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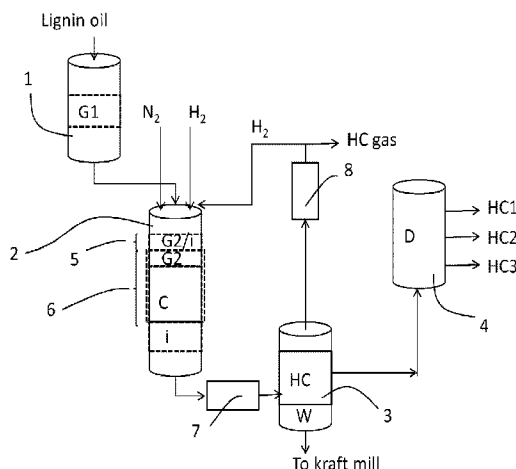
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(54) Titre : PROCEDE DE PRODUCTION D'UN PRODUIT HYDROCARBONE A PARTIR D'HUILE DE LIGNINE

(54) Title: A PROCESS FOR PRODUCING A HYDROCARBON PRODUCT FROM LIGNIN OIL



(57) **Abrégé/Abstract:**

A process for producing a hydrocarbon product from a lignin oil, said lignin oil having an oxygen content of 10-30 wt-%, an average weight molecular weight of 500-800 g/mol with a polydispersity of 2, a heating value of 25-35 MJ/kg, a water content of 0-1.5 wt-%, a sodium content of 400-500 ppm, a potassium content of 50-100 ppm, a sulfur content of 1-2.5 wt-% and a total acid number of 110-125 mg KOH/g oil, wherein the process for producing the hydrocarbon product comprises the steps of treating the lignin oil in a reactor in the presence of one or more of a hydrodesulfurization catalyst selected from NiMo on alumina or CoMo on alumina; or a hydrodesulfurization and cracking catalyst selected from NiMo on zeolite or CoMo on zeolite, or a hydrodeoxygenation and cracking catalyst selected from NiO on zeolite, zeolite alone or combinations thereof, or a hydrodeoxygenation catalyst selected from Ni/NiO, Cu/Cr, Pd/Cu, or Pt on a support material, such as chromite and/or alumina and/or zirconia and/or graphite and/or carbon and/or silica; or combinations thereof, and applying a H₂ pressure of 30-160 bar, preferably 50-150 bar, a gas to oil ratio (GTO) of 200- 2000 1/1, preferably 500-1500 1/1, at a temperature of 290-400 °C, preferably 300-360 °C, and with a liquid hourly space velocity (LHSV) of 0.25-2 h⁻¹ and preferably 0.5-1 h⁻¹ followed by cooling the reaction product from the reactor to 20-30 °C, and separating the reaction product by phase separation, into a gaseous phase, a liquid hydrocarbon product phase, and a water phase, thereby obtaining the hydrocarbon product. and a hydrocarbon product.

A PROCESS FOR PRODUCING A HYDROCARBON PRODUCT FROM LIGNIN OIL

TECHNICAL FIELD

The present application relates to a process for producing a hydrocarbon product from lignin oil, and a hydrocarbon product obtainable by the process.

5 BACKGROUND ART

There is a desire to provide renewable sources for hydrocarbon products for use as fuels and for manufacture of chemicals. There is also a desire to recover lignin and chemicals from spent black liquor, and methods for that are known in the art, for example WO2014/193289 describes a method in which lignin is precipitated from black liquor by means of an acid
10 treatment.

SUMMARY OF THE INVENTION

The present invention aims at providing a process for producing renewable hydrocarbon products from a lignin based oil.

The process of the present application relates to producing a hydrocarbon product from a
15 lignin oil, wherein the lignin oil has an oxygen content of 10-30 wt-%, an average weight molecular weight of 500-800 g/mol with a polydispersity of 2, a heating value of 25-35 MJ/kg, a water content of 0-1.5 wt-%, a sodium content of 400-500 ppm, a potassium content of 50-100 ppm, a sulfur content of 1-2.5 wt-% and a total acid number of 110-125 mg KOH/g oil.

20 The process for producing the hydrocarbon product comprises the steps of treating the lignin oil in a reactor in the presence of one or more of a hydrodesulfurization catalyst selected from NiMo on alumina or CoMo on alumina; or a hydrodesulfurization and cracking catalyst selected from NiMo on zeolite or CoMo on zeolite, or a hydrodeoxygenation and cracking catalyst selected from NiO on zeolite, zeolite alone or combinations thereof, or a
25 hydrodeoxygenation catalyst selected from Ni/NiO, Cu/Cr, Pd/Cu, or Pt on a support material, such as chromite and/or alumina and/or zirconia and/or graphite and/or carbon and/or silica; or combinations thereof, and applying a H₂ pressure of 30-160 bar, preferably 50-150 bar, a gas to oil ratio (GTO) of 200-2000 l/l (STP conditions), preferably 500-1500 l/l,

at a temperature of 290-400 °C, preferably 300-360 °C, and with a liquid hourly space velocity (LHSV) of 0.25-2 h⁻¹ and preferably 0.5-1 h⁻¹ followed by cooling the reaction product from the reactor to 20-30 °C, and separating the reaction product by phase separation, into a gaseous phase, a liquid hydrocarbon product phase, and a water phase, thereby obtaining the hydrocarbon product.

The reactor used in the process is preferably a reactor comprising a packed bed, which includes a first section of inert filling material and/or guard material and optionally a catalyst selected as defined above and a second section of the catalyst selected as defined above and optionally a guard material on top of the catalyst, and a third section of inert filling material and optionally a catalyst selected as defined above, and wherein the lignin oil passes first the first section, then the second section, and then the third section.

The reactor preferably comprises a pre-heating zone and an isothermal zone, wherein the lignin oil temperature in the isothermal zone is the reaction temperature 290-400 °C, preferably 300-360 °C, and the lignin oil temperature in the pre-heating zone is 1-10 °C below the reaction temperature, and wherein the isothermal zone comprises the second section of the packed bed, and optionally a portion of the first section of the packed bed.

The catalyst in the second section is advantageously a physical mixture of NiMo on alumina and NiO on zeolite, and the volume ratio of NiMo on alumina and NiO on zeolite is preferably 1-4:1, more preferably 1.5-2.5:1, most preferably 2:1. Alternatively, the catalyst in the second section is a physical mixture of Ni/NiO on alumina/graphite and NiO on zeolite, preferably with a volume ratio of Ni/NiO on alumina/graphite and NiO on zeolite is 1-4:1, more preferably 1.5-2.5:1, most preferably 2:1.

The process resulting hydrocarbon product is preferably separated into three fractions by means of distillation, wherein a first fraction comprises hydrocarbons having a boiling point of 35-180 °C, a second fraction comprises hydrocarbons having a boiling point of 181-340 °C, and a third fraction comprises hydrocarbons having a boiling point above 340 °C.

A fraction having a boiling point of 250-285 °C is separated from the hydrocarbon product, said fraction comprising dibenzyl, cyclohexylethylbenzene, 4-methyldiphenylmethane,

benzylcyclohexane, dicyclohexylmethane and 1,2-dicyclohexylethane may be of particular interest.

The gaseous phase separated in the phase separation is preferably led through a gas treater, whereby H₂S is removed, and H₂ is then separated and recycled to the reactor, and the rest
5 of the gases are retrieved as a gaseous hydrocarbon containing product. The gaseous hydrocarbon containing product may be led to a steam reformer producing H₂ and CO or CO₂, wherein H₂ and CO are optionally led back to the process.

Preferably, the lignin oil is desalted in a desalting unit prior to the reactor, said desalting unit comprising a bed of adsorbent, absorbent, or ion exchange material or combinations
10 thereof.

