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(54) **PROCESS FOR CONVERSION OF A CELLULOSIC MATERIAL**

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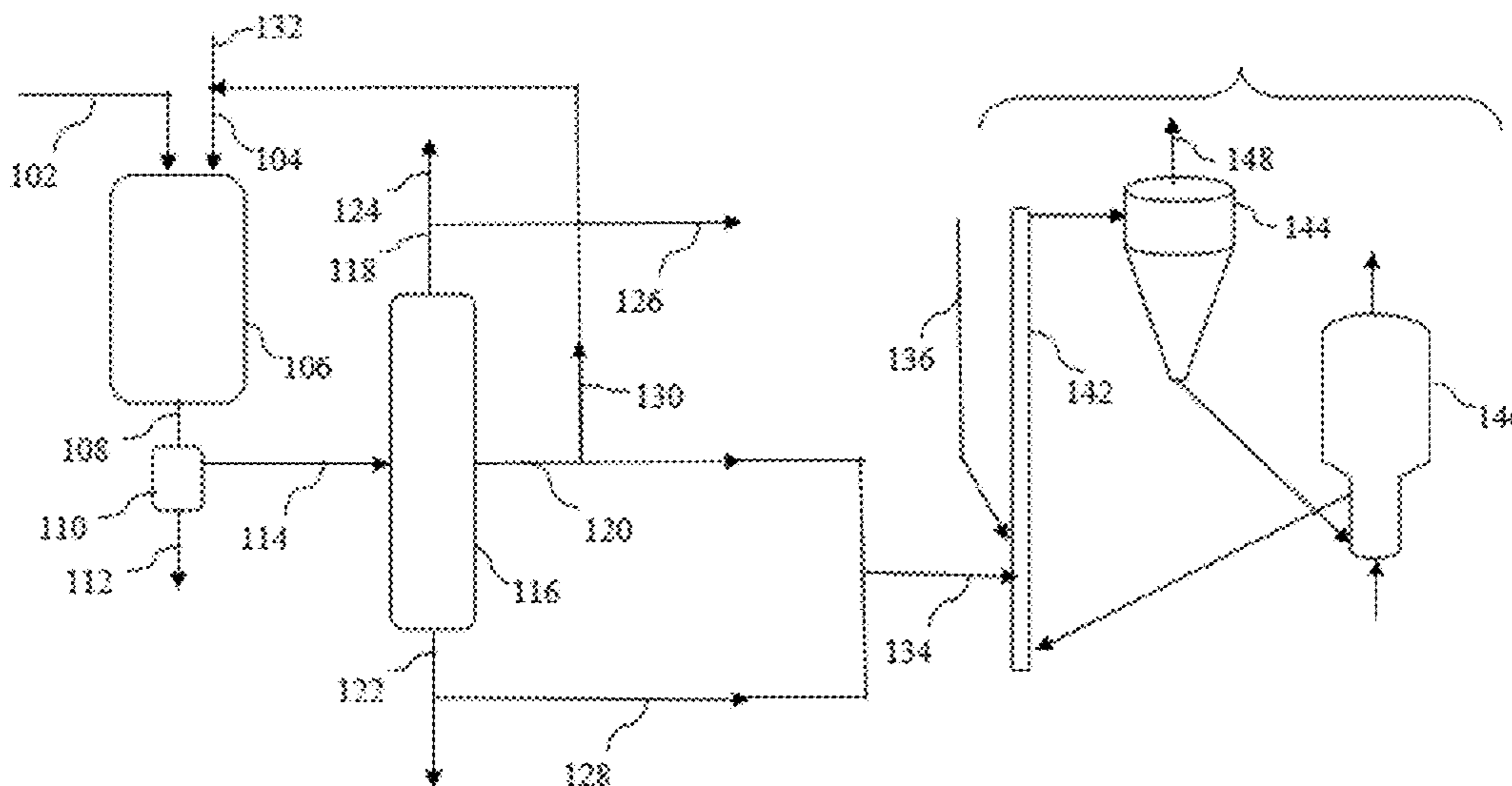
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(57) **ABSTRACT**

Methods to convert a cellulosic material into a bio-oil. In one embodiment, the method comprises (a) contacting the cellulosic material with a liquid solvent in an inert atmosphere at a reaction temperature in the range from equal to or more than about 260° C. to equal to or less than about 400° C. to produce a product mixture; (b) separating a middle fraction from the product mixture to produce a product mixture middle fraction. A first portion of the product mixture middle fraction can be recycled as part of the liquid solvent in step a). At least part of the product mixture is hydrotreated before at least a portion of a middle fraction of the treated product mixture is recycled as part of the liquid solvent in step a).



