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CN 101056882 A, 2007.10.17,CN

1656110A, 2005. 08. 17, US 3792041 A, 1974. 02. 12, Wo 9640699 A1, 1996.12.19,

Min Y G, et al. Study on a new synthesis method of sucrose vinegar. Journal of South China University of Technology (Natural Science Edition). 1995, vol. 23 (5), 149-152.

Hu J H, et al. Study on solvent-free synthesis of sucrose ester (II) A synthesis of sucrose ester from oil. China Oils and Fats, 1999, vol. 24 (6),45-46.

Fan G D, et al. Progress in the synthesis of sucrose ester, an environmentally friendly video additive. Journal of Safety and Environment, 2011, vol. 11 (1),14-16.

Yan Liang, et al. Solvent-free synthesis of high purity sucrose fatty acid ester. Chemical Production and Technology. 2010, vol. 17 (4), 23-24,27.

Chen Yong-fu, et al. Research on the improvement of sucrose ester synthesis technology. Zhejiang Chemical Industry. 2007, 38 (7),10-11.

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Claim 1 page specification 7 pages

(54) Name of invention

Method for preparing low ash sucrose fatty acid ester

(57) Abstract

The invention discloses A preparation method of low ash sucrose fatty acid ester, which comprises the following steps : A, fatty acid methyl ester and part of sucrose powder are esterified under the action of basic catalyst, after the reaction is complete, water equivalent to 0.4-1 times the volume of the product after reaction is added for dilution, and then the diluent is passed through the ion exchange column for ion exchange to remove metal ions; The basic catalyst is an alkaline metal salt or a metal hydroxide; B, after the end of the ion exchange, the material to complete the ion exchange is removed from the water, and after the removal of water, the sucrose powder is added to continue the reaction. The invention has the advantages of low cost, convenient operation and can solve the problems of low esterification degree of product, low purity of sucrose fatty acid ester and high ash content of product in the prior art.

1. A method for preparing a low ash sucrose fatty acid ester, characterized by including the following steps:

A, fatty acid methyl ester, part of sucrose powder under the action of alkaline catalyst esterification reaction, after the reaction is complete, adding water equivalent to 0.4-1 times the volume of the reaction product for dilution, and then the diluent through the ion exchange column, ion exchange to remove metal ions; The basic catalyst for the basic metal salt or metal hydroxide;

B, after the end of the ion exchange, the material to complete the ion exchange is removed from the water, and after the removal of water, the sucrose powder is added to continue the reaction;

The esterification reaction includes the following steps:

A. Fatty acid methyl ester was added to the reaction kettle, at the same time, basic catalyst with a total weight of 3%-5% of sucrose and fatty acid methyl ester was added, and vacuum heated to 127-140℃;

b. Add sucrose powder with a molar ratio of 1:2.5 to 4 of fatty acid methyl ester into the material of step A, maintain the temperature at 127-140℃, carry out vacuum esterification reaction for 1.5-2.5 hours, and draw out the reaction product methanol, and obtain.

2. The preparation method of low ash sucrose fatty acid ester as described in claim 1 is characterized by: in step A, the reaction product diluted with water is heated to 70-90 ° C and then carried out the column, and the temperature of the exchange column is maintained at 70-90 ° C.

3. As the preparation method of low ash sucrose fatty acid ester described in claim 1, its characteristics are: after the end of ion exchange, vacuum heating at 110-120 ° C to remove water, and add 2-4% of the product quality of sucrose powder to the product of water removal, stirring reaction 0.5-1.5 hours, obtain low ash sucrose fatty acid ester.

4. As any one of the low ash sucrose fatty acid ester preparation method described in claim 1-3, its characteristics are: the basic catalyst is potassium hydroxide, sodium hydroxide, potassium carbonate, sodium carbonate in one or more of the combination.

· The preparation method of low ash sucrose fatty acid ester as described in claim 4 is characterized in that the basic catalyst is potassium hydroxide.

· The preparation method of low ash sucrose fatty acid ester as described in any of the claims 1-3 is characterized in that the ion exchange column is a strong acid exchange resin column, a medium acid exchange resin column or a weak acid ion exchange resin column.

7. The preparation method of low ash sucrose fatty acid ester as described in claim 6 is characterized in that the ion exchange column is a strong acidic ion exchange resin.

The preparation method of any of the low ash sucrose fatty acid esters described in claim 1-3 is characterized in that the ion exchange column is pre-treated with an acidic solution.

9. The preparation method of low ash sucrose fatty acid ester as described in claim 8 is characterized in that the pretreatment includes the following steps:

A, the ion exchange resin in the ion exchange column soaked in the equivalent of resin volume 1-3 times the mass fraction of 7% sodium chloride solution, soaked under constant agitation for 20-24 hours, remove the water, and then rinse with deionized water until colorless;

B, step A treated resin with resin volume 2-3 times the mass fraction of 4% hydrochloric acid solution soaked for 4-6 hours, remove the water, rinse with deionized water to pH value to neutral;

C, the resin treated after step B is soaked in 4% sodium hydroxide solution with 2 to 3 times the volume of the resin for 4-6 hours, remove the water, and then rinse with deionized water to pH value to neutral

D, the resin treated in step C is soaked in 4% hydrochloric acid solution with 2 to 3 times the volume of the resin for 4-6 hours, remove the water, rinse with deionized water until the pH value is neutral, and load the column for use.

The invention relates to a preparation method of low ash sucrose fatty acid ester

Technical field

[0001] The invention relates to a method for synthesizing sucrose ester, in particular to a method for preparing a low ash sucrose fatty acid ester.

Background technology

[0002] Sucrose ester is a kind of green non-ionic surfactant with sucrose as hydrophilic base and fatty acid chain as hydrophobic group, which has good biodegradation ability, so it can be widely used in food additives, detergents, cleaning agents and cosmetics industries, and has potential application prospects in pharmaceutical, biochemistry and biomedicine. The raw materials for the production of sucrose fatty acid ester are cheap and easily available renewable resources, and have a wide range of controllable hydrophilic and lipophilic equilibrium values. In addition to good emulsifying properties, sucrose ester has complete biodegradability and environmental friendly, non-toxic, skin compatible, odorless and tasteless properties.

[0003] However, in the process of application of production technology, sucrose ester synthesis is generally used in organic solvents under the catalysis of alkaline catalyst and heating using fatty acid methyl ester and sucrose transesterification reaction to synthesize sucrose ester, the synthesis method of solvent toxicity, high cost, which will inevitably bring certain limitations to the application of solvent synthesis of sucrose ester. The current production process uses solvent-free method to produce sucrose fatty acid ester, which can solve the adverse effects of large solvent toxicity, and has been widely used as a food additive. Solveless method to use alkaline catalyst and reactants mixed catalytic reaction, resulting in a high ash content of products, sucrose fatty acid ester products ash components mainly composed of alkaline catalysts and metal ions, this is because the current prior art esterification products contain sucrose esters and fatty acids, as well as ash impurities alkaline catalysts and metal ions. And these ash impurities are not a good way to remove, which results in the final sucrose fatty acid ester of high ash, poor quality. The presence of these alkaline substances is not conducive to the application of the product and the health of the body. The application range of sucrose fatty acid ester with high ash is getting narrower and narrower, and it will be eliminated soon. For example, Nestle made it clear that the ash content of sucrose fatty acid ester purchased must be less than or equal to 1.5%. There are the following defects in the preparation of sucrose fatty acid ester by prior art method :1. Sucrose fatty acid ester has high ash content, which needs to be improved; 2. The product has low esterification degree, low purity of sucrose fatty acid ester, and the production process needs to be improved. The production of low ash, high quality sucrose fatty acid ester to meet the needs of the market has become a top priority.

Content of invention

[0004] The invention aims to provide a preparation method of low cost, easy operation and low ash sucrose fatty acid ester to solve the problems of low esterification degree, low purity of sucrose fatty acid ester and high ash content of product in the prior art.

[0005] In order to achieve the above purposes, the technical scheme of the invention is as follows:

[0006 The preparation method of low ash sucrose fatty acid ester comprises the following steps:

[0007 A, fatty acid methyl ester and part of sucrose powder are esterified under the action of alkaline catalyst. After the reaction is complete, water equivalent to 0.4-1 times the volume of the product after reaction is added for dilution, and then the diluent passes through the ion exchange column to carry out ion exchange to remove metal ions; the basic catalyst is metal salt or alkaline metal hydroxide;

[0008] B, after the end of the ion exchange, the material to complete the ion exchange is removed from the water, and after the removal of water, the sucrose powder is added to continue the reaction.