Moreover, additional viscosity modifying, and/or lubricating and/or carbonium/arenium ion scavenging components may be added to the lignin oil in an amount of 1-80 wt-%, preferably 10-20 wt% based on the weight of the lignin oil prior to the reactor and any desalting unit, said additional components being a combination of a solvent, preferably methanol, ethanol,
15 toluene, o-, m-, p-xylene, p-cymene, anisole, diesel, gasoline, benzyl alcohol; or phenol, 2-naphthol, catechol, thymol, guaiacol, cresol; and/or mixtures thereof, and the hydrocarbon product obtained by the process.

The lignin oil fed into the process is most preferably a lignin oil obtainable by a process in which a black liquor composition comprising kraft black liquor and having a hydroxide ion
20 concentration of 1-40 g/l, based on the volume of black liquor, is reacted, preferably under a H₂ or H₂/CO syngas pressure of 5-150 bar, at 220-350 °C for 10-120 minutes in the absence of a solid catalyst; or at 180-240 °C for 10-120 minutes in the presence of a solid catalyst, thereby causing depolymerization of lignin in the black liquor; the reacted composition is cooled to a temperature below the boiling point of a solvent to be added subsequently, and
25 is thereafter acidified until a pH of 4-5 is reached; and a solvent is added to the composition in order to extract oil from the composition, and the composition is separated by phase separation in a first separation step into an oil phase comprising solvent, oil, and organic acids; a first water phase comprising water, salts, and non-depolymerized lignin solids; and a second water phase comprising water and salts; the oil phase is filtered to remove any
30 particles, and is then desalted in a water wash step by adding water and separating by phase

separation into a second separation step into an oil phase comprising oil and solvent, and a water phase comprising salts; or by adding adsorbent and/or absorbent material or ion exchange material, or combinations thereof; and solvent comprised in the oil phase is evaporated, whereby the lignin oil is obtained.

- 5 The present invention also relates to a hydrocarbon product obtained by the above process said product comprising cyclohexane, methylcyclohexane, toluene, ethylcyclohexane, ethylcyclopentane, propylcyclohexane, propylbenzene, 1-methyl-4-(1-methylethyl) cyclohexane, butylcyclohexane, decalin, tetralin, methyltetralin, butylbenzene, decahydro-2-methylnaphthalene, pentylcyclohexane, hexylcyclohexane, diethylcyclohexane, bicyclohexyl, 10 biphenylmethane, 1-methyl-2-cyclohexylcyclohexane, dicyclohexylmethane, benzylcyclohexane, methyldicyclohexylmethane, 1,2-dicyclohexylethane, 1-phenyl-1-cyclohexylethane, 1-phenyl-2-cyclohexylethane, cyclohexylethylbenzene, dibenzyl, 4-methyldiphenylmethane, 3-methyldicyclohexylmethane, 1,3-dicyclohexylpropane, n-heptadecane, 1,1'-(1,4-butanediyl)-cyclohexane, n-octadecane, 1,1-dicyclohexylpropane, 15 and containing less than 0.2 wt-% oxygen.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 schematically illustrates the process of the present application.

DETAILED DESCRIPTION

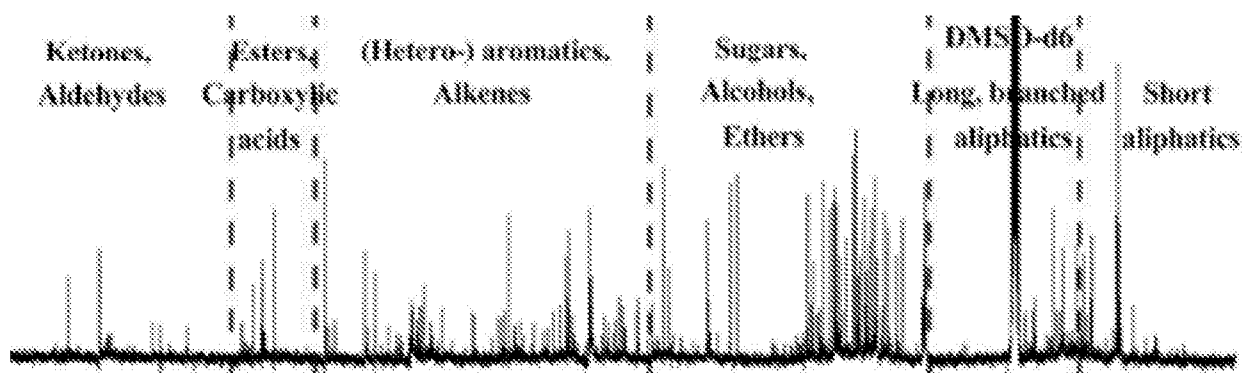
- The present invention relates to a process for producing a hydrocarbon product from a lignin oil, wherein the lignin oil is treated in a reactor in the presence of catalyst and hydrogen. The 20 lignin oil used as starting material for the process has an oxygen content of 10-30 wt-%, an average weight molecular weight of 500-800 g/mol with a polydispersity of 2, a heating value of 25-35 MJ/kg, a water content of 0-1.5 wt-%, a sodium content of 400-500 ppm, a potassium content of 50-100 ppm, a sulfur content of 1-2.5 wt-% and a total acid number (TAN) of 110-125 mg KOH/g oil (ISO 660 standard). For example, the lignin oil used herein 25 may contain no water, or 1% water and 25% oxygen. The weight average molecular weight is determined by gel permeation chromatography (GPC) with tetrahydrofuran as the solvent and where the standard is polystyrene.

The lignin oil can be obtained by a process, which is described in detail in the applications PCT/SE2015/050969 and PCT/SE2015/050970. In this process a black liquor composition comprising kraft black liquor and having a hydroxide ion concentration of 1-40 g/l, based on the volume of black liquor, is reacted, preferably under a H₂ or H₂/CO syngas pressure of 5-150 bar, at 220-350 °C for 10-120 minutes in the absence of a solid catalyst; or at 180-240 °C for 10-120 minutes in the presence of a solid catalyst, thereby causing depolymerization of lignin in the black liquor. The reacted composition is then cooled to a temperature below the boiling point of a solvent to be added subsequently, and is thereafter acidified until a pH of 4-5 is reached; and a solvent is added to the composition in order to extract oil from the composition, and the composition is separated by phase separation in a first separation step into an oil phase comprising solvent, oil, and organic acids; a first water phase comprising water, salts, and non-depolymerized lignin solids; and a second water phase comprising water and salts. The oil phase is filtered to remove any particles, and is then desalted in a water wash step by adding water and separating by phase separation into a second separation step into an oil phase comprising oil and solvent, and a water phase comprising salts; or by adding adsorbent and/or absorbent material or ion exchange material, or combinations thereof; and solvent comprised in the oil phase is evaporated, whereby the lignin oil is obtained.

