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(54) Title: PROCESS FOR THE RECOVERY OF HYDROCHLORIC ACID

(57) Abstract: Hydrochloric acid is recovered from a lignin composition in a process, comprising providing a particulate lignin composition that comprises lignin, water and hydrochloric acid; contacting the particulate lignin composition with a stream of stripping gas comprising an aprotic gas to obtain an acidified vapor stream that comprises water vapor, hydrochloric acid and aprotic gas; and recovering hydrochloric acid from the acidified vapor stream.



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Process for the recovery of hydrochloric acid

5 The present invention relates to a process for the recovery of hydrochloric acid. In particular, it relates to a process for the recovery of hydrochloric acid from a lignin composition that comprises lignin, water and hydrochloric acid.

 Lignin is one of the most common biopolymers. It comprises cross-linked phenol polymers and is believed to contain coumaryl alcohol, coniferyl alcohol and sinapyl alcohol
10 as building blocks. It constitutes a major part of various biomass materials. It is important for the formation of cell walls, especially in wood. Lignin can be obtained in the hydrolysis of wood and similar lignocellulosic materials. Such hydrolysis is typically used for the recovery of mono- and oligosaccharides from wood and such lignocellulosic biomass; lignin is often obtained as residue after the hydrolysis for saccharides recovery.

15 The hydrolysis of wood and other lignocellulosic material has been known for many years. Lignocellulosic material typically comprises cellulose and hemicellulose from which mono- and oligosaccharides can be obtained in addition to lignin. There appears to be a number of approaches to liberate mono- and oligosaccharides from lignocellulosic material. One of the approaches is enzymatic hydrolysis. This method requires a pre-treatment, such
20 as steam explosion, i.e. a method wherein biomass particles are exposed to high pressure superheated steam before a brusque pressure drop, to make the cellulose and hemicellulose accessible for enzymatic hydrolysis (cf. US 2012/0104313 and US 2013/0078677).

 A second approach is the hydrolysis with hot compressed or even supercritical water.
25 Such hydrolysis requires the application of high temperatures, e.g. 200 to 400 °C and high pressures, e.g. 50 to 250 bar, at short contact times. An example of such hydrolysis is described in US 2013/239954.

 Another approach is the use of dilute acid. Examples of such a method are the Schöller and Madison processes which are described in e.g. US 5879463 and DE 640775.
30 While sulfuric acid is used in these actual processes, the use of dilute hydrochloric acid and phosphoric acid is also known in the art.

 A further method uses concentrated acids. These methods include the Bergius Rheinau process, as described in e.g. DE 362230 and US 419937. An alternative process uses concentrated sulfuric acid (cf. US 5188673). The biomass does not require a pre-
35 treatment. The operating temperature during the hydrolysis can be relatively low; the temperature can be around room temperature and is typically at most 110 °C.

In the Bergius Rheinau process wood is shredded to chips which are treated with concentrated hydrochloric acid. During the treatment for instance about two-thirds of the wood is dissolved by the acid in the form of mono- and oligosaccharides, and the rest, e.g. about one-third remains as lignin. The dissolved fraction comprises mono- and
5 oligosaccharides, together with water and hydrochloric acid. This fraction is generally referred to as the hydrolysate. The lignin fraction is obtained as a solid fraction that comprises lignin, residual water and hydrochloric acid.

It is evident that it is desirable to recover the hydrochloric acid, both from an environmental and from an economic standpoint. In the prior art the focus has been mainly
10 on the recovery of hydrochloric acid from the hydrolysate. For example, US2011/0028710 describes a process where a polysaccharide-containing material is hydrolyzed to carbohydrates. The formed HCl-concentrate carbohydrate-containing solution is treated for partial removal of HCl, thereby forming a carbohydrate-containing dilute aqueous HCl solution. For the partial removal of HCl, HCl distillation or stripping can be used. The
15 resulting carbohydrate-containing dilute aqueous HCl solution is subsequently brought into contact with a specific water-immiscible extractant comprising an oil soluble amine, an oil soluble weak organic acid and a solvent for the amine and organic acid, whereby a HCl-depleted carbohydrate-containing solution is formed.

