

Acetic acid based refining process of biomass

Field of the invention

The present invention relates to a process for refining a biomass. The process
5 may be used for the production of cellulose pulp and/or dissolving pulp, and in addition
valuable by-products such as for example vegetable oil, hemicellulose, lignin, furans,
organic acids and monomeric and/or polymeric sugars may be recovered from the
refining process. The present invention also relates to the use of dissolving pulp
obtained by the process according to the invention for the production of cellulose
10 acetate.

Background of the invention

Biomass has been more and more recognized as the interesting CO₂-neutral
novel source for fuel and other valuable components. The processing of biomass into
15 various valuable products is referred to as refining. Over the last decades, a large
amount of research effort has been directed towards the development of processes for
the refining of biomass. Refining of biomass is often referred to as “biorefining” in
prior art.

The main valuable component of biomass is the cellulose fraction, which may
20 be isolated from the biomass in the form of a cellulose pulp. Cellulose pulp may be
further purified into a dissolving pulp. Dissolving pulp is a chemically refined and
bleached high-grade pulp with a cellulose content of more than 90%. The term
“cellulose content” usually refers to the content of high molecular, non-degraded
cellulose, i.e. pure cellulose fibre. This cellulose is resistant to dissolution in 18%
25 NaOH (R18) or 10% NaOH (R10), and is also referred to as “α-cellulose”.

Dissolving pulp has special properties such as for example a high level of
brightness and a uniform molecular weight distribution. Chemical properties that may
be used for the characterisation of dissolving pulp are for example viscosity or degree
of polymerization (DP), polymer size distribution, alkali resistance (R18, R10) and
30 carbohydrate content.

The purity of both cellulose pulp and dissolving pulp strongly depends on the
raw material used and production process applied, and determines the applicability of
the pulp. Cellulose pulp may be used for the production of for example viscose or

paper. Dissolving pulp, i.e. pulp with a cellulose content of >90% may be used for the production of cellulose derivatives such as for example rayon, cellophane, carboxymethylcellulose, cellulose acetate, etc.

As will be known to a person skilled in the art, common processes for the production of dissolving pulp include the sulphite process which produces pulp with a cellulose content up to 92% (for wood), and the prehydrolysis sulphate process, also known as the Kraft process, which produces pulp with a cellulose content of up to 96% (for wood). Additional alkaline purification and bleaching of the pulp may lead to even higher cellulose levels.

Currently, mainly wood or cotton linter is used as a feedstock for the production of cellulose pulp. Depending on the process employed, the cooking liquor includes sulphur-containing compounds, and in most cases chlorine-containing chemicals are used to purify the cellulose pulp into a dissolving pulp. The use of these chemicals results in a high environmental load.

Alternative pulping processes with organic solvents such as for example organic acids have been suggested in order to achieve a more ecologically sound pulp production. Also, organic acid pulping techniques are better suitable to the refining concept for recovering by-products as compared to traditional pulping processes. These by-products such as for example extractives, furans, xylitol and lignin may be used for added value applications, resulting in additional revenues. The main markets for furans are as a binder or resin, solvent, in pesticides and as a component in phenolic resins. Xylitol is an important sweetener for the food industry. Lignins are increasingly used, for example as surfactant, in binder systems and coating applications for the agricultural industry, and additional novel applications for lignin such as for example as phenol resource and as (plastics) additive are currently evaluated.

An organic acid based process for the production of cellulose from lignocellulosic materials is disclosed in US 3,553,076, incorporated by reference herein. The process is non-catalytic, and comprises (a) introduction of an acid solution containing essentially water and at least 50% by weight of acetic acid in the absence of a catalyst, and in an amount ranging from 1 : 1 to 12 : 1 weight ratio of acid solution to lignocellulosic material, and (b) digesting the lignocellulosic material at a temperature between 150°C and 205°C in order to substantially delignify said material. The process is preferably carried out on a continuous basis, and high-strength pulps as well as dissolving pulps may be obtained.

