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Methods for producing a manure-derived cellulose acetate at atmospheric pressure.

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A method for producing a manure-derived cellulose acetate at atmospheric pressure, by separating manure into useful components, comprising the steps of: a. flocculation treatment and a filtration treatment where fractions having different particle size are separated by using different mesh sizes to obtain solid fractions having a high lignocellulose content; b. pulping the manure-derived solid fractions with high lignocellulose content at atmospheric pressure with a monocarboxylic acid carrier solution using a bleaching process comprising of ozone or an peroxyacid to produce a dissolving-grade cellulose pulp; c. acetylation the manure-derived dissolving-grade cellulose pulp with acetic anhydride and a catalyst in the monocarboxylic acid carrier solution to produce cellulose acetate; d. extracting fermentable components from the different fractions of the manure to produce monocarboxylic acids for use in the monocarboxylic acid carrier solution.

Title: Methods for producing a manure-derived cellulose acetate at atmospheric pressure

FIELD OF THE INVENTION

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This invention relates to the separation of manure in fractions and the treatment of said fractions in order to retrieve useful components to produce manure-derived bioplastic and other manure-derived bioproducts.

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BACKGROUND OF THE INVENTION

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The current materials used by the make-industry are dominated by the use of unsustainable petrochemical based resources. There is an emergent trend of using renewable bio-based materials instead of their petrochemical alternatives. These renewable materials, often used in the pulping and bioplastic industry, rely for example mainly on harvesting trees from natural forests or other sources specifically cultivated for this purpose only. However, it is more desirable to use an already available waste stream for renewable bio-based materials for the manufacturing industry.

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One of the biggest available waste streams is manure. In contemporary agriculture manure is becoming increasingly problematic. Manure proves to be difficult to process as a fertiliser because of the large volumes that need to be transported, the limited control of nutrient balance and problems with solid particles in irrigation systems. In areas where livestock is intensively farmed this has led to a large excess of manure. Complications arise for livestock farmers because of problems with unpleasant odours, health issues, large-scale eutrophication, extra regulations and extra costs to discard the manure. In an increasing number of countries legislation is focused on limiting the amount of nitrogen or phosphorus used on their own pastures, while surplus manure needs to be disposed of. Since the composition of solid and liquid fractions of manure differ in nutrient composition, it can be favourable for the farmer to separate fractions and remove the most undesired fraction of manure. Although this excess manure is currently problematic it has high potential for refining into value added products such as protein, fibrous material, carbohydrates and nutrients.

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The current separation methods aim to optimise the solid fraction of manure for use as bedding for livestock, biochar, fertilizer and as a source for biogas fermentation

processes. However these materials are of an entirely different class when compared to materials such as bioplastics, which are useful for the manufacturing industry. Adjustments of the current separation methods are desirable in order to obtain a solid fraction more suitable as a feedstock for bioplastics.

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In terms of previous known information closest to actually producing bioplastic from manure is the method of US. Pat. No. 2013/0071890 A1, which discloses the production of bioplastic from biogas in a fermenter with aerobic methanotrophic bacteria capable of biopolymer production and a secondary fermenter in which bioplastic production is induced in the presence of methane. However, these findings use the available lignocellulose as an indirect source for bioplastic.

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A direct use of the available lignocellulose in manure as source for bioplastic would be more desirable. While methods for directly processing the lignocellulosic biomass in manure to produce end products such as crystalline cellulose have been developed, for example WO. Pat. No. 2015/101941 A1, none have been developed for end products such as bioplastic. Also, these methods are carried out high above atmospheric pressure and at high temperatures which makes these methods unnecessarily dangerous.

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These existing methods also involve processing the entire waste stream, yet treating the entire quantity of manure in a reactor prior to separation is not an economically viable process; especially with respect to the relatively low price of cellulose itself. In order to improve on these methods, it is desirable to reduce the total volume of manure and obtain an increased ratio of cellulose, by separating different components of manure into different sidestreams, prior to treatment.

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Existing traditional methods for processing non-manure based lignocellulosic biomasses in the pulping and bioplastic industry almost exclusively utilize wood and grasses, for example WO. Pat. No. 2014/122533 A2. These methods are specialised for these sources and would need specific adjustments while using manure as the source of the lignocellulose, partly due to the digestive processes that already took place in the cow's digestive system, but mostly because manure can be considered more chemically heterogeneous than more conventional lignocellulosic biomass sources. For example, manure contains more protein which can increase the use of certain process chemicals and hinder effectiveness of treatments while proteins can also be used as a valuable product. This emphasises the need for extra separation

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treatments in processing manure. Although there are methods developed to optimise extraction of cellulosic material from manure, most methods focus on hydrolysing polysaccharides to short-chain sugars for fermentation. Therefore, treatments used in these methods can be too aggressive and damage the integrity of the cellulosic fibres.

5 A method which uses less hazardous chemicals, that allows for a better recovery of the sidestreams and a better recovery of process chemicals, would be desirable.

Traditional pulping methods such as the Kraft process or bisulfite pulping and chlorine-based bleaching notoriously have a large impact on the environment due the large
10 amount of aggressive chemicals and energy required. Organosolv pulping techniques for example WO. Pat. No. 2011/126369 A1 use organic solvents for the extraction of lignin and hemicellulose. These methods have offered promising environmentally friendly alternatives because of the more environmentally friendly nature of the solvents, the high retrievability of solvents and higher quality of lignin side products.

15 Though, many of these processes are still performed at high temperatures and pressures which are demanding in terms of energy requirements, safety and equipment costs. Another advantage of organosolv techniques over the Kraft method is that the techniques are more gentle for the cellulosic fibres, which is more suited for cellulosic fibres in manure. However, no organosolv pulping method has been
20 developed for the specific source of lignocellulosic biomass in manure.

It is desirable to use the lower quality manure-derived cellulosic fibres and other manure-derived chemicals, which are not suitable for production of manure-derived bioplastic, to produce other manure-derived bio-products like paper, cardboard,
25 medium and low density fibreboard, fertiliser.

Thus, there remains a considerable need for methods that can treat manure to optimise separation into a solid and liquid fraction; use the available lignocellulose as a direct source for bioplastic; do this at atmospheric pressure; only treat that portion
30 of the waste stream that contains the lignocellulose; separate interfering compounds from the manure prior to treatment that can be used as products themselves; and utilise useful components in manure to directly convert the cellulose present in manure to cellulose derived bioplastic and other bio-products.

SUMMARY OF THE INVENTION

The present invention is directed to methods for safely producing environmentally friendly manure-derived bioplastics, having manure and manure extracted components as their direct feedstock.

Among the many different possibilities contemplated, the produced bioplastics may be directly derived from the manure-derived solid fraction with high lignocellulose content that is delignified, bleached and/or acetylated, under atmospheric pressure, in the presence of an acetylation catalyst, resulting in either cellulose based esters or cellulose based ethers. These treatment processes may include fermentable products derived from manure or sidestreams of this method, including (poly)saccharides or amino acids that can be used to produce monocarboxylic acids or the precursor of said desired monocarboxylic acids, which may form the main liquid carrier throughout the pulping and acetylation process(es).

Prior to these processes the manure may be treated to change the composition of the solid or the liquid fractions desired at the different stages of the process, in order to: obtain different grades of manure-derived lignocellulose; avoid having to treat the entire quantity of manure; extract fermentable components from the different fractions of the manure; let the livestock farmer decide if the manure obtained from the agricultural operation is either high or low in nutrients.

In preferred embodiments the concentration of the different acids, the temperature, the pressure and the acetylation catalysts may be tuned to obtain a desired treatment, and be adjusted during the processes. In some embodiments the delignification, bleaching and acetylation steps may be either combined or are consecutively. In some embodiments the spent monocarboxylic acids are retrieved by distillation. In some embodiments organic acid anhydride may be added for acetylation or to decrease the water content of the main liquid carrier. In some embodiments the cellulose pulp may be subjected to a base/alkaline extraction treatment. In some embodiments the manure-derived solid fraction with high lignocellulose content and the other fractions of manure that are not suitable for manure-derived bioplastic production may be used to produce other manure-derived products.