However, it is desirable to free also the lignin by-product from water and hydrochloric
20 acid. The literature has suggested to wash the lignin with water, but the amount of water required has been found too large to be feasible. Moreover, the result is a very dilute hydrochloric acid solution that requires extensive concentration before it can be recycled to the hydrolysis. In US 2012/0279497 and US 2012/0227733 it has been suggested to contact the wet hydrochloric acid-containing lignin with an organic solvent that is scarcely soluble in
25 water and to evaporate water, hydrochloric acid and the organic solvent to yield a lignin composition having a reduced water and hydrochloric acid content. It is evident that this process involves the application of complicated extraction, evaporation and separation treatments. In US 3251716 a process is described wherein a lignocellulosic material is hydrolyzed, also referred to as digested, with concentrated hydrochloric acid to yield a
30 hydrolysate containing mono- and oligosaccharides, hydrochloric acid and water, and a lignin composition containing aqueous hydrochloric acid and lignin. Hydrochloric acid is then separated from lignin by centrifuge. The hydrochloric acid separated is recycled to the hydrolysis of the lignocellulosic material. The remaining lignin still contains significant amounts of water and hydrochloric acid. Therefore the lignin is passed to a dryer. This is a
35 heated zone that is maintained at a temperature up to 360 °C where the lignin is in contact with a vapor. This vapor consists of a superheated mixture of water and hydrochloric acid and runs co-currently with the wet lignin. The temperature of the superheated vapor is 340

to 360 °C. After leaving the dryer a portion of the vapor is condensed, whereas the main portion is circulated through a superheater. Since the corrosive action of hydrochloric acid at higher temperatures increases, it is evident that the use of superheated hydrochloric acid vapors has the drawback that the risk of severe corrosion also increases. Further, since the hydrochloric acid vapor cools down whilst passing over the wet lignin to about 175 °C, the thermal efficiency of such an operation is flawed now that the water/hydrochloric acid vapor has to be heated to superheating temperatures of 340 to 360 °C.

Therefore, it is desirable to provide for a process wherein there is no need for heating a corrosive gas to temperatures in the range of 340 to 360 °C and wherein the energy input is limited. Accordingly, the present invention provides a process for the recovery of hydrochloric acid from a lignin composition, comprising providing a particulate lignin composition that comprises lignin, water and hydrochloric acid; contacting the particulate lignin composition with a stream of stripping gas comprising an aprotic gas to obtain an acidified vapor stream that comprises water vapor, hydrochloric acid and aprotic gas; and recovering hydrochloric acid from the acidified vapor stream.

Definitions of the specific embodiments of the invention as claimed herein follow.

According to a first embodiment of the invention, there is provided a process for the recovery of hydrochloric acid from a lignin composition, comprising

- providing a particulate lignin composition that comprises lignin, water and hydrochloric acid;
- contacting the particulate lignin composition with a stream of stripping gas comprising an aprotic gas to obtain an acidified vapor stream that comprises water vapor, hydrochloric acid and aprotic gas, wherein the aprotic gas is a combustion gas; and
- recovering hydrochloric acid from the acidified vapor stream.

According to a second embodiment of the invention, there is provided a process for the production of a lignin product, comprising hydrolyzing a particulate lignocellulosic material with hydrochloric acid to obtain a dissolved saccharides-containing hydrolysate and a particulate lignin composition that comprises lignin, hydrochloric acid and water, and contacting at least part of the particulate lignin composition with a stream of stripping gas that comprises an aprotic gas to obtain an acidified vapor stream that comprises water vapor, hydrochloric acid and aprotic gas, wherein the aprotic gas is a combustion gas, and a hydrochloric acid-lean lignin composition; and recovering the hydrochloric acid-lean lignin composition as lignin product.

The present process has the advantage that a stream of stripping gas can be used that does not have a corrosive component. It has further been found that the stream of stripping gas does not need to be heated to the very high temperatures as disclosed in

US 3251716. That mitigates the corrosive action of the stripping gas stream and also saves on heating requirements and costs. In this specification the term "aprotic" has the commonly known meaning of being incapable of acting as a proton donor.

