The present invention relates to a method of depolymerizing lignin comprising providing a lignin containing aqueous solution and adding a sulfur containing reducing agent to the solution forming a mixture, and preferably heating the formed mixture. The reducing agent is added in a 1:2 to 2:1 molar ratio to the repeating unit of the lignin.

Lignin boost lignin

Figure 1.

**Title:** DEPOLYMERISATION OF LIGNIN

**Abstract:**
DEPOLYMERISATION OF LIGNIN

FIELD OF THE INVENTION

The present invention relates to a method of depolymerizing lignin using a sulfur containing agent in order to increase the solubility of lignin in carrier liquids. The invention further relates to a composition comprising said depolymerized lignin.

BACKGROUND

There is an increasing interest in using biomass as a source for fuel production. Biomass includes, but is not limited to, plant parts, fruits, vegetables, processing waste, wood chips, chaff, grain, grasses, com, com husks, weeds, aquatic plants, hay, paper, paper products, recycled paper and paper products, lignocellulosic material, lignin and any cellulose containing biological material or material of biological origin.

An important component of biomass is the lignin present in the solid portions of the biomass. Lignin comprises chains of aromatic and oxygenate constituents forming larger molecules that are not easily treated. A major reason for difficulty in treating the lignin is the inability to disperse the lignin for contact with catalysts that can break the lignin down.

Lignin is one of the most abundant natural polymers on earth. One common way of preparing lignin is by separation from wood during pulping processes. Only a small amount (1-2 %) is utilized in specialty products whereas the rest primary serves as fuel. Even if burning lignin is a valuable way to reduce usage of fossil fuel, lignin has significant potential as raw material for the sustainable production of chemicals and fuel.

Various lignin differ structurally depending on the raw material source and subsequent processing, but one common feature is a backbone consisting of various substituted phenyl propane units that are bound to each other via aryl ether or carbon-carbon linkages. They are typically substituted with methoxy groups and the phenolic and aliphatic hydroxyl groups provide sites for e.g. further
functionalization. Lignin is known to have a low ability to sorb water compared to for example the hydrophilic cellulose.

Today lignin may be used as a component in for example pellet fuel as a binder but it may also be used as an energy source due to its high energy content. Lignin has higher energy content than cellulose or hemi celluloses and one gram of lignin has on average 2.27 kJ, which is 30% more than the energy content of cellulotic carbohydrate. The energy content of lignin is similar to that of coal. Today, due to its fuel value lignin that has been removed using the kraft process, sulphate process, in a pulp or paper mill, is usually burned in order to provide energy to run the production process and to recover the chemicals from the cooking liquor.

There are several ways of separating lignin from black or red liquor obtained after separating the cellulose fibres in the kraft or sulphite process respectively, during the production processes. One of the most common strategies is ultra-filtration. Lignoboost® is a separation process developed by Innventia AB and the process has been shown to increase the lignin yield using less sulphuric acid. In the Lignoboost® process, black liquor from the production processes is taken and the lignin is precipitated through the addition and reaction with acid, usually carbon dioxide (CO2), and the lignin is then filtered off. The lignin filter cake is then re-dispersed and acidified, usually using sulphuric acid, and the obtained slurry is then filtered and washed using displacement washing. The lignin is usually then dried and pulverized in order to make it suitable for lime kiln burners or before pelletizing it into pellet fuel.

Biofuel, such as biogasoline and biodiesel, is a fuel in which the energy is mainly derived from biomass material or gases such as wood, corn, sugarcane, animal fat, vegetable oils and so on. However the biofuel industries are struggling with issues like food vs fuel debate, efficiency and the general supply of raw material. At the same time the pulp or paper making industries produces huge amounts of lignin which is often, as described above, only burned in the mill. Two common strategies for exploring biomass as a fuel or fuel component are to use pyrolysis oils or hydrogenated lignin.

In order to make lignin more useful one has to solve the problem with the low solubility of lignin in organic solvents. One drawback of using lignin as a source for fuel production is the issue of providing lignin or lignin derivatives in a form
suitable for hydrotreaters or crackers. The problem is that lignin is not soluble in oils or fatty acids which is, if not necessary, highly wanted.

Prior art provides various strategies for degrading lignin into small units or molecules in order to prepare lignin derivatives that may be processed. These strategies include hydrogenation, deoxygenation and acid catalyst hydrolysis. WO2011003029 relates to a method for catalytic cleavage of carbon-carbon bonds and carbon-oxygen bonds in lignin. US20130025191 relates to a depolymerisation and deoxygenation method where lignin is treated with hydrogen together with a catalyst in an aromatic containing solvent. Many of the prior art methods for depolymerizing lignin involves multiple steps, high temperatures and pressure and consume a lot of reagents.

The economic benefits of producing fuels from biomass depend for example on an efficient process for preparing the lignin and on the preparation of the lignin or lignin derivatives so that the fuel production is as efficient as possible. For example the amount oxygen should be as low as possible and the number of preparation steps should be as few as possible.

SUMMARY OF THE INVENTION

The object of the present invention is present a novel method of depolymerizing lignin in a straightforward way which does not require high temperatures or high pressure. The depolymerized lignin may be used to prepare compositions which could be used to prepare a wide variety of products such as biofuels, chemicals, or additives. By depolymerizing lignin the solubility of the lignin in various solvents increases.

In a first aspect the present invention relates to a method of depolymerizing lignin comprising:

a. Providing a lignin containing aqueous solution in a container;
b. Adding a sulfur containing reducing agent to the solution forming a mixture of the sulfur containing agent and the lignin containing aqueous solution, wherein the sulfur containing reducing agent is added in a 1:2 to 2:1 molar ratio to the lignin;
c. Leaving the mixture to react.
In a second aspect the present relates to depolymerized lignin obtained by the method according to the present invention.

In a third aspect the present invention relates to a composition comprising the depolymerized lignin according to the present invention and a carrier liquid and optionally an organic solvent.

In a fourth aspect the present invention relates to a composition comprising the depolymerized lignin according to the present invention and an organic solvent.

In a fifth aspect the present invention relates to the use of the depolymerized lignin or the composition according to the present invention for preparing fuel.

In a sixth aspect the present invention relates to a fuel obtained by hydrotreating or hydrocracking the depolymerized lignin or a composition according to the present invention.

All the embodiments are applicable to all aspects of the present invention.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1, GPC of kraft lignin and products from examples 1-7.

Figure 2, GPC of starting material and depolymerized lignin from example 9.

Figure 3, GPC of starting material and depolymerized lignin from example 10.

Figure 4, GPC of starting material and depolymerized lignin from examples 11 and 12.

Figure 5, GPC of starting material and depolymerized lignin from examples 13 and 14.

Figure 6, GPC of starting material and depolymerized lignin from examples 15-19.

Figure 7, GPC of starting material and depolymerized lignin from examples 20-22.

Figure 8, GPC of starting material and depolymerized lignin from examples 23-25.

Figure 9, GPC of starting material and depolymerized lignin from examples 26-28.

DETAILED DESCRIPTION OF THE INVENTION
In the present application the term "lignin" means a polymer comprising coumaryl alcohol, coniferyl alcohol and sinapyl alcohol monomers.

