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(54) **Title:** METHOD FOR THE ACETYLATION OF WOOD

(57) **Abstract:** The present invention provides a method for the acetylation of wood comprising treating the wood with an acetylation medium under wood acetylation reaction conditions and drying the acetylated wood, wherein the drying comprises at least two steps, wherein the wood is first dried with a first drying medium and then with a second drying medium.

Title: Method for the acetylation of wood

5 The invention relates to the field of wood acetylation. Particularly, the present invention provides a method for the acetylation of wood including a step of drying the acetylated wood.

Background of the invention

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Acetylation of wood is used to improve the durability of wood and of wood elements used in the preparation various products such as fibre boards. Acetylation is typically performed in a batch or continuous type of reactor. After the acetylation process is finished, the acetylated wood is typically dried to remove the chemicals.

15 When wood is acetylated in industrial amounts, it is a general desire to acetylate in a relatively quick and economical way. This especially holds for continuous processes that often use a particular residence time of the wood in the reactor. It is therefore desired that also the drying step following the acetylation step is performed in a quick and efficient way.

20 It is an object of the present invention to provide a method for the acetylation of wood that allows fast and efficient removal of the residual chemicals from the acetylated wood.

25 **Summary of the Invention**

In order to better address one or more of the foregoing desires, the invention presents, a method for the acetylation of wood comprising treating the wood with an acetylation medium under wood acetylation reaction conditions and drying the acetylated wood, wherein the drying comprises at

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least two steps, wherein the wood is first dried with a first drying medium and then with a second drying medium.

Detailed description of the invention

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The invention, in a broad sense, is based on the judicious insight that the drying of acetylated wood following an acetylation process can be carried out more efficiently in several steps, using different drying media. Drying in the present invention refers to a post-reaction step, that is, after the acetylation reaction, or after all the acetylation reaction steps in case
10 several reaction steps are carried out. During this post-reaction drying residual chemicals are removed from the acetylated wood (particularly, the acetylation medium and reaction by-products). In some embodiments, drying aims to remove the residual amounts of acetic acid and acetic
15 anhydride after the acetylation step(s). Drying as used throughout this application is hence distinctly different from removing water from non-acetylated wood, as often done in a pre-acetylation step.

According to the present invention, the wood is dried in at least two steps. It is first dried with a first drying medium and then with a second
20 drying medium, optionally wherein the first drying medium has a higher heat capacity than the second drying medium and/or the first drying medium comprises a higher content (mol%) of acetylation medium than the second drying medium. While some conventional techniques use a hot inert gas for drying, it may take considerable time to lower the amount of
25 impurities to an acceptable level. A longer drying time is especially applicable to high pressure acetylation processes because after the pressure release following the acetylation step, the wood is cooled down due to flashing and needs to be reheated. If the drying is done using an inert gas such as nitrogen, due to its low heat capacity it takes more time before the
30 wood is dried.

This problem is solved by first drying with a first, preferably high heat capacity drying medium and then drying with a second drying medium. The first drying medium preferably has a higher heat capacity and serves two goals. Firstly, it efficiently heats up the wood and, secondly, it is able to
5 remove the chemicals from the wood to a certain level. While that level may still be too high compared to industrial requirements, using another drying medium, preferably an inert gas, in a second step allows to lower the content of the chemicals to a sufficiently low level, which meets industry standards (<0.5 wt.% for residual acetic acid). A combination of both steps,
10 therefore, achieves a quick and efficient drying of acetylated wood to a low residual acetic acid content. The use of an acetylation medium in the first step also enables efficient integration of drying purge gases in the acetylation process whilst also minimizing the use, and subsequent purification, of inert gases. The use of an inert gas in the final stage enables
15 low residual hydrocarbon levels. Thus the judicious selection of drying medium, optionally recycle and purge gas flows and residence time in each drying stage enables an improved drying efficiency.

The wood suitable for the method according to the invention can be either solid wood or wood elements. Solid wood would typically have a
20 width and a thickness of from 1 to 30 cm, and a length of from 1 to 6 m. Preferably, the wood has a width and a thickness of from 2 to 10 cm and a length of 1.5-4 m. However, other dimensions can also be used.

In a preferred embodiment, the wood is in the form of wood elements. Preferably, the wood elements have a size of a height and width
25 from 0.1 cm to 3 cm, and a length of 1 to 7 cm. In some embodiments it may be preferred to have the wood elements with a height and width from 1 to 2.5 cm, and a length of 2-5 cm, for example approximately 2.5 cm x 1.5 cm x 1.5 cm in size. The morphology of the wood elements may be, but is not limited to, wood chips, wood fibres, wood flour, wood strands, wood
30 shavings, *etc.* In a preferred embodiment, the wood elements are wood chips.