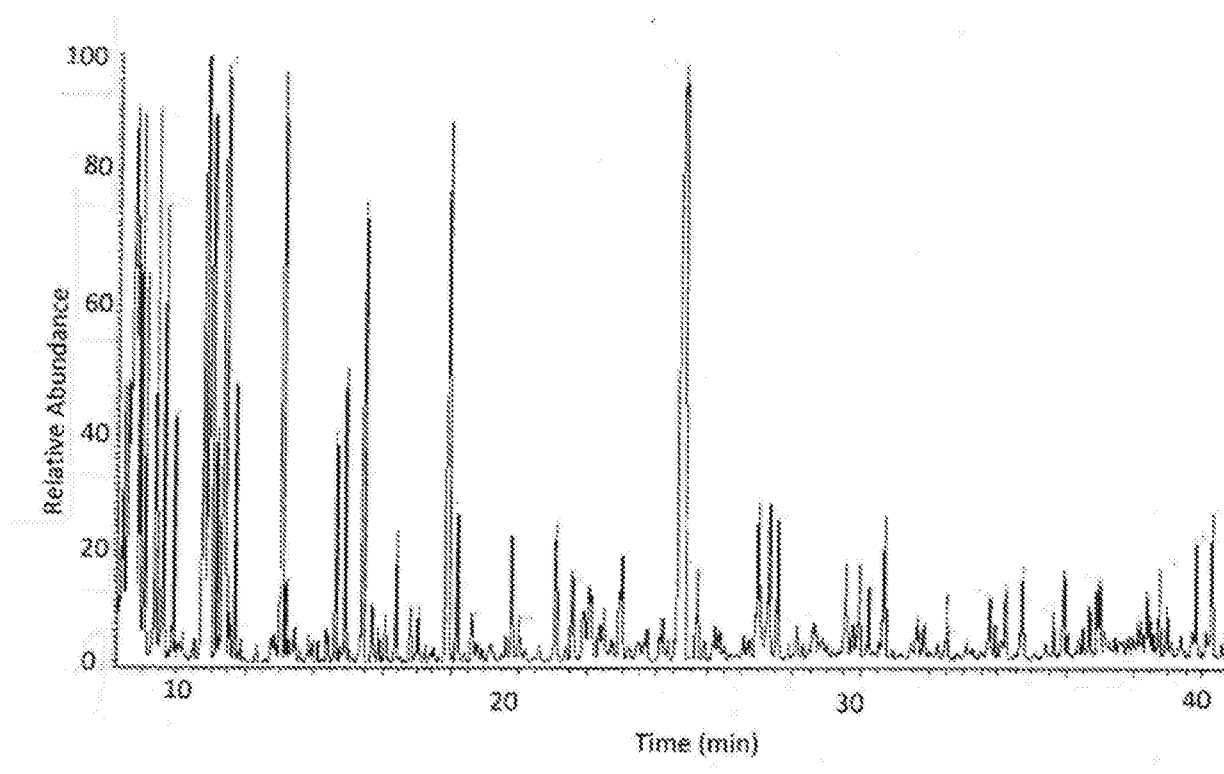
There is a large range of different bio-oils originated from different plant species (e.g. wood, sawdust, switchgrass, crop, straw, sugar cane bagasse) and produced in various ways giving a unique composition for each of them. A well-known technology is pyrolysis which is to heat biomass at 300-900 °C in the absence of air. Slow, intermediate and fast pyrolysis of almost dry (typically 4-10% moisture content) feedstock such as pine sawdust or wood chips give a pyrolysis oil of unique components and all pyrolysis oils generally contains 12-40% water and 35-40% oxygen attached to the organic components reflecting the low heating value of 16-19 MJ/kg. The water is part of the oil and the water/oil do not phase separate, meaning that the pyrolysis oil is an emulsion. The physical state of the pyrolysis oil and the range of oil components and the water content are all different to the lignin oil developed for the present process, as the lignin oil used herein typically contains no water or 1% water and 25% oxygen. The oil components obtained from pyrolysis of lignocellulosic (typically wood) material will be much broader (typically over 300 compounds) compared with the lignin oil

used herein, as the feedstock contains cellulose and all other woody components. A ^{13}C NMR spectrum of typical components obtained from pyrolysis is shown below (Zhang et al. in Sustainable Chem. Eng. 2015, DOI: 10.1021/acssuschemeng.5b00968, the supporting information).

5



A typical GC-MS spectrum and corresponding components at specific retention times (r.t.) of the lignin oil used in the present process are displayed below, and shows the following components.



r.t.	Component
9.40	3-oxobutanoic acid
10.80	4-methyl-4-hydroxy-2-pentanone
10.99	phenol

11.39	2-hydroxypropanoic acid
11.44	hydroxyisobutyric acid
11.70	hydroxyacetic acid
13.07	2-hydroxybutanoic acid
14.66	4-hydroxypentenoic acid
14.93	2-hydroxypentanoic acid
15.46	guaiacol
17.93	catechol
18.19	butanedioic acid
19.78	4-methylcatechol
21.09	2-hydroxy-2-hexenoic acid
21.56	4-hydroxyphenylethanol
24.77	Internal standard
25.20	4-hydroxy-3-methoxyacetophenone
29.56	phenylacetic acid
30.70	3,4-dihydroxyphenylacetic acid?
39.81	dehydroabietic acid
40.27	abietic acid

Also, pyrolysis oils are known to be very acidic (pH 2-3) which is another difference to the lignin oil herein. By the differences described above the same results would not be expected if a pyrolysis oil was used as feedstock for the technology developed for the present process.

- 5 This hypothesis is supported by D.C. Elliott et al. in Environ. Prog. Sustain. Energy 2009, 28(3), 441-449, which indicated that pyrolysis oil requires a two-step process utilizing different catalysts (hydrotreatment at 310 or 375 °C and hydrocracking at 400 °C) to reach an almost oxygen free hydrocarbon product.

- 10 Other processes such as liquefaction of biomass (liquefaction oil) show the same issues as for the pyrolysis oil i.e. high water content, typically 18%, acidic, and a the whole range of woody components even though the oxygen content is lower, typically 15-20%. This bio-oil is also not expected to perform as the lignin oil used in the present process.

- 15 The lignin oil used as starting material for the process is preferably first passed through a desalting unit, comprising a bed of adsorbent, absorbent, or ion exchange material or combinations thereof, prior to the reactor in order to reduce metals such as sodium and potassium.

Both the desalting unit and the reactor can be operated solvent-free or with a solvent. It may be desirable to add additional viscosity modifying, and/or lubricating and/or

carbonium/arenium ion scavenging components to the lignin oil before feeding it into the reactor, and before a possible desalting unit. The additional components can be a combination of a solvent, preferably methanol, ethanol, toluene, o-, m-, p-xylene, p-cymene, anisole, diesel, gasoline, benzyl alcohol; or additives such as phenol, 2-naphthol, catechol, thymol, guaiacol, cresol; and/or mixtures thereof; and the hydrocarbon product obtained by the present process. These additional components can be added in an amount of 1-80 wt-% based on the weight of the lignin oil prior to the reactor and any desalting unit, said. The preferred option is to use no solvent or only a small amount of solvent, such as 10-20 wt% based on the weight of the lignin oil in order to reduce the viscosity of the oil and to reduce the pressure drop over the reactor.

The solvent added to the lignin oil before the reactor or the desalting unit can be the whole hydrocarbon product or a fraction of the hydrocarbon product. The solvent also functions as a lubricant for the reactor. It has been found that the reactor lubricant function is also applicable for the process of making the lignin oil as defined in the applications

PCT/SE2015/050969 and PCT/SE2015/050970, meaning that the whole hydrocarbon product or a hydrocarbon fraction can be added to the black liquor prior producing the lignin oil.

To improve the solubility of the hydrocarbon or a fraction of the hydrocarbon product in the lignin oil a polar solvent can be added, preferably methanol alone or methanol/benzyl alcohol mixture or ethanol alone or ethanol/methanol/benzyl alcohol mixture or a mixture of toluene/methanol or toluene/ethanol, where the methanol can be a non-pure methanol obtained from the kraft mill process.

The process for producing the hydrocarbon product according to the present invention comprises treatment of the lignin oil in a reactor in the presence of one or more selected catalysts and under application of a H₂ pressure. The catalyst is one or more of a

hydrodesulfurization catalyst selected from NiMo on alumina or CoMo on alumina; or a hydrodesulfurization and cracking catalyst selected from NiMo on zeolite or CoMo on zeolite, or a hydrodeoxygenation and cracking catalyst selected from NiO on zeolite, zeolite alone or combinations thereof, or a hydrodeoxygenation catalyst selected from Ni/NiO, Cu/Cr, Pd/Cu, or Pt on a support material, such as chromite and/or alumina and/or zirconia and/or graphite and/or carbon (e.g. charcoal or activated carbon) and/or silica; or one or

more hydrodeoxygenation and a cracking catalyst selected from Cu/Cr, Cu/Ni, or NiO on zeolite or zeolite alone, or combinations thereof,

The reaction takes place at a H₂ pressure of 30-160 bar, preferably 50-150 bar, a gas to oil ratio (GTO) of 200-2000 l/l (STP conditions), preferably 500-1500 l/l, at a temperature of 290-400 °C, preferably 300-360 °C, and with a liquid hourly space velocity (LHSV) of 0.25-2 h⁻¹, preferably 0.5-1 h⁻¹. After the reactor, the reaction product is cooled to 20-30 °C, and is then separated by phase separation, into a gaseous phase, a liquid hydrocarbon product phase, and a water phase, so as to obtain the hydrocarbon product.

