



(51) International Patent Classification:

C07G 1/00 (2011.01) B01J 21/06 (2006.01)

C10G 1/00 (2006.01) B01J 23/46 (2006.01)

Declarations under Rule 4.17:

- as to the identity of the inventor (Rule 4.17(i))
- of inventorship (Rule 4.17(iv))

(21) International Application Number:

PCT/FI2016/050528

Published:

- with international search report (Art. 21(3))

(22) International Filing Date:

19 July 2016 (19.07.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(71) Applicant: UPM-KYMMENE CORPORATION

[FI/FI]; Alvar Aallon katu 1, 00100 Helsinki (FI).

(72) Inventors: DOMINE, Marcelo; Orensa 32A, Pta. 14, 46980 Paterna (ES). CHÁVEZ-SIFONTES, Marvin; Poeta Mas y Ros 79, 2º Piso, Pta. 4., 46022 Valencia (ES). GUTIERREZ, Andrea; Töölönkatu 30 bA 6, 00260 Helsinki (FI). VILONEN, Kati; Salmenrannantie 120, 23360 Kustavi (FI). STRENGELL, Timo; Tuosantie 30, 53400 Lappeenranta (FI). JOKELA, Pekka; Katri Valantie 15, 02660 Espoo (FI). EILOS, Isto; Tuurintie 3, 06150 Porvoo (FI).

(74) Agent: BOCO IP OY AB; Itämerenkatu 5, 00180 Helsinki (FI).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: PROCESS FOR CONVERTING LIGNOCELLULOSIC MATERIALS

(57) Abstract: The present invention relates to a process for converting feedstock comprising lignocellulosic material, said process comprising the steps of treating the feedstock with an alkali, whereby a mixture is obtained, hydrotreating said mixture catalytically with hydrogen in the presence of a catalyst composition comprising ruthenium supported on zirconia, where said zirconia comprises monoclinic phase of zirconia, to yield an effluent, and separating from the effluent at least one of the following: an aqueous phase, light gaseous phase, liquid organic phase and residual lignin phase.

PROCESS FOR CONVERTING LIGNOCELLULOSIC MATERIALS

5

TECHNICAL FIELD

The invention relates to converting of lignocellulosic materials and more particularly to a process for converting lignocellulosic materials to aromatic compounds, hydrocarbons and other chemicals.

10

BACKGROUND

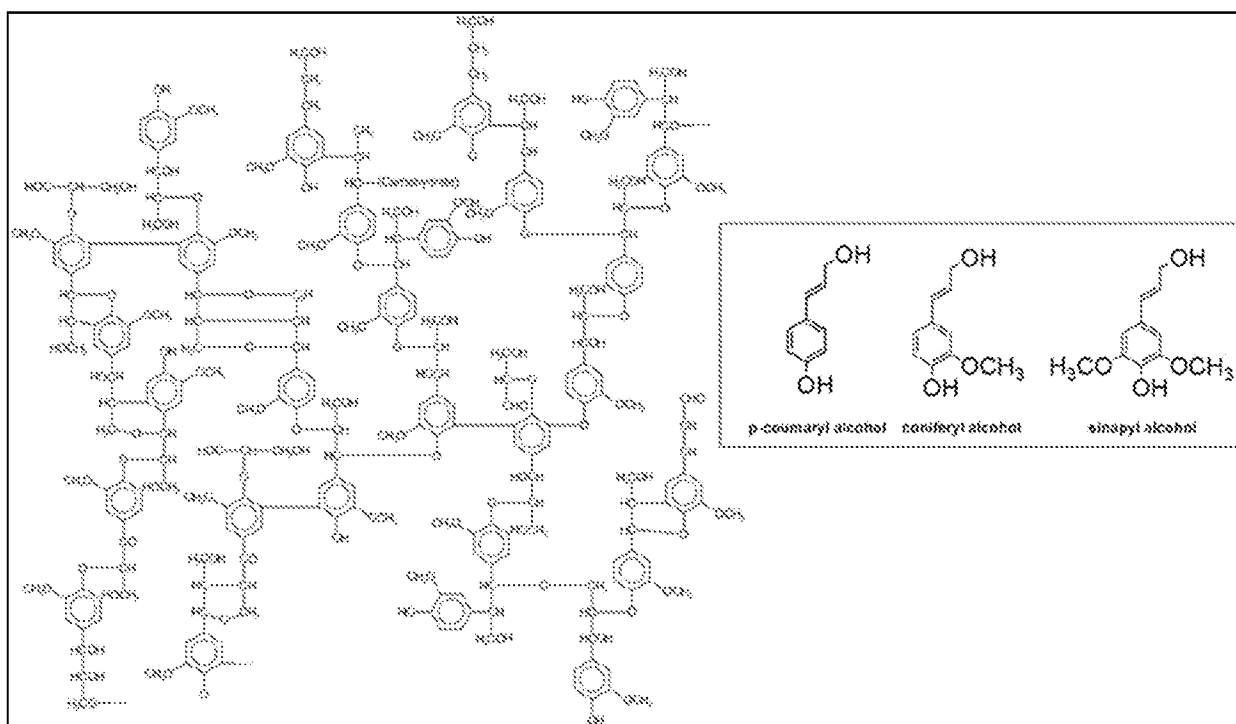
Lignin is one of the most abundant biopolymers in the nature and it is produced in large amounts in the paper industry. Global commercial yearly production of lignin is around 1.1 million metric tons and lignin is used in a wide range of low volume niche applications where typically the form but not the quality of lignin is important.

Lignin functions as a support through strengthening of wood (xylem cells). Lignin is an unusual biopolymer because of its heterogeneity and lack of defined primary structure. The building blocks of lignin are aromatic compounds and thus it is a valuable renewable source of aromatic compounds, useful for chemical and fuel production. The chemical structures of lignin and lignin precursors (coumaryl alcohol, coniferyl alcohol and sinapyl alcohol) are shown below.

25

30

35



In the conversion of lignin it may be subjected to depolymerization carried out in homogeneous or heterogeneous phases where the depolymerization may be performed in the presence of catalysts. After the depolymerization the obtained depolymerized product may be hydrotreated, followed by separation of the product obtained from hydrotreating into different fractions which may further be processed into hydrocarbons or other chemicals. Conversion of lignin may also be realized by hydrotreating without depolymerization. It is necessary to depolymerize lignin to smaller oligomers and monomers, which are suitable for further processing by hydrotreating etc.

Despite the ongoing research and development of processes for the conversion of lignocellulosic materials, there is still a need to provide an improved process for the conversion of lignocellulosic materials.

SUMMARY OF THE INVENTION

Disclosed herein is a process for converting feedstock comprising lignocellulosic material, said process comprising the following steps:

treating the feedstock comprising lignocellulosic material with an alkali in an alkali treatment step, whereby an alkali treated material is obtained,

hydrotreating the alkali treated material catalytically with hydrogen in the presence of a catalyst composition comprising ruthenium (Ru) supported on zirconia (ZrO_2), where said zirconia comprises 60-100 wt% of monoclinic phase of zirconia, to yield an effluent, and

separating from the effluent at least one of the following: an aqueous phase, light gaseous phase, liquid organic phase and residual lignin phase.

The residual lignin phase refers here to a phase or fraction separated from the effluent and comprising unreacted lignin.

Disclosed herein are also aromatic compounds and linear and branched hydrocarbons, and chemicals obtainable by the process.

Disclosed herein is also the use of said aromatic compounds and linear and branched hydrocarbons and chemicals obtainable by the process, as transportation fuels, components in transportation fuels and as industrial chemicals.

Characteristic features of said process, use of said process and products obtained by said process, are presented in the appended claims.

DEFINITIONS

The term "catalytic conversion of lignocellulosic material" refers here to treating lignocellulosic material in the presence of at least one catalytic material to effect change in the structure of the lignocellulosic material, at least to reduce the molecular size and change the functionality.

The term "lignocellulosic material" refers here to lignin or derivatives thereof and mixtures thereof. The lignin or derivatives thereof may be derived from any wood or plant based material, such as wood based raw material, woody biomass, lignin containing biomass such as agricultural residues, bagasse and corn stover, woody perennials, vascular plants, recycled brown board, deinking pulp and their combinations. The term also refers to lignin or derivatives thereof obtained from Kraft black liquor (Kraft lignin), alkaline pulping process, soda process, organosolv pulping and any combination thereof, such as lignosulfonates. The weight average molecular weight of lignin isolated from the above is $M_w = 500-10\,000$ Da, and number average molecular weight $M_n = 700-2000$ Da and polydispersity is 2-4.5. The degree of polymerization of this kind of lignin is 10-25. Lignin separated from pure biomass is sulphur-free and thus valuable in further processing.

The term "lignin" refers here to a class of complex organic polymers that form important structural materials in the support tissues of vascular plants and some algae. Chemically, lignin is a very irregular, randomly cross-linked polymer with a weight average molecular weight of 500 Daltons or higher. Said polymer is the result of an enzyme-mediated dehydrogenative polymerization of three phenyl propanoid monomer precursors, i.e. coniferyl, synapyl and coumaryl alcohols. Coniferyl alcohol is the dominant monomer in conifers (softwoods). Deciduous (hardwood) species contain up to 40% syringyl alcohol units while grasses and agricultural crops may also contain coumaryl alcohol units.

The term "zirconia" refers to zirconium oxide with the chemical formula ZrO_2 . The crystal structure of ZrO_2 exists in three polymorphic phases i.e. ZrO_2 has three different polymorphic forms: monoclinic, tetragonal and cubic. The cubic phase is formed at very high temperatures ($>2370^\circ\text{C}$), at intermediate temperatures ($1150-2370^\circ\text{C}$) the oxide has a tetragonal structure and from room temperature to 1150°C the material is stable as monoclinic structure. Each of these polymorphic phases differ structurally significantly from each other and they exhibit different acid/base properties and surface hydroxyl group concentrations.

A phase diagram for ZrO_2 is shown in Figure 1 ([www.materialdesign.com/system/files/.../ZrO₂ phase transition.pdf](http://www.materialdesign.com/system/files/.../ZrO2_phase_transition.pdf)). As can be realized from the figure, the structures cubic, tetragonal and monoclinic are different. The chemical bond is the same Zr-O but how they are organized in the space is different.

The term "monoclinic phase of zirconia" or "monoclinic zirconia" or "monoclinic ZrO_2 " refers here to a specific crystal structure of zirconia having characteristic X-ray diffraction patterns, i.e. 2θ reflections at 24.3, 28.3, 31.5 and 34.5 in the X-ray diffractogram (Joint Committee on Powder Diffraction Standards Card Numbers (JCPDS), card no. 37-1484). The X-ray diffractogram of monoclinic phase of zirconia is shown in Figure 2.