Various objects, features, aspects, and advantages of the present invention will become more apparent from the following detailed description of preferred embodiments of the invention, along with the accompanying drawings in which like numerals represent like components.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the general steps in one example embodiment of a method for directly producing a manure-derived cellulose acetate at atmospheric pressure.

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Figure 2 shows the more detailed steps of the monocarboxylic acid carrier route in one example embodiment of a method for directly producing a manure-derived cellulose acetate at atmospheric pressure.

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DESCRIPTION

Figure 1 generally depicts an example embodiment of a process for producing cellulose acetate 24 having manure 1 and manure extracted components as its direct feedstock, which includes a pre-separation treatment step 2, a partial filtration step 3, a separation optimisation treatment step 5, a filtration step 6, a pre-treatment step 8 and the monocarboxylic acid carrier route step 9. In some embodiments, the monocarboxylic acids 19 for the monocarboxylic acid carrier route step 9 are produced after a pre-fermentation treatment step 11 and a fermentation step 12. In some embodiments this method will involve a net production of different grades of cellulose products 23, fertilizer 15 and fermentation products 26 like monocarboxylic acids.

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The manure 1, as used herein, includes faeces or urine from dairy cattle. The manure can vary in composition due to different animals, different diet of animals, seasonal changes, difference in collecting and storage conditions, bedding material and mixing with other lignocellulosic waste streams. In some embodiments the manure includes faeces or urine from other animals (including humans) and can also include materials where it is mixed with during processing at an agricultural operation such as bedding material, paper, straw, grasses, wood chips, sawdust, hemp fibre or the like. Therefore, further processing is tuned to optimise treatments for variations in manure.

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Manure obtained from an agricultural operation or still present at such operation is treated in a pre-separation treatment 2. When an agricultural livestock operation uses

the liquid fraction of manure to fertilise its own pastures it can exceed legal limits on certain nutrients. An aspect of the invention is that an agricultural livestock operation can, through a pre-separation treatment 2, separate undesired parts (e.g. phosphates, nitrogen) to be processed by the invention, and thus decide if the manure obtained from his agricultural operation is either high or low in nutrients. In some embodiments a flocculant such as iron(iii)chloride (FeCl_3) or alum ($\text{Al}_2(\text{SO}_4)_3$) is mixed with the liquid fraction of manure, where after coagulation or flocculation of suspended particles takes place. After sedimentation a significant amount of nutrients especially in the form of phosphates or nitrogen are found in the sediment. By using the pre-separation treatment 2 on manure an agricultural livestock operation gains control over the separation of desired and undesired components of manure.

In some embodiments, manure 1 or pre-separation treated manure 2 is obtained in any appropriate manner that allows, through partial filtration 3, for the removal of the greater part of the liquid fraction of manure, for example by using a screw press. In some embodiments this partial filtration is performed at the agricultural operation, this ensures that the farmer retains a liquid fraction of manure that is better suited to use as fertilizer. Partial filtration at the agricultural operation also reduces the total mass that is to be transported to the processing plant. Most importantly, partial filtration reduces the to-be-treated total quantity of manure to only the necessary fractions of manure that have high lignocellulose content, which makes this process more economically viable compared to methods that process the entire waste stream like WO. Pat. No. 2015/101941 A1.

In some embodiments, the direct result of the partial filtration step 3 is a semi solid fraction 4 of manure that is to be separated into solid fractions of high lignocellulose content during the separation optimisation treatment 5 and filtration 6 steps. In some embodiments other compounds such as proteins, minerals, lipids, mono saccharides and oligosaccharides are also separated during these steps.

Since manure is considered more chemically heterogeneous than other lignocellulose sources, separation into various fractions will improve further treatments while obtaining useful sideproducts. The purpose of the separation optimisation treatment is to optimise the separation of manure into multiple fractions by "translocating" the chemical of choice to a desired state (e.g. foam, dissolved in liquid, solid particle), by treatment with heat, a chelating agent, a detergent, a flocculant, a foaming agent, enzymes, a organic solvent an acid or base. In some embodiments a foaming agent is

added to the (semi)solid fraction of manure in the form of sodium chloride and ammonium sulfate ((NH₄)₂SO₄) subsequently the manure is agitated until a foam forms. The foam consist mostly of protein and other substances interfering with lignocellulose treatments. The foam fraction is removed from the top layer of liquid (and used for further refinement). In some embodiments a chelating agent is used in order to remove metal ions that may interfere with further pulping processes or are desired in the liquid fraction. Chelating agents can include citric acid and ethylenediaminetetraacetic acid (EDTA). In some embodiments a detergent is added to separate polar from non polar substances and thereby wash the lignocellulose fibres from lipids and undesirable components. In addition a detergent is be added to increase foaming action. In some embodiments an organic solvent is used to remove lipids, oils and other soluble compounds from the solid fraction. The organic solvent includes ethanol, methanol, acetone, isopropanol, hexane or toluene and is preferably performed at high temperature. After extraction with the organic solvent the solvent is retrieved by (vacuum)distillation.

The use of a semi solid fraction 4 during the separation optimisation treatment 5 allows for the minimizing of spent water. In some embodiments, the semi solid fraction is either filtrated or diluted through addition of water to obtain a desired ratio for the separation optimisation treatment. In some embodiments, separated liquid from previous partial filtration 3 or filtration 6 steps is used to dilute the semi solid fraction.

The fraction of manure obtained after the separation optimisation treatment 5 is separated in solid 7 and liquid fractions 10 during the filtration 6 step, for example by using a filter screw press or by centrifugal separation. After which, the solid fraction is filtered by sieving, to separate fractions on particle size using different mesh sizes. The more intact lignocellulose fibers, found in large particle fractions, are separated from the more degraded compounds found in smaller particle fractions 13 to separate solid fractions 7 with high lignocellulose content. For the large particle fractions a mesh size in the range of 1-3 mm is used, for the smaller particle fractions a mesh size in the range of 0.05-1 mm is used. In some embodiments the mesh size is depending upon the nature of the manure and mixed lignocellulose sources and the upper limit can be up to 2-10 cm. In some embodiments multiple sieves are used in order to enhance the effectiveness of filtration and reducing clogging of filters.

The separation optimisation 5 and filtration 6 steps are performed multiple times with different or similar process conditions, resulting in different solid fraction's 7 with different purposes, and different liquid fractions 10. The separation optimisation treatment combines different treatments in a single step due to the complementary effect of the components. In some embodiments a foaming agent, detergent, chelating agent and acid are used as a first stage treatment where after the solid fraction is then treated with a 70% aqueous ethanol solution at a temperature of 50-60 °C.

Depending on the nature of the pulp the large particulate solid fraction 7 of high lignocellulose content is then pre-treated 8 to extract hemicelluloses. In some embodiments that pretreatment consists of base/alkaline extraction with sodium hydroxide 1-10% at a temperature of 30-95 °C. Depending on the nature of the pulp hydrogen peroxide can be added in concentrations of 0-5%. In addition this step also includes partial delignification of the lignocellulose and activation of the cellulose in order to enhance the accessibility and reactivity of cellulose to chemicals in the monocarboxylic acid carrier route 9. In one aspect of the invention the hemicellulose extraction is performed after the bleaching step using a cold caustic extraction with sodium hydroxide 1-10% at a low temperature range 20-40 °C. In some embodiments the hemicellulose 14 is extracted for use in fermentation 12.

Figure 2 generally depicts an example embodiment of the more detailed steps of the monocarboxylic acid carrier route 9, having pre-treated solid fraction of high lignocellulose content 21 as its direct feedstock, which includes a pulping step 16, a bleaching step 17, an acetylation 18 step and an recycling step 19.

After the pretreatment, the solid fractions of high lignocellulose content 21 are treated in a monocarboxylic acid carrier route 9. Here the manure-derived solid fraction of high lignocellulosic content is pulped 16 at atmospheric pressure with a acetic acid carrier solution in a concentration of 70-90% and a sodium bisulfate (NaHSO_4) catalyst in a concentration of 0-5%. In some embodiments, the monocarboxylic acid is acetic acid, formic acid, propionic acid, butyric acid or are a combination thereof in a concentration of 10-100%, preferably above 50%. In some embodiments the catalyst is nitric acid (HNO_3), sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) in concentrations of 0-10%, the concentration and type of catalyst is chosen depending on the nature of the pulp. Some pulps require a mild carrier to avoid further cellulose degradation.

