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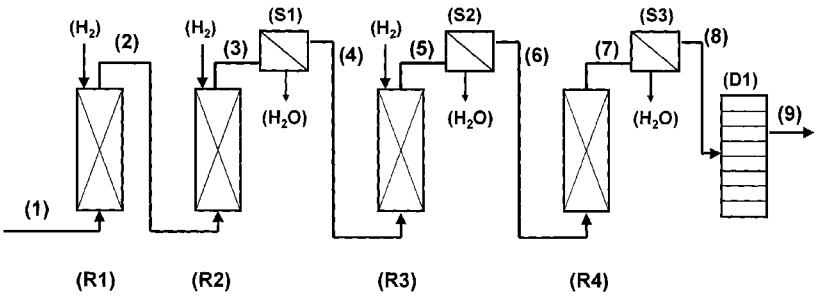

Figure 1

(57) Abstract: A process for the production of dipentyl ether from levulinic acid resulting from biomass including at least one polysaccharide comprising the following steps: (a) reacting said levulinic acid in the presence of hydrogen and at least one non-acid hydrogenation catalyst obtaining γ-valerolactone; (b) reacting said γ-valerolactone in the presence of hydrogen and at least one acid hydrogenation catalyst obtaining pentanoic acid; (c) reacting said pentanoic acid in the presence of hydrogen and at least a catalyst comprising platinum (Pt) and tin (Sn) obtaining pentyl alcohol; (d) reacting said pentyl alcohol in the presence of at least one solid acid catalyst thereby obtaining dipentyl ether. The dipentyl ether thus obtained can be advantageously used as an oxygenated component for fuels for diesel engines.

PROCESS FOR THE PRODUCTION OF DIPENTYL ETHER FROM LEVULINIC ACID RESULTING FROM BIOMASS

The present invention relates to a process for the production of dipentyl ether from levulinic acid resulting from biomass.

More in particular, the present invention relates to a process for the production of dipentyl ether from levulinic acid resulting from biomass including at least one polysaccharide comprising the following steps: (a) reacting said levulinic acid in the presence of hydrogen and at least one non-acid hydrogenation catalyst obtaining γ-valerolactone; (b) reacting said γ-valerolactone in the presence of hydrogen and at least one acid hydrogenation catalyst obtaining pentanoic acid; (c) reacting said pentanoic acid in the presence of hydrogen and at least a catalyst comprising platinum (Pt) and tin (Sn) obtaining pentyl alcohol; (d) reacting said pentyl alcohol in the presence of at least one solid acid catalyst thereby obtaining dipentyl ether.

The dipentyl ether thus obtained can be advantageously used as an oxygenated component for fuels for diesel engines.

The production of levulinic acid from biomass is known in the state of the art.

For example, Huber G. W. et al., in the review "Synthesis of transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering", "*Chemical Reviews*" (2006), Vol. 106, pag. 4044-4098, describe the production of levulinic acid from cellulosic biomass. Said review also describes the conversion of the levulinic acid into levulinic esters which can be used as oxygenated components for fuels for diesel engines.

Alonso D. M. et al., in the review "Catalytic conversion of biomass to biofuels", "*Green Chemistry*" (2010), Vol. 12, pag. 1493-1513, describe the production of levulinic acid from

biomass, in particular through the process known as Biofine. Said review also describes the conversion of the levulinic acid into levulinic methyl or ethyl esters which can be used as oxygenated components for fuels for diesel engines.

Galletti Raspolli A. M. et al., in the article "Levulinic acid production from waste biomass", "*BioResources*" (2012), Vol. 7(2), pag. 1824-1835, describe the production of levulinic acid from biomass. In particular, they describe the conversion of biomass to levulinic acid through hydrothermal treatment, in the presence of acid homogenous or heterogeneous catalysts. In said article, among other uses, the conversion of levulinic acid to γ-valerolactone is mentioned, which can be used, in turn, as liquid for producing energy and chemical products.

European patent application EP 2,684,875 describes a process for the production of furfural and levulinic acid from lignocellulosic biomass comprising:

(a) adding water and optionally an acid to said biomass so as to form a fluid biomass ("slurried biomass");

(b) subjecting said slurried biomass to hydrolysis so as to form a hydrolysate comprising C5 and C6 sugars and further comprising (insoluble) cellulose and lignin;

(c) subjecting said hydrolysate comprising said C5 and C6 sugars and said (insoluble) cellulose and lignin to solid/liquid separation to yield a first aqueous fraction comprising at least part of said C5 and C6 sugars and a first solid fraction comprising at least part of said cellulose and lignin;

(d) optionally concentrating said first aqueous fraction;

(e) adding an organic solvent to the (optionally concentrated) first aqueous fraction to form a biphasic system;

(f) heating said biphasic system to a temperature ranging from 120°C to 220°C and

maintaining said biphasic system at said temperature for a time sufficient to form furfural;

(g) cooling the biphasic system comprising furfural obtained in step (f);

(h) optionally subjecting the cooled biphasic system obtained in step (g) to solid/liquid separation and recovering the biphasic system;

(i) subjecting the cooled biphasic system obtained in step (g) or the recovered biphasic system obtained in step (h) to a separation step to yield an organic phase comprising at least part of said furfural and an aqueous phase comprising at least part of said C6 sugars and optionally further comprising furfural;

(j) optionally recovering furfural from said organic phase;

(k) optionally using the recovered organic phase obtained in step (j) to extract furfural from the aqueous phase obtained in step (i) by adding said recovered organic phase to said aqueous phase and repeating step (i) and optionally step (j);

(l) adding water and optionally an acid to the first solid fraction obtained in step (c) to form a suspension;

(m) subjecting the suspension obtained in step (l) to a temperature ranging from 140°C to 220°C to form levulinic acid;

(n) subjecting the suspension comprising levulinic acid obtained in step (m) to solid/liquid separation to yield a second aqueous fraction comprising levulinic acid and a solid fraction; and

(o) optionally recovering said levulinic acid from the second aqueous fraction.