In the present application the term "lignin derivative" means molecules or polymers derived from lignin. In the present application "lignin derivative" and "molecules or polymers derived from lignin" are used interchangeably. These molecules or polymers may be a result of chemical modification or degradation of lignin or a lignin source, for example when treating black or red liquor in order to precipitate or separate lignin. In one embodiment the lignin derivative has weight average molecular weight of not more than 1,000 g/mol, preferably not more than 800 g/mol. In one embodiment the lignin derivative has weight average molecular weight of 400-900 g/mol.

In the present invention the "repeating unit of lignin" is assumed to be 180 g/mol.

In the present application the term "carrier liquid" means a liquid selected from fatty acids or mixture of fatty acids, esterified fatty acids, rosin acid, crude oil, mineral oil, bunker fuel and hydrocarbon oils or mixtures thereof.

In the present application the terms "red liquor" and "brown liquor" denote the same liquor.

For a substance to be processed in a refinery such as an oil refinery or bio oil refinery, the substance needs to be in liquid phase. Either the substance is in liquid phase at a given temperature (usually below 80 °C) or the substance is solvated in a liquid. In this patent application, such liquid will be given the term carrier liquid. In one aspect the present invention presents a composition and a method of preparing said composition where the composition comprises a biomass material, preferably lignin or lignin derivatives, where the biomass material is in liquid phase and may be processed in a refinery.

**Biomass and sources of lignin**

Biomass includes, but is not limited to wood, fruits, vegetables, processing waste, chaff, grain, grasses, com, com husks, weeds, aquatic plants, hay, paper, paper products, recycled paper, shell, brown coal, algae, straw, bark or nut shells, lignocellulosic material, lignin and any cellulose containing biological material or material of biological origin. In one embodiment the biomass is wood, preferably particulate wood such as saw dust or wood chips. The wood may be any kind of
wood, hard or soft wood, coniferous tree or broad-leaf tree. A non-limiting list of woods would be pine, birch, spruce, maple, ash, mountain ash, redwood, alder, elm, oak, larch, yew, chestnut, olive, cypress, banyan, sycamore, cherry, apple, pear, hawthorn, magnolia, sequoia, walnut, karri, coolabah and beech.

It is preferred that the biomass contains as much lignin as possible. The Kappa number estimates the amount of chemicals required during bleaching of wood pulp in order to obtain a pulp with a given degree of whiteness. Since the amount of bleach needed is related to the lignin content of the pulp, the Kappa number can be used to monitor the effectiveness of the lignin-extraction phase of the pulping process. It is approximately proportional to the residual lignin content of the pulp.

\[ K \approx c*z \]

K: Kappa number; c: constant \( \sim 6.57 \) (dependent on process and wood); z: lignin content in percent. The Kappa number is determined by ISO 302:2004. The Kappa number is determined by ISO 302:2004. The kappa number may be 20 or higher, or 40 or higher, or 60 or higher. In one embodiment the kappa number is 10-100.

Biomass materials and derivatives thereof often have a general formula of \( C_{x}H_{y}O_{z} \) where the ratio \( z/x \) depends of origin, part of the plant and also processes of the biomass material, and where \( x \) and \( y \) each are \( \geq 1 \) and \( z \geq 0 \). Preferably \( x \) is \( \geq 2 \), or more preferably \( x \) is \( \geq 3 \), or more preferably \( x \) is \( > 6 \); \( z \) is preferably \( \geq 1 \), or \( \geq 2 \). In one embodiment \( x \) is \( \leq 20 \), in another embodiment \( x \) is \( \leq 15 \), and in yet another embodiment \( x \) is \( \leq 11 \). In one embodiment \( z \) is \( \leq 10 \) and in another embodiment \( z \) is \( \leq 5 \). The biomass material may comprise other heteroatoms such as S or N.

The following is a non-limiting list of biomass materials: cellulose \( (C_{6}H_{10}O_{5})_{n} \), glucose \( (C_{6}H_{12}O_{6}) \), glycerol \( (C_{3}H_{8}O_{3}) \), ethanol \( (C_{2}H_{6}O) \); fatty acids such as, palmitoleic oil \( (C_{16}H_{32}O_{2}) \), oleic acid \( (C_{18}H_{34}O_{2}) \), tall oil or fatty acid \( C_{17}H_{31}-35COOH \); rosin acids such as abeitic acid \( (C_{20}H_{30}O_{2}) \); lignin or lignin derivatives in the range between \( 1 \) to \( C_{20} \), such as \( (C_{10}H_{10}O_{2}) \), \( (C_{10}H_{12}O_{3}) \), \( (C_{11}H_{14}O_{4}) \), lignin in black liquor such as \( (C_{10}H_{10}O_{2}) \), \( (C_{11}H_{12}O_{3}) \) and pyrolysis oil, etc. The fatty acids such as palmitoleic oil \( (C_{16}H_{32}O_{2}) \), oleic acid \( (C_{18}H_{34}O_{2}) \), tall oil or fatty acid \( C_{17}H_{31}-35COOH \); rosin acids such as abeitic acid \( (C_{20}H_{30}O_{2}) \); may also be used as a component in the composition according to the present invention. In one embodiment the biomass material is lignin or lignin derivatives in the range
between of CI to C20, such as (C9H10O2), (C10H12O3) and (C11H14O4) or lignin in or from black liquor such as (C9H8O), (C10H10O2) and (C11H12O3). Examples of lignin derivatives are guaiacol, coniferyl alcohol, sinapyl alcohol, ethyl 4-hydroxy-3-methoxy ketone, (4-hydroxy-3-methoxy-phenyl)-propen, vanillin and phenol.

The biomass material may be a mixture of biomass materials and in one embodiment the biomass material is black or red liquor, or materials obtained from black or red liquor. Black and red liquor contains cellulose, hemicellulose and lignin and derivatives thereof. The composition according to the present invention may comprise black or red liquor, or lignin or lignin derivatives obtained from black or red liquor.

In another embodiment the biomass material comprises residual material from ethanol production such as cellulosic or corn ethanol production, hereafter called ethanol production. In another embodiment the biomass material is lignin or lignin derivatives obtained from ethanol production. In one embodiment the biomass material comprises hydroxyl groups.

Black liquor comprises four main groups of organic substances, around 30-45 weight% ligneous material, 25-35 weight% saccharine acids, about 10 weight% formic and acetic acid, 3-5 weight% extractives, about 1 weight% methanol, and many inorganic elements and sulfur. The exact composition of the liquor varies and depends on the cooking conditions in the production process and the feedstock. Red liquor comprises the ions from the sulfite process (calcium, sodium, magnesium or ammonium), sulfonated lignin, hemicellulose and low molecular resins.

The lignin may be Kraft lignin, sulfonated lignin, Lignoboost® lignin, precipitated lignin, filtrated lignin, acetosolv lignin or organosolv lignin. In one embodiment the lignin is Kraft lignin, acetosolv lignin or organosolv lignin. In another embodiment the lignin is Kraft lignin. In another embodiment the lignin is organosolv lignin. In another embodiment the lignin or lignin derivatives obtained as residual material from ethanol production. The lignin may be in particulate form with a particle size of 5 mm or less, or 1 mm or less.

