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(54) Title: PROCESS FOR THE SEPARATION OF LEVULINIC ACID FROM BIOMASS

(57) Abstract: The invention provides a process to separate levulinic acid from a composition obtained by acid hydrolysis of biomass said process comprising subjecting said composition to solvent-solvent extraction to yield an organic phase comprising levulinic acid, and an aqueous phase; subjecting said organic phase to nanofiltration to yield a permeate comprising levulinic acid and a retentate; and recovering said permeate. The process is very suitable to remove any colour and humins (soluble tar), which would otherwise form a problem in subsequent process steps, particularly in distillation. Consequently, the process is simpler and results in higher yields of levulinic acid.



PROCESS FOR THE SEPARATION OF LEVULINIC ACID FROM BIOMASS

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Field of the invention

The present invention relates to a process for the separation of levulinic from a biomass hydrolysate.

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Background of the invention

Levulinic acid is a starting molecule for the synthesis of esters known as fuel additive and is known to be useful as plasticizers and solvents. Levulinic acid can be used to synthesize methyl tetrahydrofuran (MTHF) or can be used as a solvent. Other applications of levulinic acid are for example the synthesis of delta-amino levulinic acid used as herbicides and pesticides, diphenolic acid used to synthesize polycarbonates and succinic acid used to make polyesters. Levulinic acid can also be used to produce gamma valerolactone (5-methylbutyrolactone), which in turn can be used for production of adipic acid (1,6-hexanedioic acid).

Levulinic acid can be produced from furfuryl alcohol. It is also possible to produce levulinic acid by acid hydrolysis of biomass although this is not commercially practiced.

Levulinic acid can be produced by acid hydrolysis of lignocellulosic feedstocks. Production of levulinic acid by acid hydrolysis of biomass is described e.g. in US2010312006, US5,608,105, US4,897,497, and US6,054,611. Levulinic acid can be used for the synthesis of esters known as fuel additive and known to be useful as plasticisers and solvents. Levulinic acid can be used to synthesize methyl tetrahydrofuran (MTHF), used as a solvent. Other applications of levulinic acid are for example the synthesis of delta-amino levulinic acid used as herbicides and pesticides, diphenolic acid used to synthesize polycarbonates, and succinic acid used to make polyesters. Levulinic acid can also be used to produce gamma-valerolactone (5-methylbutyrolactone), which in turn can be used for production of adipic acid (1,6-hexanedioic acid). Adipic acid is an important precursor for inter alia the production of polyamides such as Nylon 6,6. The most important process to produce adipic acid is

based on oil and starts from benzene. A disadvantage of this process is that it is based on fossil derived oil. Another disadvantage is the evolution of NO_x during the oxidation step, which either is vented to the air, which is highly undesirable as it is a greenhouse gas, or its catalytically destroyed, which is an expensive process. New processes for the production of adipic acid have been developed based on butadiene. However, such processes are also environmentally unfavourable. A third production route to produce adipic acid involves the use of levulinic acid via the following reaction sequence: levulinic acid; gamma-valerolactone; methylpentenoate; dimethyladipate, adipic acid. It is highly desirable to produce polymers such as nylon-6,6 from renewable resources. Such a process reduces the total amount of CO₂ emitted for its production and thus helps to mitigate against global warming. In addition, it helps to slow down the depletion of fossil resources. Levulinic acid may be produced from agricultural waste products or waste from the paper industry or municipal waste and therefore constitutes a renewable source of a C-5 fragment.

A disadvantage of the production of levulinic acid by acid hydrolysis of biomass is the formation of tar (also called humins, char, lignin-based char).

US2010312006 describes the isolation of levulinic acid from a biomass hydrolysate including a solvent-extraction step. In the process of US2010312006, insoluble char articles are isolated from the biomass hydrolysate at high temperature and pressurized conditions.

However, the inventors found that when a biomass hydrolysate, even when the solids have been prior removed by a solid-liquid separation step, is subjected to solvent-extraction, the resulting organic phase not only contains levulinic acid but also contains soluble tar, and has a yellow-brown colour. This means that the levulinic acid is not sufficiently pure. Moreover, such soluble tar may create problems during later isolation steps, particularly in a later distillation. For example, soluble tar may accumulate in the distillation residue and form a sticky, almost solid layer which is difficult to remove.

Summary of the invention

The present invention provides an improved process for the separation of levulinic acid from a biomass hydrolysate. The process involves a combination of solvent extraction and nanofiltration, whereby the organic phase obtained after solvent extraction is subjected to the nanofiltration. The process of the invention allows for the

removal of humins (= soluble tar) and colour, which prevents problems in the subsequent isolation of levulinic acid, particularly in distillation. This increases the yield of levulinic acid. The process makes use of ability of the solvent in the organic phase to keep the humins in solution. Thus, adding a solvent is not required. If desired, the
5 nanofiltration can be repeated (diafiltration), which removes even more colour and humins.

Legend to the Figures

Figures 1 and 2 are flow diagrams representing preferred processes. Fig 1:
10 distillation between solvent-extraction and nanofiltration and optional recycle of the distillation residue to the solvent-extraction. Fig 2: distillation after nanofiltration, and optional recycle of the distillation top fraction (solvent) to the solvent-extraction.

Detailed description of the invention

15 The invention provides a process to separate levulinic acid from a composition obtained by acid hydrolysis of biomass said process comprising:

- subjecting said composition to solvent-solvent extraction to yield an organic phase comprising levulinic acid and an aqueous phase;
- subjecting said organic phase to nanofiltration to yield a permeate comprising
20 levulinic acid and a retentate; and
- recovering said permeate.

The inventors have surprisingly found that a combination of solvent-extraction and nanofiltration is an efficient way to separate levulinic acid from colour and humins.
25 More specifically, subjecting a biomass hydrolysate to solvent-extraction, and then subjecting the resulting organic phase to nanofiltration removes most of the humins from the organic phase. Levulinic acid ends up in the permeate, whilst most of the humins end up in the retentate.

From the art, it would not be obvious to combine solvent-extraction with
30 nanofiltration. US5,608,105 and US4,897,497 describe the production of levulinic acid by acid hydrolysis of biomass. These publications do not describe or demonstrate how to isolate levulinic acid. They are silent on the use of solvent-extraction and also on the formation, or removal of soluble tar.

Alonso *et al.* (ChemSusChem 2011, vol 4, pp 1078-1081) present a schematic process to produce fuels from biomass, starting with acid hydrolysis of biomass resulting in levulinic acid including a solvent-extraction step using 2-sec-butylphenol as solvent to extract levulinic acid. Alonso *et al.* remove insoluble materials (lignin, char) from the liquid product mixture using a pressure filter system.

The conditions of the acid hydrolysis of biomass are such that they may result in the formation of levulinic acid, as well as tar and/or humins. In acid hydrolysis of biomass, C6 carbohydrates such as glucose are converted to levulinic acid and formic acid. Suitable biomass comprises cellulose and/or hemicellulose, preferably the biomass comprises lignocellulose. Suitable acids in the acid hydrolysis process are sulphuric acid, hydrochloric acid, and phosphoric acid. A preferred acid is sulphuric acid, preferably diluted sulphuric acid, for example at a concentration between 1.5 – 3%. The temperature in the acid hydrolysis process may depend on the source of carbohydrates, and may range between 150-250°C, preferably between 170-240°C, more preferably between 190-230°C, even more preferably between 200 and 220°C. Said process may comprise one, two, or more stages. The pressure may also depend on the source of carbohydrates, as well as on the temperature, and may be anywhere between 1 and 50 bar, preferably between 5 and 40 bar, even more preferably between 10 and 30 bar. Suitable reactors include plugflow reactors, backmix reactors, and CSTR reactors. Different reactors for different stages may be used. The skilled person will understand that the reaction time in the process to convert a carbohydrate to a bio-based product depends on the reaction temperature, the pressure, as well as the source of carbohydrate and the concentration of the acid. At higher reaction temperatures the reaction time may be shorter in order to obtain the desired bio-based product, whereas at lower reaction temperatures the reaction time may be longer in order to obtain the desired bio-based product. Likewise, at lower pressure, the reaction time may be longer whereas at higher pressure the reaction time may be shorter. The skilled person may therefore, without undue burden, establish suitable conditions with respect to temperature, reaction time, and pressure in order to obtain the desired bio-based product. The reaction time may vary between one second and one day, preferably between 10 seconds and one hour.