However, no processes are described in the state of the art for producing dipentyl ether from levulinic acid resulting from biomass.

The Applicant therefore set out to find a process for producing dipentyl ether from levulinic

acid resulting from biomass.

The Applicant has now found that the production of dipentyl ether from levulinic acid resulting from biomass can be carried out through a process comprising the following steps: (a) reacting said levulinic acid in the presence of hydrogen and at least one non-acid hydrogenation catalyst obtaining γ-valerolactone; (b) reacting said γ-valerolactone in the presence of hydrogen and at least one acid hydrogenation catalyst obtaining pentanoic acid; (c) reacting said pentanoic acid in the presence of hydrogen and at least a catalyst comprising platinum (Pt) and tin (Sn) obtaining pentyl alcohol; (d) reacting said pentyl alcohol in the presence of at least one solid acid catalyst thereby obtaining dipentyl ether. Said process allows dipentyl ether to be obtained with high conversion and selectivity. The dipentyl ether thus obtained can be advantageously used as an oxygenated component for fuels for diesel engines.

Hence, the subject matter of the present invention is a process for the production of dipentyl ether from levulinic acid resulting from biomass including at least one polysaccharide comprising the following steps:

(a) reacting said levulinic acid in the presence of hydrogen and at least one non-acid hydrogenation catalyst obtaining γ-valerolactone;

(b) reacting said γ-valerolactone in the presence of hydrogen and at least one acid hydrogenation catalyst obtaining pentanoic acid;

(c) reacting said pentanoic acid in the presence of hydrogen and at least a catalyst comprising platinum (Pt) and tin (Sn) obtaining pentyl alcohol;

(d) reacting said pentyl alcohol in the presence of at least one solid acid catalyst thereby obtaining dipentyl ether.

For the purpose of the present description and of the following claims, the definitions of

the numeric ranges always include the extremes unless specified otherwise.

For the purpose of the present description and of the following claims, the term "comprising" also includes the terms "which essentially consists of" or "which consists of".

In general, biomass is defined as any substance with an organic, plant or animal matrix, which can be intended for energy purposes, for example, as raw material for the production of biofuels, or of components that can be added to fuels. Therefore, biomass can constitute a source of renewable energy alternative to the traditional raw materials of fossil origin usually used for producing fuels. For that purpose, lignocellulosic biomass is particularly useful. Lignocellulosic biomass is a complex structure comprising three main components: cellulose, hemicellulose and lignin. Their relative quantities vary according to the type of lignocellulosic biomass used. For example, for plants, said quantities vary according to the species and the age of the plant.

In accordance with a preferred embodiment of the present invention, said polysaccharide can be selected from cellulose, hemicellulose, or mixtures thereof. Cellulose, or mixtures of hemicellulose and cellulose, are particularly preferred.

In accordance with a further preferred embodiment of the present invention, said biomass including at least one polysaccharide is lignocellulosic biomass. As already mentioned above the lignocellulosic biomass comprises three components: hemicellulose, cellulose and lignin.

Preferably, said lignocellulosic biomass can be selected, for example, from:

- products of crops expressly cultivated for energy use (for example, miscanthus, panic, common reed, thistle), including waste products, residues and scraps of said crops or their processing;
- products and by-products of agricultural cultivations, forestry and siviculture,

including wood, plants, residues, green wastes and waste products from agricultural processing, forestry and siviculture;

- waste of agro-food products intended for human nutrition or zootechnics;
- residues, non-chemically treated, of the paper industry;
- waste products coming from the differentiated collection of solid urban waste (for example, urban waste of a vegetable origin, paper).

For the purpose of the present invention, said levulinic acid can be obtained from biomass including at least one polysaccharide by operating according to any one of the processes of the prior art described above, incorporated herein as reference. Further details related to processes for producing levulinic acid from biomass including at least one polysaccharide can also be found, for example, in US patents US 4,897,497, US 5,608,105, US 6,054,611, or in US patent application US 2010/312006, incorporated herein as reference.

In accordance with a preferred embodiment of the present invention, in said step (a) the non-acid hydrogenation catalyst can be selected, for example, from catalysts comprising at least one metal selected from metals belonging to the groups 7-11 of the Periodic Table of the Elements, preferably a noble metal, even more preferably platinum, supported on a solid support selected, for example, from silica, titania, zirconia, alumina, or mixtures thereof, preferably silica.

It is to be noted that for the purpose of the present invention and of the following claims, the term "Periodic Table of the Elements" refers to the "IUPAC Periodic Table of the Elements", version dated 22 June 2007, available on the following website: www.iupac.org/fileadmin/user_upload/news/IUPAC_Periodic_Table-1Jun12.pdf.