Lignin is not soluble in most organic solvents, fatty acids or oils. Instead prior art have presented various techniques to depolymerize and covert the depolymerized lignin into components soluble in the wanted media. The present invention provides
a method for increasing the solubility of lignin in organic solvents and carrier liquids by depolymerizing the lignin.

In one embodiment the weight average molecular weight ($M_w$) of the lignin in the lignin containing solution is 2000-5000 g/mol

### Depolymerization of lignin

Lignin may be depolymerized according to the present invention by providing a lignin containing aqueous solution and mixing it with a sulfur containing reducing agent. The pH of the formed mixture may be adjusted to a pH of 5.0 or higher for example 6.0 or higher, or 6.5 or higher, or 7.0 or higher, or 8.0 or higher, or 9.0 or higher, but preferably 14.0 or lower, or 12 or lower, or 11.5 or lower, or 11.0 or lower. A preferred pH range is 7.0 to 10.0. The pH may be adjusted by adding a base or an acid. Any suitable base or acid may be used, however non-limiting examples of suitable bases are alkali or earth metal hydroxides such as sodium hydroxide, calcium hydroxide, potassium hydroxide, barium hydroxide, or ammonia, amines, or carbonates such as sodium carbonate, or butyl lithium, sodium amide or sodium hydride. Non-limiting examples of suitable acids are sulfuric acid, hydrochloric acid, nitric acid, perchloric acid, benzoic acid, citric acid, formic acid and acetic acid. Without being bound by theory but the inventors found that when using a sulfite as the reducing agent the pH is preferably 6.0 to 11, more preferably 7.0 to 9.0.

The sulfur containing reducing agent may be added in a 1:2 to 2:1, or a 1:1.5 to 1.5:1, or a 1:1.2 to 1.2:1, or a 1:1 molar ratio to the repeating unit of lignin or lignin derivatives. When calculating the molar ratio it is assumed that the molecular weight of the repeating unit of lignin is 180 g/mol. This repeating unit may be seen as a representative part of the repeating monomers of lignin. When calculating said molar ratio the molecular weight of the lignin or lignin derivative used is the weight average molecular weight ($M_w$). In one embodiment the amount is essentially stoichiometric to the amount of lignin based on a molecular weight of the lignin. The sulfur containing reducing agent may be a dithionite, sulfite, thiosulphate, metabisulfite, sulfinate, thiourea, thiourea oxide, thiourea dioxide, thiourea trioxide, hydroxymethane sulfinate, hydroxyethane sulfinate, hydroxypropane sulfinate, hydroxybutane sulfinate, thiophenol or sulfur dioxide, a non-limiting list of sulfur containing agents is sodium or potassium dithionite, sodium or potassium hydroxymethane sulfinate, sodium or potassium sulfite, sodium or potassium...
bisulfite, or any combination thereof. In one embodiment the agent is ditionite. In another embodiment the agent is a sulfite. In another embodiment the agent is a thiosulphate. In another embodiment the agent is a metabisulfite. In one embodiment the agent is selected from sodium dithionite, sodium or potassium sulfite, sodium hydroxymethane sulfinate or thiourea oxides. In one embodiment the sulfur containing reducing agent is a sulfite or a sulfite forming agent.

The reaction may be performed at a temperature of 20°C or higher, or 40°C or higher, or 60°C or higher, or 80°C or higher, or 100°C or higher, or 120°C or higher. One preferred temperature range at which the mixture may be heated is 60-160°C, or 100 to 150°C. The reaction may be performed during reflux. The depolymerization reaction may continue for 1 hour or longer, or 3 hours or longer, or 6 hours or longer, or 12 hours or longer and may be performed in an inert atmosphere or in an atmosphere containing inert gas. The mixture may be stirred or shaken prior to or during the depolymerization reaction. The reaction may be performed at an elevated pressure such as 2 bar or higher, or 4 bar or higher. The elevated pressure may be obtained by performing the reaction in a sealed container.

The amount of water is preferably large enough to keep the depolymerized lignin in solution. If the amount of water is too low the lignin will precipitate during the depolymerization which will lead to less effective mixing and less effective reaction conditions. The weight ratio of water to lignin may be 5:1 or higher, such as 10:1 or higher, or 20:1 or higher.

The obtained depolymerized lignin may have a weight average molecular weight of 400-1000 g/mol, for example 500-900 g/mol. The polydispersity index of the depolymerized lignin according to the present invention may be around 1.3 to 2.0.

Molecular weight in the present application is determined using GPC (Gel Permeation Chromatography) operated at 20°C and at flow rate of 1 ml/min using THF as solvent. Polystyrene Standard RedayCal Set M(p) 250-70000 (16 standards) (Sigma product no: 76552). The columns are Styrage THF (pre-colon), Styrage HR 3 THF (7.8x300 mm), Styrage HR 1 THF (7.8x300 mm), Styrage HR 0.5 THF (7.8x300 mm) all from Waters.

The composition...
The composition according to the present invention comprises depolymerized lignin, and a carrier liquid and/or an organic solvent.

The amount of depolymerized lignin or lignin derivatives in the composition may be 1 weight% or more, or 4 weight% or more, or 5 weight% or more, or 7 weight% or more, or 10 weight% or more, or 12 weight% or more, or 15 weight% or more, or 20 weight% or more, or 25 weight% or more, or 30 weight% or more, or 40 weight% or more, or 50 weight% or more, or 60 weight% or more, or 70 weight% or more, or 75 weight% or more.

In one embodiment the depolymerized lignin or lignin derivatives are dearomatized. For example the lignin or lignin derivatives are dearomatized to at least 40%, or at least 50%, or at least 60%, or at least 70%, or at least 80%, or at least 90%, or at least 95%, or at least 99%.

The purpose of the carrier liquid is to carry the wanted substrate or solution into the reactor without reacting or in any other way affecting the substrate or solution. Therefore, in the present application a carrier liquid is an inert hydrocarbon with a high boiling point, preferably at least 150°C. In one embodiment the carrier liquid is a fatty acid or a mixture of fatty acids. In another embodiment the carrier liquid is esterified fatty acids such as FAME (fatty acid methyl ester). In one embodiment the carrier liquid is a crude oil. In one embodiment the carrier liquid is bunker fuel or bunker crude. In another embodiment the carrier liquid is a hydrocarbon oil or a mineral oil. In one embodiment the carrier liquid is a mixture of esterified fatty acid and an mineral oil, hydrocarbon oil, bunker fuel or crude oil. In another embodiment the carrier liquid is a mixture of a hydrocarbon oil or a mineral oil and a fatty acid.

Bunker fuel or bunker crude are fuel mainly used for ships, usually very large ships. The bunker fuel may be divided into groups depending on if the fuel is a distillate or a residual or a mixture of both and the chain length. For example No. 1 fuel oil is a distillate with a chain length of 9-16, No. 2 fuel oil (also known as Bunker A) is a distillate with a chain length of 10-20, No. 4 and No. 5 fuel oil (also known as Bunker B) is a distillate and a residual oil respectively with a chain length of 12-70 and No. 6 fuel oil (also known as Bunker C) is a residual (heavy fuel oil) with a chain length of 20-70. No. 5 and 6 are also known as heavy fuel oil (HFO) or
furnace fuel oil (FFO). In one embodiment the bunker fuel is a Bunker B. In another embodiment the bunker fuel is a HFO or Bunker C.

