(19)中华人民共和国国家知识产权局

(12) Invention patent

(10) License Announcement No. CN 101805381BA (45) Grant Gongb 2012.01.04

(21) l No. 201010141794.5

(22) Please B 2010.04.08

(73) Chemical Engineer of Forest Products, Chinese Academy of Forestry, patentee

Research Institute of Industry

Address 16 Suojin Wu Village, Nanjing 210042, Jiangsu Province, China

(72) Inventor Wang Kui Jiang Jianchun Ying Hao Li Xiangzi

Wu Huan

(74) Nanjing Jingwei Patent and Trademark Agency Co., LTD

Company 32200

Agent Feng Hui

(51) Int. CI.

"" Breakyna 13/06 (2006.01)

") "" Microstroma 1/00 (2006.01)

Censor Cao Qian

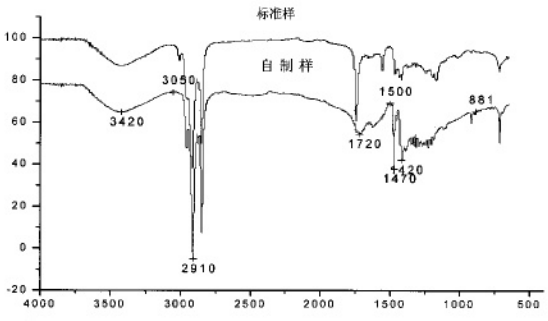
权利要求书1页 说明书8页 附图1页

(54) Issuing names

- Method of directly synthesizing sucrose fatty acid ester from bio-oil and sucrose

(57) Abstract

The invention provides a method for directly synthesizing sucrose fatty acid ester from biodiesel and sucrose, which is synthesized in N_2. Under protection and 1 atmosphere pressure, sucrose fatty acid ester is synthesized by solvent-free method, and supported solid base catalyst is prepared by equal volume impregnation method: Then, after mixing biodiesel and sucrose, add potassium stearate, reaction to the reaction system is light yellow emulsion, add the supported solid base catalyst, continue to react, stir while heating up, and pass into N_2, drive away the air in the reaction system while taking away the methanol produced in the reaction process, in N_2. Under the protection of the heating reaction, after cooling to stop the N2, add water to stop the reaction, stirred at 80° C for 10min, the crude product was processed into sucrose fatty acid ester refined products. After the crude product is purified by solvent extraction, the purity of the product is more than 98%, N_2 can be reused, and the catalyst can be recycled and reused.



1. A method of direct synthesis of sucrose fatty acid ester from biodiesel and sucrose, characterized by solvent-free synthesis of sucrose fatty acid ester under N2 protection and 1 atmosphere pressure, with specific steps as follows:

The first step, the preparation of supported solid base catalyst: according to the molar ratio of catalyst and carrier is 1: 4~25 ratio, weigh the catalyst and carrier respectively, impregnate by equal volume impregnation method, filter, filter cake drying after calcination to obtain supported solid base catalyst; The catalyst is any one of carbonate, alkali, alkaline earth metal oxide, fluoride;

The second step, the preparation of the homogeneous system: biodiesel and sucrose according to the mass ratio of biodiesel: sucrose =1~4: 1 ratio after mixing, add the biodiesel and sucrose mixture of 5%~15% of the total weight of potassium stearate, stirring while heating, stirring reaction at 60~80℃, to the reaction system is light yellow emulsion, add 1%~3% of the total weight of the mixture of supported solid base catalyst, continue stirring reaction:

The third step, the preparation of sucrose fatty acid ester: then the second step, heating up while stirring, and through N, drive away the air in the reaction system while taking away the methanol generated in the reaction process, under the protection of N, heating to 110~150℃, reaction 2~5h, after cooling to below 100℃, stop passing N, add water to stop the reaction, stirring at 80℃ for 10min;

The fourth step, the post-treatment of the crude product: adjust the pH value of the reaction system to 6~7, add NaCI solution for washing, stand stratification after stirring, remove the lower water phase and the supported solid alkali catalyst, the upper sucrose fatty acid ester phase after filtration, add the same weight of ethanol, heating and stirring at 70℃, and then stand precipitation, after filtration filter filter cake with ethyl acetate to wash, sucrose grease Fatty acid ester refined products.

2. The method of directly synthesizing sucrose fatty acid ester from biodiesel and sucrose described in Claim 1 is characterized in that the carrier is any one of activated carbon, metal oxide or molecular sieve.

According to the method of direct synthesis of sucrose fatty acid ester by biodiesel and sucrose described in claim 2, the characteristic is that the metal oxide is A10, or Mgo, and the molecular sieve is NaY type molecular sieve, NaX type molecular sieve any one of them.

4. According to the method of direct synthesis of sucrose fatty acid ester from biodiesel and sucrose described in claim 1, the carbonate is potassium carbonate, any of sodium carbonate, the base is KOH or NaOH, the alkaline earth metal oxide is calcium oxide, and the fluoride is potassium fluoride.

· The method of directly synthesizing sucrose fatty acid ester from biodiesel and sucrose according to Claim 1 is characterized in that the biodiesel is biodiesel prepared by various animal and plant oils, gutter oil, and catering waste oil.

6. According to the method of direct synthesis of sucrose fatty acid ester by biodiesel and sucrose described in claim 1, it is characterized in that the lower aqueous phase and supported solid base catalyst separated in the fourth step, in which the supported solid base catalyst is washed and dried and then reused.

7, according to the method of direct synthesis of sucrose fatty acid ester by biodiesel and sucrose described in claim 1, its characteristics are that the N used at the end of the third step, after separation and treatment, in which the separated methanol is used to prepare biodiesel, N2 is reused.

The invention relates to a method for directly synthesizing sucrose fatty acid ester from biodiesel and sucrose

Technical areas

[0001] The invention relates to the field of synthesis of sucrose fatty acid ester, in particular to a method for synthesizing sucrose fatty acid ester by using biodiesel as raw material.

Background technology

[0002] Sucrose ester as a new type of non-ionic surfactant, non-toxic to the human body, harmless, can be degraded and absorbed by the human body, with good emulsification, dispersion, solublization, penetration, foaming, viscosity regulation, prevent aging, antibacterial and other properties, is widely used in food, medicine, chemical industry, cosmetics, detergent, textile and agriculture and animal husbandry and other industries. Has been Japan, the United States, China and other countries and the United Nations Food and Agriculture Organization, the World Health Organization, the European Union and other approved as a food additive, co-solvent and other use, has a huge market demand and a wide range of application prospects. The traditional sucrose ester production process is mainly acyl chloride method, direct dehydrating method and transesterification method, transesterification method can be divided into solvent method, solven-free method and microbial method according to the process conditions, some of these methods use toxic solvents, some reaction conditions are harsh, reaction temperature is high, long time, high cost, reaction system instability, product quality can not be guaranteed. The current production methods are mainly based on the transesterification method, among which the solvent-free method has more development prospects in terms of economic cost and maneuverability.

[0003] Biodiesel and sucrose are abundant renewable resources in China, among which, biodiesel, as one of the focuses of biomass energy research, has attracted much attention in the contemporary era of fossil resources shortage, and the research of biodiesel fine chemicals also has important practical significance and market prospects. As a rich renewable resource in our country, sucrose has the advantages of wide source and low price. The end of the molecular chain of biodiesel contains an ester group, which can undergo transesterification with three primary alcohol hydroxyl groups and five secondary alcohol hydroxyl groups of sucrose to produce a sucrose fatty acid ester with both oil-wet fatty chain and water-wet alcohol hydroxyl groups. However, since sucrose and biodiesel are both macromolecules, steric hinders are relatively large, the conditions for transesterification are harsh, and the reaction conditions at high temperature are easy to make sucrose coking, which affects the yield and product quality. Therefore, it is of great significance to select the appropriate process conditions and improve the purification technology of products.

[0004] Solvent-free synthesis of sucrose ester research has been widely carried out at home and abroad, Sun Shudong in "Research on solvent-free synthesis of sucrose ester" pointed out that cottonseed oil and ethanol first under the action of alkaline catalyst reaction to prepare cottonseed oil ethyl ester, and then use sucrose and cottonseed oil ethyl ester as raw materials, in the molten state, sucrose: fatty acid ethyl ester =1: The amount of soap is 15%, the amount of catalyst is 2%, the reaction temperature is 135℃, the reaction time is 3h, and the reaction pressure is <666Pa to synthesize sucrose ester. The crude product is first extracted with aqueous solution of ethanol and sodium chloride, and then acetic acid is added to adjust the pH value. After repeated operation for many times, the refined product is obtained by washing with aqueous solution of acetic acid and sodium chloride and pumping and filtering under reduced pressure. The product yield is 80%. Hu Jianhua pointed out in the synthesis of sucrose ester using oil as raw material, sucrose, methyl stearate as raw material, sucrose: methyl stearate =1:2, the amount of soap 15%, the amount of catalyst 3%, reaction 3.5h, control vacuum 13kPa ~0.667kPa, the synthesis of sucrose ester. The crude product was neutralized, salted out, washed, dried, and finally soaked in ether for 24h to obtain the refined product with a yield of 82%. However, including the above two methods, including the vast majority of solvent-free methods to synthesize sucrose fatty acid ester have the following shortcomings:

[0005] 1. All react under vacuum conditions, the reaction conditions are harsh, the industrial feasibility is not large, and in the actual production, the vacuum and high temperature system is unstable, easy to produce foaming phenomenon, making the potassium stearate loss, sucrose is easy to coker, the product color is dark, post-processing is difficult, and the production cost is increased.

[0006] 2, the product post-treatment process is complex, the catalyst can not be recovered, the industrial production cost is high, and the amount of solvent is large, the environmental pollution is serious, and the industrial feasibility is not high.

[0007] 3. Methanol produced in the reaction is difficult to recover under vacuum conditions, resulting in greater toxicity and serious environmental pollution.

Content of invention

[0008] In order to solve the shortcomings of the prior art, such as reaction under vacuum and high temperature, the catalyst cannot be recycled, etc., the invention provides a method for directly synthesizing sucrose fatty acid ester from biodiesel and sucrose. The catalyst can be recycled and used repeatedly under normal pressure and lower temperature.

[0009] The technical scheme of the invention is as follows: a method for directly synthesizing sucrose fatty acid ester from biodiesel and sucrose, and a solvent-free method for synthesizing sucrose fatty acid ester under N protection and 1 atmosphere pressure, the specific steps are as follows:

[0010] The first step, the preparation of the supported solid base catalyst: according to the molar ratio of catalyst and carrier is 1:4~25 ratio, weigh the catalyst and carrier respectively, impregnate by equal volume impregnation, filter, and calcined the supported solid base catalyst after cake drying; The equal volume impregnation method mentioned here refers to the impregnation of the catalyst solution used in the volume and the volume of the carrier equal.