Non-acid hydrogenation catalysts of the type described above, which can be used in step

(a) of the process in accordance with the present invention are the products known by the trade names Escat™ 2351 (Pt/SiO_2) by Basf also sold by STREM (Catalog Number 78-1675), Escat™ 2941 (Pt/Al_2O_3) by Basf.

In accordance with a preferred embodiment of the present invention, said step (a) can be carried out at hydrogen pressure ranging from 5 bar to 60 bar, preferably ranging from 8 bar to 50 bar.

In accordance with a preferred embodiment of the present invention, said step (a) can be carried out at a "Gas Hourly Space Velocity" (GHSV), i.e. at a ratio of the volume of hydrogen fed in an hour to the volume of catalyst used, said ratio being measured in $hours^{-1}$, ranging from 0.2 $hours^{-1}$ to 6 $hours^{-1}$, preferably ranging from 0.25 $hours^{-1}$ to 3 $hours^{-1}$.

In accordance with a preferred embodiment of the present invention, said step (a) can be carried out at a temperature ranging from 150°C to 240°C, preferably ranging from 190°C to 210°C.

In accordance with a preferred embodiment of the present invention, said step (a) can be carried out at a "Weight Hourly Space Velocity" (WHSV), i.e. at a ratio of the amount by weight of levulinic acid fed in an hour to the amount by weight of catalyst used, said ratio being measured in $hours^{-1}$, ranging from 0.1 $hours^{-1}$ to 2 $hours^{-1}$, preferably ranging from 0.2 $hours^{-1}$ to 1 $hour^{-1}$.

Said step (a) allows a conversion of levulinic acid to be obtained calculated according to formula (Ia):

$$[(Moli_{RaI} - Moli_{RaF})/Moli_{RaI}] \times 100 \quad (Ia)$$

wherein $Moli_{RaI}$ are moles of levulinic acid at the start of the reaction and $Moli_{RaF}$ are moles of levulinic acid at the end of the reaction, ranging from 90% to 99%, and a selectivity to γ-

valerolactone calculated according to formula (IIa):

$[Moli_{Pa}/(Moli_{RaF} - Moli_{Ral}] \times 100$ (IIa)

wherein $Moli_{Pa}$ are moles of γ-valerolactone obtained and $Moli_{Ral}$ and $Moli_{RaF}$ have the same meaning described above, ranging from 80% to 95%.

In accordance with a preferred embodiment of the present invention, in said step (b), the acid hydrogenation catalyst can be selected, for example, from catalysts comprising at least one metal selected from metals belonging to the groups 7-11 of the Periodic Table of the Elements, preferably a noble metal, even more preferably platinum, supported on a solid acidic support comprising at least one zeolite in acidic form selected, for example, from zeolite Y, zeolite beta, zeolite H-ZSM-5, mordenite, preferably zeolite H-ZSM- 5 and at least one inorganic binder selected, for example, from silica, alumina, titania, zirconia, or mixtures thereof, preferably silica.

Said solid acidic support can be obtained by forming said zeolite operating according to techniques of the prior art. For example, said zeolite, in powder crystal form, can be mixed with an appropriate inorganic binder such as, for example, silica, alumina, titania, zirconia, or mixtures thereof. For the purpose of the present invention, silica is the preferred binder. Precursors of said binders can also be mixed with zeolite. Said zeolite and said binder can be mixed in different weight ratios: preferably, the zeolite/binder weight ratio can be ranging from 5/95 to 95/5, preferably ranging from 15/85 to 85/15. The zeolite/binder composite material obtained after mixing can be formed so as to obtain a zeolite having a suitable shape and size for use in the reactor used, low loss of charge and a suitable mechanical resistance and abrasion resistance.

Said zeolite/binder composite material can be formed by operating according to any extrusion, spherulization, tablet forming or granulation process of the prior art. For the

purpose of the present invention, said composite material can be formed by extrusion. Extrusion generally also envisages the use of a peptizing agent which can be mixed with the zeolite and the binder, before extrusion, until a uniform paste is obtained. At the end of said extrusion, pellets of different sizes are obtained.

For the purpose of the present invention, pellets of different shapes and sizes can be used. Pellets in the form of cylinders having a diameter ranging from 2 mm to 6 mm and a length ranging from 2 mm to 20 m, are particularly suitable for use.

After extrusion, the pellets obtained are generally subjected to a calcination step, for example, at a temperature of 550°C, in an air flow, for 10 hours.

Further details related to the forming of said zeolites in acidic form can be found, for example, in international patent application WO 2004/056475, or in European patent application EP 847 802.

Acid hydrogenation catalysts of the type described above can be obtained according to processes of the prior art as described, for example, in patent application US 2006/0162239.

For example, said catalysts can be prepared by incipient wetness impregnation of the support in acidic form. Such a technique involves wetting the support in acidic form with a solution containing the metal precursor(s) (e.g., platinum nitrate), the volume of said solution being proximal to the volume of the pores of the support in acidic form used. In the event that the quantity of metal to be introduced is high, the incipient wetness impregnation is repeated numerous times. Between one impregnation and the next, the support in acidic form impregnated is dried in a stove, for example at 120°C, for a few hours. After the impregnations, the catalyst obtained is dried, for example at 120°C, for 12 hours and then calcinated, for example at 500°C – 550°C, in the air, for 10 hours.

In accordance with a preferred embodiment of the present invention, said step (b) can be carried out at a hydrogen pressure ranging from 5 bar to 60 bar, preferably ranging from 8 bar to 50 bar.