The carrier liquid should preferably be suitable for a hydrotreater or a catalytic cracker (cat cracker), preferably a liquid suitable for both hydrotreater and catalytic cracker. Hydrotreater and catalytic cracker are steps in the refinery process where for example the sulfur content of the oil is reduced and where high-boiling, high molecular weight hydrocarbons are converted into gasoline, diesel and gases. In hydrotreaters common catalysts are cobalt-molybdenum for removing sulfur and for olefin saturation, and nickel-molybdenum for removing nitrogen and aromatic saturation. In catalytic crackers may crystalline silica alumina be used with a metal deposit where the metal may be platinum, palladium, tungsten, nickel or rare earth metals. Usually the feedstock is hydrotreated prior to catalytic cracking. The carrier liquid content may be at least 5 weight%, or at least 10 weight%, or at least 20 weight%, or at least 30 weight%, or at least 40 weight%, preferably at least 50 weight%, but preferably less than 90 weight%, or less than 80 weight%, or less than 70 weight%, or less than 60 weight%, or less than 55 weight%.

In one embodiment the carrier liquid is a fatty acid or a mixture of fatty acids. In another embodiment the fatty acid or the mixture of the fatty acids comprises unsaturated fatty acids, preferably at a concentration of more than 25 wt%, or more than 50 wt%. In one embodiment the carrier liquid is a tall oil. In another embodiment the carrier liquid is a hydrocarbon oil or a mineral oil. In yet another embodiment the carrier liquid is a mixture of a fatty acid and a hydrocarbon oil or a mineral oil. The ratio in said mixture may be 10-90 wt% fatty acid and 10-90 wt% of hydrocarbon oil or mineral oil, for example 20-40 wt% fatty acid and 60-80 wt% of hydrocarbon oil or mineral oil.

When the carrier liquid is or comprises a hydrocarbon oil the oil needs to be in liquid phase below 80 °C and preferably have boiling points of 177-371 °C. These hydrocarbon oils include different types of or gas oils and likewise e.g. Full Range Straight Run Middle Distillates, Hydrotreated, Middle Distillate, Light Catalytic Cracked Distillate, distillates Naphtha full-range straight-run, Distillates, hydrosulfurized full-range, Distillates, solvent-dewaxed straight-range, Distillates, straight-run middle sulvenylated, Naphtha clay-treated full-range straight run, Distillates full-range atm, Distillates hydrotreated full-range, Distillates, straight-run light, Distillates heavy straight-run, Distillates (oil sand),
straight-run middle-run, Naphtha (shale oil), hydrocracked, full-range straight run
(example of but not restricted to CAS nr: 68476-30-2, 68814-87-9, 74742-46-7,
64741-59-9, 64741-44-2, 64741-42-0, 101316-57-8, 101316-58-9, 91722-55-3,
91995-58-3, 68527-21-9, 128683-26-1, 91995-46-9, 68410-05-9, 68915-96-8,
128683-27-2, 195459-19-9). Moreover substances can be solvated in lighter
hydrocarbon fractions such as organic solvents e.g. mesitylene, toluene, benzene,
petroleum ether, octanes, nonanes, decanes and also isomerized derivatives of these
compounds or mixtures thereof (CAS nr: 108-88-3, 108-67-8, 71-43-2, 8032-32-4,

The composition according to the present invention may comprise a solvent or a
mixture of solvents. The solvent may be an organic solvent or a mixture of organic
solvents. In one embodiment the solvent is a mixture of an organic solvent and a
carrier liquid. The organic solvent may be but is not limited to oxygenates such as
an alcohol, ester, ketone, ether, aldehydes, furan or furfural based solvent.

Preferred solvents are C1-C10 alcohols, C1-C10 aldehydes, C2-C15 ketones, C2-
C10 ethers, and C2-C10 esters. A non-limiting list of solvents is methanol, ethanol,
propanol, isopropanol, glycerol, and butyl ether such as tert-butyl methyl ether;
diethyl ether, diglyme, diisopropyl ether, dimethoxyethane, diethylene glycol, diethyl
ether, polyethylene glycol, 1,4-dioxane and tetrahydrofuran, methylated
tetrahydrofuran, mesityl oxide, furfural, isophorone. Preferred C2-C10 esters are
organic esters, aromatic or non-aromatic esters, examples of esters are benzyl
benzoate, various acetates such as methyl acetate, ethyl acetate, cyclopentyl methyl
ether and butyl acetate, various lactates such as ethyl lactates. Solvents that are
similar to or may be converted into fuel or petrol are interesting when the
composition is to be used for fuel preparation. Such solvents could be ketones or
aldehydes. In one embodiment the solvent is a C2-C15 ketone such as a C4-C12
ketone or a C6-C8 ketone. In one embodiment the solvent is a C1-C10 aldehyde
such as a C4-C9 aldehyde or C6-C8 aldehyde. In one embodiment the solvent is
a mixture of a C2-C15 ketone and a C1-C10 aldehyde. In one embodiment the solvent
is mesityl oxide. In one embodiment the solvent is acetone. In one embodiment the
solvent is acetophenone. In one embodiment the solvent is pentanone. In one
embodiment the solvent is ethyl isopropyl ketone. In one embodiment the solvent is
isophorone. In one embodiment the organic solvent is an aromatic aldehyde or a
mixture containing an aromatic aldehyde for example furfural. In one embodiment
the solvent comprises furfural or furfuryl alcohol. In one embodiment the solvent is
benzaldehyde. In one embodiment the solvent is ethyl acetate. In one embodiment the solvent is a C1-C10 alcohol. In one embodiment the solvent is methanol. In one embodiment the solvent is isopropanol. In one embodiment the solvent is ethanol. In one embodiment the solvent is 1,4-dioxane. In one embodiment the solvent is isopropanol. In one embodiment the solvent is tetrahydrofuran or methylated tetrahydrofuran. In one embodiment the solvent is methanol. In one embodiment the solvent is a C2-C10 ester. In one embodiment the solvent is solketal. In one embodiment the solvent is C1-C10 alcohols, C2-C10 ethers and C2-C10 esters. In one embodiment the solvent comprises two C1-C10 alcohols for example ethanol and glycerol, and in another embodiment the solvent comprises propanol and glycerol. In one embodiment the solvent comprises polyethylene glycol and a C1-C10 alcohol. When the solvent is a mixture of an organic solvent and water the mixture may contain methanol and water, ethanol and water, isopropanol and water or ethyl acetate and water, preferably ethanol and water, isopropanol and water and ethyl acetate and water.

In one embodiment the solvent is a mixture of a C2-C15 ketone such as a C4-C12 ketone or a C6-C8 ketone or a C1-C10 aldehyde such as a C4-C9 aldehyde or C6-C8 aldehyde and a carrier liquid. In one embodiment the solvent is a mixture of a C1-C10 alcohol such as a C3-C8 alcohol and a carrier liquid.

In one embodiment the amount of organic solvent in the composition is 1-99 weight% of the total weight of the composition. In one embodiment the amount of solvent is 10-60 weight%, or 20-50 weight%. In one embodiment the amount of organic solvent is 70 weight% or less, or 40 weight% or less, or 20 weight% or less, or 10 weight% or less, or 5 weight% or less, or 2 weight% or less of the total weight of the composition.