The reactor is typically a reactor comprising a packed bed, which includes three different sections. In a first section the packed bed is comprised of inert filling material and/or guard material. The guard material can be a material of high specific surface area, such as alumina, and serves to minimize catalyst deactivation which can be caused by impurities in the lignin oil, and hence extending the catalyst lifetime. Some of the guard bed is sometimes replaced by inert filling material. The first section of the packed bed may optionally also comprise catalysts selected as defined above, in an amount of up to 100%.

In a second section the packed bed is comprised the catalyst selected as defined above. Optionally, an amount of guard material can be placed on top of the catalyst in the second section. The catalysts are preferably in the form of powder or extrudates. The second section does typically not comprise any inert material.

In a third section the packed bed is comprised inert filling material, and optionally a catalyst selected as defined above, in an amount of up to 100%. The lignin oil passes first the first section, then the second section, and then the third section. The lignin oil and H₂ are fed at the top of the reactor, and moves downward through the packed bed. The products are taken out at the bottom of the reactor.

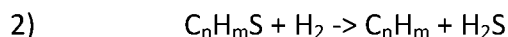
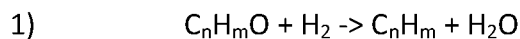
The reactor is suitably a trickle bed reactor, i.e. a reactor that uses a downward movement of a liquid and gas over a packed bed of catalyst particles.

Prior taking the reactor into operation the catalysts typically needs to be dried and activated. A nitrogen flow is preferably used for inert flushing, drying the catalysts and compacting the bed of catalysts. Hydrodesulfurization catalysts can be activated in an activation procedure,

which is sometimes called sulfidation, and includes e.g. pumping a dimethyldisulfide (DMDS) spiked mixture of paraffinic activation feed along with a hydrogen flow at a certain pressure through the catalyst bed. The DMDS generates H_2S during its decomposition, which in turn sulfides the catalyst. Hydrodeoxygenation catalysts can be dried and activated by the following chosen method; ramping up the temperature (1 K/min) from room temperature to 150 °C during 13 h in an atmospheric nitrogen flow rate of 20 l/h and then ramping up the hydrogen pressure (1 bar/min) to 31 bar hydrogen during 0.7 h at a hydrogen flow rate of 20 l/h followed by an immediate start of ramping up the temperature (1 K/min) to 400 °C for 8.5 h at a hydrogen flow rate of 87 l/h. After 2 h hold at 400 °C the temperature is preferably cooled down for 13.5 h to reach 150 °C, keeping the same hydrogen pressure and flow. This activation procedure is sometimes called reduction.

The reactor is loaded with the catalysts, i.e. hydrodesulfurization catalyst and/or hydrodeoxygenation catalyst and/or cracking catalyst and inert filling material, and optionally guard material. It has been found that hydrodesulfurization catalysts can by themselves also give near 100% hydrodeoxygenation and some cracking.

During the hydrodeoxygenation and the hydrodesulfurization processes that take place in the reactor, the oxygen and the sulfur is removed from the lignin oil by catalytic hydrogenolysis according to the two general equations below;



where C_nH_m represents the lignin oil. The oxygen and sulfur attached to the lignin also represents functional groups containing oxygen and sulfur such as OH, SH and OR where R is any carbon or carbon chain.

The high pressure of hydrogen which is applied gives a high solubility of the hydrogen in the lignin oil, and thereby high availability of hydrogen next to the catalyst surface. When water is created the availability of hydrogen reduces as the solubility of hydrogen in water is low and this is even worse if the starting oil contains a lot of water, as is the case in for example pyrolysis oil or liquefaction oil.

The catalyst in the second section is preferably a physical mixture of the hydrodesulfurization catalyst NiMo on alumina and the combined hydrodeoxygenation and cracking catalyst NiO on zeolite. The volume ratio of NiMo on alumina and NiO on zeolite is 1-4:1, preferably 1.5-2.5:1, more preferably 2:1. By a physical mixture is meant that the catalyst extrudates or powder is well blended so as to form a packed bed of catalysts, in which the two different catalysts are evenly distributed, so as to form a homogenous catalyst bed.

The intimacy of active sites for hydrogenation and hydrocracking is best when a physical mixture of the hydrogenation and hydrocracking catalyst is used. In this case, the carbonium ion formed by hydrocracking can be saturated immediately by hydrogen, which will be supported by the metal site of the hydrogenation catalyst close to the carbonium ion.

Also, high pressure hydrogen and a high gas to oil (GTO) ratio minimize any re-polymerization or re-bonding of reactive carbonium or arenium ions, carbanions, oxiranes or radicals that are generated by zeolitic cracking. It has been found that a catalyst packed bed in the form of a combined catalyst physical mixture can give substantially lower pressure drop as compared to a packed bed wherein the catalysts are not packed as a physical mixture. This indicates that close packing of two catalysts is beneficial for operational runnability of the process. It has also been found that the product result of this combination of catalysts is a hydrocarbon product of lower boiling points, without creating more very light hydrocarbons in the gas phase.

An alternative preferred catalyst in the second section is a physical mixture of the hydrodeoxygenation catalyst Ni/NiO on alumina/graphite and the combined hydrodeoxygenation and cracking catalyst NiO on zeolite. The volume ratio of Ni/NiO on alumina/graphite and NiO on zeolite is 1-4:1, preferably 1.5-2.5:1, more preferably 2:1. This combination of catalysts and packing in the reactor gives the same or a similar result as the above mentioned physical mixture of NiMo on alumina and NiO on zeolite.

The reactor preferably comprises a pre-heating zone and an isothermal zone. In the pre-heating zone the lignin oil is pre-heated to reach the reaction temperature, and the temperature in the pre-heating zone is thus 1-10 °C below the reaction temperature. The lignin oil temperature in the isothermal zone is the same as the reaction temperature 290-

400 °C, preferably 300-360 °C. The isothermal zone comprises the second section of the packed bed comprising the catalysts, and optionally a portion of the first section of the packed bed comprising guard material. The isothermal zone preferably deviates less than ± 1 K from the target value for the reaction temperature, and the pre-heating zone above the catalyst preferably deviates less than ± 10 K from the target value for the reaction temperature, and the same applies for the third section comprised of inert filling material below the second section comprising catalyst in the isothermal zone. The heating is typically obtained by means of a heating jacket, electricity or furnace based heating.

The products leaving the reactor are cooled by a heat exchanger to 25-30 °C, and are left to separate in a decanting unit. The non-condensable gases can be led to a gas treater to remove select gases such as H₂S and CO₂ and hydrogen is separated from the other gaseous products to be recycled into the process. The rest of the gaseous products contains very light hydrocarbons and are preferably led to a steam reformer producing H₂ and CO or CO₂, wherein H₂ and CO are optionally led back to the process. Another option is to recycle both hydrogen and gaseous products as carbon monoxide and methane can serve as reductive gas.

The liquid products are hydrocarbons with a wide range of boiling point and water. The water is a result from the hydrodeoxygenation of the lignin oil and can be led back to the kraft mill. The hydrocarbons may be distilled, in a distillation unit (4), into three fractions of different boiling point range. The hydrocarbon product can thus be separated into three fractions by means of distillation, wherein a first fraction is named light hydrocarbons and comprises hydrocarbons having a boiling point of 35-180 °C, a second fraction is named heavy hydrocarbons and comprises hydrocarbons having a boiling point of 181-340 °C, and a third fraction is named very heavy hydrocarbons and comprises hydrocarbons having a boiling point above 340 °C.