US 5,385,641, incorporated by reference herein, discloses a three-stage process for the delignification of cellulose-containing raw materials, wherein (a) pulping is performed with a solution of concentrated aqueous acetic acid at a temperature in the range of 140 – 230°C and at a pressure of 3 – 30 bar, and (b) treatment of the acetic acid-moist pulp with the aforementioned pulping solution with the addition of nitric acid at a temperature in the range of 60 – 140°C and at a pressure of 1 – 6 bar, followed by washing or extraction with water or with the pulping solution, and (c) treatment of the thus obtained pulp with an ozone-containing gas at a temperature in the range of 15 – 50°C and at a pressure of 1 – 12 bar.

However, even under optimum conditions the residual lignin content of the pulp obtained with the process of US 3,553,076 is rather high (Kappa numbers of 20 – 40). One of the disadvantages of the process disclosed in US 5,385,641 is the necessity of additional process steps, such as for example washing.

In the palm oil production chain large quantities of residues are produced. These residues include roots, trunks, oil palm fronds, empty fruit bunches (EFB), shells and press cake. Enhancing the sustainability of palm oil production may be achieved by fully exploiting this abundantly available biomass that comprises, amongst others, cellulose, lignin, hemicellulose and residual palm oil. So far, utilisation of this biomass is not optimised and there is a demand for other uses besides mulch or fuel.

Alkali pulping processes for the production of pulp from EFB are known from prior art. For example, a process for the production of unbleached and bleached soda pulps from oil palm EFB fibres is disclosed by Yussof *et al.* (*Paper Asia*, **2005**, 21, 29 – 33), incorporated by reference herein. Pulping of the EFB using 15% sodium hydroxide was carried out at 140°C for one hour, with a liquor to fibre ratio of 4 : 1. The pulp was obtained with a screened yield of around 40%, and could be used in the manufacture of paper. However, the residual lignin content was rather high (Kappa number 48.6).

Wan Rosli *et al.* (*Journal of Tropical Forest Science*, **2004**, 16(3), 343 – 349), incorporated by reference herein, disclose that soda pulping of oil palm EFB gives the best results when a prehydrolysis step is included. The most promising conditions included a prehydrolysis at 170°C during 60 min with a liquor to solid ratio of 6 : 1. Analysis of the prehydrolysis liquid indicated that there was minimal cellulose degradation under the applied prehydrolysis conditions. Subjecting the prehydrolysed fibres to a soda pulping cooking cycle at 170°C and with a liquor to fibre ratio of 8 : 1

resulted in an unbleached cellulose pulp with a Kappa number of 3.9 and an α -cellulose content of 96%.

One of the disadvantages of the processes known from prior art for the production of cellulose pulp from oil palm EFB is that these are alkaline processes, and as a result these processes are less suitable for a refining process, whereby the valuable by-products such as mentioned above as well as the solvents may be recovered in addition to the cellulose. The non-catalytic organic acid pulping processes known from prior art for different types of biomass may result in cellulose pulps with a high residual lignin content, and/or include additional process steps such as for example washing in order to obtain a high quality cellulose pulp.

Therefore there is a need for a process that not only integrates the production of cellulose pulp with the recovery of the other valuable components of biomass, but also results in a cellulose pulp with a low residual lignin content and a high overall quality.

15 **Summary of the invention**

The present invention relates to a process for refining a biomass having a dry matter content of 5 – 95 wt.%, based on the total weight of the biomass, wherein the process comprises the subsequent stages of (a) water extraction under atmospheric pressure conditions and at a pH of 5 to 7, (b) prehydrolysis with water, steam or a mixture thereof at a temperature of 100°C to 200°C, and (c) hydrolysis at a pH of less than 7. The term “subsequent” is herein used in the sense of “after another” or “consecutive”. Thus the process for refining a biomass comprises the sequence of steps (a), (b) and (c), in other words, the first step of this sequence is step (a), and step (b) takes place later than step (a) whereas step (c) takes place later than step (b).

25 In a specific embodiment, said biomass has a dry matter content of 5 – 50 wt%, based on the total weight of the biomass.

In a further aspect of the invention, one or more valuable by-products such as for example vegetable oil, hemicellulose, lignin, furans, organic acids and monomeric and/or polymeric sugars are recovered from the refining process.

30 The present invention also relates to a dissolving pulp obtained by the process according to the invention, and to the use of the dissolving pulp for the production of cellulose acetate.