The term "tetragonal phase of zirconia" or "tetragonal zirconia" or "tetragonal ZrO_2 " refers here to specific crystal structure of zirconia having characteristic X-ray diffraction patterns, i.e. 2θ reflections at 30.4 and 35.2 in the X-ray diffractogram (JCPDS card no. 17-0923). The X-ray diffractogram of tetragonal phase zirconia is shown in Figure 2.

The term "depolymerization/hydrotreating" or "depolymerization and hydrotreating" or "hydrotreatment" or "hydrotreating" refers to catalytic conversion of lignocellulosic materials in the presence of alkali, where depolymerization and hydrotreating of the lignocellulosic materials is carried out. The depolymerization and hydrotreating reactions, comprising one or more of the reactions of depolymerization, hydrogenation, hydrodeoxygenation hydroisomerization, hydrodenitrification, hydrodesulfurization and hydrocracking, and coke reforming, coke/carbon/char gasification, WGS (water-gas-shift) reactions and Boudouard reactions, take place in catalytic conversion of lignocellulosic materials.

All weight percentages regarding the catalyst composition are calculated from the total weight of the catalyst composition.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a phase diagram of ZrO_2 .

Figure 2 illustrates X-ray diffraction patterns of monoclinic ZrO_2 and tetragonal ZrO_2 .

Figure 3 shows an embodiment of the process where lignocellulosic material is treated with an alkali, followed by conducting the alkali treated material to catalytic hydrotreating.

Figure 4 presents another embodiment of the process where lignocellulosic material is treated with an alkali in two steps, in the first step at moderate temperature and pressure, followed by treating in the second step with the alkali at higher temperature and pressure, and then conducting the alkali treated material to hydrotreating.

Figure 5 presents another embodiment of the process where lignocellulosic material is treated with an alkali in two steps, in the first step at moderate temperature and pressure, followed by treating in the second step with the alkali in the presence of a heterogeneous catalyst to obtain alkali treated material and conducting the alkali treated material to hydrotreating.

DETAILED DESCRIPTION

It should be understood that although an illustrative implementation of one or more embodiments are provided below, the disclosed compositions and methods can be implemented using any number of techniques. The disclosure should in no way be limited to the illustrative implementation, drawings, or techniques illustrated below, including the exemplary designs describe herein, but can be modified within the scope of the appended claims along with their full scope of equivalents.

It was surprisingly found that several advantageous effects may be achieved when a catalyst composition comprising ruthenium (Ru) supported on zirconia comprising 60-100 wt% of monoclinic phase of zirconia is used in catalytic conversion of lignocellulosic materials. Said catalyst composition is particularly useful as a catalyst for conversion of lignocellulosic materials to aromatic compounds, linear and branched hydrocarbons and other chemicals. It may be used in processing of lignocellulosic materials to effect one or more of the following depolymerization, hydrogenation, hydrodeoxygenation (HDO), hydroisomerization (HI), hydrodenitrification (HDN), hydrodesulfurization (HDS) and hydrocracking (HC) reactions, and coke/carbon/char gasification, coke reforming, WGS (water-gas-shift) reactions and Boudouard reactions, also under mild conditions.

Disclosed herein is a process for converting feedstock comprising lignocellulosic material,

said process comprising the following steps:

treating the feedstock comprising lignocellulosic material with an alkali in an alkali treatment step, whereby an alkali treated material is obtained,

hydrotreating the alkali treated material catalytically with hydrogen in the presence of a catalyst composition comprising ruthenium supported on zirconia, where said zirconia comprises 60-100 wt% of monoclinic phase of zirconia, to yield an effluent, and

separating from the effluent at least one of the following: an aqueous phase, light gaseous phase, a liquid organic phase and residual lignin phase.

The residual lignin phase refers here to a phase or fraction separated from the effluent and comprising unreacted lignin.

The process comprises an alkali treatment step, which is performed in one step or in several steps, whereby an alkali treated material is obtained. The alkali treated material comprises depolymerized lignin and residual lignin (in polymeric form).

In an embodiment the alkali treatment step is performed at a temperature ranging from 30 to 300°C.

In an embodiment the alkali treatment step is performed under a pressure ranging from 0.5 to 70 bar.

In an embodiment the alkali treatment of the feedstock with an alkali is carried out under inert atmosphere.

In an embodiment the alkali treatment is performed in one step whereby an alkali treated material is obtained. The alkali treatment in one step may be carried out at moderate temperature and pressure, or alternatively at higher temperature and pressure.

In an embodiment, in the alkali treatment in one step at higher temperature and pressure, the temperature ranges from 150 to 300°C, preferably from 250 to 300°C. In said alkali treatment in one step the pressure ranges from 5 to 70 bar, preferably from 5 to 50 bar.

In another embodiment the alkali treatment step is performed in one step at moderate temperature and pressure whereby a partly depolymerized material is obtained. In the alkali treatment in one step at moderate temperature and pressure the temperature ranges from 30 to 110°C, preferably from 50 to 80°C. In said alkali treatment in one step the pressure ranges from 0.5 to 1.5 bar, preferably it is carried out under atmospheric pressure. The alkali treatment at moderate temperature and pressure may have a beneficial effect on the conversion of lignin as it may break at least some bonds in the polymeric structure of lignin, already at the mild conditions whereby at least partly depolymerized lignin is produced.

The alkali treatment carried out in one step at higher temperature and pressure produces depolymerized lignin, where significant amount of bonds in the polymeric structure of lignin are broken.

- 5 In another embodiment the alkali treatment is performed in at least two steps.

In an embodiment the alkali treatment performed in two steps may comprise a first alkali treatment step carried out at moderate temperature and pressure and a second alkali treatment step carried out at higher temperature and pressure, the first alkali treatment step producing partly depolymerized lignocellulosic material, which partly
10 depolymerized lignocellulosic material is treated in the second alkali treatment step whereby an alkali treated material is obtained.

In an embodiment the first alkali treatment step is carried out at a temperature ranging
15 from 30 to 110°C, preferably from 50 to 80°C. In an embodiment the first alkali treatment step is carried out under a pressure ranging from 0.5 to 1.5 bar, preferably under atmospheric pressure.

In an embodiment the second alkali treatment step is carried out at a temperature
20 ranging from 150 to 300°C, preferably from 250 to 300°C. In an embodiment the second alkali treatment step is carried out under a pressure ranging from 5 to 70 bar, preferably under a pressure ranging from 5 to 50 bar.

In Figure 3 an embodiment is presented where feedstock comprising lignocellulosic
25 material is treated in an alkali treatment step 101 in one step with an alkali, followed by conducting the alkali treated material to catalytic hydrotreating. Feedstock comprising lignocellulosic material 10, an aqueous solution formed of alkali 11 and a mixture 12 of ethanol and water are charged to alkali treating 100, where the feedstock comprising lignocellulosic material 10 is treated with an alkali. In an embodiment where
30 the alkali treatment is carried out at moderate temperature and pressure, an alkali treated material 13' comprising partly depolymerized lignocellulosic material, residual lignin, EtOH/water and alkali is obtained. In another embodiment where the temperature and pressure are higher (temperature from 150 to 300°C, preferably from 250 to 300°C, and pressure from 5 to 70 bar, preferably from 5 to 50 bar), an alkali
35 treated material 13 comprising depolymerized lignocellulosic material, residual lignin, EtOH/water and alkali is obtained. The alkali treated material 13 or alkali treated material 13', and hydrogen 20 are directed to hydrotreating 200 in the presence of a catalyst composition comprising ruthenium supported on zirconia, where said zirconia

comprises 60-100 wt% of monoclinic phase of zirconia, whereby an effluent 21 is obtained. The effluent 21 is directed to separation 300, where residual lignin phase 34 is separated and recycled to feedstock comprising lignocellulosic material 10, and an aqueous phase 31, light gaseous phase 32 and a liquid organic phase 33 are obtained. 5 Optionally the liquid organic phase 33 is directed to further processing 700, which may comprise hydrotreating, isomerization, cracking, fractionation etc. and combinations thereof to obtain one or more product streams 71.

Figure 4 presents another embodiment of the process where feedstock comprising lignocellulosic material is treated with an alkali in an alkali treatment step 101, in two steps comprising a first alkali treatment step 100 producing partly depolymerized lignocellulosic material and treating the partly depolymerized lignocellulosic material in a second alkali treatment step 500 whereby alkali treated material is obtained. The alkali treated material is subjected to catalytic hydrotreating 200. feedstock comprising 15 lignocellulosic material 10, an aqueous solution formed of alkali 11 and a mixture 12 of ethanol and water are charged to first alkali treatment step 100, where the feedstock comprising lignocellulosic material 10 is treated with alkali under moderate pressure and temperature, whereby a mixture 13 comprising partly depolymerized lignocellulosic material, residual lignin, EtOH/water and alkali is obtained. The mixture 13 and 20 optionally additional alkali 12 is directed to the second alkali treatment step 500 under higher pressure and temperature, whereby alkali treated material 51 comprising depolymerized lignocellulosic material, residual lignin, EtOH/water and alkali obtained. The alkali treated material 51 and hydrogen 20 are directed to hydrotreating 200 in the presence of a catalyst composition comprising ruthenium supported on zirconia, where 25 said zirconia comprises 60-100 wt% of monoclinic phase of zirconia, whereby an effluent 21 is obtained. The effluent 21 is directed to separation 300, where residual lignin phase 34 is separated and recycled to feedstock comprising lignocellulosic material 10, and an aqueous phase 31, light gaseous phase 32 and a liquid organic phase 33 are obtained.

Figure 5 presents another embodiment of the process where feedstock comprising lignocellulosic material is treated with an alkali in an alkali treatment step 101, in two steps comprising a first alkali treatment step 100 producing a partly depolymerized lignocellulosic material and treating the partly depolymerized lignocellulosic material in a second alkali treatment step 600 in the presence of a heterogeneous catalyst, 35 whereby an alkali treated material is obtained, and conducting the alkali treated material to catalytic hydrotreating 200. Feedstock comprising lignocellulosic material 10, an aqueous solution formed of alkali 11 and a mixture 12 of ethanol and water are

charged to the first alkali treatment step 100, where the feedstock comprising lignocellulosic material 10 is treated with the alkali 11 under moderate pressure and temperature, whereby a mixture 13 comprising partly depolymerized lignocellulosic material, residual lignin, EtOH/water and alkali is obtained. The mixture 13 is directed to the second alkali treatment 600 under higher pressure and temperature in the presence of a heterogeneous depolymerization catalyst 62, whereby alkali treated material 61 comprising depolymerized lignocellulosic material, residual lignin, EtOH/water and alkali is obtained. The alkali treated material 61 and hydrogen 20 are directed to hydrotreating 200 in the presence of a catalyst composition comprising ruthenium supported on zirconia, where said zirconia comprises 60-100 wt% of monoclinic phase of zirconia, whereby an effluent 21 is obtained. The effluent 21 is directed to separation 300, where residual lignin phase 34 is separated and recycled to feedstock comprising lignocellulosic material 10, and an aqueous phase 31, light gaseous phase 32 and a liquid organic phase 33 are obtained.