Afterwards a bleaching 17 process comprising of ozone at 20-40 °C and peracetic acid treatment at 50-80 °C in the monocarboxylic acid carrier is used to produce a dissolving-grade cellulose pulp. Concentration and duration of the treatments vary depending of the nature of the pulp. In some embodiments, the bleaching agent is a peracid (peroxy acid), ozone, oxygen, hydrogen peroxide or a combination thereof.

In some embodiments this cellulose pulp is used to create different grades of cellulose products 23 consisting of paper, cardboard, pulp in various grades of refinement.

After the bleaching 17 step an acetylation 18 process is used to acetylate the manure-derived dissolving-grade cellulose pulp with acetic anhydride in the monocarboxylic acid carrier solution with a concentration of 100%, with sodium bisulfate (NaHSO_4) as a catalyst to produce cellulose acetate 24. In some embodiments the catalyst added is sulfuric acid (H_2SO_4), sodium bisulfate (NaHSO_4) or a combination thereof. The hydroxyl groups of the cellulose are substituted with acetate groups directly until the desired degree of substitution or indirectly. Depending on the nature of the pulp, especially the degree of polymerisation, the cellulose can be acetylated directly to reach the desired degree of substitution to prevent cleaving of the cellulose polymers by hydrolysis. Alternatively, if the degree of polymerisation is high enough the cellulose is first fully substituted to cellulose triacetate (CTA) whereafter CTA is hydrolysed until the desired degree of substitution is reached.

In some embodiments the manure derived cellulose bioplastic consists of cellulose acetate butyrate, cellulose acetate propionate, or other cellulose derived esters. In a particular embodiment the manure derived cellulose bioplastic consist of carboxymethyl cellulose or other cellulose derived ethers.

All three of these processes use the same monocarboxylic acid solution in different concentrations as main carrier for the delignification, bleaching and acetylation processes, in which the solid fractions of high lignocellulose content are consecutively delignified, bleached and acetylated at atmospheric pressure and a temperature of 80-130 °C. In an aspect of the invention the boiling point of the monocarboxylic acid carrier is elevated by adding carboxylic acids with a higher molecular mass. The use of the monocarboxylic acid carrier solution makes countercurrent washing possible. In some embodiments these processes can take place combined to minimise spent chemicals and energy. Hereby stages in the process can be initiated by addition of chemicals and changes in temperature or the processes can be performed in a single

batch whereafter separation of undesired products can be performed after acetylation. In some embodiments these processes take place at a pressure of 0-10 bar and a temperature of 50-180 °C. In some embodiments organic acid anhydride, in particularly acetic anhydride is not only added to acetylate the manure-derived dissolving-grade cellulose pulping product but also used to decrease the water content of the monocarboxylic acid carrier solution. In some embodiments multiple chemicals are used for the monocarboxylic acid carrier solution for the different processes.

The monocarboxylic acids of the monocarboxylic acid carrier solution are partially or fully retrieved from the spent monocarboxylic acid carrier solution by distillation at low to atmospheric pressure to recycle the monocarboxylic acids. The solid fraction that remains after distillation of the spent monocarboxylic acid carrier solution consists mainly of a high quality lignin and hemicellulose. In some embodiments the lignin is used as a product after hemicellulose is extracted from the solid material and used for fermentation.

In some embodiments the monocarboxylic acid carrier is partly or fully claimed from fermentation products derived from the liquid fractions, smaller particle fractions, hemicellulose of this method, including (poly)saccharides or amino acids. In some embodiments, the fermentation products are the precursor of said desired monocarboxylic acids. In some embodiments, the fermentation products are butanoic acid, propanoic acid, acetic acid, formic acid. In some embodiments, the fermentation products are ethanol, methanol, propanol, butanol or other fermentation products.

Prior to fermentation the fermentable products are pre-treated in order to prepare the fermentable products for optimal fermentation conditions. In some embodiments the side streams from the invention are selected and mixed to achieve optimal conditions for fermentation. The liquid fractions have different compositions depending on their origins, which consist either of the partial filtration step 3, or the multiple filtration steps from the separation optimisation- and filtration cycle. Depending upon the concentration of fermentable compounds and nutrients a liquid fraction can be concentrated by reverse osmosis or diluted by mixing with side streams with lower concentration. The small particle solid fraction and low grade cellulose pulp can be hydrolysed to obtain fermentable compounds such as monosaccharides, oligosaccharides and amino acids. In some embodiments nutrients

and non-manure derived fermentable compounds can be added to the increase yield of fermentation.

Acetic acid for the monocarboxylic acid carrier solution is produced by fermentation of the product of the pre-fermentation treatment 11 to ethanol whereafter the solution is subsequently metabolised to acetic acid in a second fermentation process. In some embodiments other monocarboxylic acids are produced by changing composition of the fermentable compounds in the pre-fermentation treatment and using organisms with different metabolic pathways. Another aspect of the invention is using mixed acid fermentation where multiple useful products are produced in a single fermentation process.

In some embodiments the solid digestion residue with a high degree of bacterial cellulose produced by fermentation is used for the production of cellulose derived bioplastics.

The liquid fractions originating from the fermentation treatment are combined to produce a fertiliser product 15 that can be used for agricultural, horticultural and consumer purposes. By combining liquid fractions 10 and liquid fermentation residue, nutrients from manure can be retrieved after concentration with reverse osmosis. In some embodiments further concentrating the nutrient solution is achieved by evaporation of the solution to a fertiliser product that consists of a solid dried granular or powder product obtained by spray drying. In a particular embodiment the fertiliser product consists of a highly concentrated nutrient solution. In a preferred embodiment liquid fractions from the fermentation treatment are distilled at low or atmosphere pressure to obtain monocarboxylic acids while simultaneously the remaining solid particles are used to obtain nutrients for the fertiliser product. In some embodiments the fertiliser product is balanced to a desirable nutrient composition (e.g. N-P-K) by careful selection of process chemicals in previous steps. When it is desirable to increase the nitrogen composition of the fertiliser ammonium hydroxide (NH_4OH) is used as a base in the separation optimisation treatment. When it is desirable to increase potassium composition of the fertiliser potassium hydroxide (KOH) is used. When it is desirable to increase phosphorus composition of the fertiliser phosphoric acid (H_3PO_4) is used. In some embodiments the fertiliser product is rich in organic substances such as humic acid. In some embodiments nitrogen and phosphorus nutrients can be obtained from the liquid fractions by struvite precipitation to produce the fertiliser product or a component of the fertiliser product.

EXAMPLES

In the specific examples below different steps of the method are described as indicated previously, which are intended to be illustrative and not limiting in nature.

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Example 1: pretreatment

For the extraction of cellulose, a pretreatment was performed. The washed solids consist of light brownish fibrous materials with most fibres smaller than 2 cm.

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Four samples of 50 g of oven dried solid fraction were mixed with 500 ml of solution with different sodium hydroxide (NaOH) concentrations, namely 2.5, 5, 7.5 and 10% w/v sodium hydroxide (NaOH) and 1% hydrogen peroxide (H_2O_2) w/v. The suspension was kept for one hour at 90 °C at atmospheric pressure. after the treatment the liquid filtrate was dark brown. The fibrous solid material washed with water to neutrality.

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The colour of the fibre samples was light brown.

The pretreated samples were then the delignified with the a monocarboxylic acid carrier treatment add equal conditions to obtain a cellulose pulp. The pulp was then characterised by measuring alpha-cellulose content, brightness, Kappa number of the pulp and degree of polymerisation.

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Example 2: Separation optimisation treatment

The separation optimisation treatment was performed on the semi solid fraction. To induce foaming 0.2% of sodium chloride and of 0.5% ammonium sulfate ($(NH_4)_2SO_4$) was added. 0.5% of sodiumlaurylsulfate (SLS) was added as a detergent and to increase the effect of foaming. To increase effectiveness of the detergent and to remove metals that interfere with further processes a chelation agent was added in the form of 0.3% EDTA. The pH value of the solution was brought to 8 by using an acid or base depending on the nature of the manure. The manure solution was heavily agitated by using a strong pump to induce foam formation. The foam was mechanically removed several times until little to no foam was formed. The collected foam was liquefied and dried.