[0009] In the above step A, the reaction product diluted by adding water is heated to 70-90℃ and then carried out through the column, and the temperature of the exchange column is maintained at 70-90℃

[0010] After the end of ion exchange, vacuum heating is carried out at 110-120℃ to remove the water, and 2-4% of the product weight of sucrose powder is added to the product after the removal of water, stirring reaction is 0.5-1.5 hours, and low ash sucrose fatty acid ester is obtained.

[0011] The esterification reaction consists of the following steps:

[0012] a, the fatty acid methyl ester is added to the reaction kettle, at the same time, the basic catalyst with the total weight of sucrose and fatty acid methyl ester of 3%-5% is added, and the vacuum is heated to 127-140℃;

[0013] b. Add sucrose powder with the molar ratio of fatty acid methyl ester of 1:2.5 to the material of step A, maintain the temperature at 127-140℃, carry out vacuum esterification reaction for 1.5-2.5 hours, and draw out the reaction product methanol, and obtain.

[0014] The basic catalyst is one or more of potassium hydroxide, sodium hydroxide, potassium carbonate and sodium carbonate.

[0015] Preferably, the alkaline catalyst is potassium hydroxide.

[0016] The ion exchange column is a strong acid exchange resin column, a medium acid exchange resin column or a weak acid ion exchange resin column.

[0017] Preferably, the ion exchange column is a strong acidic ion exchange resin.

[0018] The ion exchange column is pre-treated with an acidic solution.

[0019] The pre-treatment comprises the following steps:

[0020] A. Soak the ion exchange resin in the ion exchange column in an aqueous solution of 7% sodium chloride, which is equivalent to 1-3 times the volume of the resin, soak for 20-24 hours under constant agitation, remove the water, and then rinse with deionized water until colorless;

[0021] B, step A treated resin with resin volume 2-3 times the mass fraction of 4% hydrochloric acid solution soaked for 4-6 hours, remove the water, rinse with deionized water to pH value to neutral;

[0022] C, the resin treated in step B is soaked in 4% sodium hydroxide solution with 2 to 3 times the volume of the resin for 4-6 hours, the water is removed, and then rinsed with deionized water to pH to neutral

[0023] D, the resin treated in step C was soaked in 4% hydrochloric acid solution with 2 to 3 times the volume of the resin for 4-6 hours, the water was removed, and the water was washed with deionized water until the pH value was neutral, and the column was loaded for use.

[0024] The beneficial effects of the invention are as follows:

[0025] The products of the esterification reaction of the invention contain sucrose esters, fatty acids, and alkaline ash impurities, which are mainly catalysts and metal ions. Through a large number of experimental studies, the inventor finds that the technical scheme of the invention can remove ash impurities well.

[0026] The invention adopts a two-step reaction method. The first step first heats fatty acid methyl ester and alkaline catalyst to the reaction temperature, and carries out saponification reaction, and then adds the first batch of sucrose powder for esterification reaction. After the reaction of the first batch of sucrose powder is complete, metal ions and alkaline impurities are removed by ion exchange resin, and then a small amount of the second batch of sucrose powder is added for reaction. The sucrose powder reacts with the fatty acids generated in the product to achieve the effect of reducing the acid value. The method of crushing sucrose and adding it in sections, and removing catalyst in the middle, makes the reaction more complete, and effectively reduces the ash impurity content and acid value in the reaction product. The invention is divided into a two-step reaction mode, and the ash impurities are removed after the first step, which can fully guarantee the technical effect of removing impurities by ion exchange. Because if all the sucrose powder and fatty acid methyl ester after the reaction of the product, will have a high viscosity, even if water is added at this time, it is impossible to reduce the product viscosity and dispersion products, because water and the product is difficult to miscible. The invention can overcome the technical problem that the ash impurities of this kind of chemical reaction can not be removed in the prior art by means of two-step step reaction and ion exchange in the intermediate step.

[0027] The ash impurities in the invention are removed by adding 0.4-1 times of the volume of the reaction material to reduce the viscosity of the material, and at the same time play a uniform dispersion effect on the material after esterification reaction, so that the material has the basis of ion exchange; Second, suitable.

The acid ion exchange resin, through the esterification reaction ion exchange treatment, remove impurities; The third is to control the ion exchange temperature, the inventor found that the product of the esterification reaction control temperature at 70-90℃, can get better ion exchange effect. [0028] The invention removes the metal ions in the reaction system by ion exchange, effectively reduces the ash content of the product, and timely removes the methanol generated in the reaction system, promoting the reaction to continue in the direction of generating sucrose ester, and the production process has high esterification degree, simple production process, low production cost, and is suitable for large-scale production.

Specific implementation mode

[0029] The invention is described in detail by specific embodiments.

[0030] Example 1

[0031] The method for preparing a low ash sucrose fatty acid ester of the invention comprises the following steps:

[0032] a. Add 5L fatty acid methyl ester to the reaction kettle, add 1.1L potassium hydroxide aqueous solution with A concentration of 5mo1/L, vacuum to -0.1Mpa, and steam heating to 127℃;

[0033] B. Add 3.2kg sucrose powder to the material in step A, keep the temperature at 127℃, and carry out vacuum esterification reaction for 1.5 hours. The reaction product methanol is cooled by condenser in vacuum state and then enters the methanol receiver;

[0034] C. Add 6L of water to the reaction system after step B for dilution and heating to 70℃. Then the diluent is overacidic ion exchange column for ion exchange to remove potassium ions. The temperature of the exchange column is maintained at 70℃ and the flow rate is controlled at 150mL/ min;

[0035] D, after the end of the ion exchange, vacuum heating was carried out at 110℃ to remove the water, and 300g sucrose powder was added to the product after the removal of water, stirring and reaction for 0.5 hours to obtain sucrose fatty acid ester with low ash.

[0036] The ion exchange column is pretreated with an acidic solution in advance, and the pretreatment comprises the following steps:

[0037] a. Soak the ion exchange resin in the ion exchange column in an aqueous solution of 7% sodium chloride, which is equivalent to 1 times the volume of the resin, soak for 20 hours under continuous agitation, remove the water, and then rinse with deionized water until colorless;

[0038] B. The resin treated in step A is soaked in 4% hydrochloric acid solution with twice the volume of resin for 4 hours, the water is removed, and the water is washed with deionized water until the pH value is neutral;

[0039] C. The resin treated in step B is soaked in 4% sodium hydroxide solution with twice the volume of resin for 4 hours, the water is removed, and then rinsed with deionized water until the H value is neutral

[0040] D. The resin treated in step C was soaked in 4% hydrochloric acid solution with twice the volume of resin for 4 hours, the water was removed, and the water was rinsed with deionized water until the pH value was neutral, and then loaded into columns for use.

[0041] Embodiment 2

[0042] The method for preparing a low ash sucrose fatty acid ester of the invention comprises the following steps:

[0043] a. Add 5L fatty acid methyl ester to the reaction kettle, at the same time add 1.5L sodium hydroxide aqueous solution with A concentration of 5mo1/L, vacuum to -0.1Mpa, and steam heating to 130℃;

[0044] B. Add 3.5kg sucrose powder to the material in step A, keep the temperature at 130℃, and carry out vacuum esterification reaction for 1.8 hours. The reaction product methanol is cooled by the condenser in the vacuum state and then enters the methanol receiver;

[0045] C. Add 5L of water to the reaction system after step B for dilution and heating to 75℃, and then pass the diluent through the medium acidic ion exchange column for ion exchange to remove sodium ions. The temperature of the exchange column is maintained at 75℃ and the flow rate is controlled at 200mL/ min;

[0046] D. After the ion exchange, the water was removed by vacuum heating at 112℃, and 100g sucrose powder was added to the product after water removal, stirring for 0.8 hours to obtain sucrose fatty acid ester with low ash content.

[0047] The ion exchange column is pretreated with an acidic solution in advance, and the pretreatment comprises the following steps:

[0048] a. Soak the ion exchange resin in the ion exchange column in an aqueous solution of 7% sodium chloride, which is equivalent to 2 times the volume of the resin, soak for 21 hours under continuous agitation, remove the water, and then rinse with deionized water until colorless;

[0049] B. The resin treated in step A was soaked in 4% hydrochloric acid solution with 2.5 times the volume of the resin for 5 hours, the water was removed, and the water was washed with deionized water until the pH value was neutral;

[0050] C, the resin treated in step B is soaked in the resin volume of 2.5 times the mass fraction of 4% sodium hydroxide solution for 5 hours, the water is removed, and then rinsed with deionized water until the pH is neutral

[0051] D, the resin treated in step C was soaked in 4% hydrochloric acid solution with 2.5 times the volume of the resin for 5 hours, the water was removed, and the water was rinsed with deionized water until the pH value was neutral, and the column was loaded for use.