In an embodiment the feedstock comprises lignocellulosic material selected from lignin, derivatives thereof, and mixtures thereof.

Examples of lignocellulosic materials are Kraft lignin, native lignin, liginosulfonate, lignin obtained from biorefinery processes such as enzymatic, alkaline or acid hydrolysis or steam explosion and any combinations thereof.

Lignin may be wood based, wood biomass based, corn based, bagasse based, agricultural waste based, woody perennials based, vascular plants based, recycled brown board based, deinking pulp based or nutshell based. The weight average molecular weight of lignin used as feedstock is suitably 500-10 000 Da, preferably 600-9000 Da and most preferably 700-8000 Da.

Suitably the lignocellulosic material, such as lignin may be supplied from a feed source such as the pulp and/or paper industry or ethanol production facility or any other source.

In an embodiment the feedstock comprises 60-100 wt% of lignocellulosic material. In another embodiment the feedstock comprises 80-100 wt% of lignocellulosic material.

In another embodiment the feedstock may comprise co-feed selected from benzene ring containing polymers, such as PVC, polystyrene, PET, polyamide and the like, oil refinery vacuum distillation column bottoms, black liquor, pyrolysis oil, and

combinations thereof. The feedstock may comprise co-feed not more than 40 wt%, preferably not more than 20 wt%.

Treatment with an alkali

- 5 In an embodiment the alkali is selected from alkali metal hydroxides, alkaline earth metal hydroxides, alkali metal carbonates, such as Na_2CO_3 , and alkaline earth metal carbonates. Preferably NaOH, KOH, CsOH, $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$ or $\text{Ba}(\text{OH})_2$ is used. In an embodiment, NaOH is used as alkali.
- 10 The alkali acts as a homogeneous depolymerization catalyst in the process.

In an embodiment the molar ratio of the lignocellulosic material to the alkali in the process is from 0.2:1 to 20:1, respectively.

- 15 In an embodiment the feedstock comprising lignocellulosic material is mixed in an aqueous solution to obtain a mixture, where the aqueous solution comprises water and the alkali.

The aqueous solution comprises water and the alkali.

- 20 In an embodiment the aqueous solution comprises 1-10 wt%, preferably 2-5 wt% of the alkali.

- In an embodiment the aqueous solution may comprise a co-solvent selected from lower (C1-C5) alkyl alcohols, lower (C1-C6) alkyl ethers and lower (C1-C6) alkyl esters. Preferably the alcohol is selected from methanol, ethanol, 1-propanol, iso-propanol, 1-butanol and sec-butanol.
- 25

- In another embodiment the aqueous solution may comprise a co-solvent selected from ethyl acetate, methyl tert-butyl ether, furan, methyl furan, dimethyl furan, tetrahydrofuran, methyl-tetrahydrofuran, dimethyl-tetrahydrofuran and furfuryl alcohol.
- 30

In an embodiment the co-solvent is ethanol.

- 35 In an embodiment, in the aqueous solution, the volumetric ratio of water to the co-solvent may be from 0.5:1 to 10:1, respectively, preferably from 1:1 to 5:1, and more preferably from 2:1 to 3:1, respectively.

In an embodiment in the aqueous solution the volumetric ratio of water to ethanol is from 1:1 to 5:1, preferably from 1:1 to 3:1, respectively.

Alkali treatment in one step

- 5 The alkali treatment in one step may be carried out at moderate temperature, at 30-110°C and moderate pressure, under 0.5-1.5 bar, where the alkali acts as a homogeneous catalyst which effects at least partial depolymerization of the lignocellulosic material to obtain alkali treated material, which may comprise partly depolymerized lignocellulosic material comprising organic compounds, residual lignin
10 (unreacted lignocellulosic material), and gas (typically more than 10 %). The amount of organic compounds is increased with increased temperature.

Suitably the alkali treatment in one step is carried out for 15 min to 12 hours.

- 15 The moderate temperature is 30-110°C, preferably 50- 80°C. The moderate pressure is 0.5 - 1.5 bar, preferably atmospheric pressure.

Alternatively the alkali treatment in one step may be carried out at higher temperature and under higher pressure, where alkali acts as the homogeneous catalysts, which
20 effects higher degree of depolymerization of the lignocellulosic material to obtain alkali treated material.

The higher temperature is 150-300°C, preferably 150-300°C. The higher pressure is 5-70 bar, preferably 5-50 bar.

- 25 The alkali treated material obtained from the one step alkali treatment may be directed to catalytic hydrotreating.

Alkali treatment in two steps

- 30 In an embodiment the alkali treatment is carried out in at least two steps.

In the first alkali treatment step the temperature is 30-110°C, preferably 50 - 80°C. The pressure ranges from 0.5 to 1.5 bar, preferably atmospheric pressure is used. Suitably the first step is carried out for 15 min to 12 hours.

- 35 This treatment of the lignocellulosic material with alkali yields in the alkali treatment step under moderate pressure and temperature in the first alkali treatment step partly depolymerized lignocellulosic material, which may comprise organic compounds,

residual lignin and gas (typically more than 10 %). The amount of organic compounds is increased with increased temperature.

The partly depolymerized lignocellulosic material obtained from treatment with alkali under moderate pressure in the first alkali treatment step may be directed to alkali treating in a second alkali treatment step, optionally in the presence of a heterogeneous catalyst whereby an alkali treated material is obtained.

In an embodiment the partly depolymerized lignocellulosic material, obtained from the first alkali treatment step is directed to a treatment in a second alkali treatment step. The partly depolymerized lignocellulosic material obtained from the first alkali treatment step contains alkali which effects homogeneous depolymerization of the lignocellulosic material.

If necessary, additional alkali may be added to the second alkali treatment step.

In the second alkali treatment step the temperature is in the range from 150 to 300°C, preferably in the range from 250 to 300°C.

In the second alkali treatment step the pressure is in the range from 5 to 70 bar, preferably in the range from 5 to 50 bar, more preferably in the range from 5 to 30 bar.

In an embodiment the second step is carried out for 0.5 to 10 hours, preferably for 2 to 10 hours.

In an embodiment the mixture of partly depolymerized lignocellulosic material, residual lignin, EtOH/water and alkali obtained from the first alkali treatment step carried out under moderate temperature and pressure is directed to the treatment with an alkali at higher temperature and pressure (second alkali treatment step), in the presence of a homogeneous catalyst comprising alkali.

In one embodiment the alkali carried along with the mixture of partly depolymerized lignocellulosic material, residual lignin and EtOH/water may be sufficient to affect the complete depolymerization of the lignin and no additional alkali is needed.

In one embodiment additional alkali is added to the mixture of partly depolymerized lignocellulosic material, residual lignin and EtOH/water in the second alkali treatment step.

The first and second alkali treatment steps may be carried out in one reaction vessel or in at least two vessels.

In another embodiment the alkali treatment step is carried out in the first alkali treatment step at a moderate temperature from 30 to 110°C under a moderate pressure from 0.5 to 1.5 bar, followed by increasing the temperature to 150-300°C and pressure to 5-70 bar in the second alkali treatment step. In an embodiment the treatment at moderate pressure and temperature is carried out for 0.5 to 6 hours, suitably for 1 to 6 hours and the treatment at higher temperature and pressure for 0.5 to 10 hours, suitably 2 to 10 hours. The alkali treatment may be carried out in one reaction vessel (reactor) or in at least two vessels (reactors).

In another embodiment the partly depolymerized lignocellulosic material obtained from the first alkali treatment step carried out under moderate temperature and pressure is directed to the treatment with an alkali at higher temperature and pressure (second alkali treatment step), in the presence of a heterogeneous catalyst comprising MgO or CaO. In this second alkali treatment step the treatment is carried out at the temperature of 150-300°C, preferably 250-300°C. The pressure is 5-70 bar, preferably 5-50 bar. The first and second alkali treatment steps may be carried out in one reaction vessel or in at least two vessels.

In an embodiment the heterogeneous catalyst comprises MgO or CaO, preferably MgO is used. In another embodiment the first alkali treatment step is carried out at a temperature from 30 to 110°C under a pressure from 0.5 to 1.5 bar to obtain partly depolymerized lignocellulosic material, which is then alkali treated in a second alkali treatment step in the presence of the heterogeneous catalyst comprising MgO or CaO. The second alkali treatment step is carried out at the temperature of 150-280°C, preferably at 190-220°C. The second alkali treatment step is carried out under the pressure of 5-70 bar, preferably 15-65 bar, more preferably 15-35 bar.

Suitably the alkali treatment in the first alkali treatment step is carried out for 0.5 to 6 hours and the second alkali treatment step with the heterogeneous catalyst for 0.5 to 10 hours.

In an embodiment the pressure in the second step with the heterogeneous catalyst is 20-25 bar.

The heterogeneous catalyst comprises MgO or CaO on a support selected from silica, alumina and mixtures of them.

5 In an embodiment the first alkali treatment step is carried out in one reaction vessel and the second alkali treatment step in another reaction vessel.

In another embodiment the first alkali treatment step is carried out in the same reaction vessel as the second alkali treatment step.

10 In an embodiment the second alkali treatment step with a heterogeneous depolymerization catalyst is carried out as slurry in a slurry reactor.

15 The alkali acts as a homogeneous catalyst in the depolymerization. When a solid catalyst, such as MgO or CaO is used in alkali treatment it acts as a heterogeneous depolymerization catalyst.

20 In the second alkali treatment step a high degree of depolymerization of the lignocelulosic materials takes place, whereby high amounts of depolymerized lignocellulosic material comprising organic compounds, gas (typically less than 5 %), and residual lignin are obtained.

In an embodiment, the WHSV is $0.1-10\text{h}^{-1}$ in the second alkali treatment step.

25 In an embodiment the pH of the reaction mixture is adjusted, if necessary to 10-12.5 in the second alkali treatment step.

The alkali treated material comprises depolymerized lignin and residual lignin.