Detailed description of the invention

Definitions

The verb “to comprise” and its conjugations as is used in this description and in the claims is used in its non-limiting sense to mean that items following the word are included, but items not specifically mentioned are not excluded. In addition, reference to an element by the indefinite article "a" or "an" does not exclude the possibility that more than one of the element is present, unless the context clearly requires that there is one and only one of the elements. The indefinite article "a" or "an" thus usually means "at least one".

Biomass is herein defined as plant biomass that comprises cellulose, hemicellulose and lignin.

In this description, the term cellulose pulp refers to a pulp comprising cellulose. The term dissolving pulp refers to a specific type of cellulose pulp, namely a high purity cellulose pulp. Hence, the term cellulose pulp is defined in a sense to include dissolving pulp, whereas the term dissolving pulp specifically refers to a high purity cellulose pulp. Typically, a dissolving pulp comprises over 90 wt.% of α -cellulose fibre.

20 *Process and products*

The present invention relates to a refining process for the production of cellulose pulp and other valuable components from biomass, using a multi-stage acidic pulping process.

In particular, the present invention relates to a process for refining a biomass having a dry matter content of 5 – 95 wt.%, based on the total weight of the biomass, wherein the process comprises the subsequent stages of (a) water extraction under atmospheric pressure conditions and at a pH of 5 to 7, (b) prehydrolysis with water, steam or a mixture thereof at a temperature of 100°C to 200°C, and (c) hydrolysis at a pH of less than 7. In a specific embodiment, said biomass has a dry matter content of 5 – 50 wt%, based on the total weight of the biomass.

A unique feature of the process according to the present invention is brought about by the solvents used in the process, i.e. water at the beginning of the process and acetic acid in later stages of the process. Use of these solvents advantageously results in a relatively simple and efficient solvent recovery, as opposed to the processes known

from prior art. Recycling of the solvents makes the process very suitable for application on a relatively small scale, for example next to an oil palm mill. Consequently, in a preferred embodiment of the process according to the present invention, the acid used in the hydrolysis stage and/or the bleaching stage is recycled.

5 The process starts under neutral conditions, becomes acidic during the pre-hydrolysis stage (*vide infra*) and remains acidic during the subsequent stages. The purity of the cellulose fraction obtained by the process is sufficiently high, and as a result additional alkaline purification is not necessary, thereby reducing and/or omitting the use of additional washing stages. The resulting product, cellulose pulp in acetic acid, may for example be used directly as a raw material for the production of cellulose acetate, without the need to isolate the cellulose pulp from the acetic acid.

 Furthermore, the refining process according to the present invention provides a cellulose pulp, and therefore the cellulose derivatives thereof, with unique properties. Due to the relatively mild process conditions less damage occurs to the existing cellulose structures, resulting in a higher degree of polymerization (DP) of the cellulose. The cellulose pulp is hence characterised by a high degree of crystallinity and a high degree of polymerization. In a preferred embodiment the process is used for the production of cellulose pulp, which may be used for the production of for example viscose or paper. In a further preferred embodiment of the present invention the process is used for the production of dissolving pulp, which may be used for the production of cellulose derivatives such as for example rayon, cellophane, carboxymethylcellulose and/or cellulose acetate.

 As is mentioned above, another advantage of the process according to the present invention is that the acetic acid-based pulping process for the production of dissolving pulp allows for a straightforward integration with the subsequent production of for example cellulose acetate, without the need of intermediate steps such as solvent removal, washing and/or drying. Another aspect of the present invention is therefore the use of the dissolving pulp according to the present invention for the production of cellulose acetate.

30 A further unique feature of the process according to the present invention is the integrated refining approach, aiming at maximizing the total value of output products. The process allows for the recovery of several valuable by-products, and is characterised by fully exploiting the biomass as substantially no waste streams are created. As an example, residual vegetable oil is recovered by washing with hot water,

and xylose and lignin are recovered from the prehydrolysis and hydrolysis liquids after recovery of acetic acid for recycling purposes. Additional by-products that may be recovered include hemicellulose fragments, furans, organic acids and various monomeric and/or polymeric sugars, such as for example C₅ and/or C₆ sugars.

5 In a preferred embodiment of the present invention one or more side-products selected from the group comprising vegetable oil, hemicellulose, lignin, furans, organic acids and monomeric and/or polymeric sugars, are recovered. In a further preferred embodiment, palm oil, lignin and xylose are recovered.