[0052] Embodiment 3

[0053] The method for preparing low ash sucrose fatty acid ester of the invention comprises the following steps:

[0054] a. Add 5L fatty acid methyl ester to the reaction kettle, at the same time add 1.0L potassium carbonate aqueous solution with A concentration of 5mo1/L, vacuum to -0.1Mpa, and steam heating to 135℃;

[0055] B. Add 2.8kg sucrose powder to the material in step A, keep the temperature at 135℃, and carry out vacuum esterification reaction for 2 hours. The reaction product methanol is cooled by the condenser in the vacuum state and then enters the methanol receiver;

[0056] C. Add 4L of water to the reaction system after step B for dilution and heating to 80℃, and then pass the diluent through the medium acid ion exchange column for ion exchange to remove potassium ions. The exchange column temperature is maintained at 80℃ and the flow rate is controlled at 250mL/ min;

[0057] D. After the end of ion exchange, vacuum heating was carried out at 115℃ to remove the water, and 300g sucrose powder was added to the product after water removal, stirring reaction for 1 hour to obtain sucrose fatty acid ester with low ash content.

[0058] The ion exchange column is pretreated with an acidic solution in advance, and the pretreatment includes the following steps:

[0059] a. Soak the ion exchange resin in the ion exchange column in an aqueous solution of 7% sodium chloride, which is equivalent to 3 times the volume of the resin, soak for 22 hours under continuous agitation, remove the water, and then rinse with deionized water until colorless;

[0060] B. The resin treated in step A was soaked in 4% hydrochloric acid solution with 3 times the volume of the resin for 6 hours, the water was removed, and the water was washed with deionized water until the pH value was neutral;

[0061] C, the resin treated in step B is soaked in 4% sodium hydroxide solution with 3 times the volume of resin for 6 hours to remove water, and then washed with deionized water to neutral H value

[0062] D. The resin treated in step C was soaked in 4% hydrochloric acid solution with 3 times the volume of the resin for 6 hours, the water was removed, and the water was washed with deionized water until the pH value was neutral, and then loaded into columns for use.

[0063] Embodiment 4

[0064] The method for preparing a low ash sucrose fatty acid ester of the invention comprises the following steps:

[0065] A. Add 4.51 fatty acid methyl ester to the reaction kettle, at the same time add 1.3L sodium carbonate aqueous solution with a concentration of 5mo1/L, vacuum to -0.1Mpa, and steam heating to 138℃;

[0066] B. Add 2.9kg sucrose powder to the material in step A, keep the temperature at 138℃, and carry out vacuum esterification reaction for 2.2 hours. The reaction product methanol is cooled by the condenser in the vacuum state and then enters the methanol receiver;

[0067] C, add 4.5L water to the reaction system after step B for dilution, and heat to 85℃, and then the diluent liquid liquid through the medium acid ion exchange column, ion exchange to remove sodium ions, the exchange column temperature is maintained at 85℃, the flow rate is controlled at 300mL./min;

[0068] D, after the end of the ion exchange, vacuum heating was carried out at 118℃ to remove the water, and the product after the removal of water was added

150g sucrose powder was added and stirred for 1.2 hours to obtain sucrose fatty acid ester with low ash content.

[0069] The ion exchange column is pretreated with an acidic solution in advance, and the pretreatment comprises the following steps:

[0070] a. Soak the ion exchange resin in the ion exchange column in an aqueous solution of 7% sodium chloride, which is equivalent to 2 times the volume of the resin, soak for 23 hours under continuous agitation, remove the water, and then rinse with deionized water until colorless;

[0071] B. The resin treated in step A was soaked in 4% hydrochloric acid solution with twice the volume of the resin for 4 hours, the water was removed, and the water was washed with deionized water until the pH value was neutral;

[0072] C, the resin treated in step B is soaked in 4% sodium hydroxide solution with 3 times the volume of resin for 5 hours, the water is removed, and then washed with deionized water until the pH is neutral

[0073] D, the resin treated in step C was soaked in 4% hydrochloric acid solution with twice the volume of resin for 6 hours, the water was removed, and the water was rinsed with deionized water until the pH value was neutral, and then loaded into columns for use.

[0074] Embodiment 5

[0075] The method for preparing a low ash sucrose fatty acid ester of the invention comprises the following steps:

[0076] a. Add 5L fatty acid methyl ester to the reaction kettle, at the same time add 1.0L mixed solution of potassium hydroxide and potassium carbonate with concentration of 5mo1/L, vacuum to -0.1Mpa, and steam heating to 140℃;

[0077] B. Add 3.0kg sucrose powder to the material in step A, maintain the temperature at 140℃, and carry out vacuum esterification for 2.5 hours. The reaction product methanol is cooled by the condenser in the vacuum state and then enters the methanol receiver;

[0078] C. Add 8L of water to the reaction system after step B for dilution and heating to 90℃, and then pass the diluent through the medium acidic ion exchange column for ion exchange to remove potassium ions. The temperature of the exchange column is maintained at 90℃ and the flow rate is controlled at 350mL/ min;

[0079] D. After the ion exchange, vacuum heating was carried out at 120℃ to remove the water, and 200g sucrose powder was added to the product after water removal, stirring for 1.5 hours to obtain sucrose fatty acid ester with low ash content.

[0080] the ion exchange column is pretreated with an acidic solution in advance, and the pretreatment comprises the following steps:

[0081] A, the ion exchange resin in the ion exchange column is soaked in a mass fraction of 7% equivalent to 3 times the volume of the resin

Aqueous sodium chloride solution, soaked for 24 hours under constant agitation, remove the water, then rinse with deionized water until colorless;

[0082] B, step A treated resin with resin volume 3 times the mass fraction of 4% hydrochloric acid solution soaked for 6 hours, remove the water, rinse with deionized water to pH value to neutral;

[0083] C. The treated resin after step B is soaked in 4% sodium hydroxide solution with 3 times the volume of resin for 5 hours, the water is removed, and then the H value is rinsed with deionized water to neutral

[0084] D. The resin treated in step C was soaked in 4% hydrochloric acid solution with twice the volume of resin for 6 hours, the water was removed, and the water was rinsed with deionized water until the pH value was neutral, and then loaded into columns for use.

[0085] Embodiment 6

[0086] The method for preparing a low ash sucrose fatty acid ester of the invention comprises the following steps:

[0087] a. Add 5L fatty acid methyl ester to the reaction kettle, at the same time add 1.3L sodium hydroxide and sodium carbonate mixed solution with concentration of 5mo1/L, vacuum to -0.1Mpa, and steam heating to 135℃;

[0088] B. Add 3.2kg sucrose powder to the material of step A, keep the temperature at 135℃, and carry out vacuum esterification reaction for 2 hours. The reaction product methanol is cooled by the condenser in the vacuum state and then enters the methanol receiver;

[0089] C. Add 8L of water to the reaction system after step B for dilution and heating to 85℃, and then pass the diluent through the medium acidic ion exchange column for ion exchange to remove sodium ions. The temperature of the exchange column is maintained at 85℃ and the flow rate is controlled at 250mL/ min;

[0090] D, after the end of ion exchange, vacuum heating was carried out at 115℃ to remove the water, and 300g sucrose powder was added to the product after water removal, stirring reaction for 1 hour, to obtain low ash sucrose fatty acid ester.

[0091] The ion exchange column is pretreated with an acidic solution in advance, and the pretreatment includes the following steps:

[0092] A. Immerse the ion exchange resin in the ion exchange column in A mass fraction of 7% equivalent to twice the volume of the resin

Aqueous sodium chloride solution, soaked for 24 hours under constant agitation, remove the water, then rinse with deionized water until colorless;

[0093] B, step A treated resin with resin volume twice the mass fraction of 4% hydrochloric acid solution soaked for 6 hours, remove the water, rinse with deionized water to pH value to neutral;

[0094] C, the resin treated in step B is soaked in 4% sodium hydroxide solution with twice the volume of resin for 6 hours, the water is removed, and then rinsed with deionized water until the pH is neutral

[0095] D, the resin treated in step C was soaked in 4% hydrochloric acid solution with twice the volume of resin for 6 hours, the water was removed, and the water was rinsed with deionized water until the pH value was neutral, and then loaded into columns for use.

[0096 Embodiment 7

[0097] The preparation method of low ash sucrose fatty acid ester of the invention comprises the following steps:

[0098] a. Add 5L fatty acid methyl ester to the reaction kettle, at the same time add 1.3L potassium hydroxide aqueous solution with A concentration of 5mo1/L, vacuum to -0.1Mpa, and steam heating to 135℃;

[0099] B. Add 3.2kg sucrose powder to the material in step A, keep the temperature at 135℃, and carry out the vacuum esterification reaction for 2 hours. The reaction product methanol is cooled by the condenser in the vacuum state and then enters the methanol receiver;

[0100] C. Add 8L water to the reaction system after step B for dilution, cool to room temperature, and then pass the diluent through the medium acid ion exchange column for ion exchange, with the flow rate controlled at 250mL/min;

[0101] D. After the ion exchange, vacuum heating was carried out at 115℃ to remove the water, and 300g sucrose powder was added to the product after water removal, stirring for 1 hour to obtain sucrose fatty acid ester with low ash content.