Suitable carbohydrates to be converted to levulinic acid in the acid hydrolysis reaction include sugar, such as glucose and fructose, disaccharides such as saccharose and lactose; polysaccharides such as cellulose and starch; wood; lumber

processing side products such as saw dust, wood chippings and wood shavings; cellulosic material e.g. from lignocellulosic feedstock; grass; cereal; starch; algae; tree bark; hay; straw; leaves; paper pulp, and dung, particularly herbivore dung. Paper pulp, or simply pulp, is a lignocellulosic fibrous material obtained by prepared by chemically or mechanically separating cellulose from wood, fibre crops or waste paper. Pulp is rich in cellulose and other carbohydrates. The carbohydrates may be bound to a component, such as to lignin. Lignocellulosic feedstock typically has a fibrous nature and comprises a bran fraction that contains the majority of lignocellulosic (bran) fibers. As an example, corn fiber is a heterogeneous complex of carbohydrate polymers and lignin. It is primarily composed of the outer kernel covering or seed pericarp, along with 10–25% adherent starch. Carbohydrate analyses of corn fiber vary considerably according to the source of the material.

Normally, the conditions of the acid hydrolysis reaction are such that other compounds are also formed, such as 2,5(hydroxymethyl) furfuraldehyde, ethoxymethyl furfuraldehyde, furfuraldehyde, formic acid, acetic acid, angelica lactone, and/or valerolactone. Thus, the composition preferably also comprises 2,5(hydroxymethyl) furfuraldehyde, methoxymethyl furfuraldehyde, furfuraldehyde, formic acid, acetic acid, angelica lactone, and/or (gamma)valerolactone.

The composition also comprises tar. Except when stated otherwise, in the context of the invention “tar” is understood to include char and humins. Formation of tar, for example from lignin, is well known in the production of levulinic acid and other compounds from biomass. Tar can be soluble or insoluble. Char (sometimes also referred to as “coke”) always refers to insoluble (particulate) tar, whereas soluble tar is usually referred to as humins. Yang and Sen (Chem. Sus. Chem. 2010, vol. 3, 597-603) report the formation of humins during production of fuels from carbohydrates such as fructose. They speculate that humins are formed by acid-catalyzed dehydration. According to US7,896,944 the molecular weight of humins ranges from 2.5 to 300 kDa. Char can be removed from a biomass hydrolysate by simple solid/liquid separation such as filtration. Due to their solubility, however, humins cannot be removed by solid/liquid separation step, and will be present, together with the levulinic acid, in the liquid fraction after solid/liquid filtration of the biomass hydrolysate. In the context of the invention, humins shall refer to soluble tar, whereas char shall refer to insoluble tar. The composition therefore comprises humins. Of course, the solubility of humins may depend on the solvent in which it is present. Generally, humins are soluble in water:

after solids removal, the resulting liquid fraction of a biomass hydrolysate is usually yellowish-browish colour, which is mostly caused by the (soluble) humins. At least part of these humins will end up in the organic phase after solvent-extraction. In fact, the process of the invention uses the propensity of humins to stay soluble, or even increase
5 their solubility, in an organic phase, preferably in the solvent used in solvent-extraction, e.g. MTHF.

After the acid hydrolysis reaction, levulinic acid is separated from the humins and preferably also from any other compounds such as 2,5(hydroxymethyl)furfuraldehyde, methoxymethylfurfuraldehyde, furfuraldehyde,
10 formic acid, acetic acid, angelica lactone, and valerolactone.

The first step of the process of the invention involves subjecting the composition obtained by acid hydrolysis of biomass to solvent-extraction. In the context of the invention, "extraction", "solvent extraction", and "solvent-solvent extraction" are understood to be the same. Extraction is a process for separating components (the
15 solutes) of a liquid (the feed) by contact with a second liquid phase (the solvent). The two liquids must not be completely mutually miscible. The process takes advantage of differences in the chemical properties of the feed components, such as differences in polarity and hydrophobic/hydrophilic character to separate them (T.C. Frank, L.Dahuron, B.S. Holden, W.D. Prince, A.F. Seibert, L.C. Wilson, Liquid-liquid extraction
20 and other liquid-liquid operations and equipment in Perry's Chemical Engineering Handbook, 8th Edition, Section 15). Solvent extraction commonly (but not necessarily) takes place with an aqueous solution as one liquid and an organic solvent or mixture of solvents as the other. Numerous solvents with various properties are used in solvent extraction (Y.Marcus, Principles of Solubility and Solutions, in J. Rydberg, M. Cox, C.
25 Musicas, G.R. Chopin (Editors), Solvent Extraction Principles and Practice, 2nd Edition, Chapter 2, Marcel Dekker Inc., New York). Extraction capacity of a solvent can be adjusted by changing process parameters like temperature or pH. Two streams result from the extraction: an extraction phase, which is an organic phase comprising the levulinic acid, also referred to as extract, and an aqueous phase, also referred to as
30 raffinate.

The aqueous phase may comprise salts, acid and other water-soluble components, and can be discarded.

The composition in the process of the invention may be subjected to the extraction by adding a suitable solvent to yield an organic phase and an aqueous phase. Suitable solvents include solvent as defined below.

In an embodiment, prior to the extraction, the composition is subjected to a solid / liquid separation. Any solids which may be present in the composition obtained from a process to convert carbohydrates to levulinic acid, such as char, may hamper the membrane separation or the extraction, so they are preferably removed prior to the subsequent step. Solid-liquid separation is concerned with mechanical processes for the separation of liquids and finely divided insoluble. Solid / liquid separation results in concentrated solids and a clearer solution. The solids may be discarded as co-product and the liquid can be subjected to the extraction. Examples of suitable solid / liquid separation are filtration, centrifugation, sedimentation, hydrocyclone and flotation.

In another embodiment, the composition is concentrated, e.g. by evaporation. A combination of concentration and solid-liquid fractionation is also possible. The composition is usually aqueous and may for example be in the form of a solution or a suspension.

In the next step of the process of the invention, the organic phase is subjected to nanofiltration. After the solvent-extraction, levulinic acid will predominantly be in the organic phase. However, humins will usually be distributed between the aqueous and the organic phase. This means that at least part of the humins are present in the organic phase together with the levulinic acid. These humins may cause problems, such as fouling, in subsequent separation steps, particularly in a later distillation step. Therefore, the organic phase is subjected to nanofiltration in order to remove some or all of the humins. This is particularly advantageous if the nanofiltration is done in the presence of a solvent, because the organic phase may act as the solvent. Thus, less, or even no separate solvent needs to be added prior to the nanofiltration. To facilitate the nanofiltration, a solvent as defined above may be added to the organic phase.

Nanofiltration involves separation of one or more dissolved components from one or more other dissolved components. Nanofiltration is to be distinguished from other types of filtration. For example, filtration is commonly used as a way to remove solid particles having a size larger than 5 micron. As such, it is a form of solid-liquid separation. Nanofiltration, on the other hand, relates to particles < 5 micron and dissolved particles. From suspended particles of 5 micron down to about 0.1 micron the process is termed microfiltration, while below that the term ultrafiltration applies.

Nanofiltration makes use of a (nanofiltration) membrane, and as such this technique is a membrane filtration technique, or membrane separation technique.

