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(71) Applicant: SHELL INTERNATIONALE RESEARCH
MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan
30, NL-2596 HR The Hague (NL).(71) Applicant (for US only): SHELL OIL COMPANY
[US/US]; P.O. Box 2463, One Shell Plaza, Houston, Texas
77252-2463 (US).(72) Inventors: WANG, Haisong; 189 Songling Road,
Laoshan District, Qingdao, Shandong 266101 (CN). LIU,
Chao; 189 Songling Road, Laoshan District, Qingdao,
Shandong 266101 (CN). MU, Xingdong; 189 Songling
Road, Laoshan District, Qingdao, Shandong 266101 (CN).
VAN DER HEIDE, Evert; Grasweg 31, NL-1031 HW
Amsterdam (NL). YU, Guang; 189 Songling Road,
Laoshan District, Qingdao, Shandong 266101 (CN).(74) Agent: MATTHEZING, Robert Maarten; P.O. Box 384,
NL-2501 CJ The Hague (NL).

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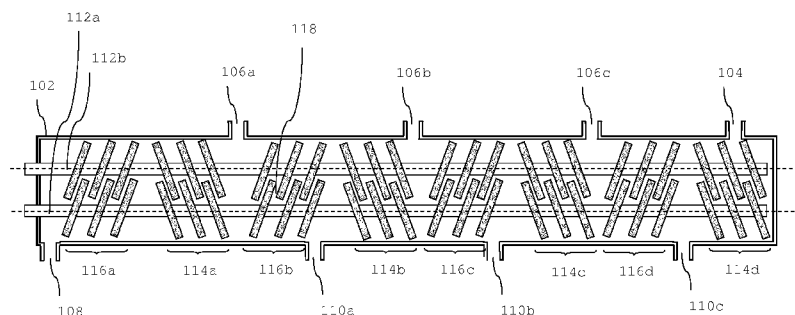
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(54) Title: PROCESS FOR PRETREATING A LIGNOCELLULOSIC MATERIAL

Figure 1



(57) Abstract: A process for pretreating a lignocellulosic material having a lignin content in the range from equal to or more than 10 wt% to equal to or less than 50 wt%, based on the total weight of the lignocellulosic material, which process comprises: mixing the lignocellulosic material and an alkaline aqueous solution, which alkaline aqueous solution has a pH of equal to or more than 9.0, in a solid to liquid weight ratio of equal to or more than 25:75 to equal to or less than 60:40, in a mixer to produce an aqueous slurry; and heat-treating the aqueous slurry at a temperature in the range from equal to or more than 50°C to equal to or less than 200°C to produce a heat-treated aqueous slurry comprising a pretreated lignocellulosic material.

PROCESS FOR PRETREATING A LIGNOCELLULOSIC MATERIAL

Technical field of the invention

The present invention relates to a process for
5 pretreating a lignocellulosic material.

Background to the invention

With the diminishing supply of crude mineral oil, use of
renewable energy sources is becoming increasingly important
for the production of fuels and chemicals. These fuels and
10 chemicals from renewable energy sources are often referred to
as biofuels, respectively biochemicals. One of the advantages
of using renewable energy sources is that the CO₂ balance is
more favorable as compared with a conventional feedstock of a
mineral source.

15 Biofuels and/or biochemicals derived from non-edible
renewable energy sources, such as lignocellulosic material,
are preferred as these do not compete with food production.
These biofuels and/or biochemicals are also referred to as
second generation or advanced biofuels and/or biochemicals.
20 Also for the production of bio-ethanol it would be preferred
to produce such from a lignocellulosic material.

A wide variety of methods for converting lignocellulosic
material into biofuels and/or biochemicals is available. The
digestibility of a lignocellulosic material, however, is
25 hindered by physical, chemical, structural and compositional
factors that give the lignocellulosic material the strength
that is needed in nature. Many of the conversion methods for
lignocellulosic materials therefore have in common that first
a pretreatment of the lignocellulosic material is required.

30 The production of bio-ethanol from a lignocellulosic
material may for example comprise as main steps: the
pretreatment of the lignocellulosic material to make the
cellulose and/or hemicellulose in the lignocellulosic

material accessible; hydrolysis of the cellulose and/or hemicellulose to produce sugars; and fermentation of the sugars to bioethanol.

The production of other biofuels and biochemicals, such as for example biodiesel, preferably also comprise a pretreatment step.

Kumar et al explain in their article titled "Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production", published in Ind. Eng. Chem. Res. 2009, volume 48, page 3713-3729, that there are several categories of pretreatment methods including: physical (milling and grinding), physicochemical (steam pretreatment/autohydrolysis, hydrothermolysis and wet oxidation), chemical (alkali, dilute acid, oxidizing agents and organic solvents), biological, electrical or a combination of these.

Alvira et al in their article titled "Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: a review", published in Bioresource Technology 101 (2010), pages 5851-4861 indicate that alkali pretreatments increase cellulose digestibility and that they are more effective for lignin solubilization, exhibiting minor cellulose and hemicellulose solubilization, than acid or hydrothermal processes. As suitable alkaline pretreatments sodium, potassium, and calcium hydroxides are mentioned.

Descriptions in the prior art of alkaline pretreatment methods of a solution of lignocellulosic material with a dry matter content of more than 15 wt% are rare.

Kumar et al. describe a radio-frequency-assisted alkali pretreatment carried out at a 20% solids content and 90°C with Alkali loadings of 0.1 to 0.25 grams of NaOH per gram of biomass.

Cheng et al. in their article titled "Evaluation of High Solids Alkaline Pretreatment of Rice Straw" describe studies with NaOH done at 55°C with a water loading of 5 grams water per gram air dried rice straw (i.e. a dry matter content of about 20 wt%) with an alkaline loading of 0,2 and 4 wt% of oven dried rice staw.

Li et al. in their article titled "Cold sodium hydroxide/urea based pretreatment of bamboo for bioethanol production: characterization of the cellulose rich fraction" describe bamboo being ground and sieved to obtain a 40-60 mesh fraction which fraction was extracted with methylbenzene/ethanol to remove fats, waxes and oils and then air dried and subsequently ball-milled. A milled sample was suspended in a 95% ethanol solution for 5 minutes and then subjected to ultrasound irradiation treatment in a ultrasonic cell crusher machine. The sample was filtrated and the residue air dried. The residue was submitted to an alkaline treatment with 7% NaOH/12% urea.

Nlewem et al, in their article titled "Comparison of different pretreatment methods based on residual lignin effect on the enzymatic hydrolysis of switch grass" describe samples of switchgrass being soaked in NaOH solutions of concentrations ranging from 0.5 to 10% w/v at a biomass loading of 0.15 g/ml and a temperature of 85-90°C for 1 hour.

Chinese Patent Application CN101121175A is directed to the problem that biological or physical or chemical processing of straw takes a long time and the degradation rate is low because the straw lignin and fibrin are hard to be degraded. As a solution it describes a pretreatment method using alkali and ozone. The method includes crushing the straw and mixing it with limewater. In the method, the dry matter of straw is about 3%-15% and the

concentration of sodium hydroxide (NaOH) is about 0.3%-1%. The obtained mixture is subsequently treated with ozone.

Chinese Patent Application CN101255479 describes a pretreatment method for saccharifying lignocellulose. In the described pretreatment, ground lignocellulose (20-60 mesh) may be mixed with an alkali solution containing for example sodium hydroxide (NaOH) or potassium hydroxide (KOH) in a concentration of 0.1% to 3%. The liquid solid ratio may lie in the range from 4:1 to 12:1. The described pretreatment process does not appear to need the addition of steam but performs pretreatment at normal temperature condition during about 1 to 4 hours. In the examples solid yields in the range from about 75% to about 93% are obtained. After enzymolysis sugar yields in the range from about 23% to about 53% are obtained. The cellulose conversion rate varied between about 48% and about 51 %.

When scaling up to a commercial process, however, the large amounts of water and low dry matter content applied in the processes of the prior art would make the prior art pretreatment processes too expensive to use.

It would therefore be an advancement in the art to provide a pretreatment process that allows one to use a feed having a dry matter content of at least 25 wt%.

