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(54) **ORGANOSOLV FRACTIONATION PROCESS FOR FRACTIONATING LIGNOCELLULOSIC BIOMASS**

(57) The invention relates to an organosolv fractionation process for fractionating lignocellulosic biomass into a biomass pulp and an organosolv liquor comprising a mild fractionation step (a) to remove lignin and hemicellulose comprising contacting the lignocellulosic biomass to the intermediate organosolv liquor originating from step (b) at a temperature in the range of 100 °C - 170 °C and a pH between 1.5 and 3.0, to obtain a mildly

treated biomass and the organosolv liquor; and a severe fractionation step (b) to obtain pulp, comprising contacting the mildly treated biomass originating from step (a) with an organosolv treatment liquid at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the intermediate organosolv liquor and a biomass pulp. The total fractionation time of steps (a) and (b) is at least 30 min.

EP 4 549 649 A1

Description

Introduction

[0001] The present invention is in the field of an organosolv fractionation process for fractionating lignocellulosic biomass.

Background of the invention

[0002] Lignocellulosic biomass is the most abundant renewable material on the Earth and it comprises cellulose and hemicelluloses (polysaccharides) and lignin (aromatic polymer). Lignocellulosic biomass is a valuable resource for the production of (bio)fuels, chemicals, performance products and energy.

[0003] The development of biorefineries converting biomass into sustainable energy carriers, chemicals, and materials is of paramount importance for the transition from a fossil-based society to a (circular) biobased one. Lignocellulosic biomass suitable for biorefining can preferably come from 2nd generation feedstocks (non-edible), e.g. agricultural residues, forestry residues, food-processing residues, dedicated energy crops, or biomass from other origins such as cattle manure and biomass from roadside verges.

[0004] Organosolv fractionation of lignocellulosic biomass is used for the production of lignocellulosic components; cellulose (a glucan), hemicellulose and lignin. The two major types of hemicellulose are xylans and (gluco)mannans. Xylans have xylose (C₅ sugar) backbones, sometimes substituted with arabinose or glucuronic acid side groups, and are predominant in hardwood and grasses, while (gluco)mannans have backbones with a glucose:mannose (both C₆ sugars) ratio of about 1:3, sometimes substituted with galactose side groups, and are predominant in softwood. Minor hemicellulose types include xyloglucans and arabino- galactans. Hemicelluloses may be chemically linked to lignin. During organosolv, the lignocellulose biomass is fractionated into a cellulose-enriched solid product stream (pulp) and a liquid product stream (liquor) comprising lignin and hemicellulose derivatives. Hemicellulose is first hydrolysed into sugar oligomers, then to sugar monomers (C₅ and/or C₆ sugars), which may subsequently dehydrate to furans such as furfural, and react further to other compounds (including condensation products with lignin ("pseudo-lignin")). Degradation products may be part of the aqueous hemicellulose stream (obtained after solvent recovery and lignin precipitation) and/or the lignin stream, which are produced by the organosolv process, thereby reducing their purity and the efficiency of further treatment of these streams to produce valuable end- products. Lignin solubilization from the feedstocks occurs via (acid-catalysed) cleavage of lignin β -O-4 linkages which starts with elimination of a hydroxyl group on the α -position of the linkage. This leads to formation of a carbenium ion, followed by linkage cleavage and Hibbert ketone end group formation. Both the carbenium ion as well as Hibbert ketone end groups are involved in undesired lignin repolymerization or condensation reactions and formation of stabile C-C bonds.

[0005] Organosolv fractionation process focusses on an efficient way to obtain high yields and quality of all lignocellulosic components. WO2015009145 discloses a batch-wise process for fractionating lignocellulosic biomass into a cellulose-enriched product stream, a hemicellulose-enriched product stream and a lignin-enriched product stream, comprising subjecting optionally pre-extracted biomass to a batch-wise organosolv step using a non-hydroxylic solvent. WO2007120210 discloses a biomass fractionation process wherein biomass is digested at 120-220 °C in an aqueous extraction mixture containing a solvent for lignin such as ethanol.

[0006] The current batch fractionation process only allows simultaneous optimisation of all three fractions, which limits the flexibility to tune the product quality of specific fractions for different applications. In this process, typical fractionation is characterized by fast solubilization of lignin and hemicellulose sugars in the early stages of fractionation, followed by slower removal of the more recalcitrant part (Figure 1). Typically, a total fractionation time of at least 30-60 min is needed to complete the process and obtain a high sugar and lignin yield in the pulping liquor. Furthermore, sufficient cellulose enrichment in the pulp is needed for both material applications and to ensure efficient enzymatic saccharification of the pulp to fermentable monomeric sugars.

[0007] Conventional organosolv processes contain three steps; fractionation, a pulp wash with an organic solvent/water mixture and a pulp water wash to remove the organic solvent. In this process, a major part of the solubilized sugars and lignin have a relatively long residence time in the hot liquor during fractionation, leading to undesired sugar degradation (Figure 2) and lignin depolymerization-condensation reactions. Recent developments in process design include very mild treatments to obtain more hemicellulose sugars and a less-condensed lignin. However, the low process severity results in limited fractionation performance and low sugar and lignin yield. Other developments focus on early removal of solubilised products by applying flow reactors or stepwise liquor replacement with fresh reaction liquid. Both approaches significantly reduce solubilised product residence time and hence improve its quality. However, such process designs involve processing with large amounts of liquid with relatively low product concentrations which is detrimental to organosolv process economics. Therefore, there is a need in the art for an efficient process to reduce the degradation of hemicellulose sugars and lignin while keeping the desired high delignification and hemicellulose solubilisation without the need for

excessive liquid usage.

Summary of the invention

[0008] The invention relates to an organosolv fractionation process for fractionating lignocellulosic biomass into a cellulose-enriched product stream (pulp) and a hemicellulose sugar/lignin-enriched product stream (liquor) thereby reducing the degradation of hemicellulose sugars and lignin. Further, the process according to the invention reduces the costs and energy usage thus, improves process economics and sustainability impact.

[0009] The inventors found that the overall severity of the organosolv treatment can be reduced such that the lignin remains more native, while at the same time the extent of delignification is not negatively affected. To accomplish these effects, the process according to the invention includes a mild treatment step (a) and a severe treatment step (b). During the mild treatment step, the majority of the lignin is extracted from the biomass at relatively mild conditions, such that the lignin degradation reactions are diminished. During this mild treatment step (a), the extent of delignification is quite significant, such that significant amounts of lignin are extracted and in view of its native state can be used beneficially. In order to obtain pulp that is sufficiently delignified for further use, it is crucial that the mild treatment step (a) is followed by a severe treatment step (b). During step (b), the conditions are more severe and most of the remaining lignin and hemicellulose can be extracted from the biomass. The occurrence of lignin degradation reactions may be bigger during step (b), but since the majority of the lignin is removed after step (a), these degradation reactions only affect a small portion of the lignin.

[0010] The inventors surprisingly found that the majority of the lignin is removed from the biomass during the first part of the organosolv treatment. They considered that stopping the organosolv treatment prematurely to remove that lignin presents an opportunity to expose that lignin to less severe conditions. However, such premature stopping of the organosolv treatments afford a biomass pulp of inferior quality, which is solved by the inventors by subjecting this pulp to a second, more severe, organosolv treatment which removes the remaining lignin from the pulp. Additionally, by using a counter-current flow of the liquid, the process requires limited amounts of liquid and collects all valuable extracted components in a single organosolv liquor.

[0011] Thus, the invention relates to an organosolv fractionation process for fractionating lignocellulosic biomass into a biomass pulp and an organosolv liquor comprising:

- (a) organosolv fractionation to remove lignin and hemicellulose, comprising contacting the lignocellulosic biomass to the intermediate organosolv liquor originating from step (b) at a temperature in the range of 100 °C - 170 °C and a pH between 1.5 and 3.0, to obtain a mildly treated biomass and the organosolv liquor;
- (b) organosolv fractionation to obtain pulp, comprising contacting the mildly treated biomass originating from step (a) with an organosolv treatment liquid at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the intermediate organosolv liquor and a biomass pulp,

wherein total fractionation time of steps (a) and (b) is at least 30 min and wherein at least one of the following applies:

- the pH during step (a) is higher than the pH during step (b);
- the temperature during step (a) is lower than the temperature during step (b);
- the duration of step (a) is shorter than the duration of step (b).

List of Figures

[0012]

Figure 1. (A) Schematic representation of batchwise processing, with a single fractionation step (b) and two washing steps (c1) and (c2). The corresponding development of the fractionation over time is given in Fig 1(B) for beech wood and Fig 1(C) for wheat straw.

Figure 2. Schematic representation of semi-continuous processing (SCP) according to the invention. Shown is a preferred embodiment with six percolating reactors with fixed solid bed positions and liquid exchange between reactors during the transfer cycle. In step (a1), the fresh biomass is contacted with the liquor obtained from (b1) and fractionation is performed at mild conditions. For feedstocks with high acid neutralizing capacity, additional dosing of acid may be required to maintain a pH of 2.1. For step (b1), acidification of the liquor obtained from (b2) is typically needed, as part of the liquor from (a1) may be transferred to step (b1) absorbed within the solids. Step (b2) is the final fractionation step, typically using 20 mM sulphuric acid being added to the liquor from (c1). Wash step (c1) involves washing the pulp with 50% acetone in water. This step may be omitted in an optimized process according to this embodiment. Wash step (c2) involves washing the pulp with water for removal of acetone. The liquid from step (c2) is

supplemented with acetone to make the washing liquid for (c1) or the treatment liquid for (b2).

Figure 3. Xylose degradation to furfural as function of acetone organosolv reaction time and liquor acidity (in mM sulphuric acid (SA)).

Figure 4. Percent polymeric C5 sugar solubilization in the liquor as oligomeric and monomeric C5 sugars as function of liquor pH (Fig 4(A)) and acid dose (Fig 4(B)), respectively, for wheat straw (WS) and pre-extracted wheat straw (WA-WS).

Figure 5. Batchwise processing reference (BR; control) and semi-continuous processing (SCP; according to the invention) of beech wood, wheat straw, roadside grass and almond shells. (Top) pH of the pulping liquors, (Bottom) C5 sugar concentrations in the obtained liquors and wash liquids.

Figure 6. Batchwise reference processing (BR; control) and semi-continuous processing (SCP; according to the invention) of beech wood (BW), wheat straw (WS), roadside grass (RG) and almond shells (AS). Shown is the correlation between feedstock polymeric C5 sugar solubilization and delignification (Fig. 6(A)), conversion to oligo and monomeric sugars (Fig 6(B)) and degradation to furfural (Fig 6(C)) for each of the four feedstocks, as well as average values (AVG).

Figure 7. Batchwise reference (BR, control) and semi-continuous processing (SCP, according to the invention) of beech wood (BW), wheat straw (WS), roadside grass (RG) and almond shells (AS). Shown is the correlation between delignification and lignin quality/nativity (Fig 7(A)), isolated lignin β -O-4 content and abundance of lignin condensed aromatic units (Fig 7(B)) for each of the four feedstocks, as well as average values (AVG).

List of preferred embodiments

[0013]

1. An organosolv fractionation process for fractionating lignocellulosic biomass into a biomass pulp and an organosolv liquor comprising:

- (a) organosolv fractionation to remove lignin and hemicellulose, comprising contacting the lignocellulosic biomass to the intermediate organosolv liquor originating from step (b) at a temperature in the range of 100 °C - 170 °C and a pH between 1.5 and 3.0, to obtain a mildly treated biomass and the organosolv liquor;
- (b) organosolv fractionation to obtain pulp, comprising contacting the mildly treated biomass originating from step (a) with an organosolv treatment liquid at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the intermediate organosolv liquor and a biomass pulp,

wherein total fractionation time of steps (a) and (b) is at least 30 min, and wherein at least one of the following applies:

- the pH during step (a) is higher than the pH during step (b);
- the temperature during step (a) is lower than the temperature during step (b);
- the duration of step (a) is shorter than the duration of step (b).

2. The organosolv fractionation process according to embodiment 1, wherein the organosolv fractionation of step (b) includes at least three distinct steps (b1), (b2) and (b3):

- (b1) contacting the mildly treated biomass originating from step (a) with the second intermediate organosolv liquor originating from step (b2) at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain a third intermediate organosolv liquor and a first treated biomass;
 - (b2) contacting the first treated biomass originating from step (b1) with the first intermediate organosolv liquor from step (b3) at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the second intermediate organosolv liquor and a second treated biomass,
 - (b3) contacting the second treated biomass originating from step (b2) with the organosolv treatment liquid at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the first intermediate organosolv liquor and a biomass pulp,
- wherein the third intermediate organosolv liquor is used in step (a).

3. The organosolv fractionation process according to embodiment 1 or 2, further comprising a washing step (c) wherein the biomass pulp obtained in step (b) is contacting with a washing liquid to obtain washed biomass pulp and spent washing liquid and wherein the spent washing liquid is used as the organosolv treatment liquid in step (b), preferably in step (b3).