The composition may further comprise at least one additive. The additive may be any additive known to a person skilled in the art. In one embodiment the additive may further enhance the dissolution of the lignin or lignin derivatives. The additive may have the function of dissolving or breaking up inter molecular bonds between the lignin chains or the lignin derivatives. In one embodiment the additive is a polar compound or a salt.

Method of preparing the composition
The composition according to the present invention may be prepared by first depolymerizing the lignin or lignin derivatives according to the present invention. The depolymerized lignin or lignin derivatives may be isolated prior to further treatment or prior to mixing with the other components of the composition.

The depolymerized lignin or lignin derivatives may be dissolved in a suitable solvent and then mixed with a carrier liquid to the wanted lignin content.

In order to further improve the dissolution of the lignin in a carrier liquid the lignin may be esterified. The esterified biomass may be isolated from the esterification reaction mixture or the esterified biomass is left in the reaction mixture when mixed with the carrier liquid. The esterification of the biomass may also be performed in situ, i.e. in the carrier liquid. Then the biomass, the esterification agent or, the first fatty acid and an esterification agent, and the carrier liquid and optionally a catalyst are mixed to form a slurry. The slurry is then preferably heated for example to 80°C or higher, or 120°C or higher. The esterification of the biomass occurs in the carrier liquid leaving a homogenous composition of carrier liquid and esterified biomass, and optionally catalyst. The catalyst and any other unwanted components may be removed afterwards. The mixing can be done by stirring or shaking or in any other suitable way. When the esterification is performed in a carrier liquid comprising a first fatty acid and together with an esterification agent such as an anhydride the obtained esterified lignin is believed to comprise ester groups derived from the anhydride alone but also ester groups derived from an anhydride bond to a first fatty acid.

The esterified lignin may be isolated by precipitation in for example hexane or water. When the degree of substitution (esterification) is high, for example 50% or more, and the lignin is substituted with C2-C4 ester groups the esterified lignin may be treated with a base for example NaHCO₃ (aq) before precipitation in order to remove free acid. When the lignin is substituted with longer ester groups celite may be used. One way of precipitating the depolymerized lignin is by adding SO₂ to the reaction, for example by bubbling SO₂ into the reaction. The precipitated lignin may then be isolated using any suitable technique. The esterified lignin according to the present invention may also be separated from metals and other additives or catalysts by simply rinsing the lignin in an aqueous solution or water. For many industries, for example the fuel refinery industry, processing lignin the amount of metals should be as low as possible since metals may damage the machinery or
disturb the process. By forming the ester groups in situ insoluble biomass may
become soluble. For example lignin substituted with acetic ester groups is not
dissolved in tall oil.

The mixing may be performed at room temperature, but may be performed at a
temperature between 50°C and 350°C, such as 50°C or higher, or 80°C or higher or
100°C or higher, or 120°C or higher, or 150°C or higher, but not higher than 350°C,
or 250°C or lower, or 200°C or lower, or 180°C or lower.

The esterification agent may be a carboxylic acid or an anhydride. The esterification
agents preferably contain an unsaturated bond. Non-limiting examples of carboxylic
acids are fatty acids or C2-C40 carboxylic esters, preferably C4 to C22. Non-limiting
examples of anhydrides are C4 to C42 anhydrides. The catalyst may be a nitrogen
containing aromatic heterocycle such as N-methyl imidazole or pyridine. The
catalyst may also be titanium based catalyst or an iron catalyst.

When the carrier liquid is a fatty acid (second fatty acid) said fatty acid may be but
is not limited to C6-C18 fatty acids, saturated or unsaturated, or a mixtures of C2-
C18 fatty acids. The second fatty acid may further be methylated or ethylated. The
second fatty acid may be a vegetable fatty acid such as a tall oil, or olive oil,
soybean oil, corn oil, hemp or coconut oil. In one embodiment the first and the
second fatty acid are the same.

In one embodiment the carrier liquid is a second fatty acid or a mixture of second
fatty acids or a mixture comprising a second fatty acid. In one embodiment the
second fatty acid is an unsaturated fatty acid or is a mixture of fatty acids in which
the mixture contains unsaturated fatty acids. In one embodiment the first and the
second fatty acids are the same, for example tall oils.

In one embodiment the composition comprises a first fatty acid or oil and lignin or
lignin derivatives; wherein at least one of the hydroxyl groups of the lignin or lignin
derivatives have been substituted with an ester groups of a second fatty acid,
preferably an unsaturated second fatty acid, forming esterified lignin or lignin
derivatives.

The degree of substitution, i.e. the degree of hydroxyl groups that has been
converted into ester groups, may be from 10% to 100%, for example 20% or more,
30% or more, or 40% or more, or 60% or more or 80% or more, or 99% or more, or
100%. It is also possible to have part of the lignin, or the hydroxyl groups on the lignin, being substituted with one type of ester group (for example C2-C6 ester groups) and another part substituted with another type of ester group (for example C8-C18 ester groups). For example 10-40% of the hydroxyl groups may be substituted with acetyl groups and 60-90% of the hydroxyl groups may be substituted with a fatty acid, preferably C12 or longer ester groups.

Fully or near fully substituted (degree of substitution of 100% or near 100%) lignin wherein the ester group is unsaturated is an oil at room temperature while lignin substituted with a saturated ester group is a solid or wax like material. By having the lignin in oil phase there is no need to heat the lignin in order for it to dissolve in the wanted solvent. In order to keep the wax like lignin in solution it needs to be kept at the elevated temperature (for example 70°C) which makes transportation and stock keeping more costly. This issue is solved with the present invention and instead the composition may be prepared at room temperature.

Substituting the hydroxyl groups of the lignin increases the solubility in organic solvents. Even at low degree of substitution (0.3 equivalents, 25% degree of substitution) the lignin becomes soluble in ethyl acetate, methyl THF, cyclopentyl methyl ether and iso-propanol. This is especially pronounced for C4 or longer ester groups. It is even more pronounced when the ester group is a C6 or longer chain, preferably C8 or longer, or C12 or longer, preferably C14 or longer chain. For the lignin to be dissolved in a carrier liquid such as an oil for example light gas oil (LGO) the degree of substitution may preferably be more than 30% for ester groups of C8 and longer, preferably 50% or more. If the carrier liquid is a mixture of a fatty acid and an oil the esterified lignin becomes more soluble.

The non-esterified groups may be capped for example with an anhydride such as acetic anhydride under common esterification conditions.

One advantage of the present invention is that a higher amount of lignin may be dissolved in a carrier liquid. The amount of lignin or lignin derivatives in the composition according to the present invention may be 4 weight% or more, or 5 weight% or more, or 7 weight% or more, or 10 weight% or more, or 12 weight% or more, or 15 weight% or more, or 20 weight% or more, or 25 weight% or more, or 30 weight% or more, or 40 weight% or more, or 50 weight% or more, or 60 weight% or more, or 70 weight% or more, or 75 weight% or more.
Pre-treatments

When the method of the present invention is performed using black or red liquor the liquor may be pre-treated by evaporation, separation or filtration or via chemical treatments such as the process described below and further defined in WO2012/121659.

