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(54) Title: METHOD FOR REDUCING POTASSIUM CONTENT IN VINASSE, ITS USE, PRECIPITATE AND PROCESS SOLUTION

(57) Abstract: The invention relates to a method for reducing potassium content in vinasse, which is a by-product from a sugar production or fermentation process, such as bioethanol or yeast production. The method comprises obtaining a process solution comprising vinasse, adding ammonium sulphate to the process solution under agitation in order to precipitate the potassium in vinasse, and separating a potassium-rich precipitate from the process solution. Ammonia is added in excess to the process solution in order to raise pH of the process solution to a value > 7 before precipitate separation. The invention relates also to use of the method and a precipitate and process solution produced.



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METHOD FOR REDUCING POTASSIUM CONTENT IN VINASSE, ITS USE, PRECIPITATE AND PROCESS SOLUTION

The invention relates to a method for reducing potassium content in vinasse, which is a by-product from sugar refining or from various fermentation processes according to the preamble of the enclosed independent claim. The invention relates also to the precipitate and process solution obtainable by the method.

Vinasse is obtained as a waste or by-product in various sugar manufacture or fermentation processes, such as production of alcohol or yeasts. Vinasse has often a relatively low dry solids content, about 5 - 30 weight-%, but it is typically rich in potassium, the potassium content being typically 0.5 - 4 weight-%, sometimes even higher. The composition of vinasse depends on the used raw material, which typically is sugar cane, sugar beet or corn. The amount of produced vinasse is increasing, as it is obtained as a by-product or waste also in production of bioethanol.

The high potassium content of vinasse makes its further use problematic. There is proposal to use it as cattle feed or as irrigation medium in agriculture. However, there are practical and legal restrictions how much potassium may be contained in cattle feed or in irrigation medium, and normally potassium content in vinasse is clearly exceeding these limits. The result is ever increasing volume of vinasse for which there is no suitable use.

Document GB 1,185,104 discloses a method for substituting ammonia for potassium in by-products of distillation of sugar fermentation products, such as distiller's wash, i.e. vinasse. The method comprises heating and concentrating the by-product and adding either sulphuric acid and ammonia, or ammonium sulphate to the by product under agitation. After cooling the formed potassium sulphate crystals are removed. The disclosed method is, however, not suitable for treating large volumes of vinasse, as it includes energy intensive and arduous heating and concentration steps.

The object of the present invention is to minimise or even totally eliminate the drawbacks existing the prior art.

- 5 An object of the present invention is to provide method for simple and economical reduction of potassium in vinasse.

Another object of the present invention is to modify the composition of vinasse in such a way that it can be used in different purposes, such as irrigation medium.

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Still another object of the present invention is to produce a potassium rich product, which in itself may have commercial use.

Typical method according to the present invention for reducing potassium content in vinasse, which is a by-product from a sugar production or fermentation process, such as bioethanol or yeast production, comprises

- 15
- obtaining a process solution comprising vinasse,
 - adding ammonium sulphate to the process solution under agitation in order to precipitate the potassium in vinasse,
 - 20 - separating a potassium-rich precipitate from the process solution,
 - adding ammonia in excess to the process solution in order to raise pH of the process solution to a value > 7 before precipitate separation.

Typical potassium-rich product according to the present invention is produced by using the method according to the present invention.

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Now it has been surprisingly found out that adding an excess of ammonia to vinasse together with addition of ammonium sulphate the precipitation of potassium is clearly and significantly increased. It is even possible to obtain a potassium reduction which is 30 % higher than the reduction obtained in the same process conditions without addition of excess ammonia. It has been surprisingly observed that the raise of pH of the vinasse to a value > 7 with the excess of

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ammonia provides a major improvement in potassium precipitation. Moreover, the method according to the invention is easy and simple to carry out and does not require complicated or expensive process steps. It is furthermore suitable for treating large volumes of vinasse. Addition of ammonia also increases the nutrient
5 value of the process solution after the separation of potassium-rich precipitate, which makes its use as irrigation medium even more advantageous.