Nanofiltration membranes can be characterized by their MWCO, Molecular Weight Cut Off, which describes the retention performance of a membrane. Cut off is defined as that molecular weight which is 90% rejected by the membrane. The retention or rejection, R , is defined as $R=100\%(1-C_p/C_f)$. Wherein C_p is the permeate concentration and C_f is the feed concentration of the membrane. In a continuous system, the feed concentration will be more or less constant, whereas in a batch-system the feed-concentration will increase. A suitable hand book for membrane separation, including nanofiltration, is "Basic principles of membrane technology by Marcel Mulder, published 1991 by Kluwer Academic in Dordrecht, Netherlands).

The membrane used in the nanofiltration is preferably impermeable for molecules having a molecular weight of 100 kDa or more. Such membranes can be easily selected by the skilled person based on the molecular weight cut off (MWCO).

In the context of the invention "impermeable for molecules having a molecular weight of 100 kDa or more" does not necessarily mean that all molecules having a molecular weight of 100 kDa or more are retained by the membrane used in the nanofiltration. "Impermeable for molecules having a molecular weight of X kDa or more" means that at least 90 wt% of an X kDa solute is retained by the membrane (wherein "X" refers to the molecular weight). Preferably the membrane used in the nanofiltration is impermeable for molecules having a molecular weight of 50 kDa or more, more preferably of 10 kDa or more, 5 kDa or more, even more preferably 2 kDa or more, 1 kDa or more, even more preferably 500 Da or more, even more preferably 300 Da or more.

The membrane used in the nanofiltration is preferably permeable to molecules having a molecular weight of 400 Da or less. "Permeable to molecules having a molecular weight of 400 Da or less" does not necessarily mean that all molecules having a molecular weight of 400 Da or less will end up in the permeate. "Permeable for molecules having a molecular weight of X Da or less" therefore means that at least 90 wt% of an X Da solute will end up in the permeate. More preferably the membrane used in the nanofiltration is permeable to molecules having a molecular weight of 200 Da or less, even more preferably to molecules having a molecular weight of 100 Da or less.

Nanofiltration membranes are commercially available and well described in "Nanofiltration: Principles and Applications" by Anthony Gordon Fane et al. 2005,

published by Elsevier, Oxford. Another hand book on membrane separation is "Filters and Filtration Handbook", Ken Sutherland, 2008, published by Elsevier, Amsterdam. Well-known nanofiltration membranes for acid separation in aqueous media are for example Koch MPS34 (pH 0-14), Nadir NP30 (pH 0-14) and GE-Osmonics KH.

5 Nanofiltration membrane separation is preferably conducted as crossflow nanofiltration which may be performed using a nanofiltration material having a cut off for normal alkanes dissolved in toluene giving 90% rejection at 300 Da.

The transmembrane pressure in the nanofiltration is preferably 5-60 bar, the crossflow velocity is preferably 0.1-10 m/s, and the temperature is preferably in the

10 range of 25-100°C.

The inventors have found that when the nanofiltration is done by subjecting the organic phase obtained by solvent-extraction, that is, in the presence of an organic solvent, humins are efficiently separated from the levulinic acid. At the same time, adding an organic solvent is not required, since the organic phase itself acts as a

15 solvent to carry out the nanofiltration. If the separation process includes a later distillation step, which will often be the case, a distillate, preferably a distillate low in or even free of levulinic acid, can be fed back to the extraction to act as a solvent. Such continuous process may require no or little addition of solvent, may efficiently separate levulinic acid from humins, and may avoid or reduce any fouling if distillation columns or

20 accumulation of residue in distillation.

Preferably at least 50% w/w, more preferably at least 70% w/w, more preferably at least 80% w/w, 90% w/w, even more preferably at least 95% w/w of any humins in the composition are retained in the retentate.

The process of the invention may comprise the step of adding a solvent,

25 preferably an organic solvent. The solvent may be added prior to the extraction and/or prior to the nanofiltration or both. If solvent is added prior to the extraction and prior to the nanofiltration preferably the same solvent is added. Suitable solvents include alcohols, such as methanol, ethanol, propanol, butanol; ketones, such as for example methylbutylketone; ethers, such as for example anisole (methyl phenyl ether), 2,5,8-trioxanonane (diglyme), diethylether, tetrahydrofuran, 2-methyl-tetrahydrofuran,

30 diphenylether, diisopropylether and the dimethylether of di-ethyleneglycol; esters, such as for example ethyl acetate, methyl acetate, dimethyl adipate and butyrolactone; amides, such as for example dimethylacetamide and N-methylpyrrolidone; sulfoxides and sulphones, such as for example dimethylsulphoxide, di-isopropylsulphone,

sulfolane (tetrahydrothiophene-2,2-dioxide) 2-methylsulfolane and 2-methyl-4-ethylsulfolane. Other organic solvents may also advantageously be used such as DCM (dichloromethane), DCE (dichloroethene), toluene, benzene, 2-Heptanone, Butyl acetate, 1,2-Dichloroethane, Methyl isobutyl ketone, Dichloromethane, Ethyl propionate, 2-Pentanone, Diethyl ether, t-Amyl alcohol, Butanol, Cyclohexanone, Ethyl acetate, Pyridine, Tetrahydrofuran, 2-Butanone, Acetone, Dioxane, Acetonitrile, Methanol, N,N-Dimethylformamide, Dimethyl sulfoxide, Formamide, Ethylene glycol, 2-ME-THF (2-methyl tetrahydrofuran), MTBE (methyl-ter-butylether), MiBK (methyl isobutylketone), HOAc (acetic acid), CPMe (cyclopentyl methylether), heptane, DMF (dimethyl formamide), NMP (N-methylpyrrolidone), 2-sec-butylphenol (SBP), 4-n-pentylphenol (NPP), 4-n-hexylphenol (NHP), THF (tetrahydrofuran), MTHF (methyl-tetrahydrofuran) and DEGDME (diethyleneglycol dimethylether).

The amount of solvent is not critical. It may not be important to keep the amount of solvent to a minimum, because the permeate including levulinic acid can be fed back to a distillation. In fact, it may be preferred to add more solvent since this may facilitate the nanofiltration.

In an embodiment, the nanofiltration is carried out using a solvent-resistant nanofiltration membrane. The inventors have surprisingly found that solvent-resistant nanofiltration results in very efficient removal of humins. Apparently, solvent-resistant nanofiltration membranes are permeable for levulinic acid, but impermeable for humins. The advantage of combining solvent-extraction with solvent-resistant nanofiltration is that the levulinic acid and humins are already in an organic phase, and thus no solvent needs to be added prior to subjecting the organic phase to the solvent-resistant nanofiltration, saving solvent and process time.

Solvent-resistant membranes are known in the field and are commercially available. The preparation of solvent-resistant membranes is known and is described e.g. by P. Vandezande et al., Chem. Soc. Rev., 2008, vol 37, 365-405. Peeva et al. [Nanofiltration Operations in Non-aqueous Systems, Comprehensive Membrane Science and Engineering, 2010, Chapter 2.05, Pages 91-113, L.G. Peeva, M. Sairam, A.G. Livingston] describe the characteristics of a number of solvent-resistant nanofiltration membranes to be used in non-aqueous systems. Suitable solvent-resistant nanofiltration membranes include STARMEM(TM) nanofiltration membranes, produced by UOP ((MET-Evonik, UK), or other polyimide based membranes. These may be employed in spiral wound modules, typically using pressure in the region of 60

bar. These preferably consist of hydrophobic integrally skinned asymmetric membranes with active surfaces manufactured from polyimides. An active skin layer of preferably less than 0.2mm in thickness with a pore size of preferably less than 5 nm covers the PI membrane body. Examples of suitable STARMEM nanofiltration membranes are StarmemTM-122, which has an MWCO of 220 g/mol, StarmemTM 120 having a MWCO of 200 g/mol, and StarmemTM 240 having a MWCO of 400 g/mol. Suitable membranes are stable in alcohols (e.g., butanol, ethanol, and iso-propanol); in alkanes (e.g., hexane and heptane); in aromatics (e.g., toluene and xylene); in ethers (e.g., methyl-tert-butyl-ether); in ketones (e.g., methyl-ethyl-ketone and methyl-isobutyl-ketone); or in other organic solvents (e.g., butyl acetate and ethyl acetate).