[0102] The ion exchange column is pretreated with an acidic solution in advance, and the pretreatment includes the following steps:

[0103] a. Soak the ion exchange resin in the ion exchange column in an aqueous solution of sodium chloride equivalent to 2 times the volume of the resin with A mass fraction of 7%, soak for 24 hours under constant agitation, remove the water, and then rinse with deionized water until colorless;

[0104] B. The resin treated in step A was soaked in 4% hydrochloric acid solution with twice the volume of resin for 6 hours, the water was removed, and the water was washed with deionized water until the pH value was neutral;

[0105] C, the resin treated in step B was soaked in 4% sodium hydroxide solution with twice the volume of resin for 6 hours, the water was removed, and then the H value was rinsed with deionized water to neutral

[0106] D, the resin treated in step C was soaked in 4% hydrochloric acid solution with twice the volume of resin for 6 hours, the water was removed, and the water was washed with deionized water until the pH value was neutral, and then loaded into columns for use.

[0107] The components of sucrose fatty acid ester were as follows: free sugar 2.5%, acid value 2.7mgKOH/g, ash 1.1%.

[0108] Embodiment 8

[0109] to scale

[0110] The preparation method of the low ash sucrose fatty acid ester of the invention comprises the following steps:

[0111A, add 5L fatty acid methyl ester to the reaction kettle, at the same time add 1.31 potassium hydroxide aqueous solution with a concentration of 5mo1/L, vacuum to -0.1Mpa, steam heating to 135℃;

[0112] B. Add 3.5kg sucrose powder to the material of step A, keep the temperature at 135℃, and carry out vacuum esterification reaction for 2 hours. The reaction product methanol is cooled by the condenser in the vacuum state and enters the methanol receiver to obtain sucrose fatty acid ester with low ash content.

[0113] Free sugar, acid value and ash content in sucrose fatty acid ester of embodiments 1-8 of the invention are respectively determined, and the results are shown in Table 1.

[0114] Table 1 shows the results of the determination of components in the products of each embodiment

[0115]

实施例	游离糖/%	酸值/(mgKOH/g)	灰分/%
实施例1	2.6	3.3	0.6
实施例2	3.5	2.3	1.0
实施例3	2.3	2.8	0.8
实施例4	2.6	2.5	1.1
实施例5	2.4	3.0	0.9
实施例6	2.5	2.7	1.1
实施例7	5.2	1.5	2.5
对比例	3.3	1.2	3.4

[0116] It can be seen from Table 1 that the ash content in the products of Embodiments 1-7 of the invention is much lower than the 3-4% ash content of commercially available sucrose ester, and it can be seen from the comparison of embodiments 6-8 that, compared with the ion exchange at room temperature in embodiments 7 and the one-time addition of sucrose powder without ion exchange in proportion, the ion exchange in embodiments 6 of the invention removes sodium ions. And the exchange column temperature is maintained at 85℃, which can achieve better ion exchange effect and ultimately achieve better ash removal effect.

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CN 101012389A, 2007. 08. 08, CN 103396460A, 2013.11.20, CN 10336043 4A, 2013.10.23,

Wang Kui, et al. Preparation of sucrose vinegar with activated carbon supported solid base catalyst. Chemical Reaction Engineering and Technology.2011, Vol. 27 (2), 139-143.

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Claims 1 page specification 5 pages

(54) Name of invention

Process for synthesizing sucrose ester using a fixed bed reactor with alkali catalyst

(57) Abstract

The invention relates to a process of synthesizing sucrose ester using a fixed bed reactor with alkali catalyst, including steps: metataric acid (also known as hydrated titanium trioxide) produced by sulfuric acid method is used as the starting raw material, purification of the raw material is completed by adjusting PH value, washing and filtering, and after dehydration and drying, it is crushed and screened and packaged into the final product. The preparation method of the invention has the advantages of simple process and material, large specific surface area and high Ti0 content of nanometer titanium dioxide.

1. A process for synthesizing sucrose ester using a fixed bed reactor with an alkali catalyst is characterized in that it comprises the following steps:

A: The preparation of the fixed bed reactor with alkali catalyst, the solid particles of the strong alkaline catalyst are filled in the fixed bed reactor. The catalyst is dry and anhydrous solid alkali particles or activated carbon particles loaded with strong alkali, and the thickness of the filling layer is 5-10cm;

B: Adding methyl stearate to the fixed bed reactor of alkali catalyst, using melted methyl stearate as raw material to melt into liquid at about 100 ℃, adding it to the fixed bed reactor of alkali catalyst while hot, and circulating in the reactor under the drive of gear pump through the solid catalyst filling layer;

C: Reaction system control and by-product collection, use temperature control heating device to heat the whole alkali catalyst fixed bed reactor, keep the temperature of the reaction system at 120-140℃, and connect the reactor exhaust port to the decompression condensing device, the methanol generated by the reaction is discharged and passed through the circulating cold water decompression condensing device to condense into liquid methanol, and then do Collection of by-products;

D: Preparation of fatty acid sucrose ester, in the process of circulating flow of methyl stearate in a fixed bed reactor with alkali catalyst, the crushed sucrose powder is added to the reaction system from the feed port of the reactor in batches, so that the sucrose is fully mixed in the liquid of methyl stearate, and repeated circulation through the solid catalyst filling layer, under the catalytic condition of basic catalyst with methyl stearate The reaction generates fatty acid sucrose ester, adding the molar ratio of the sucrose and methyl stearate is 1:3-1:7;

E: the generation of fatty acid sucrose ester, 3-5 hours after the reaction, the product is discharged from the reactor discharge port, after separation and purification, the product fatty acid sucrose ester is obtained.

2. According to the process of synthesis of sucrose ester by fixed bed reactor with alkali catalyst described in claim 1, the characteristic is that the basic solid catalyst of the solid catalyst filling layer is the solid catalyst of activated carbon supported KOH.

3. According to the claim 2, the use of alkali catalyst fixed bed reactor synthesis of sucrose ester process, its characteristics are: the activated carbon loaded KOH solid catalyst, the specific production method is: the use of heating dissolved state of susaturated KOH solution and activated carbon particles mixed stirring, half an hour later, filter and put activated carbon particles into the oven drying, drying after The activated carbon particles are put into the Muffle furnace and burned for 2 hours at a high temperature of 400-500 ° C to remove the water combined in the catalyst, and the solid catalyst of activated carbon loaded KOH is obtained, which is taken out and put into the dryer for backup.

4· According to claims 1, 2, 3 any of the use of alkali catalyst fixed bed reactor synthesis of sucrose ester process, its characteristics are: the alkali catalyst fixed bed reactor structure is as follows: the reactor is provided with a feed port and a reduced pressure evaporation port, the reactor is provided with a discharge branch, the reactor is provided with a solid catalyst filling layer, the solid catalyst filling layer is provided in front There is a baffle plate, the solid catalyst filling layer before and after the stainless steel net, the middle of the reactor is connected to the gear pump to promote the reactants in the reactor circulation flow.

The process of synthesizing sucrose ester by fixed bed reactor with alkali catalyst

[0001 【 Technical field 】]

[0002 The invention relates to a process for synthesizing sucrose ester, in particular to a process for synthesizing sucrose ester using a fixed bed reactor with an alkali catalyst conducive to continuous reaction.

[0003] 【 Background technology 】

[0004] Sucrose ester is a kind of green non-ionic surfactant with sucrose as hydrophilic base and fatty acid chain as hydrophobic group, which has good biodegradation ability, so it can be widely used in detergent, detergent and cosmetics industries, and has potential application prospects in pharmaceutical, biochemistry and biomedicine. The raw materials for the production of sugar fatty acid ester are cheap and easy to obtain renewable resources, and have a wide range of controllable hydrophilic and lipophilic balance values. In addition to good emulsification performance, sucrose ester has complete biodegradable performance and environmental friendly, non-toxic, skin compatible, odorless and tasteless properties.

[0005] The earliest synthesis of sucrose esters dates back to the middle of the nineteenth century, and from then until 1956, sucrose esters were synthesized either by direct esterification of sucrose with fatty acids or anhydrides, or by chloracylation in pyridine and fatty acid chloride. These synthetic methods were difficult to industrialize because of their low yield, high solvent toxicity and high cost. Most of the specific synthesis methods of these early sucrose esters use organic solvents that can dissolve sugar and oil at the same time, such as dimethyl alum, dimethyl acetamide, dimethyl formamide, etc. In the presence of alkaline catalysts, sugar and fatty acids are transesterification in the solvent, usually sodium hydroxide and potassium hydroxide as alkaline catalysts.