The whole hydrocarbon product itself may serve as jet fuel. The hydrocarbon products are mainly cycloalkanes and aromatic hydrocarbons and the fraction with a boiling point below 180 °C are suitable as gasoline whereas hydrocarbons with a boiling point between 180 and 340 °C are suitable as diesel. The fraction with boiling points above 340 °C may be used as fuel oil or being recycled in this process for further cracking.

Another possible use of these hydrocarbons is to make chemicals for the non-fuel market. Of particular interest is a fraction which can be separated from the second fraction and has a boiling point of 250-285 °C. This fraction comprises dibenzyl, cyclohexylethylbenzene, 4-methyldiphenylmethane, benzylcyclohexane, dicyclohexylmethane and 1,2-

dicyclohexylethane, which can be used in the manufacture of chemicals for the non-fuel market.

The hydrocarbon product obtained by the above process comprises the following compounds: cyclohexane, methylcyclohexane, toluene, ethylcyclohexane,

ethylcyclopentane, propylcyclohexane, propyl-benzene, 1-methyl-4-(1-methylethyl)

cyclohexane, butylcyclohexane, decalin, tetralin, methyltetralin, butylbenzene, decahydro-2-methylnaphthalene, pentylcyclohexane, hexylcyclohexane, diethylcyclohexane, bicyclohexyl, biphenylmethane, 1-methyl-2-cyclohexylcyclohexane, dicyclohexylmethane,

benzylcyclohexane, methyldicyclohexylmethane, 1,2-dicyclohexylethane, 1-phenyl-1-cyclohexylethane, 1-phenyl-2-cyclohexylethane, cyclohexylethylbenzene, dibenzyl, 4-

methyldiphenylmethane, 3-methyldicyclohexylmethane, 1,3-dicyclohexylpropane, n-heptadecane, 1,1'-(1,4-butanediyl)-cyclohexane, n-octadecane, 1,1-dicyclohexylpropane, and it contains less than 0.2 wt-% oxygen.

Figure 1 schematically illustrates an example of the above described process. The lignin oil starting material is fed into a desalting unit (1) which comprises a guard bed (G1) including adsorbent, ion exchanger and/or absorbent material. The desalted oil is then fed into a reactor (2), shown here as a trickle bed reactor, which includes a packed bed comprising a first section (G2/i) comprised of guard material and/or inert material, and a second section (C) comprised catalyst material and optionally an upper portion of guard material (G2), and a third section (i) comprised of inert material. The reactor (2) comprises a pre-heated zone (5) and an isothermal zone (6). After reaction the resulting composition is cooled in a heat exchanger (7) and is left to separate in a decanting unit (3), into a gaseous phase, a liquid hydrocarbon phase (HC) and a water phase (W). The water separated in the decanting unit can be led back to the kraft mill. Gaseous products are led to a gas treater where H₂S is removed, and H₂ is then separated and recycled to the reactor, and the rest of the gases are retrieved as a gaseous hydrocarbon containing product. The liquid hydrocarbon phase (HC) is distilled (D) in a distillation unit (4) into three fractions where the first fraction comprises

hydrocarbons having a boiling point of 35-180 °C (HC1), a second fraction comprises hydrocarbons having a boiling point of 181-340 °C, and (HC2), and a third fraction comprises hydrocarbons having a boiling point above 340 °C (HC3).

EXAMPLES

5 Example 1

A hydrodesulfurization catalyst, NiMo on alumina, was loaded in both the pre-heated zone and the isothermal zone of the reactor. The inert filler below the catalyst was SiC with a particle size of 125-160 µm. The inner diameter of the reactor was 4.6 mm and the length of the pre-heated zone was 155.5 mm and the length of the isothermal zone was 200 mm and
10 the length of the inert filling zone was 145 mm.

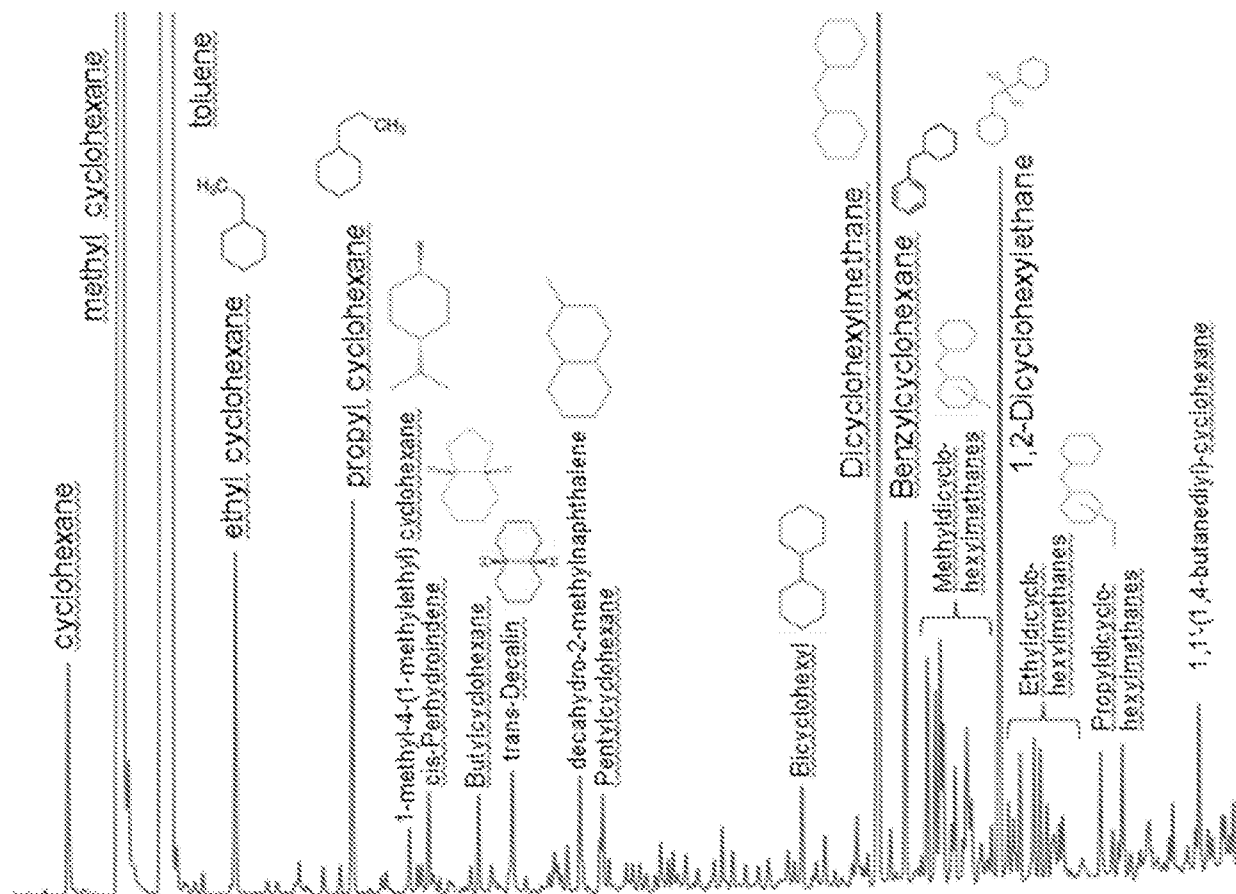
The lignin oil feedstock passing through the reactor was 20 wt-% lignin oil in benzyl alcohol. The operating conditions were set to the following:

Hydrogen pressure (bar)	160
Hydrogen flow rate (l/h)	87
Oil flow rate (ml/h)	87
GTO (l/l) (STP conditions)	1000
LHSV (h ⁻¹)	0.5
Temperature (°C)	330

The process was operating continuously for 4 days without issues. After 4 days the temperature was decreased to 310 °C and then operated continuously for 2 days without
15 issues. As a last step the temperature was decreased to 290 °C and at this temperature the rig plugged in a downstream section. Increasing the temperature again dissolves the plugging.

The pressure drop over the packed reactor after the trial was 2382 mbar.