In accordance with a preferred embodiment of the present invention, said step (b) can be carried out at a "Gas Hourly Space Velocity" (GHSV), i.e. at a ratio of the volume of hydrogen fed in an hour to the volume of catalyst used, said ratio being measured in $hours^{-1}$, ranging from 0.2 $hours^{-1}$ to 6 $hours^{-1}$, preferably ranging from 0.25 $hours^{-1}$ to 3 $hours^{-1}$.

In accordance with a preferred embodiment of the present invention, said step (b) can be carried out at a temperature ranging from 200°C to 400°C, preferably ranging from 210°C to 350°C.

In accordance with a preferred embodiment of the present invention, said step (b) can be carried out at a "Weight Hourly Space Velocity" (WHSV), i.e. at a ratio of the amount by weight of γ-valerolactone fed in an hour to the amount by weight of catalyst used, said ratio being measured in $hours^{-1}$, ranging from 0.1 $hours^{-1}$ to 2 $hours^{-1}$, preferably ranging from 0.2 $hours^{-1}$ to 1 $hour^{-1}$.

Said step (b) allows a conversion of γ-valerolactone to be obtained calculated according to formula (Ib):

$$[(Moli_{RbI} - Moli_{RbF})/Moli_{RbI}] \times 100 \quad (Ib)$$

wherein $Moli_{RbI}$ are moles of γ-valerolactone at the start of the reaction and $Moli_{RbF}$ are moles of γ-valerolactone at the end of the reaction, ranging from 90% to 97%, and a selectivity to pentanoic acid calculated according to formula (IIb):

$$[Moli_{Pb}/(Moli_{RbF} - Moli_{RbI}] \times 100 \quad (IIb)$$

wherein $Moli_{Pb}$ are the moles of pentanoic acid obtained and $Moli_{RbI}$ and $Moli_{RbF}$ have the

same meaning described above, ranging from 80% to 95%.

In accordance with a preferred embodiment of the present invention, in said step (c) the catalyst comprising platinum (Pt) and tin (Sn) can be selected, for example, from catalysts comprising platinum (Pt) and tin (Sn) in a weight ratio ranging from 0.1 to 2, preferably ranging from 0.5 to 1.5, supported on a solid support selected, for example, from silica, alumina, carbon, iron oxide, zirconia, alumina, or mixtures thereof, preferably silica.

Catalysts comprising platinum (Pt) and tin (Sn) of the type described above, which can be used in step (c) of the process in accordance with the present invention, can be prepared according to processes of the prior art as described, for example, by Cortright R. D. et al., in the article "Effects of Potassium on Silica-Supported Pt and Pt/Sn Catalysts for Isobutane Dehydrogenation", "*Journal of Catalysis*" (1997), Vol. 157, pag. 576-583. Further details related to the preparation of said catalysts can be found in the examples described below.

In accordance with a preferred embodiment of the present invention, said step (c) can be carried out at a hydrogen pressure ranging from 5 bar to 40 bar, preferably ranging from 8 bar to 30 bar.

In accordance with a preferred embodiment of the present invention, said step (c) can be carried out at a "Gas Hourly Space Velocity" (GHSV), i.e. at a ratio of the volume of hydrogen fed in an hour to the volume of catalyst used, said ratio being measured in $hours^{-1}$, ranging from 0.2 $hours^{-1}$ to 6 $hours^{-1}$, preferably ranging from 0.25 $hours^{-1}$ to 3 $hours^{-1}$.

In accordance with a preferred embodiment of the present invention, said step (c) can be carried out at a temperature ranging from 200°C to 300°C, preferably ranging from 240°C to 260°C.

In accordance with a preferred embodiment of the present invention, said step (c) can be carried out at a "Weight Hourly Space Velocity" (WHSV), i.e. at a ratio of the amount by weight of pentanoic acid fed in an hour to the amount by weight of catalyst used, said ratio being measured in $hours^{-1}$, ranging from 0.1 $hours^{-1}$ to 2 $hours^{-1}$, preferably ranging from 0.2 $hours^{-1}$ to 1 $hour^{-1}$.

Said step (c) allows a conversion of pentanoic acid to be obtained calculated according to formula (Ic):

$[(Moli_{RcI} - Moli_{RcF})/Moli_{RcI}] \times 100$ (Ic)

wherein $Moli_{RcI}$ are moles of pentanoic acid at the start of the reaction and $Moli_{RcF}$ are moles of pentanoic acid at the end of the reaction, ranging from 80% to 90%, and a selectivity to pentyl alcohol calculated according to formula (IIc):

$[Moli_{Pc}/(Moli_{RcF} - Moli_{RcI}] \times 100$

wherein $Moli_{Pc}$ are moles of pentyl alcohol obtained and $Moli_{RcI}$ and $Moli_{RcF}$ have the same meaning described above, ranging from 90% to 95%.

In accordance with a preferred embodiment of the present invention, in said step (d), the solid acid catalyst can be selected, for example, from insoluble acid catalysts, such as, for example: acid ion-exchange resins, preferably sulfonate ion-exchange resins such as, for example, sulfonated styrene-divinylbenzene matrix resins, sulfonated phenol-formaldehyde matrix resins, sulfonated benzene-formaldehyde matrix resins; perfluorosulfonic resins.

Solid acid catalyst of the type described above, which can be used in step (d) of the process in accordance with the present invention are products known by the trade names of Nafion® H by DuPont; Amberlyst® A15, Amberlyst® A35 and Dowex® 50w by Dow Chemical.