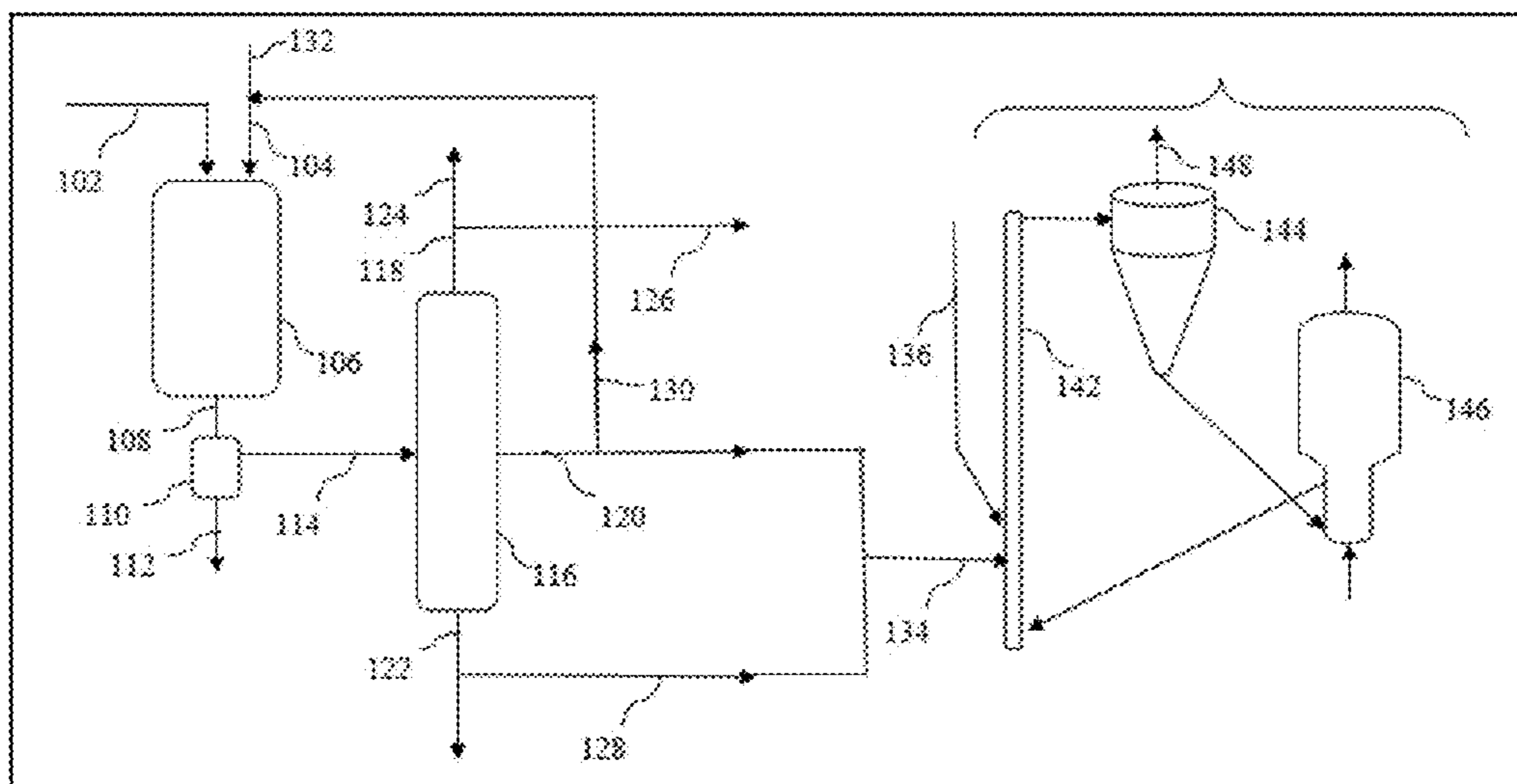


FIG. 1

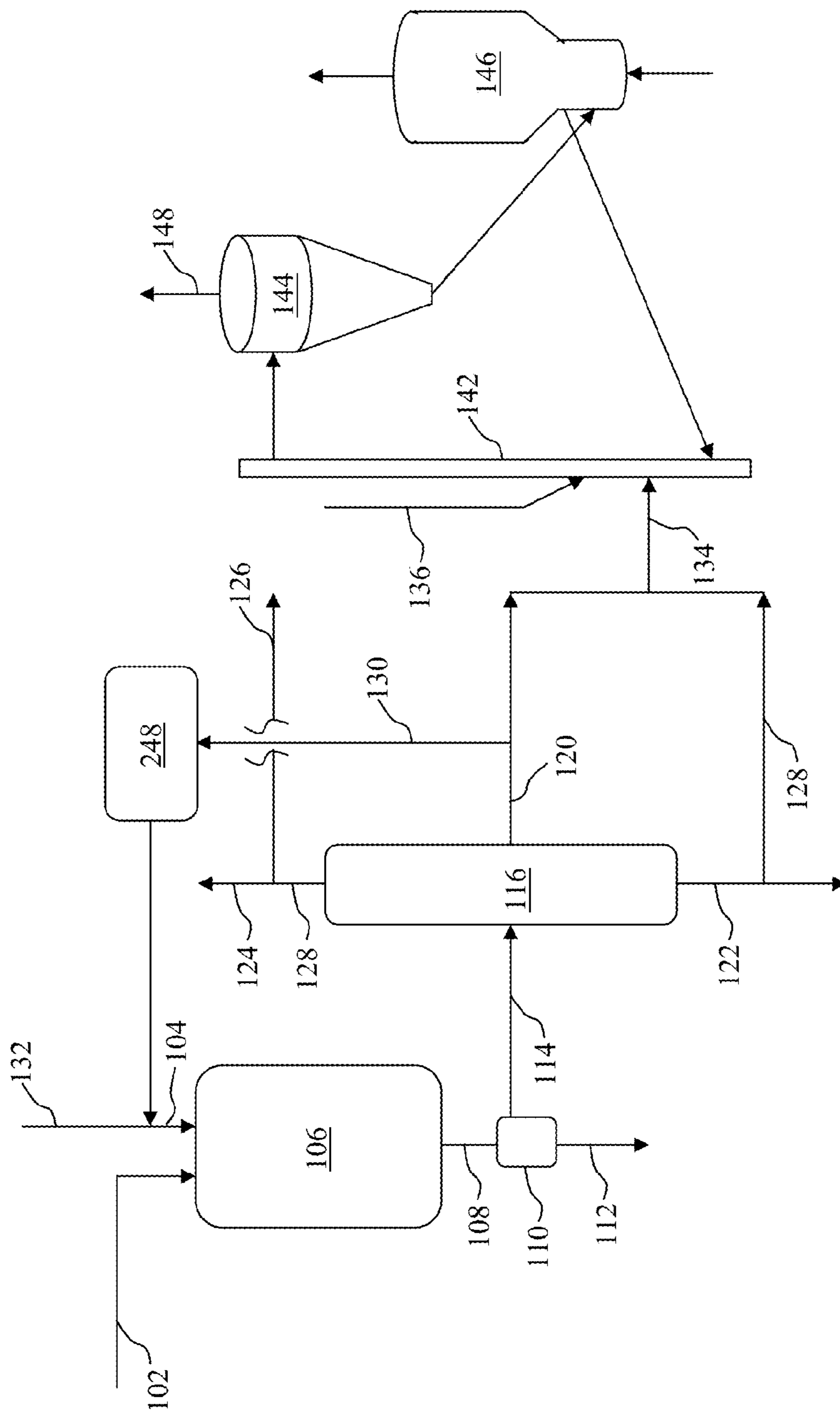


FIG. 2

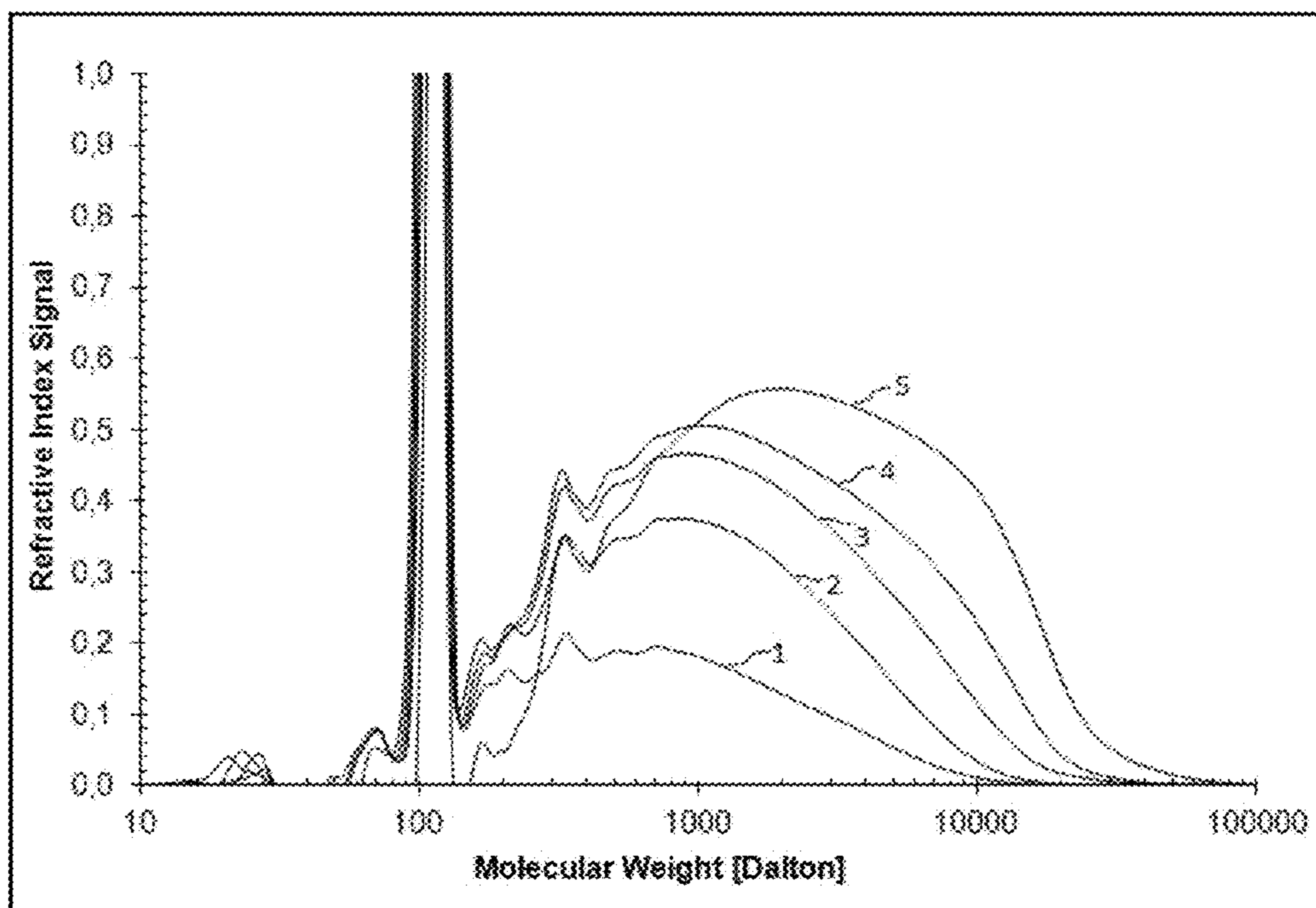


FIG. 3A

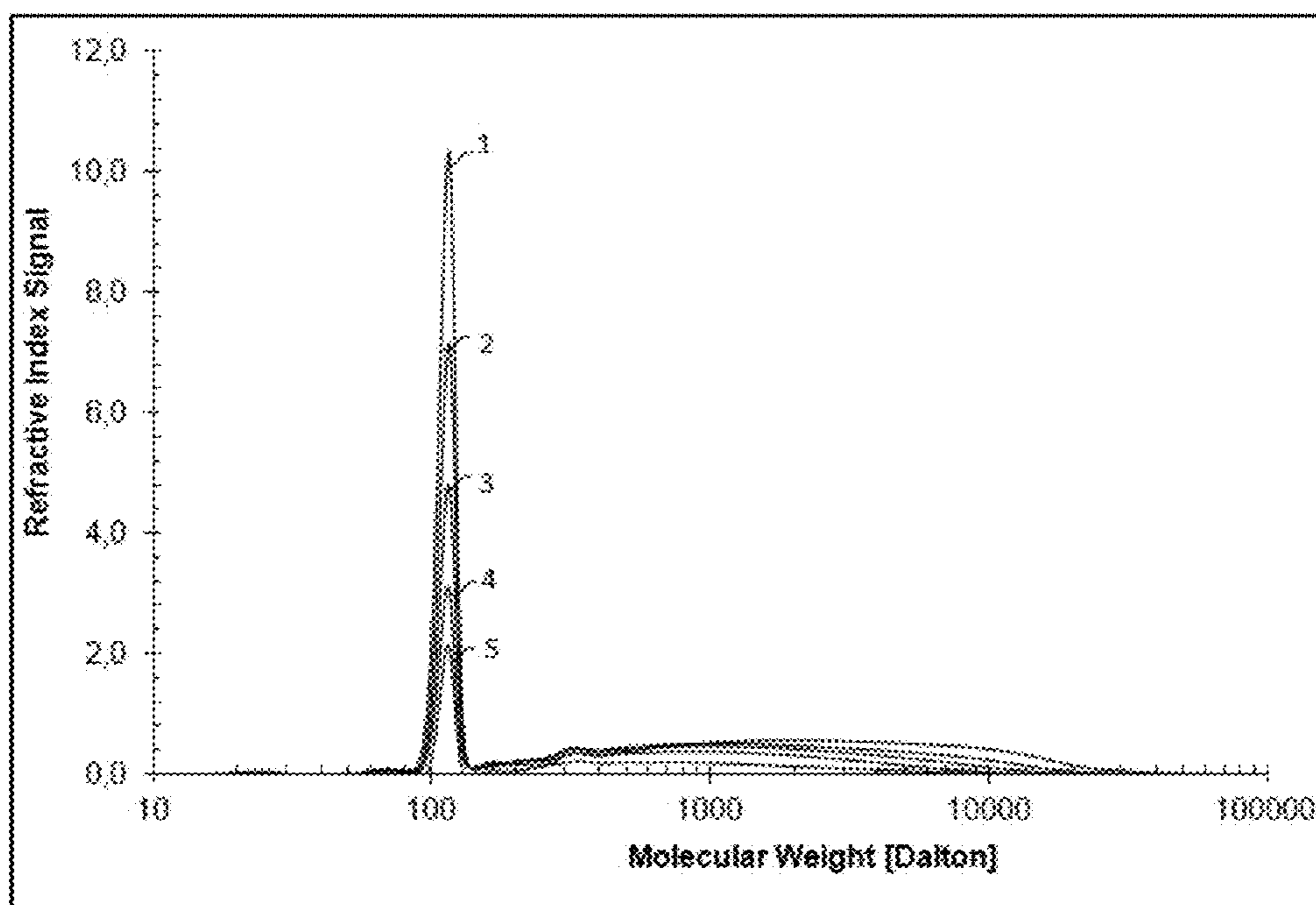


FIG. 3B

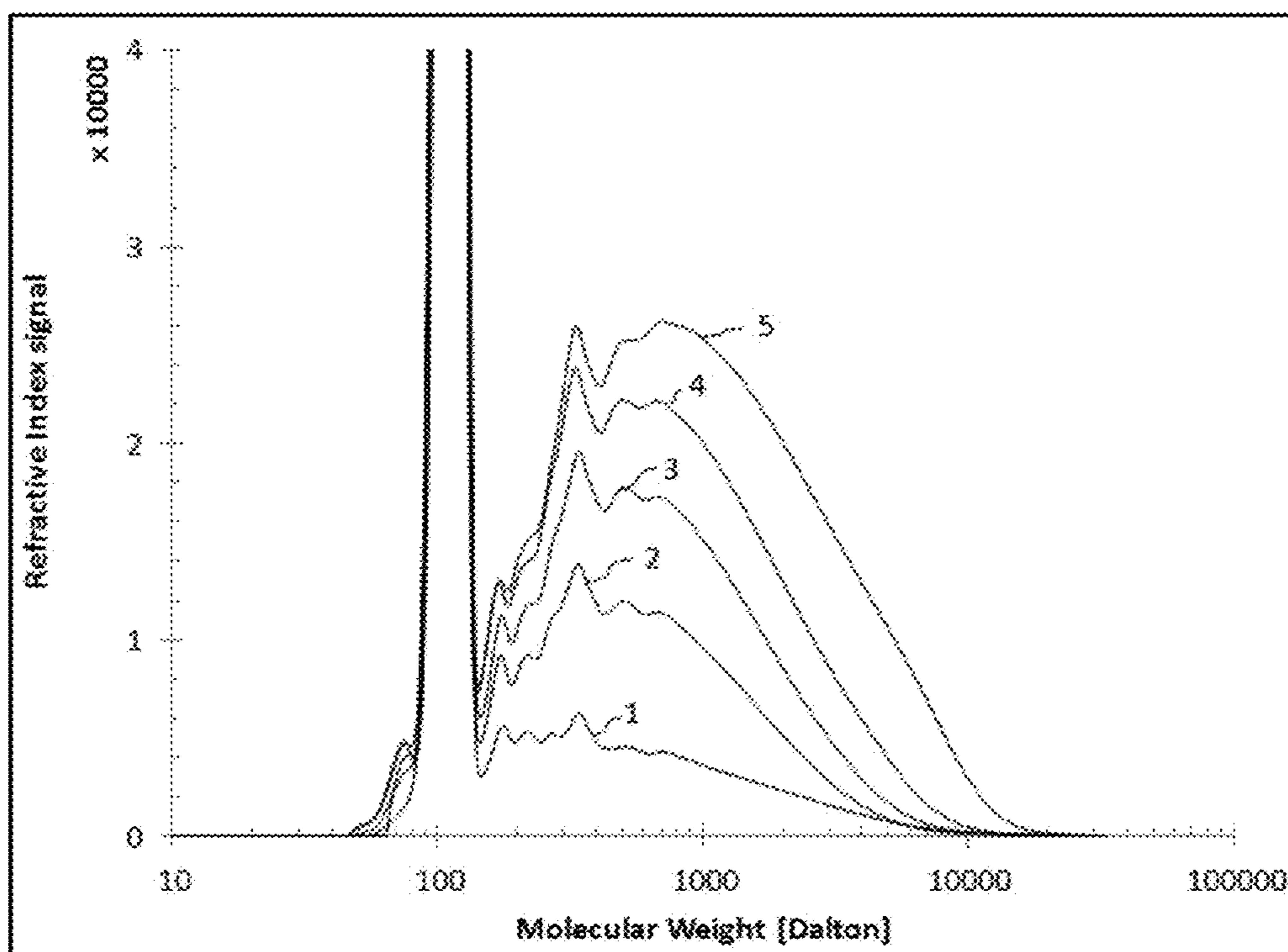


FIG. 4A

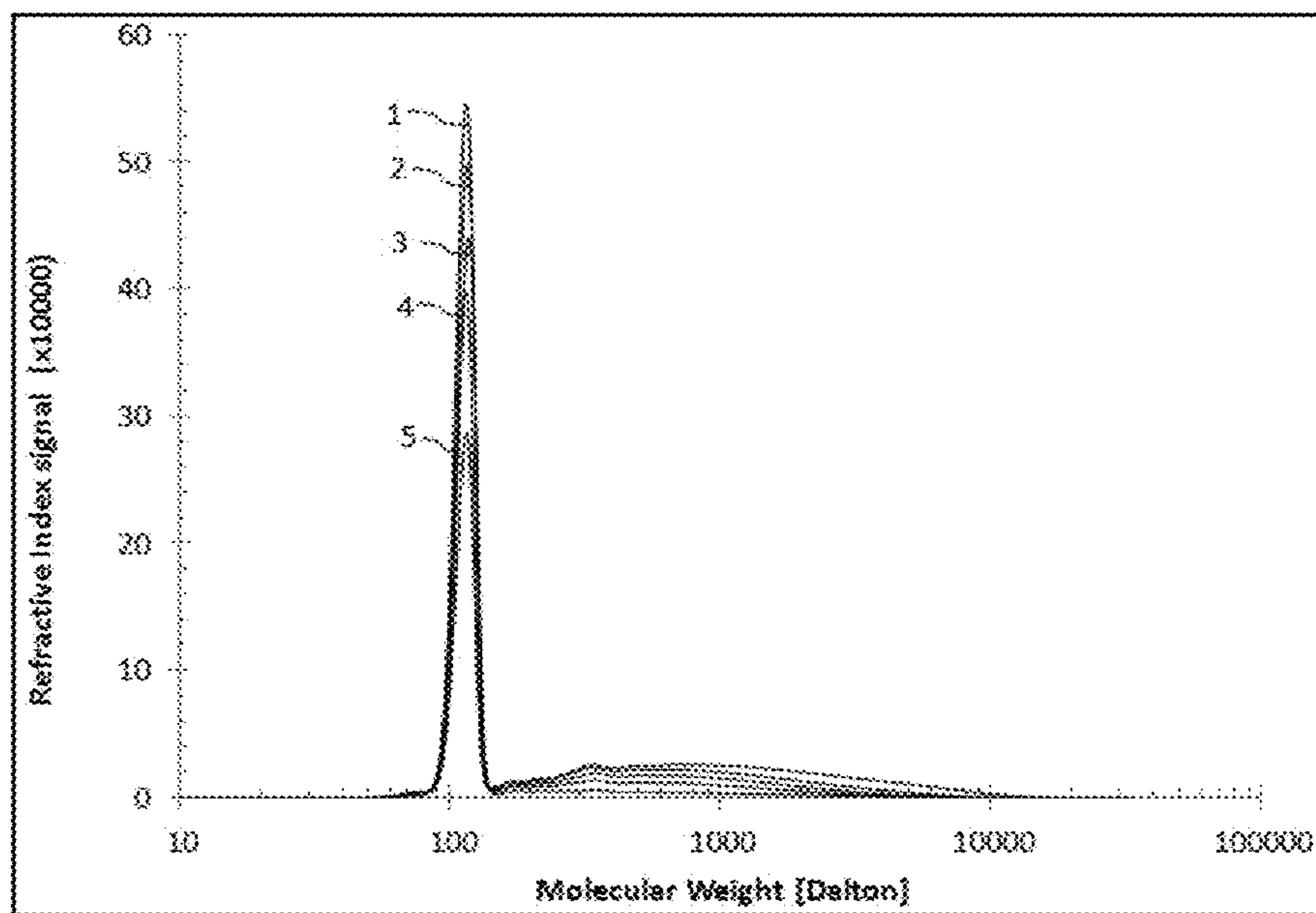


FIG. 4B

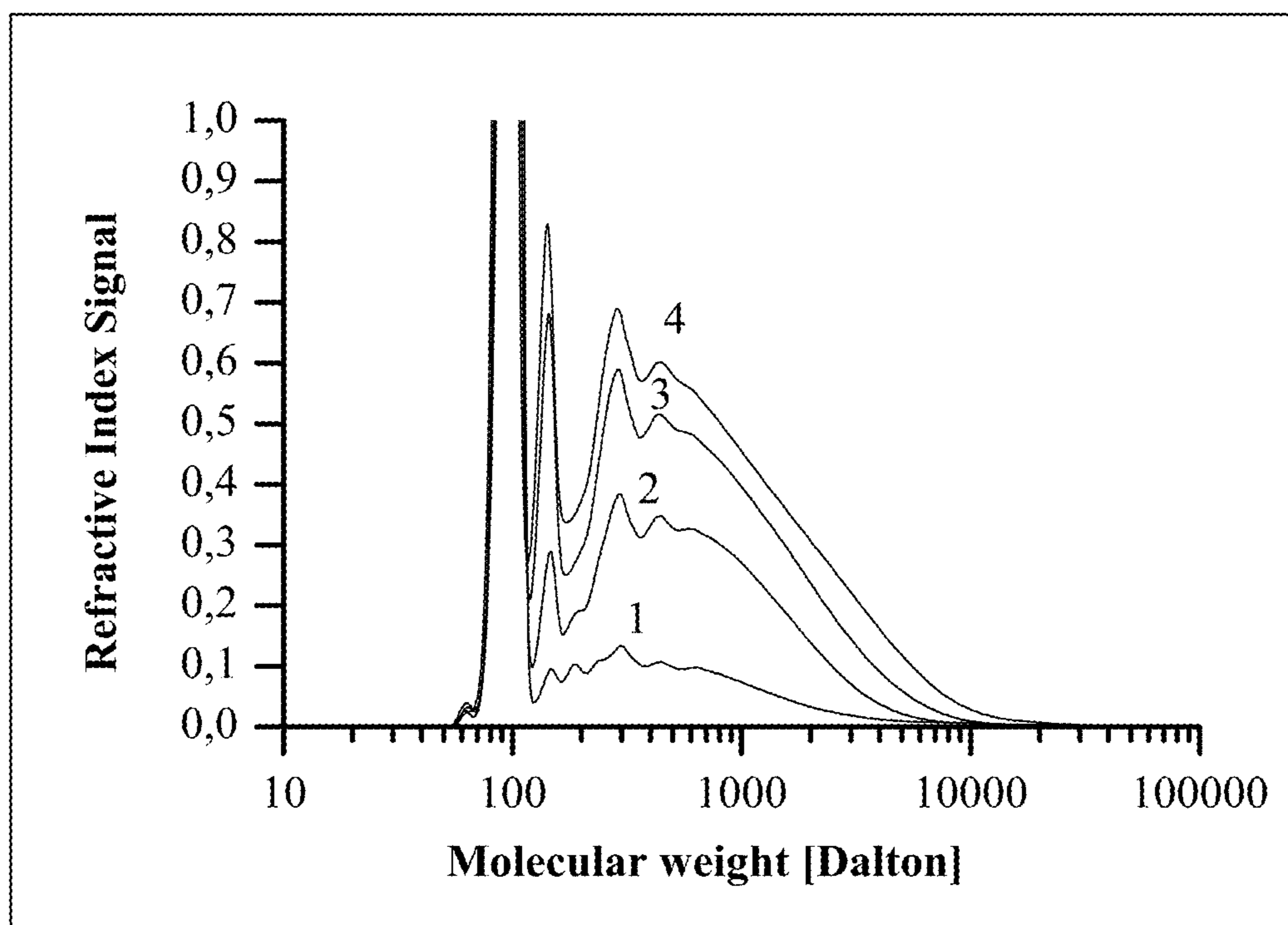


FIG. 5

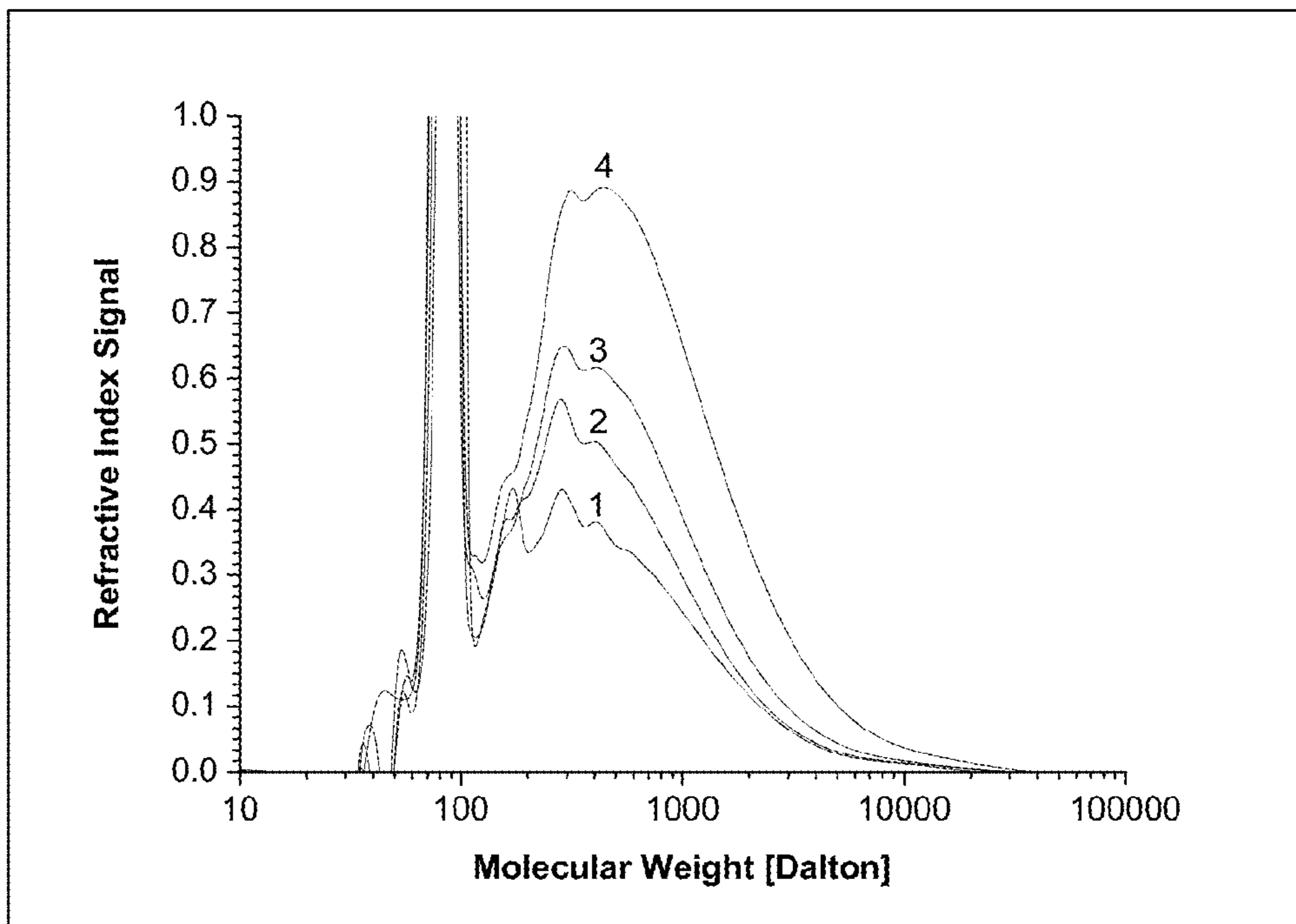


FIG. 6A

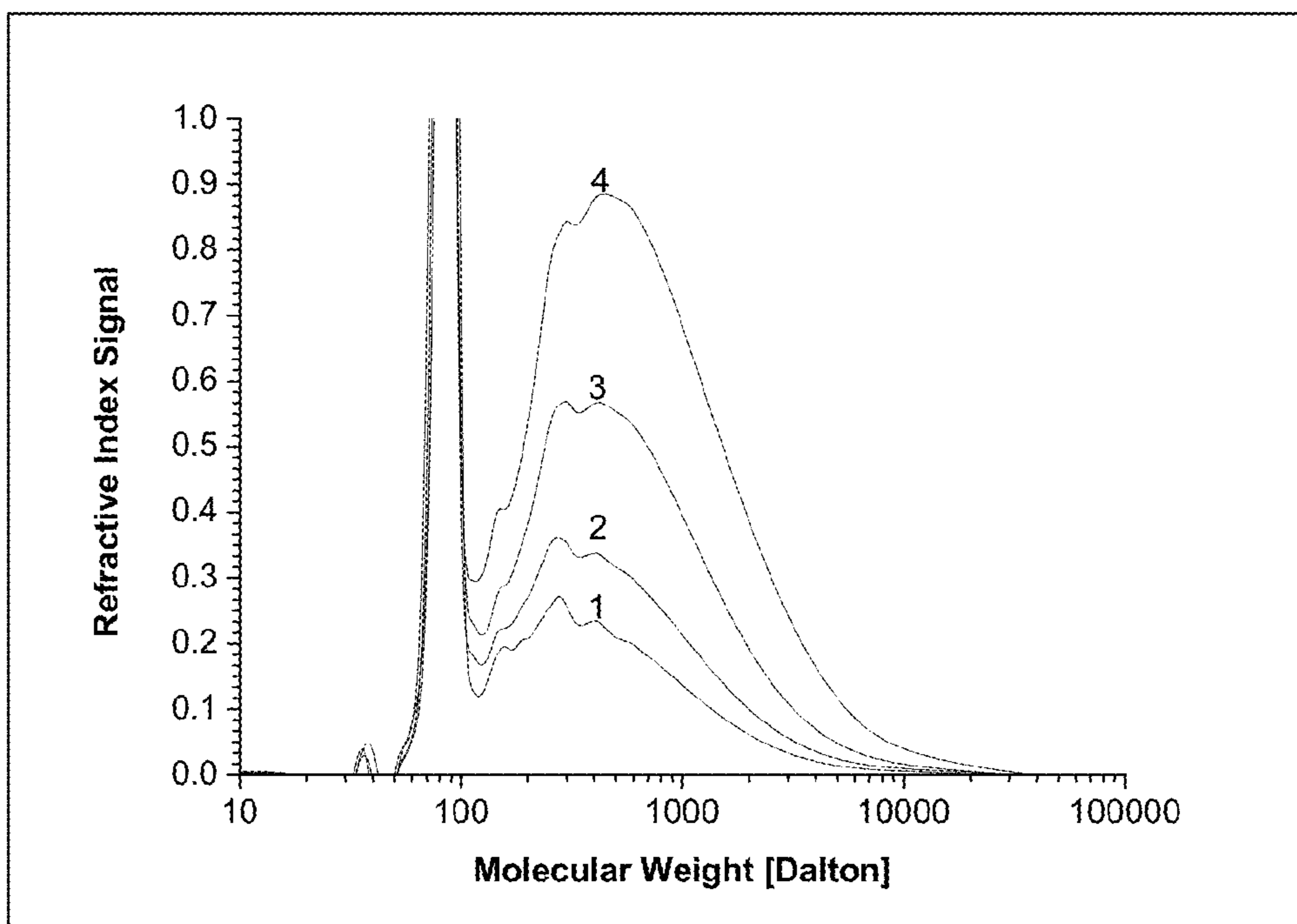


FIG. 6B

PROCESS FOR CONVERSION OF A CELLULOSIC MATERIAL

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. application Ser. No. 13/677,008, filed on Nov. 14, 2012, which claims priority to European Patent Application No. 11189056.2, filed on Nov. 14, 2011, the disclosures of which are incorporated by reference herein in their entirety.

FIELD OF THE INVENTION

[0002] Embodiments of this invention relate to a process for conversion of a cellulosic material and use of the products produced in such a process.

BACKGROUND

[0003] This section is intended to introduce various aspects of the art, which may be associated with exemplary embodiments of the present invention. This discussion is believed to assist in providing a framework to facilitate a better understanding of particular aspects of the present invention. Accordingly, it should be understood that this section should be read in this light, and not necessarily as admissions of any prior art.

[0004] With the diminishing supply of crude mineral oil, use of renewable energy sources is becoming increasingly important for the production of liquid fuels. These fuels from biological sources are often referred to as biofuels.

[0005] Biofuels derived from non-edible biological sources, such as cellulosic materials, are preferred as these do not compete with food production. These biofuels are also referred to as second generation, or advanced, biofuels. Most of these non-edible cellulosic materials, however, are solid materials that are cumbersome to convert into biofuels. A first step in conversion of these cellulosic materials is therefore a liquefaction of the cellulosic material into a liquid.

[0006] WO 2005/058856 describes a process for liquefaction of cellulosic material. In the process solid cellulosic material is heated in the presence of an acid catalyst and a solvent. The solvent comprises a compound having a gamma lactone group of a particular general molecular formula. Examples of such compounds mentioned include gamma-valerolactone. The solvent used in the liquefaction process may be obtained from furfural or levulinic acid obtained from acid hydrolysis of (ligno)cellulosic material, either via a parallel process or a process in series. In the parallel process, part of the (ligno)cellulosic material is subjected to an acid hydrolysis process to obtain levulinic acid, optionally in combination with furfural that may then be used as solvent or may be further processed to obtain a solvent. In the process in series, the (ligno)cellulosic material is first liquefied and the liquefied (ligno)cellulosic material or the residue is then subjected to an acid hydrolysis process to obtain levulinic acid, optionally in combination with furfural. Part of the thus-obtained levulinic acid or furfural or a derivative thereof is then recycled to the liquefaction process as (make-up) solvent. The process is suitable for its purpose, but the large amounts of expensive solvent make the process economically less attractive. The levulinic acid, furfural or derivative thereof can only be used as solvent if they are made in sufficient quantities. The latter may require complete separate units to be set up.

[0007] The abstract of T. Willner, titled "Direct Liquefaction as a future basis for 3th generation biofuel production," published for the 17th European Biomass Conference and Exhibition, 29 Jun.-3 Jul. 2009, in Hamburg, Germany, describes a semi-continuous reactive distillation process for the liquefaction of dry grinded biomass. In the article it is mentioned that heavy oil fractions or tars used as reaction medium support degradation of lignocellulosics (e.g. wood) as well as formation of hydrophobic oil. It notes that an atmospheric pressure process with heavy oil phase as reaction medium should be possible, if the boiling point of the applied heavy oil is above reaction temperature in the range between 250° C. and 400° C. Nitrogen is used to render the reactor atmosphere inert before heating up. During the reactive distillation, vaporized conversion products leave the reactor through the top exit together with the gas products. A so-called "heavy oil sump phase" appears to be used as liquid reaction solvent. Solid residues stay in the reactor and have to be removed separately.

[0008] Bouvier et al. in their article titled "Direct liquefaction of wood by solvolysis," published in "Pyrolysis Oils from Biomass," pages 129-138, by E. Soltes et al, for the ACS Symposium Series, American Chemical Society, Washington, D.C., 1988, describe direct liquefaction of wood based on a two steps scheme: solvolysis then upgrading. On page 135, Bouvier et al. describe that in a continuous process, it will be necessary to recycle the final product as a solvent for solvolysing wood. In a first attempt, successive solvolysis operations were carried out starting from a first solvolysis operation which solution is recycled as the solvent of the second solvolysis operation and so on. It was shown that the conversion ratio stayed close to 100%, but the viscosity increased sharply to 130 centipoises (cP), 6000 cP and 160,000 cP for the first, second and third operation. The fourth operation led to a solid mixture at room temperature. To solve this problem the solvolysis oil was upgraded via hydrotreatment to improve the solvent ability as well as to convert heavy fraction to a lighter one. Results show, however, that even with the upgraded oil, the viscosity increased with each recycle (FIG. 7 of Bouvier et al.) to exceed 10,000 cP after 6 recycles. In addition, the upgrading requires a separate hydrotreatment unit.