10 Pulping with organic solvents like acetic acid may find applications where the local situation is particularly favourable with an abundance of suitable biomass resources such as for example an oil palm mill, or in areas where the Kraft process may be restricted for economic or environmental reasons. A pulping process with acetic acid as the main delignification chemical is very suitable for the pulping of for example an oil palm, a part of an oil palm, an oil palm residue or mixtures thereof.

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Biomass

Biomass refers to plant biomass that comprises cellulose, hemicellulose and lignin. Examples of biomass are for example wood, straw, reed, forestry residues, agricultural residues and so on. In a preferred embodiment of the present invention, the biomass comprises oil palm and/or oil palm residues.

20 One of the advantages of the refining process of the present invention is that, due to simple solvent recoveries, in particular recovery of acetic acid, the process may be applied on a relatively small scale (e.g. 20 kton/year cellulose pulp production) and may therefore be installed close to the sites where the biomass is produced, for example, in the case of oil palm and/or oil palm residues, next to an oil palm mill with an average production capacity. Therefore, in a preferred embodiment the biomass comprises an oil palm, a part of an oil palm, an oil palm residue or mixtures thereof, such as for example roots, trunks, oil palm fronds, Empty Fruit Bunches, shells and/or press cake. Oil palm belongs to the family of *Arecaceae*, in particular to the genus *Elaeis*, and comprises for example *Elaeis guineensis* and *Elaeis oleifera*, and hybrids thereof.

30 In a further preferred embodiment, the biomass comprises oil palm Empty Fruit Bunches (EFB). EFB is a major biomass fraction that requires development of better conversion methodology since the large quantities that are generated at the mill site are

barely used. EFB is seldom sold as fuel since it is less suitable for storage and too bulky for transport. The specific composition and open structure of EFB makes it very suitable as a raw material for the production of various products, such as for example cellulose pulp. The texture and composition of EFB allow milder pulping and purification conditions for the cellulose extraction as compared to the commonly used wood or cotton linter. A further advantage of the use of oil palm EFB as biomass is that EFB may be used directly after removal of the oilseeds from the Fresh Fruit Bunches as is done in the oil palm mills, hence without the requirement of an energy consuming intermediate drying step. In addition, oil palm EFB contains a considerable amount of residual palm oil and it is economically viable to extract this palm oil during the process.

Depending on the nature of the biomass, a size reduction pretreatment such as for example shredding or chopping may be necessary prior to the refining process. During the pretreatment the biomass is reduced in size and/or taken apart in order to make the material more accessible for the subsequent steps of the process. In a preferred embodiment the biomass is subjected to a size reducing pretreatment, such as for example chopping or shredding, prior to the water extraction.

The biomass may have a dry matter content in the range of 5 – 95 wt.%. In one embodiment, the biomass has a dry matter content in the range of 5 – 90 wt.%, preferably in the range of 5 – 80 wt.%, more preferably in the range of 5 – 70 wt.% and even more preferably in the range of 10 – 60 wt.%, based on the total weight of the biomass. In a specific embodiment, said biomass has a dry matter content in the range of 5 – 50 wt%, preferably in the range of 10 – 40 wt.% and more preferably in the range of 20 – 30 wt.%, based on the total weight of the biomass.

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Water extraction

In the water extraction stage (a) of the process according to the present invention extractable compounds like proteins, sugars and vegetable oils may be removed by extracting said compounds from the biomass with water. If desired these extractable compounds may be recovered from the water stream. The term “water extraction” herein relates to extraction with water.

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As an example, the water extraction stage of the present process aims at extracting the abovementioned valuable compounds from fresh oil palm EFB. An

added advantage is that a further cleaning of the fibres is achieved, which may be advantageous for the subsequent processing of EFB fibres.