In accordance with a preferred embodiment of the present invention, said step (d) can be carried out at a temperature ranging from 120°C to 180°C, preferably ranging from 140°C to 160°C.

In accordance with a preferred embodiment of the present invention, said step (d) can be carried out at a "Weight Hourly Space Velocity" (WHSV), i.e. at a ratio of amount by weight of pentyl alcohol fed in an hour to the amount by weight of catalyst used, said ratio being measured in $hours^{-1}$, ranging from 0.2 $hours^{-1}$ to 2 $hours^{-1}$, preferably ranging from 0.3 $hours^{-1}$ to 1 $hour^{-1}$.

Said step (d) allows a conversion of pentyl alcohol to be obtained calculated according to formula (Id):

$$[(Moli_{RdI} - Moli_{RdF})/Moli_{RdI}] \times 100 \quad (Id)$$

wherein $Moli_{RdI}$ are moles of pentyl alcohol at the start of the reaction and $Moli_{RdF}$ are moles of pentyl alcohol at the end of the reaction, ranging from 90% to 99.9%, and a selectivity to dipentyl ether calculated according to formula (IId):

$$[Moli_{Pd}/(Moli_{RdF} - Moli_{RdI}] \times 100 \quad (IId)$$

wherein $Moli_{Pd}$ are the moles of dipentyl ether obtained and $Moli_{RdI}$ and $Moli_{RdF}$ have the same meaning described above, ranging from 90% to 99.9%.

In accordance with a preferred embodiment of the present invention, said process can be carried out in a continuous manner, for example, in one or more catalytic reactors in series, fixed bed, or fluidized bed, stirred or recirculated, or containing the catalyst in dispersion, or in one or more continuous feed slurry reactors (CSTR - "Continuous Stirred-Tank Reactor"), preferably in numerous fixed-bed reactors.

The process according to the present invention is preferably carried out in the absence of solvent. For the purpose of the present invention and of the following claims the term

"solvent" indicates a solvent that is to be added to the reaction mixture, i.e. for the purpose of the present invention and of the following claims, the reaction product(s) obtained in the aforementioned steps (a) - (d) are not considered solvent(s). The absence of solvent allows high conversions and selectivity to be obtained and is preferable both from an economic and environmental point of view.

The present invention will now be illustrated in more detail through an embodiment with reference to Figure 1 described below.

Figure 1 depicts an embodiment of the process according to the present invention. For that purpose, four fixed-bed reactors (R1), (R2), (R3) and (R4) are used. Reactor (R1) containing a non-acid hydrogenation catalyst (e.g., Pt/SiO_2), is fed with a flow (1) of levulinic acid resulting from biomass (e.g., from acid hydrolysis of lignocellulosic biomass) and with a flow of hydrogen (H_2), obtaining an outlet flow (2) comprising a homogenous mixture of water/γ-valerolactone which is fed to reactor (R2). Said reactor (R2), containing an acid hydrogenation catalyst (e.g., a platinum (Pt) based catalyst supported on an acidic support comprising H-ZSM-5 and SiO_2), is also fed with a flow of hydrogen (H_2), obtaining an outlet flow (3) comprising a biphasic mixture of water/pentanoic acid which is fed to separator (S1). From separator (S1), by decantation, an aqueous flow (H_2O) is obtained and a flow (4) comprising pentanoic acid which is fed to reactor (R3). Said reactor (R3), containing a catalyst comprising platinum (Pt) and tin (Sn) supported on silica ($PtSn/SiO_2$), is also fed with a flow of hydrogen (H_2), obtaining an outlet flow (5) comprising a biphasic mixture of water/pentyl alcohol which is fed to separator (S2). From separator (S2) an aqueous flow (H_2O) is obtained and a flow (6) comprising pentyl alcohol which is fed to reactor (R4) containing a solid acid catalyst (e.g., Nafion® H by DuPont) obtaining an outlet flow (7) comprising a biphasic mixture of water/dipentyl ether which is fed to

separator (S3). From separator (S3) an aqueous flow (H_2O) is obtained and a flow (8) comprising crude dipentyl ether which is fed to the distillation column (D1) obtaining an outlet flow (9) comprising purified dipentyl ether. The water at the outlet of the separators (S1), (S2) and (S3), can be disposed of without being subjected to any further treatments.

For the purpose of understanding the present invention better and to put it into practice, below are some illustrative and non-limitative examples thereof.

EXAMPLE 1

Synthesis of dipentyl ether from levulinic acid

The synthesis process was carried out using four fixed-bed reactors in series as represented in Figure 1 to which reference is made in the description below reported.

The levulinic acid was obtained by acid hydrolysis of lignocellulosic biomass.

(a) Synthesis of γ-valerolactone from levulinic acid

The fixed-bed reactor (R1) was loaded with a catalyst comprising platinum supported on silica (commercial product Pt/SiO_2 marketed by STREM - Catalog Number 78-1675 corresponding to Escat™ 2351 by Basf) and α–alumina in a weight ratio of 1/10: everything was kept under hydrogen flow, at 250°C, for 4 hours.