As starting material for the present process a particulate lignin composition is used that comprises water and hydrochloric acid in addition to lignin. Such a lignin composition is typically obtained in the hydrolysis of lignocellulosic material. Lignocellulosic biomass can be broadly classified into virgin biomass, waste biomass and energy crops, such as starch and sucrose-containing crops. Virgin biomass includes all naturally occurring terrestrial plants such as trees, bushes and grass. Waste biomass is produced as a low value byproduct of various industrial sectors such as agricultural, such as corn stover, sugarcane bagasse, straw, etc., waste paper, forestry, such as saw mill and paper mill discards. Energy crops are crops with high yield of lignocellulosic biomass produced to serve as a raw material for production of second generation biofuel. Examples include switch grass and miscanthus, also known as elephant grass. The hydrolysis is typically conducted to produce oligosaccharides and monosaccharides from cellulose and hemicellulose, yielding e.g. cellotriose, cellobiose and glucose from cellulose, and mannose, xylose, galactose, arabinose and their oligomers from hemicellulose. The hydrolysis may be carried out by the action of dilute hydrochloric acid or concentrated hydrochloric acid. Hence, the lignin composition used in the process according to the invention has preferably been obtained

[Text continues on page 4.]

from a hydrolysis of lignocellulosic material with hydrochloric acid. Lignin compositions obtained in the Bergius Rheinau process are particularly preferred. A summary of an example of this process is provided in F. Bergius, Current Science, 1937, 632-637.

According to such a process a battery of diffusers is loaded with wood chips, optionally
5 mixed with a proportion of saw dust. The wood chips are suitably dried to a moisture content of at most 8%wt, based on the dried wood chips. In a pseudo counter-current mode a concentrated hydrochloric acid solution in water, e.g. having a hydrochloric acid concentration of 35 to 45 %wt, based on the solution, is fed into the last diffuser. During the
10 filling of the diffuser a digestion solution will be formed containing dissolved saccharides in addition to hydrochloric acid and water. When the diffuser is filled with the digestion solution and concentrated hydrochloric acid solution is continued to be fed into the last diffuser, the digestion solution will overflow to the penultimate diffuser and so on until there is an overflow of digestion solution from the first diffuser. The digestion solution is then withdrawn from the first diffuser as the hydrolysate and saccharides are recovered therefrom. Lignin
15 stays in the diffusers. According to the prior art the lignin is washed with water. Then the washed lignin is dried and can be used e.g. in form of briquettes as fuel for the hydrolysis plant.

According to the present invention there is no need to thoroughly wash the lignin with water. Instead the lignin is preferably passed through a press or centrifuge to remove
20 adherent hydrochloric acid and water and downstream of the press or centrifuge the lignin is contacted with a stream of the stripping gas in accordance with the invention. Accordingly, the present invention also provide a process for the production of a lignin product, comprising hydrolyzing a particulate lignocellulosic material with hydrochloric acid to obtain a dissolved saccharides-containing hydrolysate and a particulate lignin composition that
25 comprises lignin, hydrochloric acid and water, and contacting at least part of the particulate lignin composition with a stream of a stripping gas that comprises an aprotic gas to obtain an acidified vapor stream that comprises water vapor, hydrochloric acid and aprotic gas, and a hydrochloric acid-lean lignin composition; and recovering the hydrochloric acid-lean lignin composition as lignin product. The particulate lignin composition comprises lignin, water and
30 hydrochloric acid. Dependent on the lignocellulosic material that is hydrolyzed, other components may also be comprised in the lignin composition. Degradation products of saccharides may be present, such as furfural, hydroxymethylfurfural, phenolic compounds and organic acids such as acetic acid and levulinic acid. Inorganic components may also be present in minor amounts. Upon combustion they form ash. Examples of inorganic
35 components include sodium and potassium salts and silica. The amount of these other components is typically at most 5 %wt, based on the particulate lignin composition. The complete particulate lignin composition may be contacted with the stripping gas. Preferably,

adherent water and hydrochloric acid is removed from the particulate lignin composition by passing it through a press. Alternatively, the particulate lignin composition may be subjected to a centrifugal separation. It is also feasible to wash some of the hydrochloric acid from the particulate lignin composition by means of water and/or an aqueous hydrochloric acid solution. Hence, the particulate lignin composition is suitably disposed of adherent hydrochloric acid by passing through a press and/or by leading into a centrifuge and/or by washing with water and/or an aqueous hydrochloric acid solution.

According to the process of US 3251716 the lignin is dried by means of hydrochloric acid/water vapor at a temperature of 340 to 360 °C. Such high temperatures are not required in the process of the present invention. It has been found that the particulate lignin composition is preferably contacted with the stream of stripping gas at a temperature in the range of 150 to 280 °C, preferably from 180 to 250 °C. When the temperature is below the lowest value of this range the drying takes too long to be feasible. It is possible to operate at temperatures exceeding the maximum value of this range. However, no additional advantages are then obtained, and such operation only leads to unnecessary costs. Moreover, by operating at a modest temperature an increase of the level of corrosive action of the acidified vapor stream that takes place at superheated temperature can be avoided.