In this context the term "vinasse" means a solution having dry solids content 5 - 50 weight-%, typically 15 - 35 weight-%, and originating from bioethanol
10 production, alcohol production, sugar production, fermentation process or yeast production, preferably from bioethanol production. The raw material for vinasse is typically corn, sugar cane or sugar beet, preferably corn or sugar cane, most preferably sugar cane. Vinasse contains > 0.1 weight-%, typically 0.2 - 7 weight-%, more typically 0.5 - 4 weight-% potassium. The present invention is suitable for
15 treating vinasse having potassium content > 1 weight-%, especially suitable for treating vinasse having potassium content > 2 weight-%. Vinasse contains also calcium, magnesium, nitrogen, phosphorous, residual sugar compounds as well as different organic residues, such as hemicelluloses, lignin, organic acids, waxes, glycerol, etc. BOD (Biological Oxygen Demand) value for vinasse may be 10 - 50
20 g/l and it has pH value 4 - 5.

According to one embodiment of the present invention ammonia is added to the process solution comprising vinasse in amount, which results pH 7 - 14, preferably 7 - 12, more preferably 8 - 10. The exact amount or volume of
25 ammonia to be added depends on the composition of the vinasse to be treated. The amount of ammonia should be such that the desired pH is obtained for the process solution. A person skilled in the art knows how to determine the pH of process solution comprising vinasse before the addition of ammonia and adjust the dosage of ammonia accordingly. For example, pH of the process solution
30 comprising vinasse may be controlled continuously on-line, and the dosing of ammonia is ended when the target pH is reached.

Ammonia may be added in gaseous form or in liquid form to the process solution comprising vinasse. Ammonia in liquid form is normally an aqueous concentrated solution of ammonia, having concentration ca. 25 - 30 weight-%. Ammonia in liquid form is added to the process solution comprising vinasse under constant
5 agitation in order to guarantee the effectivity of the reaction in the process solution. Typical amount of added ammonia in liquid form is 1 - 10 weight-%, calculated of the amount of vinasse to be treated. Depending of origin of vinasse, this addition results a pH value 8 - 10 in the process solution. In case ammonia is added in
10 gaseous form it may be bubbled through the reaction vessel or tank containing the process solution comprising vinasse. Preferably ammonia in gaseous form is added to the atmosphere of agitated reaction vessel or tank from where it is quickly dissolved into the process solution comprising vinasse.

According to one embodiment of the present invention ammonium sulphate is
15 added to the process solution comprising vinasse before or during the addition of excess ammonia. Ammonium sulphate is added in amount, which is 0.5 - 2 times, preferably 1 - 1.5 times, more preferably 1.1 - 1.5 times, the calculated stoichiometric amount for reaction with potassium in the process solution comprising vinasse. Ammonium sulphate is preferably added in excess to the
20 calculated stoichiometric amount, as the process solution usually comprises other species, such as calcium, that may react with sulphate ions and precipitate from the process solution. It should be also noted that total or complete precipitation of potassium from the process solution is not necessary, it is sufficient to attain potassium level that is under required limit values.

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The potassium content in the process solution or in vinasse, which is treated by the method, may be determined by suitable analytical methods. Samples for potassium determination may be taken at the end of an individual batch in a batch process or at predetermined time intervals. Suitable methods for determining
30 potassium content are, for example inductively coupled plasma mass spectroscopy (ICP-MS) or X-ray fluorescence (XRF). According to one embodiment of the invention the potassium content of the vinasse, which is

treated, is determined regularly at predetermined time intervals, the determined potassium content value is used for calculating the amount of ammonium sulphate needed and the result of the calculation is used to regulate the addition of ammonium sulphate to process solution comprising vinasse. Typically ammonium sulphate is added in amount from about 1.7 to about 2.5 kg per 1 kg potassium in vinasse.

Ammonium sulphate is typically added to the process solution as a solid material, e.g. powder form, or as a concentrated solution of ca. 40 weight-% under agitation. The addition of ammonium sulphate in solid, e.g. powder, form is preferred, as it improves the precipitation of potassium.