The process can be carried out using one, two or more membrane(s) or using one, two or more membrane module(s). Depending on the separation power of the membrane and the desired retention, the desired retention can be achieved by connecting a plurality of membranes or membrane modules in series. The arrangement in series can be effected so that either the retentate or the permeate, preferably the permeate, of a first nanofiltration is passed as feed to a further nanofiltration. Any further nanofiltration (s) following the first nanofiltration can be carried out under the same conditions as the first nanofiltration or under different conditions, in particular different temperatures or pressures. Also membrane cascade systems comprising ultrafiltration, nanofiltration and reverse osmosis could be used in the invention.

The nanofiltration may comprise one or more membranes. If it comprises multiple membranes, said membranes are preferably used in the form of membrane modules. In these modules, the membranes are arranged so that liquid flows over the retentate side of the membranes in such a way that the concentration polarization of the components separated off (the enrichment of the components separated off at the membrane) can be countered and, in addition, the necessary driving force (pressure) can be applied. After the membrane separation, the permeate is collected (recovered). The permeate can be collected in the permeate collection space on the permeate side of the membranes and discharged from the module. Customary membrane modules for polymer membranes have the membranes in the form of membrane disks, membrane cushions or membrane pockets. Customary membrane modules for membranes based on ceramic supports have these in the form of tubular modules. The membrane modules preferably have open-channel cushion module systems in which the membranes are thermally welded or adhesively bonded to form membrane pockets or

cushions or open-channel (wide-spacer) rolled modules in which the membranes are adhesively bonded or welded to form membrane pockets or membrane cushions and rolled up together with spacers to form a permeate collection tube or have the membrane modules in tubular modules. Membrane modules which have open-channel
5 inflow systems in which the membranes are thermally welded or adhesively bonded to form membrane pockets or membrane cushions can be procured from, for example, Solsep (The Netherlands), Borsig/GMT (Germany) Bio Pure Technology (Israel), Koch Membrane (USA) and Evonik-MET Duramem, Puramem, UOP-MET, Starmem (United Kingdom). Membrane modules which have the tubular membranes on a ceramic
10 support can be procured from, for example, Inopor (Germany) membranes, a spin-off company of HITK (Germany) / Fraunhofer_IKTS (Germany).

To avoid deposits on the membrane, the process is preferably carried out so that the nanofiltration, or, if the process comprises more two or more nanofiltration steps, the first nanofiltration, is carried out at a flow velocity at the membrane ranging
15 from 0.1 to 15 m/sec, preferably from 0.2 to 4 m/sec, more preferably from 0.3 to 1 m/sec.

The nanofiltration yields a retentate and a permeate. Preferably the yield of the levulinic acid in the permeate is preferably at least 50% w/w relative to the amount of levulinic acid in the composition prior to the nanofiltration, preferably the yield is at least
20 60% w/w, more preferably at least 70% w/w, more preferably at least 80% w/w, 90% w/w, even more preferably at least 95% w/w.

In the nanofiltration preferably at least 50% w/w, more preferably at least 70% w/w, more preferably at least 80% w/w, 90% w/w, even more preferably at least 95% w/w of humins in the composition is retained in the retentate.

25 The levulinic acid may be separated from colour. The colour may be present in the composition. Colour of the composition may be for example yellow to brown to black. Colour may be indicative of the presence of contaminants, particularly humins. Humins are a common problem in the production of bio-based products by acid hydrolysis of biomass, and although it may be difficult to define humins on molecular
30 level, they are generally regarded as soluble, coloured, undesired components. Moreover, colour itself also presents a possible problem in a levulinic acid preparation, as colour is generally undesired. Levulinic acid itself is colourless, so most of the colour in the composition or the organic phase is believed to come from humins or other products or contaminants.

The (amount of) colour of the composition, the retentate, or the composition can be quantitatively determined by absorption or extinction spectrometry. Any simple spectrophotometer is suitable which is able to measure wavelengths anywhere between 400 and 800 nanometres. Colour may be correlated with the amount of contaminants, particularly with (soluble) humins, and measuring the colour is a convenient means to quantify the amount of such contaminants in the composition, the organic phase, the permeate, and in the retentate; and thus to quantify the efficiency of the nanofiltration step in removal of contaminants such as) humins.

Colour can be expressed as OD (optical density). A suitable wavelength is 600 nm. For example, if the OD at 600 nm and 1 cm path length of the organic phase is 1.0, the OD in the retentate at 600 nm and 1 cm path length is preferably at least 0.5, more preferably at least 0.7, more preferably at least 0.8, 0.9, even more preferably at least 0.95; most preferably the OD in the retentate at 600 nm and 1 cm path length is 1.0.

If the colour is too intense to be measured, the sample (permeate, retentate etc) can be diluted with water or solvent before taking the OD. Alternatively, the shorter path length may be used, e.g. 1 mm. Suitable OD values (after optional dilution) may range between 0.1 and 2. The skilled person knows how to dilute samples prior to measuring the OD and to calculate the amount of humins, and how to correct for dilution and volume. If desired, a calibration curve can be made using a humin solution of known concentration. Alternatively, the OD can be used to quantify the efficiency of the solvent resistant nanofiltration in relative terms. For example, if the OD of a composition, at a certain wavelength and path length, corresponds to 1.0, and the OD of the retentate corresponds to 0.2 (correcting for dilution and volume), the amount of colour, and thus of humins, in the retentate has decreased by 80%.

After extraction, part of the colour of the composition will end up in the organic phase, together with the levulinic acid. In other words, solvent-extraction may not remove all of the humins. This is undesired. Using solvent-resistant nanofiltration may advantageously remove part, or even most of the colour.

In an embodiment, at least 50%, more preferably at least 70%, more preferably at least 80%, 90%, even more preferably at least 95% of colour of the composition is retained in the retentate, as measured by absorption or extinction spectrophotometry at a wavelength of between 400 and 800 nm.

In another embodiment, at least 50%, more preferably at least 70%, more preferably at least 80%, 90%, even more preferably at least 95% of colour of the

organic phase is retained in the retentate. The permeate preferably has little colour. Preferably the permeate is yellow to colourless; more preferably light-yellow to colourless.

5 The nanofiltration may comprise diafiltration. In diafiltration, the retentate obtained by a first nanofiltration is washed by adding a solvent and subjected to a subsequent nanofiltration. This may be repeated several times. Diafiltration may result in an even higher yield.

The process may further comprise distillation to yield a distillate and a distillation residue. The distillation may be done after the nanofiltration.

10 In an embodiment, the next step of the process of the invention involves subjecting the permeate of the nanofiltration to distillation to yield a distillate and a distillation residue. One or more distillates comprising one or more bio-based products, including levulinic acid, may be recovered, or may be subjected to subsequent distillation. The distillation residue may be also recovered and be subjected to a subsequent nanofiltration.

15 In another embodiment, prior to subjecting the organic phase to the nanofiltration, said organic phase is first subjected to a distillation to yield a distillate and a distillation residue, and said distillation residue is then subjected to the nanofiltration. Said distillation residue may comprise any remaining levulinic acid and any remaining humins. Optionally a solvent is added prior to subjecting the distillation residue to said nanofiltration. One or more of the distillate(s) may be fed back to extraction.

20 Depending on their boiling points, several distillation units (a so-called "train") may be required to separate more than one bio-based product. If there is more than one distillation unit, the process of the invention will comprise more than one distillate; within the context of the invention "a distillate" is understood to include the two or more distillates. The levulinic acid will normally be driven off and condensed in one or more of the distillates. The composition will typically comprise water.