Subsequently, the fixed-bed reactor (R1) was fed with a flow (1) of levulinic acid with a "Weight Hourly Space Velocity" (WHSV) of 0.5 $hours^{-1}$ and with a flow of hydrogen with a "Gas Hourly Space Velocity" (GHSV) of 2 $hours^{-1}$: said fixed-bed reactor (R1) was kept at 200°C and at a pressure of 40 bar. At the end, the outlet flow (2) from said fixed-bed reactor (R1) was analysed through gas chromatography and mass spectrometry and showed a 98% conversion of levulinic acid with a 90% selectivity to γ-valerolactone (GVL).

(b) Synthesis of pentanoic acid from γ-valerolactone

The fixed-bed reactor (R2) was previously loaded with a catalyst comprising platinum (Pt)

(0.7% w/w) supported on an acidic support comprising zeolite (H-ZSM-5) and silica (SiO_2) (zeolite/silica weight ratio 25/75): everything was kept under hydrogen flow, at 300°C, for 3 hours.

The fixed-bed reactor (R2) was then fed with the outlet flow (2) from said fixed-bed reactor (R1) comprising γ-valerolactone (GVL), the unreacted hydrogen and the reaction water, with a "Weight Hourly Space Velocity" (WHSV) of 0.5 $hours^{-1}$ and with a flow of hydrogen with a "Gas Hourly Space Velocity" (GHSV) of 2 $hours^{-1}$: said fixed-bed reactor (R2) was kept at 300°C and at a pressure of 40 bar. At the end, the outlet flow (3) from said fixed-bed reactor (R2) comprising a biphasic water/pentanoic acid mixture was analysed through gas chromatography and mass spectrometry and showed a 95% conversion of γ-valerolactone (GVL) with a 90% selectivity to pentanoic acid. Said flow (3) was fed to the separator (S1) obtaining an aqueous flow (H_2O) and a flow (4) comprising pentanoic acid.

(c) Synthesis of pentyl alcohol from pentanoic acid

The fixed-bed reactor (R3) was previously loaded with a catalyst comprising platinum (Pt) and tin (Sn) (platinum/tin ratio 1/1) supported on a support comprising silica (SiO_2) obtained by operating as follows. 1.64 g of platinum nitrate dissolved in 16 ml of water and 1.74 g of tin oxalate dissolved in 8.5 ml of 1N nitric acid, were added to 100 g of silica (SiO_2) powder (particle size: 0.2 mm) dried in the oven at 120°C, for 12 hours. The suspension obtained was subjected to stirring, for 2 hours, dried in the oven at 120°C, for 12 hours and then calcinated at 500°C (6 hours, 10°C/min).

The fixed-bed reactor (R3) was fed with the aforementioned flow (4) comprising pentanoic acid with a "Weight Hourly Space Velocity" (WHSV) of 0.5 $hours^{-1}$ and with a flow of hydrogen with a "Gas Hourly Space Velocity" (GHSV) of 2 $hours^{-1}$: said fixed-bed reactor (R3) was kept at 250°C and at a pressure of 25 bar. At the end, the outlet flow (5) from

said fixed-bed reactor (R3) comprising a biphasic water/pentyl alcohol mixture was analysed through gas chromatography and mass spectrometry and showed 85% conversion of pentanoic acid with a 93% selectivity to pentyl alcohol. Said flow (5) was fed to the separator (S2) obtaining an aqueous flow (H_2O) and a (permeated) flow (6) comprising pentyl alcohol.

(d) Synthesis of dipentyl ether from pentyl alcohol

The fixed-bed reactor (R4) was previously loaded with a solid acidic catalyst (Nafion® H by DuPont).

The fixed-bed reactor (R4) was then fed with the aforementioned flow (6) comprising pentyl alcohol with a "Weight Hourly Space Velocity" (WHSV) of 0.66 $hours^{-1}$ at 150°C. At the end, the outlet flow (7) from said fixed-bed reactor (R4) comprising a biphasic mixture of water/dipentyl ether was analysed through gas chromatography and mass spectrometry and showed 99% conversion of pentyl alcohol with a 99% selectivity to dipentyl ether. Said flow (7) was fed to the separator (S3) obtaining an aqueous flow (H_2O) and a flow (8) comprising crude dipentyl ether which was fed to the distiller (D1) obtaining a flow (9) comprising dipentyl ether with a purity of 99%.

Claims

1. A process for the production of dipentyl ether from levulinic acid resulting from biomass including at least one polysaccharide comprising the following steps:
   (a) reacting said levulinic acid in the presence of hydrogen and at least one non-acid hydrogenation catalyst obtaining γ-valerolactone;
   (b) reacting said γ-valerolactone in the presence of hydrogen and at least one acid hydrogenation catalyst obtaining pentanoic acid;
   (c) reacting said pentanoic acid in the presence of hydrogen and at least a catalyst comprising platinum (Pt) and tin (Sn) obtaining pentyl alcohol;
   (d) reacting said pentyl alcohol in the presence of at least one solid acid catalyst thereby obtaining dipentyl ether.
2. Process for the production of dipentyl ether in accordance with claim 1, wherein said polysaccharide is selected from cellulose, hemicellulose, or mixtures thereof, preferably from cellulose, or mixtures of hemicellulose and cellulose.
3. Process for the production of dipentyl ether in accordance with claim 1 or 2, wherein said biomass including at least one polysaccharide is a lignocellulosic biomass, preferably selected from:
   - products of crops expressly cultivated for energy use (such as miscanthus, panic, common reed, thistle), including waste products, residues and scraps of said crops or their processing;
   - products and by-products of agricultural cultivations, forestry and siviculture, including wood, plants, residues, green wastes and waste products from agricultural processing, forestry and siviculture;

- waste of agro-food products intended for human nutrition or zootechnics;
- residues, non-chemically treated, of the paper industry;
- waste products coming from the differentiated collection of solid urban waste (such as urban waste of a vegetable origin, paper).