[0009] It would be an advancement in the art to provide an economically attractive process for conversion of a cellulosic material, which uses a cheap solvent that can be made in large quantities and which solvent can be recycled multiple times without leading to an increased viscosity.

SUMMARY

[0010] Embodiments of the present invention can achieve such advancement. In a preferred embodiment, the process according to certain aspects of the invention advantageously provides a cheap liquid solvent, namely the product mixture middle fraction, in sufficiently large quantities, without the need of any additional upgrading unit, such as a hydrogenation unit.

[0011] Certain embodiments of the present invention further advantageously allow for multiple recycles of the product mixture middle fraction resulted in a mere moderate increase of viscosity.

[0012] In addition, it was surprisingly found that in certain embodiments, the use of multiple product mixture middle fraction recycles (preferably more than 3 recycles) resulted in an improved liquid solvent that has better liquefaction properties than the product mixture middle fraction obtained after

the first time of carrying out the liquefaction step. Some embodiments allow for a further reduction in increase of viscosity of the product mixture middle fraction by hydrotreating the middle fraction prior to recycling it.

[0013] According to one aspect of the invention, there is provided a process for the conversion of a cellulosic material into a bio-oil. The process comprises the steps of: (a) contacting the cellulosic material with a liquid solvent in an inert atmosphere at a reaction temperature in the range from equal to or more than about 260° C. to equal to or less than about 400° C. to produce a product mixture; (b) separating a middle fraction from the product mixture to produce a product mixture middle fraction; (c) recycling a first portion of the product mixture middle fraction as part of the liquid solvent (d) hydrotreating at least part of the product mixture before the recycling step (c); and using a second portion of the product mixture middle fraction to produce a bio-oil.

[0014] In one embodiment, the hydrotreating step (d) is performed after the separating step (b). In another embodiment, the hydrotreating step (d) is performed after the separating step (b). In one embodiment, the hydrotreating step (d) comprises contacting the at least part of said first portion with a hydrogenation catalyst in the presence of hydrogen. In one embodiment, the hydrogenation catalyst comprises at least one metal in groups 8-11. In another embodiment, the hydrogenation catalyst comprises at least one metal in group 6. In one embodiment, the hydrogenation catalyst further comprises a carbon carrier.

[0015] In one embodiment, the hydrotreating step is carried out at a temperature in a range of about 80 degrees C. to about 350 degrees C., about 100 degrees C. to about 250 degrees C., or about 150 degrees C. to about 200 degrees C. In one embodiment, the hydrotreating step is carried out under a pressure in a range of about 0.1 MPa to about 25 MPa, or about 1 MPa to about 15 MPa, or about 5 MPa to about 10 MPa. In one embodiment, the hydrotreating step comprises a hydrogen to liquid ratio of 10 to 10,000 mL/L, 50 to 1000 mL/L, or 100 to 500 mL/L. In one embodiment, the hydrotreating step comprises a liquid hourly space velocity in a range of about 0.1 L/L/h to about 10 L/L/h, about 0.3 L/L/h to about 3 L/L/h, or about 0.5 L/L/h to about 2 L/L/h.

[0016] Other advantages and features of embodiments of the present invention will become apparent from the following detailed description. It should be understood, however, that the detailed description and the specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] The following drawings form part of the present specification and are included to further demonstrate certain aspects of the present invention. Embodiments of the invention may be better understood by reference to the drawing in combination with the detailed description of specific embodiments presented herein.

[0018] FIG. 1 shows a schematic diagram of a first embodiment according to aspects of the invention.

[0019] FIG. 2 shows a schematic diagram of a second embodiment according to aspects of the invention.

[0020] FIG. 3A shows the SEC spectra of the liquid reaction effluent of runs 1 to 5 (R1-R5) of comparative example 1.

[0021] FIG. 3B shows the SEC spectra of the liquid reaction effluent of runs 1 to 5 (R1-R5) of comparative example 1 on an extended y-axis compared to FIG. 3A.

[0022] FIG. 4A shows the SEC spectra of the bio-oil fraction of runs 1 to 5 (R1-R5) of example 2.

[0023] FIG. 4B shows the SEC spectra of the bio-oil fraction of runs 1 to 5 (R1-R5) of example 2 on an extended y-axis compared to FIG. 4A.

[0024] FIG. 5 shows the SEC spectra of the bio-oil fraction of runs 1 to 4 (R1-R4) of example 3.

[0025] FIG. 6A shows the SEC spectra of the bio-oil fraction of runs 1 to 4 (R1-R4) of example 4.

[0026] FIG. 6B shows the SEC spectra of the bio-oil fraction of hydrotreatments 1 to 4 (T1-T4) of example 4.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0027] Embodiments of the present invention provide a process for the conversion of a cellulosic material into a bio-oil. In a preferred embodiment, the process includes a liquefaction step that produces a product mixture from which a middle fraction is separated to produce a product mixture middle fraction. The liquefaction step may be generically referred to as “step a)” without limiting it to any specific condition. Likewise, the separation step of a middle fraction from the product mixture may be generically referred to as “step b).” The product mixture obtained from the liquefaction step may also be referred to herein as a liquefaction product. In such a liquefaction step the cellulosic material can be liquefied. Step a) may therefore also be referred to as liquefaction or liquefying of cellulosic material. Such liquefaction or liquefying may be carried out by means of a liquefaction or liquefying reaction.