The particulate lignin composition may be brought to the desired temperature by means of any suitable equipment. It is thus feasible to introduce the particulate lignin composition into a heat exchanger wherein the heat is provided via indirect heat exchange via the wall and/or heat exchange elements, such as heat exchange coils or plates or tubes. The temperature of the heat exchange fluid that is used in such equipment will suitably be set at such a value that the particulate lignin composition is present at a temperature in the desired range. In some embodiments, the heat for the particulate lignin composition may at least partly be provided by the stripping gas stream. In such cases, the stream of stripping gas is suitably heated. When the stream of stripping gas is heated, it is suitably heated to a temperature in the range of 40 to 150 °C before it is contacted with the particulate lignin composition. In some embodiments the stream of stripping gas can be supplied at ambient temperature. The stream of stripping gas is thus suitably at a temperature of 20 to 150 °C before it is contacted with the particulate lignin composition. It has been found that the stripping action is most effective when the stream of stripping gas is contacted counter-currently with the particulate lignin composition.

There is no need to apply specific pressures. The process described in US 2012/0279497 and US 2012/0227733 purify the lignin by evaporating water, hydrochloric acid and the organic solvent used at pressures below 1 atm. The present process can suitably operate at atmospheric pressure, although it is feasible to carry out the process at a pressure in the range of 1 to 5 bara.

The stripping gas in the stream of stripping gas comprises an aprotic gas. The stripping gas comprises such gas at the conditions of the contact between the particulate lignin composition and the stream of stripping gas. That implies that at other conditions the aprotic gas may have a different aggregate phase, e.g. be liquid. Therefore the aprotic gas may suitably comprise an organic vapor. By organic vapor is understood a vaporous stream that comprises an organic chemical compound. The organic vapor may comprise a compound that can be selected from a variety of chemical compounds. Such compounds include hydrocarbons, by which are understood compounds that only consist of hydrogen and carbon. The organic vapor may also include compounds with one or more heteroatoms, such as oxygen or nitrogen. Suitable organic compounds may include ethers, aldehydes, ketones, esters, nitro compounds, dialkylamides and combinations thereof. The suitable organic compounds are vaporous at the conditions that prevail at the contact between lignin composition and stream of stripping gas. It is advantageous that the organic chemical compound is insoluble in water. In this specification by 'insoluble in a solvent' is understood that a substance in question dissolves for less than 1 g/100 mL of the solvent in question at 25 °C. Organic compounds that are vaporous at the desired conditions and also insoluble in water as defined herein tend not to have one or more heteroatoms. Therefore, the organic chemical compound is preferably a hydrocarbon having from 1 to 12 carbon atoms, preferably 1 to 4 carbon atoms.

When an organic compound, such as a hydrocarbon, is used that is liquid at normal conditions, i.e. at 20 °C and 1 bar, the prevailing temperature and pressure at the contact of lignin composition and stripping gas must be such that the hydrocarbon is vaporous. Upon cooling the organic compound may condense and become liquid. Such is the case when the organic compound is a hydrocarbon that has 5 or more carbon atoms. In such cases the stripping gas in the stream of stripping gas will be heated to the desired temperature range of 40 to 150 °C so that the organic compounds are vaporous. Although the use of such hydrocarbons can make their separation from aqueous solutions relatively easy, it requires significant heat exchange to condense and to re-vaporize such hydrocarbons. Therefore, it is advantageous to use as organic compounds hydrocarbons having 1 to 4 carbon atoms, which hydrocarbons are generally vaporous at the conditions that prevail throughout the hydrolysis of lignocellulosic material and the treatments of the effluents thereof.