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The remaining solution was filtered with 5 sieves with a maximum mesh size of 1.8mm to a minimum mesh size of 0.05mm. The use of multiple sieves with a mesh size smaller than 1.8mm is to prevent clogging of the subsequent sieves. Solid

fractions collected from the sieves with a mesh size smaller than the sieve with the maximum mesh size of 1.8mm were combined and were regarded as the small particle solid fraction with a higher protein content. Solid particles collected by the sieve with largest mesh size are the solid fraction with high lignocellulose content.

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The solid fraction with high lignocellulose content was washed and filtered subsequently with water of 70 °C. After this step the solid fraction was subjected to an methanol washing stage where fibres were soaked in a 70% aqueous methanol solution at 60 °C. After soaking the solid fraction was filtered and washed with water.

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The remaining solid fraction was characterised as consisting of light brown fibrous material with a high lignin cellulose content and low concentration of protein and lipids.

15 Example 3: Monocarboxylic acid carrier route

Pretreated fibres from the solid fraction are dried until fibre mass with low moisture content is obtained. 100g of the pretreated solid fraction was then treated with a monocarboxylic acid carrier solution consisting of: 1L of a 80% aqueous acetic acid solution and 2% nitric acid. The fibres were suspended and heated to boiling temperature at atmosphere pressure in a reflux apparatus. After reaching boiling temperature the fibres were treated for 1.5 hours.

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The pulped fibres were washed with 80% aqueous acetic acid to remove the nitric acid components and dissolved lignin. Then the pulped fibres were subjected twice to a ozone bleaching treatment with a liquid to pulp ratio of 1:2 at 30 °C. Duration of the bleaching treatment depended upon the nature of the pulp. After washing with 80% aqueous acetic acid the pulping solution was then brought to 70 °C for peracetic acid bleaching. (A temperature more preferable for peracetic acid formation equilibrium.)
Depening on the nature of the pulp, an amount of peracetic acid is added for a certain amount of time. After the peracetic acid bleaching of 4 hours the solution was filtrated. The solid fibres were washed two times with a 80% aqueous acetic acid solution. the pulp was then mixed in a saturated solution of sodium sulfite (NaSO_3) in a 80% aqueous acetic acid solution and left for 30 minutes to remove oxidizing agents. After filtration the fibres were washed twice with glacial (100%) acetic acid. One half of the fibres were used for acetylation while the other half was used for

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analysis on pulp quality such as brightness, alpha- cellulose content and the kappa number of pulp.

To preserve the integrity of the cellulose polymer, bleached fibres were subjected to a mild acetylation process. The whole acetylation process was performed at room temperature using a mild catalyst. The fibres were now put into a beaker glass with 200 ml of glacial (100%) acetic acid and 0.15 ml of sulfuric acid (H_2SO_4) (98%). 0.3g sodium bisulfate (NaHSO_4) were added as mild catalyst. The solution was agitated with a stirrer set at 150 rpm. 60ml of acetic anhydrid was slowly added over the course of 30 minutes. The acetylation process lasted until the desired degree of polymerisation was obtained (e.g. cellulose diacetate(CDA) with a degree of substitution of 2.4). The catalysts were neutralised by adding sodium acetate whereafter the solution was poured into a bath of distilled water in order to precipitate the cellulose acetate. The formed solids were now washed until neutral and dried until cellulose acetate products was obtained.

The cellulose acetate product was dissolved in acetone and undissolved particles separated from the solution by ultracentrifugation. The degree of polymerisation and thermal degradation was determined.

The cellulose diacetate(CDA) dissolved in acetone was concentrated until a spinning dope solution of the desirable viscosity was reached. The spinning dope was then dry spun to obtain cellulose acetate tow.

Example 4: Acetic acid carrier route for cellulose

After the separation optimisation treatment, the solid fraction was pretreated with a solution of 5% sodium hydroxide and 1% hydrogen peroxide with a liquor to biomass ratio of 4:1 this was mixed thoroughly and kept at 70 °C for one hour. After the treatment fibres were washed until neutral and dried.

100g of pretreated fibres from the solid fraction were treated with a monocarboxylic acid carrier solution consisting of 1L of an 80% aqueous acetic acid solution and 0.5% aqueous nitric acid solution. The fibres were suspended and heated to boiling temperature at atmosphere pressure in a reflux apparatus. After reaching boiling temperature the fibres were treated for 1 hour. After the treatment fibres were filtered and washed with 100ml 90% acetic acid.

Fibres were then mixed with 250ml of a 90% aqueous acetic acid solution. Sulfuric acid was added as a catalyst until a concentration of 0.3% was reached. The mixture was kept at boiling temperature for 1 hour. Depending on the nature of the pulp. After treatment 4g sodium acetate dissolved in 30ml 80% aqueous acetic acid solution was added to neutralise the sulfuric acid catalyst. Lignin content and kappa number were analysed to estimate reaction time needed for bleaching.

The pulping solution was then brought to 70 °C for peracetic acid bleaching. (A temperature more preferable for peracetic acid formation equilibrium.) Depending on the nature of the pulp an amount of hydrogen peroxide is added for a certain amount of time. 100ml of a 35% aqueous hydrogen peroxide solution was added for peracetic acid formation. After the peracetic acid bleaching of 2 hours the solution was filtrated. The solid fibres were washed with distilled water until neutral. Finally, a cold caustic extraction was performed to increase alpha cellulose content by removing residual hemicelluloses. The fibres were subjected to a solution of 8% sodium hydroxide (NaOH) under stirring at 30 °C for ten minutes. The fibres were then washed until neutral and dried. Alpha cellulose, kappa number and iso brightness were determined. A highly refined cellulose product was obtained.

Example 5: Mixed monocarboxylic acid carrier

Since pulping with a higher temperature can be more effective or time saving, it is beneficial to increase the boiling temperature of the carboxylic acid carrier liquid. In order to increase the boiling temperature while still under atmospheric pressure a monocarboxylic acid with higher boiling point was added. However, using longer chained monocarboxylic acids might decrease effectivity of the process because of fewer active groups per volume of the liquid carrier.

Butyric acid was added in various concentrations to a concentration of 90% aqueous acetic acid and boiling point was measured hereafter. 0, 5, 10, 15, 20, 30, and 40 ml of a pure butyric acid solution were added to a beakerglass, then the beaker was filled to a total of 100ml with a 90% aqueous acetic acid solution. 20 ml of 70% nitric acid was added to each solution. Boiling temperature was determined using 10ml of the mixture in a test-tube with a thermometer submerged in the liquid while the test-tube was being heated in a warm bath. When bubbles reached the surface the temperature was seen as boiling temperature.

10 g of dried and pretreated fibres from the solid fraction were mixed with each of the solutions and 0.3% sodium bisulfate (NaHSO_4) and heated until boiling point and kept at this temperature for 0.5 hours. Pulped fibres were bleached simultaneously with ozone and peracetic acid at 40 °C for 3 hours. Fibres were separated and washed thoroughly finally alpha-cellulose content, kappa number, brightness and lignin content were determined.

Example 6: Acetic acid ozone + peracetic acid route

100g of fibres from the solid fraction were treated with a monocarboxylic acid carrier solution consisting of 1L of an aqueous solution of 70% acetic acid 20% formic acid and 0.7% nitric acid and 0.2% sodium bisulfate (NaHSO_4). The fibres were suspended and heated to boiling temperature at atmosphere pressure in a reflux apparatus. Only after reaching boiling temperature the catalysts were added and were treated for 2.5 hours. After the treatment fibres were filtered and washed with 100ml 90% acetic acid. The fibres were then suspended in 200 mL of 70% acetic acid and 10% formic acid and were treated with ozone at 30 °C until a total of 4.5g ozone was reached. Subsequently the sample was bleached with 12% peracetic acid based on pulp. Peracetic acid bleaching was done at 70 °C for a total of 4 hours. Kappa number and ISO brightness were measured. Kappa number and ISO brightness were measured.