[0028] The term liquefaction or liquefying refers at least to partial conversion of a solid material, such as cellulosic material, into one or more liquefied products.

[0029] The term liquefied product refers at least to a product that is liquid at ambient temperature (about 20° C.) and pressure (about 0.1 MegaPascal) and/or a product that can be converted into a liquid by melting (for example by applying heat) or dissolving in a solvent. In a preferred embodiment, the liquefied product is liquid at a temperature of about 80° C. and a pressure of about 0.1 MegaPascal. The liquefied product may vary widely in its viscosity and may be more or less viscous.

[0030] Liquefaction of a cellulosic material can comprise cleavage of covalent linkages in that cellulosic material. For example liquefaction of lignocellulosic material can comprise cleavage of covalent linkages in cellulose, hemicellulose and/or lignin present and/or cleavage of covalent linkages between lignin, hemicelluloses and/or cellulose.

[0031] As used herein, a cellulosic material refers at least to a material containing cellulose. In a preferred embodiment, the cellulosic material is a lignocellulosic material. A lignocellulosic material comprises lignin, cellulose and optionally hemicellulose.

[0032] The liquefaction step of certain embodiments of the present invention can make it possible to liquefy not only the cellulose but also the lignin and hemicelluloses.

[0033] Embodiments of the present invention can use any suitable cellulose-containing material. The cellulosic material for use according to aspects of the invention may be obtained from a variety of plants and plant materials including agricultural wastes, forestry wastes, sugar processing

residues and/or mixtures thereof. Non-limiting examples of suitable cellulose-containing materials include agricultural wastes such as corn stover, soybean stover, corn cobs, rice straw, rice hulls, oat hulls, corn fibre, cereal straws such as wheat, barley, rye and oat straw; grasses; forestry products such as wood and wood-related materials such as sawdust; waste paper; sugar processing residues such as bagasse and beet pulp; or any combination thereof.

[0034] The liquefaction step of certain embodiments of the present invention may further comprise drying, torrefaction, steam explosion, particle size reduction, densification and/or pelletization of the cellulosic material before the cellulosic material is contacted with the liquid solvent. Such drying, torrefaction, steam explosion, particle size reduction, densification and/or pelletization of the cellulosic material may advantageously allow for improved process operability and economics.

[0035] In a preferred embodiment, the cellulosic material is processed into small particles before it is used. The cellulosic material is preferably processed into particles having a particle size distribution with an average particle size of equal to or more than about 0.05 millimeter, more preferably equal to or more than about 0.1 millimeter, most preferably equal to or more than about 0.5 millimeter and preferably equal to or less than about 20 centimeters, more preferably equal to or less than about 10 centimeters and most preferably equal to or less than about 3 centimeters. For practical purposes the particle size in the centimeter and millimeter range can be determined by sieving.

[0036] If the cellulosic material is a lignocellulosic material, it may also have been subjected to a pre-treatment to remove and/or degrade lignin and/or hemicelluloses. Non-limiting examples of such pre-treatments include fractionation, pulping and torrefaction processes.

[0037] In one embodiment, the cellulosic material may have been dried before it is used.

[0038] In another embodiment the cellulosic material has not been dried or been only partly dried to reach a water content of about 5 to 80 wt %, preferably about 20 to 50 wt %, based on the total weight of cellulosic material and water. Optionally, the cellulosic material can be impregnated with water to reach a moisture content of about 5 to 80 w %, preferably about 20 to 50 w %.

[0039] The amount of water in a cellulosic material may conveniently be determined by drying, for example according to ASTM-method D2216-98.

[0040] In a preferred embodiment, the cellulosic material used in the liquefaction step has a water content of about 5 to 80 wt %, preferably about 20 to 50 wt %, based on the total weight of cellulosic material and water. In such an embodiment, the process according to the invention may advantageously further comprise a step comprising providing a cellulosic material having a water content of about 5 to 80 wt %, preferably about 20 to 50 wt %, based on the total weight of cellulosic material and water.

[0041] The term "liquid solvent" refers at least to a solvent that is liquid at a pressure of about 0.1 MegaPascal (MPa) (about 1 bar absolute) and a temperature of about 80° C. or higher, more preferably about 100° C. or higher. Most preferably a liquid solvent is herein understood to be a solvent that is liquid at the reaction temperature and reaction pressure at which the liquefaction step is carried out.

[0042] Hence, the liquid solvent is preferably a solvent which is liquid at a temperature in the range from equal to or

more than about 260° C. to equal to or less than about 400° C. at a pressure of about 0.1 MPa. In a preferred embodiment, such liquid solvent is still liquid at a temperature in the range from equal to or more than about 260° C. to equal to or less than about 400° C. at a higher pressure, for example the pressure during the reaction as mentioned above, for example a pressure of about 4 MPa.

[0043] In a preferred embodiment, at least a portion of the reaction product of the liquefaction step is a liquid solvent. In one embodiment, at least part of the liquid solvent contains a recycled product mixture middle fraction, which may be obtained by separating a middle fraction from product mixture of the liquefaction step.

[0044] In a preferred embodiment, the liquid solvent comprises equal to or more than about 10 wt %, more preferably equal to or more than about 20 wt %, even more preferably equal to or more than about 30 wt %, still more preferably equal to or more than about 50 wt %, most preferably equal to or more than about 80 wt % and preferably equal to or less than about 100 wt %, possibly equal to or less about 90 wt %, based on the total weight of liquid solvent in the liquefaction step (or step a)), of such recycled product mixture middle fraction.

[0045] In a particular preferred embodiment, at least a portion of the liquid solvent comprises a third or higher generation reaction product; that is at least a third generation reaction product. The term third generation or n-th generation reaction product refers at least to a reaction product that has been obtained by recycling and reacting the original reaction product in the liquefaction step for n-times. For example, a third generation or higher generation reaction product may have been obtained by re-reacting a recycled preceding (e.g., 2nd or lower) generation reaction products in the liquefaction step. For example, in step a), the cellulosic material may be converted into a product mixture comprising a 1st generation reaction product; where a middle fraction comprising the 1st generation reaction product may be separated from the product mixture of the liquefaction step (or step a)). The selected product mixture middle fraction comprising the 1st generation reaction product may be recycled to step a), where the 1st generation reaction product may be converted (re-reacted) to a 2nd generation reaction product. The product mixture may be again separated (or step b)) and a middle fraction comprising the 2nd generation reaction product may be selected. The selected product mixture middle fraction comprising the 2nd generation reaction product may be recycled to step a), where the 2nd generation reaction product may be converted (re-reacted) to a 3rd generation reaction product, etc. That is, in a preferred embodiment, the liquefaction step produces a product mixture using a liquid solvent, and a middle fraction is separated from the product mixture to produce a product mixture middle fraction. In a preferred embodiment, at least a portion of this product mixture middle fraction can be recycled and used as part of the liquid solvent for the liquefaction step. When a portion of the product mixture middle fraction is used for the first time in the liquid solvent, this is a first generation reaction product. A liquid solvent contains a second generation product when it is a product mixture middle fraction obtained from a product mixture produced using a liquid solvent containing a first generation reaction product. At least a portion of this particular liquid solvent now includes materials that have been through the liquefaction process twice.

[0046] In a preferred embodiment the liquid solvent comprises at least about 10 wt %, more preferably at least about 30 wt % and most preferably at least about 50 wt % (based on the total weight of liquid solvent) of 3rd or higher generation reaction products. More preferably the liquid solvent comprises at least about 10 wt %, more preferably at least about 30 wt % and most preferably at least about 50 wt % (based on the total weight of liquid solvent) of 4th or higher generation reaction products. Most preferably the liquid solvent comprises at least about 10 wt %, more preferably at least about 30 wt % and most preferably at least about 50 wt % (based on the total weight of liquid solvent) of 5th or higher generation reaction products.

[0047] In another preferred embodiment the liquid solvent in the liquefaction step comprises equal to or more than about 10 wt %, more preferably equal to or more than about 30 wt %, even more preferably equal to or more than about 50 wt % of a steady state recycle product. By a steady state recycle product is herein preferably understood a recycle product comprising a steady composition, i.e., which does not change anymore over time.

[0048] In a preferred embodiment, the present invention provides a process for the conversion of a cellulosic material into a bio-oil, comprising the steps of:

a) contacting the cellulosic material with a liquid solvent in an inert atmosphere at a reaction temperature in the range from equal to or more than about 260° C. to equal to or less than about 400° C. to produce a product mixture comprising one or more reaction products;

b) separating a middle fraction of the product mixture to produce a product mixture middle fraction;

c) recycling at least a first portion of the product mixture middle fraction in the process by using the first portion as part of the liquid solvent in step a); and using a second portion of the product mixture middle fraction to produce a bio-oil. In another embodiment, the liquid solvent in step a) comprises at least equal to or more than about 10 wt % of 3rd or higher generation reaction products.

[0049] In another preferred embodiment, the liquid solvent in the conversion in step a) is a liquid organic solvent. By an organic solvent is herein understood to refer at least to a solvent comprising one or more hydrocarbon compounds. By a hydrocarbon compound is herein understood a compound that contains at least one hydrogen atom and at least one carbon atom, more preferably a hydrocarbon compound is herein understood to contain at least one hydrogen atom and at least one carbon atom bonded to each other via at least one covalent bond. In addition to the hydrogen atom(s) and carbon atom(s) the hydrocarbon may contain heterogeneous atoms such as for example oxygen, nitrogen and/or sulphur.

[0050] In a preferred embodiment, the organic solvent comprises one or more carboxylic acids. By a carboxylic acid is herein understood a hydrocarbon compound comprising at least one carboxyl (—CO—OH) group. More preferably the organic solvent comprises equal to or more than about 1 wt % carboxylic acids, more preferably equal to or more than about 10 wt % carboxylic acids, most preferably equal to or more than about 20 wt % of carboxylic acids, based on the total weight of organic solvent. There is no upper limit for the carboxylic acid concentration, but for practical purposes the organic solvent may comprise equal to or less than about 90 wt %, more preferably equal to or less than about 80 wt % of carboxylic acids, based on the total weight of organic solvent.

[0051] In a preferred embodiment, the liquid solvent in the liquefaction step comprises one or more methoxyphenols. Most preferably the liquid solvent comprises at least 1 wt % methoxy-phenols, more preferably at least about 10 wt % methoxy-phenols, even more preferably at least about 20 wt % methoxy-phenols, based on the total weight of the liquid solvent.

[0052] In another embodiment, the liquid solvent in the liquefaction step comprises paraffinic compounds, naphthenic compounds, olefinic compounds and/or aromatic compounds. Such compounds may be present in refinery streams such as gasoil, fuel oil and/or residue oil. These refinery streams may therefore also be suitable as organic solvent in the liquefaction step.

[0053] The weight ratio of recycled product mixture middle fraction to cellulosic material (PMMF:CM) in the liquefaction step preferably lies in the range from about 1:1 to 100:1, more preferably in the range from about 2:1 to 50:1, most preferably in the range from about 5:1 to 20:1.

[0054] Embodiments of the composition of the recycled product mixture middle fraction are described in more detail below.

[0055] In addition to the recycled product mixture middle fraction, the liquid solvent may comprise one or more hydrocarbon compound(s) that are at least partly obtained and/or derived from a source other than the cellulosic material used as a feedstock in the liquefaction step, for example a hydrocarbon compound derived from a petroleum source (herein also referred to as fossil source). These one or more hydrocarbon compounds(s) may for example be mixed with the cellulosic material before starting the conversion in the liquefaction step or may be added to the reaction mixture during the conversion in the liquefaction step.

[0056] Further in a preferred embodiment, the liquefaction step comprises contacting the cellulosic material with a liquid solvent comprising the recycled product mixture middle fraction and water. The water in the liquid solvent may for example be generated in-situ during the conversion.

[0057] Preferably, the liquid solvent in the conversion in the liquefaction step comprises water in an amount of less than or equal to about 30 wt %, more preferably an amount of less than or equal to about 25 wt %, even more preferably less than or equal to about 20 wt %, and most preferably less than or equal to about 15 wt %, based on the total weight of liquid solvent. Further water is possibly present in the liquid solvent in an amount of more than or equal to about 1 wt %, suitably more than or equal to about 5 wt %, and possibly even in an amount of more than or equal to about 10 wt % or more than or equal to about 15 wt %, based on the total weight of the liquid solvent. The liquid solvent may comprise the above water during the reaction in the liquefaction step as a consequence of the water being formed in-situ.

[0058] In a preferred embodiment, the cellulosic material and the liquid solvent in the liquefaction step are contacted in a liquid solvent-to-cellulosic material weight ratio of about 2:1 to 20:1, more preferably in a liquid solvent-to-cellulosic material weight ratio of about 3:1 to 15:1 and most preferably in a liquid solvent-to-cellulosic material weight ratio of about 4:1 to 10:1.

[0059] In another preferred embodiment, the liquefaction step is preferably carried out at a temperature in the range from equal to or more than about 280° to equal to or less than about 380° C., more preferably in the range from equal to or more than about 300° C. to equal to or less than about 350° C.,

and a pressure in the range from equal to or more than about 0.05 MPa (0.5 bar absolute), more preferably equal to or more than about 0.1 MPa, even more preferably equal to or more than about 0.5 MPa, still more preferably equal to or more than about 1 MPa, to equal to or less than about 8 MPa (80 bar absolute), more preferably equal to or less than about 6 MPa, even more preferably equal to or less than about 5 MPa, still more preferably equal to or less than about 4 MPa.

[0060] In a preferred embodiment, the liquefaction step is carried out in an inert atmosphere or environment. By an inert atmosphere is herein understood to refer at least to an atmosphere that is substantially absent of any reducing gases (such as for example hydrogen, carbon monoxide or a combination thereof) and any oxidizing gases (such as for example oxygen). In a particular preferred embodiment, the liquefaction step is carried out in an atmosphere that is substantially absent of hydrogen, carbon monoxide and/or oxygen. In another particular preferred embodiment, the liquefaction step is further carried out in an environment that is substantially absent of any hydrogenation catalyst(s).

[0061] In certain embodiments, the liquefaction step may further be carried out in the presence or absence of an externally added acid catalyst. The use of an externally added catalyst advantageously allows one to lower the reaction temperature, but at the same time may result in different reaction products. The person skilled in the art may realize that during the liquefaction step in-situ acids may be formed. Hence, by an externally added acid catalyst is understood an “ex-situ” acid catalyst that has not been generated in-situ during the process of liquefaction step a).

[0062] Preferably, the liquefaction step is carried out in an environment substantially absent of externally added acids having a pKa of equal to or less than about 3.

[0063] In one embodiment, the liquefaction step may comprise contacting a cellulosic material with a liquid solvent, in the essential absence of any externally added catalyst, for example in the essential absence of an externally added acid catalyst. When the liquefaction step is carried out in the essential absence of any externally added catalyst, or for example in the essential absence of an externally added acid catalyst, step a) is preferably carried out at a temperature of equal to or more than about 200° C., more preferably equal to or more than about 250° C., still more preferably a temperature of equal to or more than about 300° C. and preferably a temperature equal to or less than about 450° C., more preferably a temperature equal to or less than about 400° C. and most preferably a temperature equal to or less than about 350° C.

[0064] In another embodiment, the liquefaction step may comprise contacting a cellulosic material with a liquid solvent in the presence of an externally added, preferably acid, catalyst at a temperature of equal to or more than about 100° C., more preferably a temperature of equal to or more than about 150° C., still more preferably a temperature of equal to or more than about 200° C. and preferably a temperature equal to or less than about 450° C., more preferably a temperature equal to or less than about 350° C. and most preferably a temperature equal to or less than about 300° C.