[0011] The carrier is any one of activated carbon, metal oxide and molecular sieve. The metal oxide is A1203, Mg0 any one, the molecular sieve is NaY type molecular sieve, NaX type molecular sieve any one.

[0012] The catalyst is any one of carbonate, alkali, alkaline earth metal oxide and fluoride. Wherein, the carbonate is any one of potassium carbonate and sodium carbonate, the base is any one of KOH and NaOH, the alkaline earth metal oxide is calcium oxide and the fluoride is potassium fluoride.

[0013] The second step, the preparation of the homogeneous system: the biodiesel and sucrose are mixed according to the ratio of biodiesel: sucrose =1~ 4:1, and the potassium stearate accounts for 5%~15% of the total weight of the mixture, and the temperature is heated while stirring Stir reaction at 80℃, when the reaction system is light yellow emulsion, add the supported solid base catalyst accounting for 1% to 3% of the total mass of the mixture, and continue to stir the reaction; The biodiesel is biodiesel prepared by various animal and plant oils, gutter oil and catering waste oil.

[0014] The third step, the preparation of sucrose fatty acid ester: then the second step, stirring while heating, and through N, drive away the air in the reaction system while taking away the methanol produced in the reaction process, under the protection of N, heating to 110~150℃, reaction 2~ 5h, after cooling to below 100℃, stop passing N, add water to stop the reaction, stir at 80℃ for 10min; After the end of N is used, the separated methanol is used to prepare biodiesel,N, and re-used.

[0015] The fourth step, the post-treatment of the crude product: adjust the pH value of the reaction system to 6~7, add NaCl solution for washing, stir and stand for stratification, remove the lower water phase and the supported solid alkali catalyst, the upper sucrose fatty acid ester phase after filtration, add the same weight of ethanol, heat and stir at 70℃, and then stand for precipitation, and wash the filter cake with ethyl acetate after filtration to obtain sucrose grease Fatty acid ester refined products. The lower aqueous phase and the supported solid base catalyst are separated, and the supported solid base catalyst is washed and dried before being reused.

[0016] Beneficial effects:

[0017] Raw materials biodiesel and sucrose are cheap and easy to obtain, and belong to renewable green resources, low raw material cost, high industrial feasibility.

[0018] 2. The method of the invention has no special requirements for biodiesel, and can use various raw material sources of biodiesel, such as: biodiesel prepared by catering waste oil, biodiesel prepared by various woody fats, biodiesel prepared by various animal fats. The raw material sources are wide, and the added value of biodiesel products is greatly improved.

[0019] In the production method of the invention, the use of N, protection, compared with the production method requiring high vacuum, the reaction system is stable, does not produce foaming phenomenon, sucrose is not easy to coking reaction, and the post-treatment tends to be simple, and N can be reused, low industrial cost and high feasibility.

[0020] In the method of the invention, the post-treatment process of the crude product is simple, the solvent used is non-toxic or low toxic, the recovery rate is high, there is no environmental pollution, and the industrial feasibility is high.

[0021] In the method of the invention, the toxic product methanol is dissolved in water under the carrying of N, which can be collected without causing environmental pollution, and can be recycled and applied in the production process of biodiesel, thus reducing the industrial production cost.

[0022] 6. The catalyst used in the method is a supported solid base catalyst with high catalytic activity, and the catalyst can be recycled and reused, which greatly reduces the production cost, avoids environmental pollution brought by the catalyst, and has high industrial feasibility.

The attached drawings illustrate

[002] FIG. 1 is a comparison diagram of infrared spectrum between the product prepared by the invention and the standard sample.

[0024] As can be seen from the figure, the two spectra are consistent, in which the wide peak at 3420cm-1 is the absorption peak of 0-H stretching vibration, and the peak at 1720cm-1 is the absorption peak of C=0 stretching vibration on sucrose ester.

Specific implementation mode

[0025] The sucrose fatty acid ester in the invention is synthesized from the following raw materials:

[0026] Biodiesel: the main components are fatty acid methyl ester and fatty acid ethyl ester. There is no grade requirement, and it can be sold or made by itself.

[0027] Sugar: Industrial grade.

[0023] Supported solid base catalysts: lab-made.

[0029] Potassium stearate: Industrial grade.

[o030] Solvents (alcohols, acids, esters) : Industrial grade.

[0031] A method for synthesizing sucrose fatty acid esters directly from biodiesel and sucrose, including the following steps:

[0032] The first step is the preparation of supported solid base catalyst: according to the molar ratio of catalyst to support of 1:4~1: 25 ratio, weigh the catalyst and the carrier, impregnate with equal volume method for 5~24h, filter, filter cake in 100~ 120℃ for 2~5h drying, in 400~700℃ for 2~5h general burning, take out for use;

[0033] The second step, the preparation of the homogeneous system: biodiesel and sucrose according to the mass ratio of biodiesel: sucrose =1~ 4: 1, adding potassium stearate accounting for 5%~ 15% of the total weight of biodiesel and sucrose mixture, stirring while heating up, stirring at 60~80℃ for 0.5~1.5h, until the reaction system is a light yellow emulsion, adding the supported solid base catalyst accounting for 1%~3% of the total weight of the mixture, continue stirring for 0.5h;

[0034] The third step, the preparation of sucrose fatty acid ester: stirring while heating up, and through N, drive away the air in the reaction system while taking away the methanol generated in the reaction, N, under the protection of heating up to 110~150℃, reaction 2~5h, after cooling to below 100℃, stop the flow of N, add water to stop the reaction, stirring at 80℃ for 10min;

[0035] The fourth step, the post-treatment of the crude product: the pH value of the reaction system can be adjusted to 6~7 with dilute acetic acid or other dilute acids with a mass concentration of 3%, and the NaC1 solution with a mass concentration of 5%~15% is washed, and then the layer is left to stand after stirring, the lower water phase and the supported solid base catalyst are removed, and the supported solid base catalyst is washed and dried to be reused. The upper layer of sucrose fatty acids is sucrose After the ester phase is pumped and filtered, the same mass of ethanol is added, heated and stirred at 70℃, and then static precipitation is obtained. After the filter cake is pumped and washed with ethyl acetate, sucrose fatty acid ester refined products are obtained.

[0036] Embodiment 1

[0037] (1) Preparation of supported solid base catalyst: Weigh catalyst with molar ratio of 1:25 potassium carbonate and activated carbon carrier impregnated by equal volume method for 24h, filter, filter cake dried at 120℃ for 2h, calcined at 450℃ for 5h, to obtain supported solid base catalyst -K0/C catalyst;

[0038] (2) Preparation of homogeneous system: biodiesel and sucrose by mass ratio biodiesel: sucrose =1: 1, adding potassium stearate accounting for 15% of the total mass of the mixture, stirring while heating up, stirring at 80℃ for 0.5h, until the reaction system was a light yellow emulsion, adding K0/C catalyst accounting for 3% of the total mass of the mixture, continue stirring for 0.5h;

[0039] (3) The preparation of sucrose fatty acid ester: heating while stirring, and through N, drive away the air in the reaction system and take away the methanol generated in the reaction, under the protection of N, heating to 120℃, reaction for 5h, and then cooling to below 100℃, stop the flow of N, add water to stop the reaction, stirring at 80℃ for 10min;

[0040] (4) Post-treatment of crude products: Adjust the pH value of the reaction system to 6 with dilute acetic acid with a mass concentration of 3%, wash it with NaC1 solution, and then stand for stratification after stirring to remove the lower aqueous phase and the deposited supported catalyst K0/C. K0/C catalyst can be reused after washing and drying, the upper layer of sucrose fatty acid ester phase is pumped and filtered, ethanol of the same mass is added, heated and stirred at 70℃, and then static precipitation is obtained, and the filter cake is pumped and washed with ethyl acetate to obtain sucrose fatty acid ester refined products. According to the national standard of the People's Republic of China :GB8272-2009, the sensory experiment and identification test on the food additive sucrose fatty acid ester, the obtained product is sucrose ester. The yield of sucrose fatty acid ester was 88.5% based on sucrose. The infrared contrast spectra of the product and the standard sample are shown in Figure 1.

[0041] Embodiment 2

[0042] (1) Preparation of supported solid alkali catalyst: molar ratio of 1:20 potassium carbonate and activated carbon carrier impregnated by equal volume impregnation method for 24h, filtration, filter cake dried at 110℃ for 3h, calcined at 600℃ for 3h, take out for use;

[0043] (2) Preparation of homogeneous system: biodiesel and sucrose by mass ratio biodiesel: sucrose =2: After mixing, potassium stearate accounting for 10% of the total mass of the mixture was added, stirring while heating up, stirring at 80℃ for 1.0h until the reaction system was a light yellow emulsion, adding K,0/C catalyst accounting for 2% of the total mass of the mixture, and stirring for 0.5h;

[0044] (3) The preparation of sucrose fatty acid ester: heating up while stirring, and through N, drive away the air in the reaction system,N, heating up to 130℃ under protection, reaction for 3.5h, and then cooling down to below 100℃, stop passing N2, add water to stop the reaction, stir at 80℃ for 10min;

[0045] (4) Post-treatment of the crude product: adjust the PH value of the reaction system to 6 with dilute acetic acid with a concentration of 3%, wash with NaCI solution, stand for stratification after stirring, remove the lower aqueous phase and the deposited catalyst, the catalyst is washed and dried for use, the upper sucrose ester phase is pumped and filtered, ethanol of the same weight is added, heated and stirred at 70℃, and then settle, and the filter cake is pumped After washing with ethyl acetate, the refined product of sucrose ester is obtained. The yield of sucrose ester was 86.0% based on sucrose.

[0046] Illustrative embodiment 3

[0047] (1) Preparation of supported solid base catalyst: the Ko0/C catalyst recovered in Embodiment 1 is washed twice with deionized water and acetate respectively, dried at 110℃, and reserved;

[0048] (2) Preparation of homogeneous system: biodiesel and sucrose by mass ratio biodiesel: sucrose =2: After mixing, potassium stearate accounting for 5% of the total mass of the mixture is added, stirring while heating, stirring at 80℃ for 0.5h until the reaction system is a light yellow emulsion, adding K0/C catalyst recovered from embodiment 1 accounting for 3% of the total mass of the mixture, continue stirring for 0.5h;

[0049] (3) The preparation of sucrose fatty acid ester: heating up while stirring, and through N, drive away the air in the reaction system,N, heating up to 135 ° C under protection, reaction for 3h, and then cooling down to below 100 ° C, stop passing N, add water to stop the reaction, stir #10min at 80 ° C;

[0050] (4) Post-treatment of crude products: adjust the PH value of the reaction system with 3% dilute acetic acid, add 5% NaC1 solution for water washing, stand stratification after stirring, remove the lower aqueous phase and deposited catalyst, the catalyst is washed and dried for use, the upper sucrose ester phase is pumped and filtered, and the same mass of ethanol is added. Heating and stirring at 70℃, then resting and settling, filter cake after pumping and filtering and washing with ethyl acetate, sucrose ester refined products are obtained. The yield of sucrose ester was 84.7% based on sucrose.