[0006] However, in the application process, the general used for sucrose ester synthesis is in organic solvents under the catalysis of alkaline catalyst and heating using methyl stearate and sucrose transesterification reaction to synthesize sucrose ester, however, organic solvents such as dimethyl sulfoxide, dimethyl acetamide, dimethyl formamide, etc., have certain toxicity, which will inevitably give solvent synthesis of sucrose ester application Bring certain limitations, at the same time, the use of alkaline catalyst and reactant mixed catalysis, which will bring further difficulties to the subsequent purification of the product, resulting in higher ash content of the product, the catalyst can be recycled is poor.

[0007] The existing process of synthesizing sucrose ester is to react by mixing reactants and catalysts, and steaming the product from the reaction system during the reaction process. This method belongs to intermittent production, long production cycle, high production cost, product conversion rate is not high, not suitable for large-scale industrial production.

[0008] 【 Content of invention

[0009] The invention aims to provide a low cost, non-toxic and side effect solvent, rapid production, strong continuous production capacity for continuous reaction by alkali catalyst fixed bed reactor synthesis of sucrose ester technology, in order to solve the prior art sucrose ester production cost, low efficiency, strong restriction, product ash.

[0010] The technical scheme of the invention is: a process for synthesizing sucrose ester using a fixed bed reactor with alkali catalyst, which comprises the following steps:

[0011] A: Preparation of the alkaline catalyst fixed bed reactor, the solid particles of the strong basic catalyst are filled in the fixed bed reactor, the catalyst is dry and anhydrous solid alkali particles or activated carbon particles loaded with strong alkali, the thickness of the filling layer is 5-10cm;

[0012] B: Adding methyl stearate to the fixed bed reactor of alkali catalyst, using melted methyl stearate as raw material to melt into liquid at about 100℃, adding it to the fixed bed reactor of alkali catalyst while hot, and circulating in the reactor under the drive of gear pump through the solid catalyst filling layer;

[0013] C: reaction system control and by-product collection, use temperature control heating device to heat the whole alkali catalyst fixed bed reactor, keep the temperature of the reaction system at 120-140℃, and access the reactor exhaust port to reduce pressure condensing load

In place, the methanol generated by the reaction is discharged and condensed into liquid methanol through a decompression condensing device that passes into circulating cold water, and then collected as a by-product;

[0014] D: The preparation of fatty acid sucrose ester, in the process of circulating flow of methyl stearate in a fixed bed reactor with alkali catalyst, the crushed sucrose powder is added to the reaction system from the feed port of the reactor in batches, so that the sucrose is fully mixed in the liquid of methyl stearate, and repeated circulation through the solid catalyst filling layer, under the catalytic condition of basic catalyst and methyl stearate occurs The reaction generates fatty acid sucrose ester, adding the molar ratio of the sucrose and methyl stearate is 1:3-1:7;

[0015] E: The production of fatty acid sucrose ester, 3-5 hours after the reaction, the product is discharged from the reactor discharge port, through

Separation and purification to obtain the product fatty acid sucrose ester.

[0016] The further technical scheme of the invention is that the basic solid catalyst of the solid catalyst filling layer is a solid catalyst of activated carbon supported KOH.

[0017] The further technical scheme of the invention is: the solid catalyst of the activated carbon loaded with KOH, the specific production method is: the susaturated KOH solution in the state of heating dissolution is mixed and stirred with activated carbon particles, half an hour later, filter and put the activated carbon particles into the oven to dry, and put the dried activated carbon particles into the Muffle furnace and at a high temperature of 400-500℃ The solid catalyst of KOH supported by activated carbon is obtained by burning at temperature for 2 hours to remove the water combined in the catalyst, and then the solid catalyst is taken out and put into the dryer for use.

[0018] The further technical scheme of the invention is that the structure of the alkali catalyst fixed bed reactor is as follows: a feed port and a vacuum evaporation port are arranged above the reactor, a discharge branch is arranged in the middle of the reactor, a solid catalyst filling layer is arranged below the reactor, a baffle is arranged in front of the solid catalyst filling layer, the solid catalyst filling layer is provided with a stainless steel net before and after the solid catalyst filling layer, and the middle of the reactor is connected with teeth The wheel pump pushes the reactant to circulate and flow in the reactor.

[0019] The invention has the following beneficial effects: Due to the adoption of the technical scheme, the process of synthesizing sucrose ester by using a fixed bed reactor with alkali catalyst has the following beneficial effects:

[0020] 1. The invention adopts solvent-free method in the process of synthesizing sucrose ester, and does not add any toxic organic solvent in the whole preparation process. The product obtained is simple, safe and non-toxic, and meets the requirements of food and other industries for product purity and non-toxic quality, and has a wide application range;

[0021] The invention adopts a fixed bed reactor to synthesize and prepare sucrose ester. The preparation process is simple, can be continuously fed and produced, has high product yield, high raw material utilization rate, low production cost, and is suitable for large-scale production;

[0022] 3, the filling layer in the fixed bed reactor is a solid basic catalyst, the reaction raw materials flow through the filling layer under the push of the gear pump and catalytic reaction occurs, the catalyst will not be broken, loss and other phenomena, reduce the difficulty of product separation and purification, reduce the ash content in the product, and the catalyst can be recycled, the production process saves resources and environmental protection;

[0023] 4, the reactants in the reactor because in the reaction process under the push of the gear pump kept circulating flow and mixing, so the reaction is uniform and effectively prevent the caramelization reaction;

[0024] 5. The sucrose ester prepared by the invention has good color, high purity, the reaction yield can reach more than 70%, the raw material is cheap and easy to obtain, the reactor operation process is simple, and the unreacted raw material can be repeatedly put into the reactor to continue the reaction.

[0025 [Specific implementation method]

(0026 The following is a further description of the invention in combination with the specific embodiments.

[0027 Embodiment 1:

[002 Use the susaturated KOH solution in the state of heating dissolution to mix and stir the activated carbon particles, half an hour later, filter and put the activated carbon particles into the oven to dry, put the dried activated carbon particles into the Muffle furnace and heat at 400-500℃ for 2 hours to remove the water bound in the catalyst, get the solid catalyst supported by activated carbon KOH, remove and

Put it in the dryer for use. The solid catalyst of the activated carbon supported KoH has large specific surface area and strong adsorption capacity, so the catalytic effect is good.

[0029] The solid particles of the strong basic catalyst were filled in the fixed bed reactor. The catalyst was dry and anhydrous solid alkali particles or activated carbon particles loaded with strong alkali, and the thickness of the filling layer was 5-10cm.

[0030] The 500g methyl stearate is heated to the melting state under the heating condition of about 100℃, and then the melted liquid methyl stearate is added to the alkali catalyst fixed bed reactor while it is hot. The gear pump in the reactor is opened, and the flow rate of the gear pump is 18.3L/min. At the same time, the constant temperature oil bath heating device is opened to adjust the temperature to 150℃, and the whole reaction in the reactor is taken After the system temperature balance, in the process of reactor operation batch to the reactor to add crushed sucrose powder a total of 188.3g, an average of 10min added once, each time the amount of sucrose is 10.5g, a total of 5 hours of reaction, and in the reaction process will be connected to the reactor vacuum distillation device to maintain the reaction system of negative pressure state, distillation device collected at the end The methanol generated by the reaction, after the end of the reaction, open the discharge port, collect the crude product sucrose ester discharged from the discharge port, and then the product is washed in solvent for many times after vacuum drying to obtain pure sucrose ester, the yield of the product is 75%(relative sucrose). The sucrose ester prepared in this embodiment was tested according to GB8272-2009 "Food Additive - sucrose fatty acid Ester", and the results were as follows: free sugar 3.6%, acid value 3.5mgkOH/g, ash content 0.6%

[0031] Embodiment 2:

[0032] The technical scheme provided in this embodiment is similar to the above technical scheme, except that:

[003 The 600g methyl stearate is heated to the melting state under the heating condition of about 100℃, and then the melted liquid methyl stearate is added to the fixed bed reactor with alkali catalyst while it is hot. The gear pump in the reactor is opened, and the flow rate of the gear pump is 18.3L/min. At the same time, the constant temperature oil bath heating device is opened, and the temperature is adjusted to 140℃, with the whole reaction in the reactor After the system temperature balance, in the process of reactor operation batch to the reactor to add crushed sucrose powder a total of 225.9g, an average of 10min added once, each time the amount of sucrose is 12.6g, a total of 5 hours of reaction, and in the reaction process will be connected to the reactor vacuum distillation device to maintain the reaction system of negative pressure state, distillation device collected at the end The methanol generated by the reaction, after the end of the reaction, open the discharge port, collect the crude product sucrose ester discharged from the discharge port, and then the product is washed in solvent for many times after vacuum drying to obtain pure sucrose ester, the yield of the product is 73.2%(relative sucrose). The sucrose ester prepared in this embodiment was tested according to GB8272-2009 "Food Additive - sucrose fatty acid Ester", and the results were as follows: free sugar 4.0%, acid value 3.0mgKOH/g, ash 0.9%

[0034 Embodiment 3:

[0035] The technical scheme provided in this embodiment is similar to the above technical scheme, except in the following

[0036] 700g methyl stearate is heated to the melting state under the heating condition of about 100℃, and then the melted liquid methyl stearate is added to the fixed bed reactor with alkali catalyst while it is hot. The gear pump in the reactor is opened, and the flow rate of the gear pump is 18.3L/min. At the same time, the constant temperature oil bath heating device is opened, and the temperature is adjusted to 130℃, and the whole reaction in the reactor is taken After the system temperature equilibrium, in the process of reactor operation batch to the reactor to add crushed sucrose powder a total of 263.6g, an average of 10min added once, each time the amount of sucrose is 14.6g, a total of 5 hours of reaction, and in the reaction process will be connected to the reactor vacuum distillation device to maintain the reaction system of negative pressure state, distillation device end collection The methanol generated by the reaction, after the end of the reaction, open the discharge port, collect the crude product sucrose ester discharged from the discharge port, and then the product is washed in solvent for many times after vacuum drying to obtain pure sucrose ester, the yield of the product is 71.4%(relative sucrose). The sucrose ester prepared in this embodiment was tested according to GB8272-2009 "Food Additive - sucrose fatty acid Ester ", and the results were as follows: free sugar 4.8%, acid value 2.7mgKOH/g, ash content 0.5%

[0037] Embodiment 4:

[0038] The technical scheme provided in this embodiment is similar to the above technical scheme, except that:

[0039 The 700g methyl stearate is heated to the melting state under the heating condition of about 100℃, and then the melted liquid methyl stearate is added to the alkali catalyst fixed bed reactor while it is hot. The gear pump in the reactor is opened, and the flow rate of the gear pump is 18.3L/min. At the same time, the constant temperature oil bath heating device is opened, and the temperature is adjusted to 150℃, with the whole reaction in the reactor After the system temperature equilibrium, in the process of reactor operation batch to the reactor to add crushed sucrose powder a total of 158.2g, an average of 10min added once, each time the amount of sucrose is 8.8g, a total of 5 hours of reaction, and in the reaction process will be connected to the reactor vacuum distillation device so that the reaction system to maintain negative pressure state, distillation device end collection reverse The methanol should be generated, after the end of the reaction, open the discharge port, collect the crude product sucrose ester discharged from the discharge port, and then the product is washed in solvent for many times after vacuum drying to obtain pure sucrose ester, the yield of the product is 80%(relative sucrose). The sucrose ester prepared in this embodiment was tested according to GB8272-2009 "Food Additive - sucrose fatty acid Ester", and the results were as follows: free sugar 2.6%, acid value 3.3mgKoH/g, ash 0.6%

[0040] Embodiment 5:

[0041] The technical scheme provided in this embodiment is similar to the above technical scheme, except that:

[0042] The 700g methyl stearate is heated to the melting state under the heating condition of about 100℃, and then the melted liquid methyl stearate is added to the fixed bed reactor with alkali catalyst while it is hot. The gear pump in the reactor is opened, and the flow rate of the gear pump is 18.3L/min. At the same time, the constant temperature oil bath heating device is opened, and the temperature is adjusted to 140℃, and the whole reaction in the reactor is taken After the system temperature equilibrium, in the process of reactor operation batch to the reactor after the pulverized sucrose powder a total of 158.2g, an average of 15min added once, each time the amount of sucrose is 13.2g, a total of 4 hours of reaction, and in the reaction process will be connected to the reactor vacuum distillation device to maintain the reaction system of negative pressure state, distillation device end collection The methanol generated by the reaction, after the end of the reaction, open the discharge port, collect the crude product sucrose ester discharged from the discharge port, and then the product is washed in solvent for many times after vacuum drying to obtain pure sucrose ester, the yield of the product is 78%(relative sucrose). The sucrose ester prepared in this embodiment was tested according to GB8272-2009 "Food Additive - sucrose fatty acid ester", and the results were as follows: 2.8% free sugar, 3.6mgKOH/g acid value, and 1.0% ash content

[0043] Embodiment 6:

[0044] The technical scheme provided in this embodiment is similar to the above technical scheme, except that:

[0045 The 700g methyl stearate is heated to the melting state under the heating condition of about 100℃, and then the melted liquid methyl stearate is added to the alkali catalyst fixed bed reactor while it is hot. The gear pump in the reactor is opened, and the flow rate of the gear pump is 18.3L/min. At the same time, the constant temperature oil bath heating device is opened, and the temperature is adjusted to 130℃, with the whole reaction in the reactor After the system temperature equilibrium, in the process of reactor operation batch to the reactor after the pulverized sucrose powder a total of 158.2g, an average of 10min added once, each time the amount of sucrose is 13.2g, a total of 3 hours of reaction, and in the reaction process will be connected to the reactor vacuum distillation device to maintain the reaction system of negative pressure state, distillation device end collection The methanol generated by the reaction, after the end of the reaction, open the discharge port, collect the crude product sucrose ester discharged from the discharge port, and then the product is washed in solvent for many times after vacuum drying to obtain pure sucrose ester, the yield of the product is 77.5%(relative sucrose). The sucrose ester prepared in this embodiment was tested according to GB8272-2009 "Food N-Additive - sucrose fatty acid ester", and the results were as follows: free sugar 3.1%, acid value 2.9mgKOH/g, ash content 0.8%.

[0046 Embodiment 7:

[0047] The technical scheme provided in this embodiment is similar to the above technical scheme, except that:

[0048 Heat 700g methyl stearate to the melting state under the heating condition of about 100℃, and then add the melted liquid methyl stearate to the fixed bed reactor with alkali catalyst while it is hot, open the gear pump in the reactor, and the flow rate of the gear pump

18.31/min, at the same time open the constant temperature oil bath heating device, adjust the temperature to 150℃, with the reactor in the whole reaction system temperature equilibrium, in the process of reactor operation batch to the reactor after the pulverized sugar powder a total of 113g, an average of 10min added once, each time the amount of sugar added is 6.3g, a total reaction of 5 hours , and in the reaction process will be connected to the reactor vacuum distillation device to keep the reaction system in a state of negative pressure, distillation device at the end of the collection reaction generated methanol, after the end of the reaction, open the discharge port, collect the discharge port of the crude product sucrose ester, and then the product after solvent washing several times after vacuum drying sucrose ester pure product, product yield of 86%(relative sucrose). The sucrose ester obtained in this embodiment was tested in accordance with GB8272-2009 "Food additive - sucrose fatty acid ester", and the results were as follows: free sugar 2.0%, acid value 2.3mgKOH/g, ash 0.5%

[0049 Embodiment 8:

[0050] The technical scheme provided in this embodiment is similar to the above technical scheme, except that:

[0051] 700g methyl stearate is heated to the melting state under the heating condition of about 100℃, and then the melted liquid methyl stearate is added to the fixed bed reactor with alkali catalyst while it is hot. The gear pump in the reactor is opened, and the flow rate of the gear pump is 18.3/min. At the same time, the constant temperature oil bath heating device is opened, and the temperature is adjusted to 150℃, with the whole reactor After the temperature balance, in the process of reactor operation batch to the reactor to add crushed sucrose powder a total of 113g, an average of 10min added once, each time the amount of sucrose is 9.4g, a total of 4 hours of reaction, and in the reaction process will be connected to the reactor vacuum distillation device so that the reaction system to maintain negative pressure state, distillation device end collection reaction generated Methanol, after the end of the reaction, open the discharge port, collect the discharge port of the crude product sucrose ester, and then the product after solvent washing several times after vacuum drying to obtain sucrose ester pure products, the yield of the product is 84%(relative sucrose). The sucrose ester prepared in this embodiment was tested according to GB8272-2009 "Food Additive - sucrose fatty acid ester", and the results were as follows: free sugar 2.4%, acid value 2.7mgKOH/g, ash 0.8%

[0052] Due to the adoption of the technical scheme, the process of synthesizing sucrose ester using a fixed bed reactor with alkali catalyst has the following beneficial effects:

[0053] 1. The invention adopts solvent-free method in the process of synthesizing sucrose ester, and does not add any toxic organic solvent in the whole preparation process. The product obtained is simple, safe and non-toxic, and meets the requirements of food industry for product purity and non-toxic quality, and has a wide application range;

[0054] 2. The invention adopts a fixed bed reactor to synthesize and prepare sucrose ester. The preparation process is simple, continuous feeding can be produced continuously, the product yield is high, the raw material utilization rate is high, the production cost is low, and is suitable for large-scale production;

[0055] 3, the filling layer in the fixed bed reactor is a solid basic catalyst, the reaction raw materials flow through the filling layer under the push of the gear pump and catalytic reaction occurs, the catalyst will not be broken, loss and other phenomena, reduce the difficulty of product separation and purification, reduce the ash content in the product, and the catalyst can be recycled, the production process saves resources and environmental protection;

[0056] 4, the reactants in the reactor because in the reaction process under the push of the gear pump keep circulating flow and mixing, so the reaction is uniform and effectively prevent the caramelization reaction;

[0057] 5. The sucrose ester prepared by the process of the invention has good color, high purity, the reaction yield can reach more than 70%, the raw material is cheap, the reactor operation process is simple, and the unreacted raw material can be repeatedly put into the reactor to continue the reaction.