[0065] If the liquefaction step is carried out in the presence of a catalyst, the catalyst is preferably an acid catalyst. The acid catalyst may be in-situ formed or may be an externally added acid catalyst. The acid catalyst may for example be any acid catalyst known in the art to be suitable for liquefying of cellulosic material. The acid catalyst may be a Brönsted acid

or a Lewis acid. Further the acid catalyst may be a homogeneous catalyst or a heterogeneous catalyst. Preferably the acid catalyst is a homogeneous or finely dispersed heterogeneous catalyst, most preferably the acid catalyst is a homogeneous catalyst.

[0066] In a preferred embodiment, the acid catalyst is a Brönsted acid. The acid catalyst can be an inorganic or organic acid.

[0067] Non-limiting examples of suitable organic acid catalysts include levulinic acid, acetic acid, oxalic acid, formic acid, lactic acid, citric acid, trichloroacetic acid and any combination thereof.

[0068] If present, the acid catalyst is preferably an organic acid catalyst. Preferably, the liquefaction step is carried out in the absence of any inorganic acid catalyst. If present, the acid catalyst preferably has a pKa value equal to or less than about 5.0, more preferably equal to or less than about 4.25, and equal to or more than about 2.5, more preferably equal to or more than about 3.0. The liquefaction step can be carried out batch-wise, semi-batch wise, continuously and/or in any combination thereof.

[0069] The liquefaction step may further for example be carried out in a continuously stirred tank reactor or in a plug flow reactor or a combination thereof. In a preferred embodiment, the liquefaction step is carried out in a plug flow reactor.

[0070] Preferably, the residence time in any reactor during the liquefaction step lies in the range from equal to or more than about 5 minutes, more preferably equal to or more than about 10 minutes, even more preferably equal to or more than about 15 minutes, still more preferably equal to or more than about 20 minutes; to equal to or less than about 120 minutes, more preferably equal to or less than 60 minutes, even more preferably equal to or less than about 45 minutes, still more preferably equal to or less than about 30 minutes.

[0071] The product mixture obtained from the liquefaction step may contain solids (such as unconverted cellulosic material and/or humins and/or char); liquids (such as water and/or hydrocarbon compounds); and/or gas.

[0072] Embodiments of the process of the invention advantageously allow for the production of a product mixture with a viscosity preferably in the range from about 1 to 2000 centipoises (cP) at about 30° C., more preferably a viscosity in the range from about 1 to 1000 centipoises (cP) at about 30° C., and most preferably a viscosity in the range from about 2 to 500 centipoises (cP) at about 30° C. As explained herein a middle fraction of the product mixture is recycled and used as part of the liquid solvent in the liquefaction step. Therefore the liquid solvent in the liquefaction step may also have a viscosity preferably in the range from about 1 to 2000 centipoises (cP) at about 30° C., more preferably a viscosity in the range from about 1 to 1000 centipoises (cP) at about 30° C., and most preferably a viscosity in the range from about 2 to 500 centipoises (cP) at about 30° C. The viscosity may depend on the number of recycles completed. For example, a liquid solvent containing an n-th generation product may comprise at least about 10 wt %, more preferably at least about 30 wt % and most preferably at least about 50 wt % (based on the total weight of the liquid solvent containing an n-th generation product) of a 3rd generation or higher generation reaction products and preferably have a viscosity in the range from about 2 to 500 centipoises (cP) at about 30° C., more preferably a viscosity in the range from about 2 to 100 centipoises (cP); or for example a product mixture respectively liquid solvent may comprise at least about 10 wt %,

more preferably at least about 30 wt % and most preferably at least about 50 wt % (based on the total weight of the liquid solvent containing an n-th generation product) of a 5th generation or higher generation reaction products and preferably have a viscosity in the range from about 10 to 1000 centipoises (cP) at about 30° C., more preferably a viscosity in the range from about 20 to 500 centipoises (cP) at about 30° C.

[0073] In a still further embodiment, the present invention allows for a process where a product composition, in which the cumulative weight of cellulosic material equals the initial weight of liquid solvent, preferably has a viscosity in the range from about 1 to 2000 centipoises (cP) at about 30° C. For example, when cellulosic material is continuously or gradually supplied to the liquefaction step, such cellulosic material may continuously or gradually be converted into a product mixture, of which product mixture in a middle fraction may be separated and partly recycled to be used as part of the liquid solvent in the liquefaction step as described herein. The liquid solvent used may therefore be more and more replaced with such recycled product mixture middle fraction. At a certain moment, the weight of continuously or gradually added cellulosic material from the recycled product mixture middle fraction may equal the initial weight of the liquid solvent (i.e. the weight of liquid solvent at start up); that is, the weight ratio of cumulative weight cellulosic material to initial weight liquid solvent may be about 1:1. At this moment in time, the product mixture and/or the liquid solvent may preferably have a viscosity in the range from about 1 to 2000 centipoises (cP) at about 30° C.

[0074] In a preferred embodiment, step b) involves separating a middle fraction from the product mixture of the liquefaction step to produce a product mixture middle fraction.

[0075] Preferably, the product mixture middle fraction is a fraction of which at least about 90 wt % has a boiling temperature of equal to or more than about 150° C. at about 0.1 MPa and of which about 90 wt % melts at a temperature equal to or less than the reaction temperature.

[0076] Preferably, the product mixture middle fraction is a fraction in which at least about 70 wt %, more preferably at least about 80 wt %, still more preferably at least about 90 wt %, even more preferably at least about 95 wt %, boils in the range from equal to or more than about 150° C. to equal to or less than about 650° C. at about 0.1 MPa. More preferably, the product mixture middle fraction is a product mixture middle fraction in which at least about 90 wt %, preferably at least about 95 wt %, boils in the range from equal to or more than about 150° C. to equal to or less than about 500° C. at about 0.1 MPa. Still more preferably the product mixture middle fraction is a product mixture middle fraction in which at least about 90 wt %, preferably at least about 95 wt %, boils in the range from equal to or more than 180° C. to equal to or less than about 400° C. at about 0.1 MPa. Even more preferably the product mixture middle fraction is a product mixture middle fraction in which at least about 90 wt %, preferably at least about 95 wt %, boils in the range from equal to or more than about 180° C. to equal to or less than about 370° C. at about 0.1 MPa. In a most preferred embodiment, the product mixture middle fraction may have a boiling range in the range as preferred above for the liquid solvent.

[0077] The product mixture middle fraction preferably comprises a mixture of three or more compounds, more preferably a mixture of four or more compounds, which compounds preferably have a molecular weight in the range of equal to or more than about 100 grams per mol, more prefer-

ably equal to or more than about 150 grams per mol, even more preferably equal to or more than about 300 grams per mol, to equal to or less than about 10,000 grams per mol, more preferably equal to or less than about 3000 grams per mol. Preferably the product mixture middle fraction has an average molecular weight of equal to or more than about 100 grams per mol, more preferably equal to or more than about 150 grams per mol, even more preferably equal to or more than about 300 grams per mol to equal to or less than about 10,000 grams per mol, more preferably equal to or less than about 3,000 grams per mol, and most preferably equal to or less than about 1,000 grams per mol.

[0078] In a further preferred embodiment the product mixture middle fraction is a fraction of which at least about 90 wt %, preferably at least about 95 wt %, most preferably about 100 wt %, boils above about 150° C. at about 0.1 MPa and which fraction only comprises compounds having a molecular weight below about 10,000 gram per mol.

[0079] In a still further preferred embodiment the product mixture middle fraction is a fraction that has a viscosity in the range from about 1 to 2000 centipoises (cP) at about 30° C., more preferably a viscosity in the range from about 1 to 1000 centipoises (cP) at about 30° C., and most preferably a viscosity in the range from about 2 to 500 centipoises (cP) at about 30° C.

[0080] In one preferred embodiment, separating a middle fraction from the product mixture of the liquefaction step comprises a step wherein

[0081] a top fraction of the product mixture having a boiling temperature of less than about 150° C. at about 0.1 MPa, more preferably a top fraction of the product mixture having a boiling temperature of less than about 200° C., is removed from the product mixture; and

[0082] a bottom fraction of the product mixture having a melting point higher than the reaction temperature in the liquefaction step is removed from the product mixture.

[0083] In one embodiment, the product mixture middle fraction in this case is a fraction of which at least about 90 wt % has a boiling temperature of equal to or more than about 150° C. at about 0.1 MPa and of which about 90 wt % melts at a temperature equal to or less than the reaction temperature.

[0084] In another preferred embodiment, separating a middle fraction from the product mixture of the liquefaction step comprises a step where the product mixture is separated into a light fraction comprising compounds having a molecular weight of less than about 100 grams per mol; a middle fraction comprising compounds having a molecular weight in the range from equal to or more than about 100 grams per mol to equal to or less than about 10,000 grams per mol; and a heavy fraction comprising compounds having a molecular weight of more than about 10,000 grams per mol; and selecting the middle fraction to produce the product mixture middle fraction.

[0085] In a still further embodiment, separating a middle fraction from the product mixture of the liquefaction step comprises a step wherein the product mixture is separated into a light fraction comprising compounds having a molecular weight of less than about 100 grams per mol; a middle fraction comprising compounds having a molecular weight in the range from equal to or more than about 100 grams per mol to equal to or less than about 3,000 grams per mol; and a heavy fraction comprising compounds having a molecular

weight of more than about 3,000 grams per mol; and selecting the middle fraction to produce the product mixture middle fraction.

[0086] The middle fraction may be separated from the product mixture using any kind of separation technique known by the person skilled in the art, including for example filtration, settling, fractionation (including atmospheric or vacuum distillation and/or flashing), centrifugation, cyclone separation, membrane separation and/or membrane filtration, phase separation, (solvent) extraction and/or a combination thereof.

[0087] Preferably, the top fraction or light fraction is separated from the product mixture by fractionation. The fractionation may be carried out in any manner known to the person skilled in the art to be suitable.

[0088] The fractionation may further be carried out at a wide range of pressures, for example a pressure in the range from equal to or less than about 2 MPa (20 bar absolute) to equal to or more than about 0.0001 MPa (0.001 bar absolute).

[0089] In a preferred embodiment the fractionation may comprise two or more fractionation steps, wherein each subsequent fractionation step is carried out at a lower pressure than the preceding fractionation step.

[0090] Examples of a fractionation include flashing and/or distillation.

[0091] For example, the fractionation may be carried out in a fractionation unit comprising one or more fractionation towers, preferable two or more fractionation towers. The fractionation unit may for example comprise a high-pressure, high-temperature (HPHT) fractionators, optionally followed by a high-pressure, low-temperature (HPLT) fractionators, and/or atmospheric distillation and/or vacuum distillation.

[0092] The product mixture middle fraction separated in step b) may comprise one or more hydrocarbon compounds and preferably contains two or more different hydrocarbon compounds, more preferably three or more different hydrocarbon compounds, most preferably four or more different hydrocarbon compounds boiling in the above mentioned ranges. By a hydrocarbon compound is herein understood to at least refer to a compound that contains at least one hydrogen atom and at least one carbon atom, more preferably a hydrocarbon compound is herein understood to contain at least one hydrogen atom and at least one carbon atom bonded to each other via at least one covalent bond. In addition to hydrogen and carbon, the hydrocarbon compound may contain for example heteroatoms such as sulphur, oxygen and/or nitrogen.

[0093] In certain embodiments of the invention, the product mixture middle fraction selected in step b) preferably comprises one or more oxygenates, more preferably two or more oxygenates. By an oxygenate is herein understood to refer at least to a hydrocarbon compound that contains at least one oxygen atom, more preferably by an oxygenate is herein understood a hydrocarbon compound further containing at least one oxygen atom bonded to a carbon atom via at least one covalent bond. Non-limiting examples of oxygenates include hexanoic acid (boiling at about 205° C. at 0.1 MPa), pentanoic acid (boiling at about 186-187° C. at 0.1 MPa), levulinic acid (boiling at about 245-246° C. at 0.1 MPa), guaiacol (boiling at about 204-206° C. at 0.1 MPa), syringol (boiling at about 261° C. at 0.1 MPa) and/or gamma-valerolactone (boiling at about 207-208° C. at 0.1 MPa).

[0094] Embodiments of the present invention further include recycling of a first portion of the product mixture middle fraction by using it as part of the liquid solvent in the liquefaction step.

[0095] For example, the portion being recycled can be in the range from equal to or more than about 10 wt %, more preferably equal to or more than about 30 wt %, more preferably equal to or more than about 50 wt %, more preferably equal to or more than about 80 wt % to equal to or less than about 99 wt %, more preferably equal to or less than about 95 wt %, most preferably equal to or less than about 90 wt % of the product mixture middle fraction, based on the total weight of the product mixture middle fraction.

[0096] Embodiments of the present invention also further include using a second portion of the product mixture middle fraction to produce a bio-oil.

[0097] In a preferred embodiment, the process further comprises an additional step comprising hydrotreatment of at least part of the produced bio-oil. The hydrotreatment may for example comprise hydrogenation, hydroxyoxygenation and/or hydrodesulphurization.

[0098] Preferably, the hydrotreatment step comprises contacting at least part of the bio-oil with a source of hydrogen in the presence of a hydrotreatment catalyst at a temperature of equal to or more than about 150° C.

[0099] The hydrotreatment catalyst can be any hydrotreatment catalyst known to the person skilled in the art to be suitable for a hydrotreatment process.

[0100] For example, the hydrotreatment catalyst can comprise a heterogeneous and/or homogeneous catalyst. In a preferred embodiment, the hydrotreatment catalyst is a homogeneous catalyst. In another preferred embodiment the hydrotreatment catalyst is a heterogeneous catalyst. The hydrotreatment catalyst preferably comprises a hydrogenation metal known to be suitable for hydrogenation reactions, such as for example iron, molybdenum, cobalt, nickel, copper ruthenium, rhodium, palladium, iridium, platinum and gold, or mixtures thereof. The hydrogenation catalyst comprising such a hydrogenation metal may be sulfided.

[0101] In a further embodiment, sulfided hydrogenation catalysts may be used such as for example a catalyst based on molybdenum sulfide, potentially including Cobalt and/or Nickel as a promotor.

[0102] If the hydrotreatment catalyst is a heterogeneous catalyst, the catalyst preferably comprises a hydrogenation metal supported on a carrier. Non-limiting examples of suitable carriers include carbon, alumina, titanium dioxide, zirconium dioxide, silicon dioxide and mixtures thereof. Non-limiting examples of preferred heterogeneous hydrogenation catalysts include ruthenium, platinum or palladium supported on a carbon carrier. Other non-limiting preferred examples of heterogeneous hydrogenation catalysts include ruthenium supported on titanium dioxide (TiO₂), platinum supported on titanium dioxide and ruthenium supported on zirconium dioxide (ZrO₂). The heterogeneous catalyst and/or carrier may have any suitable form including the form of a mesoporous powder, granules or extrudates or a megaporous structure such as a foam, honeycomb, mesh or cloth. The heterogeneous catalyst may be present in a hydrogenation reactor comprised in a fixed bed or ebullated slurry. Preferably the heterogeneous catalyst is present in a hydrogenation reactor as a fixed bed.

[0103] If the hydrotreatment catalyst is a homogeneous hydrogenation catalyst, the catalyst preferably comprises an

organic or inorganic salt of the hydrogenation metal, such as for example the acetate-, acetylacetonate-, nitrate-, sulphate- or chloride-salt of ruthenium, platinum or palladium.

[0104] The source of hydrogen may be any source of hydrogen known to be suitable for hydrogenation purposes. It may for example include hydrogen gas, but also an hydrogen-donor such as for example formic acid. Preferably the source of hydrogen is a hydrogen gas. Such a hydrogen gas can be applied in the process of the invention at a partial hydrogen pressure that preferably lies in the range from about 0.2 to 20 MPa, more preferably in the range from about 1 to 17 MPa, and most preferably in the range from about 3 to 15 MPa.

[0105] The hydrogenation step can for example be carried out under a total pressure that preferably lies in the range from about 0.2 to 20 MPa, more preferably in the range from about 1 to 17 MPa, and most preferably in the range from about 3 to 15 MPa.

[0106] The at least part of the bio-oil is further preferably contacted with the source of hydrogen in the presence of the hydrotreatment catalyst at a temperature in the range from equal to or more than about 150° C., more preferably equal to or more than about 300° C. to equal to or less than about 450° C., more preferably equal to or less than about 400° C.