The biomass material in the composition may have been treated with the process described in WO2012/121659 which is hereby incorporated by reference. The process relates to reduction of a substrate wherein said substrate can be but is not limited to primary, secondary and tertiary benzylic or allylic alcohol, benzylic or allylic ether, benzylic or allylic carbonyl, and benzylic or allylic ester, or olefins to the corresponding hydrocarbon. The substrate may be lignin or any other compound or polymer comprising said functional group, or black or red liquor. A general method comprises adding a catalyst, a transition metal catalyst, to a reaction flask or container. Adding a solvent mixture of at least two solvents where one of the solvents is water and a base. The mixture is then heated followed by addition of a hydrogen donor and the substrate to be reduced. In order to inhibit disproportionation, a base or carbon dioxide should be added to the solvent mixture and catalyst prior to addition of a hydrogen donor and the substrate. The hydrogen donor may for example be formic acid or an alcohol, it may even be hydrogen gas.

The reduction is performed at a temperature of 40-100°C. In one embodiment the amount of base is not stoichiometric to the amount of the substrate. The biomass material or preferably the separated lignin and lignin derivatives obtained from the reduction method may then be used as the biomass material in the composition according to the present invention. In one embodiment the obtained biomass material from the chemical reduction is further treated with filtration, ultra-filtration or cross-flow ultra-filtration; or treated with acidification and separation such as the Lignoboost® technique for example as described in WO2006/031175.

In another embodiment the composition of the present invention may comprise a biomass material comprising lignin or lignin derivatives obtained through precipitation and separation of lignin and lignin derivatives for example by acidification and separation, such as filtration. Lignoboost® or any other similar separation technique are examples of such technique and may be used. The separated lignin and lignin derivatives may then be used as the biomass material in the composition according to the present invention. In another embodiment the
separated lignin and lignin derivative may further be chemically reduced using the method described above and in WO2012/ 121659.

Another method or a complimentary method for purifying or separating specific components in a biomass material is through filtration, ultra-filtration or cross-flow ultra-filtration. When the biomass material comprises lignin or lignin derivatives, the lignin may be separated in respect to size through any of said filtration techniques. The lignin or lignin derivatives may also be separated in respect to size through a depolymerisation technique; this separation may be performed in combination with filtration, ultra-filtration or cross-flow ultra-filtration. By using filtration, membrane filtration, ultra-filtration or cross-flow ultra-filtration on black or red liquor lignin or lignin derivatives with molecular weights of 10,000 g/mol or less may be separated, preferably the separated lignin or lignin derivatives have a molecular weight of 2,000g/mol or less, such as 1,000 g/mol or less. The separated lignin and lignin derivatives may then be used as the biomass material in the composition according to the present invention. In one embodiment the lignin and lignin derivatives obtained from said filtration may further be chemically reduced using the method described above and in WO2012/ 121659.

The lignin may also be extracted using an appropriate solvent such an alcohol for example methanol, ethanol or iso-propanol.

Applications

The composition according to the present invention may be used in a refinery process or as a pre-step to a refinery process for preparing fuel such as diesel and petrol, or diesel and petrol analogues; or biogasoline or biodiesel; or fuel additives. Any hydrotreatment or hydroprocessing may be used, and any catalytic cracking process may be used. In one embodiment the composition is hydrotreated prior to the catalytic cracking.

The composition according to the present invention may also be used as an additive, for example as a concreted grinding aid, set retarder for cement, strengthener of cement, antioxidant, enhancer of thermal protection, stabilizer in asphalt, emulsifying agent, fiber strengthening additive, cross-linking agent, board binder, anti-corrosion additive, wear resistant additive, antifriction addictive, binder, emulsifier or dispersing agent.
The composition may further be used to prepare foams, plastics, rubbers or paint. The esterified lignin may be used as a cross-linking or curing agent, or as a water absorption inhibitor or as a fluidization agent. Mechanical properties may also be enhanced by the use of the composition. The composition and the method according to the present invention may further be used for preparing fine chemicals such as aromatic compounds using conventional techniques.

The composition may be added to surfaces to obtain dust control, or the composition may be used to prepare batteries.

EXAMPLES

Example 1.

Kraft lignin (0.50 g, 2.78 mmol of repeating unit), Na₂S₂O₄ (0.73 g, 4.19 mmol), water (5 ml) and NaOH (0.16 g) were loaded into a microwave vial with a magnet. The vial was capped, purged with argon and heated at 140 °C for 21 h. The reaction was cooled to room temperature, diluted with water (5 ml) and tetrahydrofuran (5 ml), and acidified with cone. HCl. After phase separation the aqueous phase was further extracted with tetrahydrofuran (10 ml). The combined organic extracts were washed with brine (20 ml) and dried over Na₂SO₄. Evaporation of solvents afforded 0.31 g of brown solid.

Example 2.

As in example 1, following amounts were used: kraft lignin (0.50 g), Na₂S₂O₃ (0.66 g), water (5 ml) and NaOH (0.16 g). The reaction proceeded for 19 h.

Example 3.

As in example 1, following amounts were used: kraft lignin (0.50 g), Na₂SO₃ (0.53 g), water (5 ml) and NaOH (0.16 g). The reaction proceeded for 19 h.

Example 4.

As in example 1, following amounts were used: kraft lignin (0.50 g), Na₂S₂O₃ (0.22 g), Na₂SO₄ (0.35 g), water (5 ml) and NaOH (0.16 g). The reaction proceeded for 19 h.

Example 5.
As in example 1, following amounts were used: kraft lignin (0.10 g), Na2S03 (0.28 g), water (2 ml) and NaOH (62 mg). The reaction proceeded for 19 h.

Example 6.

As in example 1, following amounts were used: kraft lignin (0.10 g), Na2S2O4 (0.22 g), water (2 ml) and NaOH (62 mg). The reaction proceeded for 19 h.

Example 7.

Kraft lignin (10.00 g) and Na2S03 (5.25 g) were suspended in water (100 ml).

Na2S2O5 (3.96 g) (pH around 7) was added and reaction was refluxed under argon for 120 h. SO2 was bubbled through the reaction mixture until pH reached 5. The obtained suspension was filtered to remove most of the solvent, dried in air and grind to give 12.97 g of brown powder.

Example 8

Into 5 microwave vials was benzyl phenyl ether (0.10 g) (model substrate), 2,2'-biphenol (0.10 g), diphenyl ether (0.10 g), bibenzyl (0.10 g) and kraft lignin (0.10 g) added respectively. Each vial was charged with Na2S2O4 (0.20 g) and NaOH (0.16), purged with argon and filled with a suitable solvent: water (2 ml) in 2,2'-biphenol sample, water:dioxane (1:1 ml) in all other samples. The reactions were heated at 140 °C for 16 h. After cooling to room temperature, acidification with cone. HCl, solutions were extracted with chloroform (or THF in kraft lignin sample), dried over Na2SO4 and the solvents were carefully evaporated. The residues were analysed with H NMR and in some cases with GC MS or GPC. The model compounds didn't show any sign of degradation or modification, while the GPC of the kraft lignin reaction displayed the expected depolymerization.