For a long time, the value of oil palm EFB was neglected due to an assumed low level of residual palm oil (1 – 2 wt.%), a high water content in the range of 70 – 80 wt.% water, and difficulty in handling due to its bulky and fibrous nature. As a comparison, in order to make EFB suitable for fuel purposes it is necessary to remove water by a screw press. However, for the process according to the present invention it is an advantage if the EFB remains wet, preferably with a dry matter content in the range of 5 – 50 wt.%, more preferably in the range of 20 – 30 wt.%, based on the total weight of the oil palm EFB. First of all, drying of EFB may induce irreversible changes to the EFB fibres that may complicate extraction of cellulose during subsequent stages. Secondly, fresh EFB contains approximately 6 wt.% of extractives. The largest part of these extractives (approximately 60 – 70 wt.%) comprises residual palm oil, the remaining part comprises water soluble material such as free sugars and proteins.

The water extraction stage of the process takes place under atmospheric pressure conditions and at a pH of 5 to 7, preferably at a pH of 5 to less than 7. The water extraction stage may take place at ambient temperature or at an elevated temperature. In a preferred embodiment, the water extraction stage takes place at a temperature in the range of 50 – 100°C, more preferably at a temperature in the range of 60 – 80°C.

Prehydrolysis

The prehydrolysis stage (b) is included in the process in order to achieve the removal of predominantly hemicellulose and lignin.

In water prehydrolysis, organic acid is liberated from the fibres by natural deacetylation of polysaccharides, providing an acidic medium for hydrolysis reactions of hemicelluloses. Although hemicelluloses are more prone to hydrolysis than cellulose due to their amorphous state and relatively low degree of polymerisation, severe hydrolytic conditions should be avoided in order to prevent concomitant hydrolysis of the cellulose, which would result in lower yields and a lower degree of polymerisation of the cellulose.

The prehydrolysis stage of the process according to the present invention results in an efficient removal of hemicelluloses, and also increases the extractability of lignin during subsequent steps. During the prehydrolysis of the biomass in water the pH

decreases from about 6 – 7 to 3 – 4 due to the autocatalysed formation of organic acids such as for example acetic acid and formic acid. Xylose is extracted from the biomass in oligomeric form, whereas the monomeric sugars may be further degraded to acids and furans. Furthermore, the crystallinity of the cellulose, *i.e.* the fraction of crystalline cellulose, is increased due to the removal of amorphous segments.

Since the process according to the present invention results in the recovery of cellulose from the biomass with an overall yield of over 90%, cellulose degradation during the pre-hydrolysis stage appears to be minimal.

The prehydrolysis takes place with water, steam or a mixture thereof at a temperature in the range of 100 – 200°C. In a preferred embodiment, the prehydrolysis takes place at a temperature in the range of 140 – 180°C, more preferably in the range of 150 – 170°C.

In another preferred embodiment, the prehydrolysis stage takes place at a pressure of 4 – 8 bar, more preferably 5 – 7 bar.

In yet another embodiment, the prehydrolysis stage lasts less than about 2 hours, more preferably less than about 1 hour, even more preferably less than about 55 minutes. Most preferably, the pre-hydrolysis stage lasts about 50 minutes.

In a further preferred embodiment, the weight ratio of the liquid phase to the solid phase in the prehydrolysis stage is between 20 : 1 to 5 : 1. With the liquid phase is meant the prehydrolysis solvent, *i.e.* water, and with the solid phase is meant the remaining biomass after the extraction phase. Preferably, the weight ratio of the liquid phase to the solid phase is between 15 : 1 to 6 : 1, more preferably between 11 : 1 and 7 : 1, and even more preferably between 10 : 1 and 8 : 1, based on the total weight of the liquid phase and the solid phase. Most preferably, the weight ratio of the liquid phase to the solid phase is about 9 : 1, based on the total weight of the liquid phase and the solid phase.

The yield of the prehydrolysis step may be in the range of 60 – 80%, and a hemicellulose removal of more than 70% and a lignin removal of 20 – 30% may be obtained. Valuable by-products from the prehydrolysis step are acetic acid that may be recovered for recycling, xylose and lignin.

Hydrolysis

The hydrolysis stage (c) of the process according to the present invention is predominantly aimed at the removal of lignin. Native lignin is hardly soluble in most

solvents due to its 3D-crosslinked structure. In order to extract lignin from biomass, cleavage of the covalent bonds between lignin and hemicellulose is necessary, and lignin has to be partially degraded to lower molecular weight fragments that may dissolve in the hydrolysis liquid or hydrolysate. This hydrolysate will contain the hemicellulose and lignin fragments. When organic acids are used as hydrolysis liquid, lignin may be recovered as insoluble precipitate by diluting the hydrolysate with water, whereas the sugars originating from hemicellulose will remain solubilised in the water fraction.