[0107] It may be advantageous to further convert the optionally hydrotreated, bio-oil or part of the bio-oil in one or more refinery units into a base fuel.

[0108] Preferably, the process according to the invention further comprises an additional catalytic cracking step, preferably a fluidized catalytic cracking step, for example comprising contacting a feed comprising at least part of the bio-oil—which bio-oil may optionally have been hydrotreated—with a fluidized catalytic cracking catalyst at a temperature of equal to or more than about 400° C., preferably a temperature in the range of equal to or more than about 450° C. to equal to or less than about 800° C., to produce one or more cracked products.

[0109] In a preferred embodiment the catalytic cracking step comprises contacting a fluid hydrocarbon co-feed and a feed comprising at least part of the bio-oil with the fluidized catalytic cracking catalyst at a temperature of equal to or more than about 400° C., to produce the one or more cracked products. That is, in a preferred embodiment also a fluid hydrocarbon co-feed other than the feed may be added into a fluidized catalytic cracking reactor.

[0110] By a hydrocarbon co-feed is herein understood a co-feed that contains one or more hydrocarbon compounds. By a fluid hydrocarbon co-feed is herein understood a hydrocarbon feed that is not in a solid state. The fluid hydrocarbon co-feed is preferably a liquid hydrocarbon co-feed, a gaseous hydrocarbon co-feed, or a mixture thereof. The fluid hydrocarbon co-feed and/or the feed comprising the (part of the) product mixture and/or the part of the product mixture middle fraction selected in step b) can be fed to a catalytic cracking reactor in an essentially liquid state, in an essentially gaseous state or in a partially liquid-partially gaseous state. When entering the catalytic cracking reactor in an essentially or partially liquid state, the feed and/or the co-feed preferably vaporizes upon entry and preferably is contacted in the gaseous state with the fluidized catalytic cracking catalyst.

[0111] The fluid hydrocarbon co-feed can be any non-solid hydrocarbon co-feed known to the skilled person to be suitable as a co-feed for a catalytic cracking unit.

[0112] The fluid hydrocarbon co-feed can for example be obtained from a conventional crude oil (also sometimes

referred to as a petroleum oil or mineral oil), an unconventional crude oil (that is, oil produced or extracted using techniques other than the traditional oil well method) or a Fisher Tropsch oil and/or a mixture thereof.

[0113] The fluid hydrocarbon co-feed may even be a fluid hydrocarbon co-feed from a renewable source, such as for example a vegetable oil.

[0114] In one embodiment, the fluid hydrocarbon co-feed is derived from a, preferably conventional, crude oil. Non-limiting examples of conventional crude oils include West Texas Intermediate crude oil, Brent crude oil, Dubai-Oman crude oil, Arabian Light crude oil, Midway Sunset crude oil or Tapis crude oil.

[0115] More preferably, the fluid hydrocarbon co-feed comprises a fraction of a, preferably conventional, crude oil or renewable oil. Preferred fluid hydrocarbon co-feeds include straight run (atmospheric) gas oils, light cycle oil, heavy cycle oil, hydrowax, flashed distillate, vacuum gas oils (VGO), coker gas oils, diesel, gasoline, kerosene, naphtha, liquefied petroleum gases, atmospheric residue (“long residue”) and vacuum residue (“short residue”) and/or any combination thereof. Most preferably the fluid hydrocarbon co-feed comprises a long residue.

[0116] The composition of the fluid hydrocarbon co-feed may vary widely. The fluid hydrocarbon co-feed may for example contain paraffins, olefins and aromatics.

[0117] Preferably, the fluid hydrocarbon co-feed comprises equal to or more than about 1 wt % paraffins, more preferably equal to or more than about 5 wt % paraffins, and most preferably equal to or more than about 10 wt % paraffins, and preferably equal to or less than about 100 wt % paraffins, more preferably equal to or less than about 90 wt % paraffins, and most preferably equal to or less than about 30 wt % paraffins, based on the total fluid hydrocarbon co-feed. By paraffins both normal-, cyclo- and branched-paraffins are understood.

[0118] When a fluid hydrocarbon co-feed is present, the weight ratio of fluid hydrocarbon co-feed to the feed is preferably equal to or more than about 50 to 50 (5:5), more preferably equal to or more than about 70 to 30 (7:3), still more preferably equal to or more than about 80 to 20 (8:2), even still more preferably equal to or more than about 90 to 10 (9:1). For practical purposes the weight ratio of fluid hydrocarbon co-feed to the feed is preferably equal to or less than about 99.9 to 0.1 (99.9:0.1), more preferably equal to or less than about 95 to 5 (95:5). The fluid hydrocarbon co-feed and the feed are preferably being fed to a fluidized catalytic cracking reactor in a weight ratio within the above ranges.

[0119] The catalytic cracking step is preferably carried out in a fluidized catalytic cracking reactor. The fluidized catalytic cracking reactor can be any fluidized catalytic cracking reactor known in the art to be suitable for the purpose, including for example a fluidized dense bed reactor or a riser reactor.

[0120] The fluidized catalytic cracking catalyst can be any catalyst known to the skilled person to be suitable for use in a cracking process. Preferably, the fluidized catalytic cracking catalyst comprises a zeolitic component. In addition, the fluidized catalytic cracking catalyst can contain an amorphous binder compound and/or a filler. Examples of the amorphous binder component include silica, alumina, titania, zirconia and magnesium oxide, or combinations of two or more of them. Examples of fillers include clays (such as kaolin).

[0121] The zeolite is preferably a large pore zeolite. The large pore zeolite includes a zeolite comprising a porous,

crystalline aluminosilicate structure having a porous internal cell structure on which the major axis of the pores is in the range of about 0.62 nanometer to about 0.8 nanometer. The axes of zeolites are depicted in the 'Atlas of Zeolite Structure Types', of W. M. Meier, D. H. Olson, and Ch. Baerlocher, Fourth Revised Edition 1996, Elsevier, ISBN 0-444-10015-6. Examples of such large pore zeolites include FAU or faujasite, preferably synthetic faujasite, for example, zeolite Y or X, ultra-stable zeolite Y (USY), Rare Earth zeolite Y (=REY) and Rare Earth USY (REUSY). According to the present invention USY is preferably used as the large pore zeolite.

[0122] The fluidized catalytic cracking catalyst can also comprise a medium pore zeolite. The medium pore zeolite that can be used according to the present invention is a zeolite comprising a porous, crystalline aluminosilicate structure having a porous internal cell structure on which the major axis of the pores is in the range of about 0.45 nanometer to about 0.62 nanometer. Examples of such medium pore zeolites are of the MFI structural type, for example, ZSM-5; the MTW type, for example, ZSM-12; the TON structural type, for example, theta one; and the FER structural type, for example, ferrierite. According to the present invention, ZSM-5 is preferably used as the medium pore zeolite.

[0123] According to another embodiment, a blend of large pore and medium pore zeolites may be used. The ratio of the large pore zeolite to the medium pore size zeolite in the cracking catalyst is preferably in the range of about 99:1 to about 70:30, more preferably in the range of about 98:2 to about 85:15.

[0124] The total amount of the large pore size zeolite and/or medium pore zeolite that is present in the cracking catalyst is preferably in the range of about 5 wt % to about 40 wt %, more preferably in the range of about 10 wt % to about 30 wt %, and even more preferably in the range of about 10 wt % to about 25 wt % relative to the total mass of the fluidized catalytic cracking catalyst.

[0125] In the catalytic cracking step one or more cracked products are produced. In a preferred embodiment this/these one or more cracked products is/are subsequently fractionated and/or hydrotreated to produce one or more base fuels.

[0126] Such a base fuel may conveniently be blended with one or more other components to produce a biofuel or biochemical. Non-limiting examples of such one or more other components include anti-oxidants, corrosion inhibitors, ashless detergents, dehazers, dyes, lubricity improvers and/or mineral fuel components, but also conventional petroleum derived gasoline, diesel and/or kerosene fractions.

[0127] By a biofuel is herein understood to refer at least to a fuel that is at least partly derived from a renewable energy source. The biofuel may advantageously be used in the engine of a transportation vehicle.

[0128] One exemplary embodiment of the process according to the invention has further been illustrated by non-limiting FIG. 1.

[0129] FIG. 1 illustrates a process where a feed of birch wood chips (102) is fed together with a liquid solvent (104) in a liquefaction reactor (106). In the liquefaction reactor (106), the birch wood chips (102) and the liquid solvent (104) are contacted at a temperature of about 300° C. and a product mixture (108) is produced that comprises gases, solids and liquids (including also water). The solids are separated from the liquids and gases in solid-liquid separator (110). From the solid-liquid separator (110) a solid stream (112) is obtained and a combined liquid and gas stream (114) is obtained. The

combined liquid and gas stream (114) is forwarded to fractionator (116). In the fractionator (116) the combined liquid and gas stream (114) is fractionated into a top fraction (which will include volatile liquids and gases) (118), a middle fraction (120) and a bottom fraction (122). From the top fraction (118) gases (124) and a light fraction (126), which light fraction boils in the range from about 35° C. to about 150° C. at about 0.1 MPa, are obtained. The middle fraction (120) is a product mixture middle fraction according to the invention, which product mixture middle fraction boils above about 150° C. at about 0.1 MPa and comprises compounds having a molecular weight below about 10,000 gram per mol. From the bottom fraction (122) a heavy fraction (128) is obtained, which comprises compounds having molecular weights above about 10,000 grams per mol.

[0130] About 90 wt % of the middle fraction (120) is withdrawn and recycled with recycle stream (130) to be combined with fresh liquid solvent stream (132) and to be used as liquid solvent (104) in liquefaction reactor (106). The remainder of the middle fraction (120) is combined with the heavy fraction (128) and forwarded as feed (134) to fluidized catalytic cracking unit (140). This fluidized catalytic cracking unit comprises a riser reactor (142), a separator (144) and a catalyst regenerator (146). The feed (134) is fed to the riser reactor (142) together with co-feed (136).

[0131] From the fluidized catalytic cracking unit (140) cracked products (148) are obtained. The cracked products (148) can be fractionated and optionally hydrotreated to obtain one or more base fuels.

[0132] FIG. 2 shows a second embodiment. The numerals and corresponding descriptions for FIG. 1 are equally applicable to FIG. 2 where the numbers are the same and will not be repeated for the sake of brevity. Referring to FIG. 2, at least a portion of the product mixture (108) is subjected to a hydrotreatment (248) before it is combined with fresh liquid solvent stream (132) and to be used as liquid solvent (104) in liquefaction reactor (106). The hydrotreatment (248) can take place before or after the product mixture (108) is separated into different fractions, such as a middle fraction (120), a bottom fraction (122), and a heavy fraction (128). In the embodiment shown in FIG. 2, at least a portion of the middle fraction (120), particularly at least a portion of the middle fraction being recycled (130) is subject to the hydrotreatment (248). That is, as shown, the product mixture (108) is subject to the hydrotreatment (248) after the product mixture (108) passes through the fractionators and a middle fraction (120, 130) has been obtained. In another embodiment, the product mixture (108) is subject to hydrotreatment (248) before it is routed to the fractionators (116), and a middle fraction (120) is obtained and recycled (130). In a preferred embodiment, the hydrotreatment (248) comprises contacting at least a portion of the middle portion (130) to be recycled with a hydrogenation catalyst in the presence of hydrogen.

[0133] The hydrotreatment catalyst for treating at least a portion of the product mixture before part of a middle fraction of the treated product mixture is recycled can comprise a heterogeneous and/or homogeneous catalyst. In a preferred embodiment, the hydrotreatment catalyst is a homogeneous catalyst. In another preferred embodiment, the hydrotreatment catalyst is a heterogeneous catalyst. The hydrotreatment catalyst preferably comprises a hydrogenation metal known to be suitable for hydrogenation reactions. In one embodiment, exemplary hydrogenation metals include metals in groups 8-11 metal and their alloys, for example iron, cobalt,

nickel, copper ruthenium, rhodium, palladium, iridium, platinum and gold, and any combination thereof. In another embodiment, exemplary hydrogenation metals include metals in group 6, such as molybdenum or tungsten, optionally promoted with metals in groups 8-11 described above, and such a hydrogenation metal is sulfided.

[0134] If the hydrotreatment catalyst is a heterogeneous catalyst, the catalyst preferably comprises a hydrogenation metal supported on a carrier. Non-limiting examples of suitable carriers include carbon, oxides containing silicon, aluminum, titanium, zirconium, and phosphorus, such as alumina, titanium dioxide, zirconium dioxide, silicon dioxide, and any combination thereof. Non-limiting examples of preferred heterogeneous hydrogenation catalysts include ruthenium, platinum or palladium supported on a carbon carrier. Other non-limiting preferred examples of heterogeneous hydrogenation catalysts include ruthenium supported on titanium dioxide (TiO₂), platinum supported on titanium dioxide and ruthenium supported on zirconium dioxide (ZrO₂). The heterogeneous catalyst and/or carrier may have any suitable form including the form of a mesoporous powder, granules or extrudates or a megaporous structure such as a foam, honeycomb, mesh or cloth. The heterogeneous catalyst may be present in a hydrogenation reactor comprised in a fixed bed or ebullated slurry. Preferably the heterogeneous catalyst is present in a hydrogenation reactor as a fixed bed.

[0135] In another embodiment, the heterogeneous hydrotreatment catalyst is in the form of colloidal suspension of hydrogenation metal. In one embodiment, the metal can be supported on a suitable support as defined above or can be stabilized as colloid by various additives known to those skilled in the art. Non-limiting examples of such additives include high-boiling carboxylic acids, amine or S-containing components (for sulfided catalysts), monoaromatic compounds or polyaromatic compounds (being in monomeric, oligomeric or polymeric form), and any combination thereof.

[0136] The source of hydrogen may be any source of hydrogen known to be suitable for hydrogenation purposes. Preferably the source of hydrogen is a hydrogen gas. Such a hydrogen gas can be applied in the process of the invention at a partial hydrogen pressure that preferably lies in the range from about 0.2 to 20 MPa, more preferably in the range from about 1 to 17 MPa, and most preferably in the range from about 3 to 15 MPa.

[0137] In a preferred embodiment, the hydrotreatment of the product mixture before recycling can be carried out at a temperature in a range of about 80 degrees C. to about 400 degrees C., more preferably in a range of about 100 degrees C. to about 300 degrees, and most preferably in a range of about 150 degrees C. to about 250 degrees C. In another preferred embodiment, the hydrotreatment of the product mixture before recycling can be carried out under a total pressure in a range of about 0.1 to 25 MPa, more preferably in the range from about 1 to 15 MPa, and most preferably in the range from about 5 to 10 MPa. In another embodiment, the pressure is preferably at least about 0.1 MPa, more preferably at least about 1 MPa, and most preferably at least about 5 MPa. In yet another embodiment, the pressure is preferably less than about 25 MPa, more preferably less than about 15 MPa, and most preferably less than about 10 MPa.

[0138] In one preferred embodiment, the hydrogen to liquid ratio for the hydrotreatment of the middle fraction before it is recycled is in a range of about 10 to 10,000 mL/L, more preferably in a range of about 50 to 1000 mL/L, and most

preferably in a range of about 100 to 500 mL/L. In yet another preferred embodiment, the liquid hourly space velocity (LHSV) is in a range of about 0.1 to 10 L/L/h, more preferably in a range of about 0.3 to 3 L/L/h, and most preferably about 0.5 to 2 L/L/h.

[0139] In the second embodiment, it has been observed that hydrotreating (248) at least a portion of the recycled middle fraction (130) provides stable product yields. It has also been observed that there was no or minimal increase in heavies fraction and no or minimal additional polymerization. While there was an increase in viscosity with each subsequent recycle round, the increase in viscosity was less than if at least a portion of the recycled middle fraction (130) had not been hydrotreated (248).

[0140] The examples described below further demonstrate certain aspects of the present invention. The examples are merely illustrative and not exhaustive and are presented to provide a better understanding of embodiments of the present invention.