Lamsal et al. in their article titled "Extrusion as a thermo-chemical pretreatment for lignocellulosic ethanol", published in Biomass and Bioenergy vol. 34 (2010) pages 1703-1710, describe the mixing of a solution of sodium hydroxide, urea and thiourea (10wt% each) with wheat bran to achieve a moisture content of 20-25% w/w (i.e. 75%-80% dry matter) and soybean hull to achieve a moisture content of 30 and 35% w/w (i.e. 65%-70% dry matter). Samples were stored overnight at ambient temperature for equilibration and subsequently extruded at 7 Hz and maximum barrel temperature of 150°C in a

twin-screw extruder. Lamsal et al. explain that the sugar yield from wheat bran, which wheat bran had a lignin content of approximately 7% w/w resulted in a sugar yield from 18 to 20%. Lamsal et al. explain, however, that sugar yields (9-
5 12%) from soybean hull, which soybean hull had a lignin content of 14%, were much lower than wheat bran irrespective of the pre-treatment method. In fact, the preliminary data indicated that extrusion negatively affected sugar release as compared to hammer milling. Lamsal et al. further suggest
10 that extrusion may have led to a greater complexation of the hemicellulose and lignin fractions resulting in even lower sugar yields.

It would be an advancement in the art to provide a pretreatment process that allows one to apply a feed with
15 a dry matter content of at least 25 wt% for a lignocellulosic material containing equal to or more than 10 wt% lignin.

Summary of the invention

Such a process has now been found. Accordingly the
20 present invention provides a process for pretreating a lignocellulosic material having a lignin content in the range from equal to or more than 10 wt% to equal to or less than 50 wt%, based on the total weight of the lignocellulosic material, which process comprises:

25 mixing the lignocellulosic material and an alkaline aqueous solution, which alkaline aqueous solution has a pH of equal to or more than 9.0, in a solid to liquid weight ratio of equal to or more than 25:75 to equal to or less than 60:40, in a mixer to produce an aqueous slurry;

30 and heat-treating the aqueous slurry at a temperature in the range from equal to or more than 50°C to equal to or less than 200°C to produce a heat-treated aqueous slurry comprising a pretreated lignocellulosic material.

As indicated above, Lamsal et al. suggest that for lignocellulosic materials having a higher lignin content (for example 14 wt%) extrusion may lead to a greater complexation of the hemicellulose and lignin fractions resulting in even lower sugar yields. It has now been found, however, that this does not apply in the process according to the invention. To the contrary, surprisingly it was found that when applying a solid to liquid weight ratio in the claimed range, improved sugar yields - even as high as 50 wt% - may be obtained.

10 Brief description of the drawings

The invention has been illustrated by the following non-limiting following figures:

Figure 1 shows a shear mixer that can be used in an embodiment according to the invention.

15 Figure 2 shows a schematic flowsheet of an embodiment according to the invention.

Detailed description of the invention

By a lignocellulosic material is herein understood a material containing cellulose, hemicellulose and lignin.

20 Suitably the lignocellulosic material is a solid lignocellulosic material. The lignocellulosic material may be obtained from a wide variety of sources, including for example plants, forestry residues, agricultural residues, herbaceous material, municipal solid wastes, waste and recycled paper, pulp and paper mill residues, sugar processing residues and/or combinations of one or more of the above.

The lignocellulosic material can comprise for example, corn stover, wheat stover, soybean stover, corn cobs, corn fibre, straw (including cereal straws such as wheat straw, 30 barley straw, rye straw and/or oat straw), bagasse, beet pulp, miscanthus, sorghum residue, rice straw, rice hulls, oat hulls, grasses (including switch grass, cord grass, rye

grass, reed canary grass or a combination thereof), bamboo, water hyacinth, wood and wood-related materials (including hardwood, hardwood chips, hardwood pulp, softwood, softwood chips, softwood pulp and/or sawdust), waste paper and/or a combination of one or more of these.

The lignocellulosic material is a lignocellulosic material having a lignin content in the range from equal to or more than 10 wt% to equal to or less than 50wt%, based on the total weight of the lignocellulosic material. The lignocellulosic material preferably has a lignin content of equal to or more than 14 wt%, more preferably equal to or more than 15wt%, still more preferably equal to or more than 16 wt% and most preferably equal to or more than 17%, based on the total weight of the lignocellulosic material.

Further the lignocellulosic material preferably has a lignin content of equal to or less than 40 wt%, more preferably of equal to or less than 35 wt%, and most preferably equal to or less than 30 wt%, based on the total weight of the lignocellulosic material. Preferably the lignocellulosic material contains in the range from equal to or more than 15 wt% lignin to equal to or less than 40 wt% lignin, based on the total weight of the lignocellulosic material.

For example, willow wood may contain about 25 wt% lignin, larch wood may contain about 35 wt% lignin, straw may contain about 14 wt% lignin, beech wood may contain about 12-23 wt% lignin and coniferous wood may contain about 25-35 wt% lignin.

Suitably the weight percentages based on the total weight of the lignocellulosic material herein are determined on the total weight of the lignocellulosic material on a dry basis.

The lignin may for example include polymers of p-coumaryl alcohol, coniferyl alcohol, sinapyl alcohol, methoxylated coumaryl alcohol, methoxylated coniferyl alcohol, methoxylated sinapyl alcohol and mixtures thereof.

5 The lignocellulosic material preferably contains equal to or more than 20 wt%, more preferably equal to or more than 30 wt% and most preferably equal to or more than 40 wt% cellulose, based on the total weight of the lignocellulosic material. Preferably the lignocellulosic material contains
10 equal to or less 90 wt%, more preferably equal to or less than 85 wt% cellulose, based on the total weight of the lignocellulosic material. For example the lignocellulosic material may comprise in the range from equal to or more than 20wt% to equal to or less than 90 wt% cellulose, suitably in
15 the range from equal to or more than 30wt% to equal to or less than 80 wt% cellulose, based on the total weight of the lignocellulosic material.

 In a preferred embodiment the lignocellulosic material is washed one or more times with water before being supplied to
20 the mixer.

 The lignocellulosic material may be supplied to the mixer as a wetted lignocellulosic material comprising both lignocellulosic material and water, whereafter the wetted lignocellulosic material is mixed with the alkaline aqueous
25 solution.

 Preferably, however, the lignocellulosic material is supplied to the mixer as a dewatered and/or deaired lignocellulosic material; and/or the lignocellulosic material is dewatered and/or deaired during mixing with the alkaline
30 aqueous solution in the mixer (for example in an extruder). This may for example be achieved by drying and/or deairing of the lignocellulosic material before mixing it with the alkaline aqueous solution. Mixing of the alkaline aqueous

solution and a lignocellulosic material, which lignocellulosic material has been dewatered and/or deaired, may advantageously improve penetration of the lignocellulosic material with the alkaline aqueous solution.

5 If the lignocellulosic material is supplied to the process as a feed comprising both lignocellulosic material and water, the feed preferably has a solid to liquid weight ratio of equal to or more than 25:75 to equal to or less than 60:40 (i.e. the feed contains in the range from equal
10 to or more than 25wt% to equal to or less than 60wt% of dry matter).

 If the lignocellulosic material is supplied to the process as a dewatered feed, the feed preferably has a solid to liquid weight ratio of equal to or more than 40:60 to
15 equal to or less than 90:10 (i.e. the feed contains in the range from equal to or more than 40wt% to equal to or less than 90wt% of dry matter).

 In the process according to the invention the lignocellulosic material is mixed with an alkaline aqueous
20 solution. By an "alkaline aqueous solution" is herein understood an aqueous solution having a pH of equal to or more than 7.0. In the process according to the invention, the lignocellulosic material is mixed with an alkaline aqueous solution having a pH of equal to or more than 9.0.
25 Preferably the alkaline aqueous solution has a pH of equal to or more than 11.0, more preferably a pH of equal to or more than 12.0. More preferably the alkaline aqueous solution has a pH in the range from equal to or more than 9.0 to equal to or less than 15.0, still more preferably a
30 pH in the range from equal to or more than 11.0 to equal to or less than 14.5, and most preferably a pH in the range from equal to or more than 12.0 to equal to or less than 14.0.