30 In an embodiment, after the alkali treatment is completed, the alkali treated material may be subjected to separation, where solids containing residual lignin are separated and they may be recycled to the feedstock. In an embodiment an aqueous phase is separated from an organic phase.

35 In another embodiment, after the alkali treatment no separation is carried out and the alkali treated material or the partly depolymerized material is conducted as such to the hydrotreating.

In an embodiment the alkali treatment may be carried out in at least one reaction vessel and the subsequent hydrotreating may be carried out in at least one other reaction vessel.

5 **Hydrotreating**

The hydrotreating is carried out in the presence of hydrogen. The hydrotreating comprises depolymerization reactions and any combination of the reactions of hydrogenation, hydrodeoxygenation, hydroisomerization, hydrodenitrification, hydrodesulfurization, hydrocracking, coke/carbon/char gasification and coke reforming
10 reactions, water-gas-shift reactions and Boudouard reactions.

In an embodiment the alkali treated material obtained from alkali treatment is hydrotreated with hydrogen in the presence of a catalyst composition comprising ruthenium supported on zirconia, where said zirconia comprises 60-100 wt% of
15 monoclinic phase of zirconia.

In an embodiment the catalytic hydrotreating is carried out in the presence of water, originating from the alkali treatment. The catalyst Ru supported zirconia comprising monoclinic phase of zirconia, used in the hydrotreating tolerates aqueous environment.
20

In an embodiment the catalyst composition comprises ruthenium supported on zirconia, where said zirconia comprises 80-100 wt% of monoclinic phase of zirconia.

In an embodiment the zirconia comprises 85-100 wt% of monoclinic phase of zirconia.
25

In an embodiment the zirconia comprises 90-100 wt% of monoclinic phase of zirconia.

In another embodiment the zirconia comprises 95-100 wt% of monoclinic phase of zirconia.
30

In another embodiment the zirconia comprises 98-100 wt% of monoclinic phase of zirconia.

The remaining part of zirconia may exist as tetragonal phase or another crystal form.
35

In an embodiment the catalyst composition comprises 0.2 - 5 wt% of Ru. In another embodiment the catalyst composition comprises 0.3 - 3 wt% of Ru. In still another embodiment the catalyst composition comprises 0.5 - 2.5 wt% of Ru.

In an embodiment in the catalyst composition comprises metallic Ru particles having small average particle size, in the range from 0.1 to 30 nm. In another embodiment the catalyst composition comprises metallic Ru particles having average particle size in the range from 0.5 to 20 nm. In still another embodiment the catalyst composition comprises metallic Ru particles having average particle size in the range from 1 to 15 nm. The particle size determination may suitably be carried out by methods based on SEM (Scanning Electron Microscope) or HR-TEM (High Resolution Transmission Electron Microscope).

In an embodiment, in the catalyst composition, the Ru metallic particles are highly dispersed onto the support. In an embodiment the metal dispersion of Ru measured by CO chemisorption method, is in the range from 15 to 45% where the specific surface area (BET) of zirconia is not more than 100 m²/g and the Ru loading is not more than 2 wt%, in the catalyst composition.

In another embodiment the catalyst composition may additionally comprise at least one dopant selected from Pd, Pt, Vn, Ni, Sn, La, Ga, Co and combinations thereof. The amount of the dopant in the catalyst composition is not more than 2 wt%. The total amount of Ru and the dopant is not more than 5 wt%.

ZrO₂ comprising 60-100 wt% of monoclinic phase of zirconia interacts strongly with the active phase (Ru), it inhibits sintering of supported oxides in the presence of water and high temperatures, it possesses high thermal stability and good chemical stability, and it is more inert than the classical supported oxides. Further, ZrO₂ comprising 60-100 wt% of monoclinic phase of zirconia possesses acidity, basicity as well as reducing and oxidizing ability.

In an embodiment the catalyst composition comprises ZrO₂ comprising 60-100 wt% of monoclinic phase of zirconia only as the support.

In another embodiment the catalyst composition may comprise as an additional support an oxide selected from CeO₂, TiO₂, MgO, ZnO, SiO₂, Al₂O₃ and combinations thereof. Examples of suitable mixtures are ZrO₂-SiO₂, ZrO₂-Al₂O₃, ZrO₂-TiO₂, ZrO₂-ZnO, ZrO₂-CeO₂ and ZrO₂-MgO, where ZrO₂ refers to ZrO₂ comprising 60-100 wt% of monoclinic phase of zirconia.

In an embodiment the support may comprise ZrO₂ comprising 60-100 wt% of monoclinic phase of zirconia and less than 50 wt% of an additional support.

In another embodiment the support may comprise zirconia comprising ZrO_2 comprising 60-100 wt% of monoclinic phase of zirconia and less than 40 wt% of the additional support, suitably less than 30 wt% of the additional support, and even more suitably less than 20 wt% of the additional support.

5

In still another embodiment the support may comprise ZrO_2 comprising 60-100 wt% of monoclinic phase of zirconia and less than 10 wt% of the additional support, suitably less than 5 wt% of the additional support, and even more suitably less than 2 wt% of the additional support.

10

In an embodiment the hydrotreating is carried out at the temperature from 180 to 420°C. In another embodiment the hydrotreating is carried out at the temperature from 200 to 350°C. In another embodiment the hydrotreating is carried out at the temperature from 220 to 280°C.

15

In an embodiment the hydrotreating is carried out under the pressure from 5 to 140 bar. In another embodiment the hydrotreating is carried out under a pressure from 10 to 120 bar. In another embodiment the hydrotreating is carried out under a pressure from 10 to 70 bar.

20

In an embodiment the hydrotreating is carried out under the initial pressure from 20 to 35 bar in batch wise operation. Reaction time in batch wise operation may be from 20 min to 24 hours.

25

In an embodiment the hydrotreating is carried out under the pressure from 10 to 140 bar in continuous operation.

WHSV in the hydrotreating may be $0.1\text{-}10\text{ h}^{-1}$

30

WHSV in the hydrotreating and in the alkali treatment may be $0.1\text{-}10\text{ h}^{-1}$.

In another embodiment WHSV in the hydrotreating and in the alkali treatment may be $0.5\text{-}5\text{ h}^{-1}$.

35

The catalyst composition is water tolerant. Thus it is capable of carrying out hydrotreating reactions in an environment where water (or aqueous solution) forms a part of the material to be treated.

Hydrogen partial pressure at feed is typically from 60 to 100 % from total pressure.

The hydrotreating may be carried out in any reactor or reactor system comprising one or more reactors suitable for the purpose, such as a slurry reactor, CSRT (continuous stirred tank reactor), a continuous flow fixed-bed reactor, fixed bed (trickle or gas phase), loop reactor, tubular reactor (plug-flow reactor PFR and packed-bed reactor) or ebullated bed reactor.

In an embodiment the effluent obtained from the process, comprising aromatic compounds, alcohols, ethers, esters, gases and some residual lignin may be subjected separation, whereby light gaseous components, residual lignin and an aqueous phase are separated from a liquid organic phase. The liquid organic phase may be further fractionated and/or subjected to further processing, such as one or more of hydrotreating, isomerizing, cracking etc. for obtaining components suitable as biofuels, biofuel components and other chemicals. The residual lignin may be recycled to the feedstock.

The liquid organic phase comprises aromatic compounds, alcohols, ethers, esters and hydrocarbons.

The light gaseous phase comprises light gaseous components, which are mainly gases, such as unreacted (excess) H_2 , CO and CO_2 , methane, ethane, ethene, propane, propene, butanes and butenes that can be used in the production of H_2 after optional separation of excess hydrogen (H_2). This H_2 produced or separated excess H_2 can be recycled to the hydrotreating step. The optional separation of excess H_2 may be carried out by membrane or pressure swing absorption technique.

The aqueous phase typically comprises sugars, acids, some aromatic compounds (phenols) and inorganic impurities. The aromatics may be separated and used as chemicals. Low molecular weight acids in water phase may be condensed for example via ketonization and consecutive aldol condensation reactions to produce hydrocarbon mixtures for further applications. The aqueous water phase may also be used in H_2 production, particularly in steam reforming.

The liquid organic phase may be fractionated and/or subjected to further processing, such as hydrotreating to provide chemical compounds and hydrocarbon boiling in the liquid fuel range, particularly the gasoline and diesel range.

The catalyst composition comprising Ru supported on ZrO₂ comprising 60-100 w% of monoclinic phase may be obtained by a method comprising the steps, where
in the first step an aqueous solution of Ru precursor is mixed with ZrO₂ comprising 60-100 wt% of monoclinic phase of zirconia, at a temperature from 5 to 85 °C to obtain a mixture,

in the second step the pH of the mixture is adjusted to 7.5 – 10 with a alkali and mixing is continued for 0.5 to 30 hours,

in the third step solid material is recovered from the mixture obtained in the second step,

in the fourth step the solid material is dried at a temperature from 50 to 200 °C and a catalyst composition comprising Ru supported on ZrO₂ comprising 60-100 w% of monoclinic phase of zirconia is obtained.

ZrO₂ comprising 60-100 w% of monoclinic phase may be obtained using hydrothermal synthesis methods or other methods known in the art.

Incorporation of Ru onto ZrO₂ comprising 60-100 w% of monoclinic phase of zirconia may be performed by means of the above described co-precipitation method.

The Ru precursor may be selected from salts and organometallic complexes of Ru(II). The Ru precursor may be selected from [Ru₃(CO)₁₂], Ru(NH₃)₄Cl₂, [((Cy)RuCl₂)₂], [(Cp)Ru(PPh₃)₂Cl)], [((pMeCp)RuCl₂)₂], RuCl₃·3H₂O and Ru(NO₃)₂. In a preferable embodiment the Ru precursor is selected from [Ru₃(CO)₁₂], Ru(NH₃)₄Cl₂, RuCl₃·3H₂O and Ru(NO₃)₂.

In an embodiment RuCl₃·3H₂O is used as Ru precursor and 0.0065 – 0.1424 grams of this precursor are diluted in an aqueous solution (20 – 30 ml) to attain 0.2 – 5.0wt% of Ru in the final solid. In an embodiment the aqueous solution of the Ru precursor is mixed with 1 gram of the ZrO₂ comprising 60-100 w% of monoclinic phase of zirconia.

In an embodiment the concentration of the Ru precursor in the aqueous solution is 0.01 – 1 wt%.

The mixing in the first step is carried at a temperature from 5°C to 85°C, preferably from 15°C to 70°C, and most preferably from 20°C to 50°C.

In an embodiment the ZrO_2 comprising 60-100 w% of monoclinic phase is pretreated at 150-300°C, suitably in air, to eliminate humidity and other organic impurities from the solid.