The wood or wood elements preferably belong to non-durable wood species such as soft woods, for example, coniferous trees, spruce, pine or fir or to non-durable hardwoods, typically spruce, pine or fir beech, birch, eucalyptus, poplar or alder.

5 Preferably, the wood has a moisture content of at most 6 wt.% dry base, before the acetylation. After chipping the trees, the green wood has a typical natural moisture content (MC) of > 100 wt.% based on the dry weight. The moisture content of the wood is preferably lowered to below 6 wt.% dry weight, before the wood is treated in the acetylation process. At
10 higher moisture contents too much of the acetylation medium (typically containing acetic anhydride) will be consumed in a reaction with water in the wood instead of with the hydroxyl groups in the wood, which makes the acetylation process less efficient. Another disadvantage of a too high MC is that the strong exothermic reaction of acetic anhydride with water in the
15 wood can lead to local overheating in the wood and discoloration of the wood may occur. More preferably, the moisture content is less than 4 wt.%, ideally less than 3 wt.%. Lowering of the moisture content can be achieved by conventional continuous or batch drying techniques.

 According to the method of the present invention, the wood is
20 acetylated to obtain acetylated wood. Acetylation is achieved by treating the wood with an acetylation medium under wood acetylation reaction conditions. Under "acetylation medium" it is understood a compound or a mixture of compounds that are able to acetylate the hydroxyl groups of cellulose in the wood. For example, acetic acid or acetic anhydride are
25 suitable acetylation media. Preferably, the acetylation medium comprises acetic acid, acetic anhydride or a mixture thereof. More preferably, the acetylation medium comprises a mixture of acetic acid and acetic anhydride. Particularly, such mixture preferably comprises at least 50 wt.%, more preferably at least 85 wt.% of acetic anhydride.

Under "wood acetylation reaction conditions" the conditions are understood under which the wood undergoes acetylation. A skilled person is aware of specific temperature and pressure conditions to achieve acetylation of wood. Usually acetylation is performed under an elevated temperature, 5 *e.g.* at a temperature 70-190°C. An example of an acetylation process is the one described in EP 680810. Preferably, the acetylation conditions comprise heating at a temperature in the range 160-190°C.

In a particularly preferred embodiment, the acetylation takes place at an increased pressure, preferably at least 1 barg. More preferably, 10 the pressure in the acetylation reactor is in the range 1.5-5 barg, yet more preferably 2-3.5 barg. When the acetylation takes place under an increased pressure, the pressure is ideally released before entering the finishing step, *i.e.* prior to drying. Since the wood still contains liquid from the acetylation step after the acetylation, the release of the pressure will result in a rapid 15 cooling of the wood due to flashing. In the method according to the present invention, the two-step drying provides for a rapid and efficient re-heating of the cooled wood to the temperature of drying and removal of remaining chemicals from the wood.

The unreacted acetylation medium from the acetylation step is 20 preferably recycled and re-used in the process. This can be realised by condensing the vapour at the exit part of the reactor and separating by distillation of acetic anhydride. Separated acetic anhydride can then be re-used in the process and separated acetic acid can be stored or used in another process, or converted to acetic anhydride by known methods.

25 In case the acetylation is conducted at an elevated pressure, the pressure is substantially released at the end of the acetylation reaction. Preferably the pressure drops to about -0.4 barg to 0.3 barg.

In one embodiment of the present process the acetylated wood at the end of acetylation contains at least 55 wt.% liquid on dry basis of the

acetylated wood weight. When an elevated pressures is used, the above-mentioned liquid content refers to the wood before depressurization.

In one embodiment, depressurisation is achieved by discharging the acetylated material from the reactor using a an arrangement of one or
5 more rotary valves and/or sluice gates.

In a further step, the acetylated wood is dried. Drying means the removal of the acetylation medium and reaction products from the acetylated wood. During drying acetic acid and unreacted acetic anhydride are removed, preferably to a level of below 0.5 wt.%.

10 An important characteristic of the present invention is that the drying comprises at least two steps wherein different drying media are used.

In a first step, the wood is dried with a first drying medium, which preferably comprises an acetylation medium vapour and more preferably comprises superheated acetylation medium vapour. Superheated
15 medium means heated to a temperature higher than its boiling point, without boiling. By its nature, the superheated acetylation medium is suitable for drying the acetylated wood containing liquid acetylation medium and other acetylation residues. The first drying medium has preferably a higher heat capacity than the heat capacity of the second
20 drying medium, used in a following step. The first drying medium preferably comprises a higher content (mol%) of acetylation medium than the second drying medium.

The acetylation medium vapour preferably comprises acetic acid, acetic anhydride or a mixture thereof. Suitably, the acetylation medium
25 vapour can comprise the unreacted acetylation medium from the acetylation step, which is preferably recycled and re-used in the process.