The alkaline aqueous solution suitably comprises an alkaline pretreatment agent. Preferably such an alkaline pretreatment agent is chosen from the group consisting of sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate sodium sulfide, potassium sulfide and mixtures thereof. In a preferred embodiment the alkaline aqueous solution is an alkaline aqueous solution comprising sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate or mixtures thereof. More preferably the alkaline aqueous solution is an alkaline aqueous solution containing sodium hydroxide and/or potassium hydroxide. Most preferably the alkaline aqueous solution is an alkaline aqueous solution containing sodium hydroxide.

If the alkaline aqueous solution is an alkaline aqueous solution containing sodium hydroxide, such alkaline aqueous solution preferably contains in the range from 0.04 gram/liter to 500 gram/liter of sodium hydroxide, more preferably in the range from 4 gram/liter to 450 gram/liter of sodium hydroxide, still more preferably in the range from 10 to 300 gram/liter of sodium hydroxide, and most preferably in the range from 20 to 80 gram/liter of sodium hydroxide.

In the process according to the invention, the lignocellulosic material and the alkaline aqueous solution are mixed in a solid to liquid weight ratio of equal to or more than 25:75 to equal to or less than 60:40. By a solid to liquid weight ratio of equal to or more than 25:75 to equal to or less than 60:40 is herein preferably understood that an aqueous slurry is formed that appropriately has a dry matter content in the range from equal to or more than 25 wt% to equal to or less than 60 wt%, based on the total weight of the aqueous slurry.

Preferably the lignocellulosic material and the alkaline aqueous solution are mixed in a solid to liquid weight ratio of equal to or more than 30:70, more preferably equal to or more than 32:68. Further the

5 lignocellulosic material and the alkaline aqueous solution are preferably mixed in a solid to liquid weight ratio of equal to or less than 55:45. Most preferably the lignocellulosic material and the alkaline aqueous solution are mixed in a solid to liquid weight ratio of equal to or

10 more than 30:70 to equal to or less than 55:45.

During mixing suitably a sufficient amount of alkaline aqueous solution and/or additional water and/or steam may be added to bring the solid to liquid weight ratio into the claimed solid to liquid weight ratio. The exact amount

15 of alkaline aqueous solution and/or additional water and/or steam to be added to the mixer may depend on the amount of water that may already be provided in a feed comprising the lignocellulosic material.

In one embodiment the lignocellulosic material may be

20 supplied to the mixer as a feed comprising both lignocellulosic material and water (herein also referred to as wetted lignocellulosic material), as described in more detail above. When such a wetted lignocellulosic material is used, the wetted lignocellulosic material is

25 preferably mixed in the mixer with a suitable amount of alkaline aqueous solution to provide an aqueous slurry having the claimed solid to liquid weight ratio.

In another embodiment the lignocellulosic material may be supplied to the process as a dewatered lignocellulosic

30 material as described in more detail above. When such a dewatered lignocellulosic material is used, the dewatered lignocellulosic material is preferably mixed in the mixer with a suitable amount of alkaline aqueous solution and/or

additional water and/or steam to provide an aqueous slurry having the claimed a solid to liquid weight ratio.

The lignocellulosic material and alkaline aqueous solution are mixed in a mixer to produce an aqueous slurry.

5 A wide range of mixers may be used including for example extruders, screw mixers, CSTR type mixers , squeezer-type mixers and grinder-type mixers.

In a preferred embodiment the mixer comprises or consists of one or more a shear mixer(s). By a shear mixer
10 is herein preferably understood a mixer that is suitable to disperse a solid into a liquid phase by applying shear force. In the process according to the invention a shear mixer may advantageously improve penetration of the internal structure of the lignocellulosic material with the
15 alkaline aqueous solution by applying shear force to the aqueous slurry. By shear force is herein preferably understood a force applied in a direction co-planar to a material cross-section. Application of such shear force may cause one layer of lignocellulosic material to slide over
20 another layer of lignocellulosic material and/or over a fixed surface. The energy applied by the shear mixer is herein referred to as shear energy.

As explained in respect to screw conveyers in R.H. Perry, C.H. Chilton, Chemical Engineers' Handbook, McGraw-Hill Chemical Engineering Series, 5th ed., McGraw-Hill Book
25 Company, New York, 1973, Section 7, p.6. "required power is made up of two components: that necessary to drive the screw empty and that necessary to move the material. The first component is a function of conveyer length, speed of
30 rotation, and friction in the conveyor bearings. The second is a function of the total weight of material conveyed per unit of time, conveyed length, and depth to which the trough is loaded. The latter power item is in turn a function of the

internal friction and friction on metal of the conveyed material". Preferably shear energy is understood to refer to this internal friction and friction on metal of the conveyed material.

5 Shear energy can be determined by determining the energy needed to operate the mixer after loading the mixer with the lignocellulosic material and subtracting the energy input needed to operate the mixer without loading (i.e. when empty).

10 In a preferred embodiment the shear energy applied by the shear mixer is in the range of from equal to or more than 1% to equal to or less than 25%, more preferably equal to or more than 2% to equal to or less than 10% of the gross energy contained in the lignocellulosic material. The
15 gross energy (sometimes also referred to as higher heating value HHV or gross calorific value) of the lignocellulosic material is equal to its thermodynamic heat of combustion and can be determined at a standard temperature of 25°C. If so desired, one may for example use ASTM D5865 - 11a
20 Standard Test Method for Gross Calorific Value of Coal and Coke to determine the gross energy.

In another preferred embodiment the shear energy applied by the shear mixer lies in the range from equal to or more than 0.05 MegaJoule to equal to or less than 25
25 MegaJoule per kilogram of lignocellulosic material (as measured at a dry basis). More preferably the shear energy applied by the shear mixer lies in the range from equal to or more than 0.10 MegaJoule to equal to or less than 2.0 MegaJoule per kilogram of lignocellulosic material (as
30 measured at a dry basis). Most preferably the shear energy applied by the shear mixer lies in the range from equal to or more than 0.10 to equal to or less than 0.20 MegaJoule

per kilogram of lignocellulosic material (as measured at a dry basis).

Preferably the one or more shear mixer(s) comprise or consist of one or more screw mixer(s), one or more
5 extruder(s) or a combination thereof.

In one preferred embodiment the shear mixer comprises or is a screw mixer. The screw mixer preferably comprises a tubular shaped vessel containing a screw. Preferably the tubular shaped vessel is oriented in an essentially
10 horizontal direction. Via the screw, shear energy can be applied to the lignocellulosic material. In a preferred embodiment the shear mixer is a screw reactor. Such a screw reactor comprises a tubular shaped reactor containing a screw. The screw in such a screw reactor may advantageously
15 forward the lignocellulosic material from the inlet of the reactor to the outlet of the reactor and in addition mix the lignocellulosic material with a liquid. Advantageously the screw can be used to apply shear energy to the lignocellulosic material.

20 In another preferred embodiment the shear mixer comprises or is an extruder. Preferably the extruder is a single screw extruder or a twin screw extruder. Most preferably the shear mixer is a twin screw extruder. A schematic example of a twin screw extruder is provided in figure 1. Figure 1 shows a twin
25 screw extruder (102) having a solids inlet (104) for lignocellulosic material; several liquid inlets (106 a, b and c) for water and/or the alkaline aqueous solution; a slurry outlet (108) for the aqueous slurry and several liquid outlets (110 a, b and c). The twin screw extruder (102)
30 further comprises two parallel screws (112 a and b) that rotate in the same direction. The helixes of the two screws are forward directed (114a, b, c and d) and reverse directed (116 a, b, c and d) in an alternate manner. In the space

between the helixes (118) shear energy can be applied to the lignocellulosic material and/or the aqueous slurry.

Advantageously the process according to the invention can be carried out without preheating of the lignocellulosic material before mixing it with the alkaline aqueous solution; and/or without applying external heating during the mixing of the lignocellulosic material and the alkaline aqueous solution. Due to the friction between the fibers of the lignocellulosic material and the friction between the lignocellulosic material and the mixer, a substantial amount of friction heat may be generated. In the process of the invention, friction heat that may be in-situ generated during the mixing of the lignocellulosic material and the alkaline aqueous solution may advantageously be used to increase the temperature. The use of a shear mixer is especially advantageous in this respect as the use of a shear mixer increases the amount of friction heat that may be generated. If the mixer is a shear mixer the friction heat may be generated by the shear energy as described herein before, and the friction heat may also be referred to as shear energy.