[0051] Embodiment 4

[0052] (1) Preparation of supported solid base catalyst: The K0/C catalyst recovered in Embodiment 3 is washed twice with deionized water and ethyl acetate, dried at 110℃, and reserved;

[0053] (2) Preparation of homogeneous system: biodiesel and sucrose by mass ratio biodiesel: sucrose =2: After mixing, potassium stearate accounting for 15% of the total mass of the mixture is added, stirring while heating, stirring at 80℃ for 1.0h, until the reaction system is a light yellow emulsion, adding K0/C catalyst recovered from (1) treated embodiment 3, accounting for 3% of the total mass of the mixture, continue stirring for 0.5h;

[0054] (3) The preparation of sucrose fatty acid ester: heating up while stirring, and through N, drive away the air in the reaction system,N, heating up to 130℃ under protection, reaction for 3h, and then cooling down to below 100℃, stop passing N, add water to stop the reaction, and stir at 80℃ for 10min;

[0055] (4) Post-treatment of the crude product: adjust the PH value of the reaction system to 6 with dilute acetic acid with a concentration of 3%, wash with NaC1 solution, stand for stratification after stirring, remove the lower aqueous phase and the deposited catalyst, the catalyst is washed and dried for use, the upper sucrose ester phase is pumped and filtered, ethanol of the same weight is added, heated and stirred at 70℃, and then settle, and the filter cake is pumped After washing with ethyl acetate, sucrose ester refined products are obtained. The yield of sucrose ester is 82.2% based on sucrose.

[0056]

Example 5

[0057] (1) Preparation of supported solid base catalyst: The K0/C catalyst recovered in Embodiment 4 is washed twice with deionized water and ethyl acetate, dried at 110℃, and reserved;

[0058] (2) Preparation of homogeneous system: biodiesel and sucrose by mass ratio biodiesel: sucrose =4: After mixing in the ratio of 1, potassium stearate accounting for 10% of the total mass of the mixture is added, stirring while heating, stirring at 80℃ for 1.5h, until the reaction system is a light yellow emulsion, adding K20/C catalyst recovered from embodiment 4 accounting for 2% of the total mass of the mixture, continue stirring for 0.5h;

[0059] (3) The preparation of sucrose fatty acid ester: heating up while stirring, and passing N, driving away the air in the reaction system,N, heating up to 140℃ under protection, reacting for 2h, and then cooling down to below 100℃, stopping passing N, adding water to stop the reaction, stirring at 80℃ for 10min;

[0060] (4) Post-treatment of the crude product: adjust the PH value of the reaction system to 6 with dilute acetic acid with a concentration of 3%, wash with NaCl solution, stand for stratification after stirring, remove the lower aqueous phase and the deposited catalyst, the catalyst is washed and dried for use, the upper sucrose ester phase is pumped and filtered, ethanol of the same weight is added, heated and stirred at 70℃, and then settle, and the filter cake is pumped and filtered After washing with ethyl acetate, sucrose ester refined products can be obtained. The yield of sucrose ester is 79.2% based on sucrose.

[0061] Embodiment 6

[0062] (1) Preparation of supported solid base catalyst: The K0/C catalyst recovered in Embodiment 5 is washed twice with deionized water and ethyl acetate, dried at 110℃, and reserved;

[0063] (2) Preparation of homogeneous system: biodiesel and sucrose by mass ratio biodiesel: sucrose =4: After mixing, potassium stearate accounting for 10% of the total mass of the mixture is added, stirring while heating, stirring at 60℃ for 0.5h until the reaction system is a light yellow emulsion, adding KO/C catalyst recovered from embodiment 5 accounting for 2% of the total mass of the mixture, continue stirring for 0.5h;

[0064] (3) The preparation of sucrose fatty acid ester: heating while stirring, and through N, drive away the air in the reaction system, under the protection of N, heating to 140℃, reaction for 2h, and then cooling to below 100℃, stop the flow of N, add water to stop the reaction, stir at 80℃ for #10min;

[0065] (4) Post-treatment of the crude product: adjust the PH value of the reaction system to 6 with dilute acetic acid with a concentration of 3%, wash with NaC1 solution, stand for stratification after stirring, remove the lower aqueous phase and the deposited catalyst, the catalyst is washed and dried for use, the upper sucrose ester phase is pumped and filtered, ethanol of the same weight is added, heated and stirred at 70℃, and then settle, and the filter cake is pumped After washing with ethyl acetate, sucrose ester refined products are obtained. The yield of sucrose ester is 74.9% based on sucrose.

[0066] As can be seen from the above embodiments, the catalytic activity of the supported solid base catalyst used in the invention is still high after recycling for more than four times, and the catalyst utilization rate is high, which can effectively reduce the production cost.

[0067] Embodiments 7

[0068] (1) Preparation of supported solid base catalyst: Firstly, A1,0 is activated at 550℃ for 4h, then potassium carbonate with molar ratio of 1:4 is weighed and A120g is impregnated by equal volume method for 24h, dried at 110℃ and ground, calcined at 700℃ for 5h, Ko/Al0 is removed, and the catalyst is left for use

[0069] (2) Preparation of homogeneous system: biodiesel and sucrose by mass ratio Biodiesel: sucrose =2: After mixing, potassium stearate accounting for 10% of the total mass of the mixture was added, stirring while heating up, stirring at 60℃ for 1.5h, until the reaction system was a light yellow emulsion, adding K0/A120 catalyst accounting for 3% of the total mass of the mixture, continue stirring for 0.5h;

[0070] (3) The preparation of sucrose fatty acid ester: heating up while stirring, and through N, drive away the air in the reaction system,N, heating up to 135℃ under protection, reaction for 3h, and then cooling down to below 100℃, stop passing N, add water to stop the reaction, stirring at 80℃ for 10min;

[0071] (4) Post-treatment of the crude product: adjust the pH value of the reaction system to 6 with dilute acetic acid with a concentration of 3%, wash with NaCI solution, then stand for stratification after stirring, remove the lower aqueous phase and the deposited catalyst, the catalyst is washed and dried for use, after the upper sucrose ester phase is pumped and filtered, the same weight of ethanol is added to the filter cake, heated and stirred at 70℃, after static precipitation, pumped and filtered After the filter cake is washed with ethyl acetate, sucrose ester refined products are obtained. The yield of sucrose ester was 81.6% based on sucrose.

[0072] Embodiment 8

[0073] (1) Preparation of supported solid base catalyst: NaY type molecular sieve was activated at 400℃ for 4h, and calcium oxide with molar ratio of 1:25 was weighed with NaY molecular sieve, impregnated by equal-volume method for 24h, dried at 110℃ and ground, burned at 600℃ for 5h, and removed for use;

[0074] (2) Preparation of homogeneous system: biodiesel and sucrose by mass ratio biodiesel: sucrose =2: After mixing, potassium stearate accounting for 10% of the total mass of the mixture was added, stirring while heating up, stirring at 60℃ for 1.5h, until the reaction system was a light yellow emulsion, adding Ca0/NaY catalyst accounting for 3% of the total mass of the mixture, and stirring for 0.5h;

[0075] (3) The preparation of sucrose fatty acid ester: heating up while stirring, and through N, drive away the air in the reaction system,N, heating up to 135℃ under protection, reaction for 3h, and then cooling down to below 100℃, stop passing N, add water to stop the reaction, stir at 80℃ for # 10min;

[0076] (4) Post-treatment of the crude product: adjust the pH value of the reaction system to 7 with dilute acetic acid with a concentration of 3%, wash with NaC1 solution, stand for stratification after stirring, remove the lower aqueous phase and the deposited catalyst, wash and dry the catalyst for use, after the upper sucrose ester phase filtration, add the same weight of ethanol into the filter cake, heat and stir at 70℃, and then settle and filter After the filter cake is washed with ethyl acetate, sucrose ester refined products are obtained. The yield of sucrose ester was 82.0% based on sucrose.

[0077] Embodiment 9

[0078] (1) Preparation of supported solid base catalyst: The NaX molecular sieve is activated at 400℃ for 4h, and the mole is weighed

KOH and NaX zeolite with a ratio of 1:10 were impregnated for 24h by equal volume impregnation method, dried at 110℃, ground, calcined at 600℃ for 5h, and removed for use

[0079] (2) Preparation of homogeneous system: biodiesel and sucrose by mass ratio Biodiesel: sucrose =2: After mixing, potassium stearate accounting for 10% of the total mass of the mixture was added, stirring while heating up, stirring at 60℃ for 1.5h, until the reaction system was a light yellow emulsion, adding KOH/NaX catalyst accounting for 3% of the total mass of the mixture, continue stirring for 0.5h;

[0080] (3) The preparation of sucrose fatty acid ester: heating up while stirring, and through N, drive away the air in the reaction system, N, heating up to 135℃ under protection, reaction for 3h, and then cooling down to below 100℃, stop passing N, add water to stop the reaction, and stir at 80℃ for 10min;

[0081] (4) Post-treatment of the crude product: adjust the pH value of the reaction system to 6 with dilute acetic acid with a concentration of 3%, wash with NaCl solution, stand for stratification after stirring, remove the lower aqueous phase and the deposited catalyst, wash and dry the catalyst for use, after the upper sucrose ester phase is pumped and filtered, the same weight of ethanol is added to the filter cake, heated and stirred at 70℃, after static precipitation, pumped and filtered After the filter cake is washed with ethyl acetate, sucrose ester refined products can be obtained. The yield of sucrose ester was 79.4% based on sucrose.