[0058] The above is only a better embodiment of the invention and is not used to limit the invention, and any modification, equivalent replacement and improvement made within the spirit and principle of the invention shall be included in the scope of protection of the invention.

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(56) Contrast files

CN 101805381 A,2010.08.18,

CN 103087118 A,2013.05.08, WO 2002/057282 A1,2002.07.25,

WO 2007/125328 A1,2007.11.08,

CN 102827213 A, December 19, 2012,

CN 1687096A,2005.10.26,CN

101913638A,2010.12.15,

Zhu JL et al., solvent-free preparation and characterizatio n of sucrose esters. Journal of Nantong University (Natural Science Edition), 2009, vol. 8 (2), p. 3439.

Tian Heng et al., Cao solid catalysts prepared by different processes have effects on the performance of biochemicals. Biomass Chemical Engineering.2010, vol. 44 (4), pp. 40-42.

Peng Min-Min, Solvo-free synthesis of sucrose fatty acid ester. Journal of Guangdong University of Technology. 2003, vol.20 (2), p. 8183.

Zhou Jian-Ping, et al. Synthesis of sucrose stearate vinegar by solid superbase catalysis. Applied Chemical Industry.2005, vol. 34 (7), pp. 453-454.

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Claims 1 page specification 4 pages

(54) State the name

Method of preparing sucrose

(57) Abstract

The invention discloses a method for preparing sucrose ester, belonging to the technical field of non-ionic surfactant. The method first removes a small amount of water and free fatty acids in fatty acid methyl ester, and then adds the solid catalyst into the fatty acid methyl ester after water removal, and adds sucrose in a certain proportion under the condition of stirring evenly. In the prior art, alkali metal hydroxide is often used as the catalyst for the preparation of sucrose ester in industry, which is easy to cause tedious purification steps of subsequent products, resulting in a large amount of waste water, while the invention adopts common industrial alkali earth metal oxide as a solid catalyst, the reaction condition is mild, the solid catalyst will not remain in the product and can be reused, which is environmentally friendly and reduces the cost.

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1. A method for preparing sucrose ester, characterized by including the following steps:

(1) Pretreatment method of calcium oxide: calcium oxide is burned at 1100℃~1200℃ for pretreatment for 5~6 hours and then transferred to the dryer for preservation;

(2) part of the steps (1) obtained after the burning of calcium oxide and methyl stearate in the reactor for stirring 5 minutes to 15 minutes, the amount of calcium oxide is methyl stearate quality of 7wt%~9wt%;

(3) The pulverized and ground sucrose is added to the methyl stearate obtained after burning in step (2), and then the calcium oxide obtained after burning and pretreatment as described in step (1) is rapidly stirred and evenly dispersed for 30~40 minutes, and the reaction is carried out at the oil bath temperature of 90° C ~ 175℃ to combine the crude sucrose ester; The molar ratio of the sucrose and methyl stearate is 1:1 ~7, the amount of calcium oxide is methyl stearate and the total mass of 4 wt% ~6 wt%;

(4) the crude sucrose ester obtained in step (3) at 90℃ ~175℃ to continue stirring reaction 2~6 hours after the stop heating, filtration, remove as a catalyst calcium oxide;

(5) Step (4) the obtained material into the separation funnel, add 1-3 times water shake to stand stratification, remove the lower water phase, and then wash the upper oil phase with water, until neutral, and then at 80℃ vacuum distillation to obtain a purest sucrose ester.

The preparation method of sucrose ester

Technical field

[0001] The invention relates to the technical field of a non-ionic surfactant, in particular to a method for sucrose ester.

Background technology

[0002] There are four main methods for the synthesis of sucrose ester: solvent method, microemulsification method, solvo-free method and enzyme catalysis method. The solvent method uses DMF or DMSO as the solvent, but both solvents are toxic, which limits the application of sucrose ester in food and other industries. Microemulsification method uses propylene glycol or water to replace the toxic solvent used in solvent method, and adds emulsifier, so that the reaction system is approximately homogeneous system. Solvent-free rule is by adding emulsifier or surfactant in the reaction system to melt each other homogeneous phase, the reaction is stable. However, the general solvent-free reaction temperature is high, the reaction is not easy to carry out, the yield is low, and the product quality is not guaranteed. At present, solvent-free method usually uses alkali metal hydroxide such as potassium hydroxide or sodium hydroxide as a catalyst, and the residual phenomenon of catalyst in the product is serious, which strictly limits its application in the food industry, and the subsequent separation and purification steps are more complicated and easy to produce a large amount of wastewater.

[0003] The invention adopts heterogeneous catalyst calcium oxide, calcium oxide as heterogeneous catalyst for transesterification reaction, has been widely used in the field of biodiesel, the pre-treated calcium oxide alkaline strong specific surface area, has good stability, long catalytic life, can be used several times continuously, so it is more and more chemists and chemical experts pay attention to.

The content of the invention

[0004] The invention aims to provide a method for preparing sucrose ester by using solid catalyst, which has high catalytic efficiency, an average yield of up to 55%, high product purity and bright color, and can be applied to food chemical industry.

[0005] To achieve the above purpose, the technical scheme of the invention is as follows:

[0006] The method for preparing sucrose ester comprises the following specific steps:

[0007] (1) Pretreatment method of alkaline earth metal oxide: the alkaline earth metal oxide is pre-treated by burning at 1100℃~1200℃ for 5~6 hours, and then transferred to the dryer for preservation;

[0008] (2) part of the steps (1) obtained after the alkaline earth metal oxide after burning pretreatment and fatty acid methyl ester is placed in the reactor for stirring 5 minutes to 15 minutes, remove a small amount of water and free fatty acid methyl ester, the amount of alkaline earth metal oxide is 7wt% to 9wt% of the mass of fatty acid methyl ester;

[0009] (3) Add the pulverized and ground sucrose to the fatty acid methyl ester obtained after the burning step (2), and then add the alkaline earth metal oxide obtained after the burning pretreatment of the part of the step (1) with it for rapid stirring and uniform dispersion 30~40 minutes, reaction at 90℃ ~ 175℃ oil bath temperature, combined with the cost of crude sucrose ester; The molar ratio of the sucrose and the fatty acid methyl ester is 1:1~7, the amount of the alkaline earth metal oxide is 4 wt% ~6 wt% of the total mass of fatty acid methyl ester and sucrose;

[0010] (4) The crude sucrose ester obtained from step (3) is stirred at 90℃ ~175℃ for 2~6 h, then the heating is stopped, and the alkaline earth metal oxides as catalysts are removed by filtration;

[0011] (5) Transfer the obtained product of step (4) into the liquid separation funnel, add 1~3 times water to shake and stand stratification, remove the lower water phase, and then wash the upper oil phase with water until neutral, and then vacuum distillation at 80 ° C to obtain a purest sucrose ester.

[0012] In the above technical scheme, the more specific scheme can also be: the alkali earth metal oxide is calcium oxide, the fat

The methyl fatty acid is methyl stearate.

[0013] Above, the alkali earth metal oxides mentioned in step (1) can be better removed at 1100℃~1200℃ impurities, such as calcium carbonate, calcium hydroxide, water and carbon dioxide in the alkali earth metal oxides; In step (2), the alkaline earth metal oxide is mainly used as a dehydrating agent to remove a small amount of water and free fatty acids in fatty acid methyl ester; The alkaline earth metal oxide in step (3) is mainly used as a solid catalyst.

[0014] Compared with the prior art, the invention has the following beneficial effects:

[0015] 1. The preparation method is composed of commonly used chemical raw materials, mild reaction conditions and simple operation.