4. Process for the production of dipentyl ether in accordance with any one of the preceding claims, wherein in said step (a) the non-acid hydrogenation catalyst is selected from catalysts comprising at least one metal selected from metals belonging to the groups 7-11 of the Periodic Table of the Elements, preferably a noble metal, even more preferably platinum, supported on a solid support selected from silica, titania, zirconia, alumina, or mixtures thereof, preferably silica.

5. Process for the production of dipentyl ether in accordance with any one of the preceding claims, wherein said step (a) is carried out:
   - at a hydrogen pressure ranging from 5 bar to 60 bar, preferably ranging from 8 bar to 50 bar; and/or
   - at a "Gas Hourly Space Velocity" (GHSV), i.e. at a ratio of the volume of hydrogen fed in an hour to the volume of catalyst used, said ratio being measured in $hours^{-1}$, ranging from 0.2 $hours^{-1}$ to 6 $hours^{-1}$, preferably ranging from 0.25 $hours^{-1}$ to 3 $hours^{-1}$; and/or
   - at a temperature ranging from 150°C to 240°C, preferably ranging from 190°C to 210°C; and/or
   - at a "Weight Hourly Space Velocity" (WHSV), i.e. a ratio of the amount by weight of levulinic acid fed in an hour to the amount by weight of catalyst used, said ratio being measured in $hours^{-1}$, ranging from 0.1 $hours^{-1}$ to 2 $hours^{-1}$, preferably ranging from 0.2 $hours^{-1}$ to 1 $hour^{-1}$.

6. Process for the production of dipentyl ether in accordance with any one of the preceding claims, wherein in said step (b) the hydrogenation catalyst is selected from acid catalysts comprising at least one metal selected from metals belonging to the groups 7-11 of the Periodic Table of the Elements, preferably a noble metal, even more preferably platinum, supported on a solid acidic support comprising at least one zeolite in acidic form selected from zeolite Y, zeolite beta, zeolite H-ZSM-5, mordenite, preferably zeolite H-ZSM- 5 and at least one inorganic binder selected from silica, alumina, titania, zirconia, or mixtures thereof, preferably silica.

7. Process for the production of dipentyl ether in accordance with any one of the preceding claims, wherein said step (b) is carried out:
   - at a "Gas Hourly Space Velocity" (GHSV), i.e. at a ratio of the volume of hydrogen fed in an hour to the volume of catalyst used, said ratio being measured in $hours^{-1}$, ranging from 0.2 $hours^{-1}$ to 6 $hours^{-1}$, preferably ranging from 0.25 $hours^{-1}$ to 3 $hours^{-1}$; and/or
   - at a temperature ranging from 200°C to 400°C, preferably ranging from 210°C to 350°C; and/or
   - at a "Weight Hourly Space Velocity" (WHSV), i.e. a ratio of the amount by weight of γ-valerolactone fed in an hour to the amount by weight of catalyst used, said ratio being measured in $hours^{-1}$, ranging from 0.1 $hours^{-1}$ to 2 $hours^{-1}$, preferably ranging from 0.2 $hours^{-1}$ to 1 $hour^{-1}$.

8. Process for the production of dipentyl ether in accordance with any one of the preceding claims, wherein in said step (c) the catalyst comprising platinum (Pt) and tin (Sn) is selected from catalysts comprising platinum (Pt) and tin (Sn) in a weight ratio ranging from 0.1 to 2, preferably ranging from 0.5 to 1.5, supported on a solid

support selected from silica, alumina, carbon, iron oxide, zirconia, alumina, or mixtures thereof, preferably silica.

9. Process for the production of dipentyl ether in accordance with any one of the preceding claims, wherein said step (c) is carried out:
   - at a hydrogen pressure ranging from 5 bar to 40 bar, preferably ranging from 8 bar to 30 bar; and/or
   - at a "Gas Hourly Space Velocity" (GHSV), namely at a ratio of the volume of hydrogen fed in an hour to the volume of catalyst used, said ratio being measured in $hours^{-1}$, ranging from 0.2 $hours^{-1}$ to 6 $hours^{-1}$, preferably ranging from 0.25 $hours^{-1}$ to 3 $hours^{-1}$; and/or
   - at a temperature ranging from 200°C to 300°C, preferably ranging from 240°C to 260°C; and/or
   - at a "Weight Hourly Space Velocity" (WHSV), i.e. a ratio of the amount by weight of the pentanoic acid fed in an hour to the amount by weight of catalyst used, said ratio being measured in $hours^{-1}$, ranging from 0.1 $hours^{-1}$ to 2 $hours^{-1}$, preferably ranging from 0.2 $hours^{-1}$ to 1 $hour^{-1}$.

10. Process for the production of dipentyl ether in accordance with any one of the preceding claims, wherein in said step (d) the solid acid catalyst is selected from insoluble acid catalysts such as acid ion-exchange resins, preferably sulfonated ion-exchange resins such as sulfonated styrene-divinylbenzene matrix resins, sulfonated phenol-formaldehyde matrix resins, sulfonated benzene-formaldehyde matrix resins; perfluorosulfonic resins.