- 5 In an embodiment, the mixture is stirred in the first step for 10 min to 10 hours.

In an embodiment, in the second step the alkali is selected from alkali metal hydroxides and alkaline earth metal hydroxides, preferably KOH or NaOH is used. Preferably an aqueous solution of NaOH, having concentration ranging from 0.1M to 2.0M is used.

10

In an embodiment in the second step the mixture is stirred at the temperature from 5 to 35°C. In an embodiment the mixture is stirred for 0.5-30 hours, suitably from 1 to 24 hours.

- 15 In an embodiment in the third step the solid material is recovered by filtration, centrifuging, spray drying or the like. The solid material is suitably washed with water until pH is in the range of 6.5 – 7.5.

- 20 In an embodiment in the fourth step the solid material is dried (under air, atmospheric pressure) at 50-200°C. Suitably the drying temperature is 60 – 140°C.

The Ru content in the thus obtained catalyst composition may be determined by ICP (inductively coupled plasma mass spectrometry) measurements.

- 25 In an embodiment the dried final solid material (the catalyst composition) is thermally activated (reduced) at 80-350°C, suitably under H_2 , *in situ* or separately, prior to its use in catalytic processing. In another embodiment the dried solid material is thermally activated at 100-300°C, suitably at 200-300°C.

- 30 The process for converting lignocellulosic materials to aromatic compounds, linear and branched hydrocarbons and other chemicals has several advantageous effects. It was surprising that low temperatures and pressures can be used, whereby there is no need for equipment designed for high temperature/pressure processing. Further, less side-reactions and less cracking occur, whereby less light compounds are formed, and better
35 conversion and high organic yields, and products of high quality are achieved.

Varying lignocellulosic materials may be used as feedstock, such as lignin or derivatives thereof, Kraft lignin, native lignin, liginosulfonate, lignin obtained from biorefinery

processes such as enzymatic, alkaline or acid hydrolysis or steam explosion, and any combinations thereof.

The liquid organic phase may be fractionated using methods well known in the art to several fractions comprising aromatics, linear and branched hydrocarbons boiling in the liquid fuel range and other chemicals. The aromatics, hydrocarbons and chemicals may be used as fuels and fuel components and as starting materials in industrial processes. The liquid organic phase may also be processed further by hydrotreating, cracking, isomerizing and combinations thereof.

Disclosed herein are also aromatic compounds and linear and branched hydrocarbons obtainable by the process. The aromatics comprise benzene, toluene, ortho- and para-xylenes, ethyl-benzene, propyl-benzene, iso-propyl-benzene, di- and tri-alkyl substituted benzenes, where alkyl substituents are selected from methyl-, ethyl-, propyl- or iso-propyl.

The linear and branched hydrocarbons comprise C4-C12 linear and branched hydrocarbons selected from C4-C12 n-alkanes; and C4-C12 mono-alkyl-substituted alkanes, where alkyl substituents are selected from methyl-, ethyl, propyl-, and iso-propyl; and also C4-C10 di- and tri- alkyl substituted alkane, where alkyl groups are selected from methyl-, ethyl-, propyl-, and iso-propyl; and additionally C4-C9 alkyl substituted cycloalkanes, where alkyl groups are selected from methyl-, ethyl-, propyl, and iso-propyl.

Particularly the catalyst composition comprising Ru supported on ZrO₂ comprising 60-100 w% of monoclinic phase of zirconia is very efficient in the conversion of lignocellulosic materials to aromatic monomers and other hydrocarbonaceous component, particularly to effect one or more of the following: depolymerization, hydrogenation, hydrodeoxygenation, hydroisomerization hydrodenitrification, hydrodesulfurization, hydrocracking, coke reforming and coke/carbon/char gasification reactions, WGS (water-gas-shift) reactions and Boudouard reactions, simultaneously and/or in parallel, in any order.

The catalyst composition comprising Ru supported on ZrO₂ is very stable and resistant at reactions conditions and it is more tolerant than commercial sulfided hydrotreatment catalysts under the harsh conditions.

The catalyst composition comprising Ru supported on ZrO₂ is active and effective even at low temperatures and pressures.

With the process, less residual lignin and less gases are obtained in converting lignocellulosic materials, and further, the oxygen content of the products is lower, when compared with prior art processes.

The metal loading of the catalyst may be low, still maintaining the desired activity, whereby the need for expensive ruthenium is reduced.

Yields of the liquid organic phase of around 70 wt-% may be achieved when the process is used.

Examples

The following examples are illustrative embodiments of the present invention, as described above, and they are not meant to limit the invention in any way.

Example 1

Alkali treatment of lignin in two steps

In the first alkali treatment step lignin (1.0 g) was treated with an aqueous solution comprising NaOH (0.4 g) and a mixture (10,0 g) of ethanol and water (1:3). The operation conditions for the first step were 70°C and atmospheric pressure for 3 hours. A mixture comprising partly depolymerized lignin was obtained. The mixture comprising the partly depolymerized lignin was treated in the second alkali treatment step carried out A) with NaOH (homogeneous catalyst, originating from the first step) at 250°C and 22 bar (initial pressure pressurized at room temperature with N₂, before heating) and B) with MgO (0.3 g) (heterogeneous catalyst) at 200°C and 22 bar (initial pressure pressurized at room temperature with N₂ before heating) yielding alkali treated material. Compositions of alkali treated materials are presented in table 1 below.

Table 1: Compositions of alkali treated materials

Composition of alkali treated material (wt%)	First Step: NaOH + EtOH/ water (1:3) 70°C Second step : NaOH+ EtOH/water (1:3), 250°C	First step: NaOH + EtOH/water (1:3) 70°C Second step: MgO (0.3 g) + EtOH/water 81:3), 250°C
Organic compounds	44.01	49.66
Gas	3.15	2.14

Residual lignin	39.53	58.94
Light oxygenated		0.24
2,2-diethylpropene		0.01
Acetic acid	0.51	
Acetaldehyde	0.10	
Guaiacol	3.14	1.51
4-methylguaiacol	0.35	
4-ethylguaiacol	0.90	0.75
Syringol	0.09	0.44
vanillin	0,35	0.35
iso-eugenol	0.03	0.94
acetovanillone	0.29	0.67
syringaldehyde	1.67	3.12
acetosyringone	0.04	8.00
Comp.1	2.42	2.18
Comp.2	0.55	0.30
Comp.3	0.73	
Comp.4	0.57	
Oligomers	88.26	81.73

This example shows that depolymerization happens with the homogeneous catalyst and with the heterogeneous catalyst.

- 5 The use of MgO as heterogeneous depolymerization catalyst in the second step of the alkali treatment increased the organic yield when compared with the product obtained when the second step of the alkali treatment is performed without MgO. No significant differences were detected in the product distribution achieved with or without MgO.
- 10 The alkali treatment may also be carried out without EtOH, simplifying the process and making it less expensive.

Example 2

Alkali treatment of lignin in one step

- 15 Lignin was treated with alkali in one step at a) 200°C/20-22 bar, using an aqueous solution comprising NaOH, and b) 250°C/32 bar, using 10 g of an aqueous solution comprising NaOH and EtOH, where the ratio of ethanol and water was (1:3). 10 wt% of lignin was mixed with the aqueous solution. In both cases the NaOH concentration

was 4-5 wt%. No alkali treatment at moderate temperature and pressure was carried out. After the alkali treatment alkali treated material was obtained. Compositions of the alkali treated materials are presented in table 2 below.

5 **Table 2:** Compositions of the alkali treated materials

Compositions of alkali treated materials (wt%)	NaOH with water (200°C/20-22 bar)	NaOH with EtOH + water (1:3, 250°C/32 bar)
Organic compounds	29.55	40.49
Gas	16.79	21.17
Residual lignin	45.89	37.50
light oxygenates	-	3.04
2,2-diethoxypropane	0.16	0.01
Guaiacol	1.09	2.65
4-ethylguaiacol	0.12	1.33
Syringol	0.11	0.94
vanillin	1.89	1.36
iso-eugenol	0	0
acetovanillone	2.22	0.59
syringaldehyde	0.21	0.31
acetosyringone	0.77	1.18
Comp.1	1.99	0.94
Comp.2	0.78	0.15
Comp.3	0.27	0
Oligomers in the organic phase	90.39	90.54

This example shows that the alkali treatment can also be carried out without the alkali treatment at moderate temperature and pressure (first alkali treatment step) and a liquid organic phase containing high amounts of about 90 wt% of oligomers is obtained.

Performing the alkali treatment at the higher temperature and pressure, with an aqueous solution comprising water, ethanol, and NaOH as homogeneous catalyst has a positive effect on the organic yield. However, this organic yield also includes the alcohol added. The beneficial effect of ethanol addition can be seen in the amount of residual

lignin. This amount is less than when the aqueous solution does not contain ethanol. The presence of ethanol enhances the production of aromatics which can then later be processed further.

5

Example 3.

One step alkali treatment of lignin followed by hydrotreating

Ru supported on monoclinic ZrO₂ comprising more than 90 w% of monoclinic phase of zirconia was used as catalyst in hydrotreating for processing lignin in a process comprising an alkali treatment where lignin was at least partly depolymerized with homogenous catalyst, that is NaOH, followed by hydrotreating under mild conditions. In the alkali treatment lignin was treated in the alkali treatment step with an aqueous solution comprising NaOH and EtOH/water mixture, at 70°C/atmospheric pressure, the alkali treated material (slurry) was hydrotreated under H₂ atmosphere (initial pressure 22 bar) and at 250 °C temperature in the presence of a metal supported catalyst in a slurry reactor. Results of the evaluation of the catalytic activity of Ru and Ni supported catalysts in the two step processing of lignin are summarized in Table 3, respectively. The catalysts used in the evaluation were Ru supported on monoclinic ZrO₂, and as comparative Ru/C and Ni supported on monoclinic ZrO₂.

20

In addition, the treatment with alkali may also be carried out using aqueous alkali without EtOH, avoiding thus the use of EtOH.

Table 3: Results of the evaluation of the catalytic activity of Ru and Ni supported catalysts

25

Alkali treatment and hydrotreating			
Alkali treatment	70/atmospheric	70/atmospheric	70/atmospheric
T (°C)/P(bar)			
Catalyst	NaOH	NaOH	NaOH
Hydrotreating T(°C)/P(bar)	250/<50	250/<50	250/<50
Catalyst	5% Ru/C (commercial)	1.9% Ru/ZrO ₂ (monoclinic)	10% Ni/ZrO ₂ (monoclinic)
EtOH/water ratio	1/3	1/3	1/3
Yields:			
Organic (%)	73.50	79.73	29.28
Gas (%)	20.81	14.91	10.36
Residual lignin (%)	11.26	10.70	55.38

Total identified prod. (%)	20.10	11.80	4.46
Oligomeric products (%)	79.90	88.20	95.54
Alcohols (%)	10.16	3.35	1.39
Other lights (%)	4.26	1.09	0.94
Aromatics (%)	5.02	6.64	2.12

In this approach, the conversion of lignin to hydrocarbons can be done without the need of using a high temperature and high pressure in the alkali treatment step.