4. The organosolv fractionation process according to embodiment 3, wherein washing step (c) includes at least two

distinct steps (c1) and (c2):

(c1) contacting the biomass pulp originating from step (b), preferably from step (b3) with the intermediate washing liquid originating from step (c2) at a temperature in the range of 100 °C - 170 °C, to obtain a spent washing liquid and an intermediate washed biomass pulp;

(c2) washing the intermediate washed biomass pulp originating from step (c1) with a washing liquid to obtain the intermediate washing liquid and washed biomass pulp.

5. The organosolv fractionation process according to any one of embodiments 1 - 4, comprising:

(a) contacting lignocellulosic biomass to the third intermediate organosolv liquor originating from step (b1) at a temperature in the range of 100 °C - 170 °C and an acidic pH above 2.0, to obtain a mildly treated biomass and the organosolv liquor;

(b1) contacting the mildly treated biomass originating from step (a) with the second intermediate organosolv liquor originating from step (b2) at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the third intermediate organosolv liquor and a first treated biomass;

(b2) contacting the first treated biomass originating from step (b1) with the first intermediate organosolv liquor at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the second intermediate organosolv liquor and a second treated biomass,

(b3) optionally contacting the second treated biomass originating from step (b2) with the organosolv treatment liquid at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the first intermediate organosolv liquor and a third treated biomass,

wherein the organosolv treatment liquid comprises 40 - 70 wt% organic solvent and 30 - 60 wt% water, wherein the treated biomass obtained in step (b2), or step (b3) if performed, is the biomass pulp.

6. The organosolv fractionation process according to any one of embodiments 1 - 4, comprising:

(a) contacting lignocellulosic biomass to the third intermediate organosolv liquor originating from step (b1) at a temperature in the range of 100 °C - 170 °C and an acidic pH above 2.0, to obtain a mildly treated biomass and the organosolv liquor;

(b1) contacting the mildly treated biomass originating from step (a) with an organosolv treatment liquid, which is the spent washing liquid originating from step (c1) or optionally the intermediate organosolv liquor originating from step (b2) or (b3), at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the third intermediate organosolv liquor and a first treated biomass;

(b2) optionally contacting the first treated biomass originating from step (b1) with the spent washing liquid originating from step (c1) or optionally with the first intermediate organosolv liquor from step (b3), at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the second intermediate organosolv liquor and a second treated biomass;

(b3) optionally contacting the treated biomass originating from step (b1) or optionally from step (b2) with the spent washing liquid originating from step (c1) at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the first intermediate organosolv liquor and a third treated biomass;

(c1) washing the treated biomass originating from step (b1) or optionally originating from step (b2) or (b3) with a washing liquid comprising 40 - 70 wt% organic solvent and 30-60 wt% water at a temperature in the range of 100 °C - 170 °C, to obtain the spent washing liquid and the biomass pulp.

7. The organosolv fractionation process according to any one of embodiments 1 - 4 comprising:

(a) contacting lignocellulosic biomass to the third intermediate organosolv liquor originating from step (b1) at a temperature in the range of 100 °C - 170 °C and an acidic pH above 2.0, to obtain a mildly treated biomass and the organosolv liquor;

(b1) contacting the mildly treated biomass originating from step (a) with an organosolv treatment liquid, which is the spent washing liquid originating from step (c1) or optionally the intermediate organosolv liquor originating from step (b2) or (b3), at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the third intermediate organosolv liquor and a first treated biomass;

(b2) optionally contacting the first treated biomass originating from step (b1) with the spent washing liquid originating from step (c1) or optionally with the first intermediate organosolv liquor from step (b3), at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the second intermediate organosolv liquor and a second treated biomass;

(b3) optionally contacting the treated biomass originating from step (b1) or optionally from step (b2) with the spent washing liquid originating from step (c1) at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the first intermediate organosolv liquor and a third treated biomass;

(c1) washing the treated biomass originating from step (b1) or optionally originating from step (b2) or (b3) with an intermediate washing liquid originating from (c2) at a temperature in the range of 100 °C - 170 °C, to obtain a spent washing liquid and an intermediate washed biomass pulp;

(c2) washing the intermediate washed biomass pulp originating from step (c1) with water to obtain the biomass pulp and the intermediate washing liquid.

8. The organosolv fractionation process according to any one of the preceding embodiments, wherein the organosolv treatment liquid comprises water, an organic solvent and an acid catalyst, preferably wherein the organic solvent is a ketone, more preferably acetone.

9. The organosolv fractionation process according to any one of the preceding embodiments, wherein the steps (a) and (b) are performed at a temperature in the range of 110 °C - 160 °C, more preferably in the range of 120 °C - 150 °C.

10. The organosolv fractionation process according to embodiments 3-9, wherein the step (c) is performed at a temperature in the range of 110 °C - 160 °C, more preferably in the range of 120 °C - 150 °C.

11. The organosolv fractionation process according to any one of the preceding embodiments, wherein step (a) is performed at a pH between 1.6 and 2.8, preferably between 1.8 and 2.6.

12. The organosolv fractionation process according to any one of the preceding embodiments, wherein step (b) is performed at a pH between 1.5 and 2.0, preferably between 1.6 and 1.8.

13. The organosolv fractionation process according to any one of the preceding embodiments, wherein the lignocellulosic biomass is selected from herbaceous biomass, softwood, hardwood and combinations thereof, preferably the lignocellulosic biomass comprises herbaceous biomass.

14. The organosolv fractionation process according to any one of the preceding embodiments, wherein the biomass is extracted with an extracting liquid before conducting the organosolv treatment step in step (a), preferably wherein the extracting liquid comprises at least 50 wt% of an organic solvent selected from lower alcohols and ketones at a temperature below 100 °C.

15. The organosolv fractionation process according to embodiment 14, comprising:

(x1) optionally an aqueous pre-extraction, comprising contacting the lignocellulosic biomass with an aqueous extraction liquid to obtain an aqueous biomass extract and aqueous extracted biomass;

(x2) an organic pre-extraction, comprising contacting the lignocellulosic biomass or the aqueous extracted biomass with an organic extraction liquid to obtain an organic biomass extract and extracted biomass;

(a) organosolv fractionation to remove lignin and hemicellulose, comprising contacting the extracted biomass to the intermediate organosolv liquor originating from step (b) at a temperature in the range of 100 °C - 170 °C and a pH between 1.5 and 3.0, to obtain a mildly treated biomass and the organosolv liquor;

(b) organosolv fractionation to obtain pulp, comprising contacting the mildly treated biomass originating from step (a) with an organosolv treatment liquid at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the intermediate organosolv liquor and a biomass pulp.

16. The organosolv fractionation process according to any one of the preceding embodiments, comprising a separation step wherein lignin is isolated from the organosolv liquor of step (a).

17. The organosolv fractionation process according to any one of the preceding embodiments, wherein the total fractionation time is in the range of 60 - 180 min.

18. The organosolv fractionation process according to any one of the preceding embodiments, wherein each individual step has a duration that deviates at most 50 %, preferably at most 25 %, from the average fractionation time defined as the total fractionation time divided by the total number of steps.

19. The organosolv fractionation process according to any one of the preceding embodiments, wherein the pH of the liquid is continuously monitored and if needed adjusted to the target pH for fractionation, preferably using a sensor or probe and acid and/or alkaline dosing system.

20. The organosolv fractionation process according to any one of the preceding embodiments, wherein the liquid is directly transferred from reactor to reactor and preferably the duration of the liquid outside of the reactors during the transfer is below 1 min, more preferably below 10 s per transfer.

Detailed description of the invention

[0014] The present invention relates to an organosolv fractionation process for fractionating lignocellulosic biomass and reducing the degradation of hemicellulose sugars and lignin during that process. The inventors have found that it is

possible to extract sugar and lignin before substantial degradation took place, by conducting fractionation in two sub-steps (a) and (b). Furthermore, the organosolv fractionation process according to the invention allows to increase the yield of lignin and hemicellulose sugars and reduce the residual lignin in the pulp.

[0015] In the process according to the present invention, the following (optional or essential) stages can be identified: (1)

Pre-extraction, wherein the biomass is contacted with a solvent in order to remove soluble components such as minerals and organics. During pre-extraction, the conditions are such that no hydrolysis of the structural components of the biomass takes place. (2) Fractionation, wherein the biomass is contacted with a liquid under conditions that enable the hydrolysis of the structural components of the biomass, in particular of the chemical bonds that exists between lignin and (hemi) cellulose. Fractionation of the biomass is also referred to organosolv and affords a liquor wherein the solubilized components of the biomass are dissolved and a cellulose pulp containing the solid cellulose residues of the pulp. (3) Washing, wherein the biomass (pulp) is contacted with a solvent to remove remaining solubilized components from the biomass (pulp). During washing, the conditions are such that hardly any hydrolysis takes place.

[0016] The organosolv fractionation process according to the invention is typically conducted as a semi-continuous process (SCP). Different than the batch-wise processing, in this process the reactors are coupled allowing for liquor (containing solubilised sugars/lignin) exchange between percolation reactors. In a preferred configuration, the solids remain in their respective reactors and only liquids are transferred, wherein this transfer of liquids is typically directly between the reactors without the use of storage tanks. This way, a stepwise counter-current flow can be achieved while maintaining the robustness of batch-wise processing. The organosolv fractionation process according to the invention is not only different in terms of process design but also in terms of fractionation process severity. The severity of fractionation depends on the liquor acidity. In the process of the invention, fractionation is divided to two steps: mild and severe fractionation.

[0017] The process of the present invention helps to minimise hemicellulose sugar and lignin degradation and improve hemicellulose and lignin solubilisation thereby producing a cellulose enriched pulp with improved quality. Further, this process helps to reduce the pulp washing requirements, consumption of acids and energy and reduce overall process costs.

[0018] The success of processing according to the invention, with regard to improved sugar yield and lignin quality/nativity, is directly related to the efficiency of the liquid transfer where preferably all liquor is transferred to a next step. One aspect severely impacting these criteria is the liquid absorbance capacity of biomass which significantly limits liquid transfer between semi-continuous processing cycles. Another important parameter that needs careful control is the liquor acidity. Therefore, one of the most important aspect for successful semi-continuous processing is optimal fractionation conditions during mild fractionation step (a). As fractionation time and temperature are fixed values for the entire process, liquor acidity is one of the most important parameters ensuring sufficient fractionation with reduced product degradation.

The biomass feedstock

[0019] Any lignocellulosic biomass is suitable for the process according to the invention. Preferably, the biomass is selected from herbaceous biomass, softwood, hardwood and combinations thereof, preferably the lignocellulosic biomass comprises herbaceous biomass. Preferably, herbaceous biomass in the form of agricultural residues and/or biodegradable municipal waste is used in the process according to the invention, more preferably, the herbaceous biomass is selected from straw, leaves, (fresh or dried) grasses and combinations thereof, most preferably straw (e.g. rice straw, barley straw, wheat straw). Such biomass comprises in general 20 to 80 wt.% carbohydrates (based on dry matter), which are valuable starting materials for production of fuels and chemicals. Preferably, the biomass has a lignin content of at least 5 wt%, more preferably at least 10 wt%, such as 20-35 wt%, based on total dry weight.

[0020] The biomass subjected to the process according to the invention may be fresh or dried biomass, optionally after removal of large impurities such as stones and pieces of metal, and optionally chopped or milled to pieces for ease of handling (e.g. pieces of 0.01 to 50 cm, in particular 0.1-10 cm in length or diameter, depending on the type of biomass).

[0021] The biomass may be subjected to a pre-treatment prior to being subjected to step (a). In a preferred embodiment, the biomass is subjected to a pre-extraction step to remove non-lignocellulose compounds (extractives) prior to fractionation. A pre-extraction steps enables valorisation of biomass extractives (e.g., bioactive compounds, nutrients), improved fractionation performance (i.e., increased sugar yield and lignin purity) at reduced acid doses and provides potential for reduced equipment corrosion (by chloride removal). The pre-extraction may be an aqueous extraction or an organic extraction. Since both extractions remove different components from the biomass, it is especially preferred that an aqueous and an organic extraction is performed as pre-extraction.

[0022] In an embodiment, the biomass is extracted with an extracting liquid before conducting the organosolv treatment step in step (a), preferably wherein the extracting liquid comprises at least 50 wt% of an organic solvent selected from lower alcohols and ketones at a temperature below 100 °C. Herein, "lower" means containing 1-6 carbon atoms (C₁-C₆), especially C₁-C₄. Examples of suitable organic solvent include methanol, ethanol, propanol, isopropanol, butanol and its isomers, ethylene glycol, propylene glycol, methoxy- ethanol, dimethoxyethane, diethylene glycol, dioxane, acetone,

methylethyl ketone, tetrahydrofuran, dimethyl formamide, dimethyl acetamide, N-methylpyrrolidone, and mixtures thereof. Preferably, the organic solvent used during pre-extraction is the same as the organic solvent used during the organosolv treatment. The extracting liquid may comprise between 0 and 50 vol. % of water. The extraction step can be performed with an organic solvent and/or water, wherein the extracting liquid has a temperature between its melting temperature and its boiling temperature (or higher if pressurised). Preferred extracting temperatures are from 10 to 100 °C and have a duration in the range of 30 s - 15 min. The skilled person will appreciate how to control the temperatures for optimal results when using a mixture of water and organic solvent. The extraction step may be performed using any extraction technique known in the art.