[0082] Embodiment 10

[0083] (1) Preparation of supported solid base catalyst: Mg0 is activated at 500℃ for 4h, KF and MgO with molar ratio of 1:5 are weighed, impregnated by equal volume method for 24h, dried at 110℃ and ground, calcined at 600℃ for 6h, KF/Mgo catalyst is taken out for use

[0084] (2) Preparation of homogeneous system: biodiesel and sucrose by mass ratio Biodiesel: sucrose =2: After mixing, potassium stearate accounting for 10% of the total mass of the mixture was added, stirring while heating up, stirring at 80℃ for 1.5h, until the reaction system was a light yellow emulsion, adding KF/Mg0 catalyst accounting for 3% of the total mass of the mixture, continue stirring for 0.5h;

[0085] (3) The preparation of sucrose fatty acid ester: heating up while stirring, and through N, drive away the air in the reaction system, heating up to 135℃ under the protection of N, reaction for 3h, and then cooling down to below 100℃, stop passing N, add water to stop the reaction, stir at 80℃ for #10min;

[0086] (4) Post-treatment of the crude product: adjust the PH value of the reaction system to 6 with dilute acetic acid with a concentration of 3%, wash with NaC1 solution, then stand for stratification after stirring, remove the lower aqueous phase and the deposited catalyst, the catalyst is washed and dried for use, after the upper sucrose ester phase is pumped and filtered, the same weight of ethanol is added to the filter cake, heated and stirred at 70℃, after static precipitation, pumped and filtered After the filter cake is washed with ethyl acetate, sucrose ester refined products are obtained. The yield of sucrose ester is 80.7% calculated by sucrose.

[0087 Embodiment 11

[008] (1) Preparation of supported solid base catalyst: sodium carbonate and activated carbon with molar ratio of 1:20 were weighed, impregnated by equal volume method for 24h, dried at 110℃ and ground, calcined at 450℃ for 6h, to obtain supported solid base catalyst Na,0/ C for use;

[0089] (2) Preparation of homogeneous system: biodiesel and sucrose by mass ratio biodiesel: sucrose =2: After mixing, potassium stearate accounting for 10% of the total mass of the mixture was added, stirring while heating up, stirring at 80℃ for 1.5h, until the reaction system was a light yellow emulsion, adding Na0/C catalyst accounting for 3% of the total mass of the mixture, continue stirring for 0.5h;

[0090] (3) The preparation of sucrose fatty acid ester: heating up while stirring, and through N, drive away the air in the reaction system, N, heating up to 135℃ under protection, reaction for 3h, and then cooling down to below 100℃, stop passing N, add water to stop the reaction, stirring at 80℃ for 10min;

[0091] (4) Post-treatment of the crude product: adjust the PH value of the reaction system to 6 with dilute acetic acid with a concentration of 3%, wash with NaCl solution, stand for stratification after stirring, remove the lower aqueous phase and the deposited catalyst, wash and dry the catalyst for use, after the upper sucrose ester phase is pumped and filtered, the same weight of ethanol is added to the filter cake, heated and stirred at 70℃, after static precipitation, pumped and filtered after

After the filter cake is washed with ethyl acetate, the refined product of sucrose ester is obtained. The yield of sucrose ester is 78.5% based on sucrose.

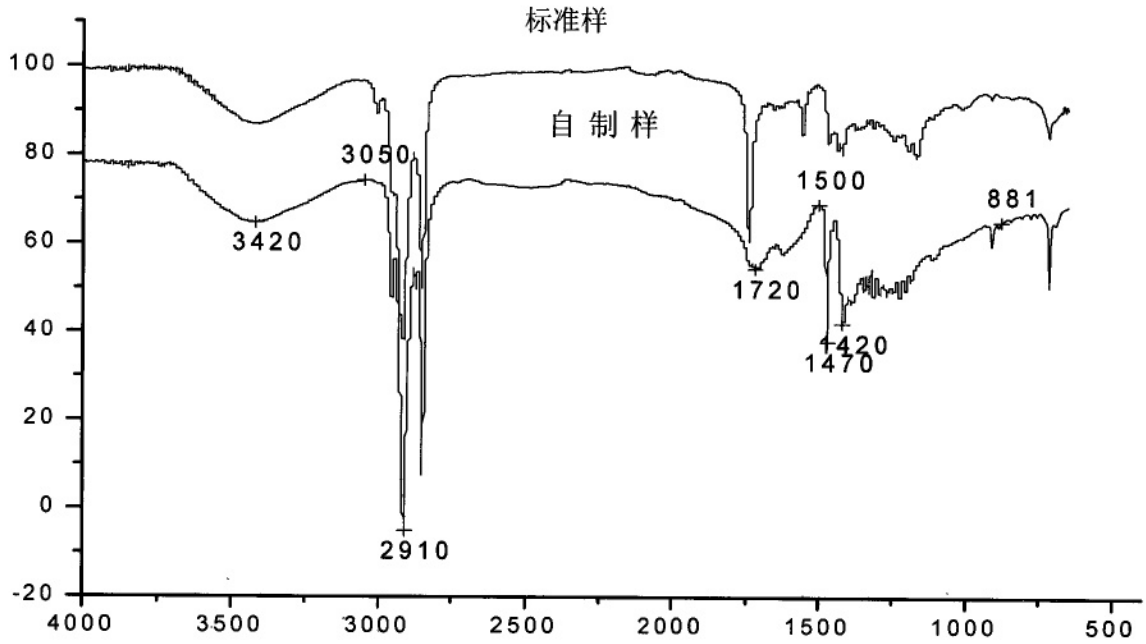

标准样
自 制 样
3420
3050
2910
1720
1500
1470
1420
881
100
80
60
40
20
0
-20
4000
3500
3000
2500
2000
1500
1000
500

Figure 1

(19)中华人民共和国国家知识产权局

(12) Invention patent

(10) License Notice No. CN 101514218dobeca
(45) Grant t B 2012.01.11

(21) l No. 200910096837.X

Examiner Li Shikun

(22) Please B 2009. 03.16
(73) Patentee Yuan Changgui

Address: Yangtang Road, Tonglu County, Hangzhou City, Zhejiang 311500, China

279 Hangzhou Ruilin Chemical Co., LTD

(72) The inventor Yuan Changgui

(74) Patent Agency, Hangzhou Tianxin Patent Office 33209

Agent Chen Hong
(51) Int. CI.

"" Breakyna 13/06 (2006.01)

"Particulars 1/00 (2006.01)")

(56) Compare files

CN 1232036A, 1999. 10.20, Requirements 1-3.

Zhang Wei et al. Synthesis of sucrose esters by solvent-free method. Food Science and Technology. 2003, (4), 68-70.

1 page of claims and 5 pages of instructions

(54) Issue name

The invention relates to a raw material formula for the synthesis of sucrose fatty acid ester and a synthesis method thereof

(57) Abstract

The invention relates to a raw material formula for synthesizing sucrose fatty acid ester and a synthesis method thereof, belonging to the field of chemical industry. The formula of the invention is: sucrose: 50-200 weight parts, fatty acid methyl or ethyl ester: 20-80 weight parts, catalyst :0.2-8 weight parts; Fatty acid cationic soap salt :5--50 weight parts; Modified phospholipids: 1-20 parts by weight; Sucrose esters (HLB 5-15) :0-8 parts by weight; Sodium lactate (HLB 5-15) :0-6 weight parts. The invention adopts a method of adding a composite catalyst in a solvent-free method to synthesize sucrose ester system. The addition of modified phospholipid compounds can make the reaction of sucrose ester synthesis system more uniform, and can reach the eutectic state quickly, so as to effectively improve the conversion of sucrose ester as a reaction product and the content of single and total sucrose ester in the product.

1. A raw material composition for the synthesis of sucrose fatty acid ester, the type and dosage of the composition are:

Sucrose :50-200 weight parts, fatty acid methyl ester or ethyl ester :20-80 weight parts, catalyst :0.2-8 weight parts; Fatty acid cationic soap salts :5-50 parts by weight; Modified phospholipids :1-20 parts by weight; Sucrose esters with HLB value of 5-15:0-8 parts by weight; Sodium lactate :0-6 weight parts, the modified phospholipid compound is modified soybean phospholipid, modified corn phospholipid, modified egg phospholipid, modified cottonseed phospholipid, modified rapeseed phospholipid, modified peanut phospholipid one or several, the modified method is hydroxylation modification, hydrogenation modification, acylation modification, enzymatic hydrolysis modification of one or several.

2. The raw material composition for the synthesis of sucrose fatty acid ester in accordance with claim 1 is characterized as follows: the fatty acid cationic soap salt is potassium stearate and/or magnesium stearate and/or lithium stearate.

3. The raw material composition for the synthesis of sucrose fatty acid ester according to claim 1 is characterized as: the modified phospholipid compound is hydroxylated modified soybean phospholipid.

4. The raw material composition for the synthesis of sucrose fatty acid ester according to claim 1 or 3 is characterized by the catalyst being one or more of carbonate, calcium oxide, potassium hydroxide, phosphate.

5. A method of synthesizing sucrose fatty acid ester using any of the raw materials mentioned in Claim 1-4, the process steps are:

a. Heating 20-80 weight parts of fatty acid methyl ester or ethyl ester to 70-110℃ in an oil bath or steam;

b, then add 5-50 parts by weight fatty acid cationic soap salt under stirring, then add 0.2-8 parts by weight catalyst and 1-20 parts by weight modified phospholipid compounds, stir well, and add 50-200 parts by weight sucrose powder; When adding fatty acid cationic soap salt, add 0-8 weight parts of sucrose ester with HLB value of 5-15, and add 0-6 weight parts of sodium lactate when adding catalyst and modified phospholipids;

c, increase the reaction temperature to 120-180℃, while maintaining the vacuum degree 1000-5500Pa, under stirring reaction 10-480 minutes, to obtain sucrose ester crude products;

d, the crude product of sucrose ester was washed, extracted with organic solvent, and the impurities of soap body and catalyst were removed to obtain the purified product of sucrose ester.

6, according to the synthesis method of sucrose fatty acid ester described in claim 5, it is characterized by: the temperature range of the oil bath or steam heating is 90-100℃.

· The method of synthesis of sucrose fatty acid ester described in claim 5 is characterized as follows: in step c, the reaction temperature is raised to 140-160℃.

· According to the synthesis method of sucrose fatty acid ester described in claim 5, it is characterized as follows: in the step c, maintain the vacuum degree 2000-4000Pa.

The invention relates to a raw material formula for the synthesis of sucrose fatty acid ester and a synthesis method thereof

Technical field

[0001] The invention relates to a raw material formula for synthesizing sucrose fatty acid ester and a synthesis method thereof, belonging to the field of chemical industry.

Background technology

[0002] Sucrose Fatty Acid (Sucrose Fatty Acid) Esters, referred to as SE, are a kind of excellent performance and very safe non-ionic surfactant, as a food additive approved by the World Health Organization (WHO), the United Nations Food Organization (FAO), the European Community and Japan, China, the United States and other countries, can be used in food as emulsifier, stabilizer, lubricant, regulator and antibacterial agent, in medicine As a drug and adjuvant, as an emulsifier and moisturizer in cosmetics and detergents, as a fruit preservative, pesticide additives and plant growth aid in agriculture. Because sucrose ester is non-toxic and widely used, its synthesis and application research has attracted much attention.