25 The process may comprise one, two, or more distillations and/or one, two, or more nanofiltration steps. In the context of the invention, the term "the distillation" does not necessarily mean that there is only one distillation. Similarly, "the nanofiltration" does not necessarily mean that there is only one nanofiltration; the process may comprise other, previous and/or subsequent nanofiltration steps.

Said distillation residue preferably comprises levulinic acid and/or humins. If the distillation residue comprises humins, it may also contain levulinic acid, and this levulinic acid may be dissolved in these humins. Even though humins are soluble, they may accumulate over the course of the distillation which may result in a viscous distillation residue. The viscosity may depend on the concentration of the distillation residue and/or the concentration of tar and/or humins therein, and may be anywhere from slightly viscous to solid. It may have the consistency of syrup, or a gum. It may even be very hard, almost glass-like. Without using the nanofiltration step, such accumulated humins would eventually become so viscous, that it would not be flowable anymore, and it would stick to the wall of the distillation. To keep the distillation residue flowable (so it can be removed from the distillation), the inventors realized that a certain amount of levulinic acid had to be present in the residue. This levulinic acid acts as a solvent for the humins. However, when such distillation residue is discarded from the distillation, the levulinic acid is discarded with it, which is undesired as it constitutes a loss.

In contrast, in the process of the invention, where the organic phase is subjected to nanofiltration, humins can be effectively removed, resulting in less or even no humin accumulation in the distillation residue, and this avoids the necessity to keep levulinic acid in the distillation residue. This increases the yield of levulinic acid.

The distillation may yield one, two, three, four, or more distillates, depending on the number of other bio-based products in the composition and their boiling points. The concentration % (w/w) of levulinic acid in the distillate is preferably higher than the concentration % (w/w) of said levulinic acid in the distillation residue, both based on total dry weight. Preferably the ratio of the concentration % (w/w) of levulinic acid in the distillate over the concentration of levulinic acid in the distillation residue is at least 2, more preferably at least 4.

The distillation residue may be fed to a subsequent extraction or a subsequent nanofiltration. The distillation residue may be diluted with a solvent before it is subjected said subsequent extraction or a subsequent distillation, preferably using a solvent which is suitable for dilution of the distillation residue. Preferably such solvent is also suitable to be used in said distillation. The way in which the distillation residue is diluted is not critical. An easy way of diluting the distillation residue is to simply add the solvent to the distillation residue and mix. It may be preferred to stir so as to ensure that the solvent and the distillation residue are well mixed. Diluting the distillation residue

with the solvent may reduce the viscosity of said distillation residue. This may facilitate removal of the distillation residue from the distillation unit.

In an embodiment, the process comprises recycling solvent from the distillation back to the solvent-extraction. Recycling the solvent (e.g. the top fraction of the distillation) to the solvent-extraction may advantageously save consumption of solvent and may allow operating the process in a continuous way. Not necessarily all solvent is to be recycled to the solvent-extraction. The solvent of the solvent-extraction can be collected as the top fraction of the distillation, and part or all of said top fraction may be recycled to the solvent-extraction.

In another embodiment, the process of the invention comprises recycling the distillation residue back to the solvent-extraction. Levulinic acid may be recovered as a distillate. However, some levulinic acid may be present in the distillation residue. Feeding such distillation residue back to the solvent-extraction advantageously allows for the process to be operated in a continuous mode, i.e. the process is preferably a continuous process, and may result in an increase in the yield of levulinic acid. The process of the invention can be operated in a continuous way without the need to remove humins from a distillation unit: levulinic acid can easily be separated and collected in the distillate and any levulinic acid present in the distillation residue can simply be recycled to the solvent-extraction.

In a levulinic acid separation process comprising a solvent-extraction step and a distillation step, but without the nanofiltration step, humins would end up in the distillation residue, together with a certain amount of levulinic acid in order to keep the residue flowable. If one tried to conduct such a process in a continuous fashion, recycling such distillation residue to the solvent-extraction would result in accumulation of humins in the process stream. Humins would build up in the distillation residue, resulting in fouling. Instead, such a process would require to discard the distillation residue, and any levulinic acid present with it, meaning suboptimal yield of levulinic acid.

The process also allows for lower temperatures in subsequent distillation steps. High distillation temperatures, which are commonly used in the art, may not be required in order to recover as much as possible from the levulinic acid, because the levulinic acid, may not end up in a distillation residue. Lower distillation temperatures may also be advantageous from a cost (energy) perspective, they may be environmentally beneficial, safe in operation to personnel, and may require less stringent distillation

equipment. Lower distillation temperatures may also be desired to prevent deterioration or degradation of levulinic acid. For example, US5,189,215 describes that high distillation temperatures may negatively affect storage stability of levulinic acid and may result to browning of the product. The distillation may be done using smaller distillation columns, requiring less vacuum requirements, meaning lower energy costs, lower installation costs, and less waste (less product may be degraded into waste), contributing to sustainability. It also leads to less fouling of the distillation columns and/or less downtime of the process.

The invention will be further elucidated with reference to the following examples, without however being limited thereto.

EXAMPLES

Example 1

Reaction mixtures were obtained via acid hydrolysis of a carbohydrate. Levulinic acid (LA), formic acid (FA) and furfuraldehyde (F) were measured with HPLC analysis in the resulting mixture. The concentration range of various aqueous solutions was: 1-5 wt% of LA, 0.5 to 3 wt% of FA and 0.1 to 5 wt% F. The aqueous solution contained also about 2 w% of sulphuric acid. The aqueous solution was contacted with the MTHF to test its capacity for the extraction of the carboxylic acids. Equal volumes (50 ml) of the aqueous and organic phase were placed in a jacketed vessel. In such a vessel temperature was controlled and maintained constant at a pre-set value. The experiments were performed at 25°C and 60°C. After a predetermined time (minimum 5 minutes) in which the equilibrium is attained, samples from both phases were taken and diluted with acetonitrile to prevent phase splitting. The composition of each phase was analysed. At 25°C measured partitioning coefficients between MTHF and water were: levulinic acid 1.44, formic acid 1.62, furfuraldehyde 6.00. At 60°C measured partitioning coefficients between MTHF and water were: levulinic acid 1.34, formic acid 1.09, furfuraldehyde 6.02.

Example 2

A reaction mixture is obtained via acid hydrolysis of wood (sieved fraction less than 1 mm in size) in an aqueous environment. Reaction conditions: H₂SO₄, 4% w/w;

temperature, 195°C; pressure, 20 bar (kept constant using nitrogen); time, 30 minutes. Levulinic acid (LA), furfuraldehyde (F), and 2,5(hydroxymethyl)furfuraldehyde (HMF) are measured with GC-FID analysis in the resulting mixture. Formic acid (FA) is also measured. Via a solid/liquid separation, using a 0.2 µm filter, the undissolved tar and suspended humins are separated. The dissolved tar and humins in the mixture are estimated at 15 wt% of the total mixture. Presence of these dissolved humins and dissolved tar is indicated by a strong dark brown color of the solution. The prefiltrated solution is extracted with methyltetrahydrofuran (MTHF) as solvent. The organic phase is separated from the aqueous phase. An amount of 150 kg of the organic phase is fed to a distillation column operated at ambient pressure to reclaim the MTHF. Subsequently the bio-based products are fed to a sequence of vacuum distillation columns, operated at a top pressure of respectively 500 mbars, 200 mbars, 50 mbars and 20 mbars to remove the furfuraldehyde, MMF, HMF and LA as topproducts. 5 kg is left in the residue of the final column, containing the humins and dissolved tars. An amount of 5 kg of the residue is mixed with 30 kg gram of solvent and then nanofiltrated on a pilot crossflow membrane test unit. Pressure is set on 30 bars and temperature kept on 40°C. The tested membrane is a spiral wound membrane (7 m²), Starmem 122 solvent resistant nano filtration membrane, produced by UOP ((MET-Evonik, UK). An amount of 15 kg permeate is produced. The color of the clear obtained permeate is light yellow. The flux on average is 12 l/m².h. The permeate and the feed are analysed. The calculated retention $(1 - C_{\text{permeate}}/C_{\text{feed}})$ for LA, F, and HMF range from -10 to 3%. Subsequently, 15 kg of solvent is added to 15 kg retentate and nano-filtrated again. This diafiltration step is repeated 3 times in total, allowing more than 80% recovery of the products for LA, F, and HMF and full retention of the humins and dissolved tar. The 45 kg permeate is recycled and combined with a new batch 150 kg of phase-E and processed in the same way as described above. The final product yield of levulinic acid is in this process 10% higher than without recycle.