[0023] If performed, the pre-extraction may be a separate step, which is conducted completely independent of the steps (a), (b) and optionally (c) of the process of the present invention. Alternatively, the pre-extraction may be integrated into the sequence of steps (a), (b) and optionally (c) of the process of the present invention, wherein the biomass is subjected to step (a) immediately after the pre-extraction, preferably wherein the biomass is kept in the same reactor from which the extract obtained during the pre-extraction step is removed. Thus, in a preferred embodiment, a pre-extraction step is performed wherein the biomass is contacted with an extraction liquid to obtain a biomass extract and extracted biomass, wherein the extracted biomass is subjected to organosolv fractionation according to the present invention.

Organosolv fractionation

[0024] The organosolv fractionation process according to the present invention separates the lignocellulose biomass into a cellulose-enriched product stream (the pulp) and a hemicellulose/lignin-enriched product stream (the liquor). Organosolv processes to delignify biomass are known in the art, and can be performed as deemed appropriate by the skilled person.

[0025] Performing organosolv fractionation process at reduced temperatures, such as between 100 °C - 170 °C is desirable in order to reduce the costs and to already reduce degradation of valuable hemicellulose derivatives and lignin, when compared with conventional organosolv typically at temperatures around 200 °C. The organosolv fractionation process according to the invention is performed at a temperature between 100 °C - 170 °C, preferably between 110 °C - 160 °C, more preferably between 120 °C - 150 °C. Steps (a) and (b) may be performed at the same temperature or at different temperature. In one embodiment, the temperature of step (b) is the same as or higher than the temperature in step (a). Most preferably, the temperature in both steps is the same. These temperature ranges provide optimal results in that no undesirable solvent loss is observed and delignification remains high. Optimal results have been obtained at 140 °C.

[0026] The organosolv fractionation step can be performed at any suitable pressure as known in the art, which typically is about 0.5 to 50 bar (absolute), preferably between 1 and 25 bar (absolute). Typically, the process is performed at atmospheric pressure wherein the only pressure increase is the result of the heating within a pressurized reactor.

[0027] The total fractionation time of the organosolv fractionation process is at least 30 minutes. Herein, the total fractionation time refers to the duration of steps (a) and (b), as during these steps the biomass is fractionated into a liquor and a pulp. Even if some minor additional fractionation would take place before (e.g. during a pre-extraction) or after (e.g. during washing) steps (a) and (b), this is not included in the total fractionation time. In the context of the present invention, steps (a) and (b) together make up the organosolv process. Preferably, the total fractionation time is in the range of 60 - 180 minutes. Longer times can be used but provide no further benefit, as the biomass will be completely fractionated, and may lead to unnecessary degradation of the components in the liquor, whereas shorter times typically lead to undesired results in view of incomplete fractionation. Also, it is desired that the duration of the individual steps (a) and (b) is such that significant fractionation takes place in each step. Therefore, it is preferred that each individual step has a duration that deviates at most 50 %, preferably at most 25 %, from the average fractionation time defined as the total fractionation time divided by the total number of steps. In one embodiment, the individual steps may refer to the two steps (a) and (b). For example, for a total fractionation time of 60 min, the average fractionation time would be 30 min, such that the duration of step (a) and the duration of step (b) deviates at most 50 %, i.e. 15 min, from this average. In other words, step (a) and step (b) both have a duration in the range of 15 to 45 min, and together have a duration of 60 min. Alternatively or additionally, the individual steps may refer to each individual substep within steps (a) and (b). For example, the process may contain one step (a) and two sub-steps (b1) and (b2) for step (b). Then, for a total fractionation time of 60 min, the average fractionation time would be 20 min, such that the duration of steps (a), (b1) and (b2) deviates at most 50 %, i.e. 10 min, from this average. In other words, steps (a), (b1) and (b2) all have a duration in the range of 10 to 30 min, and together have a duration of 60 min. In a preferred embodiment, the total fractionation time is in the range of 60 - 180 minutes, preferably 60 - 120 minutes, and the duration of each individual step is in the range of 5 - 45 minutes, more preferably 10 - 30 min.

[0028] Typically, the suspension of biomass and treatment liquid is obtained by mixing at most 50 L and at least 0.1 L of treatment liquid per kg dry weight of the biomass, preferably between 1.0 L and 20 L, most preferably between 3 L and 15 L. Thus, organosolv treatment of biomass uses 1 L of treatment liquid per between 20 g and 10 kg of biomass, preferably per between 50 and 1000 g, most preferably per between 67 and 333 g of biomass (dry weight). The optimum ratio of treatment liquid to biomass depends on the type of biomass. For procedural economy, the liquid to solid weight ratio (L/S in liter/kg) of

the organosolv fractionation step is preferably as low as possible, preferably lower than 20/1, more preferably lower than 12/1, most preferably lower than 8/1. In one embodiment, the L/S ratio is at least 0.5/1, preferably at least 1/1, even more preferably at least 1.5/1, most preferably at least 2/1.

[0029] The organosolv process involves contacting the biomass with an organosolv treatment liquid. Any organosolv treatment liquid may be used during the process according to the invention. Typically, an organosolv treatment liquid comprises water, an organic solvent and optionally an acid catalyst. The acid is preferably present to enable working at reduced pH as defined for steps (a) and (b). A compound is considered to be a solvent in the context of the present invention, when it is liquid under ambient conditions. The presence of water in the treatment liquid allows hydrolysis reactions to take place during organosolv, in order to break up the network of structural components. Preferably, the organosolv treatment liquid comprises at least 5 wt% water, more preferably at least 10 wt%, even more preferably between 20 wt% and 80 wt%, even more preferably between 30 wt% and 75 wt% water, most preferably between 40 wt% and 70 wt% water. The weight ratio of organic solvent to water is preferably between 20/80 and 80/20, more preferably between 30/70 and 75/25, even more preferably between 40/60 and 70/30, even more preferably between 40/60 and 65/35, more preferably between 40/60 and 60/40.

[0030] Any organic solvent suitable for organosolv may be used in the treatment liquid, including mixtures of organic solvents. Suitable solvents include alcohols, esters, ethers and/or ketones, more preferably the organic solvent is an alcohol or a ketone, most preferably a ketone solvent. Preferred alcohols include methanol, ethanol, (iso)propanol, butanol, ethylene glycol, methoxyethanol and mixtures thereof, most preferred the alcohol is ethanol. Preferred ethers include dimethoxyethane, tetrahydrofuran (THF), 1,4-dioxane and 1,3-dioxolane. Preferred ketones include acetone, butanone (methyl-ethyl-ketone or MEK), methyl isobutyl ketone (MIBK), cyclohexanone, acetoacetic (3-oxo-butanoic) acid esters and levulinic (4-oxopentanoic) esters, such as methyl levulinate and ethyl levulinate, most preferred the ketone is acetone. Herein, solvents having both a ketone and an ester functionality are listed as ketones. Preferred esters, i.e. solvents not having a separate ketone functionality, include C₃-C₅ esters such as ethyl acetate. In a preferred embodiment, the organic solvent is methanol, ethanol or acetone. Most preferably, the organosolv treatment liquid comprises acetone as organic solvent. The inventors have obtained excellent results using acetone as organic solvent. Organosolv fractionation occurs at acidic pH, to enable optimum fractionation into cellulose pulp and lignin-containing liquor. The amount of acid used for optimum performance of the organosolv reaction may vary depending on the strength of the acid (pKa) and the acid neutralisation capacity (ANC) of the biomass, as well as on the process conditions. The skilled person will appreciate how to adjust the amount of acid in order to obtain optimal results. Working at decreased L/S ratios favours an increase in acid concentration in the treatment liquid, but at the same a reduction in acid load per kg biomass. Preferably, the pH of the liquid is continuously monitored and if needed adjusted to the target pH for fractionation, using a sensor or probe and acid and/or alkaline dosing system. Suitable acids include sulfuric acid, sulfurous acid, hydrochloric acid, phosphoric acid, perchloric acid, sulfonic acids such as methanesulfonic acid and *para*-toluenesulfonic acid, formic acid, oxalic acid, benzoic acid, lactic acid, malonic acid, maleic acid, dichloroacetic acid, trichloroacetic acid, trifluoroacetic acid, and combinations thereof. Preferably the acid is selected from sulfuric acid, sulfurous acid, hydrochloric acid, phosphoric acid, *para*-toluenesulfonic acid, and combinations thereof. Most preferably, sulfuric acid is used. Herein, "the acid" may refer to a single compound, or to a mixture of different acids. Preferably, a single acid is used.

[0031] During organosolv fractionation, biomass is contacted with a treatment liquid and fractionated into a pulp and a liquor. Thus, biomass, which may optionally be pre-treated as defined below, and treatment liquid, which has optionally been used as washing liquid in step (c) as defined below, are fed into the organosolv process. A key aspect of the present invention is that the optionally pre-treated biomass is fed into the mild fractionation of step (a), whereas the treatment liquid is fed into the severe fractionation of step (b). The "liquor" or "organosolv liquor" is obtained from step (a), whereas the "pulp" or "biomass pulp" is obtained from step (b), optionally after it has been subjected to a washing step (c). The liquid fraction that is obtained from step (b) is herein referred to as "intermediate organosolv liquor" and the solid fraction that is obtained from step (a) is herein referred to as "mildly treated biomass".

[0032] The process according to the invention operates in counter-current mode, whereby the liquid stream starts at step (b) - or even step (c) if present - and ends at step (a), while the solid stream starts at step (a) and ends at step (b) - or even (c) if present. The process typically runs semi-continuously, where organosolv treatment liquid is fed into step (b) (semi-)continuously and biomass is fed into step (a) (semi-)continuously, while during the process the liquids move from the severe treatment of step (b) to the mild treatment of step (a), while the solids remain in the same reactor. Thus, reactors containing solids shift from step (a) to step (b), while liquids flow from reactor to reactor. The duration that the liquid is outside of the reactors during the transfer of the liquid from steps (b) to (a) and from steps (c) to (b) is preferably kept as low as possible, preferably below 1 min, more preferably below 10 s per transfer.

[0033] The aim of step (a) is to conduct a mild fractionation of the biomass thereby solubilizing the most labile part of the hemicellulose and lignin. The aim of step (b) is to increase the liquor acidity to promote fractionation and separate as much lignin as possible from the cellulose. Most hemicellulose and lignin solubilization occurs during the mild fractionation step (a) followed by consecutively lower solubilization during the severe fractionation step (b). Preferably, the biomass feedstock is either pre-extracted or pre-wetted with 50% organic solvent, preferably with acetone prior to fractionation

steps. Pre-wetting can be done to ensure the sufficient liquid transfer.

Mild fractionation (step (a))

[0034] The mild fractionation step is applied to remove hemicellulose and lignin at a temperature in the range of 100 °C - 170 °C and a pH between 1.5 and 3.0. The organosolv fractionation process according to the invention comprises step (a), which involves contacting fresh or pre-extracted lignocellulosic biomass to the intermediate organosolv liquor originating from step (b). The contacting of step (a) occurs at a temperature in the range of 100 °C - 170 °C and at a pH between 1.5 and 3.0. In step (a), a mildly treated biomass and the organosolv liquor are obtained. The organosolv liquor obtained in step (a) is one of the key end-products of the process according to the present invention.

[0035] To ensure that step (a) is a mild fractionation with respect to the severe fractionation of step (b), it is preferred that at least one of the following should apply: The pH during step (a) is higher than the pH during step (b); the temperature during step (a) is lower than the temperature during step (b); the duration of step (a) is shorter than the duration of step (b). Preferably, at least the pH is higher and/or the temperature is lower. In a most preferred embodiment, step (a) operates at a higher pH than step (b). The inventors found that a small pH difference already provides a significantly reduced sugar and lignin degradation. Thus, in one embodiment, the pH during step (a) is at least 0.1 pH-point higher than the pH during step (b), preferably 0.1 - 1.0 pH-point higher, more preferably 0.2 - 0.5 pH-point higher. Optimal results have been obtained with step (a) at a pH of about 2.1 and step (b) at a pH of about 1.8.

[0036] The incoming intermediate organosolv liquor may be more acidic than desired for step (a), depending on the conditions at which step (b) is conducted. A significant part of the liquor acidity can be removed when contacted with the biomass in step (a), depending on the acid neutralising capacity of biomass. Thus, step (a) will typically be conducted at a higher pH than step (b). During step (a) the liquor acidity of step (b) is partly removed to create mild fractionation conditions for first lignin and hemicellulose hydrolysis and solubilisation. By keeping the addition of acid to the liquid between steps (a) and (b) to a minimum, or preferably completely avoiding any acid addition at that moment, the acidity of the intermediate organosolv liquor originating from step (b) is conveniently reduced upon contacting with the biomass in step (a). Optionally, automatic pH control is applied using a sensor or probe and an inline acid and/or alkaline dosing system to ensure a milder fractionation in step (a) as compared to step (b). Hence, step (a) is performed at a pH preferably between 1.6 and 2.8, more preferably between 1.8 and 2.6. Liquor acidity is one of the most important parameter for this step in order to ensure sufficient fractionation with reduced product degradation.