[0003] At present, most of the industrial synthesis methods of sucrose ester are transesterification. Industrial transesterification of sucrose esters can be divided into solvent method and solvent-free method two categories. Although the solvent free method is non-toxic, short in time and low in cost, it is difficult for sucrose and fatty acid methyl ester (or ethyl ester) in the reaction system to reach eutectic under the action of a single fatty acid soap body, causing the synthetic reaction system to be uneven and difficult to reach the homogeneous level, resulting in low content of single sucrose ester and total sucrose ester in the reaction products and low conversion rate. However, sucrose ester products with high single ester content are widely used in many fields such as food and medicine, and the market demand is the largest, so the promotion and application of solvent-free synthesis is greatly limited.

Content of invention

[0004] The technical problem to be solved by the invention is to provide a raw material formula of synthetic sucrose fatty acid ester with ingenious raw material formula, reasonable formula content, high single ester content and high product yield.

[0005] Another technical problem to be solved by the invention is to provide a synthesis process method of sucrose fatty acid ester with advanced process design, reasonable process steps, high product yield, high content of sucrose single ester and total ester, and wide application range.

[0006] The technical solution adopted by the invention to solve the above technical problems is a raw material formula for synthesizing sucrose fatty acid ester, and the type and dosage of the formula are:

[0007] Sucrose :50--200 weight parts, fatty acid methyl ester or ethyl ester :20--80 weight parts, catalyst :0.2--8 weight parts; Fatty acid cationic soap salts :5--50 parts by weight; Modified phospholipids :1-20 parts by weight; Sucrose esters (HLB 5-15) :0-8 parts by weight; Sodium lactate (HLB 5-15) :0-6 weight parts.

[0008] As a preferred option, the modified phospholipids are one or several of the modified soybean phospholipids, modified corn phospholipids, modified egg phospholipids, modified cottonseed phospholipids, modified rapeseed phospholipids, modified peanut phospholipids, and the methods used for the modification are one or several of the hydroxylation modification, hydrogenation modification, acylation modification, and enzymatic hydrolysis modification.

[00□□ as an option, the fatty acid cationic soap salts are potassium stearate and/or magnesium stearate and/or lithium stearate. [0010] As an option, the modified phospholipid compounds are hydroxylated modified soybean phospholipids.

[0011] As a preference, the catalyst is one or more of carbonate, calcium oxide, potassium hydroxide, phosphates. The technical scheme adopted by the invention to solve the technical problem is also a synthesis process method of sucrose fatty acid ester, the process steps are as follows:

[0012] a. The fatty acid methyl ester or ethyl ester is heated to 70-110° C by oil bath or steam;

[0013] b, then add fatty acid cationic soap salt under stirring, then add catalyst and modified phospholipid compounds, stir well, and then add sucrose powder;

[0014] c, increase the reaction temperature to 120-180℃, while maintaining the vacuum degree 1000-5500Pa, reaction under stirring for 10-480 minutes, to obtain sucrose ester crude products;

[0015] d, the crude product of sucrose ester was washed, extracted with organic solvent, and impurities such as soap body and catalyst were removed to obtain the purified product of sucrose ester.

[o016] As preferred, the temperature range of the oil bath or steam heating is 90-100 ° C.

[0017] As a preference, in step c, the reaction temperature is raised to 140-160 ° C.

[0018] As a preference, in the step c, the vacuum degree is maintained at 2000-4000Pa.

[0019] As a preference, in step b, sucrose ester is added when fatty acid cationic soap salt is added, and sodium lactate is added when catalyst and modified phospholipid compound are added.

[0020] Compared with the prior art, the invention has the following advantages and effects :1. The invention adopts a variety of emulsifiers to catalyze the synthesis of sucrose fatty acid ester, so that the sucrose fatty acid ester synthesis system becomes thin and homogeneous, increases the contact area of the reaction molecules, and improves the content of sucrose monoester and the conversion rate of sucrose ester reaction. 2. The invention adopts the addition of different amounts of fatty acid soap salt and phospholipid compounds. The sucrose in the synthesis system produces eutectic, the sucrose ester synthesis system becomes homogeneous, the contact area of the reaction molecules is increased, the content of the product sucrose single ester and total ester is increased, and the transesterification synthesis reaction of sucrose ester is accelerated.

Specific implementation mode

[0021] The following are further detailed descriptions of the invention in conjunction with embodiments. The following embodiments are interpretations of the invention and the invention is not limited to the following embodiments.

[0022] Embodiment 1:

[0023] In a 1000ml three-flask with stirring stick and defoamer, 35 g of fatty acid methyl ester was added, the oil bath was heated to 80-100℃, and under agitation 3 g of accelerator sucrose ester (HLB11), 30 g of potassium stearate, 1.5 g of magnesium carbonate and 2 g of calcium oxide were added. After stirring well, 8 g of hydroxylated modified soybean phospholipids were added. After stirring well, finally add 160 grams of powdered sucrose. Increase the temperature to 140-142℃, while maintaining the vacuum of 1500Pa, stirring reaction for 65 minutes, to obtain the crude product of sucrose ester. Then using the method of prior art, that is, extraction by organic solvent and purification by calcium oxide (refer to European Patent EP0448996), the purified product of sucrose ester was obtained at 137.25 grams. The yield was 69.32%. By HPLC analysis, the content of single sucrose ester was 57.82%, and the total sucrose ester content was 95.76%.

[0024] Example 2:

[0025] In a 1000ml three-neck bottle with stirring stick and defoamator, 40 g of fatty acid methyl ester was added, the oil bath was heated to 90-100℃, and under agitation 5 g of accelerator sucrose ester (HLB 15), 20 g of potassium stearate, 1.5 g of sodium carbonate and 2 g of dipotassium hydrogen phosphate were added. After stirring well, add 6 grams of hydroxylated modified soybean phospholipid, stir for 1-5 minutes, and finally add 140 grams of sucrose powder, raise the temperature to 143-145℃, maintain the vacuum degree at 3800Pa, stir reaction for 165 minutes, to obtain sucrose ester crude product. Then with the method of prior art, that is, by organic solvent extraction and calcium oxide purification treatment (refer to European patent EP 0448996), the purified product of sucrose ester is 151.7 grams, the yield is 82.0%, the high performance liquid chromatography analysis, the content of sucrose mono ester is 49. 27%, the total content of sucrose ester is 96.82%.

[0026] i Case 3:

[0027] Add 38 grams of fatty acid ethyl ester to a 1000ml three-neck bottle with stirring stick and defoamer and heat the oil bath until

80-100℃, and stir to add the accelerator sucrose ester (HLB 13)5 grams, potassium stearate and lithium stearate 15 grams each, then add Na2HP04.12H20 2 grams and t1.5 grams of carbonate were stirred,m into the hydrogenated modified corn phospholipid 10 grams and then stirred for 1 to 5 minutes, and finally added 166 grams of sucrose powder, increasing the temperature to 138-140℃, while maintaining the vacuum 1350Pa, stirring reaction for 70 minutes, to obtain sucrose ester crude products. Then using the method of prior art, that is, by organic solvent extraction and calcium oxide purification treatment (refer to European patent EP 0448996), sucrose ester purified product 149.15 grams, the yield is 71.36%. By HPLC analysis, the content of single sucrose ester was 58.27%, the content of total sucrose ester was 94.96%.
[0028] Example 4:

[0029] In a 1000ml three-neck flask with stirring stick and defoamer, 35 g of fatty acid methyl ester is added, the oil bath is heated to 80-100 ° C, and the accelerator sucrose ester (HLB) is added under agitation 7)5 g, 20 g potassium stearate, 15 g magnesium stearate, then add 3.5 g calcium oxide and 1 g potassium hydroxide, add 12 g enzymatic hydrolysis modified cottonseed phospholipid. After stirring well, finally add 165 grams of sucrose powder. The temperature was raised to 140-160℃, the vacuum was maintained at 3450Pa, and the reaction was stirred for 55 minutes to obtain the crude sucrose ester product. Then by the method of prior art, that is, by organic solvent extraction and calcium oxide purification treatment (refer to European patent EP 0448996), the purified product of sucrose ester was 135.69g, with a yield of 66.19%. By HPLC analysis, the content of single sucrose ester was 63.15%, the content of total sucrose ester was 96.03%.

[0030] Example 5:

[0031] In a 1000ml three-neck bottle with stirring stick and defoamator, add 60g of fatty acid methyl ester, heat the oil bath to 70-90℃, and add 50g of potassium stearate under stirring, after stirring well, add 5g of potassium carbonate, 5g of hydroxylated modified egg phospholipid and 5g of sodium lactate, continue to stir for 1-5 minutes, then add 140g of powdered sucrose. The high temperature was raised to 148-150℃ while maintaining the vacuum degree of 2100Pa, stirring and reacting for 200 minutes to obtain the crude product of sucrose ester. Then with the method of prior art, that is, by organic solvent extraction and calcium oxide purification treatment (refer to European patent EP 0448996), the purified product of sucrose ester was obtained 159.72 grams. The yield was 79.86%. The content of sucrose monoester and total sucrose ester were 45% and 95.28% respectively by HPLC.

[0032] Example 6:

[0033] In a 1000ml three-necked bottle with stirring stick and defoamer, add 32 grams of fatty acid methyl ester, heat the oil bath to 80-100℃, and add 15 grams of accelerator potassium stearate, 10 grams of magnesium stearate, 5 grams of calcium oxide, 3 grams of potassium carbonate and 12 grams of acylated modified egg phospholipid under stirring, continue to stir well, and finally add 168 grams of sucrose powder, rise to high temperature Degree to 150-152℃, while the vacuum degree was maintained at 4500Pa, stirring reaction for 50 minutes, to obtain the sucrose ester reaction crude product. Then using the method of prior art, that is, by organic solvent extraction and calcium oxide purification treatment (refer to European patent EP 0448996), the purified product of sucrose ester was 136.38 grams, the yield was 68.19%, by HPLC analysis, the content of sucrose monoester was 62.27%, the total content of sucrose ester was 96.17%.