Example 3

A reaction mixture is obtained via acid hydrolysis of wood (sieved fraction less than 1 mm in size) in an aqueous environment. Reaction conditions: H₂SO₄, 4% w/w; temperature, 195°C; pressure, 20 bar (kept constant using nitrogen); time, 30 minutes. Levulinic Acid (LA), Furfuraldehyde (F), and 2,5(hydroxymethyl) furfuraldehyde (HMF) are measured with GC-FID analysis in the resulting mixture. Formic acid (FA) is also

measured. Via a solid/liquid separation, using a 0.2 μm filter, the undissolved tar and suspended humins are separated. The dissolved tar and humins in the mixture are estimated at 15 wt% of the total mixture. Presence of these dissolved humins and dissolved tar is indicated by a strong dark brown color of the solution. The prefiltrated solution is extracted with methyltetrahydrofuran as solvent. The solvent is separated from water. An amount of 150 kg of the organic phase is nanofiltrated on a pilot crossflow membrane test unit. Pressure is set on 30 bars and temperature kept on 40°C. The tested membrane is a spiral wound membrane (7 m²), Starmem 122 solvent resistant nano filtration membrane, produced by UOP ((MET-Evonik, UK). An amount of 135 kg permeate is produced. The color of the clear obtained permeate is light yellow. The flux on average is 10 l/m².h. The permeate and the feed are analysed. The calculated retention $(1 - C_{\text{permeate}}/C_{\text{feed}})$ for LA, F, and HMF ranges from -10 to 3%. An amount of 135 kg of permeate is distilled in a sequence of vacuum distillation columns, operated at a top pressure of respectively 500 mbars, 200 mbars, 50 mbars and 20 mbars to remove the furfuraldehyde, MMF and HMF. LA is obtained in the distillation residue of the final column; 0.5 kg distillation residue is recycled to the nanofiltration and combined with a new batch 150 kg of the organic phase and processed in the same way as described above. The final product yield of levulinic acid is in this process 15% higher than without recycle.

Example 4

A reaction mixture was obtained via acid hydrolysis of a carbohydrate. Levulinic Acid (LA), Formic Acid (FA) and Acetic Acid (AA) were measured with HPLC analysis in the resulting mixture. Presence of humins and dissolved tar was indicated by brown color of the solution and via UV-VIS spectrophotometry. The absorption of a dilute sample was measured at 425 nm. The samples were diluted with solvent (15 g Sample + 85 g MTHF). In addition the transmission was recorded. An amount of 547.9 gram of reaction mixture was mixed for 2 hours with 453,4 gram solvent MTHF at 25 °C. The MTHF top layer was darker in color than the water layer. The MTHF top layer had an pH of 0.85 and a conductivity of 7 $\mu\text{S}/\text{cm}$. The water bottom layer had an pH of 0.89 and a conductivity of 115 mS/cm. Subsequently, the top layer was separated and 408.4 gram of this layer was subjected to Solvent Resistant Nano Filtration, SRNF. The MTHF layer contained 1.07 w% LA, 0.19 w% FA and 0.10 w% AA. An amount of 327.9 gram of this reaction mixture was nanofiltrated on a laboratory crossflow membrane test unit,

type CM Celfa P28. Pressure was set up to 9 bars and temperature constant kept on 40°C. The six tested flat-sheet membranes had a surface area of 28 cm². ONF-1, ONF-2 were obtained from Borsig-GMT, Puramem-S from Evonik-MET, Starmem 122 and 240 from UOP (via Evonik-MET), Solsep 030705 from Solsep. Results see Table 1.

5

Table 1.

		LA	FA	AA	Color	Color
		(w/w)%	(w/w)%	(w/w)%	T%	Abs (-)
Retentate	Borsig ONF-2	1,07	0,19	0,10	12,4	0,897
Permeate	Borsig ONF-2	0,73	0,16	0,09	96,0	0,025
Retentate	Borsig ONF-1	1,19	0,19	0,10	4,6	1,339
Permeate	Borsig ONF-1	0,85	0,17	0,09	89,3	0,051
Retentate	Puramem-S	1,19	0,19	0,10	3,1	1,573
Permeate	Puramem-S	0,93	0,16	0,09	88,3	0,052
Retentate	Starmem 122	1,17	0,19	0,09	1,6	1,807
Permeate	Starmem 122	1,12	0,18	0,09	83,6	0,077
Retentate	Solsep 030705	1,17	0,19	0,09	1,1	2,021
Permeate	Solsep 030705	1,07	0,17	0,09	13,8	0,860
Retentate	Starmem 240	1,14	0,18	0,09	0,6	2,235
Permeate	Starmem 240	0,97	0,16	0,08	85,0	0,069

The flux at concentration factor 1.2, was between 8 and 37 l/m².h. The permeate and retentate, at a concentration factor 1.2, were analysed. The retention ($1 - C_{\text{permeate}}/C_{\text{retentate}}$) for LA, FA, AA and humins were calculated and presented in Table 2.

10

Table 2

Membrane	Flux [kg/m ² /h] CF < 1.2	Pressure [bar]	LA Ret [%]	FA Ret [%]	AA Ret [%]	Humin Ret [%]
ONF-2	24	9	32	16	14	97
ONF-1	25	9	28	14	11	96
Puramem-S	25	9	22	18	13	97
Starmem 122	29	5	4	3	1	96
Solsep 030705	37	3	9	8	10	57
Starmem 240	8	9	15	7	6	97

The colour of all permeates were light yellow, except for the Solsep 030705 permeate which was brown. This difference in color/humins is confirmed by the transmission and absorption numbers. The Starmem 122 shows good humin and dissolved tar retention and excellent permeability for LA, FA and AA.

5

Example 5

A reaction mixture was obtained via acid hydrolysis of a carbohydrate. Levulinic Acid (LA), Formic Acid (FA) and Acetic Acid (AA) were measured with HPLC analysis in the resulting mixture. Furfuraldehyde (F) is also measured. An amount of 725 gram of reaction mixture was mixed for 2 hours with 600 gram solvent MTHF at 25 °C. Subsequently, the top layer was separated. The MTHF layer contained 1.07 w% LA, 0.19 w% FA and 0.10 w% AA. An amount of 501 gram of this MTHF with reaction mixture was nanofiltrated on a laboratory crossflow membrane test unit, type CM Celfa P28. Pressure was set on 5 bars and temperature kept on 40°C. The tested membrane was a flatsheet membrane (28 cm²), Starmem 122 solvent resistant nano filtration membrane. An amount of 204 grams permeate was produced. The color of the clear permeate was light yellow. At a concentration factor of 2, the flux was of 24 l/m².h. The flux at concentration factor 1.4, 2.5, 4, 6, 9 was respectively 28, 25, 22, 18 and 15 l/m².h. The permeate, at a concentration factor 9, and the feed were analysed. The calculated retention $(1 - C_{\text{permeate}}/C_{\text{retentate}})$ for F, LA, FA, AA and color/humins were respectively 1%, -4%, 2%, 3% and 95%. Subsequently, 400 gram of MTHF was added to 100 gram retentate and nano-filtrated again. This diafiltration step is repeated 4 times in total, allowing more than 98% recovery of the products for F, LA, FA and AA and good retention of the humins and dissolved tar. In total 2000 g of permeate was distilled via two falling film distillation units to remove the solvent. The first falling film distillation unit was operating at 90°C and 500 mbars pressure. A second falling film distillation unit was operated at 120°C and 200 mbars. 80% of FA, 90% of AA, 100% of F and 100% of LA was recovered in the bottom of the second falling film evaporator and the solvent level was reduced to less than 1 %. Subsequently the furfuraldehyde, LA, F, AA and FA mixture was distilled in a batch distillation column operated with a top pressure of 20 mbars to separate and purify the components.