If so desired, external heating may be applied in addition to the friction heat. Advantageously the amount of external heating may be limited to providing a further temperature increase (ΔT) in the range from equal to or more than 5°C to equal to or less than 100°C, more preferably in the range equal to or more than 5°C to equal to or less than 30°C.

In one embodiment, the lignocellulosic material and optionally water may be supplied to a shear mixer; after dewatering and deairing the lignocellulosic material within such shear mixer, the lignocellulosic material may be mixed with the alkaline aqueous solution in the same or another shear mixer. Preferably the shear mixer for this embodiment

is a twin screw extruder as illustrated in figure 1, wherein
an, optionally wetted, lignocelulosic material is supplied
at a solids inlet (104); a part of water is added to the
lignocellulosic material at a first liquid inlet (106c) along
5 the extruder; at least part of the water is removed via one
or more liquid outlets (110c and 110b) of the extruder;

followed by one or more parts of an alkaline aqueous solution
being added to the lignocellulosic material at one or more
subsequent liquid inlets (for example at 106a and/or 106b)

10 along the extruder. In this embodiment, outlet 110a is
preferably closed before liquid inlet 106b is opened for
addition of any alkaline aqueous solution, to avoid the
unnecessary loss of alkaline aqueous solution. Suitably
residual alkaline aqueous solution and/or water and/or any
15 dissolved lignin may be removed via one or more of the liquid
outlets (110a and/or 110b). The aqueous slurry comprising the
pretreated lignocellulosic material can be obtained from
outlet (108).

Within the process of the invention it may be
20 advantageous to feed the alkaline aqueous solution to the
mixer in a staged manner. For example the alkaline aqueous
solution may be added to the mixer via two or more subsequent
inlets. More preferably the alkaline aqueous solution is fed
to the mixer via two or more subsequent inlets; and water
25 and/or residual alkaline aqueous solution and/or any
dissolved lignin is removed from the mixer via two or more
subsequent outlets. Feeding the alkaline aqueous solution to
the mixer in a staged manner may advantageously result in a
better wetting of the lignocellulosic material. In addition
30 removal of water and/or residual alkaline aqueous solution
and/or any dissolved lignin via two or more outlets may
result in an improved removal of for example dirt and soil.

Mixing of the lignocellulosic material and the alkaline aqueous solution in the mixer may be carried out at a wide range of temperatures and pressures. In a preferred embodiment, the mixing is carried out at a temperature in the range from equal to or more than 50°C to equal to or less than 150°C, more preferably equal to or more than 50°C to equal to or less than 120°C, still more preferably at a temperature in the range from equal to or more than 65°C to equal to or less than 100°C, most preferably at a temperature in the range from equal to or more than 90°C to equal to or less than 96°C. Preferably the mixing is carried out at a pressure in the range from equal to or more than 0.1 MegaPascal (about 1 bar) to equal to or less than 2.0 MegaPascal (about 20 bar), more preferably a pressure of about 0.1 MegaPascal.

Further the residence time of the lignocellulosic material in the mixer may vary widely. Preferably this residence time of the lignocellulosic material in the mixer is equal to or more than 10 seconds, more preferably equal to or more than 20 seconds, still more preferably equal to or more than 1 minutes, and most preferably equal to or more than 2 minutes. Preferably the residence time of the lignocellulosic material in the mixer is further equal to or less than 10 hours, more preferably equal to or less than 5 hours, still more preferably equal to or less than 1 hour, and most preferably equal to or less than 30 minutes. More preferably the residence time of the lignocellulosic material in the mixer ranges from equal to or more than 10 seconds to equal to or less than 2 hours, even more preferably from equal to or more than 20 seconds to equal to or less than 1 hour. Most preferably the residence time ranges from equal to or more than 1 minute to equal to or less than 20 minutes.

In the mixer an aqueous slurry is produced. The aqueous slurry preferably comprises pretreated lignocellulosic material, water, and optionally some dissolved alkaline pretreatment agent. Preferably the aqueous slurry has a dry matter content in the range from equal to or more than 25 wt% to equal to or less than 60 wt%, based on the total weight of the aqueous slurry, more preferably a dry matter content in the range from equal to or more than 30 wt% to equal to or less than 55 wt%, based on the total weight of the aqueous slurry. Further the aqueous slurry preferably has a pH of equal to or more than 9.0, more preferably of equal to or more than 10.0 and most preferably of equal to or more than 11.0. Most preferably the aqueous slurry has a pH in the range from equal to or more than 9.0 or more than 11.0 to equal to or less than 14.0.

In the process according to the invention the aqueous slurry is heat-treated at a temperature in the range from equal to or more than 50°C to equal to or less than 200°C.

The pressure during this heat-treatment is preferably similar to the pressure in the mixer and is preferably a pressure in the range from equal to or more than 0.1 MegaPascal (1 bar) to equal to or less than 2.0 MegaPascal (20 bar), more preferably a pressure of about 0.1 MegaPascal.

The mixing of the lignocellulosic material and the alkaline aqueous solution and the heat-treating can be carried out in sequence or simultaneously.

In one embodiment the mixing and heat-treating are carried out simultaneously in one step and the invention advantageously provides a process for pretreating a lignocellulosic material having a lignin content in the range from equal to or more than 10 wt% to equal to or

less than 50 wt%, based on the total weight of the lignocellulosic material, which process comprises: mixing the lignocellulosic material and an alkaline aqueous solution, which alkaline aqueous solution has a pH
5 of equal to or more than 9.0, at a temperature in the range from equal to or more than 50°C to equal to or less than 200°C, more preferably to equal to or less than 150°C, in a solid to liquid weight ratio of equal to or more than 25:75 to equal to or less than 60:40, in a mixer
10 to produce a heat-treated aqueous slurry comprising a pretreated lignocellulosic material. This process is hereafter also referred to as one-step process.

Preferences for such a one-step process, for example preferences for the mixer and the aqueous slurry, are as
15 described herein above in general.

Preferably the mixer in such a one-step process is a shear mixer as described herein above.

In such a one-step process the residence time of the lignocellulosic material in the mixer more preferably
20 ranges from equal to or more than 20 seconds to equal to or less than 10 hours, even more preferably from equal to or more than 1 minute to equal to or less than 5 hours; and most preferably from equal to or more than 20 minutes to equal to or less than 2 hours.

25 In another embodiment the mixing and heat-treating are carried out in a two-step process and the invention advantageously provides a process for pretreating a lignocellulosic material having a lignin content in the range from equal to or more than 10 wt% to equal to or
30 less than 50 wt%, based on the total weight of the lignocellulosic material, which process comprises:

mixing the lignocellulosic material and an alkaline aqueous solution, which alkaline aqueous solution has a pH

of equal to or more than 9.0, in a solid to liquid weight ratio of equal to or more than 25:75 to equal to or less than 60:40, in a mixer to produce an aqueous slurry;

transporting the aqueous slurry from the mixer into a
5 reaction vessel; and

heat-treating the aqueous slurry in the reaction vessel at a temperature in the range from equal to or more than 50°C to equal to or less than 200°C to produce a heat-treated aqueous slurry comprising a pretreated
10 lignocellulosic material. This process is hereafter also referred to as two-step process. Preferences for such a two-step process, for example preferences for the mixer and the aqueous slurry, are as described herein above in general.

15 Preferably the mixer in such a two-step process is a shear mixer as described herein above.

In such a two-step process the temperature applied during the mixing step may advantageously differ from the temperature applied during the heat-treating step. In the
20 two-step process the lignocellulosic material and the alkaline aqueous solution are preferably mixed in the mixer at a temperature equal to or below 150°C, more preferably at a temperature equal to or below 120°C and even more preferably at a temperature equal to or below
25 100°C. Still more preferably the lignocellulosic material and the alkaline aqueous solution are mixed in the mixer at a temperature in the range from equal to or more than 20°C to equal to or less than 120°C, even more preferably in the range from equal to or more than 50°C to equal to
30 or less than 120°C and still more preferably in the range from equal to or more than 50°C to equal to or less than 100°C. Most preferably the two-step process comprises mixing of the lignocellulosic material and the alkaline

aqueous solution at a temperature in the range from equal to or more than 80°C to equal to or less than 96°C. The pressure during the mixing step in the two-step process is preferably about 0.1 MegaPascal.