[0034] Exemplar 7:

[0035] In a 1000ml three-flask with stirring stick and defoamer, 20 g of fatty acid methyl ester was added, the oil bath was heated to 80-100℃, and under agitation, 2 g of accelerator sucrose ester (HLB14), 25 g of potassium stearate were added, 0.2 g of calcium oxide, 2.5 g of hydroxylated modified soybean phospholipid and 1 g of sodium lactate were added. After stirring well, 50 g of powdered sucrose was finally added. Increase the temperature to 120-140℃, while maintaining the vacuum of 5500Pa, stirring reaction for 100 minutes, to obtain the crude product of sucrose ester. Then by the method of prior art, that is, by organic solvent extraction and calcium oxide purification treatment (refer to European patent EP 0448996), 43.72 grams of sucrose ester purified product was obtained. The yield was 60.72%. By HPLC analysis, the content of single sucrose ester was 62.08%, and the content of total sucrose ester was 96.72%.

[0036] Embodiment 8:

[0037] In a 1000ml three-flask with stirring stick and defoamer, 80g of fatty acid methyl ester was added, the oil bath was heated to 70-100℃, and under agitation 1 g of accelerator sucrose ester (HLB5), 35 g of potassium stearate, 0.3 g of potassium hydroxide, 1 g of enzymatic hydrolysis modified rapeseed phospholipid and 0.5 g of sodium lactate were added. After stirring well, 130g of powdered sucrose was finally added. Increase the temperature to 150-180℃, while maintaining the vacuum degree 4000Pa, stirring reaction for 460 minutes, to obtain sucrose ester crude product. Then by the method of prior art, that is, by organic solvent extraction and calcium oxide purification treatment (refer to European patent EP 0448996), 168.78 grams of sucrose ester purified product was obtained. The yield was 83.55%. By HPLC analysis, the content of single sucrose ester was 45.23% and the total sucrose ester content was 96.75%.

[0038] Case 9:

[0039] 25 g of fatty acid methyl ester was added to a 1000ml three-neck bottle with stirring stick and defoamer. The oil bath was heated to 70-110℃, and the accelerator sucrose ester (HLB6) was added under agitation. 4 g, 18 g potassium stearate, then add 0.5 g potassium hydroxide, 1.2 g disodium hydrogen phosphate, 3 g hydroxylated modified peanut phospholipid and 3 g sodium lactate. After mixing well, add 75g of powdered sucrose at the end. The temperature was raised to 120-150℃, the vacuum was maintained at 1000Pa, and the crude product of sucrose ester was obtained after the stirring reaction for 480 minutes. Then with the method of prior art, that is, by organic solvent extraction and calcium oxide purification treatment (refer to European patent EP 0448996), 77.98 grams of sucrose ester purified product was obtained. The yield was 74.98%. By HPLC analysis, the content of single sucrose ester was 60.87%, and the content of total sucrose ester was 97.82%.

[0040] Example 10:

[0041] In a 1000ml three-necked flask with stirring stick and defoamer, 30 g fatty acid methyl ester was added, the oil bath was heated to 80-110℃, and under agitation 3 g of accelerator sucrose ester (HLB10), 15 g of magnesium stearate, 4.5 g of calcium oxide, 3.5 g of potassium carbonate, 20 g of hydrogenated modified soybean phospholipid and 4 g of sodium lactate were added. After being stirred well, 100g of powdered sucrose was finally added. Increase the temperature to 160-180℃, while maintaining the vacuum degree 2000Pa, stirring reaction for 10 minutes, to obtain sucrose ester crude products. Then by the method of prior art, that is, extraction by organic solvent and purification by calcium oxide (refer to European Patent EP0448996), 79.96 grams of sucrose ester purified product was obtained. The yield was 60.12%. By HPLC analysis, the content of single sucrose ester was 65.12%, and the total sucrose ester content was 96.25%.

[0042] Example 11:

[0043] In a 1000ml three-necked flask with stirring stick and defoamer, add 55 grams of fatty acid methyl ester, heat the oil bath to 90-110℃, and add 8 grams of accelerator sucrose ester (HLB13), 20 grams of magnesium stearate, 20 grams of potassium stearate under agitation, add 3 grams of calcium oxide, 2 grams of potassium hydroxide, 3 grams of sodium hydrogen phosphate, 20 grams of acylated modified soybean phospholipid and 6g sodium lactate. After mixing well, add 185 grams of powdered sucrose at the end. Increase the temperature to 150-170℃, while maintaining the vacuum of 5000Pa, stirring reaction for 400 minutes, to obtain the crude product of sucrose ester. Then by the method of prior art, that is, by organic solvent extraction and calcium oxide purification treatment (refer to European patent EP 0448996), 168.04 grams of sucrose ester purified product was obtained. The yield was 80.79%. By HPLC analysis, the content of single sucrose ester was 45.29%, and the total sucrose ester content was 96.83%.

[0044]

Example 12:

[0045] In a 1000ml three-neck bottle with stirring stick and defoamer, add 28 g of fatty acid methyl ester, oil bath heated to 70-90℃, and add 7 g of accelerator sucrose ester (HLB9), 5 g of lithium stearate, 5 g of magnesium stearate under agitation, then add 3.5 g of sodium carbonate, 3.5 g of dipotassium hydrogen phosphate, 18 g of enzymatic hydrolysis modified rapeseed phospholipid and 5 g of sodium lactate . After mixing well, add 200g of powdered sucrose at the end. The temperature was raised to 130-160℃, the vacuum was maintained at 5300Pa, and the reaction was stirred for 20 minutes to obtain the crude sucrose ester product. Then using the method of prior art, that is, by organic solvent extraction and calcium oxide purification treatment (refer to European patent EP 0448996), the purified product of sucrose ester was obtained 144.55 grams. The yield was 59.00%. By HPLC analysis, the content of single sucrose ester was 62.89% and the total sucrose ester was 96.38%.

[0046] Embodiment 13:

[0047] In a 1000ml three-flask with stirring stick and defoamer, 48 g of fatty acid methyl ester was added, the oil bath was heated to 80-100℃, and under agitation 6 g of accelerator sucrose ester (HLB6), 5 g of potassium stearate, 5 g of magnesium carbonate, 14 g of hydroxylated modified soybean phospholipid and 2 g of sodium lactate were added. After stirring well, 152g of powdered sucrose was finally added. The temperature was raised to 125-145℃, while the vacuum was maintained at 2500Pa, and the stirring reaction was carried out for 360 minutes to obtain the crude sucrose ester product. Then by the method of prior art, that is, by organic solvent extraction and calcium oxide purification treatment (refer to European patent EP 0448996), 161.9 grams of sucrose ester purified product was obtained. The yield was 78.59%. By HPLC analysis, the content of single sucrose ester was 56.10% and the total sucrose ester content was 97.12%.

[0048] Embodiment 14:

[004] In a 1000ml three-necked flask with stirring stick and defoamer, add 35g of fatty acid methyl ester, heat the oil bath to 90-100℃, and add 4 g of accelerator sucrose ester (HLB13), 25 g of magnesium stearate under agitation, add 2.5 g of calcium carbonate, 1.5 g of potassium hydroxide, 16 g of hydrogenated modified corn phospholipid and 3.5 g of sodium lactate. After being stirred well, 125g of powdered sucrose was finally added. Increase the temperature to 145-175℃, while maintaining the vacuum 1200Pa, stirring reaction for 280 minutes, to obtain sucrose ester crude product. Then by the method of prior art, that is, extraction by organic solvent and purification by calcium oxide (refer to European Patent EP0448996), the purified product of sucrose ester was obtained at 116.10 grams. The yield was 70.79%. By HPLC analysis, the content of single sucrose ester was 62.93%, and the content of total sucrose ester was 99.12%.

[0050] In the present invention, the applicant, after a lot of tests, adopts the method of synthesizing sucrose ester system by solvent-free method and adding compound catalyst. In addition to the strong alkaline inorganic catalyst such as carbonate or calcium oxide, the composite catalyst also contains three (or more) components such as modified phospholipid compounds and fatty acid cationic soap salts. Among them, the addition of modified phospholipids can make the reaction of sucrose ester synthesis system more uniform, and can reach the eutectic state quickly, so as to effectively improve the conversion of sucrose ester as a reaction product and the content of sucrose single ester and total ester in the product.

[0051] The yield of sucrose ester in the reaction products can reach 60-82%. After purification, the total ester content of sucrose ester products can reach 90-99%, and the single ester content of sucrose can reach 45-65%, which is in line with domestic and international industrial standards for sucrose ester products. The invention has been successfully developed on a small scale and achieved industrial production results in Hangzhou Ruilin Chemical Company. After a small range of trials, it has been highly appraised by customers. After purification, the product conforms to the national standard of sucrose ester in China, the United States and Japan, and has broad application prospect and market prospect.

[0052] The purification process of the crude product of the sucrose ester is the prior art and will not be repeated.

[0053] Although embodiments of the invention have been disclosed as above, they are not intended to limit the scope of protection of the invention, and changes and refinements made by any skilled person familiar with the technology within the concept and scope of the invention shall fall within the scope of protection of the invention.

(19)国家知识产权局

(12) Application for invention patent

(10) Application Publication No. CN 114929720 A (43) Application EKT B 2022.08.19

(21) Application No. 202280001930.1

(22) Apply B 2022.04.15

(85) PCTE International please proceed to \ ER stage E 2022.06.28

(86) Application data for PCTE International application PCT/CN2022/086961 2022. 04. 15

7 (51) Int. CI. C O H 13/06 (2006. 01) C H O 7 1/00 (2006.01)

(71) The applicant Guangzhou Jiadele Biochemical Technology Co., LTD

Address 6 Huafeng Road, Yonghe District, Guangzhou Economic and Technological Development Zone, Guangzhou 510530, China

(72) Inventor Xu Liangzhenming Juping Shaorei and Xu Huaiyi

(74) Beijing Pinyuan Patent Agency Co., LTD 11332

Liu Cuo Hu Bin, patent agent

Claim 1 page specification 9 pages

(54) State the name

A solvent-free synthesis method of sucrose ester with high monoester content

(57) Abstract

This paper presents a solvent-free synthesis method of sucrose ester with high monoester content. The method includes the following steps: (1) the mixture of sucrose, higher fatty acid ester and higher fatty acid salt is preheated at 70-90° C to obtain the mixture; (2) Mix the mixture with a catalyst and react at 120-140 ° C to obtain the sucrose ester. The synthesis method involved in this application adopts solve-free transesterification method, which forms a co-melting state of sucrose and advanced fatty acid ester, advanced fatty acid salt and catalyst according to a certain proportion at high temperature, and catalyzed the synthesis of sucrose ester under reaction conditions conducive to kinetics. The synthesis method avoids the use of solvent, solves the toxicity problem, so that the product can reach the standard for medical consumption, the content of single sucrose ester in the product is high, and the obtained product has good color, the synthesis method is simple and easy to industrial production, and has important application value.