[0016] 2. The use of solid catalyst calcium oxide reduces the catalyst cost to a great extent, meets the requirements of food industry for the purity and non-toxic quality of sucrose ester products, and the calcium oxide has higher alkaline strength than the surface, can be reused, low carbon environmental protection.

[0017] 3. The catalyst pretreatment method of the invention is simple, and the sintered calcium oxide at this temperature is characterized by XRD with good lattice arrangement and morphology characteristics, and the macro performance is large specific surface area. CO2-TPD shows that the calcium oxide sintered at this temperature has much more base potential than the similar alkaline earth metal oxides.

[0018] 4. The sucrose ester prepared by the invention has bright color and purity up to more than 98%, and can be applied to food industry.

[0019] 5. The raw materials of the method provided by the invention are cheap and easy to obtain, and the sucrose ester based surfactant product is safe and pollution-free, non-toxic to human body, does not stimulate skin and mucous membranes, and can be biodegradable.

Specific embodiments

[0020] The present invention is further elaborated in combination with specific examples: The calcium oxides used in the following specific embodiments are pretreated calcium oxides by placing calcium oxide in crucible for 6 hours at 1200 ° C for the purpose of removing a small amount of water, calcium carbonate, calcium hydroxide and carbon dioxide in the catalyst, so that the catalyst after treatment has a high catalytic performance The activity is transferred to the dryer immediately after the treatment, so that the catalyst can maintain the best catalytic performance.

[0021] Embodiment 1

[0022] Add 4g calcium oxide as a dehydrating agent into 30g methyl stearate, stir, remove a small amount of water and free fatty acids in methyl stearate, then transfer the dehydrated methyl stearate to a three-neck bottle, add 51g of crushed and ground sucrose, use 3.2 grams of calcium oxide as catalyst, quickly stir and disperse evenly for 30 minutes, adjust and set the oil bath temperature to 130℃ Under normal pressure or pressure reduction, the synthesis of sucrose ester, continue to stir, the reaction for 4h after the stop heating, the product filtration to remove the catalyst, the reaction liquid into the liquid separation funnel, stand stratification, remove the lower water phase, and then wash the upper oil phase with distilled water, to neutral so far, and then at 80 ° C on the product of vacuum distillation can be obtained more pure sucrose ester.

[0023] Embodiments 2

[0024] Add 6g calcium oxide as a dehydrating agent to 36g methyl stearate, stir, remove a small amount of water and free fatty acids in methyl stearate, then transfer the dehydrated methyl stearate to a three-neck bottle, add 103g crushed and ground sucrose, use 6.9g calcium oxide as a catalyst, quickly stir and disperse evenly for 30 minutes, adjust and set the oil bath temperature to 90℃ Under normal pressure or vacuum synthesis of sucrose ester, continue to stir, the reaction for 2 hours after the stop heating, the product filtration to remove the solid catalyst, the reaction liquid into the liquid separation funnel, stand stratification, remove the lower water phase, and then wash the upper oil phase with distilled water, to neutral so far, and then at 80℃ on the product of vacuum distillation can be obtained more pure sucrose ester.

[0025] Embodiment 3

[0026] 7g calcium oxide was added into 42g methyl stearate as a dehydrating agent, stir, remove a small amount of water and fatty acids in methyl stearate, then transfer the dehydrated methyl stearate to a three-neck bottle, add 217g of crushed and ground sucrose, use 15.5g calcium oxide as catalyst, stir and disperse evenly for 30 minutes, adjust and set the oil bath temperature to 16 0°C, often

Pressure or pressure reduction under the case of synthesis of sucrose ester, continue to stir, the reaction after 42h to stop heating, the product filtration to remove the solid catalyst, the reaction liquid into the liquid separation funnel, stand stratification, remove the lower water phase, and then wash the upper oil phase with distilled water, to neutral so far, and then the product at 80 ° C vacuum distillation can be obtained more pure sucrose ester.

[0027] Embodiment 4

[0028] 8g calcium oxide was added into 48g methyl stearate as a dehydrating agent, stir, remove a small amount of water and free fatty acids in methyl stearate, then transfer the dehydrated methyl stearate to a three-necked bottle, add 275g crushed and ground sucrose, use 12.9g calcium oxide as catalyst, stir and disperse evenly for 30 minutes, adjust and set the oil bath temperature to 17 5C, the synthesis of sucrose ester under atmospheric pressure or pressure reduction, continue to stir, the reaction after 6h to stop heating, the product filtration to remove the solid catalyst, the reaction liquid into the liquid separation funnel, stand stratification, remove the lower water phase, and then wash the upper oil phase with distilled water to neutral so far, and then at 80℃ the product of vacuum distillation can be obtained more pure sucrose ester.

[0029] Embodiment 5

[0030] Add 9g calcium oxide as a dehydrating agent to 54g methyl stearate, stir, remove a small amount of water and free fatty acids in methyl stearate, then transfer the dehydrated methyl stearate to a three-flask, add 433.8g crushed and ground sucrose, use 24.4 calcium oxide as a catalyst, quickly stir and disperse evenly for 30 minutes, adjust and set the oil bath temperature to 9 0℃, under normal pressure or reduced pressure, the sucrose ester was synthesized, and the reaction continued to stir, 3 After h, the heating is stopped, the product is filtered to remove the solid catalyst, the reaction liquid is transferred into the liquid separation funnel, the stratification is static, the lower water phase is removed, and then the upper oil phase is washed with distilled water to neutral so far, and then the product is distilled at 80 ° C to obtain a purest sucrose ester.

[0031] Embodiment 6

[0032] Add 10g calcium oxide as a dehydrating agent to 60g methyl stearate, stir, remove a small amount of water and free fatty acids in methyl stearate, then transfer the dehydrated methyl stearate to a three-necked bottle, add 413g of crushed and ground sucrose, use 28.4g calcium oxide as catalyst, stir quickly and disperse evenly for 40 minutes, adjust and set the oil bath temperature to 1 40℃, under normal pressure or pressure reduction, the synthesis of sucrose ester, continue to stir, the reaction after 5h to stop heating, the product filtration to remove the solid catalyst, the reaction liquid into the liquid separation funnel, stand stratification, remove the lower water phase, and then wash the upper oil phase with distilled water, to neutral so far, and then the product at 80 ° C vacuum distillation can be obtained more pure sucrose Ester.

[0033] Embodiment 7

[0034] Add 11g calcium oxide as a dewatering agent to 66g methyl stearate, stir, remove a small amount of water and free fatty acids in methyl stearate, then transfer the dehydrated methyl stearate to a three-neck bottle, add 151g of crushed and ground sucrose, use 8.7g calcium oxide as a catalyst, stir quickly and disperse evenly for 30 minutes, adjust and set the oil bath temperature to 15 0° C, under normal pressure or vacuum synthesis of sucrose ester, continue to stir, the reaction carried out 4 After h, the heating is stopped, the product is filtered to remove the solid catalyst, the reaction liquid is transferred to the liquid separation funnel, the stratification is placed, the lower water phase is removed, and the upper oil phase is washed with distilled water to neutral so far, and then the product is distilled at 80 ° C to obtain a purest sucrose ester.

[0035] Embodiment 8

[0036] Add 12g calcium oxide as a dehydrating agent to 72g methyl stearate, stir, remove a small amount of water and free fatty acids in methyl stearate, then transfer the dehydrated methyl stearate to a three-neck bottle, add 330.5g of crushed and ground sucrose, use 20g calcium oxide as a catalyst, quickly stir and disperse evenly for 40 minutes, adjust and set the oil bath temperature to 1 00° C, Under normal pressure or pressure reduction, sucrose ester is synthesized, continue to stir, the reaction is stopped after 6h, the product is filtered to remove the solid catalyst, the reaction liquid is transferred into the liquid separation funnel, stand stratification, remove the lower water phase, and then wash the upper oil phase with distilled water, until neutral, and then the product at 80℃ vacuum distillation can be obtained more pure sucrose ester.

[0037] The sucrose esters obtained in the above embodiments 1~8 were tested according to GB8272-2009 "Food Additive - sucrose fatty Acid Ester"

The main performance indexes are as follows:

[0038]

项目	游离糖（%）	酸值（mgKOH/g）	灰分（%）
国家标准	≤10.0	≤6.0	≤4.0
实施例 1	2.3	5.0	1.2
实施例 2	1.8	4.5	0.9
实施例 3	2.6	5.3	1.0
实施例 4	2.5	5.2	1.8
实施例 5	2.8	4.0	1.4
实施例 6	2.0	4.5	1.6
实施例 7	2.8	4.6	1.8
实施例 8	2.8	4.8	1.3