5 The temperature during the heat-treating step in the two-step process is preferably equal to or higher than the temperature during the mixing step. In the two-step process the aqueous slurry is preferably heat-treated in the reaction vessel at a temperature in the range from
10 equal to or more than 65°C to equal to or less than 200°C, more preferably in the range from equal to or more than 100°C to equal to or less than 150°C. The pressure during the heat-treating step in the two-step process is preferably a pressure in the range from equal to or more
15 than 0.0 to equal to or less than 1.6 MegaPascal.

Such a two-step process may further have the advantages that the residence time in the mixer may be reduced allowing for a higher throughput during commercial operation. Preferably the residence time in the mixer is
20 equal to or lower than the residence time in the reaction vessel.

In the above two-step process the residence time of the lignocellulosic material in the mixer preferably ranges from equal to or more than 10 seconds to equal to
25 or less than 2 hours, more preferably from equal to or more than 20 seconds to equal to or less than 1 hour. Most preferably from equal to or more than 1 minutes to equal to or less than 20 minutes.

The residence time of the aqueous slurry in the
30 reaction vessel may vary widely. Preferably the residence time of the aqueous slurry in the reaction vessel ranges from equal to or more than 1 minute to equal to or less

than 10 hours, more preferably from equal to or more than 5 minutes to equal to or less than 5 hours.

The total residence time of the aqueous slurry in the mixer and any reaction vessel (i.e. the combined residence
5 time) preferably lies in the range from equal to or more than 20 seconds to equal to or less than 10 hours, more preferably in the range from equal to or more than 1 minute to equal to or less than 5 hours. Most preferably from equal to or more than 20 minutes to equal to or less
10 than 2 hours.

The aqueous slurry may be transported from the mixer into the reaction vessel by any transporting means known to the skilled person to be suitable for this purpose. These transporting means may for example include pipes,
15 pumps, conveyer belts or other types of conveyers. In a preferred embodiment the aqueous slurry is transported from the mixer into the reaction vessel with the help of one or more screw pumps. During the transport from the mixer into the reaction vessel, the aqueous slurry may or
20 may not be heated to keep the aqueous slurry at a certain temperature. In addition the transporting means may be heat-insulated to prevent leakage of heat from the process.

The reaction vessel may be any vessel known to the person
25 skilled in the art to be suitable for carrying out a reaction. It may for example be an extruder, plug flow reactor, screw reactor, continuously stirred tank reactor (CSTR), Pandia digester, moving belt reactor or L&G type reactor. Also combinations thereof may be used. Preferably
30 the reaction vessel is a vessel that can be heated and/or insulated and/or pressurized. In one preferred embodiment the reaction vessel may be an adiabatic reaction vessel, where the heat generated during the mixing is used as the main

heating source. In another preferred embodiment the reaction vessel may be a heat insulated reaction vessel to prevent heat from leaking away.

5 In the two-step process, friction heat that may be in-situ generated during the mixing of the lignocellulosic material and the alkaline aqueous solution may advantageously be used to increase the temperature of the aqueous slurry.

10 In one embodiment it is therefore not needed to add any external heat to the reaction vessel. In this embodiment friction heat generated during the mixing in the mixer may advantageously be used as the sole heat source for the heat-treating in the reaction vessel.

15 In another embodiment, heat is supplied to the reaction vessel by an external heat source. In this case a first part of the heat needed for the heat-treating may advantageously be supplied by the friction heat generated during the mixing, whilst a second part of the heat needed for the heat-treating is supplied to the reaction vessel by an external heat source. A preferred external heat source is steam. The
20 addition of extra heat may advantageously accelerate the pretreatment.

The reaction vessel may contain mechanical displacement means. In a preferred embodiment however, the reaction vessel contains no or only limited displacement means. Examples of
25 mechanical displacement means include stirrers or screws.

In the above two-step process, one, two or more reaction vessels may be used. If two or more reaction vessels are used, such two or more reaction vessels may be any combination of the reaction vessels as described above. In an
30 advantageous embodiment, the aqueous slurry is transported into and heat-treated in two or more reaction vessels. Such two or more reaction vessels may be applied in parallel or in sequence. The use of two or more reaction vessels

advantageously allows one to operate the mixer in a continuous manner. For example, when the residence time in the mixer is lower than the residence time in the reaction vessel, the use of two or more reaction vessels in parallel may advantageously allow one to fill up a subsequent reaction vessel, whilst a previous reaction vessel is still being used for the heat-treatment or whilst a previous reaction vessel is being emptied. The use of two or more reaction vessels in sequence may advantageously allow one to spread the residence time for the heat-treatment over multiple reaction vessels, also allowing for continuous operation.

During heat-treating of the aqueous slurry, a heat-treated aqueous slurry is produced. The heat-treated aqueous slurry preferably comprises pretreated lignocellulosic material, water, optionally dissolved lignin and optionally some dissolved alkaline pretreatment agent. Preferably the heat-treated aqueous slurry has a dry matter content in the range from equal to or more than 25 wt% to equal to or less than 60 wt%, based on the total weight of the aqueous slurry, more preferably a dry matter content in the range from equal to or more than 30 wt% to equal to or less than 55 wt%, based on the total weight of the heat-treated aqueous slurry.

The heat-treated aqueous slurry may be further processed in one or more subsequent steps before the pretreated lignocellulosic material contained therein is converted into an end-product. For example, in a subsequent step, part of the water and optionally any dissolved lignin may be removed from the heat-treated aqueous slurry. Water may for example be at least partly removed with the help of a filter, a cyclone, drum vacuum washer, horizontal belt washer.

The pretreated lignocellulosic material produced in the process according to the invention may advantageously be subjected to other steps, such as for example a neutralization step, a steam blasting step or a hydrolysis step.

In a preferred embodiment the pretreated lignocellulosic material produced in the process according to the invention is converted into a biofuel and/or biochemical. For example the pretreated lignocellulosic material can be converted to one or more hydrocarbons, for example hydrocarbons comprising in the range from 6 to 20 carbon atoms. Such hydrocarbons can for example be useful as a component in a gasoline and/or diesel fuel or in a lubricant. The pretreated lignocellulosic material may also be converted to one or more alkanol(s), for example ethanol and/or butanol. Most preferably the pretreated lignocellulosic material produced in the process according to the invention is converted into ethanol.

Depending on the pH of the pretreated lignocellulosic material and the envisaged subsequent processing steps it may be advantageous to neutralize the pretreated lignocellulosic material to a pH in the range from equal to or more than 4.0 to equal to or less than 7.0. Such a neutralization may for example be carried out by means of washings with water and/or washings with a limited amount of an acidic aqueous solution.

The neutralized pretreated lignocellulosic material may conveniently be converted to one or more alkanol(s), such as for example ethanol and/or butanol with the help of enzymatic hydrolysis.

The current invention therefore also provides a process for the production an alkanol, preferably ethanol, comprising

a) pretreating a lignocellulosic material having a lignin content in the range from equal to or more than 10 wt% to equal to or less than 50 wt%, based on the total weight of the lignocellulosic material, which pretreating
5 comprises mixing the lignocellulosic material and an alkaline aqueous solution, which alkaline aqueous solution has a pH of equal to or more than 9.0, in a solid to liquid weight ratio of equal to or more than 25:75 to equal to or less than 60:40, in a mixer to produce an
10 aqueous slurry; and heat-treating the aqueous slurry at a temperature in the range from equal to or more than 50°C to equal to or less than 200°C to produce a heat-treated aqueous slurry containing pretreated lignocellulosic material;

15 b) converting the pretreated lignocellulosic material into an alkanol, preferably ethanol.

Preferences for step a) are as described herein above. In addition to the pretreated lignocellulosic material, the heat-treated aqueous slurry obtained from step a) may
20 contain water. In a preferred embodiment at least part of the water and optionally any dissolved lignin is removed from the heat-treated aqueous slurry containing the pretreated lignocellulosic material before subjecting the pretreated lignocellulosic material to step b).

25 In a further preferred embodiment the pretreated lignocellulosic material obtained from step a) is washed and/or neutralized before subjecting it to step b). As explained above, it may be advantageous to neutralize the pH of the pretreated lignocellulosic material to a pH in
30 the range from equal to or more than 4.0 to equal to or less than 7.0, before subjecting it to step b).