The acidic pulp may be further delignified by a bleaching stage. The hydrolysis and bleaching stages are both aimed at the removal of lignin. As will be clear to a person skilled in the art, the bleaching stage may be performed directly following the hydrolysis stage, i.e. without any intermediate isolation or solvent recovery steps. The combination of hydrolysis and bleaching is often referred to as “pulping”.

The hydrolysis stage is performed at a pH of 0 to less than 7, preferably at a pH of less than 7, more preferably at a pH of less than 5. Preferably, the hydrolysis is performed in the presence of acetic acid, and preferably at a temperature of 120°C to 200°C. In a preferred embodiment, the hydrolysis stage takes place (i) in the presence of acetic acid, (ii) at a temperature of 120°C to 200°C, and (iii) at a pH of less than 5.

In a preferred embodiment, pulping is performed in 60 – 90 wt.% acetic acid, more preferably in 70 – 80 wt.% acetic acid. As will be clear to a person skilled in the art, the pH of the pulp depends on the concentration of acetic acid. In a preferred embodiment, the pH in the hydrolysis stage is in the range of about 0 to 5, more preferably in the range of 0 to 2, even more preferably in the range of 1 to 2.

Preferably, the weight ratio of the liquid phase to the solid phase is between 15 : 1 to 5 : 1, more preferably between 12 : 1 and 7 : 1, and even more preferably between 11 : 1 and 8 : 1, based on the total weight of the liquid phase and the solid phase.

Preferably, the hydrolysis stage takes place at a temperature in the range of 140 – 190°C, more preferably in the range of 150 – 180°C, and most preferably in the range of 160 – 170°C.

In yet another embodiment, the hydrolysis stage lasts less than about 3 hours, more preferably less than about 2 hours, even more preferably less than about 100 minutes. Most preferably, the hydrolysis stage lasts about 90 minutes.

The yield of the hydrolysis stage may be about 50 – 60%, and the resulting cellulose fraction is characterised by a kappa number of 5 or lower. As will be known

to a person skilled in the art, the kappa number is a measure for the residual lignin content in a pulp. The kappa number may be in the range of 1 – 100, and the lower the kappa number, the lower the amount of residual lignin in the pulp. A standard method for the determination of the kappa number is specified by ISO 302:2004.

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Bleaching

The pulp may be further purified by a bleaching stage. Therefore, in a preferred embodiment of the process of the present invention, the process further comprises a bleaching stage subsequent to the hydrolysis stage. Preferably, the bleaching stage is a chlorine-free bleaching stage, whereby “chlorine-free” means that no additional chlorine-containing chemicals are added. This bleaching stage may be executed according to the methods from prior art as known to a person skilled in the art, such as for example alkaline peroxide bleaching, oxygen bleaching, ozone bleaching or chelating stage.

However, in a preferred embodiment the bleaching step is performed under acidic conditions as the unbleached cellulose is wetted with acetic acid. The advantages of these bleaching conditions include that the necessity for excessive washing, the need for solvent recovery systems and the occurrence of waste streams may be avoided substantially. In a further preferred embodiment the bleaching stage comprises an ozone bleaching step or a peracetic acid bleaching step, or both, and in an even more preferred embodiment the bleaching stage comprises an ozone bleaching step followed by a peracetic acid bleaching step.

Preferably, the ozone bleaching step takes place at or below ambient temperature, ambient temperature meaning without additional heating or cooling. Since the process according to the present invention is likely to be executed in areas with a tropical climate, ambient temperature may comprise temperatures of up to for example 45°C. In a preferred embodiment the ozone bleaching step is carried out at a temperature in the range of 15 – 45°C, more preferably 16 – 40°C. Most preferably, the ozone bleaching step is executed at a temperature in the range of 17 – 35°C. The lower limit of this temperature range is dictated by the melting point of glacial acetic acid, which is 16.6°C.

In a preferred embodiment the peracetic acid bleaching step takes place at a temperature in the range of 40 – 80°C, more preferably at a temperature in the range of

50 – 70°C, even more preferably at a temperature in the range of 55 – 65°C. Most preferably, the peracetic acid bleaching step takes place at a temperature of about 60°C.