Instead of organic vapors it is advantageous to select the aprotic gas from inorganic gases. Suitable inorganic gases are inter alia air, nitrogen, carbon monoxide, carbon dioxide, noble gases and combinations thereof. Although noble gases, i.e. the gases from group 18 of the Periodic Table of Elements, can also be applied, such as helium, neon or argon, their use is not practical when much cheaper and more abundant gases, such as air or nitrogen, are available. As the temperature of the process of the present invention is

modest, the risk of combusting the lignin when air is used is minimal. Obviously, the use of air is very convenient as it is abundantly available. A very suitable alternative is formed by combustion gases. The combustion gases may originate from whatever combustion process, e.g. from a heater that supplies energy to the hydrolysis of lignocellulosic material, or from a heater that provides the energy for heating the particulate lignin composition. The use of a combustion gas has the advantage that it generally becomes available at elevated temperature and also that it contains suitable aprotic gases such as nitrogen, carbon dioxide and optionally carbon monoxide. The oxygen content in combustion gases has been significantly reduced compared to air, so that any risk for combustion of the lignin is further reduced. The use of the above-mentioned inorganic gases and also that of non-condensable organic gases, such as C₁-C₄ hydrocarbons, creates the possibility to pass these gases as stripping gas along the lignin composition without heating these gases. In this case, the heat required for the evaporation of water and hydrochloric acid can be provided by indirect means, such as via surfaces heated by a heat exchange medium, such as hot oil or steam. When the inorganic gases are used in the stripping gas, these gases can be discharged after having recovered the hydrochloric acid from them. That is economic and environmentally safe.

The duration of the contact between the particulate lignin composition and the stream of stripping gas is not critical. Factors that may influence the desired duration include the temperature of the particulate lignin composition, the temperature of the stream of stripping gas, the heat capacity of the aprotic gas, the rate at which the stream of stripping gas is supplied, expressed as volume of stripping gas per kilogram particulate lignin composition, and the desired level of moisture and/or hydrochloric acid in the lignin product. Typically the amount of stripping gas per kilogram of particulate lignin composition is in the range of 0.1 to 25 Nm³/kg, preferably from 0.5 to 10 Nm³/kg. The duration of the contact may typically be varied from 5 to 300 minutes, preferably from 20 to 120 minutes. The duration can be varied by applying different flow rates for the stripping gas. Suitable values for the flow rate of the stream of stripping gas are in the range of 25 to 1000 Nm³ stripping gas per kg lignin composition per hour, preferably from 50 to 400 Nm³/kg/h, more preferably from 100 to 250 Nm³/kg/h.

The skilled person will realize what equipment suitably can be used for operating the process according to the present invention. It is feasible to pass the stripping gas through or along a bed of the lignin composition. Such can be achieved in a column reactor. Alternatively, the lignin composition can be subjected to a stripping gas in a dryer. Equipment that is at his disposal includes flash dryers, paddle dryers, rotary drum dryers, rotary tube dryers, rotary louver dryers, fluidized bed dryers, cabinet dryers, tunnel dryers and conveyor dryers. A very suitable dryer appears to be a rotary tube dryer. The

particulate lignin composition therein is rotated thereby reducing the effect of diffusion, and the stream of stripping gas is passed through in a counter-current or co-current mode, thereby promoting the separation of water and hydrochloric acid from the lignin composition. The heat for drying is provided by a heat exchange medium that flows through the tubes in
5 the rotary tube dryer.

It is advantageous to recover the hydrochloric acid from the acidified vapor stream. There are several methods for achieving the recovery of hydrochloric acid. Suitably the acidified vapor stream can be subjected to absorption or adsorption to recover hydrochloric acid. One suitable method involves passing the acidified vapor stream along an adsorbent
10 that selectively adsorbs hydrochloric acid, which can be followed by desorption. Typically such adsorbents include metal oxides that have a significant surface area, e.g. a BET surface area of at least 200 m²/g. Suitable adsorbents include alumina, zeolite-alumina mixtures and alumina that is promoted with an alkali metal oxide. Examples of such adsorbents are disclosed in e.g. US 4762537 and US 5316998.