Example 6

A reaction mixture is obtained via acid hydrolysis of wood (sieved fraction less than 1 mm in size) in an aqueous environment. Reaction conditions: H₂SO₄, 4% w/w; temperature, 195°C; pressure, 20 bar (kept constant using nitrogen); time, 30 minutes. Levulinic Acid (LA), Formic Acid (FA) and Acetic Acid (AA) are measured with HPLC analysis in the resulting mixture. Furfuraldehyde (F) is also measured. Via a solid/liquid separation, using a 0.2 µm filter, the undissolved tar and suspended humins are separated. The dissolved tar and humins in the mixture are estimated at 15 wt% of the total mixture. Presence of these dissolved humins and dissolved tar is indicated by a strong dark brown color of the solution. The prefiltrated solution is extracted with methyltetrahydrofuran (MTHF) as solvent. The organic phase is separated from the aqueous phase. An amount of 150 kg of the organic phase is fed to a distillation column operated at ambient pressure to reclaim the MTHF. Subsequently the biobased products are fed to a sequence of vacuum distillation columns, operated at a top pressure of respectively 500 mbars, 200 mbars, 50 mbars and 20 mbars to remove the Furfuraldehyde (F), Formic Acid (FA) and Acetic Acid (AA) and Levulinic Acid (LA), top-products. An amount of these valuable products are left in the residue of the final column, containing the humins and dissolved tars. An amount of 5 kg of the residue is mixed with 30 kg gram of solvent and then nanofiltrated on a pilot crossflow membrane test unit. Pressure is set on 30 bars and temperature kept on 40°C. The tested membrane is a spiral wound membrane (7 m²), Starmem 122 solvent resistant nano filtration membrane, produced by UOP ((MET-Evonik, UK). An amount of 15 kg permeate is produced. The color of the clear obtained permeate is light yellow. The flux on average is 12 l/m².h. The permeate and the feed are analysed. The calculated retention ($1 - C_{\text{permeate}}/C_{\text{retentate}}$) for Levulinic Acid (LA), Formic Acid (FA), Furfuraldehyde (F) and Acetic Acid (AA) range from -5 to 3%. Subsequently, 15 kg of solvent is added to 15 kg retentate and nano-filtrated again. This diafiltration step is repeated 3 times in total, allowing more than 80% recovery of the products for LA, AA, F, and FA and full retention of the humins and dissolved tar. The 45 kg permeate is recycled and combined with a new batch 150 kg of phase-E and processed in the same way as described above. The final product yield of levulinic acid is in this process 10% higher than without recycle.

Example 7

A reaction mixture is obtained via acid hydrolysis of wood (sieved fraction less than 1 mm in size) in an aqueous environment. Reaction conditions: H₂SO₄, 4% w/w; temperature, 195°C; pressure, 20 bar (kept constant using nitrogen); time, 30 minutes. Levulinic Acid (LA), Formic Acid (FA) and Acetic Acid (AA) are measured with HPLC analysis in the resulting mixture. Furfuraldehyde is also measured. Via a solid/liquid separation, using a 0.2 µm filter, the undissolved tar and suspended humins are separated. The dissolved tar and humins in the mixture are estimated at 15 wt% of the total mixture. Presence of these dissolved humins and dissolved tar is indicated by a strong dark brown color of the solution. The prefiltrated solution is extracted with methyltetrahydrofuran as solvent. The solvent is separated from water. An amount of 150 kg of the organic phase is nanofiltrated on a pilot crossflow membrane test unit. Pressure is set on 30 bars and temperature kept on 40°C. The tested membrane is a spiral wound membrane (7 m²), Starmem 122 solvent resistant nano filtration membrane, produced by UOP ((MET-Evonik, UK). An amount of 135 kg permeate is produced. The color of the clear obtained permeate is light yellow. The flux on average is 10 l/m².h. The permeate and the feed are analysed. The calculated retention ($1 - C_{\text{permeate}}/C_{\text{retentate}}$) for Levulinic Acid (LA), Formic Acid (FA), Furfuraldehyde (F) and Acetic Acid (AA) range from -5 to 3%. An amount of 135 kg of permeate is distilled in a sequence of vacuum distillation columns, operated at a top pressure of respectively 500 mbars, 200 mbars, 50 mbars and 20 mbars to remove the Levulinic Acid (LA), Furfuraldehyde (F), Formic Acid (FA) and Acetic Acid (AA) via the top. An amount of these valuable products are left in the residue of the final column, containing the humins and dissolved tars. An amount of 0.5 kg of this distillation residue is recycled to the nanofiltration and combined with a new batch 150 kg of the organic phase and processed in the same way as described above. The final product yield of levulinic acid is in this process 15% higher than without recycle.

CLAIMS

1. Process to separate levulinic acid from a composition obtained by acid hydrolysis of biomass said process comprising:
 - 5 - subjecting said composition to solvent-solvent extraction to yield an organic phase comprising levulinic acid, and an aqueous phase;
 - subjecting said organic phase to nanofiltration to yield a permeate comprising levulinic acid and a retentate; and
 - recovering said permeate.
- 10 2. Process according to claim 1 wherein said composition comprises colour, and where at least 50% of said colour is retained in the retentate, as measured by absorption or extinction spectrophotometry at a wavelength of between 400 and 800 nm.
3. Process according to claim 1 or 2 wherein said composition comprises humins and wherein at least 50 % w/w of said humins are retained in the retentate.
- 15 4. Process according to any one of claim 1-3 wherein said nanofiltration is carried out using a membrane which is impermeable for molecules having a molecular weight of 1 kDa or more.
5. Process according to any one of claim 1-4 wherein said nanofiltration is carried out using a solvent-resistant nanofiltration membrane.
- 20 6. Process according to any one claim 1-5 wherein the process comprises the step of adding an organic solvent prior to subjecting the organic phase to said nanofiltration.
7. Process according to any one of claim 1-6 further comprising distillation to yield a distillate and a distillation residue.
- 25 8. Process according to claim 7 comprising subjecting the permeate of the nanofiltration to said distillation.
9. Process according to claim 7 wherein prior to subjecting the organic phase to the membrane separation said organic phase is first subjected to said distillation to yield a distillate and a distillation residue, and wherein said distillation residue is subjected to the nanofiltration.
- 30 10. Process according to any one of claim 7-9 further comprising recycling solvent from the distillation back to the solvent-extraction.

11. Process according to any one of claim 7-10 further comprising recycling said distillation residue back to the solvent-extraction.