The overall conversion was very high at 310 and 330 °C. The hydrogen consumption was 40-
20 60% of the hydrogen flow giving a product mix of hydrocarbons (analyzed by off-line GC-MS) shown below.



GC-MS analysis indicate no oxygenates, not even for a derivatized sample. The water product also contain no oxygenates.

The sulfur content in the hydrocarbon product was 23 ppm after 2 days of operation at 330 °C. A transparent and colorless hydrocarbon product was collected after 4 days at 330 °C whereas at lower temperatures a weak green coloring was observed.

The heat value of the hydrocarbon product was 43.8 MJ/kg.

The elemental analysis of the hydrocarbon product (ASTM D 5291 for carbon, hydrogen, nitrogen and ASTM D 1552 for sulfur) show 88.1 wt-% carbon, 11.6 wt-% hydrogen, <0.1 wt-% nitrogen, <0.05 wt-% sulfur and 0.2 wt-% oxygen by difference.

Example 2

A hydrodesulfurization catalyst, CoMo on alumina, and a combined hydrodeoxygenation and cracking catalyst, NiO on zeolite, were loaded in the reactor. The packing design was hydrodesulfurization catalyst on top of the hydrodeoxygenation and cracking catalyst, at a

volume ratio of 2:1 within the isothermal zone. The pre-heated zone contained the same hydrodesulfurization catalyst alone. The inert filler below the catalysts were SiC with a particle size of 125-160 μm . The inner diameter of the reactor was 4.6 mm and the length of the pre-heated zone was 155.5 mm, the length of the isothermal zone was 200 mm, and the length of the inert filling zone was 145 mm.

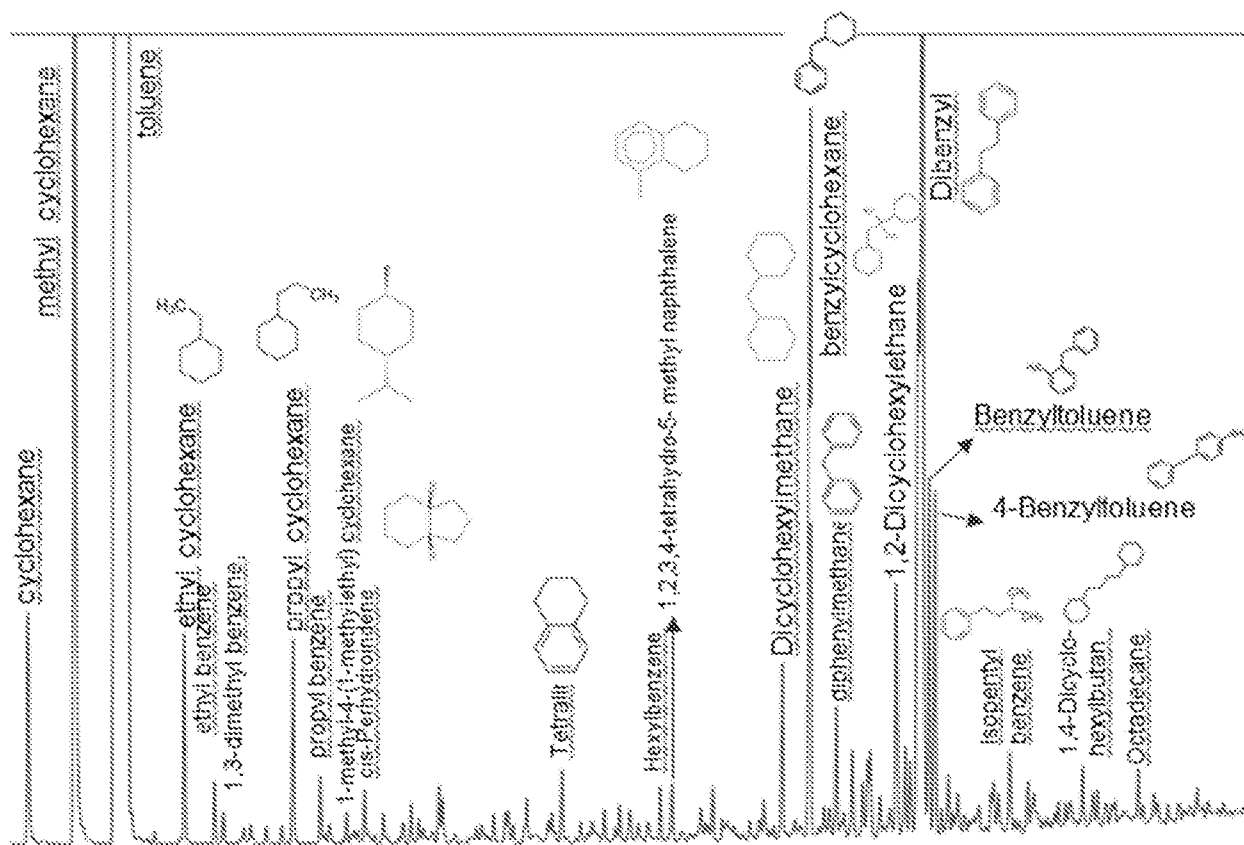
The lignin oil feedstock passing through the reactor was 20 wt% lignin oil in benzyl alcohol. The operating conditions were set to the following:

Hydrogen pressure (bar)	160
Hydrogen flow rate (l/h)	87
Oil flow rate (ml/h)	87
GTO (l/l)	1000
LHSV (h^{-1})	0.5
Temperature ($^{\circ}\text{C}$)	330

The process was operating continuously for 4 days without issues. After 4 days the temperature was decreased to 310 $^{\circ}\text{C}$ and then operated continuously for 2 days without issues. As a last step the temperature was decreased to 290 $^{\circ}\text{C}$ and at this temperature the rig plugged in a downstream section. Increasing the temperature again dissolves the plugging.

The pressure drop over the packed reactor after the trial was 2384 mbar.

The overall conversion is very high at 310 and 330 $^{\circ}\text{C}$. The hydrogen consumption was 40-60% of the hydrogen flow giving a product mix of hydrocarbons (analyzed by off-line GC-MS) shown below.



The components shown in the GC-MS spectra above indicate that this combination of catalysts gives a less saturated mixture of components compared with Example 1. The CoMo catalyst gives some hydrodeoxygenation of the solvent benzyl alcohol to toluene whereas the NiMo catalyst in Example 1 provides more hydrogenation of toluene to methylcyclohexane.

The sulfur content in the hydrocarbon product was 35 ppm after 2 days of operation at 330 °C. A transparent and weakly colored hydrocarbon product was collected after 4 days at 330 °C whereas after 6.5 days at 310 °C the weak coloring swift from being green to orange like.

10 Example 3

A hydrodesulfurization catalyst, NiMo on alumina, and a combined hydrodeoxygenation and cracking catalyst, NiO on zeolite, were loaded in the reactor. The packing design was a physical mixture of the hydrodesulfurization catalyst and the hydrodeoxygenation and cracking catalyst at a volume ratio of 2:1 within the isothermal zone. The pre-heated zone contained the same hydrodesulfurization catalyst alone. The inert filler below the catalysts were SiC with a particle size of 125-160 μm. The inner diameter of the reactor was 4.6 mm

and the length of the pre-heated zone was 155.5 mm and the length of the isothermal zone was 200 mm and the length of the inert filling zone was 145 mm.

The lignin oil feedstock passing through the reactor was 20 wt% lignin oil in benzyl alcohol.

The operating conditions were set to the following:

Hydrogen pressure (bar)	160
Hydrogen flow rate (l/h)	87
Oil flow rate (ml/h)	87
GTO (l/l) (STP conditions)	1000
LHSV (h ⁻¹)	0.5
Temperature (°C)	330

5

The process was operating continuously for 4 days without issues. After 4 days the temperature was decreased to 310 °C and then operated continuously for 2 days without issues. As a last step the temperature was decreased to 290 °C and at this temperature the rig plugged in a downstream section. Increasing the temperature again dissolves the plugging.

10

The pressure drop over the packed reactor after the trial was 974 mbar. A physical mix of catalysts gives the lowest pressure drop.