CN 114929720 A

1. A solvent-free synthesis method of sucrose ester with high monoester content, which includes:

(1) sucrose, advanced fatty acid ester and advanced fatty acid salt are mixed and preheated at 70-90℃ to obtain the mixture;

(2) Mix the mixture with the catalyst and react at 120-140℃ to obtain the sucrose ester.

2. Solvent-free synthesis method of sucrose esters with high monoester content as described in Claim 1, wherein the higher fatty acid esters described in step (1) include any one or at least a combination of methyl stearate, ethyl stearate, isopropyl stearate or butyl stearate.

3. Solvent-free synthesis method of sucrose ester with high monoester content according to Claim 2, wherein the advanced fatty acid ester described in step (1) is methyl-cool stearate.

· Solvent-free synthesis of sucrose esters with a high monoester content as described in any item of Claim 1-3, where the higher fatty acid salts described in step (1) include any one or at least a combination of sodium stearate, calcium stearate, magnesium stearate, potassium stearate or zinc stearate.

· Solvent-free synthesis method of sucrose ester with high monoester content as described in Claim 4, where the higher fatty acid salt described in step (1) is potassium stearate.

· Solvent-free synthesis method of sucrose ester with high monoester content as described in any of the claims 1-5, where the molar ratio of sucrose to the higher fatty acid ester described in step (1) is 2:5-3:2, preferably 1:1.3-1.3:1.

7. Solvent-free synthesis method of sucrose ester with high monoester content as described in any item of claim 1-6, where the mass of the higher fatty acid salt described in step (1) is 5-25% of the total mass of sucrose and higher fatty acid ester, preferably 7-13%.

· Solvent-free synthesis method of sucrose ester with high monoester content as described in any item of Claim 1-7, where the preheating time described in step (1) is 20-40min.

· Solventless synthesis method of sucrose ester with high monoester content as described in any item of Claim 1-8, where the catalyst in step (2) comprises any one or at least two of potassium carbonate, sodium carbonate, potassium hydroxide or sodium hydroxide, preferably a combination of potassium carbonate and potassium hydroxide or sodium hydroxide;

Preferably, the molar ratio of potassium and/or sodium ions to sucrose in said catalyst is 1: (1-5), preferably 1: (2.2-2.7)

10. Solvent-free synthesis of sucrose esters with a high monoester content as described in either of the claims 1-9, where the reaction described in step (2) is carried out under pressure of 200-2000Pa, preferably 200-1000Pa;

Preferably, the temperature of the reaction in step (2) is 132-138 ° C;

Preferably, the reaction time in step (2) is 0.5-6h, preferably 3.7-6h.

11· Solvent-free synthesis method of sucrose ester with high monoester content as described in any item of claim 1-10, wherein the purification of sucrose ester after the reaction described in step (2) also includes: mixing sucrose ester obtained in step (2) with solvent, adjusting pH to 6-7, adding sedimentation agent, filtering, collecting filtrate, drying, recrystallization, i.e The purified sucrose ester is obtained.

12· Solvent-free synthesis method of sucrose ester with a high monoester content as described in claim 11, where, in the purification step, the solvent includes any one or at least two combinations of water, butanone, n-butanol, tert-butanol or isopropanol, preferably a combination of water and butanone;

Preferably, the volume ratio of said water to butanone is 1: (1-3);

Preferably, the settler comprises calcium chloride;

Preferably, the reagent used in the recrystallization is 90-98% ethanol.

- A solvent-free process for sucrose esters with a high E content

Technical fields

[0001] The embodiment of this application relates to the technical field of sucrose ester synthesis, such as a solvent-free synthesis method of sucrose ester with high monoester content, in particular to a sucrose ester synthesis method without the use of solvent, high monoester content, and good product color.

Background Technology

[0002] Sucrose ester, short for sucrose fatty acid ester, is usually obtained by esterification or transesterification of sucrose and long-chain fatty acid or fatty acid ester. It has hydrophilic sugar group and oleophilic fatty acid side chain at the same time, and is a kind of non-ionic surfactant. Studies have shown that sucrose ester has good emulsifying ability, non-toxic, and easy to be biodegradable, so it is widely used in medicine, cosmetics and food industries. Due to the existence of multiple hydroxyl reaction sites on the structure of sucrose, the reaction product is a mixture of single ester, ester and polyester. Among them, the water solubility of sucrose monoester is better, and it has certain antibacterial activity, which makes the sucrose monoester has high economic value.

[0003] In the process of synthesis of sucrose ester, in order to solve the insolubility of sucrose and fatty acids and their derivatives, most modern industries use strong polar solvents to assist the synthesis of sucrose ester. Solvent method has simple process, mild reaction conditions and high yield of sucrose ester. However, the reaction cost of solvent method is expensive, and the residual solvent is difficult to remove clean, and the product is difficult to meet the standards of medical consumption. The solven-free method can avoid the use of organic reagents well and solve the toxicity problem, but the sucrose ester produced by the solven-free method is generally not high in yield, low in single ester content and dark in color.

[0004] Therefore, how to develop a synthesis method of sucrose ester without the use of solvent, high single ester content, and good product color is an urgent problem for technicians in this field.

Content of invention

[0005] The following is an overview of the topics described in detail in this article. This overview is not intended to limit the scope of protection of the claims.

[0006] This application provides a solvent-free synthesis method of sucrose ester with high monoester content, specifically a method of sucrose ester synthesis without the use of solvents, high monoester content, and good color of the product.

[0007] First, the present application embodiment provides a solvent-free synthesis method of sucrose esters with a high monoester content, which comprises the following steps:

[0008 (1) The sucrose, higher fatty acid ester and higher fatty acid salt are mixed and preheated at 70-90℃ to obtain the mixture

[0009☒] (2) The mixture is mixed with a catalyst and reacts at 120-140℃ to obtain the sucrose ester.

[o010] The high monoester content referred to in this application means that in the synthesized sucrose ester product, the content of sucrose monoester is greater than 30%. [0011] the specific values such as in the 70-90 ℃ 70 ℃. 72 ℃, 75 ℃, 77 ℃, 80 ℃, 82 ℃, 85 ℃, 87 ℃, 90 ℃, etc.

[0012] The specific values in the above 120-140℃ are such as 120℃,122℃, 125℃, 130℃,132℃,135℃, 138 ℃ or 140℃.

[0013] This application chooses to mix sucrose, advanced fatty acid ester and advanced fatty acid salt first, preheat, and then add catalyst because: if sucrose, advanced fatty acid ester, advanced fatty acid salt and catalyst are mixed together, it is not conducive to reaction

Fully carried out, the obtained product color is darker. Moreover, compared with other temperatures, this application chooses to preheat at 70-90℃, which is more conducive to the full progress of the reaction, so that the obtained product color is good. The reaction in step (2) is carried out at 120-140℃, which is conducive to increasing the content of sucrose monoester in the product.

[0014] Preferably, the higher fatty acid esters described in step (1) include any or at least two combinations of methyl stearate, ethyl stearate, isopropyl stearate or butyl stearate, combinations of at least two such as a combination of methyl stearate and ethyl stearate, a combination of ethyl stearate and isopropyl stearate, a combination of isopropyl stearate and butyl stearate, etc., and any other Any combination of means can be preferred for methyl stearate.

[0015] Preferably, the higher fatty acid salts described in step (1) include any one or at least two combinations of sodium stearate, calcium stearate, magnesium stearate, potassium stearate, or zinc stearate, combinations of at least two such as a combination of sodium stearate and t stearate, a combination of calcium stearate and magnesium stearate, a combination of calcium stearate and zinc stearate, and any other combination may be used , preferably potassium stearate.

[0016] Preferably, the molar ratio of sucrose to higher fatty acid esters in step (1) is 2:5-3:2, e.g. 2:5, 1:22:3,1:1.3, 1:1.2, 1:1:1,1:1, 1.1:1, 1.1: 1, 1.2:1, 1.2:1, 1.3:1, etc., preferably 1:1.3-1.3:1.

(step 1) [0017] optimization, referred to the quality of higher fatty acid salt for sugar and senior fatty acid ester 5-25% of the total quality, cases of 15% 7%, 8%, 9%, 10%, 11%, 12%, 13%, 14%, 15%, 18% 20% ☒ 22% 25%, optimization of 7 to 13%.

[0018] Preferably, the preheating time described in step (1) is 20-40min, e.g. 20min.22min,25min,27min 30min, 32min.35min, 37min, 40min, etc.

[0019] The preheating time described in this application is preferably 20-40min, within this range, it is conducive to the full mixing of raw materials, and then to the full progress of the reaction, so that the color of the product is good. If the preheating time is short, it will lead to insufficient mixing and reaction of raw materials, resulting in darker color of the product.

[0020] Preferably, the catalyst in step (2) comprises any one or at least two combinations of potassium carbonate, sodium carbonate, potassium hydroxide or sodium hydroxide, such as a combination of potassium carbonate and potassium hydroxide, a combination of sodium carbonate and potassium hydroxide, a combination of sodium carbonate and sodium hydroxide, etc. Any other combination may be used, preferably potassium carbonate and potassium hydroxide Combination or sodium hydroxide.

[0021] Preferably, the molar ratio of potassium and/or sodium ions in the catalyst to sucrose is 1: (1-5), e.g. 1:1, 1:1.5, 1:2:1:2.1 :2. 3, 1:2.4, 1:2.5, 1:2.6, 1:2.7, 1:3, 1:4, 1:5, etc., preferably 1: (2.2-2.7) o.o

[0022 Preferably, the reaction described in step (2) is carried out at pressures of 200-2000Pa, e.g. 200Pa, 300Pa, 400Pa, 500Pa,600Pa 700Pa, 800Pa.900Pa, 1000Pa, 1400Pa, 1500Pa, 1520Pa 1550Pa, 1570Pa 1600Pa, 1620Pa, 1650Pa, 1670Pa 1700Pa, 1800Pa,2000Pa, etc., preferably 200-1000Pa.

[0023] Preferably, the temperature of the reaction described in step (2) is 132-138 ° C, for example 132 ° C, 133 ° C, 134 ° C, 135 ° C, 136 ° C. 137 ° C, 138 ° C, etc.

[0024] Preferably, the reaction time described in step (2) is 0.5-6h, such as 0.5h, 1h, 1.5h, 2h, 2.5h,.3h 3.5h, 3.7h, 3.7h, 4h, 4.2h, 4.5h, 4.5h, 5.2h, 5.7h, 5.7h, 5.7h, 5.7h, 5.7h, and so on, preferably 3.7-6h.