15 Adsorbents are most commonly used as means to purify contaminated gas streams. Their capacity therefore tends to be rather limited. If large amounts of hydrochloric acid are to be recovered from a large acidified vapor stream the equipment for the adsorbents must be large, too. The sheer size of such equipment may render the recovery very expensive. Therefore, it is preferred to subject the acidified vapor stream to absorption with a liquid
20 wherein the hydrochloric acid is selectively dissolved. The liquid may consist of organic compounds, such as amines. Suitable amines include alkanolamines, di- and tri-alkyl amines. The amines may be primary, secondary and tertiary amines and have at least 10, and preferably at least 14, carbon atoms and at least one hydrophobic group. Examples of such amines are di-isopropanol amine, methyl diethanol amine, triethanol amine, tri(2-
25 ethylhexyl)amine, tri-octyl amine, tri-isooctyl amine, tridecylamine, tricapyryl amine and combinations thereof. Other suitable amines are listed in US 3548282. It has been found that the hydrochloric acid may also be easily absorbed in an aqueous absorbent. Therefore, the acidified vapor stream is preferably subjected to absorption with an aqueous absorbent, to yield acid-loaded absorbent. The aqueous absorbent comprises water. In an embodiment
30 the absorbent may comprise one or more additives to promote the absorption of hydrochloric acid and/or to facilitate the work up of the acid-loaded absorbent. The absorption may be promoted by using water-soluble amines, such as triethanol amine, di-isopropanol amine or methyl diethanol amine. Also inorganic basic compounds can be used to promote absorption of hydrochloric acid. However, when the acid-loaded absorbent is to be re-used in e.g. the
35 hydrolysis of lignocellulosic material, it is advantageous that the aqueous absorbent comprises mainly water. It may consist of water, but in practice the aqueous absorbent may contain some hydrochloric acid. Dependent on the process the aqueous absorbent may also

comprise minor amounts organic compounds, such as methanol and/or acetic acid. In this way the acid-loaded absorbent comprises mainly hydrochloric acid and water, preferably substantially consists of hydrochloric acid and water. Since the solubility of hydrochloric acid in water is very good, the aqueous absorbent may comprise an aqueous solution of

5 hydrochloric acid. Suitably, such a solution comprises hydrochloric acid in relatively low concentrations, e.g. up to 5%wt, based on the aqueous absorbent. The content of water in the aqueous absorbent may vary from 80 to 100%wt, preferably from 95 to 100 %wt, based on the aqueous absorbent. The use of such dilute hydrochloric acid solutions as aqueous

10 absorbent has the advantage that other gases that may have a tendency to dissolve in water, such as carbon dioxide, are to a certain extent prevented from dissolving into the absorbent. The use of an aqueous absorbent that comprises water, optionally containing hydrochloric acid, or preferably substantially consists of water or substantially consists of water and hydrochloric acid, is further advantageous, as the absorbent can be used until an acid-loaded absorbent having the desired hydrochloric acid concentration is obtained. If so,

15 the acid-loaded absorbent can then be recycled to a hydrolysis of lignocellulosic material. If the hydrolysis is conducted with diluted hydrochloric acid, no further treatment of the acid loaded absorbent may be necessary. If the hydrolysis is carried out with concentrated hydrochloric acid, such as in the Bergius Rheinau process, an acid-loaded absorbent as a relatively concentrated solution of hydrochloric acid is obtained. The concentration of

20 hydrochloric acid in such acid-loaded absorbents may be as high as more than 20%wt, calculated as hydrochloric acid based on the acid-loaded absorbent. Nevertheless, some further concentration to even higher concentrations of hydrochloric acid may be desired.

The use of an aqueous absorbent is also advantageous when an organic compound that under standard conditions is liquid, is used as aprotic gas. For instance, when the

25 aprotic gas is a hydrocarbon with five or more carbon atoms, and the acidified vapor stream is contacted with an aqueous absorbent, the organic compound condenses and is easily separated from the aqueous absorbent by phase separation. The organic compound is then isolated and can be re-heated and re-used as aprotic gas in the stream of stripping gas.

As indicated above, the acid-loaded absorbent can be used to recycle hydrochloric

30 acid to earlier steps in the process, e.g. the hydrolysis of lignocellulosic material. When the hydrolysis is carried out with a dilute solution of hydrochloric acid the acid-loaded absorbent may be used as such. Alternatively, some treatment of the absorbent may be carried out to obtain a solution with the desired hydrochloric acid concentration. When the hydrolysis is conducted with concentrated hydrochloric acid concentration, as in the Bergius Rheinau