The overall conversion is very high at 310 and 330 °C. The hydrogen consumption was 40-60% of the hydrogen flow giving a product mix different to example 1 at temperatures above 300 °C. The hydrocarbon product was shown to contain more components of lower boiling points without creating more C1 and C2 in the gas phase. The sulfur content in the hydrocarbon product was 63 ppm after 2 days of operation at 330 °C

15

A transparent and less weakly colored hydrocarbon product than Example 2 was collected after 4 days at 330 °C and at lower temperatures the coloring effect was slightly more progressed than Example 1.

20

The hydrocarbon product was grouped by GC-MS analysis into the following component classes where the area-% of the hydrocarbons can be estimated to be weight-%, not the oxygen or nitrogen components due to a different GC-MS response factor.

Components	Area-%
Aromates	48.58
Naphthenes	45.86
Paraffines	0.47
Olefines	0.96
Oxygen compounds	2.39
Nitrogen compounds	1.3
Rest	0.43

Example 4

A hydrodesulfurization catalyst, NiMo on alumina, and a physical mixture of the same hydrodesulfurization and a zeolite cracking catalyst, (a 1:2 volume ratio), were loaded in the reactor. The packing design was a NiMo on alumina catalyst on top of the physical mixture of NiMo on alumina and zeolite catalyst at a volume ratio of 1:1 within the isothermal zone. The pre-heated zone contained the same hydrodesulfurization catalyst. The inert filler below the catalysts were SiC with a particle size of 125-160 μm . The inner diameter of the reactor was 4.6 mm and the length of the pre-heated zone was 155.5 mm and the length of the isothermal zone was 200 mm and the length of the inert filling zone was 145 mm.

The lignin oil feedstock passing through the reactor was 20 wt-% lignin oil in benzyl alcohol.

The operating conditions were set to the following:

Hydrogen pressure (bar)	160
Hydrogen flow rate (l/h)	87
Oil flow rate (ml/h)	87
GTO (l/l) (STP conditions)	1000
LHSV (h^{-1})	0.5
Temperature ($^{\circ}\text{C}$)	330

The process was operating continuously for 4 days without issues. After 4 days the temperature was decreased to 310 $^{\circ}\text{C}$ and then operated continuously for 2 days without issues. As a last step the temperature was decreased to 290 $^{\circ}\text{C}$ and at this temperature the rig plugged in a downstream section. Increasing the temperature again dissolves the plugging.

The overall conversion is very high at 310 and 330 °C. The hydrogen consumption was 40-60% of the hydrogen flow giving a product mix no different to example 1 at temperatures above 300 °C.

The pressure drop over the packed reactor after the trial was 1354 mbar indicating a higher pressure drop for a stack of catalysts compared with physical mix in Example 3. The sulfur content in the hydrocarbon product was 23 ppm after 2 days of operation at 330 °C.

A transparent and equally weakly colored hydrocarbon product as Example 3 was collected after 4 days at 330 °C and at lower temperatures the coloring effect was more progressed than Example 1 and 3.

Example 5

A guard (alumina of high surface area and low NiMo content) and a hydrodesulfurization catalyst, NiMo on alumina, were loaded in the reactor. The packing design was a guard bed on top of the hydrodesulfurization catalyst at a volume ratio of 1:2 within the isothermal zone. The pre-heated zone contained the same hydrodesulfurization catalyst alone. The inert filler below the catalysts were SiC with a particle size of 125-160 µm. The inner diameter of the reactor was 4.6 mm and the length of the pre-heated zone was 155.5 mm and the length of the isothermal zone was 200 mm and the length of the inert filling zone was 145 mm.

The lignin oil feedstock passing through the reactor was 20 wt% crude bio-oil in benzyl alcohol. The operating conditions were set to the following:

Hydrogen pressure (bar)	160
Hydrogen flow rate (l/h)	87
Oil flow rate (ml/h)	87
GTO (l/l) (STP conditions)	1000
LHSV (h ⁻¹)	0.5
Temperature (°C)	330

The process was operating continuously for 4 days without issues. After 4 days the temperature was decreased to 310 °C and then operated continuously for 2 days without issues. As a last step the temperature was decreased to 290 °C and at this temperature the

rig plugged in a downstream section. Increasing the temperature again dissolves the plugging.

The pressure drop over the packed reactor after the trial was 2383 mbar. The overall conversion is very high at 310 and 330 °C. The hydrogen consumption was 40-60% of the hydrogen flow giving a product mix no different to example 1 at temperatures above 300 °C. The pressure drop was 2383 mbar indicating similar pressure drop as Example 1 and 2. The sulfur content in the hydrocarbon product was 89 ppm after 2 days of operation at 330 °C

A transparent and colorless hydrocarbon product was collected after 4 days at 330 °C and at lower temperatures the coloring effect was even less progressed than Example 1.

10 Example 6

A hydrodeoxygenation catalyst, Ni/NiO on alumina/graphite, and a combined hydrodeoxygenation and cracking catalyst, NiO on zeolite, were loaded in the reactor. The packing design was a physical mixture of the hydrodeoxygenation catalyst and the hydrodeoxygenation and cracking catalyst at a volume ratio of 2:1 within the isothermal zone. The pre-heated zone contained the same hydrodeoxygenation catalyst alone. The inert filler below the catalysts were SiC with a particle size of 125-160 µm. The inner diameter of the reactor was 4.6 mm and the length of the pre-heated zone was 155.5 mm and the length of the isothermal zone was 200 mm and the length of the inert filling zone was 145 mm.

The lignin oil feedstock passing through the reactor was 20 wt% lignin oil in benzyl alcohol.

20 The operating conditions were set to the following:

Hydrogen pressure (bar)	160
Hydrogen flow rate (l/h)	87
Oil flow rate (ml/h)	87
GTO (l/l) (STP conditions)	1000
LHSV (h ⁻¹)	0.5
Temperature (°C)	330

The process was operating continuously for 1 day- without issues.

The overall conversion is very high at 330 °C. The hydrogen consumption was 80 % of the hydrogen flow during the first day giving a hydrocarbon product mix similar to example 1. A transparent and colorless hydrocarbon product was collected after 1 day at 330 °C.

CLAIMS

1. A process for producing a hydrocarbon product from a lignin oil, said lignin oil having an oxygen content of 10-30 wt-%, an average weight molecular weight of 500-800 g/mol with a polydispersity of 2, a heating value of 25-35 MJ/kg, a water content of 0-1.5 wt-%, a sodium content of 400-500 ppm by weight, a potassium content of 50-100 ppm by weight, a sulfur content of 1-2.5 wt-% and a total acid number of 110-125 mg KOH/g oil,

wherein the process for producing the hydrocarbon product comprises the steps of treating the lignin oil in a reactor in the presence of one or more of:

a hydrodesulfurization catalyst selected from the group consisting of NiMo on alumina and CoMo on alumina;

a hydrodesulfurization and cracking catalyst selected from the group consisting of NiMo on zeolite and CoMo on zeolite;

a hydrodeoxygenation and cracking catalyst selected from the group consisting of NiO on zeolite, zeolite alone and combinations thereof;

a hydrodeoxygenation catalyst selected from the group consisting of Ni/NiO, Cu/Cr, Pd/Cu, and Pt on a support material;

or combinations thereof, and

applying a H₂ pressure of 30-160 bar, a gas to oil ratio (GTO) of 200-2000 l/l (STP conditions), at a temperature of 290-400 °C, and with a liquid hourly space velocity (LHSV) of 0.25-2 h⁻¹, followed by cooling the reaction product from the reactor to 20-30 °C, and

separating the reaction product by phase separation, into a gaseous phase, a liquid hydrocarbon product phase, and a water phase, thereby obtaining the hydrocarbon product.