A particularly preferred embodiment for the bleaching stage therefore comprises an ozone bleaching step that takes place at ambient temperature, followed by a
5 peracetic acid bleaching step taking place at a temperature of in the range of 40 – 80°C.

The final cellulose pulp as obtained by the process according to the present invention is characterized by a α -cellulose content of more than 90% and a Kappa number in the range of 1.5 – 2.5.

10 *Hydrolysis of oil palm and/or oil palm residues under acidic conditions*

The invention of the present application further relates to a process for the pulping of oil palm and/or oil palm residues under acidic conditions, in particular a process for the hydrolysis of oil palm and/or oil palm residues under acidic conditions. Oil palm and oil palm residues comprise for example an oil palm, a part of an oil palm,
15 an oil palm residue or mixtures thereof, such as for example roots, trunks, oil palm fronds, Empty Fruit Bunches, shells and/or press cake. In a preferred embodiment, the oil palm residues comprise oil palm Empty Fruit Bunches (EFB).

The hydrolysis takes place under acidic conditions at a pH of 0 to less than 7, preferably at a pH of less than 7, more preferably less than 5, even more preferably at a
20 pH in the range of 0 to 2, most preferably in the range of 1 to 2. Preferably, the hydrolysis takes place in the presence of acetic acid, and in a preferred embodiment, hydrolysis takes place in 60 – 90 wt.% acetic acid, more preferably in 70 – 80 wt.% acetic acid.

Preferably, the weight ratio of the liquid phase to the solid phase is between 15 :
25 1 to 5 : 1, more preferably between 12 : 1 and 7 : 1, and even more preferably between 11 : 1 and 8 : 1, based on the total weight of the liquid phase and the solid phase.

The hydrolysis stage takes place at an elevated temperature, preferably at a temperature in the range of 120 – 200°C, more preferably in the range of 140 – 190 °C, even more preferably in the range of 150 – 180°C, and most preferably in the range of
30 160 – 170°C.

In yet another preferred embodiment, the hydrolysis stage lasts less than about 3 hours, more preferably less than about 2 hours, even more preferably less than about 100 minutes. Most preferably, the hydrolysis stage lasts about 90 minutes.

The hydrolysis process according to the invention may be used for the production of a cellulose pulp and/or a dissolving pulp. As will be clear to a person skilled in the art, the hydrolysis process may be preceded by one or more process stages, such as for example an extraction stage and/or a prehydrolysis stage as described above. Furthermore, the hydrolysis process may be followed by additional process stages, such as for example a bleaching stage, as described above.

Examples

10 Example 1

Shredded EFB fibres were subjected to washing with warm water. After the water extraction the amount of extractives on oven-dry material was determined by TAPPI method T264 om-82. With these extractions substances like proteins, waxes, fats, resins, tannins, gums, starches and coloring materials (like chlorophyll) can be removed. EFB fibres and washed EFB fibres were analysed in order to determine the effect of the water extraction. The results are given in table 1.

Table 1: Amount of extractives based on oven-dry material

Sample	Ethanol/Toluene (wt%)	EtOH (wt%)	Hot water (wt%)
EFB	17.2	0.6	7.9
Washed EFB	5.3	1.0	5.6

20 An empty fruit bunch is composed of various different tissues, and the dry matter content varies substantially within one bunch. For this reason it is very difficult to determine the dry matter content of the EFB material, and experiments showed that the dry matter content varies between 20 and 30 wt%. Considering this variation in dry matter content, fresh EFB contains 5 – 8 wt% extractives of which the largest part comprises residual palm oil (70%), whereas washed EFB contains 2 – 4 wt% extractives of which 50% comprises oil. The remaining part consists of water soluble material such as proteins and free sugars. It is expected that some part of the palm oil is difficult to extract with water and remains in the fibres.

30 Example 2

Prehydrolysis of EFB fibres was performed at 160 and 170 °C for 50 min at 5 – 7 bar. Due to this treatment mainly hemicellulose and lignin were degraded and dissolved in the prehydrolysis liquid. The results of this pretreatment are illustrated in table 3. Analysis of the prehydrolysis liquid revealed that in general more organic acids and furfural are formed at higher prehydrolysis temperature due to sugar degradation. In most cases xylose was found as oligomers as the monomeric sugars easily degrade further to acids and furans.