35 process, the acid-loaded absorbent may require additional concentrating in order to render it suitable for recycle to the hydrolysis. A challenge is then provided by the fact that hydrochloric acid and water form an azeotrope, wherein the hydrochloric acid concentration

is about 18 to 23 %wt, depending on the pressure. Since the Bergius Rheinau process and similar processes operate at higher hydrochloric acid concentrations, the azeotrope is typically unsuitable for direct re-use in the hydrolysis. It is known in the art to obtain hydrochloric acid at higher concentration than in the azeotrope. A feasible method is to feed
5 a dilute solution into a distillation column that operates at low pressure, e.g. 0.01 to 0.9 bar, to obtain a top stream of water and a hydrochloric acid stream at the bottom. The concentration of the bottom stream is suitably that of the azeotrope, e.g. about 23%wt hydrochloric acid. A portion of the bottom stream is then fed into a second distillation column that operates at higher pressure, e.g. from 2 to 5 bar, resulting in a concentrated
10 hydrochloric acid stream over the top, having a concentration above 30 %wt and a bottom stream that has a low hydrochloric acid concentration, suitably that of the azeotrope, e.g. about 18 %wt. The bottom stream is then recycled to the first distillation column. In this way all hydrochloric acid is obtained in concentrated form.

Alternatively, the loaded absorbent may be subjected to extractive distillation where a
15 dilute hydrochloric acid solution is fed into a distillation column wherein aqueous hydrochloric acid is contacted with an azeotrope-breaking component, typically a chloride salt, such as calcium or magnesium chloride. This leads to a top product of concentrated hydrochloric acid and a bottom product of a dilute solution that contains the chloride salt. The chloride salt is concentrated in a separate vessel and recycled to the distillation column.

20 An extractive distillation process is e.g. described in US 3779870. Since the use of a Bergius Rheinau process is preferred, the acid-loaded absorbent is preferably subjected to one or more distillation steps to yield a hydrochloric acid-rich fraction with a higher concentration than the acid-loaded absorbent. Preferably, at least a portion of this hydrochloric acid-rich fraction, optionally after further acid concentration, is recycled to a
25 hydrolysis of lignocellulosic material.

The particulate lignin composition that is produced in the process according to the present invention contains minor amounts of water and hydrochloric acid. In that it differs from the lignin produced in the process according to US 3251716, that is contacted with superheated water and hydrochloric acid. By this treatment the lignin will absorb significant
30 quantities of hydrochloric acid.

The particulate lignin composition also differs from the treated lignin composition obtained in the process of US 2012/0279497. This treated lignin may contain less than 10,000 ppm hydrochloric acid and is water-free. The absolute dryness entails a risk. The treated lignin is not only dry but also tends to have a high degree of dustiness. Both the
35 dryness and the dustiness are factors that raise the risk of explosion or fire. Such risk represents a considerable disadvantage of the treated lignin according to US 2012/0279497.

The present process results in a particulate lignin composition that has enough water to eliminate the risk of explosion and has a sufficiently low amount of hydrochloric acid to be safe. Accordingly, the present invention also provides a particulate lignin composition comprising lignin, hydrochloric acid and water, wherein the content of hydrochloric acid is in the range of 100 to 10,000 parts by weight per million (ppmw), preferably from 500 to 5000 ppmw, based on the weight of the particulate lignin composition and the content of water is in the range of 0.1 to 2 %wt, based on the weight of the particulate lignin composition. The lignin content in the particulate lignin composition will suitably be in the range of 98 to 99.9%wt.

The invention will be further illustrated by means of the following example.

EXAMPLE

A series of vessels were loaded with a lignin composition that comprised about 49.5 %wt of lignin, on a dry basis, and about 50.5 %wt of a concentrated hydrochloric acid solution, containing 37%wt of hydrochloric acid. The hydrochloric acid content in the lignin composition was therefore 18.7%wt.

Nitrogen gas was passed as stream of stripping gas along the bed of the lignin composition at a flow rate of 87.3 or 174.5 Nm³/kg/h. The nitrogen gas was supplied at ambient temperature, i.e. about 20 °C, and pre-heated to the drying temperature before being contacted with the lignin composition. The lignin compositions were heated to various temperatures. At different periods of supply of the stripping gas the hydrochloric content of the lignin product then obtained was determined.

The results are shown in the Table below. The Table indicates the temperature at which the lignin composition is contacted with the stripping gas ("T"), the flow rate of the stream of stripping gas ("Flow"), the time during which the lignin composition was contacted with the stripping gas ("t"), the total amount of stripping gas supplied per weight unit of lignin composition when the lignin product was removed for determination of the hydrochloric acid content ("Gas") and the content of hydrochloric acid on the lignin product, expressed as hydrochloric acid on the lignin product ("HCl_{prod}").