2. The process of claim 1, wherein the support material is selected from the group consisting of chromite, alumina, zirconia, graphite, carbon, silica, and combinations thereof.
3. The process of claim 1 or 2, wherein the H₂ pressure is 50-150 bar.
4. The process of any one of claims 1 to 3, wherein the a gas to oil ratio (GTO) is 500-1500 l/l.
5. The process of any one of claims 1 to 4, wherein the H₂ pressure is applied at a temperature of 300-360 °C.
6. The process of any one of claims 1 to 5, wherein the liquid hourly space velocity (LHSV) is 0.5-1 h⁻¹.
7. The process of any one of claims 1 to 6, wherein the reactor is a reactor comprising a packed bed, which includes
 - a first section of inert filling material or guard material and optionally the hydrodesulfurization catalyst defined in claim 1, and
 - a second section of the hydrodesulfurization catalyst defined in claim 1 and optionally a guard material on top of the catalyst, and

a third section of inert filling material and optionally the hydrodesulfurization catalyst defined in claim 1,

and wherein the lignin oil passes first the first section, then the second section, and then the third section.

8. The process of any one of claims 1 to 6, wherein the reactor is a reactor comprising a packed bed, which includes

a first section of inert filling material or guard material and optionally the hydrodesulfurization and cracking catalyst defined in claim 1, and

a second section of the hydrodesulfurization and cracking catalyst defined in claim 1 and optionally a guard material on top of the catalyst, and

a third section of inert filling material and optionally the hydrodesulfurization and cracking catalyst defined in claim 1,

and wherein the lignin oil passes first the first section, then the second section, and then the third section.

9. The process of claims 7 or 8, wherein the reactor comprises a pre-heating zone and an isothermal zone, wherein the lignin oil temperature in the isothermal zone is the reaction temperature 290-400 °C, and the lignin oil temperature in the pre-heating zone is 1-10 °C below the reaction temperature, and wherein the isothermal zone comprises the second section of the packed bed, and optionally a portion of the first section of the packed bed.

10. The process of claim 7 or 8, wherein the reactor comprises a pre-heating zone and an isothermal zone, wherein the lignin oil temperature in the isothermal zone is

the reaction temperature 300-360 °C, and the lignin oil temperature in the pre-heating zone is 1-10 °C below the reaction temperature, and wherein the isothermal zone comprises the second section of the packed bed, and optionally a portion of the first section of the packed bed.

11. The process of any one of claims 7 to 10, wherein the catalyst in the second section is a physical mixture of NiMo on alumina and NiO on zeolite.
12. The process of claim 11, wherein the volume ratio of NiMo on alumina and NiO on zeolite is 1-4:1.
13. The process of claim 11, wherein the volume ratio of NiMo on alumina and NiO on zeolite is 1.5-2.5:1.
14. The process of claim 11, wherein the volume ratio of NiMo on alumina and NiO on zeolite is 2:1.
15. The process of claims any one of claims 7 to 10, wherein the catalyst in the second section is a physical mixture of Ni/NiO on alumina/graphite and NiO on zeolite.
16. The process of claim 15, wherein the volume ratio of Ni/NiO on alumina/graphite and NiO on zeolite is 1-4:1.
17. The process of claim 15, wherein the volume ratio of Ni/NiO on alumina/graphite and NiO on zeolite is 1.5-2.5:1.

18. The process of claim 15, wherein the volume ratio of Ni/NiO on alumina/graphite and NiO on zeolite is 2:1.
19. The process of any one of claims 1 to 18, wherein the resulting hydrocarbon product is separated into three fractions by means of distillation, wherein a first fraction comprises
- hydrocarbons having a boiling point of 35-180 °C,
- a second fraction comprises hydrocarbons having a boiling point of 181-340 °C,
- and a third fraction comprises hydrocarbons having a boiling point above 340 °C.
20. The process of claim 19, wherein a fraction having a boiling point of 250-285 °C is separated from the hydrocarbon product, said fraction comprising dibenzyl, cyclohexylethylbenzene, 4-methyldiphenylmethane, benzylcyclohexane, dicyclohexylmethane and 1,2-dicyclohexylethane.
21. The process of any one of claims 1 to 20, wherein the gaseous phase separated in the phase separation is led through a gas treater, whereby H₂S is removed, and H₂ is then separated and recycled to the reactor, and the rest of the gases are retrieved as a gaseous hydrocarbon containing product.
22. The process of claim 21, wherein the gaseous hydrocarbon containing product is led to a steam reformer producing H₂ and CO or CO₂, wherein H₂ and CO are optionally led back to the process.

23. The process of any one of claims 1 to 22, wherein the lignin oil is desalted in a desalting unit prior to the reactor, said desalting unit comprising a bed of adsorbent, absorbent, ion exchange material, or combinations thereof.
24. The process of any one of claims 1 to 23, comprising addition of additional viscosity modifying, lubricating or carbonium/arenium ion scavenging components to the lignin oil in an amount of 1-80 wt-%, based on the weight of the lignin oil prior to the reactor and any desalting unit, said additional components being a combination of a solvent, and the hydrocarbon product obtained by the process.
25. The process of claim 24, wherein the additional viscosity modifying, lubricating or carbonium/arenium ion scavenging components are added to the lignin oil in an amount of 10-20 wt% based on the weight of the lignin oil.
26. The process of claim 24 or 25, wherein the solvent is methanol, ethanol, toluene, o-xylene, m-xylene, p-xylene, p-cymene, anisole, diesel, gasoline, benzyl alcohol, phenol, 2-naphthol, catechol, thymol, guaiacol, cresol, and mixtures thereof.
27. The process of any one of claims 1 to 26, wherein the lignin oil fed into the process is lignin oil obtained by a process in which
a black liquor composition comprising kraft black liquor and having a hydroxide ion concentration of 1-40 g/l, based on the volume of black liquor, is reacted at 220-350 °C for 10-120 minutes in the absence of a solid catalyst; or at 180-240 °C for 10-120 minutes in the presence of a solid catalyst, thereby causing depolymerization of lignin in the black liquor;

the reacted composition is cooled to a temperature below the boiling point of a solvent to be added subsequently, and is thereafter acidified until a pH of 4-5 is reached; and a solvent is added to the composition in order to extract oil from the composition, and the composition is separated by phase separation in a first separation step into an oil phase comprising solvent, oil, and organic acids; a first water phase comprising water, salts, and non-depolymerized lignin solids; and a second water phase comprising water and salts;

the oil phase is filtered to remove any particles, and is then desalted in a water wash step by adding water and separating by phase separation into a second separation step into an oil phase comprising oil and solvent, and a water phase comprising salts; or by adding adsorbent or absorbent material, ion exchange material, or combinations thereof; and

solvent comprised in the oil phase is evaporated, whereby the lignin oil is obtained.

28. The process of claim 27, wherein the black liquor composition is reacted under a H₂ or H₂/CO syngas pressure of 5-150 bar.

29. A hydrocarbon product obtained by the process of any one of claims 1 to 21, said product comprising:

Cyclohexane

Methylcyclohexane

Toluene

Ethylcyclohexane

Ethylcyclopentane

Propylcyclohexane
Propylbenzene
1-methyl-4-(1-methylethyl) cyclohexane
Butylcyclohexane
Decalin
Tetralin
Methyltetralin
Butylbenzene
Decahydro-2-methylnaphthalene
Pentylcyclohexane
Hexylcyclohexane
Diethylcyclohexane
Bicyclohexyl
Biphenylmethane
1-Methyl-2-Cyclohexylcyclohexane
Dicyclohexylmethane
Benzylcyclohexane
Methyldicyclohexylmethane
1,2-Dicyclohexylethane
1-Phenyl-1-cyclohexylethane
1-Phenyl-2-cyclohexylethane
Cyclohexylethylbenzene
Dibenzyl
4-Methyldiphenylmethane
3-Methyldicyclohexylmethane

1.3- Dicyclohexylpropane

n-Heptadecane

1,1'-(1,4-butanediyl)-cyclohexane

n-Octadecane

1,1-Dicyclohexylpropane

and containing less than 0.2 wt-% oxygen.

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