Example 7: Liquid fraction fermentation

A spent monocarboxylic acid carrier solution consisting of 80% acetic acid and 3% nitric acid that has been used for delignification of the solid fraction was recycled while useful components were extracted. 1L of solution was put into a distillation apparatus and fully distilled. The distilled liquids were collected and could be reused for further delignification processes. The obtained solids from the spent monocarboxylic acid carrier solution were soaked with hot water in a ratio of 10:1 (volume of obtained solids: volume of hot water). After soaking under continuous stirring for 4 h the suspension was filtered. The solid residue contains a high value lignin product.

The filtrate contains dissolved fermentable products in the form of hemicellulose, sugars. To obtain a fermentable solution rich in sugars the filtrate was mixed with solutions (concentrated with reverse osmosis) from the separation optimisation treatment and hydrolysed components from the solid fraction. The solution was fermented with a yeast strain to obtain ethanol which can be used as a product or

further fermentation by acetic acid bacteria to form acetic acid that can be used for making a monocarboxylic acid carrier solution or as a product.

Examples 8: Farmer example manure separation flocculant

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A dairy farm operation has an excess of manure that contains minerals and other fertilizer compounds that need to be removed from the slurry pit and deported. It is more desirable to the dairy farm operation to use a liquid for fertilizing meadows with a spraying/injecting system while it is more desirable to transport the solid fraction of manure. However, the liquid fraction still contains more fertilizer compounds than desired (mainly concerning nitrogen and phosphorous) for fertilizing the agricultural land of the dairy farm operation. Therefore, a flocculant is added to the manure storage pit to precipitate fertilizer compounds in order to move compounds to the solid fraction.

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At the farmer iron(III)chloride (FeCl_3) is added to the manure storage tank to reach a concentration of 2g per liter (amount should be tuned desirable for the farming operation) while agitating the tank for 1 hour. After agitation the tank is left to form sediment for 2 days. Then the tank is filtered with a screwpress to separate the liquid from the solid fraction. The liquid fraction now contains 30% less nitrogen and 40% less phosphorous than before flocculation. The solid fraction can now be used for the separation optimisation treatment.

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Example 9: Fertilizer

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Liquid fractions were processed to create a balanced fertiliser product. The digested solution of the fermentation treatment for the production of acetic acid was filtered. The solid materials were filtrated and used as lignocellulose feedstock for use in monocarboxylic acid carrier route. The fermented liquid fraction containing acetic acid was distilled by vacuum distillation to obtain acetic acid for use in the monocarboxylic acid carrier. The solid residue remaining after distillation, high in nutrients originating from manure, was used to create a nutrient rich powder.

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To balance this fertiliser product and to retrieve as much nutrients from the original manure as possible. A liquid fraction from the partial filtration and a liquid fraction of the separation treatment was characterised as low in fermentable products but high in nutrients with a total solid content of 67 mg/L. These fractions were concentrated by

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reverse osmosis to concentration containing 438 mg/L total solids. This concentrated fraction was spray dried to obtain a solid powder that was mixed with the nutrient rich powder obtained from the digested liquid fraction. Composition of the fertilizer was analysed on nutrient composition.

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Example 10: Cellulose diacetate thermoplast

Manure derived cellulose pulp was treated with the monocarboxylic acid carrier route and acetylated under mild conditions using sulfuric acid H_2SO_4 and sodium bisulfate (NaHSO_4) in a ratio of 1:3 as catalyst. First cellulose was acetylated to a cellulose triacetate and then hydrolysed to obtain a cellulose diacetate with the desired degree of substitution. A cellulose diacetate with the degree of substitution of 2.08 was obtained and mixed with a plasticiser (e.g. diethyl phthalate (DEP)) to obtain a thermal mouldable material. The product was made into a granulate product.

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CONCLUSIES

1. Werkwijze ter bereiding van een mest-afgeleide celluloseacetaat bij atmosferische druk, door het scheiden van mest in nuttige componenten, 5
omvattende de volgende stappen:
 - a. onderwerpen van de mest aan een flocculatie-behandeling (waarbij het vlokmiddel optioneel ijzerchloride (FeCl_3) of aluminiumsulfaat ($\text{Al}_2(\text{SO}_4)_3$) bevat) en aan een filtratiebehandeling waarbij fracties met verschillende deeltjesgrootte 10
worden gescheiden door het toepassen van verschillende maaswijdten om vaste fracties te verkrijgen met een hoog gehalte aan lignocellulose;
 - b. pulpen van de mest-afgeleide vaste fracties met een hoog gehalte aan lignocellulose, bij atmosferische druk met een monocarbonzuur drageroplossing 15
(waarbij het monocarbonzuur optioneel azijnzuur bevat) door het toepassen van een bleekproces met ozon of peroxyzuur om een oplosbare kwaliteit cellulosepulp te verkrijgen;
 - c. acetyleren van de mest-afgeleide oplosbare kwaliteit cellulosepulp met 20
azijnzuuranhydride en een katalysator (die eventueel zwavelzuur (H_2SO_4) en natriumbisulfaat (NaHSO_4) bevat) in de monocarbonzuur drageroplossing om celluloseacetaat te verkrijgen;
 - d. extraheren van vergistbare componenten uit de verschillende fracties van de 25
mest om monocarbonzuren te verkrijgen voor toepassing in de monocarbonzuur dragervloeistof.
2. Werkwijze volgens conclusie 1, waarbij de mest-afgeleide oplosbare kwaliteit cellulosepulp wordt gebruikt om cellulose-esters of cellulose-ethers te verkrijgen. 30
3. Werkwijze volgens conclusie 1, waarbij de vergistbare componenten (poly)sachariden of aminozuren zijn, die worden gebruikt om monocarbonzuren te verkrijgen.
- 35 4. Werkwijze volgens conclusie 3, waarbij het vergistingsproduct een precursor is van de monocarbonzuren.

5. Werkwijze volgens conclusie 3 waarbij het monocarbonzuur azijnzuur, mierenzuur, propionzuur, boterzuur is, of een combinatie daarvan is.
- 5 6. Werkwijze volgens conclusie 1, waarbij de mest-afgeleide vaste fractie met een hoog gehalte aan lignocellulose wordt gedelignificeerd, gebleekt en/of geacetylerd tijdens stap b en/of c, hetzij gecombineerd of achtereenvolgend.
- 10 7. Werkwijze volgens conclusie 6, waarbij de monocarbonzuren van de monocarbonzuur drageroplossing volgens conclusies 3 – 5 geheel of gedeeltelijk worden toegepast.
8. Werkwijze volgens conclusie 6, waarbij de monocarbonzuren een gehalte hebben van 10 - 100%, bij voorkeur boven 50%, ideaal 70 - 90%.
- 15 9. Werkwijze volgens conclusie 6, waarbij de gehalten aan monocarbonzuren gedurende de werkwijze worden aangepast.
- 20 10. Werkwijze volgens conclusie 6, waarbij de monocarbonzuur-oplossing de belangrijkste dragervloeistof is tijdens stap b en/of c.
11. Werkwijze volgens conclusie 6, waarbij salpeterzuur wordt toegevoegd met een gehalte van 0 - 20%, bij voorkeur 0,5 - 5%.
- 25 12. Werkwijze volgens conclusie 6, waarbij zwavelzuur of zoutzuur wordt toegevoegd met een gehalte van 0 - 10%, bij voorkeur 0 - 5%.
13. Werkwijze volgens conclusie 6, waarbij natriumbisulfaat wordt toegevoegd met een gehalte van 0 - 15%, bij voorkeur 0 - 5%.
- 30 14. Werkwijze volgens conclusie 6, waarbij het bleekmiddel een perzuur, ozon, zuurstof, waterstofperoxide of een combinatie daarvan is.
- 35 15. Werkwijze volgens conclusie 6, waarbij carbonzuuranhydride, in het bijzonder azijnzuuranhydride, wordt toegevoegd om de mest-afgeleide oplosbare kwaliteit cellulosepulp te acetyleren of om het watergehalte van de monocarbonzuur drageroplossing te verminderen.