Table 2: Results of prehydrolysis

Prehydrolysis T (°C)	Yield (wt%)	End pH	Cellulose yield (wt%)	Hemicellulose removal (wt%)	Lignin removal (wt%)
160	79	3.9	95	47	14
170	72	3.7	99	70	23

Example 3

Hydrolysis of prehydrolysed EFB fibres was performed at 150 – 170 °C for 90 min with 76% acetic acid. Properties of the resulting pulps are listed in table 3. With this example the effect of hydrolysis temperature is illustrated: by increasing the severity of the treatment the degradation of the fibres is more pronounced. Lignin and hemicellulose is degraded and dissolved in the hydrolysis liquid, whereas the most resistant cellulose fraction stays intact to a sufficiently high level.

Table 3: Pulp properties after hydrolysis

Hydrolysis T (°C)	Yield (wt%)	Kappa	DP	Alpha cellulose (%)
150	55	3	2100	82
160	62	2	1800	85
170	55	2	1000	90

Example 4

During the hydrolysis stage hemicellulose and lignin is dissolved in the acidic liquid phase. Lignin was recovered from this liquor by evaporating acetic acid and washing the precipitated lignin with water. Analysis of the dried lignin revealed that a highly

pure lignin was obtained (94.4 wt% lignin, 0.3 wt% residual sugars) with a molecular weight of 3700 Da determined by Size Exclusion Chromatography.

Claims

1. Process for refining a biomass having a dry matter content of 5 – 95 wt.%, based on the total weight of the biomass, wherein the process comprises the subsequent stages of:
 - (a) Water extraction under atmospheric pressure conditions and at a pH of 5 to 7;
 - (b) Prehydrolysis with water, steam or a mixture thereof at a temperature of 100°C to 200°C; and
 - (c) Hydrolysis at a pH of less than 7.
2. Process according to claim 1, wherein the biomass has a dry matter content of 5 – 50 wt%, based on the total weight of the biomass.
3. Process according to claim 1 or claim 2, wherein the biomass comprises an oil palm, a part of an oil palm, an oil palm residue or mixtures thereof.
4. Process according to any one of claims 1 – 3, wherein the water extraction stage (a) takes place at a temperature in the range of 50 – 100°C.
5. Process according to any one of claims 1 – 4, wherein the prehydrolysis stage (b) takes place at a temperature in the range of 140 – 180°C.
6. Process according to any one of claims 1 – 5, wherein the prehydrolysis stage (b) takes place at a pressure of 4 – 8 bar.
7. Process according to any one of claims 1 – 6, wherein the weight ratio of the liquid phase to the solid phase in the prehydrolysis stage (b) is between 20 : 1 to 5 : 1, based on the total weight of the liquid phase and the solid phase.
8. Process according to any one of claims 1 – 7, wherein the hydrolysis stage (c) takes place (i) in the presence of acetic acid, (ii) at a temperature of 120°C to 200°C, and (iii) at a pH of less than 5.

9. Process according to any one of claims 1 – 8, wherein the pH in the hydrolysis stage (c) is in the range of 1 to 2.
- 5 10. Process according to any one of claims 1 – 9, wherein the hydrolysis stage (c) takes place at a temperature of 150 – 180°C.
11. Process according to any one of claims 1 – 10, wherein the process further comprises a bleaching stage subsequent to the hydrolysis stage (c).
- 10 12. Process according to claim 11, wherein the bleaching stage comprises an ozone bleaching step or a peracetic acid bleaching step, or both.
13. Process according to claim 12, wherein the bleaching stage comprises an ozone bleaching step followed by a peracetic acid bleaching step.
- 15 14. Process according to any one of claims 12 – 13, wherein the peracetic acid bleaching step takes place at a temperature of 40 – 80°C.
- 15 15. Dissolving pulp obtained by the process according to any one of claims 1 – 14.
- 20 16. Process according to any one of claims 1 – 14, wherein acid used in the hydrolysis stage and/or the bleaching stage is recycled.
- 25 17. Use of a dissolving pulp according to claim 15 for the production of cellulose acetate.