11. A process for the production of dipentyl ether in accordance with any one of the preceding claims, wherein said step (d) is carried out:

- at a temperature ranging from 120°C and 180°C, preferably ranging from 140°C to 160°C; and/or
- at a "Weight Hourly Space Velocity" (WHSV), i.e. a ratio of the amount by weight of pentyl alcohol fed in an hour to the amount by weight of catalyst used, said ratio being measured in $hours^{-1}$, ranging from 0.2-$hours^{-1}$ to 2 $hours^{-1}$, preferably ranging from 0.3 $hours^{-1}$ to 1 $hour^{-1}$.

12. Process for the production of dipentyl ether in accordance with any one of the preceding claims, wherein said process is carried out in a continuous manner, in one or more catalytic reactors in series, a fixed bed, or fluidized bed, stirred or recirculated, or containing the catalyst in dispersion, or in one or more continuous feed slurry reactors (CSTR - "Continuous Stirred-Tank Reactor"), most preferably in numerous fixed-bed reactors.

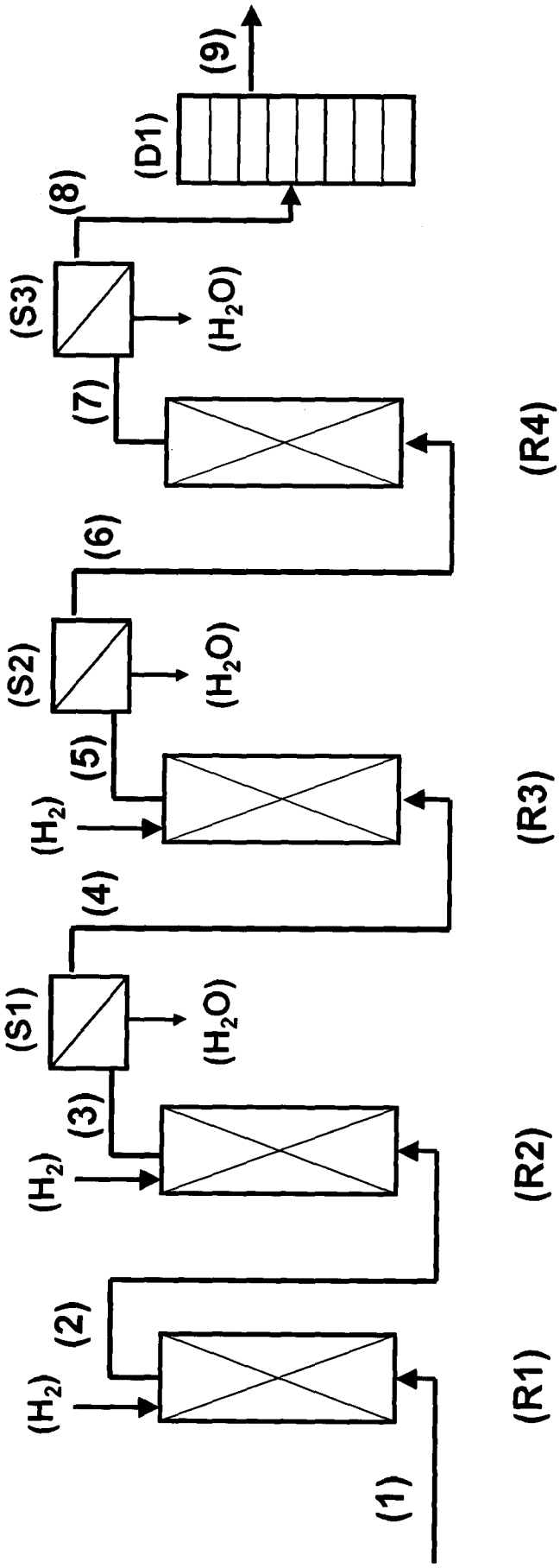

Figure 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2015/059539

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C29/149 C07C41/09 C07C51/09 C07D307/33 C07C43/04
C07C31/125 C07C53/126
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C C07D

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	J. TEJERO ET AL: "Dehydration of 1-pentanol to di-n-pentyl ether over ion-exchange resin catalysts", JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL, vol. 182-183, 1 May 2002 (2002-05-01), pages 541-554, XP055203713, ISSN: 1381-1169, DOI: 10.1016/S1381-1169(01)00492-7 page 547 - page 549; figure 3; tables 3, 4 ----- -/--	1-12

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 March 2016	18/03/2016

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1

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2015/059539

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	G.A. OLAH ET AL: CATALYSIS LETTERS, vol. 46, no. 1/2, 1 January 1997 (1997-01-01), pages 1-4, XP055203714, ISSN: 1011-372X, DOI: 10.1023/A:1019069107667 table 1 page 2, column 2 - page 4, column 1	1-12
A	WO 2014/190161 A1 (VIRENT INC [US]; BLOMMEL PAUL [US]; HELD ANDREW [US]; GOODWIN RALPH [U) 27 November 2014 (2014-11-27) paragraph [0078] - paragraph [0079] paragraph [0083]	1-12
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A	& WO 2006/067171 A1 (SHELL INT RESEARCH [NL]; VAN DEN BRINK PETER JOHN [NL]; VON HEBEL KLAA) 29 June 2006 (2006-06-29) page 7, line 23 - line 26	1-12
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1

INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/IB2015/059539

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		EP 2619163 A2	31-07-2013