The first drying medium preferably comprises at least 90 wt.% of the acetylation medium (preferably, a mixture of acetic acid and acetic anhydride) and a maximum of 10 wt.% of an inert gas such as nitrogen or
30 the like. Preferably, the acetylation medium is a mixture of acetic acid and

acetic anhydride. An example of a preferred composition of the first drying medium is 20-50 wt.% acetic acid, 50-80 wt.% acetic anhydride and 0-3 wt.% of nitrogen.

Preferably, the residence time in the first drying step is 5-25 min.

5 The gas to solid flow rate in first drying step is preferably 1-6 mass ratio.

In a second drying step, the wood is dried with a second drying medium, which is preferably an inert gas. Inert gas means that it is inert to the wood or the acetylation reaction. Preferably, the inert gas is nitrogen, carbon dioxide or flue gas. More preferably, the inert gas is nitrogen.

10 In both steps, conventional drying techniques can be used, for example blowing with a (hot) gas over the wood. Preferably, the acetylated wood is dried in either or both of the drying steps at a temperature in the range 150-190°C, more preferably in the range 160-180°C. The drying in the first and/or the second step is preferably carried out at a pressure lower
15 than the acetylation reaction pressure. Preferably, ambient pressure is used during drying, more preferably the pressure from -0.4 barg to 0.3 barg is used.

The residence time in the second drying step is preferably 15-40 min. The gas to solid flow rate in first drying step is preferably 0.7-5 mass
20 ratio.

Preferably, the acetylated wood before discharging or depressurization contains at least 55 wt.% liquid on dry basis of the acetylated wood weight; after flashing —*i.e.* at beginning of the first drying step, the liquid content is typically reduced to at least 30 wt.%. During the
25 first drying step this liquid content is typically reduced to 2-8 wt.%, at most 10 wt.%. During the second drying step this is further reduced to max 0.5 wt.% on dry basis.

The described two drying steps can suitably take place in vessels that ensure a minimum residence time for all wood elements and that
30 provide for good, preferably uniform distribution, of the drying medium

through the wood elements in the dryer. The drying medium may flow in a counter-current or cross-current manner relative to the wood elements. The drying medium used for each drying step is preferably recycled to achieve the required drying flowrate with minimum make-up gas requirement.

5 Each such recycle loop may be provided with (i) cooling to condense and then separate degassed hydrocarbons from the recycled drying medium and/or (ii) a vapor make-up or purge to maintain mass balance. The drying medium fed to each step is preferably heated prior to introduction into the drying vessel.

10 The drying vessel may be a batch or continuous, optionally a plug flow, vessel or silo. The drying vessel may alternatively be a screw device with a cross-flow of drying gas.

The acetylation reaction and the drying steps can be each performed in a continuous manner or batchwise. Preferably, the acetylation
15 reaction and/or each of drying steps are carried out as a continuous process, more preferably all the three mentioned steps are carried out in a continuous manner. In an alternative embodiment, the acetylation reaction and/or any of the drying steps is carried out batchwise. Preferably, all the three mentioned steps are carried out batchwise.

20 One or more of the acetylation reaction and each of the drying steps may be effected in the same or in separate vessels. In one embodiment, the acetylation reaction and each of the drying steps are performed in a separate vessel, preferably with each step being continuous. In an alternative embodiment, the acetylation reaction and each of the
25 drying steps are performed in the vessel, preferably with each step being batchwise.

The dried acetylated wood can be cooled down to room temperature. Conventional techniques can be used for that such as air cooling or water cooling.

An important advantage of the method according to the present invention is that it allows the obtaining of acetylated wood with a high acetylation degree and low residual acid content in a quick and efficient way. Due to the above-described two-step drying procedure with different
5 drying media, the wood can efficiently and fast be (re-)heated and the residual chemicals be removed in a relatively short period of time. The total drying time is preferably under 90 min, more preferably in the range 20-65 min.

Preferably, the acetyl content of the acetylated wood is from 17%
10 to 26%, as measured by high-pressure liquid chromatography (HPLC), preferably at least 19%, more preferably 21%.

The residual acetic acid (RA) content is a measure of the residual, non-bound acetic acid or from hydrolysis of residuals of unreacted acetic anhydride contained in the wood. Acetic acid may also originate from the
15 wood itself, therefore the RA measures both the original acetic acid and the acetic acid left from the acetylation reaction. For determining the residual acid (RA) a well defined amount of 3-5 g of sample material is shaken in demineralised water for 1 hr. After this extraction step the sample is separated from the water fraction by filtration. Subsequently this water
20 fraction is titrated with a known sodium hydroxide (NaOH) solution, using phenolphthalein as an indicator, from which the residual acid concentration of the sample can be calculated.