- 5 To have one alkali treatment step at low temperatures (70°C) and atmospheric pressure makes this process more suitable for the large scale application as is less expensive and complicated than those of prior art.

These examples show several advantages, which are listed in the following:

- 10 - The organic yields achieved with Ru/monoclinic ZrO₂ catalyst are higher than with the other catalysts that contain even higher metal loading
- The residual lignin content (non-converted lignin) is low
- More aromatics are produced with the Ru/monoclinic ZrO₂ supported catalyst than with any other catalyst.
- 15 - The compounds obtained as product can be converted further in downstream processes.
- Products containing large amounts of aromatics can be used as drop-in components in jet fuel
- 20 Further, the amount of non-identified compounds in the product indicates that there are compounds that have high boiling points and thus they can't be identified by gas chromatography (GC) but they could be hydrotreated in downstream processes.

Claims

1. A process for converting feedstock comprising lignocellulosic material,
5 said process comprising the steps:
treating the feedstock comprising lignocellulosic material with an alkali in an alkali
treatment step, whereby an alkali treated material is obtained,
hydrotreating the alkali treated material catalytically with hydrogen in the presence of
a catalyst composition comprising ruthenium supported on zirconia, where said zirconia
10 comprises 60-100 wt% of monoclinic phase of zirconia, to yield an effluent, and
separating from the effluent at least one of the following: an aqueous phase, light
gaseous phase, a liquid organic phase and residual lignin phase.
2. The process according to claim 1, wherein the alkali treatment step is performed in
15 one step or in several steps.
3. The process according to claim 1 or 2, wherein the alkali treatment step is performed
at the temperature from 30 to 300°C under the pressure from 0.5 to 70 bar.
- 20 4. The process according to any one of claims 1-3, wherein the feedstock comprising
lignocellulosic material is mixed in an aqueous solution comprising water and the alkali.
5. The process according to claim 4, wherein the aqueous solution comprises 1-10 wt%,
preferably 2-5 wt% of the alkali.
- 25 6. The process according to any one of claims 1-5, wherein the alkali is selected from
alkali metal hydroxides, alkaline earth metal hydroxides, alkali metal carbonates, and
alkaline earth metal carbonates, preferably the alkali is NaOH, KOH, CsOH, Ca(OH)₂,
Sr(OH)₂ or Ba(OH)₂.
- 30 7. The process according to any one of claims 4-6, wherein the aqueous solution
comprises a co-solvent selected from C1-C5 alkyl alcohols, C1-C6 alkyl ethers and C1-
C6 alkyl esters, preferably the co-solvent is selected from ethyl acetate, methyl tert-
butyl ether, furan, methyl furan, dimethyl furan, tetrahydrofuran, methyl-
35 tetrahydrofuran, dimethyl-tetrahydrofuran, furfuryl alcohol, methanol, ethanol, 1-
propanol, iso-propanol, 1-butanol and sec-butanol, particularly preferably the co-
solvent is ethanol.

8. The process according to claim 7, wherein in the aqueous solution the volumetric ratio of water to the co-solvent is from 0.5:1 to 10:1, preferably from 1:1 to 5:1.

9. The process according to any one of claims 1-8, wherein the feedstock comprising lignocellulosic material is treated in the alkali treatment step in one step at a temperature from 150 to 300°C, preferably from 250 to 300°C.

10. The process according to any one of claims 1-9, wherein the feedstock comprising lignocellulosic material is treated in alkali treatment step in one step under a pressure from 5 to 70 bar, preferably from 5 to 50 bar.

11. The process according to any one of claims 1-8, wherein the feedstock comprising lignocellulosic material is treated in the alkali treatment step in one step at a temperature from 30 to 110°C, preferably from 50 to 80°C.

12. The process according to any one of claims 1-8 and 11, wherein the feedstock comprising lignocellulosic material is treated in the alkali treatment step in one step under a pressure from 0.5 to 1.5 bar, preferably under atmospheric pressure.

13. The process according to any one of claims 1-8, wherein the feedstock comprising lignocellulosic material is treated in the alkali treatment step in at least two steps where said steps comprise a first alkali treatment step and a second alkali treatment step, the first alkali treatment step producing a partly depolymerized lignocellulosic material which is treated in the second alkali treatment step whereby an alkali treated material is obtained.

14. The process according to claim 13, wherein the first alkali treatment step is carried out at a temperature from 30 to 110°C, preferably from 50 to 80 °C and under a pressure of 0.5 to 1.5 bar, preferably under atmospheric pressure, and the second alkali treatment step is carried out at a temperature from 150 to 300°C preferably from 250 to 300°C and under a pressure of 5 to 70 bar, preferably under a pressure from 5 to 50 bar.

15. The process according to any one of claims 1-8 and 13-14, wherein the second alkali treatment step is carried out in the presence of a heterogeneous catalyst comprising MgO or CaO, preferably MgO.

16. The process according to any one of claims 15, wherein the lignocellulosic material is selected from lignin, derivatives of lignin and mixtures thereof.

17. The process according to any one of claims 1-16, wherein the hydrotreating comprises depolymerization reactions and any combination of the reactions of hydrogenation, hydrodeoxygenation, hydroisomerization, hydrodenitrification, hydrodesulfurization, hydrocracking, coke/carbon/char gasification and coke reforming reactions, water-gas-shift reactions and Boudouard reactions.

18. The process according to any one of claims 1-17, wherein the catalyst composition comprising ruthenium supported on zirconia comprises 0.2-5 wt% of Ru, preferably 0.3-3 wt% of Ru, particularly preferably 0.5-2.5 wt% of Ru.

19. The process according to any one of claims 1-18, wherein the catalyst composition comprises Ru particles having average particle size in the range from 0.1 to 30 nm, preferably 0.5 to 20 nm, and more preferably 1 to 15 nm.

20. The process according to any one of claims 1 - 19, wherein dispersion of Ru in the catalyst composition is in the range from 15 to 45 %, where the specific surface area of zirconia is not more than 100 m²/g and the Ru loading is not more than 2 wt%.

21. The process according to any one of claims 1-20, wherein the zirconia comprises at least 80-100 wt% of monoclinic phase of zirconia, preferably 90-100 wt% of monoclinic phase of zirconia, and more preferably 95-100 wt% of monoclinic phase of zirconia.

22. The process according to any one of claims 1-21, wherein the catalyst composition comprising ruthenium supported on zirconia comprises at least one dopant selected from Pd, Pt, Vn, Ni, Sn, La, Ga, Co and combinations thereof.

23. The process according to claim 22, wherein the amount of the dopant in the catalyst composition comprising ruthenium supported on zirconia is not more than 2 wt% and the total amount of Ru and the dopant is not more than 5 wt%.

24. The process according to any one of claims 1-23, wherein the catalyst composition comprising ruthenium supported on zirconia comprises an oxide selected from CeO₂, TiO₂, MgO, ZnO, SiO₂, Al₂O₃ and combinations thereof.

25. The process according to any one of claims 1-24, wherein the residual lignin phase is recycled to the feedstock.

5 26. The process according to any one of claims 1-25, wherein the hydrotreating is carried out at the temperature from 180 to 420°C, preferably from 200 to 350°C and particularly preferably from 220 to 280°C.

10 27. The process according to any one of claims 1-26, wherein the hydrotreating is carried out under the pressure from 5 to 140 bar, preferably from 10 to 120 bar and particularly preferably from 10 to 70 bar.

15 28. The process according to any one of claims 1-27, wherein the liquid organic phase is fractionated to fractions comprising aromatic compounds and linear and branched hydrocarbons boiling in the liquid fuel range.

29. The process according to any one of claims 1-27, wherein the liquid organic phase is processed further by one or more of hydrotreating, cracking or isomerizing.