Example 9

Water (5ml) was added to a reaction flask containing Lignoboost® lignin with a dryness of 95% (0.5g, 2.8mmol), sodium hydroxide (0.18g, 4.5mmol) and sodium dithionite (0.37g, 2.1mmol). The flask was sealed and heated during stirring for 5 days at 150°C. After cooling THF (2ml) was added and stirred until all precipitated material had dissolved (~lh). A homogeneous sample was taken, and diluted with THF, for GPC-analysis (figure 2).

Example 10
Water (5ml) was added to a reaction flask containing Lignoboost® lignin with a dryness of 95% (0.503g, 2.8mmol), sodium hydroxide (0.306g, 7.6mmol) and sodium dithionite (3.189g, 18.3mmol). The flask was sealed and heated during stirring for 3 days at 110°C. After cooling THF (2ml) was added and stirred until all precipitated material had dissolved (~1h). A homogeneous sample was taken and diluted with THF, neutralized with HCl filtered and then injected on GPC (figure 3).

Example 11

Water (5ml) was added to a reaction flask containing Lignoboost® lignin with a dryness of 95% (0.496g, 2.8mmol), sodium hydroxide (0.130g, 3.2mmol) and sodium dithionite (0.740g, 4.3mmol). The flask was sealed and heated during stirring for 24h at 140°C. After cooling THF (2ml) was added and stirred until all precipitated material had dissolved (~1h). A homogeneous sample was taken and injected on GPC (figure 4).

Example 12

Lignoboost® lignin with a dryness of 95% was extracted using isopropanol in order to obtain lignin large fractions ("large fraction lignin"). The lignin was isolated using filtration. Water (5ml) was added to a reaction flask containing "large fraction lignin" (0.504g, 2.8mmol), sodium hydroxide (0.127g, 3.2mmol) and sodium dithionite (0.725g, 4.2mmol). The flask was sealed and heated during stirring for 24h at 140°C. After cooling THF (2ml) was added and stirred until all precipitated material had dissolved (~1h). A homogeneous sample was taken and injected on GPC (figure 4).

Example 13

Water (5ml) was added to a reaction flask containing ultrafiltrated lignin (from CleanFlow AB) (0.500g, 2.8mmol), sodium hydroxide (0.150g, 3.8mmol) and sodium dithionite (0.739g, 4.2mmol). The flask was sealed and heated during stirring for 24h at 140°C. After cooling THF (2ml) was added and stirred until all precipitated material had dissolved (~1h). A homogeneous sample was taken and injected on GPC (figure 5).

Example 14

Ultrafiltrated lignin (from MoRe Research Ornskoldsvik AB) (5 ml) and sodium dithionite (0.737g, 4.2mmol) was added to a reaction flask. The flask was sealed
and heated during stirring for 24h at 140°C. After cooling THF (2ml) was added and stirred until all precipitated material had dissolved (~1h). A homogeneous sample was taken and injected on GPC (figure 5).

Example 15

Lignoboost® lignin with a dryness of 95% was extracted using isopropanol in order to obtain lignin large fractions. The lignin was isolated using filtration. Water (5ml) was added to a reaction flask containing "lignin large fractions" (0.5g, 2.8mmol), sodium hydroxide (0.182g, 4.6mmol) and sodium dithionite (0.0487g, 0.28mmol, 0.1 eq). The flask was sealed and heated during stirring for 24h at 140°C. After cooling THF (2ml) was added and stirred until all precipitated material had dissolved (~1h). A homogeneous sample was taken, diluted with THF and injected on GPC (figure 6).

Example 16

Lignoboost® lignin with a dryness of 95% was extracted using isopropanol in order to obtain lignin large fractions. The lignin was isolated using filtration. Water (5ml) was added to a reaction flask containing "lignin large fractions" (0.5g, 2.8mmol), sodium hydroxide (0.159g, 3.9mmol) and sodium dithionite (0.146g, 0.84 mmol, 0.3 eq.). The flask was sealed and heated during stirring for 24h at 140°C. After cooling THF (2ml) was added and stirred until all precipitated material had dissolved (~1h). A homogeneous sample was taken, diluted with THF and injected on GPC (figure 6).

Example 17

Lignoboost® lignin with a dryness of 95% was extracted using isopropanol in order to obtain lignin large fractions. The lignin was isolated using filtration. Water (5ml) was added to a reaction flask containing "lignin large fractions" (0.5g, 2.8mmol), sodium hydroxide (0.171g, 4.2mmol) and sodium dithionite (0.292g, 1.7mmol, 0.6eq). The flask was sealed and heated during stirring for 24h at 140°C. After cooling THF (2ml) was added and stirred until all precipitated material had dissolved (~1h). A homogeneous sample was taken, diluted with THF and injected on GPC (figure 6).

Example 18

Lignoboost® lignin with a dryness of 95% was extracted using isopropanol in order to obtain lignin large fractions. The lignin was isolated using filtration. Water (5ml)
was added to a reaction flask containing "lignin large fractions" (0.5g, 2.8mmol), sodium hydroxide (0.177g, 4.4mmol) and sodium dithionite (0.439g, 2.5mmol, 0.9eq). The flask was sealed and heated during stirring for 24h at 140°C. After cooling THF (2ml) was added and stirred until all precipitated material had dissolved (~1h). A homogeneous sample was taken, diluted with THF and injected on GPC (figure 6).

Example 19

Lignoboost® lignin with a dryness of 95% was extracted using isopropanol in order to obtain lignin large fractions. The lignin was isolated using filtration. Water (5ml) was added to a reaction flask containing "lignin large fractions" (0.5g, 2.8mmol), sodium hydroxide (0.173g, 4.3mmol) and sodium dithionite (0.5846g, 3.4mmol, 1.2eq). The flask was sealed and heated during stirring for 24h at 140°C. After cooling THF (2ml) was added and stirred until all precipitated material had dissolved (~1h). A homogeneous sample was taken, diluted with THF and injected on GPC (figure 6).

Example 20

A microwave (MW)-vial was loaded with kraft lignin (0.50 g, 1 eq, 2.78 mmol), Na₂S₂O₄ (0.73 g, 1.5 eq, 4.19 mmol), water (5 ml) and NaOH (0.16 g, ca 1.5 eq, 4.0 mmol). The vial was heated at 140 °C for 20 hours. After cooling, water (5 ml) and THF (10 ml) were added. The solution was acidified with concentrated HCl and an aqueous phase and an organic phase were formed. The aqueous phase was extracted with THF (10 ml). The combined organic phase was washed with brine (10 ml), dried over Na₂S₂O₄ and solvent was evaporated to afford 0.31 g product.

Example 21

The reaction was performed as in Example 20 with the following amounts: kraft lignin (0.50 g, 1 eq, 2.78 mmol), Na₂S₂O₃ (0.66 g, 1.5 eq, 4.17 mmol), water (5 ml) and NaOH (0.16 g, ca 1.5 eq, 4.0 mmol). After the same work up as in Example 20 the product was analysed by GPC.

Example 22

The reaction was performed as in Example 20 with the following amounts: kraft lignin (0.50 g, 1 eq, 2.78 mmol), Na₂S₂O₃ (0.53 g, 1.5 eq, 4.21 mmol), water (5 ml) and NaOH (0.16 g, ca 1.5 eq, 4.0 mmol). After the same work up as in Example 20
the product was analysed by GPC.