Severe fractionation (step (b))

[0037] The severe fractionation step is applied to obtain pulp at a temperature in the range of 100 °C - 170 °C and a pH below 2.0. The organosolv fractionation process according to the invention comprises step (b) wherein the mildly treated biomass originating from step (a) is contacted with an organosolv treatment liquid at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the intermediate organosolv liquor and a biomass pulp. This step is performed at a pH preferably between 1.5 and 2.0, more preferably between 1.6 and 1.8. The biomass pulp obtained in step (b), which is optionally washed in step (c), is one of the key end-products of the process according to the present invention.

[0038] The organosolv treatment liquid that is used in step (b) may be a fresh organosolv treatment liquid, i.e. a liquid which has not yet been subjected to a process step, in particular no fractionation step or washing step. Alternatively, the organosolv treatment liquid that is used in step (b) may be a spent washing liquid that originates from a washing step, typically a washing step (c) as defined below.

[0039] To ensure that step (b) is a severe fractionation with respect to the mild fractionation of step (a), at least one of the following should apply: The pH during step (b) is lower than the pH during step (a); the temperature during step (b) is higher than the temperature during step (a); the duration of step (b) is longer than the duration of step (a). Preferably, at least the pH is lower and/or the temperature is higher. In a most preferred embodiment, step (b) operates at a lower pH than step (a). Preferably, the pH during step (b) is at least 0.1 pH-point lower than the pH during step (a), preferably 0.1 - 1.0 pH-point lower, more preferably 0.2 - 0.5 pH-point lower.

[0040] According to the present invention, the severe organosolv fractionation of step (b) preferably includes at least two distinct sub-steps, more preferably at least three distinct steps (b1), (b2) and (b3). These sub-steps operate with the conditions as defined above for step (b), although some variation in conditions within the defined ranges may occur. The advantage of having additional fractionation steps is a more efficient transfer of components to the liquor of step (a) with very little degradation thereof, especially when low L/S ratios are applied. Thus, in one embodiment, step (b) of the process according to the invention includes steps (b1), (b2) and (b3) as follows:

(b1) contacting the mildly treated biomass originating from step (a) with the second intermediate organosolv liquor originating from step (b2) to obtain a third intermediate organosolv liquor and a first treated biomass;

(b2) contacting the first treated biomass originating from step (b1) with the first intermediate organosolv liquor from

step (b3) to obtain the second intermediate organosolv liquor and a second treated biomass,
 (b3) contacting the second treated biomass originating from step (b2) with the organosolv treatment liquid to obtain the
 first intermediate organosolv liquor and a biomass pulp, wherein the third intermediate organosolv liquor is used in
 step (a).

[0041] Preferably, higher acid concentrations are applied in step (b1) in order to increase hydrolysis power and thus hemicellulose/lignin solubilisation in this step. Acid concentrations in step (b2) and step (b3) are preferably kept constant to solubilise the remaining hemicellulose and lignin to obtain a cellulose-enriched pulp.

[0042] In one embodiment, the present invention relates to an organosolv fractionation process comprising:

(a) contacting lignocellulosic biomass to the third intermediate organosolv liquor originating from step (b1) at a temperature in the range of 100 °C - 170 °C and an acidic pH above 2.0, to obtain a mildly treated biomass and the organosolv liquor;

(b1) contacting the mildly treated biomass originating from step (a) with the second intermediate organosolv liquor originating from step (b2) at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the third intermediate organosolv liquor and a first treated biomass;

(b2) contacting the first treated biomass originating from step (b1) with the first intermediate organosolv liquor from step (b3) at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the second intermediate organosolv liquor and a second treated biomass,

(b3) optionally contacting the second treated biomass originating from step (b2) with the organosolv treatment liquid at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the first intermediate organosolv liquor and a third treated biomass.

[0043] Herein, if step (b3) is not performed, the second treated biomass from step (b2) is the biomass pulp obtained from step (b). If step (b3) is performed, the third treated biomass from step (b3) is the biomass pulp obtained from step (b). Likewise, if step (b3) is not performed, the first intermediate organosolv liquor fed to step (b2) is the intermediate organosolv liquor fed to step (b). Preferably, step (b3) is performed.

[0044] In the context of the present embodiment, it is preferred that the organosolv treatment liquid comprises 40 - 70 vol% organic solvent and 30 - 60 vol% water, preferably wherein the organic solvent comprises acetone, most preferably wherein the organic solvent is acetone.

Washing step (step (c))

[0045] The organosolv fractionation process according to the present invention may comprise a pulp washing step (c). In the washing step, the biomass pulp obtained in step (b) is contacted with a washing liquid to obtain washed biomass pulp and spent washing liquid. It is highly preferred that the spent washing liquid is used as the organosolv treatment liquid in step (b), preferably as the first intermediate organosolv liquor in step (b2), when step (b3) is not performed, or as the organosolv treatment liquid in step (b3), when step (b3) is performed. The skilled person understands that the composition of the spent washing liquid may need to be changed in order to make it suitable as the treatment liquid in step (b). For example, some organic solvent and/or acid may need to be added. Since washing step (c) removes organic solvent from the pulp, the spent washing liquid will at all times contain some organic solvent, but this may be insufficient for the treatment of step (b). As long as at least part of the spent washing liquid, including the solutes present therein, is used in the treatment liquid, the benefits of the present invention are obtained. Depending on the composition of the spent washing liquid, especially the water to organic solvent ratio, and the desired composition of the organosolv treatment liquid, the spent washing liquid may be partially or fully used for the organosolv treatment liquid. In case not all of the spent washing liquid is used, the remainder may be used for recovery of the organic solvent or can be used in a pre-extraction step.

[0046] The purpose of the washing step is to remove any remaining solvents from the treatment liquid as well as the solutes contained therein from the pulp. As such, the pulp will contain less residual lignin and hemicellulose, which will be contained in the liquor. So the washing step also increases the yield of lignin and hemicellulose in the final organosolv liquor that is obtained in step (a). At the same time, organic solvent is beneficially removed from the pulp before it is further used or processed. Typically, the pulp may be subjected to enzymatic hydrolysis into glucose, for which the presence of organic solvent is detrimental.

[0047] According to the present invention, the washing step (c) may include at least two distinct steps (c1) and (c2) as follows:

(c1) contacting the biomass pulp originating from step (b), preferably from step (b3), with the intermediate washing liquid originating from step (c2) at a temperature in the range of 100 °C - 170 °C, to obtain a spent washing liquid and an intermediate washed biomass pulp, wherein the spent washing liquid is used as the organosolv treatment liquid in step

(b);

(c2) washing the intermediate washed biomass pulp originating from step (c1) with a washing liquid to obtain the intermediate washing liquid and washed biomass pulp.

[0048] Multiple washing steps are preferably performed in order to improve the effectiveness. Washing step (c1) typically occurs at elevated temperature, which is close to the temperature at which the severe treatment step (b) is performed. As such, the heat of the biomass pulp can effectively be used for washing step (c1) and the effectiveness of the washing is increased. At such elevated temperatures, the solubility of the solutes (mainly lignin and hemicellulose residues) is higher than at ambient temperature, and therefore these are more effectively removed. To further improve the effectiveness of the washing step (c1) at elevated temperatures, it is preferred that the washing liquid used in step (c1), also referred to as the "intermediate washing liquid", comprises organic solvent and water in similar ratios as the treatment liquid to be used in step (b). As such, the spent washing liquid may immediately be suitable as treatment liquid in step (b), without the need for addition of organic solvent, optionally with the addition of acid.

[0049] Washing step (c2) typically occurs at lower temperatures than washing step (c1). As such, the passive cooling of the biomass pulp after the treatment of step (b) can be used as the temperature at which the washing steps are performed. In one embodiment, the washing of step (c2) occurs at ambient temperature. In order to effectively remove the organic solvent from the biomass pulp, it is preferred that water is used as washing liquid in step (c2). The intermediate washing liquid obtained in step (c2) may contain 10-25 vol% organic solvent. It may be beneficial to supplement the intermediate washing liquid with organic solvent before it is used in step (c1). As such, the spent washing liquid may contain about 50 vol% organic solvent. In a preferred embodiment, when the spent washing liquid is used as an organosolv treatment liquid in step (b), organic solvent can be added to the intermediate washing liquid or the spent washing liquid to make sure the content of organic solvent is suitable for step (b).

[0050] In one embodiment, the present invention relates to an organosolv fractionation process comprising:

(a) contacting lignocellulosic biomass to the third intermediate organosolv liquor originating from step (b1) at a temperature in the range of 100 °C - 170 °C and an acidic pH above 2.0, to obtain a mildly treated biomass and the organosolv liquor;

(b1) contacting the mildly treated biomass originating from step (a) with an organosolv treatment liquid, which is the spent washing liquid originating from step (c1) or optionally the intermediate organosolv liquor originating from step (b2) or (b3), at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the third intermediate organosolv liquor and a first treated biomass;

(b2) optionally contacting the first treated biomass originating from step (b1) with the spent washing liquid originating from step (c1) or optionally with the first intermediate organosolv liquor from step (b3), at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the second intermediate organosolv liquor and a second treated biomass;

(b3) optionally contacting the treated biomass originating from step (b1) or optionally from step (b2) with the spent washing liquid originating from step (c1) at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the first intermediate organosolv liquor and a third treated biomass;

(c1) washing the treated biomass originating from step (b1) or optionally originating from step (b2) or (b3) with a washing liquid comprising 40 - 70 wt% organic solvent and 30 - 60 wt% water at a temperature in the range of 100 °C - 170 °C, to obtain the spent washing liquid and the biomass pulp.

[0051] In the context of this embodiment, it is preferred that step (b2) is performed, more preferably steps (b2) and (b3) are both performed.

[0052] In one embodiment, the present invention relates to an organosolv fractionation process comprising:

(a) contacting lignocellulosic biomass to the third intermediate organosolv liquor originating from step (b1) at a temperature in the range of 100 °C - 170 °C and an acidic pH above 2.0, to obtain a mildly treated biomass and the organosolv liquor;

(b1) contacting the mildly treated biomass originating from step (a) with an organosolv treatment liquid, which is the spent washing liquid originating from step (c1) or optionally the intermediate organosolv liquor originating from step (b2) or (b3), at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the third intermediate organosolv liquor and a first treated biomass;

(b2) optionally contacting the first treated biomass originating from step (b1) with the spent washing liquid originating from step (c1) or optionally with the first intermediate organosolv liquor from step (b3), at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the second intermediate organosolv liquor and a second treated biomass;

(b3) optionally contacting the treated biomass originating from step (b1) or optionally from step (b2) with the spent

washing liquid originating from step (c1) at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the first intermediate organosolv liquor and a third treated biomass;

(c1) washing the treated biomass originating from step (b1) or optionally originating from step (b2) or (b3) with an intermediate washing liquid originating from (c2) at a temperature in the range of 100 °C - 170 °C, to obtain a spent washing liquid and an intermediate washed biomass pulp;

(c2) washing the intermediate washed biomass pulp originating from step (c1) with a washing liquid comprising water to obtain the biomass pulp and the intermediate washing liquid;

[0053] In the context of this embodiment, it is preferred that step (b2) is performed, more preferably steps (b2) and (b3) are both performed.

[0054] In a further preferred embodiment, it is preferred that a pre-extraction step is part of the step sequence of the process according to the invention. Thus, in one embodiment, the present invention relates to an organosolv fractionation process comprising:

(x) a pre-extraction step, comprising contacting the lignocellulosic biomass with an extraction liquid to obtain a biomass extract and extracted biomass;

(a) organosolv fractionation to remove lignin and hemicellulose, comprising contacting the extracted biomass to the intermediate organosolv liquor originating from step (b) at a temperature in the range of 100 °C - 170 °C and a pH between 1.5 and 3.0, to obtain a mildly treated biomass and the organosolv liquor;

(b) organosolv fractionation to obtain pulp, comprising contacting the mildly treated biomass originating from step (a) with an organosolv treatment liquid at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the intermediate organosolv liquor and a biomass pulp.

[0055] In a further preferred embodiment, the present invention relates to an organosolv fractionation process comprising:

(x1) optionally an aqueous pre-extraction, comprising contacting the lignocellulosic biomass with an aqueous extraction liquid to obtain an aqueous biomass extract and aqueous extracted biomass;

(x2) an organic pre-extraction, comprising contacting the lignocellulosic biomass or the aqueous extracted biomass with an organic extraction liquid to obtain an organic biomass extract and extracted biomass;

(a) organosolv fractionation to remove lignin, comprising contacting the extracted biomass to the intermediate organosolv liquor originating from step (b) at a temperature in the range of 100 °C - 170 °C and a pH between 1.5 and 3.0, to obtain a mildly treated biomass and the organosolv liquor;

(b) organosolv fractionation to obtain pulp, comprising contacting the mildly treated biomass originating from step (a) with an organosolv treatment liquid at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the intermediate organosolv liquor and a biomass pulp.