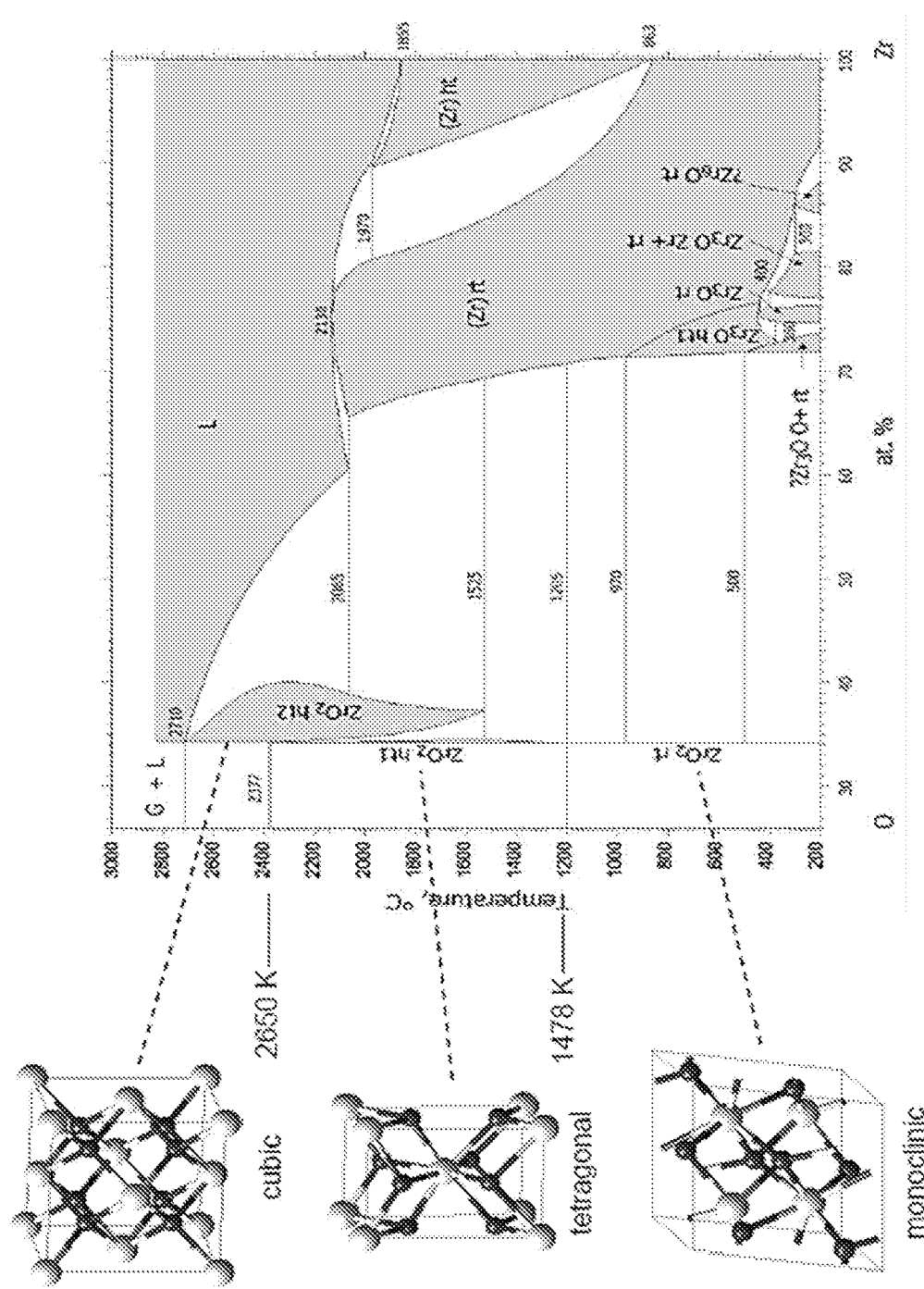


Fig. 1

2/4

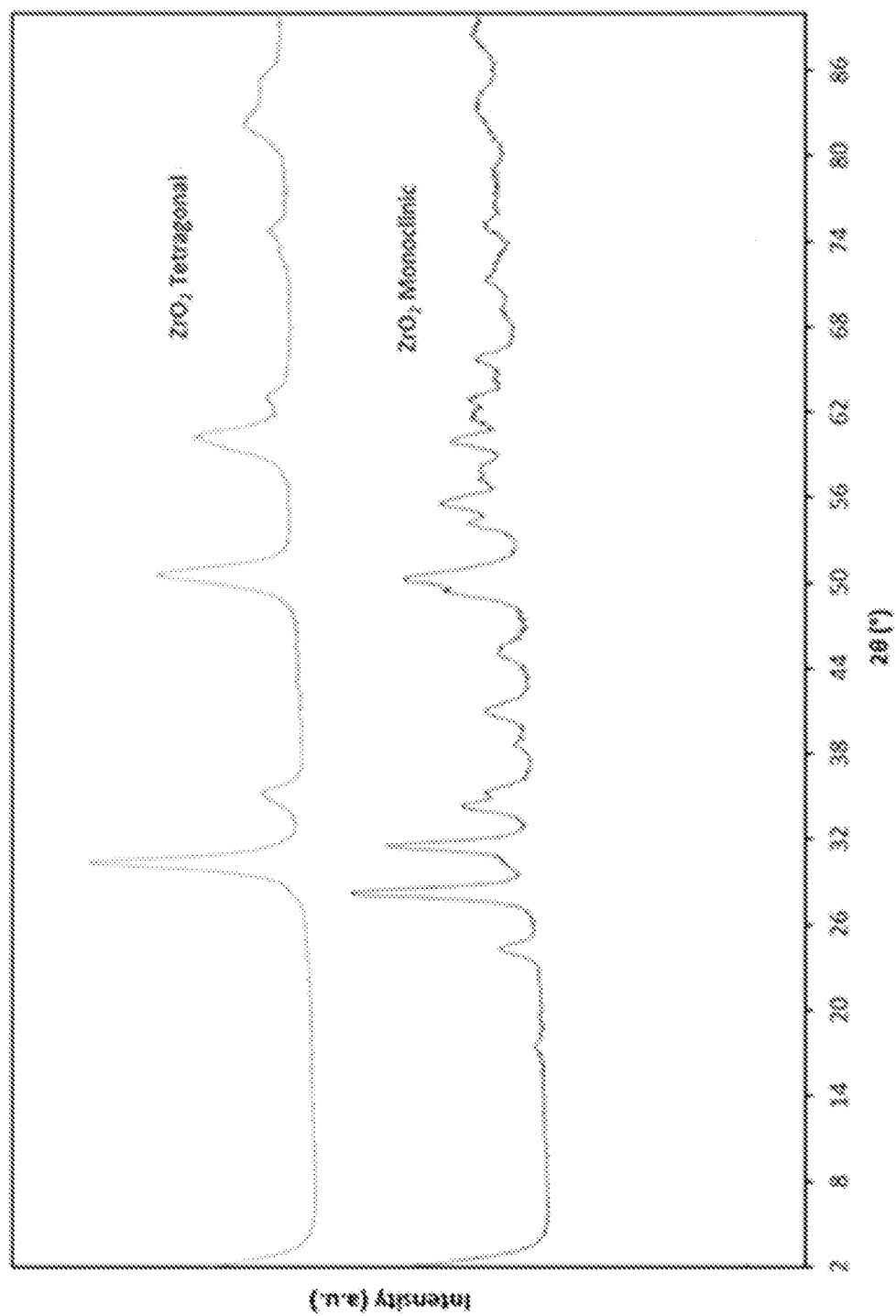


Fig. 2

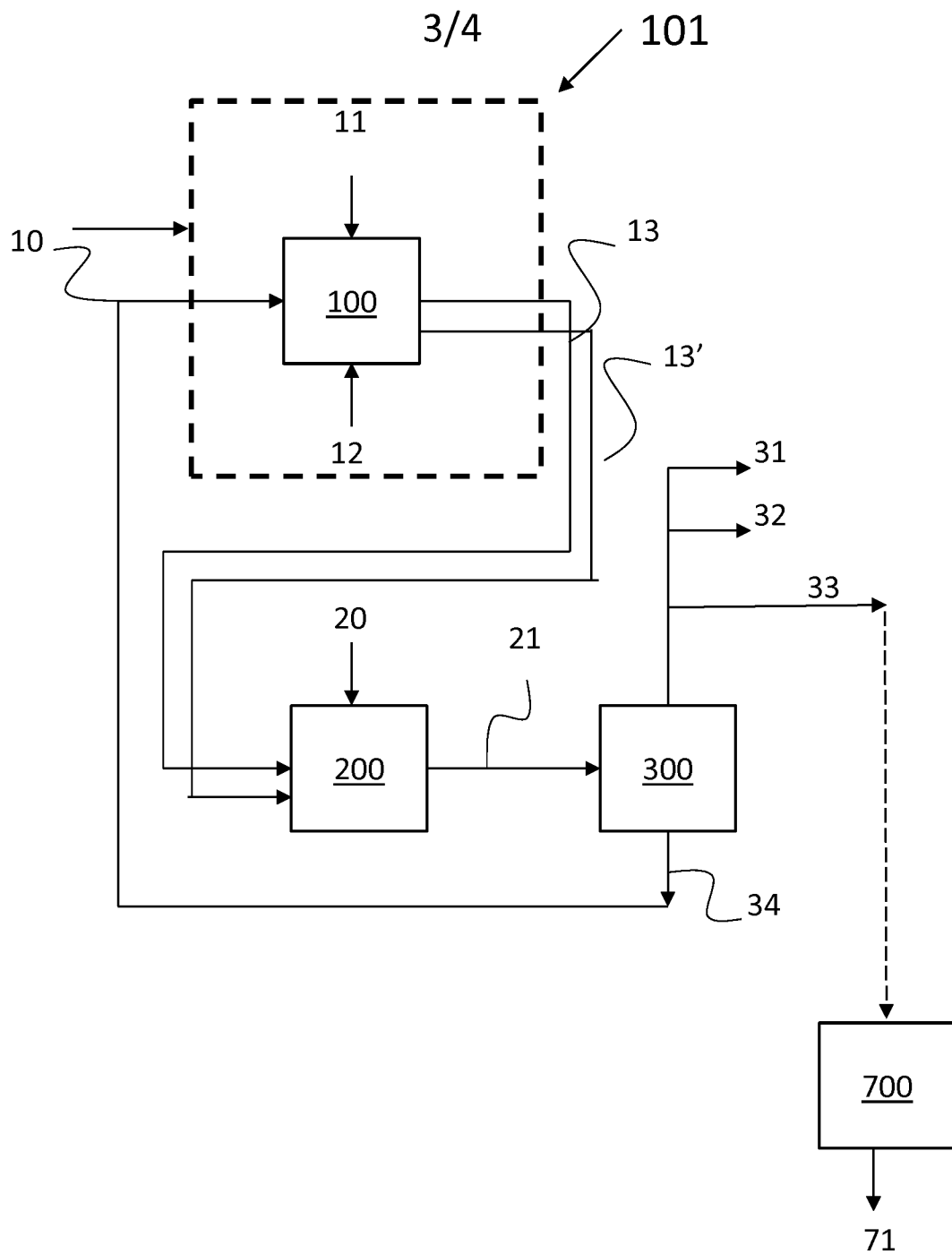


Fig. 3

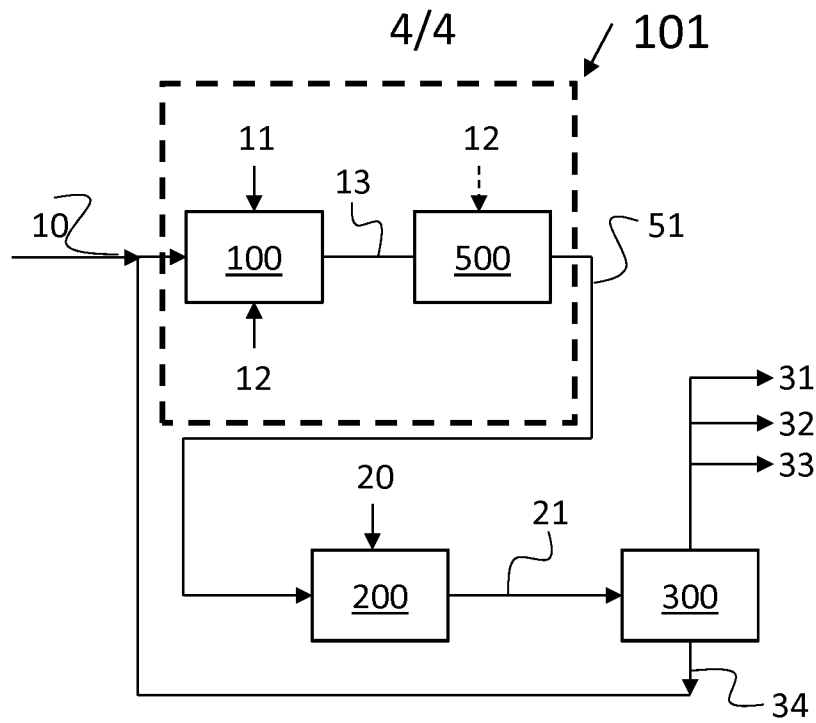


Fig. 4

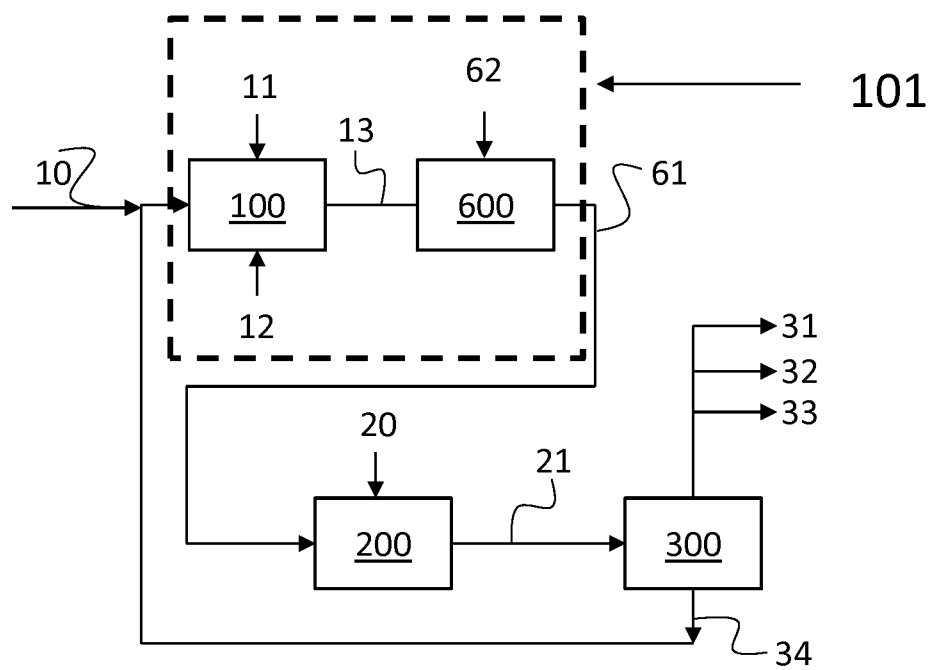


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2016/050528

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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)

IPC: C07G, C10G, B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
FI, SE, NO, DK

Electronic data base consulted during the international search (name of data base, and, where practicable, search terms used)

EPODOC, EPO-Internal full-text databases, Full-text translation databases from Asian languages, WPIAP, PRH-Internal, XPAIP, XPESP, NPL, BIOSIS, EMBASE, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2010137663 A1 (CHEN JOHN Q [US] et al.) 03 June 2010 (03.06.2010) paragraphs [0014]-[0017], [0020], claims	1-29
A	US 2014275468 A1 (KELLETT PATTI JEAN [US] et al.) 18 September 2014 (18.09.2014) paragraphs [0039], [0056], claims	1-29
Y	US 2012318258 A1 (QIAO MING [US] et al.) 20 December 2012 (20.12.2012) paragraph [0083], example 4, figure 1, claims	1-29
A	WO 2012162403 A1 (VIRENT INC [US]) 29 November 2012 (29.11.2012) examples 16 and 17, claims	1-29
A	US 2012172588 A1 (QIAO MING [US] et al.) 05 July 2012 (05.07.2012) example 9, figures 20-22, claims	1-29

☒ Further documents are listed in the continuation of Box C.
☒ See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search

26 October 2016 (26.10.2016)

Date of mailing of the international search report

26 October 2016 (26.10.2016)

Name and mailing address of the ISA/FI
Finnish Patent and Registration Office
P.O. Box 1160, FI-00101 HELSINKI, Finland
Facsimile No. +358 9 6939 5328

Authorized officer
Antti Hoikkala
Telephone No. +358 9 6939 500

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2016/050528

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2014163652 A1 (UNIV WASHINGTON STATE [US]) 09 October 2014 (09.10.2014) page 11, line 18-page 12, claims	1-29
A	WO 9910450 A1 (UNIV UTAH RES FOUND [US]) 04 March 1999 (04.03.1999) examples, figure 1, claims	1-29

INTERNATIONAL SEARCH REPORT
Information on Patent Family Members

International application No.
PCT/FI2016/050528

Patent document cited in search report	Publication date	Patent family members(s)	Publication date
US 2010137663 A1	03/06/2010	US 8871989 B2	28/10/2014
		AU 2009341104 A1	08/09/2011
		AU 2009341104 B2	19/09/2013
		PI 0924309	26/01/2016
		CA 2753355 A1	02/09/2010
		CA 2753355 C	28/01/2014
		CN 102414297 A	11/04/2012
		CN 102414297 B	17/09/2014
		EP 2401344 A1	04/01/2012
		MX 2011009040 A	15/09/2011
		MY 156665 A	15/03/2016
		SG 173805 A1	29/09/2011
		WO 2010098801 A1	02/09/2010
US 2014275468 A1	18/09/2014	US 9452422 B2	27/09/2016
		CA 2901590 A1	02/10/2014
		CN 105189413 A	23/12/2015
		EP 2970040 A1	20/01/2016
		JP 2016513626 A	16/05/2016
		WO 2014159040 A1	02/10/2014
US 2012318258 A1	20/12/2012	US 9157031 B2	13/10/2015
		AU 2012258767 A1	21/11/2013
		BR 112013016145 A2	20/09/2016
		BR 112013016322 A2	04/10/2016
		CA 2820753 A1	05/07/2012
		CA 2820755 A1	05/07/2012
		CA 2820757 A1	05/07/2012
		CA 2835287 A1	29/11/2012
		CN 103298770 A	11/09/2013
		CN 103298770 B	07/09/2016