16. Werkwijze volgens conclusie 6, waarbij het pulpen en het acetyleren wordt uitgevoerd bij een druk van 0 - 10 bar, bij voorkeur bij atmosferische druk.
- 5 17. Werkwijze volgens conclusie 6, waarbij het pulpen en het acetyleren wordt uitgevoerd bij een temperatuur van 50 - 180 °C, bij voorkeur 80 - 130 °C.
18. Werkwijze volgens conclusie 6, waarbij de lignine wordt toegepast voor het vervaardigen van producten.
- 10 19. Werkwijze volgens conclusie 6, waarbij de verbruikte monocarbonzuur drageroplossing wordt teruggewonnen door destillatie bij lage tot atmosferische druk.
- 15 20. Werkwijze volgens conclusie 6, waarbij de mest-afgeleide vaste fractie met een hoog gehalte aan lignocellulose wordt onderworpen aan een alkalische extractie behandeling vóór, tijdens of na de monocarbonzuur-behandeling.
- 20 21. Werkwijze volgens conclusie 1, waarbij de mest (gedeeltelijk) wordt gefiltreerd, of wordt verdund door het toevoegen van water, om een gewenste verhouding van de behandeling te verkrijgen met minimaal verbruik van water.
- 25 22. Werkwijze volgens conclusie 21, waarbij de scheidingsbehandeling wordt herhaald, onder verschillende of soortgelijke omstandigheden, met gedeeltelijk of volledig hergebruik van het filtraat verkregen uit de vorige filtratie-stappen.
- 30 23. Werkwijze volgens conclusie 21, waarbij de mest wordt behandeld met warmte, met een chelerend middel, een zeep, een vlokmiddel, enzymen, een organisch oplosmiddel, een zuur of een base.
- 35 24. Werkwijze volgens conclusie 21, waarbij de mest wordt behandeld met een schuimmiddel en vervolgens geagiteerd, waarbij de chemische componenten die zich ophopen in het schuim uit de suspensie worden afgescheiden met behulp van geschikte mechanische middelen.
25. Werkwijze volgens conclusie 24, waarbij het schuimmiddel bestaat uit ammoniumsulfaat (NH_4SO_4) of ammoniumsulfaat (NH_4SO_4) bevat.

26. Werkwijze volgens conclusie 21, waarbij de behandelingen worden uitgevoerd op een landbouwbedrijf, tijdens opslag of tijdens transport.
- 5 27. Werkwijze volgens conclusie 1, waarbij de mest-afgeleide vaste fractie met een hoog gehalte aan lignocellulose, of andere fracties van de mest, worden gebruikt om verschillende soorten celluloseproducten te maken zoals: papier, karton, vezelplaat met gemiddelde en lage dichtheid, pulp in verschillende zuiveringskwaliteiten.
- 10 28. Werkwijze volgens conclusie 27, waarbij de mest-afgeleide vaste fractie met een hoog gehalte aan lignocellulose wordt gecombineerd met koude keramiek, epoxyhars, polycondensaat hars of polymeer, om een samengesteld materiaal te vormen.
- 15 29. Werkwijze volgens conclusie 1, waarbij elke zijstroom van de verschillende fracties van de mest wordt gebruikt voor de vervaardiging van een meststof, welke kan worden gebruikt voor land-, tuin- en consumenten-doeleinden.
- 20 30. Werkwijze volgens conclusie 29, waarbij de meststofproducten voedselrijke hooggeconcentreerde vloeistoffen of poeders zijn.
- 25 31. Werkwijze volgens conclusie 29, waarbij het meststofproduct is vervaardigd uit de vloeibare fracties van de mest door het verwijderen van water of door extractie van nutriënten met behulp van struviet precipitatie.
- 30 32. Werkwijze volgens conclusie 29, waarbij de flocculatie-behandeling (waarbij het vlokmiddel optioneel ijzer(iii)chloride (FeCl_3) of aluminiumsulfaat ($\text{Al}_2(\text{SO}_4)_3$) omvat) is ingericht om een gewenste samenstelling van voedingsstoffen te verkrijgen in het meststofproduct.
- 35 33. Werkwijze volgens een van de voorgaande conclusies, waarbij de mest of mestfracties, geproduceerd door dieren inclusief mensen, is vermengd met urine of lignocellulose bevattende biomassa zoals: strooisel, stro, hout, papier, vergister afvalproducten, vergistingsproducten.