[0056] Pre-extraction step (x), or steps (x1) and (2), as defined above, are compatible with all the above embodiments.

Further process steps

[0057] The liquor obtained in step (a) typically contains lignin, carbohydrates (notably hemicellulose and its degradation products), organic acids, salts and possibly other compounds originating from the biomass. It may be used as deemed fit by the skilled person. For example, it may be further treated or separated for the purpose of isolating valuable products. In particular, the liquor may be depleted in lignin by precipitation of lignin through decreasing the organic solvent content of the liquor, e.g. by dilution with water and/or by evaporation of organic solvent, e.g. followed by centrifugation. Alternatively, the ratio within a mixture of organic solvents may be altered, which may lead to phase separation between the aqueous and organic phases, facilitating the separation which may e.g. be performed by decantation. For example, reducing the acetone content (e.g. by evaporation) or increasing the butanone content (e.g. by addition thereof) leads to such phase separation.

[0058] The biomass pulp obtained in step (b), or in step (c) if performed, contains cellulose and typically some hemicellulose residues. Although minor amounts of lignin may be present in the pulp, the delignification rate of the process according to the invention is high such that content of residual lignin is low. The biomass pulp may be used as deemed fit by the skilled person. For example, it may be further treated by enzymatic hydrolysis of the cellulose polymers into glucose monomers, which in turn is a suitable intermediate for the manufacture of biofuels.

[0059] The advantages of the invention are most pronounced within the following preferred embodiments:

- Preferably, the solids remain in the same reactor throughout the process, and liquids are transported between the

reactors to effectuate the fractionation and optional washing and pre-extraction steps. As such, the process is robust by not requiring extensive solid transfer but the benefits of the invention are fully obtained.

- Advantageously, performing a mild fractionation step (a) and a severe fractionation step (b) ensures that most components are solubilized during the mild fractionation, leading to less lignin and hemicellulose sugar degradation and thus a higher yield and quality of these fractions.
- These advantages are especially obtained by varying the acidity of the treatment liquid, which can conveniently be controlled using the acid-neutralizing capacity of the biomass and/or keeping the addition of acid between step (a) and (b) to a minimum. Further finetuning of the pH can then be achieved through automated pH control.

Examples

[0060] The following examples are intended to illustrate the invention, not to limit the scope.

Feedstock composition

[0061] The ambient dry beech wood (BW), wheat straw (WS), roadside grass (RS) and almond shells (AS) were selected as feedstocks considering composition, physical characteristics and fractionation performance. WS, RS and AS were pre-extracted. WS and RS were extracted by premixing 2.5 kg feedstock (dry weight) with 7.5 L demineralised water before loading into a pre-extraction unit. The wetted feedstocks were transferred to the pre-extraction unit and preheated at 50 °C for 2 h. Demineralised water of 48 °C was sprayed onto the top of the biomass bed with a flow rate of 200 mL/min. After water addition, the liquid was allowed to percolate down the biomass bed for 30 min and collected in a vessel. Then, 50 % w/w aqueous acetone was added following the same procedure followed by the addition of 10 L of 100 % acetone. AS was extracted by stepwise soaking 3 kg of the shells in extraction liquid followed by draining rather than using percolation to maintain a comparable contact time for all feedstock extractions.

[0062] The biochemical composition of the biomass feedstock was analysed according to the method described in Smit, A. T.; van Zomeren, A.; Dussan, K.; Riddell, L. A.; Huijgen, W. J.; Dijkstra, J. W.; Bruijninx, P. C., Biomass Pre-Extraction as a Versatile Strategy to Improve Biorefinery Feedstock Flexibility, Sugar Yields, and Lignin Purity. ACS sustainable chemistry & engineering 2022. The compositions of BW and pre-extracted WS, RG and AS are shown in Table 1. All (pre-extracted) feedstocks have a comparable glucan and xylan content with one exception for almond shells glucan content. Both BW and AS have relatively higher lignin and lower ash content as compared to WS and RG. RG and WS have a low bulk density and a high liquor absorbance capacity.

Table 1: Feedstock composition and characteristics

		Unit	BEECH WOOD	WHEAT STRAW	ROADSIDE GRASS	ALMOND SHELLS
Pre-extraction			no	yes	yes	yes
Extractives	Water (organic)	% w/w	2.8	1.5	1.5	3.2
	Solvent (acetone)	% w/w	0.7	1.9	1.8	1.7
Cellulose	Glucan	% w/w	37.6	37.6	34.4	24.1
Hemicellulose	Xylan	% w/w	17.6	20.2	19.4	23.3
	Arabinan	% w/w	0.6	2.7	3.3	0.8
	Galactan	% w/w	0.8	0.9	1.2	0.9
	Mannan	% w/w	1.5	0.4	0.0	0.0
	Rhamnan	% w/w	0.4	0.0	0.1	0.4
Lignin	AIL +ASL	% w/w	25.5	16.7	16.9	29.0
Ash		% w/w	0.7	7.0	4.2	0.5
Bulk density	Feedstock	kg/m ³	294	195	212	605
Liquor absorbing capacity	Feedstock	g/g feed	1.3	3.7	4.0	0.7
Acid neutralizing capacity	Feedstock	mmol H ⁺ /g	0.16	0.35	0.31	0.14

Organosolv Fractionation Process

[0063] A series of integrated 2 L autoclave experiments were conducted to simulate semi-continuous processing (SCP) according to the invention. The semi-continuous processing experiments were conducted as shown in Figure 2: Fresh or pre-extracted dry feedstock was pre-wetted with 50% acetone and fractionated through three fractionation stages (steps (a), (b1) and (b2)) and the pulp washed (step (c)) and dried. The SCP experiments for each feedstock consisted of two startup cycles (each cycle comprising of steps (a), (b1) and (b2)), followed by two or three cycles from which the average values are presented in the results. The mixtures were heated to 140 °C and kept isothermal for the specified reaction time (Table 2) while stirring. In step (b2) 1200 mL of 50% acetone/water mixture containing 20 mM sulfuric acid was used as treatment liquid. After the (b2) fractionation step, the organosolv liquor was acidified (Table 2) and transferred to step (b1). After the (b1) fractionation step the organosolv liquor was transferred to step (a). After the step (a) fractionation step the final organosolv liquor was obtained for further processing. The wet pulp was then washed with 600 ml 50% acetone in step (c1) followed by a wash with 1200 ml water to remove the acetone in step (c2). The pH of the liquid streams was determined with a pH meter.

Table 2: Experimental conditions

Experiment	Time (min)	L/S (L per kg feed)	Acid added (mM H ₂ SO ₄)		
			BR	SCP (b1)	SCP (b2)
BW-BR	3 × 30	6	40		
BW-SCP	3 × 30	6		20	20
WS-BR	3 × 20	10	60		
WS-SCP	3 × 20	10		30	20
RG-BR	3 × 20	10	50		
RG-SCP	3 × 20	10		30	20
AS-BR	3 × 20	10	30		
AS-SCP	3 × 20	10		10	20

Compositional analyses

[0064] A wet pulp sample was dried for determining pulp yield and duplicate biochemical composition analysis. The remainder of the wet pulp was stored frozen for subsequent pulp enzymatic saccharification. The obtained liquors were processed using the lab-scale LigniSep lignin precipitation method as described in Smit, A. T.; Verges, M.; Schulze, P.; van Zomeren, A.; Lorenz, H., Laboratory-to Pilot-Scale Fractionation of Lignocellulosic Biomass Using an Acetone Organosolv Process. ACS sustainable chemistry & engineering 2022.

[0065] The precipitated lignin was washed, dried and their biochemical composition was analysed. Lignin was also precipitated from the washing liquids obtained from the step (c1) at 60 °C.

[0066] Liquor samples from all (intermediate) process steps were analysed for monomeric sugar, organic acid and furanic content. Additionally liquors were post-hydrolysed in 1 M sulfuric acid for 2 h at 100 °C and analysed for total monomeric sugars to determine the oligomeric sugar content. Wash liquids obtained from step (c1) and (c2) were only analysed for total monomeric sugars after post-hydrolysis, no distinction was made between monomers and oligomers and these sugars were added to the mass balance as monomeric sugars. Due to the low concentration of sugars in these streams, the contribution of sugar oligomers is minimal.

Control experiments

[0067] A batch-wise processing experiment was conducted for each feedstock as a reference for the semi-continuous processing experiments (Table 2). In batch-wise processing, the fractionation mixture and process conditions were the same as for the semi-continuous processing but conducted with a single fractionation liquor and separate washing liquids as shown in Figure 1A. Downstream processing of pulp and liquor was identical to the semi-continuous processing. Due to

the higher sugar concentrations in the wash liquor obtained in step (c1) as compared to semi-continuous processing wash liquors, both monomeric and oligomeric sugars (after post-hydrolysis) were quantified. The results of semi-continuous processing (SCP) and the batch-wise processing (BR) experiments are compared.

Results

[0068] The development of beech wood and wheat straw fractionation is shown in Figure 1 A and B. As can be seen from Figure 1 A and B, fractionation proceeds fast in the early stages of the process (0 - 30 min). Fractionation of wheat straw is slightly slower than the fractionation of beech wood due to the higher acid neutralising capacity of wheat straw. The later stages of fractionation (after 30 min) are slower but still important to reach sufficient fractionation levels and cellulose enrichment in the pulp. The early release of (oligomeric) sugars during fractionation results in relatively long residence time in the hot liquor leading to undesired sugar degradation and lignin depolymerization-condensation reactions during batch-wise processing, despite the relatively mild process conditions. Contrary to the batch-wise processing, counter-current flow during the fractionation of semi-continuous processing shortens the residence time of a major part of the solubilised products which leads to reduced sugar degradation and increased lignin quality/nativity.

[0069] The degradation of xylose (25 g/L in 50% acetone and 10-30 mM H_2SO_4) to furfural over time is shown in Figure 3. As can be seen from this figure, there is a correlation between the fractionation time, liquor acidity and furfural formation. The degradation of xylose to furfural increases with the fractionation time and liquor acidity. Therefore, relatively long residence time of the sugar and lignin in the hot liquor during batch wise fractionation process results in undesired sugar degradation and lignin depolymerisation-condensation reactions.

[0070] Further, Figure 4 A shows the fractionation performance of wheat straw (WS) and pre-extracted wheat straw (WA-WS) as a function of liquor acidity and Figure 4 B shows the fractionation performance of wheat straw (WS) and pre-extracted wheat straw (WA-WS) as a function of acid dose. Figure 4 A shows no difference between the fractionation of WS and WA-WS at similar liquor acidities but Figure 4 B shows a difference at similar acid dose. The reason for this is the effect of pre-extraction step. Pre-extraction removes organic extractives as well as minerals and reduces the acid neutralising capacity of the feedstock. As a result, acid dose requirements decreases for fractionation.

[0071] Overall, Figure 3, 4 A and B show that liquor acidity controls the fractionation performance and sugar stability. Therefore, it is concluded that oligomeric and monomeric C5 sugar yield and degradation as well as lignin characteristics are not only affected by process design (batchwise - semi-continuous) but also by process severity (liquor acidity).

[0072] The fractionation results of batchwise reference processing (BR) and semi-continuous processing (SCP) are shown in Figure 5. The combination of applied acid dose, feedstock acid neutralising capacity and fractionation L/S ratio resulted in variation of the fractionation liquor pH which affects the fractionation performance in both batchwise reference processing and semi-continuous processing. It is observed that the liquor acidity of BW and RG is lower than the liquor acidity of WS and AS in batch-wise processing. Similar variations in liquor acidity also observed in semi-continuous processing. This difference is related to the acid neutralising capacity of the feedstocks. Further, it is observed that the liquor transfer is lowest for WS-SCP and is highest for AS-SCP due to the applied L/S ratio of and liquor absorbance capacity of each feedstocks. Differences in liquor transfer are reflected on C5 sugars and lignin concentrations. In batch-wise processing, relatively high concentrations of C5 sugar and lignin were obtained in the wash liquid of BW and WS and less in RG and AS. Also, as can be seen from Figure 5, in semi-continuous processing, most sugar and lignin solubilization occur during step (a), followed by consecutively lower solubilization during step (b1) and (b2). Overall, it is clear that semi-continuous processing results in high product concentrations in the resulting pulping liquor and low concentrations in the wash liquids.

[0073] The fractionation results in Figures 6 and 7 are shown as function of C5 sugar solubilization as a proxy for process severity allowing for more accurate comparison between feedstocks and experiments. In Figure 6 A, the extent of C5 sugar solubilization correlates well with feedstock delignification. Overall, solubilization of C5 sugars and lignin is relatively high for herbaceous biomass (RG, WS) and lower for AS in both batch-wise processing and semi-continuous processing. Also, it is shown that semi-continuous processing results in slightly improved delignification. Figure 6 B shows higher sugar yields for semi-continuous processing than batch-wise processing. The higher yields come from slightly improved C5 sugar solubilization (Figure 6 A) and reduced sugar degradation. Further, Figure 6 C shows an inverse relation to the sugar yield with furfural formation decreasing from batchwise processing to semi-continuous processing. It is concluded that the compositions of the cellulose pulp obtained from batchwise and semi-continuous processing are mostly affected by feedstock type and fractionation process severity (liquor acidity). Overall, the results in Figures 4 - 6 show that early removal of sugars during semi-continuous fractionation increases the sugar yield, mostly by reduced degradation to furanics.