In a preferred embodiment step b) comprises

i) hydrolyzing at least part of the, optionally neutralized, pretreated lignocellulosic material produced in step a) to produce a hydrolysis product; and

ii) fermenting at least part of the hydrolysis product produced in step i) to produce a fermentation broth comprising the one or more alkanol(s).

Preferably such steps i) and ii) are followed by: an optional step iii) comprising retrieving the one or more alkanols from the fermentation broth produced in step ii).

10 The hydrolysis in step i) may be carried out in any manner known to the skilled person in the art to be suitable for the hydrolysis of a lignocellulosic material. Preferably the, optionally neutralized, pretreated lignocellulosic is hydrolyzed in step i) by enzymatic hydrolysis. In an especially preferred embodiment step i) comprises hydrolyzing the, optionally neutralized, pretreated lignocellulosic material with the help of one or more cellulase enzymes, one or more glucosidase enzymes, one or more xylanase enzymes or a combination thereof. By hydrolysis of the, optionally neutralized, pretreated lignocellulosic material a hydrolysis product is produced. The hydrolysis product may contain one or more sugars. The sugars may comprise for example monosaccharides and disaccharides. For example the hydrolysis product may contain glucose, xylose, galactose, mannose, arabinose, fructose, rhamnose and/or mixtures thereof.

In step ii) at least part of the hydrolysis product produced in step i) can be fermented to produce a fermentation broth.

30 The fermentation in step ii) may for example be carried out with the help of a microorganism. The microorganism may be any kind of microorganism known to be capable of fermenting part or whole of the hydrolysis product. For example, it may be a microorganism capable of fermenting part

or whole of the hydrolysis product to a fermentation broth containing ethanol and/or butanol. Preferably the microorganism is a yeast or bacterium. More preferably the microorganism is chosen from the group consisting of

5 Saccharomyces spp., Saccharomyces cerevisiae, Escherichia, Zymomonas, Candida, Pichia, Streptomyces, Bacillus, Lactobacillus, Clostridium and mixtures thereof.

In one embodiment the hydrolyzing of step i) and the fermentation of step ii) are carried out simultaneously in
10 the same reactor. It is, however, most preferred to carry out the hydrolyzing of step i) and the fermentation of step ii) separately to allow for optimal temperatures for each step.

The fermentation broth generated in step ii) may contain one or more alkanols. Preferably the fermentation broth
15 contains ethanol and/or butanol. Most preferably the fermentation broth is a fermentation broth containing ethanol.

In optional step iii) the one or more alkanols are retrieved from the fermentation broth produced in step ii).

20 Preferably step iii) comprises distillation of the fermentation broth to produce one or more distillation fraction(s) comprising the one or more alkanol(s), for example a distillation fraction comprising ethanol and/or a distillation fraction comprising butanol and/or a
25 distillation fraction comprising ethanol and butanol.

The one or more alkanol(s), for example the butanol and/or ethanol, may advantageously be blended with one or more other components to produce a biofuel or a biochemical. Examples of one or more other components with which the one
30 or more alkanol(s) may be blended include anti-oxidants, corrosion inhibitors, ashless detergents, dehazers, dyes, lubricity improvers and/or mineral fuel components and/or other fuel components, such as for example so-called Fischer-

Tropsch derived fuel components or other renewable fuel components.

The present invention therefore also provides a process for the production of a fuel comprising steps a) and b) as described herein above and further comprising an additional step of blending the one or more alkanols produced in step b) with one or more other fuel components to produce a fuel.

Unless indicated otherwise, any weight percentages described herein are determined on a dry basis, i.e. after removal of any residual water.

The process according to the invention is further illustrated by figure 2. In figure 2 a lignocellulosic material (202) is wetted and washed with water (204) in a first screw mixer (206) to produce a wetted lignocellulosic material composition (208) and waste water (209). The wetted lignocellulosic material composition (208) is mixed with an alkaline aqueous solution (210) in a second screw mixer (212) at a temperature of 90°C during 10 minutes. From the second screw mixer (212) an aqueous slurry (214) having a solid to liquid weight ratio of 35:65 is obtained. The aqueous slurry (214) is forwarded to one of the two heat-insulated reaction vessels (216a and 216b). In the heat-insulated reaction vessels (216a and 216b) the aqueous slurry is heat-treated during 3 hours to produce a heat-treated aqueous slurry containing pretreated lignocellulosic material and water (218). The heat-treated aqueous slurry (218) is subsequently forwarded to a purification and neutralization unit (220) where the pretreated lignocellulosic material is retrieved from the heat-treated aqueous slurry (218) and subsequently washed with water (221) to produce a neutralized pretreated lignocellulosic material (222). The neutralized pretreated lignocellulosic material (222) is thereafter forwarded to a hydrolysis unit (224) where the neutralized pretreated

lignocellulosic material (222) is hydrolyzed with the help of cellulase enzymes to produce a hydrolysis product containing sugars (226). The sugars (226) are fermented in fermentation unit (228) with the help of a yeast to produce a fermentation
5 broth (230) containing ethanol. The fermentation broth (230) is subsequently distilled in distiller (232) to produce ethanol (234) and other products (236).

Examples

Example 1

10 Air dried corn stover having a lignin of about 21 wt% on a dry basis was cut into 3-5 cm pieces and loaded into a twin screw extruder (TEP80 commercially obtainable from Hebei Tianzheng Screening pulp-making Device Co. Ltd) via its feed inlet. Water was added via the feed inlet for washing and the
15 water content of the squeezed material was adjusted via the liquid outlet to produce an aqueous slurry having a dry matter concentration of about 50 wt% (corresponding to a solid to liquid weight ratio of 50:50). An aqueous sodium hydroxide solution having a concentration of about 60 grams
20 sodium hydroxide per litre was added via a liquid inlet. This aqueous sodium hydroxide solution had a pH of about 14.2. The amount of aqueous sodium hydroxide solution was controlled so that the dry matter content of the slurry was reduced to about 33 wt%, corresponding to a solid to liquid
25 weight ratio of 33:67. (i.e. the weight of the added sodium hydroxide solution was equal to 1 time the weight of dry matter already present in the aqueous slurry). The main shaft rotation speed of the twin screw extruder was set as 375 rpm. An aqueous slurry having a dry matter content of about 33 wt%
30 was collected from the discharge outlet of the twin screw extruder and was placed in a heat insulated reaction vessel during 3 hours. The temperature in the twin screw extruder

and heat-insulated reaction vessel during pretreatment was about 94°C.

The reaction conditions are summarized in table 1.

After standing, the material was washed to be neutral,
5 then its chemical components were analyzed according to the methods as described in NREL/TP-510-42618 (<http://www.nrel.gov/biomass/pdfs/42618.pdf>), and a high performance liquid chromatography (HPLC, Model 1200, Agilent Technologies, USA) was used according to the
10 instructions from the manufacturer to detect its carbohydrate content.

The pretreatment recovery rate (i.e. weight of the residue obtained) on the basis of the initial material, and the weight percentages of respectively glucan, xylan
15 and lignin in the residue obtained are listed in table 2. This indicated that after the pretreatment according to the process of the present invention, the lignin in the corn stalk was effectively removed.

Under pH 4.8 and 50°C, cellulase (Celluclast 1.5L) of
20 20FPU/g substrate and β -glucosidase (Novozyme 188) of 5IU/g substrate were used to hydrolyze the pretreated material in 2% substrate concentration for 48h. A high performance liquid chromatography (HPLC, Model 1200, Agilent Technologies, USA) was used according to the
25 instructions of the manufacturer to analyze the hydrolysis product, and the hydrolysis efficiency of glucose, the hydrolysis efficiency of xylose and the total sugar yield were calculated.

The hydrolysis efficiency of glucose; the hydrolysis
30 efficiency of xylose and the total sugar yield are listed in table 2. The results indicate that the corn stover could be easily enzymatically degraded after the pretreatment according to the process of the present

invention, and both the hydrolysis efficiencies and the total sugar yield were high.