Example 23

The reaction was performed as in Example 20 with following amounts: kraft lignin (0.50 g, 1 eq, 2.78 mmol), Na$_2$S$_2$O$_3$ (0.22 g, 0.5 eq, 1.39 mmol), Na$_2$SO$_3$ (0.35 g, 1 eq, 4.21 mmol), water (5 ml) and NaOH (0.16 g, ca 1.5 eq, 4.0 mmol). After the same work up as in Example 20 the product was analysed by GPC.

Example 24

The reaction was performed as in Example 20 with following amounts: kraft lignin (0.50 g, 1 eq, 2.78 mmol), Na$_2$S$_2$O$_3$ (0.35 g, 1 eq, 2.78 mmol), Na$_2$S$_2$O$_5$ (0.26 g, 0.5 eq, 1.37 mmol), water (5 ml) and NaOH (0.16 g, ca 1.5 eq, 4.0 mmol). After the same work up as in Example 20 the product was analysed by GPC.

Example 25

The reaction was performed as in Example 20 with following amounts: kraft lignin (0.50 g, 1 eq, 2.78 mmol), Na$_2$S$_2$O$_5$ (0.40 g, 0.75 eq, 2.10 mmol), water (5 ml) and NaOH (0.16 g, ca 1.5 eq, 4.0 mmol). After the same work up as in Example 20 the product was analysed by GPC.

Example 26

A solution was prepared from 50% black liquor (10.03 g), water (40 ml) and NaOH (3.15 g, 78.8 mmol) and S0$_2$ was bubbled until pH reached around 6.9. The resulting suspension was transferred with a small amount of water (10 ml) to a flask with a condenser and the content was refluxed for 20 hours. After cooling, water (50 ml) was added, the solution was acidified to pH 3 with concentrated HCl. The solution was saturated with NaCl (s) and extracted with dioxane (2x100 ml), dried over Na$_2$SO$_4$. The removal of solvent afforded 2.09 g of product.

Example 27

As a reference test sulfuric acid was used in the following example. A solution of 50% black liquor (4.00 g) and water (10 ml) was neutralised (pH 7.0) with H$_2$SO$_4$ and heated at 140 °C for 18 hours. After a similar work up as in Example 20 the product was analysed by GPC, no depolymerization was seen.
As a reference test carbon dioxide was used in the following example. A solution of 50% black liquor (4.00 g) and water (10 ml) was neutralised (pH 7.3) with CO₂ (g) and heated at 140 °C for 18 hours. After a similar work up as in Example 20 the product was analysed by GPC, no depolymerization was seen.
CLAIMS

1. A method of depolymerizing lignin comprising:
   a. Providing a lignin containing aqueous solution in a container;
   b. Adding a sulfur containing reducing agent to the solution forming a
      mixture of the sulfur containing agent and the lignin containing
      aqueous solution, wherein the sulfur containing reducing agent is
      added in a 1:2 to 2:1 molar ratio to the repeating unit of lignin;
   c. Leaving the mixture to react.

2. The method of claim 1 wherein the sulfur containing reducing agent is added
   in a 1:1.5 to 1.5:1 molar ratio to the repeating unit of lignin.

3. The method according to claim 1 or 2 wherein the sulfur containing reducing
   agent is sodium dithionite, sodium or potassium sulfite, sodium
   hydroxymethane sulfinate or thiourea oxides.

4. The method according to any one of claims 1 to 3 wherein the pH in the
   mixture is 6.0 or higher, or 6.5 or higher, or 7.0 or higher, or 8.0 or higher,
   or 9.0 or higher.

5. The method according to any one of claims 1 to 4 wherein the reaction is
   performed at 80°C or higher, or 100°C or higher, or 120°C or higher.

6. The method according to any of the preceding claims wherein the obtained
   weight average molecular weight of the obtained depolymerized lignin is 400-
   1000 g/mol, for example 500-900 g/mol.

7. The method according to any of the preceding claims wherein the lignin is
   pre-treated by extraction using an appropriate solvent or ultrafiltration.

8. The method according to any of the preceding claims wherein the weight
   ratio of water to lignin is 20:1 or higher.

9. The method according to any of the preceding claims wherein the pressure in
   the container is 4 bar or higher.

10. Depolymerized lignin obtained by the method according to claims 1 to 9.

11. A composition comprising depolymerized lignin according to claim 10, a
    carrier liquid and optionally a solvent.

12. A composition comprising depolymerized lignin according to claim 10 and an
    organic solvent.
13. The composition according to claim 11 or 12 wherein the lignin concentration is at least 10 weight%, or at least 20 weight%, or preferably at least 30 weight%.

14. The composition according to any one of claims 11 or 12 wherein the depolymerized lignin is esterified.

15. The composition according to claim 14 wherein the degree of esterification is 10% to 100%, for example 20% or more, 30% or more, or 40% or more, or 60% or more or 80% or more, or 99% or more, or 100%.

16. The composition according to any one of claim 14 or 15 wherein the depolymerized lignin is esterified with a fatty acid or C2-C40 carboxylic ester.

17. The composition according to any one of claims 11 or 12 wherein the solvent concentration is not more than 66 weight%, or 60 weight% or less, or 55 weight% or less, or 50 weight% or less or 45 weight% or less, or 35 weight% or less, or 20 weight% or less, or 10 weight% or less.

18. The composition according to any one of claims 11 or 12 wherein the solvent is selected from THF, 1,4-dioxane, furfural, methanol, ethanol or iso-propanol, methyl acetate or ethyl acetate or a mixture thereof.

19. The use of the depolymerized lignin or the composition according to any one of claim 10 to 18 for preparing fuel.

20. A fuel obtained by hydrotreating or hydro cracking the depolymerized lignin or the composition according to any one of claim 10 to 18.
Figure 4.

Figure 5.

Figure 6.
Figure 7.

Figure 8.

Figure 9.
### A. CLASSIFICATION OF SUBJECT MATTER

**IPC**: 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**: C07C, C07G, C08H, C08L, C10L

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

SE, DK, FI, NO classes as above

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

EPO-Internal, PAJ, WPI data, COMPENDEX, IBM-TDB

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>A</td>
<td>WO 2013135485 A1 (BTU COTTBUS), 19 September 2013 (2013-09-19); page 4, line 36 - line 41</td>
<td>1-20</td>
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<td>A</td>
<td>WO 2013130101 A1 (EMPIRE TECHNOLOGY DEV LLC ET AL), 6 September 2013 (2013-09-06); paragraph [0040]</td>
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<td>A</td>
<td>US 2002021991 0 A1 (LIGHTNER GENE E), 19 September 2002 (2002-09-19); claims 1, 6</td>
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<td>A</td>
<td>US 20030221 804 A1 (LIGHTNER GENE E), 4 December 2003 (2003-12-04); paragraph [0008]</td>
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Further documents are listed in the continuation of Box C.

See patent family annex.

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Form PCT/ISA/210 (second sheet) (January 2015)
Continuation of: second sheet

International Patent Classification (IPC)

C08H 7/00 (2011.01)
C07C 37/52 (2006.01)
C07C 37/54 (2006.01)
C07G 7/00 (2011.01)
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C10L 1/183 (2006.01)
C08L 97/02 (2006.01)
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