[0074] Contrary to the sugar chemistry, lignin structural changes during fractionation are more complex. Lignin solubilisation from the feedstocks occur via (acid-catalysed) cleavage of lignin β -O-4 linkages which starts with elimination of a hydroxyl group on the α -position of the linkage. This leads to formation of a carbenium ion, followed by linkage cleavage and Hibbert ketone end group formation. Both the carbenium ion as well as Hibbert ketone end groups are

involved in lignin condensation reactions and formation of stable C-C bonds. Overall, a more condensed and altered lignin hampers its application in biobased materials. In Figure 7 A, the β -O-4 content of all BR and SCP lignins are related to the feedstock delignification to include a measure for process severity. Despite some (feedstock related) variation, the SCP lignins show both improved delignification and a higher β -O-4 content as compared to the BR lignins. Reduced β -O-4 bond cleavage in the SCP lignin in turn results in less formation of condensed lignin structures as shown in Figure 7 B. This further supports the results from the C5 sugar mass balance, with again improved product yield and quality through the application of stepwise counter-current flow.

Claims

1. An organosolv fractionation process for fractionating lignocellulosic biomass into a biomass pulp and an organosolv liquor comprising:

- (a) organosolv fractionation to remove lignin and hemicellulose, comprising contacting the lignocellulosic biomass to the intermediate organosolv liquor originating from step (b) at a temperature in the range of 100 °C - 170 °C and a pH between 1.5 and 3.0, to obtain a mildly treated biomass and the organosolv liquor;
- (b) organosolv fractionation to obtain pulp, comprising contacting the mildly treated biomass originating from step (a) with an organosolv treatment liquid at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the intermediate organosolv liquor and a biomass pulp,

wherein total fractionation time of steps (a) and (b) is at least 30 min, and wherein at least one of the following applies:

- the pH during step (a) is higher than the pH during step (b);
- the temperature during step (a) is lower than the temperature during step (b);
- the duration of step (a) is shorter than the duration of step (b).

2. The organosolv fractionation process according to claim 1, wherein the organosolv fractionation of step (b) includes at least three distinct steps (b1), (b2) and (b3):

- (b1) contacting the mildly treated biomass originating from step (a) with the second intermediate organosolv liquor originating from step (b2) at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain a third intermediate organosolv liquor and a first treated biomass;
 - (b2) contacting the first treated biomass originating from step (b1) with the first intermediate organosolv liquor from step (b3) at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the second intermediate organosolv liquor and a second treated biomass,
 - (b3) contacting the second treated biomass originating from step (b2) with the organosolv treatment liquid at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the first intermediate organosolv liquor and a biomass pulp,
- wherein the third intermediate organosolv liquor is used in step (a).

3. The organosolv fractionation process according to claim 1 or 2, further comprising a washing step (c) wherein the biomass pulp obtained in step (b) is contacting with a washing liquid to obtain washed biomass pulp and spent washing liquid and wherein the spent washing liquid is used as the organosolv treatment liquid in step (b), preferably in step (b3), preferably wherein the washing step (c) includes at least two distinct steps (c1) and (c2):

- (c1) contacting the biomass pulp originating from step (b), preferably from step (b3) with the intermediate washing liquid originating from step (c2) at a temperature in the range of 100 °C - 170 °C, to obtain a spent washing liquid and an intermediate washed biomass pulp;
- (c2) washing the intermediate washed biomass pulp originating from step (c1) with a washing liquid to obtain the intermediate washing liquid and washed biomass pulp.

4. The organosolv fractionation process according to any one of claims 1 - 3, comprising:

- (a) contacting lignocellulosic biomass to the third intermediate organosolv liquor originating from step (b1) at a temperature in the range of 100 °C - 170 °C and an acidic pH above 2.0, to obtain a mildly treated biomass and the organosolv liquor;
- (b1) contacting the mildly treated biomass originating from step (a) with the second intermediate organosolv liquor

originating from step (b2) at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the third intermediate organosolv liquor and a first treated biomass;

(b2) contacting the first treated biomass originating from step (b1) with the first intermediate organosolv liquor at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the second intermediate organosolv liquor and a second treated biomass,

(b3) optionally contacting the second treated biomass originating from step (b2) with the organosolv treatment liquid at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the first intermediate organosolv liquor and a third treated biomass,

wherein the organosolv treatment liquid comprises 40 - 70 wt% organic solvent and 30 - 60 wt% water,

wherein the treated biomass obtained in step (b2), or step (b3) if performed, is the biomass pulp.

5. The organosolv fractionation process according to any one of claims 1 - 3, comprising:

(a) contacting lignocellulosic biomass to the third intermediate organosolv liquor originating from step (b1) at a temperature in the range of 100 °C - 170 °C and an acidic pH above 2.0, to obtain a mildly treated biomass and the organosolv liquor;

(b1) contacting the mildly treated biomass originating from step (a) with an organosolv treatment liquid, which is the spent washing liquid originating from step (c1) or optionally the intermediate organosolv liquor originating from step (b2) or (b3), at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the third intermediate organosolv liquor and a first treated biomass;

(b2) optionally contacting the first treated biomass originating from step (b1) with the spent washing liquid originating from step (c1) or optionally with the first intermediate organosolv liquor from step (b3), at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the second intermediate organosolv liquor and a second treated biomass;

(b3) optionally contacting the treated biomass originating from step (b1) or optionally from step (b2) with the spent washing liquid originating from step (c1) at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the first intermediate organosolv liquor and a third treated biomass;

(c1) washing the treated biomass originating from step (b1) or optionally originating from step (b2) or (b3) with a washing liquid comprising 40 - 70 wt% organic solvent and 30-60 wt% water at a temperature in the range of 100 °C - 170 °C, to obtain the spent washing liquid and the biomass pulp.

6. The organosolv fractionation process according to any one of claims 1 - 3 comprising:

(a) contacting lignocellulosic biomass to the third intermediate organosolv liquor originating from step (b1) at a temperature in the range of 100 °C - 170 °C and an acidic pH above 2.0, to obtain a mildly treated biomass and the organosolv liquor;

(b1) contacting the mildly treated biomass originating from step (a) with an organosolv treatment liquid, which is the spent washing liquid originating from step (c1) or optionally the intermediate organosolv liquor originating from step (b2) or (b3), at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the third intermediate organosolv liquor and a first treated biomass;

(b2) optionally contacting the first treated biomass originating from step (b1) with the spent washing liquid originating from step (c1) or optionally with the first intermediate organosolv liquor from step (b3), at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the second intermediate organosolv liquor and a second treated biomass;

(b3) optionally contacting the treated biomass originating from step (b1) or optionally from step (b2) with the spent washing liquid originating from step (c1) at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the first intermediate organosolv liquor and a third treated biomass;

(c1) washing the treated biomass originating from step (b1) or optionally originating from step (b2) or (b3) with an intermediate washing liquid originating from (c2) at a temperature in the range of 100 °C - 170 °C, to obtain a spent washing liquid and an intermediate washed biomass pulp;

(c2) washing the intermediate washed biomass pulp originating from step (c1) with water to obtain the biomass pulp and the intermediate washing liquid.

7. The organosolv fractionation process according to any one of the preceding claims, wherein the organosolv treatment liquid comprises water, an organic solvent and an acid catalyst, preferably wherein the organic solvent is a ketone, more preferably acetone; and/or wherein the lignocellulosic biomass is selected from herbaceous biomass, softwood, hardwood and combinations thereof, preferably the lignocellulosic biomass comprises herbaceous biomass.

8. The organosolv fractionation process according to any one of the preceding claims, wherein the steps (a) and (b) are performed at a temperature in the range of 110 °C - 160 °C, more preferably in the range of 120 °C - 150 °C; and/or wherein the step (c) is performed at a temperature in the range of 110 °C - 160 °C, more preferably in the range of 120 °C - 150 °C.
9. The organosolv fractionation process according to any one of the preceding claims, wherein step (a) is performed at a pH between 1.6 and 2.8, preferably between 1.8 and 2.6, preferably wherein step (b) is performed at a pH between 1.5 and 2.0, more preferably between 1.6 and 1.8.
10. The organosolv fractionation process according to any one of the preceding claims, wherein the biomass is extracted with an extracting liquid before conducting the organosolv treatment step in step (a), preferably wherein the extracting liquid comprises at least 50 wt% of an organic solvent selected from lower alcohols and ketones at a temperature below 100 °C.
11. The organosolv fractionation process according to claim 10, comprising:
 - (x1) optionally an aqueous pre-extraction, comprising contacting the lignocellulosic biomass with an aqueous extraction liquid to obtain an aqueous biomass extract and aqueous extracted biomass;
 - (x2) an organic pre-extraction, comprising contacting the lignocellulosic biomass or the aqueous extracted biomass with an organic extraction liquid to obtain an organic biomass extract and extracted biomass;
 - (a) organosolv fractionation to remove lignin and hemicellulose, comprising contacting the extracted biomass to the intermediate organosolv liquor originating from step (b) at a temperature in the range of 100 °C - 170 °C and a pH between 1.5 and 3.0, to obtain a mildly treated biomass and the organosolv liquor;
 - (b) organosolv fractionation to obtain pulp, comprising contacting the mildly treated biomass originating from step (a) with an organosolv treatment liquid at a temperature in the range of 100 °C - 170 °C and a pH below 2.0, to obtain the intermediate organosolv liquor and a biomass pulp.
12. The organosolv fractionation process according to any one of the preceding claims, comprising a separation step wherein lignin is isolated from the organosolv liquor of step (a).
13. The organosolv fractionation process according to any one of the preceding claims, wherein the total fractionation time is in the range of 60 - 180 min, preferably each individual step has a duration that deviates at most 50 %, preferably at most 25 %, from the average fractionation time defined as the total fractionation time divided by the total number of steps.
14. The organosolv fractionation process according to any one of the preceding claims, wherein the pH of the liquid is continuously monitored and if needed adjusted to the target pH for fractionation, preferably using a sensor or probe and acid and/or alkaline dosing system.
15. The organosolv fractionation process according to any one of the preceding claims, wherein the liquid is directly transferred from reactor to reactor and preferably the duration of the liquid outside of the reactors during the transfer is below 1 min, more preferably below 10 s per transfer.