Example 2

Example 2 was carried out in a similar manner as example 1, except as indicated herein below. The air dried corn stover having a lignin of about 21 wt% on a dry basis was shredded by a shredder into 1-3 cm pieces. Water was added via the feed inlet for washing and the water content of the squeezed material was adjusted via the liquid outlet to

produce an aqueous slurry having a dry matter concentration of about 45 wt% (corresponding to a solid to liquid weight ratio of 45:55). An aqueous sodium hydroxide solution having a concentration of about 100 grams sodium hydroxide per litre was added via a liquid inlet. This aqueous sodium hydroxide solution had a pH of about 14.4. The amount of aqueous sodium hydroxide solution was controlled so that the dry matter content of the aqueous slurry was reduced to about 35 wt%, corresponding to a solid to liquid weight ratio of 35:65.

(i.e. the weight of the added sodium hydroxide solution was equal to 0.6 time the weight of dry matter already present in the aqueous slurry). An aqueous slurry having a dry matter content of about 35 % w/w was collected from the discharge outlet of the twin screw extruder and was placed in a heat insulated reaction vessel during 1 hours. The temperature in the twin screw extruder and heat-insulated reaction vessel during pretreatment was about 98°C.

The reaction conditions are summarized in table 1. The pretreatment recovery rate (i.e. weight of the residue obtained) on the basis of the initial material, and the weight percentages of respectively glucan, xylan and lignin in the residue obtained are listed in table 2. Also the hydrolysis efficiency of glucose; the hydrolysis

efficiency of xylose and the total sugar yield are listed in table 2.

Example 3:

Poplar wood pieces with a lignin content of about 23 wt% on a dry basis and a size of about 4cm*4cm were washed with water, then loaded into a twin screw extruder (TEP80 from Hebei Tianzheng Screening Pulp-making Device Co., Ltd.) via its feed inlet. The first 2 squeezing zones of the twin screw extruder were used to remove a part of water and gas from the wood pieces so that the material had a dry matter content of about 60wt% (corresponding to a solid to liquid weight ratio of 60:40).

An aqueous sodium hydroxide solution with a concentration of about 430 grams sodium hydroxide per litre was added via a liquid inlet. This aqueous sodium hydroxide solution had a pH of about 15.0. The amount of sodium hydroxide solution was controlled so that the dry matter content was further decreased to about 40% (i.e., the weight of the used aqueous sodium hydroxide solution was equivalent to 0.83 times the weight of absolute dry material).

The main shaft rotation speed of the twin screw extruder was set as 350 rpm. The pretreated material with a dry matter concentration of about 40wt% was collected from the discharge outlet. The temperature of the material at the discharge outlet of the extruder was measured as 98°C. The material was placed in a thermal insulation tank for 1 hour. The reaction conditions are summarized in table 1.

For the remainder example 3 was carried out as example 1.

The pretreatment recovery rate (i.e. weight of the residue obtained) on the basis of the initial material, and the weight percentages of respectively glucan, xylan

and lignin in the residue obtained are listed in table 2. Also the hydrolysis efficiency of glucose; the hydrolysis efficiency of xylose and the total sugar yield are listed in table 2.

Table 1: Reaction conditions of examples 1 to 3.

Example	1	2	3
Lignin content of the LM (wt%)	21	21	23
NaOH (grams/liter) in AAS and pH of the solution	6 (13.2)	10 (13.4)	43 (14.0)
Dry matter in aqueous slurry after addition of AAS (wt%)	33	35	40
Temperature in twin screw extruder (°C)	94	98	98
Temperature in heat- insulated reaction vessel	94	98	98
Total energy consumption* (MegaJoule/kilogram lignocellulosic material)	0.21	0.20	0.25
Shear energy** (MegaJoule/kilogram lignocellulosic material)	0.16	0.15	0.20
Total Residence time at reaction conditions, including both the residence time in the extruder and in the reactor vessel (hours)	3	1	1

LM = lignocellulosic material

AAS = alkaline aqueous solution

* Energy consumption is the energy required to operate the
5 twin screw extruder, this includes the shear energy.

** calculated by subtracting the energy consumed when the
extruder was running empty (i.e. 0.05 MegaJoule/Kilogram
lignocellulosic material) from the total energy consumption.

Table 1: Product characteristics of examples 1 to 3

Example	1	2	3
Pretreatment recovery rate (wt % based on the weight of the initial material)	63.6	61.7	78.6
glucan (wt% on residue)	55.2	61.5	51.8
glucan (wt% on initial material)	35.1	37.9	40.7
xylan (wt% on residue)	22.5	21.0	19.2
xylan (wt% on initial material)	14.3	13.0	15.1
lignin (wt% on residue)	8.6	8.6	20.3
lignin (wt% on initial material)	5.5	5.3	16.0
hydrolysis efficiency of glucose (wt% on glucan in the residue)	81.3	89.0	85.3
Yield of glucose (wt% on initial material)	28.5	33.7	34.7
hydrolysis efficiency of xylose (wt% on xylan in the residue)	88.4	84.6	78.1
Yield of xylose (wt% on initial material)	12.6	11.0	11.8
Total sugar yield (wt% on initial material)	46	50	52

CLAIMS

1. A process for pretreating a lignocellulosic
5 material having a lignin content in the range from equal
to or more than 10 wt% to equal to or less than 50 wt%,
based on the total weight of the lignocellulosic material,
which process comprises:

mixing the lignocellulosic material and an alkaline
10 aqueous solution, which alkaline aqueous solution has a pH
of equal to or more than 9.0, in a solid to liquid weight
ratio of equal to or more than 25:75 to equal to or less
than 60:40, in a mixer to produce an aqueous slurry;

and heat-treating the aqueous slurry at a temperature
15 in the range from equal to or more than 50°C to equal to
or less than 200°C to produce a heat-treated aqueous
slurry comprising a pretreated lignocellulosic material.

2. The process according to claim 1, wherein the
20 lignocellulosic material contains in the range from equal
to or more than 15 wt% lignin to equal to or less than 40
wt% lignin, based on the total weight of the
lignocellulosic material.

3. The process according to any one of the preceding
25 claims, wherein the alkaline aqueous solution is an
alkaline aqueous solution comprising sodium hydroxide,
potassium hydroxide, sodium carbonate, potassium carbonate
and/or mixtures thereof.

30 4. The process according to any one of the preceding
claims, wherein the alkaline aqueous solution is an
alkaline aqueous solution containing in the range from
0.04 gram/liter to 500 gram/liter of sodium hydroxide.

5. The process according to any one of the preceding claims, wherein the lignocellulosic material and the alkaline aqueous solution are mixed in a solid to liquid weight ratio of equal to or more than 30:70 to equal to or less than 55:45.

6. The process according to any one of the preceding claims, wherein the mixer is a shear mixer.

7. The process according to claim 6, wherein an amount of shear energy is applied by the shear mixer in a range of from equal to or more than 1% to equal to or less than 25% of the gross energy contained in the lignocellulosic material.

8. The process according to claim 6, wherein an amount of shear energy is applied by the shear mixer in the range from equal to or more than 100 Joule to equal to or less than 20,000 Joule per gram of lignocellulosic material.

9. The process according to any one of the preceding claims, wherein the mixer is a twin screw extruder.

10. The process according to any one of the preceding claims, wherein residence time of the lignocellulosic material in the mixer ranges from equal to or more than 10 seconds to equal to or less than 10 hours.

11. The process according to anyone of the preceding claims, wherein the mixing and the heat-treating are carried out in sequence or simultaneously.

12. The process according to any one of the preceding claims, which process comprises mixing the lignocellulosic material and an alkaline aqueous solution, which alkaline aqueous solution has a pH of equal to or more than 9.0, at
5 a temperature in the range from equal to or more than 50°C to equal to or less than 200°C, in a solid to liquid weight ratio of equal to or more than 25:75 to equal to or less than 60:40, in a mixer to produce a heat-treated aqueous slurry comprising a pretreated lignocellulosic
10 material

13. The process according to any one of the preceding claims, which process comprises mixing the lignocellulosic material and an alkaline aqueous solution, which alkaline
15 aqueous solution has a pH of equal to or more than 9.0, in a solid to liquid weight ratio of equal to or more than 25:75 to equal to or less than 60:40, in a mixer to produce an aqueous slurry;

transporting the aqueous slurry from the mixer into a
20 reaction vessel; and

heat-treating the aqueous slurry in the reaction vessel at a temperature in the range from equal to or more than 50°C to equal to or less than 200°C to produce a heat-treated aqueous slurry comprising a pretreated
25 lignocellulosic material.