		CN 103313955 A	18/09/2013
		CN 103313955 B	13/07/2016
		CN 103339090 A	02/10/2013
		CN 103562160 A	05/02/2014
		CN 103562160 B	23/03/2016
		EP 2658832 A1	06/11/2013
		EP 2658833 A1	06/11/2013
		EP 2658834 A1	06/11/2013
		EP 2714625 A1	09/04/2014
		KR 20130132947 A	05/12/2013
		KR 20130132948 A	05/12/2013
		KR 20130132954 A	05/12/2013
		RU 2013154067 A	27/06/2015

INTERNATIONAL SEARCH REPORT
Information on Patent Family Members

International application No.
PCT/FI2016/050528

Patent document cited in search report	Publication date	Patent family members(s)	Publication date
		US 2012172579 A1	05/07/2012
		US 8642813 B2	04/02/2014
		US 2014107353 A1	17/04/2014
		US 9045383 B2	02/06/2015
		US 2013019859 A1	24/01/2013
		US 9157030 B2	13/10/2015
		US 2012167876 A1	05/07/2012
		US 9212104 B2	15/12/2015
		US 2012167875 A1	05/07/2012
		US 9212314 B2	15/12/2015
		US 2012323053 A1	20/12/2012
		US 9212315 B2	15/12/2015
		US 2013023702 A1	24/01/2013
		US 9212316 B2	15/12/2015
		US 2013036660 A1	14/02/2013
		US 9212320 B2	15/12/2015
		US 2016024711 A1	28/01/2016
		US 9388528 B2	12/07/2016
		US 2016096996 A1	07/04/2016
		US 2016097108 A1	07/04/2016
		US 2016102372 A1	14/04/2016
		WO 2012092436 A1	05/07/2012
		WO 2012092440 A1	05/07/2012
		WO 2012092475 A1	05/07/2012
		WO 2012162403 A1	29/11/2012
.....			
WO 2012162403 A1	29/11/2012	AU 2012258767 A1	21/11/2013
		BR 112013016145 A2	20/09/2016
		BR 112013016322 A2	04/10/2016
		CA 2820753 A1	05/07/2012
		CA 2820755 A1	05/07/2012
		CA 2820757 A1	05/07/2012
		CA 2835287 A1	29/11/2012
		CN 103298770 A	11/09/2013
		CN 103298770 B	07/09/2016
		CN 103313955 A	18/09/2013
		CN 103313955 B	13/07/2016
		CN 103339090 A	02/10/2013
		CN 103562160 A	05/02/2014
		CN 103562160 B	23/03/2016
		EP 2658832 A1	06/11/2013
		EP 2658833 A1	06/11/2013
		EP 2658834 A1	06/11/2013
		EP 2714625 A1	09/04/2014
		KR 20130132947 A	05/12/2013
		KR 20130132948 A	05/12/2013

INTERNATIONAL SEARCH REPORT
Information on Patent Family Members

International application No.
PCT/FI2016/050528

Patent document cited in search report	Publication date	Patent family members(s)	Publication date
		KR 20130132954 A	05/12/2013
		RU 2013154067 A	27/06/2015
		US 2012172579 A1	05/07/2012
		US 8642813 B2	04/02/2014
		US 2014107353 A1	17/04/2014
		US 9045383 B2	02/06/2015
		US 2013019859 A1	24/01/2013
		US 9157030 B2	13/10/2015
		US 2012318258 A1	20/12/2012
		US 9157031 B2	13/10/2015
		US 2012167876 A1	05/07/2012
		US 9212104 B2	15/12/2015
		US 2012167875 A1	05/07/2012
		US 9212314 B2	15/12/2015
		US 2012323053 A1	20/12/2012
		US 9212315 B2	15/12/2015
		US 2013023702 A1	24/01/2013
		US 9212316 B2	15/12/2015
		US 2013036660 A1	14/02/2013
		US 9212320 B2	15/12/2015
		US 2016024711 A1	28/01/2016
		US 9388528 B2	12/07/2016
		US 2016096996 A1	07/04/2016
		US 2016097108 A1	07/04/2016
		US 2016102372 A1	14/04/2016
		WO 2012092436 A1	05/07/2012
		WO 2012092440 A1	05/07/2012
		WO 2012092475 A1	05/07/2012
.....			
US 2012172588 A1	05/07/2012	WO 2012092431 A1	05/07/2012
.....			
WO 2014163652 A1	09/10/2014	US 2015099868 A1	09/04/2015
.....			
WO 9910450 A1	04/03/1999	US 5959167 A	28/09/1999
.....			

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2016/050528

CLASSIFICATION OF SUBJECT MATTER

IPC

C07G 1/00 (2011.01)

C10G 1/00 (2006.01)

B01J 21/06 (2006.01)

B01J 23/46 (2006.01)