EXAMPLES

Comparative Example 1 for Comparison with Example 2

[0141] Example 1 was carried out using a 45 mL Inconel 825 autoclave that was equipped with mechanical stirrer, manometer and internal thermocouple. In the autoclave, 5 consecutive liquefaction runs were carried out (R1-R5).

[0142] For the first run (R1) the autoclave was loaded with 22.43 grams of guaiacol and 7.47 grams of dry pine wood particles (<0.5 mm). The guaiacol was used as a liquid solvent in R1. The autoclave was sealed, pressurized with 6 bar (0.6 MPa) of N₂ and immersed in a hot fluidized sand bed that was set at 300° C. The autoclave was held in the hot sand for 30 min (its content reached 270° C. within some 4 minutes). A summary of the reaction conditions of the first run (R1) of comparative example 1 can be found in Table 1. At the end of the first run the autoclave was quenched in a water bath to ambient temperature (about 20° C.) and vented to release the gases for analysis. The autoclave was then opened for sampling the liquid reaction effluent. A summary of the results of the first run (R1) of comparative example 1 can be found in Table 1.

[0143] After the first run the contents of the autoclave were removed and the autoclave was cleaned. Subsequently a weighted amount of the contents of the autoclave as specified in Table 1 for the second run (R2) was returned to the autoclave, to be used as a liquid solvent in R2. This procedure may be considered to mimic a recycle of the complete reaction effluent of the first run (R1) for use as liquid solvent in the second run (R2). Subsequently a second weighted amount of dry pine wood as listed in Table 1 for second run (R2) was added to the autoclave and the autoclave was sealed and subjected to a second run.

[0144] This procedure was repeated to achieve 5 consecutive runs, during which the operating pressure increased from 55 bar (5.5 MegaPascal) for the first run (R1) to 87 bar (8.7 MegaPascal) for the fifth run (R5). The liquid reaction effluent appeared to become increasingly viscous, being syrup-like after the third run (R3) and bitumen-like after the fifth run (R5). The viscosity of the liquid reaction effluent after the fifth run (R5), measured using a rotational viscosimeter (Brookfield DV) at 98° C., ranged from 2847 to 4250 centipoise (cP), depending on the rotating speed. The overall

degree of liquefaction could not be determined since the viscosity of the product hindered separation of the char.

[0145] A summary of the reaction conditions and results for runs 1-5 (R1-5) of comparative example 1 can be found in table 1 below. As indicated the liquid solvent was guaiacol for the first run (R1) and a weighted amount of the reaction effluent of the preceding run (including water, tar and char) for each consecutive run (R2-R5).

[0146] The liquid reaction effluent was analyzed by Gas Chromatography-Mass Spectroscopy (GC-MS) as well as Size Exclusion Chromatography (SEC). SEC analyses used Tetrahydrofuran (THF) as mobile phase and a series of polystyrene for molecular weight (Mw) calibration.

[0147] The concentration of guaiacol in the liquid reaction effluent was measured by Gas Chromatography-Mass Spectroscopy (GC-MS). In addition the percentage of the distillates fraction (i.e. compounds having a molecular weight of less than 146 Dalton); vacuum gas oil fraction (VGO, i.e. compounds having a molecular weight in the range from 146 to 10,000 Dalton); and residual oil fraction (i.e. compounds having a molecular weight of more than 10,000 Dalton) in the SEC spectra was determined. The SEC spectra for comparative example 1 have been included in FIG. 3A and FIG. 3B. The values on the Y-axis may be considered to be arbitrary and may for example depend on the amount of sample used and the specific apparatus used.

[0148] GC-MS revealed that the guaiacol content decreased from 70.8 wt % in the liquid reaction effluent of the first run (R1) to 18.6 wt % in the liquid reaction effluent of the fifth run (R5). SEC analysis confirmed the strong decrease of distillates (compounds having a molecular weight of <146 Dalton) and showed steady increase of vacuum gas oil (compounds having a molecular weight of 146-10,000 Dalton). However, it also revealed the buildup of increasingly residual oil (compounds having a molecular weight above 10,000 Dalton).

stirrer, manometer and internal thermocouple. In the autoclave, 5 consecutive liquefaction runs were carried out (R1-R5).

[0150] For the first run (R1) the autoclave was loaded with 23.91 grams of guaiacol and 3.08 grams of dry pine wood particles (<0.5 mm) that were impregnated with 3 grams of water. The guaiacol was used as a liquid solvent in R1. The autoclave was sealed, pressurized with 6 bar (0.6 MPa) of N₂ and immersed in a hot fluidized sand bed that was set at 300° C. The autoclave was held in the hot sand for 30 min (its content reached 270° C. within some 4 minutes). A summary of the reaction conditions of the first run (R1) for example 2 can be found in Table 2. At the end of the run, the autoclave was cooled to 200° C. and vented to remove the gases and light condensable products, including much of the water, to top the reaction effluent. The gases and light condensable products removed at 200° C. are in this example also referred to as "lights". The autoclave was subsequently quenched in a water bath at ambient temperature (about 20° C.) and opened and its contents poured over a 1 micron filter to separate the solid residue from the liquid reaction effluent to produce a middle fraction (in this example also referred to as bio-oil or bio-oil fraction). This last step may also be referred to as tailing and is considered to remove tar and char. The autoclave was rinsed with acetone and the rinsing liquid as well as clean acetone were used to wash the solid residue. The solid residue was dried to deliver char. Evaporation of the acetone wash liquor yielded a residual oil (tar).

[0151] The bio-oil fraction was sampled for SEC and GC-MS analyses. The remaining part of the bio-oil fraction was used for viscosity measurement using a rotational viscosimeter (Brookfield DV) at 30° C. and subsequently reloaded in the autoclave, to be used as a liquid solvent in the second run (R2). This procedure may be considered to mimic a recycle of the middle fraction of the reaction effluent of the first run (R1) for use as liquid solvent in the second run (R2). Subsequently

TABLE 1

	Run				
	R1	R2	R3	R4	R5
Weighted amount of liquid solvent (grams)	22.43	20.01	18.88	18.71	19.41
Type of liquid solvent	Guaiacol	Reaction effluent of R1	Reaction effluent of R2	Reaction effluent of R3	Reaction effluent of R4
Weighted amount of dry pine wood (grams)	7.47	6.75	6.33	6.28	6.35
weight ratio of dry pine wood to liquid solvent (w:w)	25:75	25:75	25:75	25:75	25:75
cumulative weight percentage of dry pine wood*** (wt %)	25	40	50	57	63
guaiacol in liquid reaction effluent (wt %)	64.1	48.6	34.8	23.7	17.0
Distillates in liquid reaction effluent (%)	76	53	36	24	13
VGO in liquid reaction effluent (%)	23	46	62	72	75
Residual oil in liquid reaction effluent (%)	0.1	0.3	1.8	4.4	11.2
Viscosity (cP at 98° C.)	n.m.	n.m.	n.m.	n.m.	3000-4000

n.m. = not measured;

***based on total weight of dry pine wood and weight of initial liquid solvent (guaiacol) (wt %)

Example 2

According to an Embodiment of the Invention

[0149] Example 2 was carried out using a 45 mL using a 45 mL Inconel 825 autoclave that was equipped with mechanical

a second weighted amount of dry pine wood impregnated with a second weighted amount of water as listed in Table 2 for second run (R2) was added to the autoclave and the autoclave was sealed and subjected to a second run. The weight ratio of liquid solvent, fresh pine wood and water in the second run (R2) was 8:1:1 bio-oil:wood:water.

[0152] A summary of the results of the first run (R1) of example 2 can be found in Table 2.

The second run was performed as described above and followed by a 3rd and 4th that also used an bio-oil:wood:water weight ratio of about 8:1:1. The 4th run was followed by a 5th and more severe run that used an bio-oil:wood:water weight ratio of 7:2:1. The oil obtained after the 5th run was still very fluid at room temperature.

[0153] A summary of the reaction conditions and results for runs 1-5 (R1-5) of example 2 can be found in table 2 below. As indicated the liquid solvent was guaiacol for the first run (R1) and a weighted amount of the middle fraction of the reaction effluent of the preceding run (free of gas, lights, tar and char) for each consecutive run (R2-R5).

[0154] For each run, the middle fraction of the reaction effluent (also referred to as bio-oil or bio-oil fraction in this example) was analyzed by Gas Chromatography-Mass Spectroscopy (GC-MS) as well as Size Exclusion Chromatography (SEC). SEC analyses used Tetrahydrofuran (THF) as mobile phase and a series of polystyrene for molecular weight (Mw) calibration.

[0155] The concentration of guaiacol in the bio-oil fraction was measured by Gas Chromatography-Mass Spectroscopy (GC-MS). In addition the percentage of the distillates fraction (i.e. compounds having a molecular weight of less than 146 Dalton); vacuum gas oil fraction (VGO, i.e. compounds having a molecular weight in the range from 146 to 10,000 Dalton); and residual oil fraction (i.e. compounds having a molecular weight of more than 10,000 Dalton) in the SEC spectra was determined. The SEC spectra for example 2 have been included in FIG. 4A and FIG. 4B. The values on the Y-axis may be considered to be arbitrary and may for example depend on the amount of sample used and the specific apparatus used.

sis revealed a decrease in guaiacol concentration (from 76.6 to 54.1 wt %) in the bio-oil. SEC analysis confirmed the decrease in distillate (mainly guaiacol), showed a significant increase in vacuum gas oil (compounds having a molecular weight in the range from 146 to 10,000 Dalton) and a stable and low concentration of residual oil (compounds having a molecular weight of >10,000 Dalton). These observations indicate that the bio-oil has a higher liquefaction power than the starting solvent, guaiacol. Meanwhile, the viscosity of the oil remained low by increasing only from 8 cP to 64 cP after 4 consecutive runs.

[0157] Run 5 applied more severe conditions by using a higher loading of wood. Nevertheless, the yield in oil+tar remained high (80.5 wt %), the yield in gas, lights and char remained low and the guaiacol concentration of the oil dropped further (37.5 wt %). The fraction of Distillates decreased further, that of VGO increased further but the fraction of residual oil remained low. Consistently, the viscosity increased significantly to 320 cP measured. When measured at 60° C., the viscosity dropped to ~40 cP. One skilled in the art may therefore expect that if the temperature would be raised further to 98° C., the viscosity may even drop further. It should be stressed that the oil remained very fluid at room temperature, which contrasts with the bitumen syrup and behavior observed after run 3 and 5 of comparative example 1.

[0158] Examples 1 and 2 illustrate that the combined addition of water in the feed and the removal of light and heavy products allows the build-up of bio-oil through consecutive refill of wood without severe increase (10×) in the by-production of heavy residual oil and the resulting increase (10×) in oil viscosity.

TABLE 2

Reaction conditions and results for Runs 1 to 5 (R1-5) of example 2.					
	Run				
	R1	R2	R3	R4	R5
Weighted amount of liquid solvent (grams)	23.91	19.00	17.50	10.59	7.01
Type of liquid solvent	Guaiacol	Middle fraction of R1	Middle fraction of R2	Middle fraction of R3	Middle fraction of R4
Weighted amount of dry pine wood (grams)	3.08	2.45	2.31	1.33	2.21
Weighted amount of water* (grams)	3.00	2.46	2.23	1.29	1.03
weight ratio of liquid solvent:pine wood:water (w:w:w)	80:10:10	80:10:10	79:11:10	80:10:10	68:22:10
cumulative weight percentage of dry pine wood*** (wt %)	11	20	28	34	44
Yield Gas (wt %)	11.4	15.9	13.4	8.1	13.1
Yield Lights (wt %)	11.0	0.2	0.0	7.5	5.9
Yield Char (wt %)	6.3	0.8	0.9	0.7	0.5
Yield oil + tar** (wt %)	71.3	83.2	85.7	83.6	80.5
guaiacol in bio-oil fraction (wt %)	76.6	71.0	62.4	54.1	37.5
Distillates in bio-oil fraction (%)	90	78	68	59	43
VGO in bio-oil fraction (%)	10	22	32	41	56
Residual oil in bio-oil fraction (%)	0.1	0.0	0.0	0.1	0.5
Viscosity (cP at 30° C.)	8	15	28	64	320

n.m. = not measured;

*water was impregnated into the wood;

**oil + tar yields were calculated as 100% minus gas yield, minus lights yield and minus char yield (100%-gas-% lights-% char);

***based on total weight of dry pine wood and weight of initial liquid solvent (guaiacol)(wt %)

[0156] Compared to run 1, the subsequent runs showed a decrease in undesired by-products, gas, lights and char and, thereby, an increase of 12-14 wt % in the desired oil+tar yield (defined as 100-char-gas-lights). Meanwhile, GC-MS analy-

Comparative Example 3 for Comparison with Example 4

[0159] Example 3 was carried out using a 560 mL Inconel 825 autoclave that was equipped with mechanical stirrer,

manometer and internal thermocouple. In the autoclave, 4 consecutive liquefaction runs were carried out (R1-R4).

[0160] For the first run (R1) the autoclave was loaded with 239.39 grams of guaiacol and 30.45 grams of dry pine wood particles (<0.5 mm) that were impregnated with 30.44 grams of water. The guaiacol was used as a liquid solvent in R1. The autoclave was sealed and pressurized with 6 bar (0.6 MPa) of N₂. The autoclave was then heated using an electric jacket which was placed around the reactor and was set at 325° C. The autoclave was kept for 30 minutes above reactor temperature of 270° C. (its content reached 270° C. within around 90 minutes). A summary of the reaction conditions of the first run (R1) for example 4 can be found in Table 4. At the end of the run, the autoclave was cooled to 200° C. via natural convection and vented to remove the gases and light condensable products, including much of the water, to top the reaction effluent. The gases and light condensable products removed at 200° C. are in this example also referred to as "lights." The autoclave was subsequently cooled to ambient temperature (about 20° C.) and opened and its contents poured over a 1 micron filter to separate the solid residue from the liquid reaction effluent to produce a middle fraction (in this example also referred to as bio-oil or bio-oil fraction). This last step may also be referred to as tailing and is considered to remove tar and char. The autoclave was rinsed with acetone and the rinsing liquid, as well as clean acetone, were used to wash the solid residue. The solid residue was dried to deliver char. Evaporation of the acetone wash liquor yielded a residual oil (tar).

[0161] The bio-oil fraction was sampled for SEC and GC-MS analyses. The remaining part of the bio-oil fraction was used for viscosity measurement using a rotational viscosimeter (Brookfield DV) at 30° C. and subsequently reloaded in the autoclave, to be used as a liquid solvent in the second run

(R2). This procedure may be considered to mimic a recycle of the middle fraction of the reaction effluent of the first run (R1) for use as liquid solvent in the second run (R2). Subsequently a second weighted amount of dry pine wood impregnated with a second weighted amount of water as listed in Table 2 for second run (R2) was added to the autoclave and the autoclave was sealed and subjected to a second run. This second run (R2) was performed at more severe conditions, with a weight ratio of liquid solvent, fresh pine wood and water of 7:2:1 bio-oil:wood:water. It was followed by a 3rd and 4th runs (R3 and R4) that also used a bio-oil:wood:water weight ratio of about 7:2:1.

[0162] A summary of the reaction conditions and results for runs 1-4 (R1-4) of example 3 can be found in Table 3 below. As indicated the liquid solvent was guaiacol for the first run (R1) and a weighted amount of the middle fraction of the reaction effluent of the preceding run (free of gas, lights, tar and char) for each consecutive run (R2-R4).

[0163] For each run, the middle fraction of the reaction effluent (also referred to as bio-oil or bio-oil fraction in this example) was analyzed Size Exclusion Chromatography (SEC). SEC analyses used Tetrahydrofuran (THF) as mobile phase and a series of polystyrene for molecular weight (Mw) calibration.

[0164] In addition the percentage of the distillates fraction (i.e. compounds having a molecular weight of less than 146 Dalton); vacuum gas oil fraction (VGO, i.e. compounds having a molecular weight in the range from 146 to 10,000 Dalton); and residual oil fraction (i.e. compounds having a molecular weight of more than 10,000 Dalton) in the SEC spectra was determined. The SEC spectra for example 3 have been included in FIG. 5. The values on the Y-axis may be considered to be arbitrary and may for example depend on the amount of sample used and the specific apparatus used.