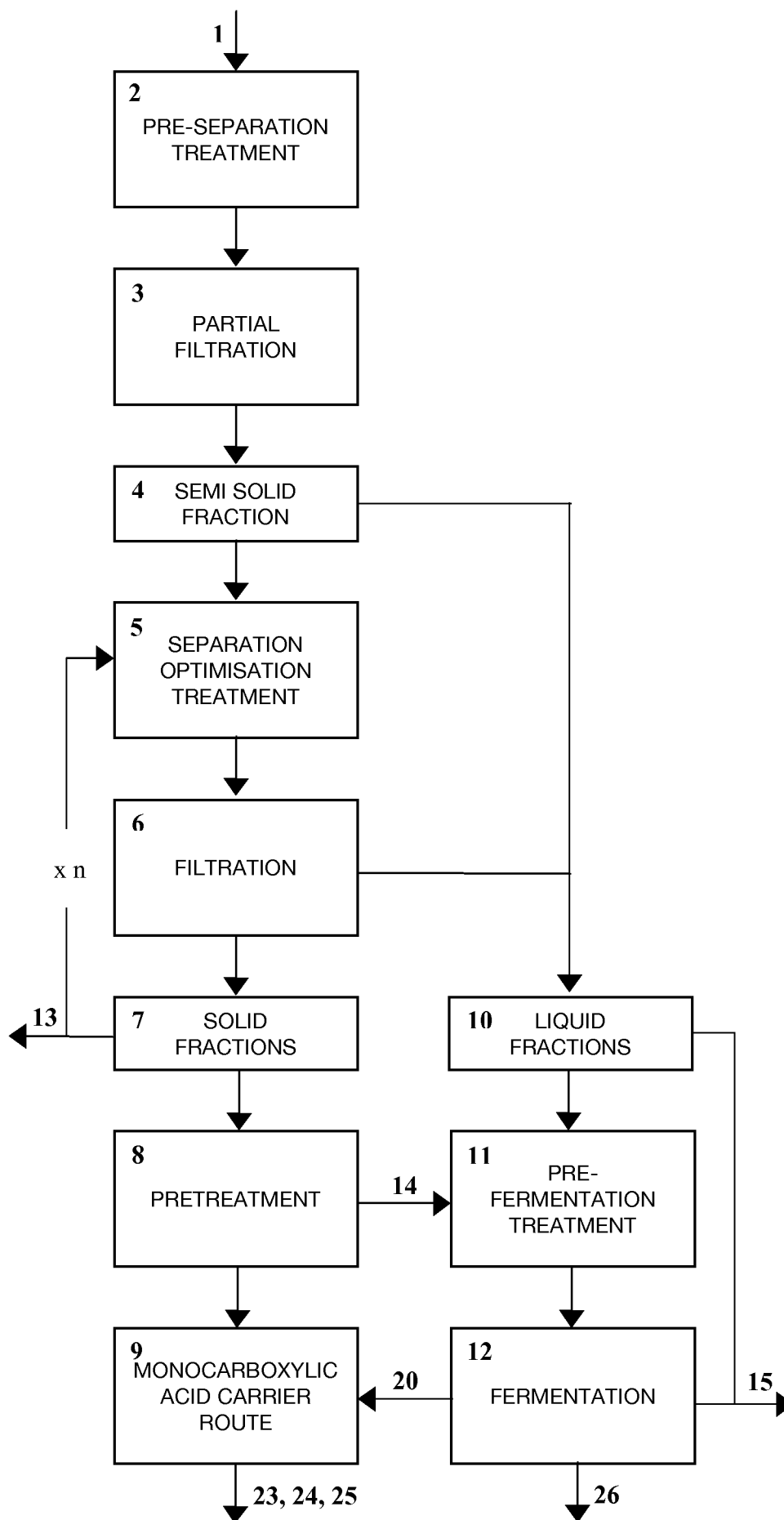


FIGURE 1

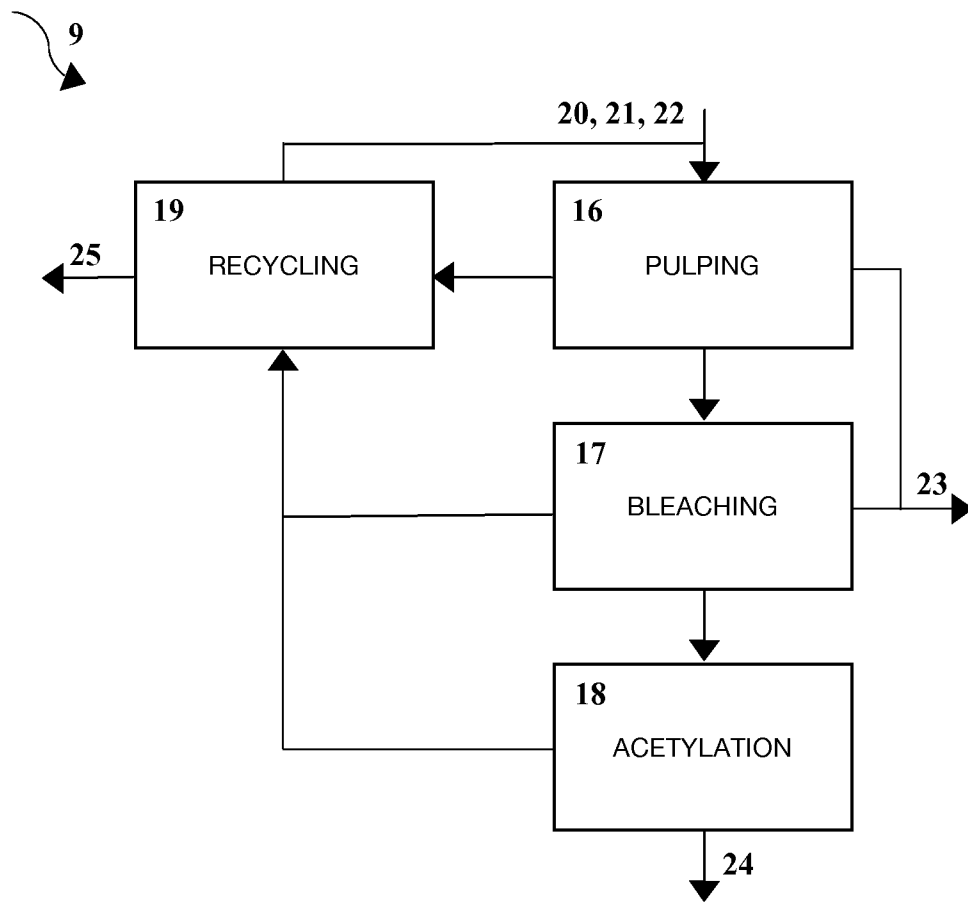


FIGURE 2

ABSTRACT

A method for producing a manure-derived cellulose acetate at atmospheric pressure, by separating manure into useful components, comprising the steps of: a. flocculation treatment and a filtration treatment where fractions having different particle size are separated by using different mesh sizes to obtain solid fractions having a high lignocellulose content; b. pulping the manure-derived solid fractions with high lignocellulose content at atmospheric pressure with a monocarboxylic acid carrier solution using a bleaching process comprising of ozone or an peroxyacid to produce a dissolving-grade cellulose pulp; c. acetylation the manure-derived dissolving-grade cellulose pulp with acetic anhydride and a catalyst in the monocarboxylic acid carrier solution to produce cellulose acetate; d. extracting fermentable components from the different fractions of the manure to produce monocarboxylic acids for use in the monocarboxylic acid carrier solution.



RAPPORT BETREFFENDE HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK

Octrooiaanvraag 2016798

Classificatie van het onderwerp ¹ : C08B 3/06; A01C 3/00; D21C 3/20	Onderzochte gebieden van de techniek ² : C08B, D21C
Computerbestanden: EPODOC, WPI	Omvang van het onderzoek: Volledig
Datum van de onderzochte conclusies: 19 mei 2016	Niet onderzochte conclusies: –

Van belang zijnde literatuur

Categorie ²	Vermelding van literatuur met aanduiding, voor zover nodig, van speciaal van belang zijnde tekstgedeelten of figuren.	Van belang voor conclusie(s)
A	US 2013/0115654 A (PETERSON JOHN R) 9 mei 2013 * samenvatting; figuren 1, 6 * - - -	
A	WO 92/12944 A (FLOCCO TEC APS) 6 augustus 1992 * samenvatting; pagina 4, regels 26-30 * - - -	
A	NL 2010993 C (VEENHUIS MACHINES) 18 december 2014 * samenvatting; pagina 3, regels 20-31 * - - -	
A	H. SATO, et al.; "New process for producing cellulose acetate from wood in concentrated acetic acid"; Cellulose, 2003, Vol. 10, pp 397-404 * hele document * - - -	
A	US 4649113 A (US AGRICULTURE) 10 maart 1987 * samenvatting * - - - - -	
Datum waarop het onderzoek werd voltooid: 20 februari 2017		De bevoegde ambtenaar: Dr. R. Boers Octrooiencentrum Nederland, onderdeel van Rijksdienst voor Ondernemend Nederland

1 Gedefinieerd volgens International Patent Classification (IPC).

2 Verklaring van de categorie-aanduiding: zie apart blad.

Categorie van de vermelde literatuur:

- X: op zichzelf van bijzonder belang zijnde stand van de techniek
- Y: in samenhang met andere geciteerde literatuur van bijzonder belang zijnde stand van de techniek
- A: niet tot de categorie X of Y behorende van belang zijnde stand van de techniek
- O: verwijzend naar niet op schrift gestelde stand van de techniek
- P: literatuur gepubliceerd tussen voorrangs- en indieningsdatum
- T: niet tijdig gepubliceerde literatuur over theorie of principe ten grondslag liggend aan de uitvinding
- E: octrooiliteratuur gepubliceerd op of na de indieningsdatum van de onderhavige aanvraag en waarvan de indieningsdatum of de voorrangsdatum ligt voor de indieningsdatum van de onderhavige aanvraag.
- D: in de aanvraag genoemd
- L: om andere redenen vermelde literatuur
- &: lid van dezelfde octrooifamilie; corresponderende literatuur



AANHANGSEL

Behorende bij het Rapport betreffende het Onderzoek naar de Stand van de Techniek, Octrooiaanvraag 2016798

Het aanhangsel bevat een opgave van elders gepubliceerde octrooiaanvragen of octrooien (zogenaamde leden van dezelfde octrooifamilie), die overeenkomen met octrooigeschriften genoemd in het rapport. De opgave is samengesteld aan de hand van gegevens uit het computerbestand van het Europees Octrooibureau per 20 februari 2017. De juistheid en volledigheid van deze opgave wordt noch door het Europees Octrooibureau, noch door Octrooiencentrum Nederland gegarandeerd; de gegevens worden verstrekt voor informatiedoeleinden.