According to one embodiment of the invention the process solution comprising vinasse is cooled to a temperature 15 - 50 °C, preferably to a temperature 20 - 35 °C before addition of ammonium sulphate. Vinasse to be treated typically comes straight from the bioethanol production, and it is usually warm, as the temperature in the end of distillation is typically around 80 °C. Vinasse or process solution comprising vinasse may be cooled by keeping it in a cooling vessel, such as tank, basin, or reservoir, possibly under agitation, so long that its temperature is decreased under desired level. Vinasse may be alternatively actively cooled by using cooling with double-walled cooling tanks with circulating cooling water or by using tanks with cooling coils. Cooling of vinasse or the process solution improves the addition of the ammonia, as it is more easily added to a solution with decreased temperature. However, the cooling of vinasse or process solution is not normally necessary.

Vinasse may be treated as slightly concentrated solution or as such, directly obtained from the previous process step, e.g. from production of bioethanol. Typically vinasse has a solids content less than 50 weight-%. According to one preferred embodiment of the invention the method is free from any active concentration steps of vinasse. This means that vinasse from the preceding process, such as bioethanol distillation, is obtained as such and used as process

solution in the present method. In that case vinasse has solids content 5 - 50 weight-%, typically 15 - 35 weight-%. Natural slight evaporation may occur, but vinasse is preferably not concentrated by using active process steps, for example by exposure to heat, and vinasse may be considered unconcentrated.

- 5 Furthermore, the process solution comprising vinasse is not concentrated before or after the addition of ammonia and/or ammonium sulphate. Concentration steps would reduce the amount of water in the process solution that is available for irrigation, whereby they are preferably excluded.
- 10 The potassium-rich precipitate, which is obtained by using the present invention, may be separated from the process solution by any suitable method for separating solid material from liquid. Preferably the potassium rich precipitate is separated by using filtration, settling or centrifugal separation. The precipitate comprises, in addition to potassium compounds, also other inorganic compounds, such as
- 15 calcium and magnesium compounds, as well as organic material.

According to one embodiment of the invention the separated potassium-rich precipitate is formed into granules. The granules may be used as fertilizer or as a component in a fertilizer, especially in NPK-fertilizer mixture. The organic material

20 in the precipitate improves its granulation tendency, whereby the precipitate is easily formed into granules of desired size, by using conventional granulation methods, such as a drum or pan granulator or compacting. Typical size of the granules is 1 - 4 mm.

- 25 After separation of the potassium-rich precipitate the separated liquid phase of the process solution is transferred to a storage reservoir, basin, container or the like. The process solution after the separation of potassium-rich precipitate may be used as irrigation medium in agriculture, for example for irrigation of sugar cane or corn fields.

According to one embodiment it is possible to concentrate the vinasse to be treated, or the process solution comprising vinasse before addition of ammonium sulphate and/or ammonia.

5 EXPERIMENTAL

Example 1

A molasses based vinasse containing originally 3.60 weight-% potassium is treated according to the present invention by adding ammonium sulphate in stoichiometric ratios of approximately 0.5 to 1.6 with and without pH adjustment by min. 25 weight-% ammonia solution. The results shown in Table 1 indicate that in addition to the conventional process parameters like stoichiometric ratio and mixing time, the pH adjustment by ammonia clearly improves the potassium reduction in the solution due to potassium salt precipitation.

Table 1. Different parameters employed in Example 1, and obtained potassium reduction results.

$(\text{NH}_4)_2\text{SO}_4$ (g/kg)	stoichiom. ratio to K	mixing time (h)	final pH ¹⁾	K (w-%) in filtrate	K reduction (%)
experimental set 1					
31.30	0.51	0.5	5.0	2.61	27.5
64.16	1.05	0.5	5.1	2.51	30.3
96.90	1.59	0.5	5.1	2.42	32.8
62.72	1.03	24 ²⁾	5.0	2.31	35.8
62.72	1.03	24	5.1	2.20	38.9
62.72	1.03	0.5	9.9	2.13	40.8
experimental set 2					
62.70	1.03	0.5	8.0	2.44	32.2
62.64	1.03	24	8.0	2.40	33.3
75.10	1.23	24	8.0	2.37	34.2

1) adjusted by NH_4OH (min. 25 w-%)

2) heating/cooling up to 80 °C

Even if the invention was described with reference to what at present seems to be the most practical and preferred embodiments, it is appreciated that the invention shall not be limited to the embodiments described above, but the invention is intended to cover also different modifications and equivalent technical solutions

5 within the scope of the enclosed claims.