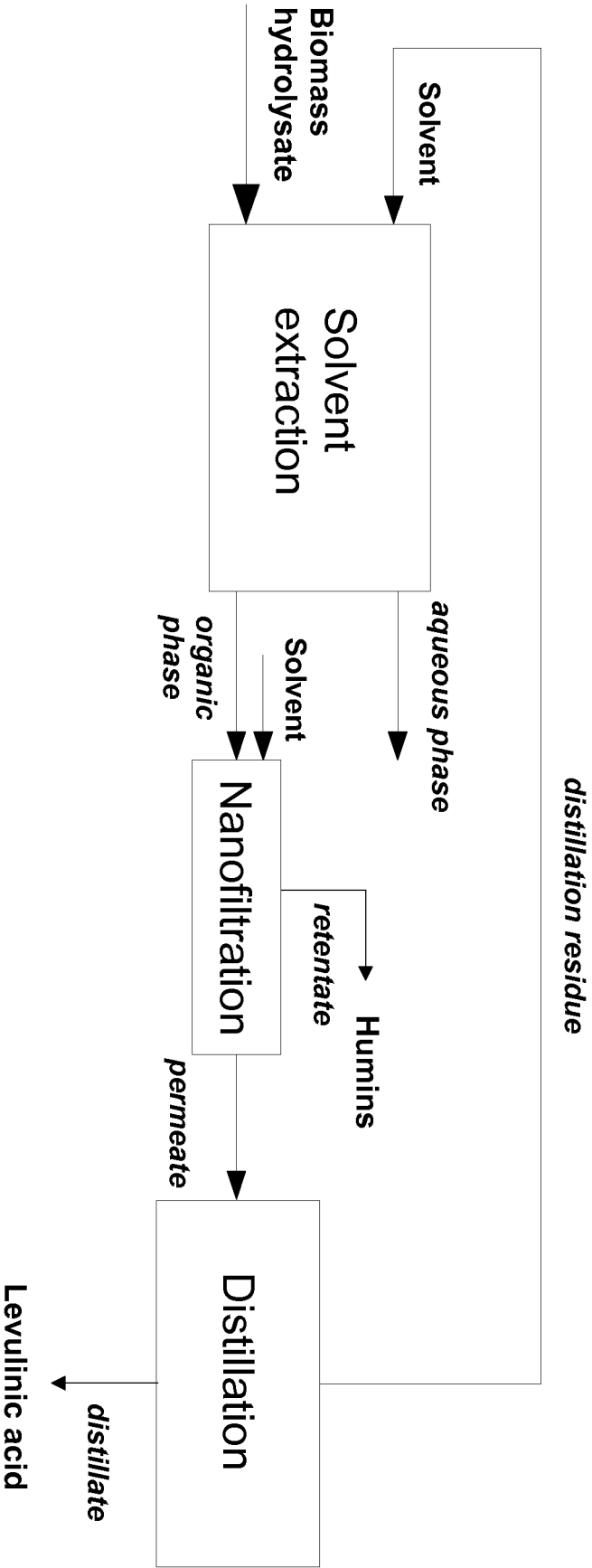


Fig. 1

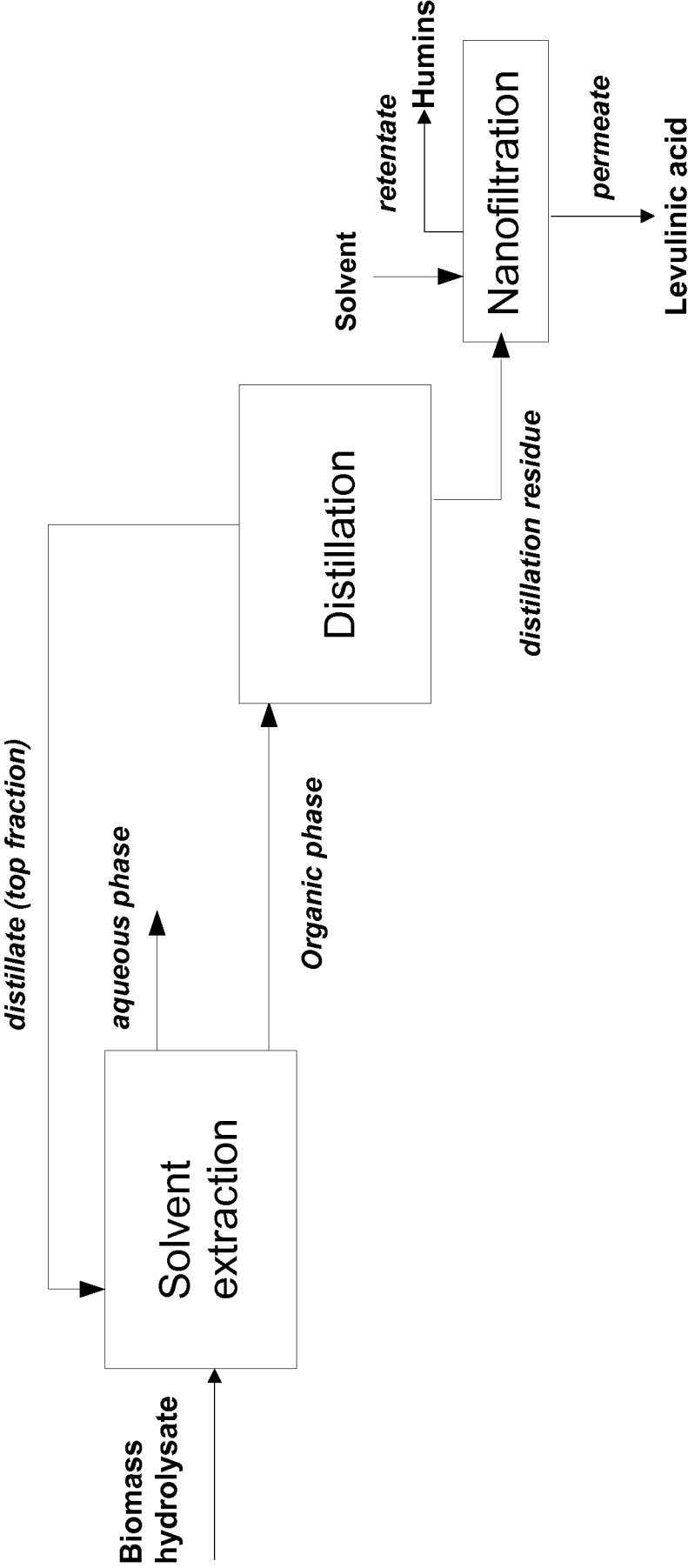


Fig 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/068595

A. CLASSIFICATION OF SUBJECT MATTER INV. C07C51/00 B01D11/04 C07D307/50 C07D309/30 B01D61/36 C07C59/185 C07C53/08 C07C53/02 ADD. According to International Patent Classification (IPC) or to both national classification and IPC														
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C07C B01D C07D Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, INSPEC, WPI Data														
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category*</th> <th style="width: 70%;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="width: 20%;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>WO 92/13849 A1 (REPAP TECHNOLOGIES INC [US]) 20 August 1992 (1992-08-20) page 5; figures 5-6 page 16, line 33 - page 17, line 12 page 19 - page 22, line 28 pages 26-27; claims -----</td> <td style="text-align: center; vertical-align: top;">1-11</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>WO 2011/057413 A1 (FPINNOVATIONS [CA]; YUAN ZHIRUN [CA]; BROWNE THOMAS CARL [CA]; ZHANG X) 19 May 2011 (2011-05-19) the whole document -----</td> <td style="text-align: center; vertical-align: top;">1-11</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US 2009/008235 A1 (GOEL MANISH [US] ET AL) 8 January 2009 (2009-01-08) pages 4-5, paragraphs 7-8,14,20,30; claims ----- -/-</td> <td style="text-align: center; vertical-align: top;">1-11</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	Y	WO 92/13849 A1 (REPAP TECHNOLOGIES INC [US]) 20 August 1992 (1992-08-20) page 5; figures 5-6 page 16, line 33 - page 17, line 12 page 19 - page 22, line 28 pages 26-27; claims -----	1-11	Y	WO 2011/057413 A1 (FPINNOVATIONS [CA]; YUAN ZHIRUN [CA]; BROWNE THOMAS CARL [CA]; ZHANG X) 19 May 2011 (2011-05-19) the whole document -----	1-11	Y	US 2009/008235 A1 (GOEL MANISH [US] ET AL) 8 January 2009 (2009-01-08) pages 4-5, paragraphs 7-8,14,20,30; claims ----- -/-	1-11
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Y	US 2009/008235 A1 (GOEL MANISH [US] ET AL) 8 January 2009 (2009-01-08) pages 4-5, paragraphs 7-8,14,20,30; claims ----- -/-	1-11												
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.														
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Date of the actual completion of the international search 18 December 2013		Date of mailing of the international search report 07/01/2014												
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Seelmann, Marielle												

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/068595

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Information on patent family members

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