The method according to the present invention allows to achieve the RA of the acetylated wood below 1% by weight, preferably below 0.9%,
25 more preferably below 0.5% by weight. Most preferably, the acetylated wood contains less than 0.2% of residual acid by weight. In a preferred embodiment, the RA content is from 0.05 to 0.9 wt.%. One of the advantages of the low levels of residual acetic acid is that the wood does not have any odour of acetic acid.

Acetylated wood obtained according to the method of the present invention may be used in various applications. Acetylated wood elements may usefully be refined and converted to board, such as medium density fibreboard, which will possess the superior dimensional stability, durability, stability to ultra-violet light and thermal conductivity, compared with boards derived from non-acetylated wood elements.

The following non-limiting example serves to illustrate the invention. In this example and throughout this specification, all percentages, parts and ratios are by weight unless indicated otherwise.

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Example

A mixture of wood chips with dimensions 2.5 cm x 1.5 cm x 1.5 cm consisting of 80% Sitka Spruce with 20% Loblolly Pine has been dried to a moisture content of 2.5%. This mixture is fed to an acetylation step where it is sprayed with liquid acetic anhydride/acetic acid mixture and heated with superheated acetic anhydride/acetic acid mixture (where the liquid to gas ratio is 1:2.5 wt:wt) to a temperature of 180°C at a pressure of 2.5 barg. The weight ratio of acetic anhydride to acetic acid in the acetylation medium mixture is 90:10. After a residence time of 30 minutes at these conditions the pressure is released and the wood chips are transferred to the drying step, which proceeds at 0 barg. The first drying step occurs with a gas flow to solid flow ratio of 3.2:1 (mass:mass) with a gas phase composition of 33% acetic acid, 65% acetic anhydride and 2% nitrogen. The residence time for this step is 15 minutes, where the chips are heated with a temperature of 170°C. Subsequently the chips are transferred to the second drying step, where the chips are heated with nitrogen at 170°C for 25 additional minutes. This process resulted in acetylated wood chips with an acetyl content (AC) of 23.2% and a residual acid content of 0.3 wt.%.

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Claims

1. Method for the acetylation of wood comprising treating the wood with an acetylation medium under wood acetylation reaction conditions and drying the acetylated wood, wherein the drying comprises at least two steps, wherein the wood is first dried with a first drying medium and then with a
5 second drying medium.
2. The method according to claim 1, wherein the first drying medium has a higher heat capacity than the second drying medium.
- 10 3. The method according to claim 1 or 2, wherein the first drying medium comprises an acetylation medium vapour.
4. The method according to any of the preceding claims, wherein the second drying medium is an inert gas, preferably nitrogen.
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5. The method according to claim 1, wherein the acetylation reaction conditions comprise a pressure of at least 1 barg.
6. The method according to claim 1, wherein the drying in the first
20 and/or the second step is carried out at a pressure lower than the acetylation reaction pressure.
7. The method according to any one of the preceding claims, wherein the acetylation medium comprises acetic acid, acetic anhydride or a mixture
25 thereof.
8. The method according to claim 4, wherein the acetylation medium comprises a mixture of acetic acid and acetic anhydride, preferably

comprising at least 50 wt.%, more preferably at least 85 wt.% of acetic anhydride.

9. The method according to any one of the preceding claims, wherein
5 the acetylation conditions comprise heating to a temperature in the range 160-190°C.

10. The method according to any one of the preceding claims, wherein
10 the drying temperature in either one or both of the drying steps is in the range 150-190°C.

11. The method according to any one of the preceding claims, wherein
in the first drying step the residence time is 5-25 min and, optionally, the
gas to solid flow rate is 1-6 mass ratio.

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12. The method according to any one of the preceding claims, wherein
in the second drying step the residence time is 15-40 min and, optionally,
the gas to solid flow rate is 0.7-5 mass ratio.

20 13. The method according to any one of the preceding claims, wherein
the liquid content in the acetylated wood after acetylation and before drying
is at least 55 wt.% on dry basis.

14. The method according to claim any one of the preceding claims,
25 wherein the liquid content in the acetylated wood is reduced during the first
drying step to at least 2-8 wt.% on dry basis and in the second drying step to
max 0.5 wt.% on dry basis.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/058147

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08B3/06 C08B3/20 C08H8/00
 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)
 C08B C08H

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 , BIOSIS, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	W0 2012/037481 AI (TITAN WOOD LTD [GB] ; ROWELL ROGER M [US]) 22 March 2012 (2012-03-22) cl aims ; exampl es -----	1-14

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"P" document published prior to the international filing date but later than the priority date claimed	

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2016/058147

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