CLAIMS

1. Method for reducing potassium content in vinasse, which is a by-product from a sugar production or fermentation process, such as bioethanol or yeast production, the method comprising
- 5 - obtaining a process solution comprising vinasse,
- adding ammonium sulphate to the process solution under agitation in order to precipitate the potassium in vinasse,
- separating a potassium-rich precipitate from the process solution,
- 10 **characterised** in
- adding ammonia in excess to the process solution in order to raise pH of the process solution to a value > 7 before precipitate separation.
2. Method according to claim 1, **characterised** in adding ammonia to the process solution during or after ammonium sulphate addition.
- 15 3. Method according to claim 1 or 2, **characterised** in adding ammonia to the process solution comprising vinasse in amount resulting pH 7 - 14, more preferably 8 - 10.
- 20 4. Method according to claim 1, 2 or 3, **characterised** in adding ammonia in gaseous form or in liquid form.
5. Method according to claim 4, **characterised** in adding ammonia in liquid form as an aqueous concentrated solution of ammonia, having concentration ca. 25 - 30 weight-%, in amount 1 - 10 weight-%, calculated of the amount of vinasse to be treated.
- 25 6. Method according to any of preceding claims 1 - 5, **characterised** in adding ammonium sulphate in amount, which is 0.5 - 2 times the calculated stoichiometric amount.
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7. Method according to claim 6, **characterised** in adding ammonium sulphate in excess to the calculated stoichiometric amount.

5 8. Method according to claim 6 or 7, **characterised** in adding ammonium sulphate to the process solution as a solid material, e.g. in powder form, or as a concentrated solution of ca. 40 weight-%.

9. Method according to any of preceding claims 1 - 8, **characterised** in
10 - determining regularly at predetermined time intervals the potassium content of the vinasse,
- using the determined potassium content value for calculating the amount of ammonium sulphate needed, and
- using the result of the calculation to regulate the addition of ammonium sulphate to process solution comprising vinasse.

15 10. Method according to any of preceding claims 1 - 9, **characterised** in cooling the process solution comprising vinasse to a temperature 15 - 50 °C, preferably to a temperature 20 - 35 °C, before addition of ammonium sulphate.

20 11. Method according to claim 1, **characterised** in separating the potassium-rich precipitate by filtration, settling or centrifugal separation from the process solution.

12. Method according to claim 1, **characterised** in forming the separated potassium-rich precipitate into granules, having size of 1 - 4 mm.

25 13. Method according to claim 1 or 12, **characterised** in using the separated precipitate or granules as fertilizer or as a component in a fertilizer, especially in NPK-fertilizer mixture.

30 14. Method according to claim 1, **characterised** in using the process solution after the separation of potassium-rich precipitate as irrigation medium.

15. Method according to any of preceding claims 1 - 14, **characterised** in that the method is free from any concentration steps of vinasse.

16. Use of a method according any of claims 1 to 15 for treating vinasse having
5 potassium content > 1 weight-%, preferably > 2 weight-%, more preferably > 3 weight-%.

17. Use according to claim 16, **characterised** in that the vinasse originates from bioethanol production and is in form of a solution having dry solids content 5 - 50
10 weight-%, typically 15 - 35 weight-%.

18. Use according to claim 16 or 17, **characterised** in that raw material for vinasse is corn, sugar cane or sugar beet.

15 19. Potassium-rich precipitate obtainable by using a method according to any of claims 1 - 15.

20. Process solution obtainable by using a method according to any of claims 1 - 15.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI201 1/051 104

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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)

IPC: A23K, C05D, C05F, C12F, C12P

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

FI, SE, NO, DK

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

EPO-Internal, WPI, AGRICOLA, BIOSIS, CABA, CAPLUS, EMBASE, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 11851 04 A (LESAFFRE & CIE) 18 March 1970 (18.03.1970) cited in the application, the whole document	1-20
A	FR 2573088 A1 (BEGHIN SAY SA) 16 May 1986 (16.05.1986) the whole document	1-20
A	EP 0794246 A1 (GIST BROCADES BV - DSM NV) 10 September 1997 (10.09.1997) the whole document	1-20



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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

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

"&" document member of the same patent family

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