14. The process according to claim 13, wherein the residence time in the mixer is equal to or lower than the residence time in the reaction vessel.

30

15. A process for the production of an alkanol, comprising

a) pretreating a lignocellulosic material having a lignin content in the range from equal to or more than 10 wt% to equal to or less than 50 wt%, based on the total weight of the lignocellulosic material, which pretreating
5 comprises mixing the lignocellulosic material and an alkaline aqueous solution, which alkaline aqueous solution has a pH of equal to or more than 9.0, in a solid to liquid weight ratio of equal to or more than 25:75 to equal to or less than 60:40, in a mixer to produce an
10 aqueous slurry; and heat-treating the aqueous slurry at a temperature in the range from equal to or more than 50°C to equal to or less than 200°C to produce a heat-treated aqueous slurry containing pretreated lignocellulosic material;

15 b) converting the pretreated lignocellulosic material into an alkanol.

Figure 1

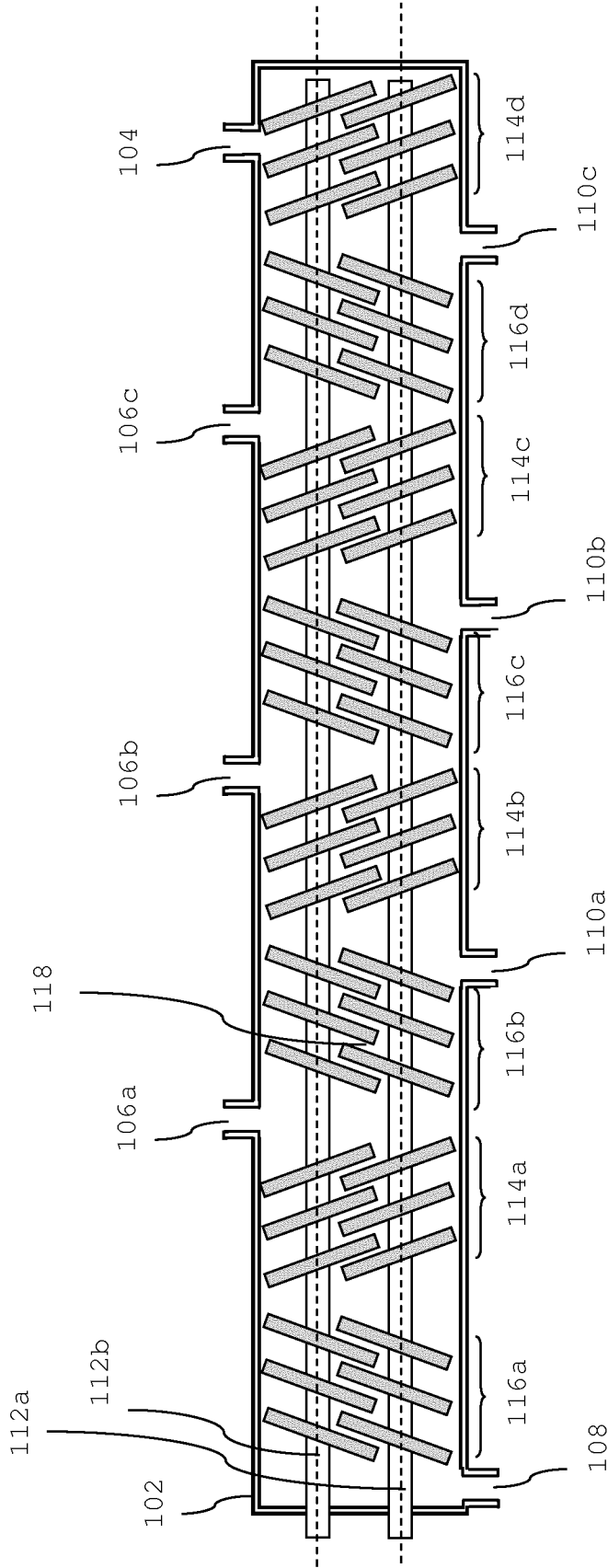
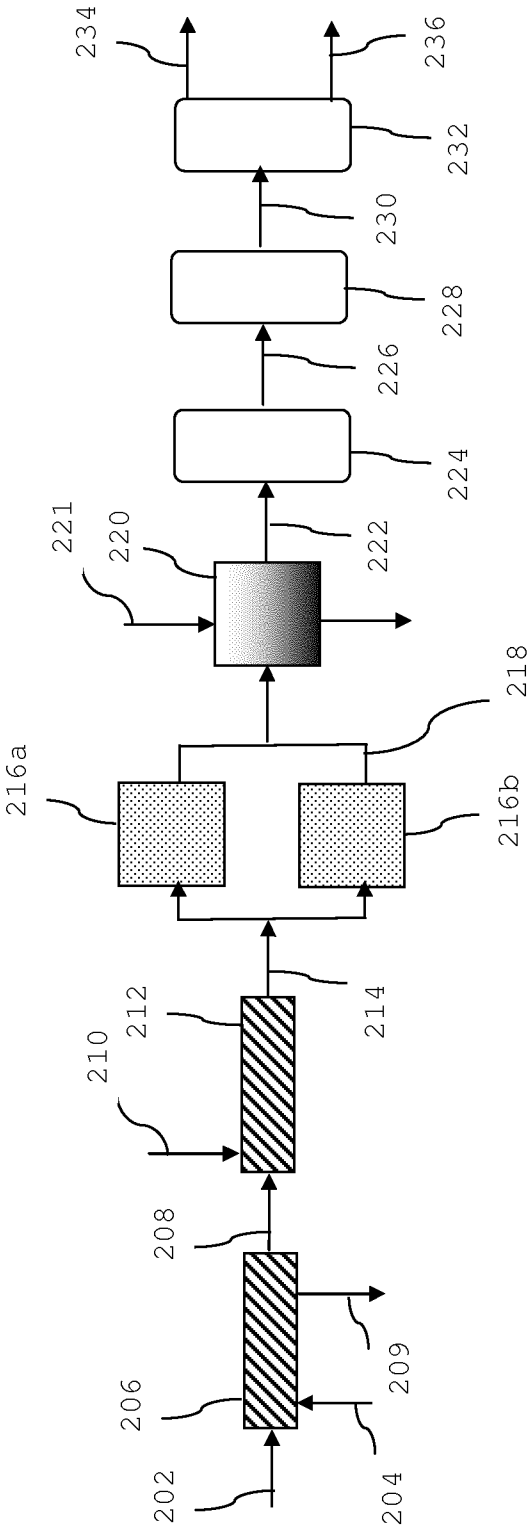


Figure 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/072650

A. CLASSIFICATION OF SUBJECT MATTER
INV. C12P7/02 C08H7/00 D21C1/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C12P C08H D21C

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

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

EPO-Internal, WPI Data, BIOSIS, EMBASE, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 997 488 A (GOULD JOHN M [US] ET AL) 5 March 1991 (1991-03-05) column 2, line 23 - line 36 column 3, line 64 - column 5, line 11 -----	1-15
X	WO 2010/078930 A2 (BORREGAARD IND [NO]; SJOEDE ANDERS [NO]; FROELANDER ANDERS [NO]; LERSC) 15 July 2010 (2010-07-15) page 10, line 30 - line 34 page 12, line 7 - line 10 page 14, line 28 - page 16, line 3 -----	1-15
X	WO 2011/061400 A1 (VALTION TEKNILLINEN [FI]; KALLIOINEN ANNE [FI]; VUORELA SATU [FI]; VON) 26 May 2011 (2011-05-26) page 6, line 27 - page 8, line 12 ----- -/-	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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Date of the actual completion of the international search

14 February 2014

Date of mailing of the international search report

03/03/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Schönwasser, D

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/072650

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PARVEEN KUMAR ET AL: "Methods for Pretreatment of Lignocellulosic Biomass for Efficient Hydrolysis and Biofuel Production", INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH, AMERICAN CHEMICAL SOCIETY, US, vol. 48, no. 8, 15 April 2009 (2009-04-15), pages 3713-3729, XP008147200, ISSN: 0888-5885, DOI: 10.1021/IE801542G [retrieved on 2009-03-20] cited in the application -----	1-15

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International application No

PCT/EP2013/072650

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