In het rapport genoemd octrooigeschrift		Datum van publicatie	Overeenkomende octrooigeschriften		Datum van publicatie
US 2013115654	A1	09-05-2013	(geen)		
WO 9212944	A1	06-08-1992	NO 932599	A	22-09-1993
			FI 933309	A	22-07-1993
			ES 2070633	T3	01-06-1995
			EP 0568597	A1	10-11-1993
			DK 0568597	T3	24-07-1995
			DE 69201789	T2	03-08-1995
			AU 1227492	A	27-08-1992
			AT 120161	T	15-04-1995
NL 2010993	C	18-12-2014	(geen)		
US 4649113	A	10-03-1987	CA 1242191	A	20-09-1988



SCHRIFTELIJKE OPINIE

Octrooiaanvraag 2016798

Indieningsdatum: 19 mei 2016	Vorrangsdatum:																
Classificatie van het onderwerp ¹ : C08B 3/06; A01C 3/00; D21C 3/20	Aanvrager: Jalila Essaidi																
Deze schriftelijke opinie bevat een toelichting op de volgende onderdelen: <table><tr><td>☒ Onderdeel I</td><td>Basis van de schriftelijke opinie</td></tr><tr><td>☐ Onderdeel II</td><td>Vorrang</td></tr><tr><td>☐ Onderdeel III</td><td>Vaststelling nieuwheid, inventiviteit en industriële toepasbaarheid niet mogelijk</td></tr><tr><td>☐ Onderdeel IV</td><td>De aanvraag heeft betrekking op meer dan één uitvinding</td></tr><tr><td>☒ Onderdeel V</td><td>Gemotiveerde verklaring ten aanzien van nieuwheid, inventiviteit en industriële toepasbaarheid</td></tr><tr><td>☐ Onderdeel VI</td><td>Andere geciteerde documenten</td></tr><tr><td>☐ Onderdeel VII</td><td>Overige gebreken</td></tr><tr><td>☒ Onderdeel VIII</td><td>Overige opmerkingen</td></tr></table>		☒ Onderdeel I	Basis van de schriftelijke opinie	☐ Onderdeel II	Vorrang	☐ Onderdeel III	Vaststelling nieuwheid, inventiviteit en industriële toepasbaarheid niet mogelijk	☐ Onderdeel IV	De aanvraag heeft betrekking op meer dan één uitvinding	☒ Onderdeel V	Gemotiveerde verklaring ten aanzien van nieuwheid, inventiviteit en industriële toepasbaarheid	☐ Onderdeel VI	Andere geciteerde documenten	☐ Onderdeel VII	Overige gebreken	☒ Onderdeel VIII	Overige opmerkingen
☒ Onderdeel I	Basis van de schriftelijke opinie																
☐ Onderdeel II	Vorrang																
☐ Onderdeel III	Vaststelling nieuwheid, inventiviteit en industriële toepasbaarheid niet mogelijk																
☐ Onderdeel IV	De aanvraag heeft betrekking op meer dan één uitvinding																
☒ Onderdeel V	Gemotiveerde verklaring ten aanzien van nieuwheid, inventiviteit en industriële toepasbaarheid																
☐ Onderdeel VI	Andere geciteerde documenten																
☐ Onderdeel VII	Overige gebreken																
☒ Onderdeel VIII	Overige opmerkingen																
	De bevoegde ambtenaar: Dr. R. Boers Octrooicentrum Nederland, onderdeel van Rijksdienst voor Ondernemend Nederland																

¹ Gedefinieerd volgens International Patent Classification (IPC).

Onderdeel I Basis van de schriftelijke opinie

Deze schriftelijke opinie is opgesteld op basis van de op 19 mei 2016 ingediende conclusies.

Onderdeel V Gemotiveerde verklaring ten aanzien van nieuwheid, inventiviteit en industriële toepasbaarheid

1. Verklaring

Nieuwheid	Ja: Conclusie(s)	1-33
	Nee: Conclusie(s)	-
Inventiviteit	Ja: Conclusie(s)	1-33
	Nee: Conclusie(s)	-
Industriële toepasbaarheid	Ja: Conclusie(s)	1-33
	Nee: Conclusie(s)	-

2. Literatuur en toelichting

In het rapport betreffende het onderzoek naar de stand van de techniek worden de volgende publicaties genoemd:

- D1: US 2013/0115654 A (PETERSON JOHN R) 9 mei 2013
- D2: WO 92/12944 A (FLOCCO TEC APS) 6 augustus 1992
- D3: NL 2010993 C (VEENHUIS MACHINES) 18 december 2014
- D4: H. SATO, et al.; "New process for producing cellulose acetate from wood in concentrated acetic acid"; Cellulose, 2003, Vol. 10, pp 397-404
- D5: US 4649113 A (US AGRICULTURE) 10 maart 1987

D1 openbaart een werkwijze voor het verkrijgen van biobased materialen verkregen uit landbouwafval. Vanuit dit afval wordt in verschillende stappen diverse verbindingen gewonnen en eventueel omgezet tot andere nuttige producten, waaronder cellulose esters (zie figuur 6). In een van de eerste stappen wordt uit de een versnipperde massa o.a. vetten, oliën en andere extraheerbare verbindingen gewonnen ("chemical processing" 14). Dit is vergelijkbaar met stappen 5 en 6 van figuur 1 van de onderhavige aanvraag. Vervolgens worden cellulose, hemi-cellulose en lignine van elkaar gescheiden, bijvoorbeeld door een alkalische oxidatieve behandeling. Deze volgens deze werkwijze verkregen verbindingen kunnen vervolgens verder omgezet worden in diverse producten, zoals carbonzuren en cellulose acetaat.

Dit document laat zien welke stappen er genomen kunnen worden om van landbouwafval, nuttige producten te verkrijgen.

Het document noemt niet het omzetten van mest, als startmateriaal, tot celluloseacetaat en gebruikt niet de stappen a en c van de onderhavige conclusie 1.

D2 openbaart een werkwijze voor het scheiden van mest in een vaste fractie en vloeibare fracties, waarbij het N-gehalte van de vloeibare fase kan worden geregeld door flocculatie. Zodoende kan een vloeibare fase met een gewenste hoeveelheid voedingsstoffen verkregen worden.

Ook D3 openbaart een werkwijze voor het scheiden van mest in een vaste fractie en vloeibare fracties, waarbij een vlokmiddel wordt gebruikt om de hoeveelheid fosfaat in de vloeibare fractie te verlagen. Zodoende kan er een grotere hoeveelheid dunne fractie over het land uitgereden worden.

D2 en D3 openbaren daarmee de basis van stap a van de onderhavige conclusie, ook al is dit met een andere algemeen bekende alternatieve scheidingsmethode.

D4 openbaart een werkwijze voor de bereiding van cellulose acetaat uit hout, waarbij de stappen van pulpen en acetyleren volledig in geconcentreerd azijnzuur plaats vinden. Dit document openbaart daarmee het principe achter stappen b en c van de onderhavige conclusie 1.

D5 openbaart een werkwijze voor het delignificeren van lignocellulose houdende stromen. Hiertoe wordt deze behandeld met waterstofperoxide onder basische omstandigheden. Er wordt vermeld dat bij een pH hoger dan 11,8 de hemi-cellulose oplost.

D5 openbaart daarmee het principe van de materie van conclusie 20.

Geen van de documenten openbaart de gehele materie van de onderhavige conclusie 1. De conclusies zijn derhalve nieuw.

Voor de inventiviteitsvraag is het belangrijk of de verschillende stappen in de onderhavige conclusie moeten worden gezien als een geheel of dat deze elk afzonderlijk op inventiviteit beoordeeld moeten worden. Aangezien de resultaten van de ene stap gevolgen heeft voor de te behalen kwaliteit en zuiverheid in de daarop volgende stappen dienen de stappen in hun verband beoordeeld te worden op inventiviteit en niet los van elkaar.

Uit de bovenstaande documenten blijkt dat de principes achter elk van de stappen van de onderhavige aanvraag onafhankelijk van elkaar op zich bekend zijn, echter uitgaande van andere uitgangsstoffen dan (afkomstig van) mest.

De inventiviteitsvraag is nu gelegen in de vraag of de deskundige – zonder inventieve arbeid te verrichten – de in de onderhavige aanvraag genoemde combinatie van stappen zou selecteren uit de stand van de techniek zelfs als die gericht is op een ander uitgangsmateriaal. Aangezien er geen aanwijzingen gevonden zijn dat zulk een combinatie voor de hand liggend is, wordt de materie van conclusie inventief bevonden.

De hiervan afhankelijke conclusies worden daardoor ook nieuw en inventief bevonden.

Onderdeel VIII Overige opmerkingen

De volgende opmerkingen met betrekking tot de duidelijkheid van de conclusies, beschrijving, en figuren, of met betrekking tot de vraag of de conclusies nawerkbaar zijn, worden gemaakt:

Schriftelijke Opinie

Octrooiaanvraag 2016798

De optionele maatregelen in conclusie 1 zijn niet beperkend voor deze conclusie.