Table

Exp. No.	T, °C	t, hr	Flow, Nm ³ /kg/h	Gas, Nm ³ /kg	HCl _{prod} , %wt
1	170	1.30	174.5	3.78	1.08
2	170	2.30	174.5	6.69	0.88
3	170	3.67	174.5	10.67	0.71
4	170	6.10	174.5	17.74	0.59
5	200	0.17	87.3	0.36	0.73

6	200	0.43	87.3	0.95	0.50
7	200	0.67	87.3	1.45	0.45
8	200	1.83	87.3	4.00	0.39
9	200	6.00	87.3	17.09	0.36
10	200	0.25	174.5	1.09	0.69
11	200	0.62	174.5	2.69	0.55
12	200	0.80	174.5	3.49	0.47
13	200	1.25	174.5	5.45	0.34
14	220	0.17	174.5	0.72	0.46
15	220	0.43	174.5	1.89	0.38
16	220	0.80	174.5	3.49	0.35
17	220	1.00	174.5	4.36	0.26
18	220	1.25	174.5	5.45	0.26

The results show that hydrochloric acid can be efficiently removed from hydrochloric acid-containing lignin compositions. Especially at elevated temperatures and at flow rates above 100 Nm³/kg/h, the level of hydrochloric acid that remains in the lignin product can be reduced to a low value within a short period and thus with the use of a limited amount of stripping gas. That has the advantage that a smaller amount of stripping gas has to be subjected to e.g. absorption to recover the hydrochloric acid entrained.

The term “comprise” and variants of the term such as “comprises” or “comprising” are used herein to denote the inclusion of a stated integer or stated integers but not to exclude any other integer or any other integers, unless in the context or usage an exclusive interpretation of the term is required.

Any reference to publications cited in this specification is not an admission that the disclosures constitute common general knowledge in Australia.

CLAIMS

1. Process for the recovery of hydrochloric acid from a lignin composition, comprising
 - providing a particulate lignin composition that comprises lignin, water and hydrochloric acid;
 - contacting the particulate lignin composition with a stream of stripping gas comprising an aprotic gas to obtain an acidified vapor stream that comprises water vapor, hydrochloric acid and aprotic gas, wherein the aprotic gas is a combustion gas; and
 - recovering hydrochloric acid from the acidified vapor stream.

2. Process according to claim 1, wherein the particulate lignin composition has been obtained from a hydrolysis of lignocellulosic material with hydrochloric acid.

3. Process according to claim 1 or 2, wherein the particulate lignin composition is contacted with the stream of stripping gas at a temperature in the range of 150 to 280 °C, preferably in the range of 180 to 250 °C.

4. Process according to any one of claims 1 to 3, wherein the stream of stripping gas is at a temperature in the range of 20 to 150 °C before it is contacted with the particulate lignin composition.

5. Process according to any one of claims 1 to 4, wherein the stream of stripping gas is contacted counter-currently with the particulate lignin composition.

6. Process according to any one of claims 1 to 5, wherein the aprotic gas comprises an organic vapor.

7. Process according to claim 6, wherein the organic vapor comprises a hydrocarbon having from 1 to 12 carbon atoms, preferably 1 to 4 carbon atoms.

8. Process according to any one of claims 1 to 7, wherein the acidified vapor stream is subjected to absorption or adsorption to recover hydrochloric acid.

9. Process according to claim 8, wherein the acidified vapor stream is subjected to absorption with an aqueous absorbent, to yield acid-loaded absorbent.

10. Process according to claim 9, wherein the aqueous absorbent substantially consists of water.

11. Process according to claim 9 or 10, wherein the acid-loaded absorbent is subjected to one or more distillation steps to yield a hydrochloric acid-rich fraction with a higher acid concentration than the acid-loaded absorbent.

12. Process according to claim 11, wherein at least a portion of the hydrochloric acid-rich fraction, optionally after further acid concentration, is recycled to a hydrolysis of lignocellulosic material.

13. Process for the production of a lignin product, comprising hydrolyzing a particulate lignocellulosic material with hydrochloric acid to obtain a dissolved saccharides-containing hydrolysate and a particulate lignin composition that comprises lignin, hydrochloric acid and water, and contacting at least part of the particulate lignin composition with a stream of stripping gas that comprises an aprotic gas to obtain an acidified vapor stream that comprises water vapor, hydrochloric acid and aprotic gas, wherein the aprotic gas is a combustion gas, and a hydrochloric acid-lean lignin composition; and recovering the hydrochloric acid-lean lignin composition as lignin product.

Date: 20 February 2020