Fig. 1A

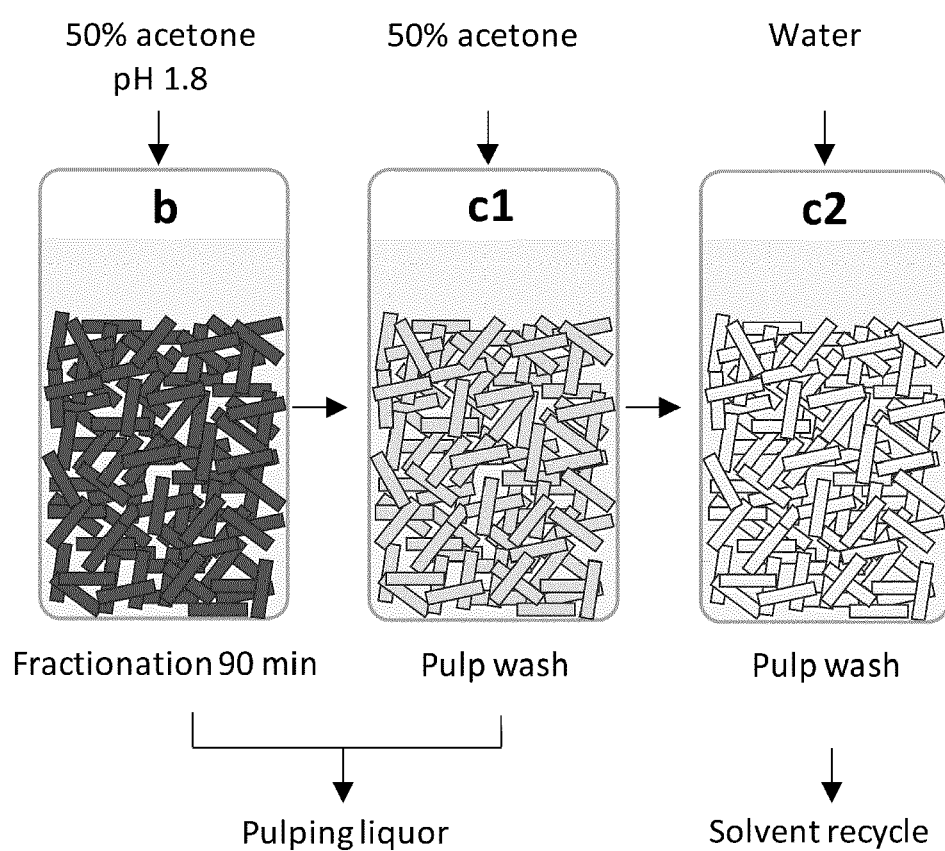


Fig. 1B

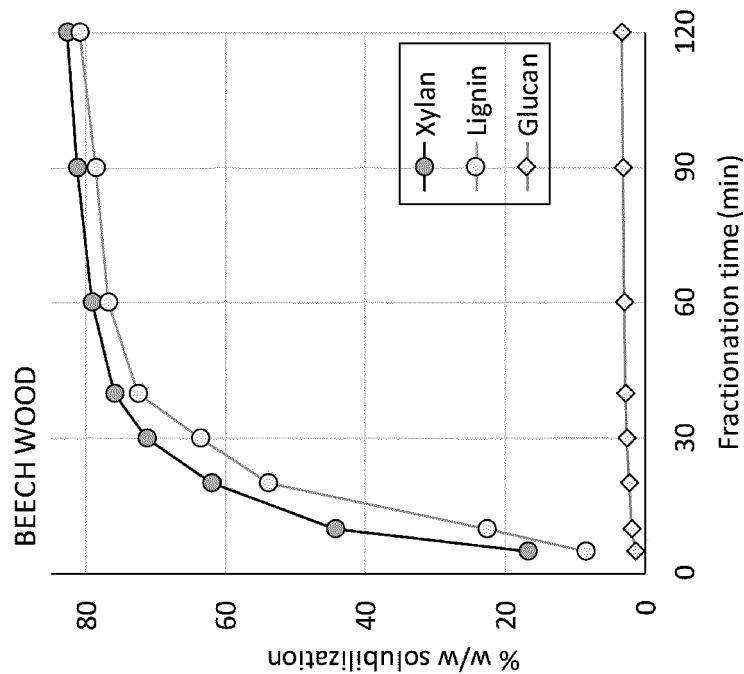


Fig. 1C

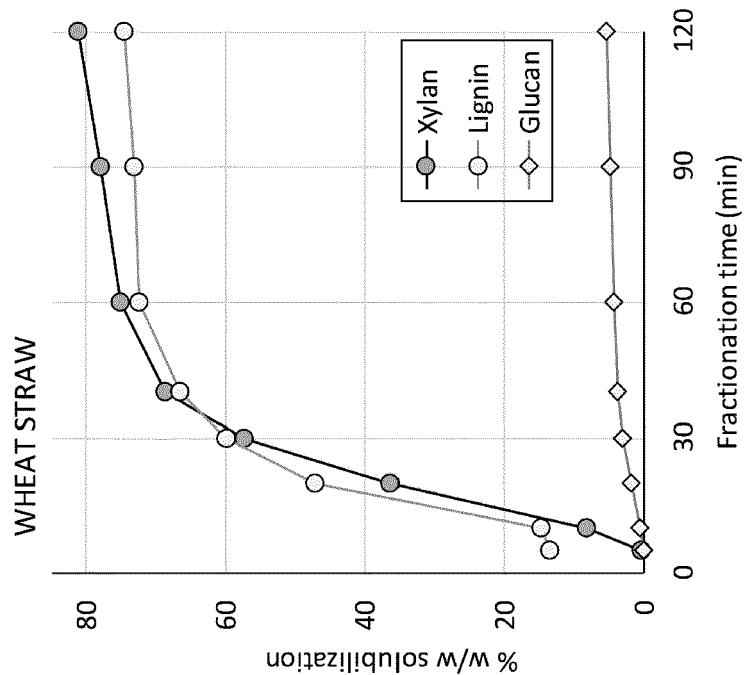


Fig. 2

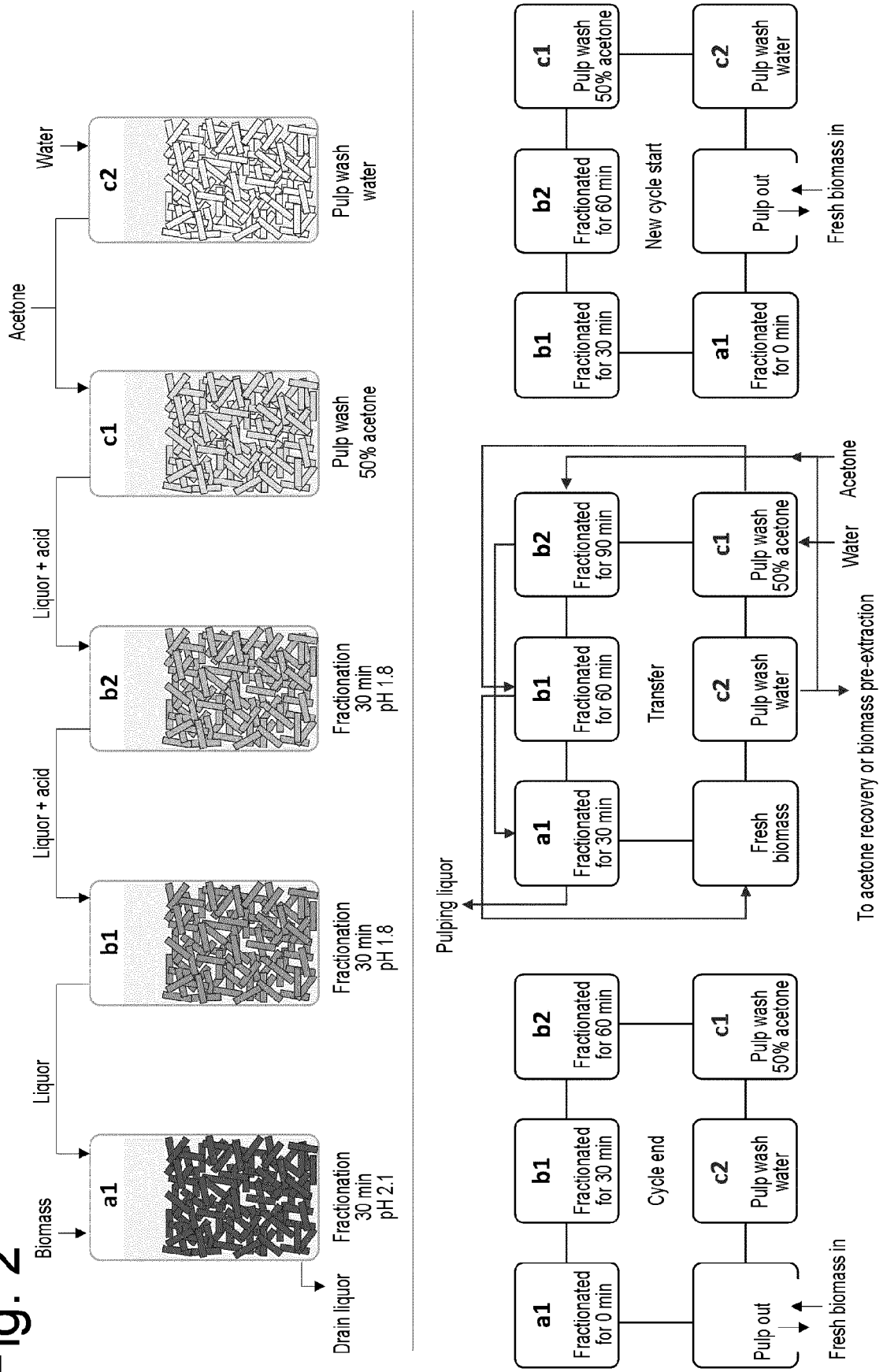


Fig. 3

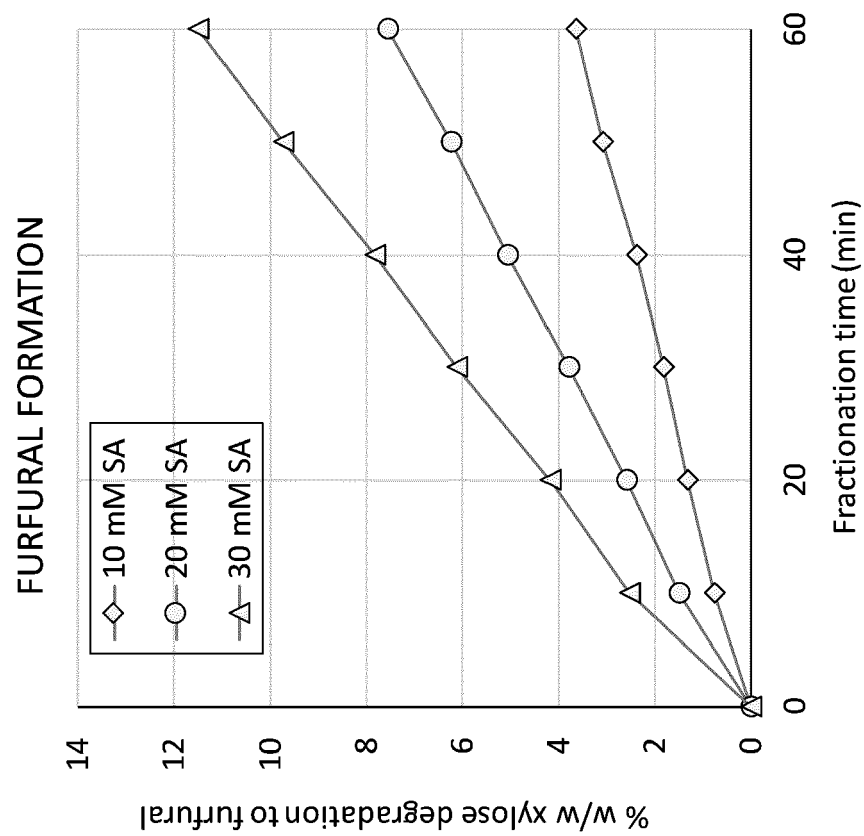


Fig. 4A

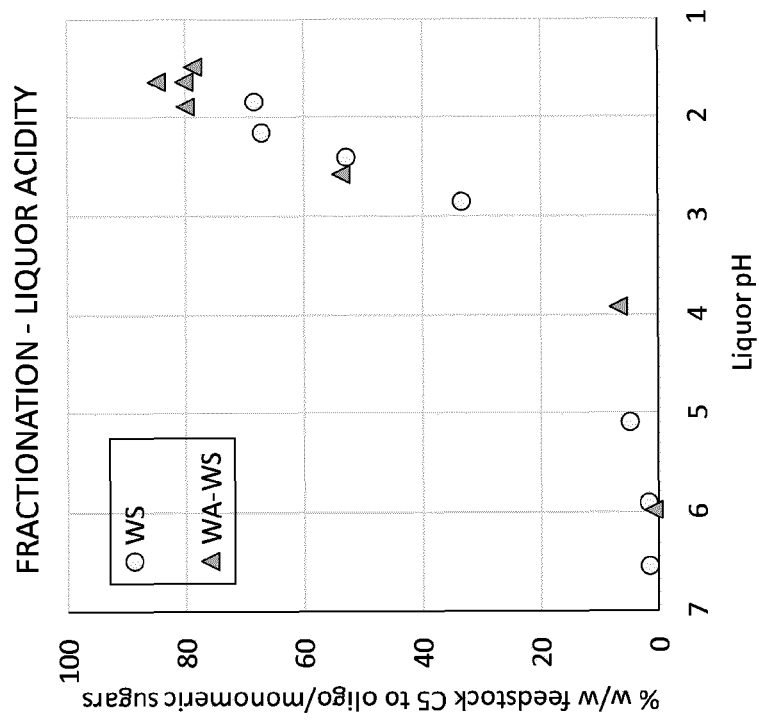


Fig. 4B

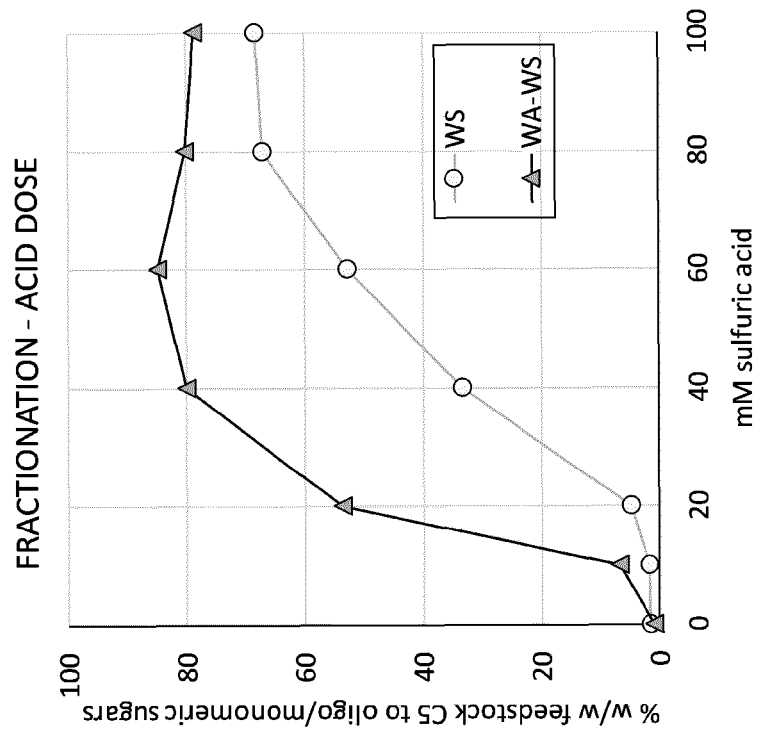


Fig. 5

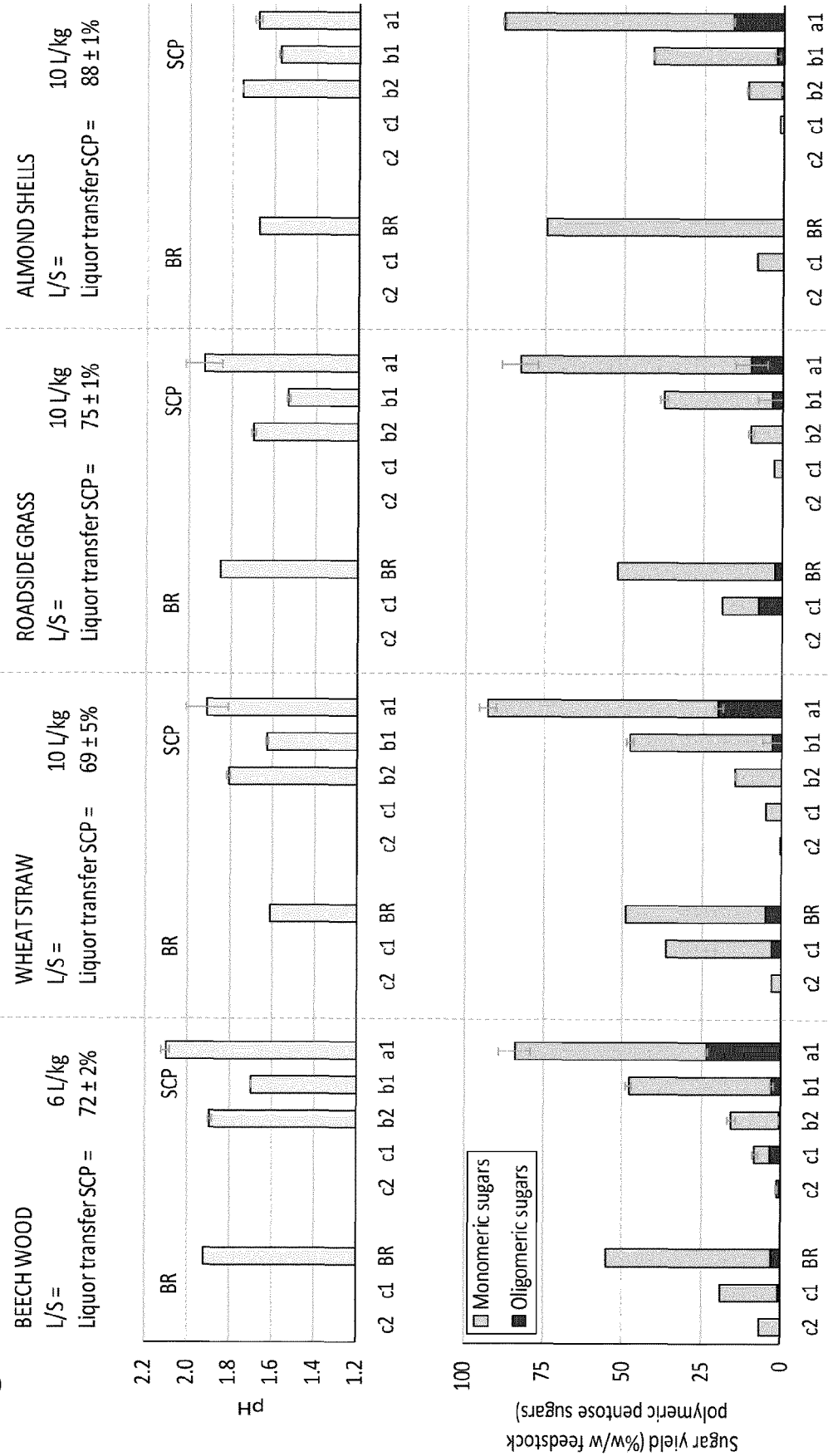


Fig. 6A

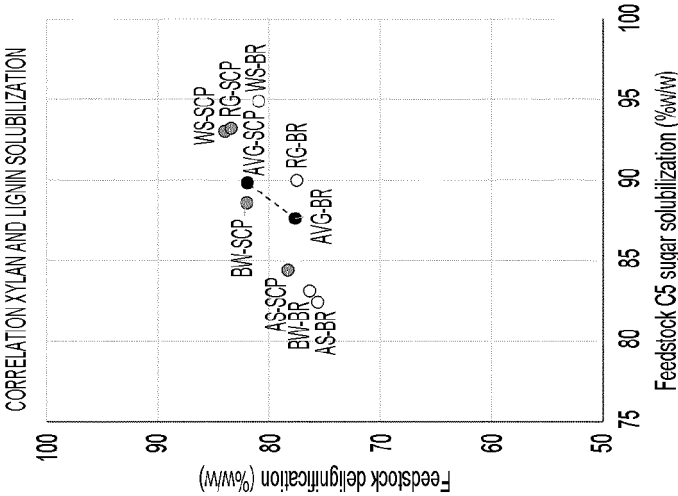


Fig. 6B

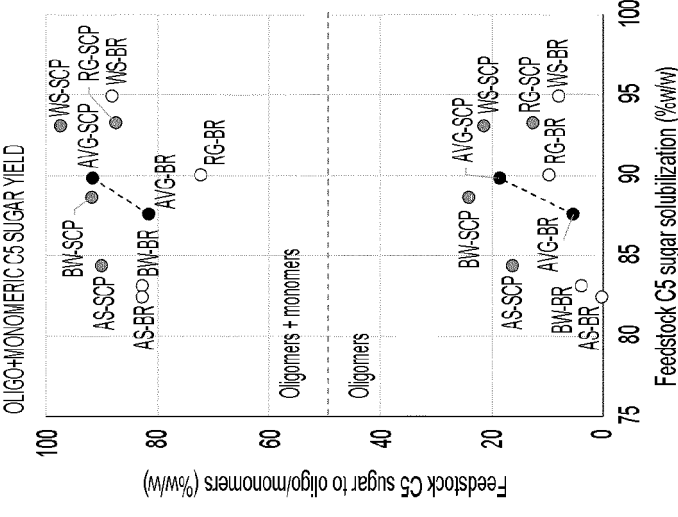


Fig. 6C

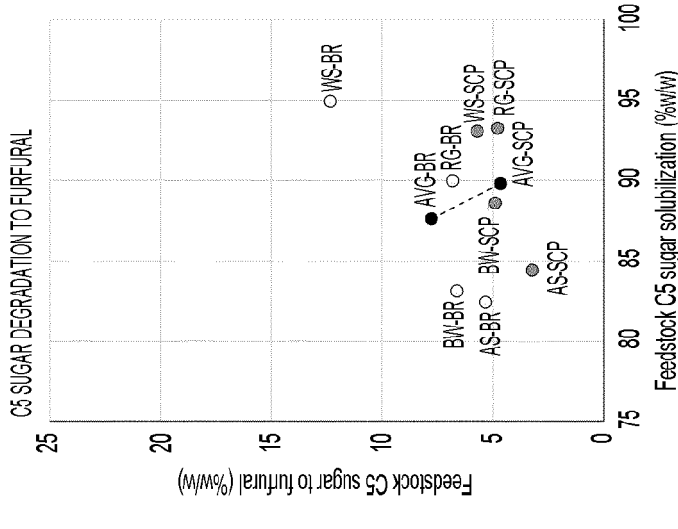


Fig. 7A

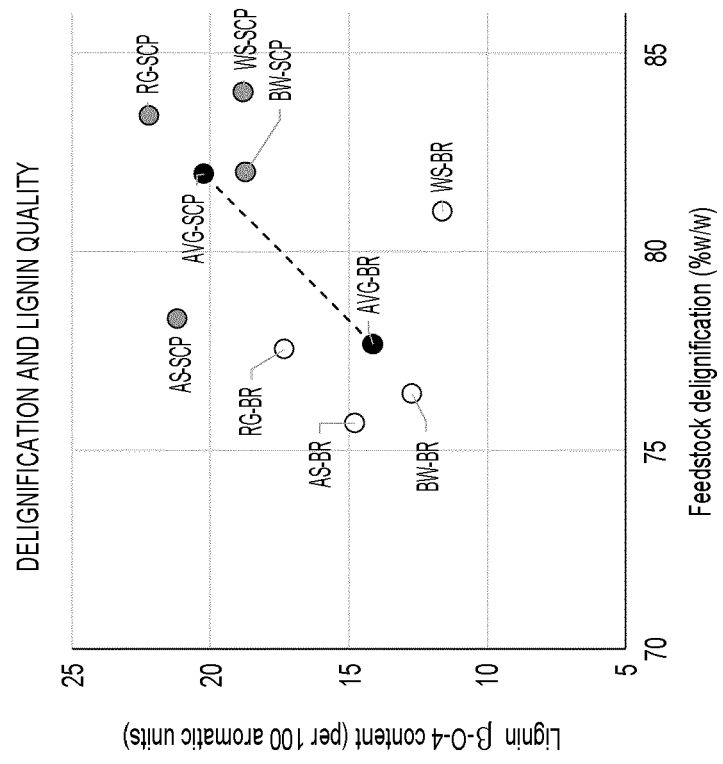
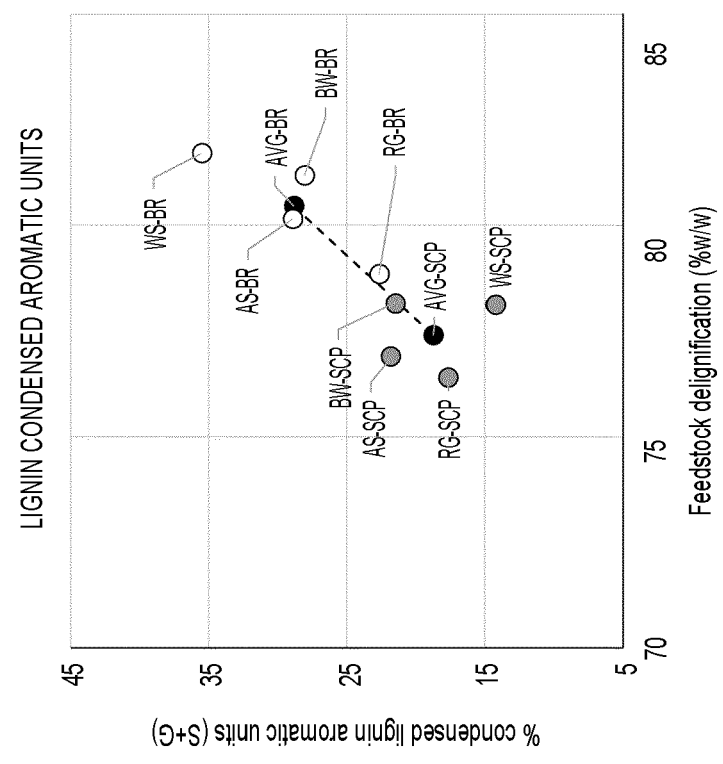


Fig. 7B





EUROPEAN SEARCH REPORT

Application Number

EP 23 20 6718

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 4 941 944 A (CHANG ROBERT P [CA]) 17 July 1990 (1990-07-17) * column 2, line 24 - line 60 * * column 3, line 30 - line 38 * * column 4, line 59 - column 5, line 15; figure 1 * * column 5, line 39 - line 68 * * claims 1-14 * -----	1-15	INV. D21C3/04 C08H8/00 D21C3/20 D21C11/00
A	US 2012/184721 A1 (WINGERSON RICHARD C [US] ET AL) 19 July 2012 (2012-07-19) * paragraphs [0007], [0018], [0019] * * paragraphs [0067], [0068]; figure 1 * -----	1-15	
A	US 4 100 016 A (DIEBOLD VINCENT B ET AL) 11 July 1978 (1978-07-11) * claims 1-15; figure 1 * -----	1-15	
A	WOUTER J. J. HUIJGEN ET AL: "Pretreatment and Fractionation of Wheat Straw by an Acetone-Based Organosolv Process", INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH, vol. 49, no. 20, 20 October 2010 (2010-10-20), pages 10132-10140, XP055112723, ISSN: 0888-5885, DOI: 10.1021/ie101247w * abstract * * page 10133 * -----	1-15	TECHNICAL FIELDS SEARCHED (IPC) D21C C09J C08H
A	WO 2008/017145 A1 (EMICELLEX ENERGY CORP [CA]; FALLAVOLLITA JOHN ALLAN [CA]) 14 February 2008 (2008-02-14) * paragraph [0080] - paragraph [0087] * -----	1-15	
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 3 April 2024	Examiner Billet, Aina
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 23 20 6718

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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03-04-2024

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