TABLE 3

	Run			
	R1	R2	R3	R4
Reaction conditions and results for Runs 1 to 4 (R1-R4) of example 3.				
Weighted amount of liquid solvent (grams)	239.39	228.66	207.88	136.27
Type of liquid solvent	Guaiacol	Middle fraction of R1	Middle fraction of R2	Middle fraction of R3
Weighted amount of dry pine wood (grams)	30.45	66.09	60.24	48.92
Weighted amount of water* (grams)	30.44	33.45	30.71	24.52
weight ratio of liquid solvent:pine wood:water (w:w:w)	80:10:10	70:20:10	70:20:10	65:23:12
cumulative weight percentage of dry pine wood** (wt %)	10	27	39	49
Yield Gas (wt %)	n.m.	n.m.	n.m.	n.m.
Yield Lights (wt %)***	11.8	8.0	22.6	24.2
Yield Char (wt %)***	0.2	0.2	0.5	n.m.****
Yield oil + tar (wt %)	84.7	76.2	70.8	80.1*****
guaiacol in bio-oil fraction (wt %)	n.m.	n.m.	n.m.	n.m.
Distillates in bio-oil fraction (%)	89	66	47	34
VGO in bio-oil fraction (%)	11	34	53	66
Residual oil in bio-oil fraction (%)	0.1	0.2	0.2	0.5
Viscosity (cP at 30° C.)	7	44	1227	12600*****

n.m. = not measured;

*water was impregnated into the wood;

**Cumulative wood % = [% solvent_{exp. n} * (% cumulative wood_{exp. (n-1)} / 100)] + % wood_{exp. n};

***based on cumulative wood intake + guaiacol;

****Oil and solid could not be completely separated, yields are reported together as Yield oil + tar;

*****Viscosity estimated from viscosity(40° C.) = 4000 cp assuming $v(T) = A * e(11000/T)$ with T expressed in Kelvin.

Example 4

According to Another Embodiment of the Invention

[0165] Example 4 was carried out using a 560 mL Inconel 825 autoclave that was equipped with mechanical stirrer, pressure sensor and internal thermocouple. In the autoclave, 4 consecutive liquefaction runs were carried out (R1-R4).

[0166] For the first run (R1) the autoclave was loaded with 174.39 grams of guaiacol, 24.69 grams of water and 49.02 grams of dry pine wood particles (<0.5 mm). The guaiacol was used as a liquid solvent in R1. The autoclave was sealed, pressurized with 5 bar (0.5 MPa) of N₂. The autoclave was then heated using an electric jacket which was placed around the reactor and was set at 330° C. The autoclave was kept for 30 minutes above reactor temperature of 270° C. (its content reached 270° C. within around 60 minutes). A summary of the reaction conditions of the first run (R1) for example 3 can be found in Table 3. At the end of the run, the autoclave was cooled to around 200° C. via natural convection and further it was cooled to ambient temperature (about 20° C.) by spraying water to the outer wall of the reactor and opened. The bio-oil fraction was sampled for SEC and GC-MS analyses and for Karl Fischer titration to determine water content. The remaining part of the bio-oil fraction was used for viscosity measurement using a rotational viscosity meter (Brookfield DV) at 30° C. and subsequently reloaded in the autoclave for a first hydrotreatment (T1).

[0167] For a first hydrotreatment (T1) the autoclave was then loaded with around 5 wt % (11.41 g) of Ru/C (5 wt % Ru on C, obtained from Sigma-Aldrich). A baffle was placed inside the reactor to have good mixing. The reactor was first pressurized with N₂ at 130 bar. If the leak test was successful, N₂ was vented out, at the same time removing the remaining air inside the reactor. Afterwards a second leak test was done by pressurizing the reactor with H₂ at 180 bar. The H₂ was vented out also removing N₂. The reactor was then pressurized with H₂ at around 130 bar and an electric jacket was placed around the reactor. The stirrer and the heater were turned on and were set to 300 rpm and 230° C. respectively. Heating of the reactor caused an initial increase in reactor pressure that was followed by stabilization and, subsequently, pressure decrease as reaction started. Whenever reactor pressure dropped, additional hydrogen was supplied and the reactor pressure was kept in the range of 170-200 bar. The autoclave was heated for 2 hours that gave the final reactor temperature around 210° C. Thereafter, the heater was turned off and when reactor temperature reached 190° C., gas sampling line was opened to vent out the gases and light condensable products, including much of the water. The gases and light condensable products were passed through a condenser where vapors were condensed and off gases were sampled for GC analyses. The gases and light condensable products, removed at 190° C. are in this example also referred to as "lights." The autoclave was subsequently cooled to ambient temperature and opened and its contents poured over a 5 micron filter to separate the solid residue and the hydrotreatment catalyst from the liquid reaction effluent to produce a middle fraction (in this example also referred to as bio-oil or bio-oil fraction). This last step may also be referred to as tailing and is considered to remove char. The autoclave was rinsed with acetone and the rinsing liquid as well as clean acetone were used to wash the solid residue. The solid residue was dried to deliver char and the hydrotreatment catalyst.

Evaporation of the acetone wash liquor yielded a residual oil which was added to the filtered oil.

[0168] The bio-oil fraction was sampled for SEC and GC-MS analyses. Water content was measured using Karl Fischer Titration (787 KF Titrino—Metrohm). The remaining part of the bio-oil fraction was used for viscosity measurement using a rotational viscosity meter (Brookfield DV) at 30° C. and subsequently reloaded in the autoclave, to be used as a liquid solvent in the second run (R2).

[0169] This procedure may be considered to mimic a recycle of the middle fraction of the reaction effluent of the first run and hydrotreatment (R1 and T1) for use as liquid solvent in the second run (R2). Subsequently a second weighted amount of dry pine wood mixed with a second weighted amount of water as listed in Table 3 for second run (R2) was added to the autoclave and the autoclave was sealed and subjected to a second run. The weight ratio of liquid solvent, fresh pine wood and water in the second run (R2) was 7:2:1 bio-oil:wood:water. A summary of the results of the second run (R12 of example 3 can be found in Table 3.

[0170] The second run was followed by a second hydrotreatment (T2) that was performed as the first treatment (T1). A summary of the results of the second treatment (T2) of example 3 can be found in Table 3.

[0171] The second treatment was followed by a 3rd run (R3) and 3rd treatment (T3) and a 4th run (R4) and 4th treatment (T4) as described above. the bio-oil:wood:water weight ratio of the R3-4 amounted to 7:2:1. For T3-4, the light components were purged at 190° C. while the autoclave temperature was kept at 210° C. instead of being allowed to cool down further, as applied for T1-2. The oil obtained after the 4th run was still very fluid at room temperature.

[0172] A summary of the reaction conditions and results for runs 1-4 (R1-4) and hydrotreatment 1-4 (T1-4) of example 4 can be found in Table 4 below. As indicated the liquid solvent was guaiacol for the first run (R 1) and a weighted amount of the middle fraction of the reaction effluent of the preceding run (free of gas, lights and char) for each consecutive run (R2-R4).

[0173] For each run, the middle fraction of the reaction effluent (also referred to as bio-oil or bio-oil fraction in this example) was analyzed by Gas Chromatography-Mass Spectroscopy (GC-MS) as well as Size Exclusion Chromatography (SEC). SEC analyses used Tetrahydrofuran (THF) as mobile phase and a series of polystyrene for molecular weight (Mw) calibration.

[0174] The percentage of the distillates fraction (i.e. compounds having a molecular weight of less than 146 Dalton); vacuum gas oil fraction (VGO, i.e. compounds having a molecular weight in the range from 146 to 10,000 Dalton); and residual oil fraction (i.e. compounds having a molecular weight of more than 10,000 Dalton) in the SEC spectra was determined. The SEC spectra for example 3 have been included in FIG. 6A and FIG. 6B. The values on the Y-axis may be considered to be arbitrary and may for example depend on the amount of sample used and the specific apparatus used.

[0175] SEC analysis confirmed the decrease in distillate (mainly guaiacol), showed a significant increase in vacuum gas oil (compounds having a molecular weight in the range from 146 to 10,000 Dalton) and a stable and low concentration of residual oil (compounds having a molecular weight of >10,000 Dalton). These observations indicate that the bio-oil has a higher liquefaction power than the starting solvent,

guaiacol. Meanwhile, the viscosity of the oil increase from 17.6 cP to 3400 cP after 4 consecutive runs and 4 consecutive hydrotreatments. It will be noticed that the viscosity of the bio-oil is higher after hydrotreatment than before it. This increase is due to the removal of light components after hydrotreatment, which resulted in a thickening of the bio-oil. These light components accounted for 14 to 34 w % of the total intake, depending on the conditions, as shown in Table 4.

[0176] Examples 3 and 4 illustrate that the addition of an hydrotreatment and removal of light and heavy products before recycling of the middle fraction allows the build-up of bio-oil through consecutive refill of wood without severe increase in the by-production of heavy residual oil and, consequently, with a lower increase in oil viscosity.

[0177] Indeed, the oil produced at 50% cumulative wood intake without HDO (Run 4 of example 3) shows a viscosity of 12600 cp (30° C.), which is more than 10x the 866 cp observed after comparable cumulative wood loading but with interstage HDO (T3 of example 4).

[0178] Further modifications and alternative embodiments of various aspects of the invention will be apparent to those skilled in the art in view of this description. Accordingly, this description is to be construed as illustrative only and is for the purpose of teaching those skilled in the art the general manner of carrying out the invention. It is to be understood that the forms of the invention shown and described herein are to be taken as the presently preferred embodiments. Elements and materials may be substituted for those illustrated and described herein, parts and processes may be reversed, and certain features of the invention may be utilized independently, all as would be apparent to one skilled in the art after having the benefit of this description of the invention. Changes may be made in the elements described herein without departing from the spirit and scope of the invention as described in the following claims.

What is claimed is:

1. A process for the conversion of a cellulosic material into a bio-oil, comprising the steps of:

TABLE 4

Reaction conditions and results for Runs 1 to 4 (R1-4) and hydrotreatments 1 to 4 (T1-4) of example 4.								
Run	R1	T1	R2	T2	R3	T3	R4	T4
Weighted amount of liquid solvent (grams)	174.39	234.97	196.46	266.35	215.06	292.21	179	241.83
Type of liquid solvent	Guaiacol	Bio-oil from R1	Middle fraction of T1	Bio-oil from R2	Middle fraction of T2	Bio-oil from R3	Middle fraction of T3	Bio-oil from R4
Weighted amount of dry pine wood (grams)	49.02	0	56.46	0	61.68	0	51.08	0
Weighted amount of water* (grams)	24.69	0	28.05	0	30.44	0	25.40	0
weight ratio of liquid solvent:pine wood:water (w:w:w)	70:20:10	n.a.	70:20:10	n.a.	70:20:10	n.a.	70:20:10	n.a.
cumulative weight percentage of dry pine wood** (wt %)	21.9	n.a.	37.7	n.a.	48.9	n.a.	55.6	n.a.
Maximum Temperature (° C.)	292	213	290	213	290	211	284	213
Maximum Pressure (bar)	74.2	185	92.3	190	92.3	200	74.1	189
Absolute yield***								
Yield Gas (wt %)	1.8	0.7	1.9	0.2	1.9	0.6	2.1	0.3
Yield Lights (wt %)		14.9		13.6		33.9		22.6
Yield Char (wt %)****		1.3		1.8		2.1		1.2
Yield Oil + tar (wt %)	96.6 ^a	84.8	96.3	83.1	96.4	62.6	96.7	75.3
Mass Closure (wt %)*****	98.4	101.7	98.2	98.7	98.3	99.2	98.8	99.4
H ₂ consumption (gm)		11.6		5.10		3.0		1.9
Combined yield based on wood*****								
Yield Lights + Oil + tar (wt %) ^b		81.1		80.9		77.4		82.3
Yield Char (wt %)		6.3		8.8		10.1		5.5
Yield gas (wt %)		12.6		10.3		12.5		12.2
Bio-oil analysis								
Distillates in bio-oil (%)	80.7	68.0	52.9	50.7	40.1	34.9	28.0	23.9
VGO in bio-oil (%)	19.2	31.8	46.8	49.0	59.5	64.7	71.3	75.3
Residual oil in bio-oil (%)	0.1	0.2	0.3	0.3	0.4	0.4	0.7	0.8
Viscosity (cP at 30° C.)	17.6	21.6	26.4	39.6	57.2	866	360	3400
Water in the oil (wt %)	13.3	6.4	18.7	11.6	22.5	1.4	14.9	1.1
Water formed (wt %)*****	14.7		17.5		18.1		17.5	

n.m. = not measured;

*water was first mixed in the liquid then wood was introduced;

**based on total weight of dry pine wood and weight of initial liquid solvent (guaiacol) (wt %);

***calculated based on total feed i.e. liquid and wood;

****calculated by subtracting amount of catalyst intake from the total solid obtained;

*****H₂ consumption was not accounted in mass closure;

*****based on the wood intake in the liquefaction run;

^aYield of oil + tar in runs R1-4 also include char. A duplicate run of R1 under same conditions gave very low char yield 0.7 wt % on wood intake;

^bLights + oil + tar yields were calculated as 100% minus gas yield, minus char yield (100%-gas-% char);

- (a) contacting the cellulosic material with a liquid solvent in an inert atmosphere at a reaction temperature in the range from equal to or more than about 260° C. to equal to or less than about 400° C. to produce a product mixture;
- (b) separating a middle fraction from the product mixture to produce a product mixture middle fraction;
- (c) recycling a first portion of the product mixture middle fraction by using said first portion as part of the liquid solvent;
- (d) hydrotreating at least part of said first portion of the product mixture before the recycling step (c); and
- (e) using a second portion of the product mixture middle fraction to produce a bio-oil.
- 2.** The process of claim **1** wherein the hydrotreating step (d) is performed before the separating step (b).
- 3.** The process of claim **1** wherein the hydrotreating step (d) is performed after the separating step (b).
- 4.** The process of claim **1**, wherein the hydrotreating step comprises contacting the at least part of said first portion with a hydrogenation catalyst in the presence of hydrogen.
- 5.** The process of claim **4**, wherein the hydrogenation catalyst comprises at least one metal in groups 8-11.
- 6.** The process of claim **5**, wherein the hydrogenation catalyst further comprises a carbon carrier.
- 7.** The process of claim **4**, wherein the hydrogenation catalyst comprises at least one metal in group 6.
- 8.** The process of claim **1**, wherein the hydrotreating step is carried out at a temperature in a range of about 80 degrees C. to about 350 degrees C.
- 9.** The process of claim **8**, wherein the hydrotreating step is carried out at a temperature in a range of about 100 degrees C. to about 250 degrees C.
- 10.** The process of claim **9**, wherein the hydrotreating step is carried out at a temperature in a range of about 150 degrees C. to about 200 degrees C.
- 11.** The process of claim **1**, wherein the hydrotreating step is carried out under a pressure in a range of about 0.1 MPa to about 25 MPa.
- 12.** The process of claim **11**, wherein the hydrotreating step is carried out under a pressure in a range of about 1 MPa to about 15 MPa.
- 13.** The process of claim **12**, wherein the hydrotreating step is carried out under a pressure in a range of about 5 MPa to about 10 MPa.
- 14.** The process of claim **1**, wherein the hydrotreating step comprises a hydrogen to liquid ratio of 10 to 10,000 mL/L.
- 15.** The process of claim **14**, wherein the hydrotreating step comprises a hydrogen to liquid ratio of 50 to 1000 mL/L.
- 16.** The process of claim **15**, wherein the hydrotreating step comprises a hydrogen to liquid ratio of 100 to 500 mL/L.
- 17.** The process of claim **1**, wherein the hydrotreating step comprises a liquid hourly space velocity in a range of about 0.1 L/L/h to about 10 L/L/h.
- 18.** The process of claim **17**, wherein the hydrotreating step comprises a liquid hourly space velocity in a range of about 0.3 L/L/h to about 3 L/L/h.
- 19.** The process of claim **18**, wherein the hydrotreating step comprises a liquid hourly space velocity in a range of about 0.5 L/L/h to about 2 L/L/h.

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