[0025] Optimally, the reaction of step (2) also includes the purification of sucrose ester, the purification includes: the sucrose ester obtained in step (2) is mixed with a solvent, the pH is adjusted to 6-7, the sedimentation agent is added, the filtrate is collected, drying, recrystallization, and the purified sucrose ester is obtained.

[0026] The specific values in the 6-7 are for example 6, 6.1, 6.2, 6.3, 6.4, 6.5, 6.6, 6.7, 6.8, 6.9.7, etc.

[0027] Preferably, in the purification step, the solvent comprises any one or a combination of at least two of water, butanone, n-butanol, tert-butanol, or isopropyl alcohol, the butyl ketone, n-butanol, tert-butanol, and isopropyl alcohol, all referring to anhydrous reagents, the combination of at least two of the said, such as a combination of water and butanone, a combination of water and tert-butanol, a combination of water and isopropyl alcohol, etc., and any other combination May, preferably for the combination of water and butanone.

[0028] When a combination of water and butanone is selected for recrystallization, the color of the purified product is the best.

[0029] Preferably, the volume ratio of the water to the butanone is 1: (1-3), such as 1:1, 1:1.5, 1:2.5, 1:3, etc.

[0030] Preferably, the settler comprises calcium chloride.

[0031] Preferably, the reagent used in the recrystallization is 90-98% ethanol, and the 90-98% refers to the percentage content of anhydrous ethanol by volume, such as 90%.91%, 92%, 93%, 94%, 95%, 96%.97%, 98%, etc.

[0032] The range of values described in this application includes not only the point values listed above, but also any point values in between the above value ranges that are not listed. Due to space limitations and for reasons of brevity, this application does not enumerate the specific point values covered by the range.

[0033] In comparison with related techniques, this application has the following beneficial effects:

[0034] The synthesis method involved in the embodiment of the present application adopts solven-free transesterification, which forms a co-melting state of sucrose with higher fatty acid ester, higher fatty acid salt and catalyst in a certain proportion at high temperature, and catalyzes the synthesis of sucrose ester under reaction conditions favorable to kinetics. In the reaction process, sucrose reacts with long-chain fatty acid ester to form a single ester. When the external energy supply is greater than the esterification activation energy of the single ester, the single ester participates in the reaction to form a diester, and the same can be used to generate multiple esters. Therefore, by controlling the external conditions, the reaction can be carried out to the maximum extent in the direction of the formation of monomers. (1) The synthetic method avoids the use of solvents, solves the toxicity problem, and enables the product to meet the standards for medical consumption. (2) The synthetic reaction of sucrose ester is a balanced reaction. This application optimizes the steps and specific parameters to maximize the reaction in the direction of the generation of sucrose monoester. The sucrose monoester in the product can reach more than 30% purity without purification, and can reach more than 70% purity after purification. (3) The embodiment of this application through the optimization of each step and specific parameters, so that the product color is good, to solve the problem of deep color of the product prepared by the relevant technology. (4) The embodiments of this application have simple steps (synthesis steps and purification steps are very simple), which is convenient for industrial production and has important application value.

[0035] After reading and understanding the detailed description, other aspects can be understood

Specific implementation

[0036] In order to further elaborate the technical means adopted in the present application and their effects, the technical scheme of the present application is further described below in combination with the preferred embodiment of the present application, but the present application is not limited to the scope of the embodiment.

[0037] The sucrose used in the following embodiments is sucrose obtained by grinding it with a mill and passing through a 100-mesh screen. The catalysts are all in powder state.

[0038 Embodiments

[0039 The present embodiment provides a method for the synthesis of sucrose esters by the following steps:

[0040 Sucrose, methyl stearate, and potassium stearate were added to a three-way bottle, stirred at 80℃ for 30min, and then catalyst (t carbonate and potassium hydroxide mixed at 1:2 molar ratio) was added to it, and the temperature was raised to 135C, and the reaction was carried out at 1.6kPa at 400rpm stirring speed for 4h to obtain the product.

[0041] Among them, the molar ratio of sucrose to methyl stearate was 1:1; Potassium stearate is 10% of the total weight of sucrose and methyl stearate; The molar ratio of potassium ions to sucrose in the catalyst is 2:5.

[0042] Embodiments 2-4

[0043] Embodiments 2-4 provide three methods for the synthesis of sucrose esters, which differ from Embodiment 1 only in that methyl stearate is successively replaced by equal molar amounts of ethyl stearate, isopropyl stearate, and butyl stearate, with reference to Embodiment 1 for other conditions.

[0044] Embodiments 5-8

[0045] Embodiments 5-8 provide four methods for the synthesis of sucrose esters, which differ from Embodiment 1 only in that potassium stearate is replaced sequentially with sodium stearate, calcium stearate, magnesium stearate, and zinc stearate of equal mass, with reference to Embodiment 1 for other conditions

[0046] Embodiments 9-12

[0047] Embodiments 9-12 provide four methods for the synthesis of sucrose esters, which differ from Embodiment 1 only by replacing the catalyst in turn with equal molar quantities of potassium carbonate, potassium hydroxide, sodium carbonate, and sodium hydroxide, with reference to Embodiment 1 for other conditions.

[0048] Embodiments 13-16

[0049] Embodiments 13-16 provide four methods for the synthesis of sucrose esters, which differ from Embodiment 1 only in that the molar ratio of sucrose to methyl stearate is 3:2, 2:3, 1:2:5, and other conditions refer to Embodiment 1.

[0050] Embodiment 17-19

[0051] Embodiment 17-19 provides three methods for the synthesis of sucrose esters, which differ from Embodiment 1 only in that the mass of potassium stearate is 5%, 15%, and 20% of the total mass of sucrose and methyl stearate, in turn, with reference to Embodiment 1 for other conditions.

[0052] Embodiments 20-23

[0053] Embodiment 20-23 provides four synthesis methods of sucrose esters, which differ from Embodiment 1 only in that the molar ratio of potassium ions to sucrose in the catalyst is 1:53:10, 1:2:3:5, and other conditions refer to Embodiment 1.

[0054] Embodiments 24-27

[0055] Embodiments 24-27 provide four synthesis methods of sucrose esters, which differ from Embodiments 1 only in that "temperature rise to 135 ° C" is sequentially changed to temperature rise to 120 ° C, 125 ° C, 130 ° C, 140 ° C, and other conditions are referred to Embodiments 1.

[0056] Embodiments 28-31

[0057] Embodiments 28-31 provide four synthesis methods of sucrose esters, which differ from Embodiments 1 only in that the reaction time is successively replaced by "4h" with 0.5h,.2.5h, 3.5h, 6h, and other conditions refer to Embodiments 1.

[0058] on ratio 1

[0059] This ratio provides a method for the synthesis of sucrose ester, which differs from Embodiment 1 only in the absence of potassium stearate, all other conditions being the same.

[0060] Test Example 1- Evaluation of the purity of the crude product:

[0061] The products prepared in Example 1-31 were ground to powder and the contents of sucrose mono-ester, sucrose diester, sucrose and stearate were detected using WATERS UPC-SQ detector 2, as shown in Table 1-Table 8.

[0062]

Table 1

[0063]

组别	反应原料	蔗糖单酯	标准差	蔗糖二酯	标准差	蔗糖	标准差
实施例1	硬脂酸甲酯	36.3%	0.2%	21.1%	0.1%	10.7%	0.6%
实施例2	硬脂酸乙酯	1.9%	0.2%	＜1%	/	29.0%	1.7%
实施例3	硬脂酸异丙酯	＜1%	/	＜1%	/	27.5%	0.4%
实施例4	硬脂酸丁酯	＜1%	/	＜1%	/	27.6%	1.2%

[0064] As can be seen from the results of Table 1, when methyl stearate is selected as the synthesis method involved in this application, the synthesis effect is significantly better than that of other types of advanced fatty acid ester, and the content of sucrose monoester and sucrose diester in the product is high.

[0065] Table 2

[0066]

组别	类型	蔗糖单酯	标准差	蔗糖二酯	标准差	蔗糖	标准差	硬脂酸甲酯含量	标准差
实施例1	硬脂酸钾	36.3%	0.2%	21.1%	0.1%	10.7%	0.6%	7.4%	0.5%
实施例5	硬脂酸钠	17.0%	0.2%	36.2%	0.5%	23.3%	2.7%	5.6%	0.1%
实施例6	硬脂酸钙	5.6%	0.2%	14.2%	0.1%	26.3%	0.5%	9.5%	1.5%
实施例7	硬脂酸镁	11.5%	0.3%	11.6%	0.1%	33.5%	3.4%	12.2%	0.2%
实施例8	硬脂酸锌	10.6%	0.0%	11.1%	0.3%	29.0%	9.1%	12.3%	0.7%

[0067]

[0068] As can be seen from the results of Table 2, when potassium stearate is used as the synthesis method involved in this application, the synthesis effect is better and the content of sucrose monoester in the product is higher than that of other types of higher fatty acid salts.

[0069] Table 3

[0070]

组别	催化剂	蔗糖单酯	标准差	蔗糖二酯	标准差	蔗糖	标准差	硬脂酸甲酯含量	标准差
实施例1	碳酸钾+氢氧化钾	36.3%	0.2%	21.1%	0.1%	10.7%	0.6%	7.4%	0.5%
实施例9	碳酸钾	10.8%	0.8%	29.5%	0.6%	12.1%	0.4%	7.0%	0.5%
实施例10	氢氧化钾	25.6%	2.8%	29.9%	0.1%	10.2%	0.4%	7.1%	1.5%
实施例11	碳酸钠	16.6%	0.2%	26.5%	0.2%	32.3%	1.2%	3.6%	0.6%
实施例12	氢氧化钠	32.5%	0.7%	21.6%	0.5%	22.4%	0.7%	<1%	/

[0071] It can be seen from the results of Table 3 that the synthesis method involved in this application has better effect when the combination of potassium carbonate and potassium hydroxide is used as catalyst, and the content of sucrose monoester in the product is higher. When sodium hydroxide is used, the high content of sucrose monoester can be reached to more than 32%.

[0072] Table 4

组别：Group.**摩尔比：** Molby. 蔗糖酯/蔗糖单酯：Sucrose ester.标准差： Standard deviation. 蔗糖二酯：Sucrose diester. **蔗糖：** sucrose.硬脂酸甲酯含量：The content of methyl stearate.**类型：**Type.催化剂：Catalyst. 实施例：An embodiment. 反应原料：Reaction material. **添加量：**Addition amount

[0073]

组别	蔗糖/硬脂酸甲酯	蔗糖单酯	标准差	蔗糖二酯	标准差	蔗糖	标准差	硬脂酸甲酯含量	标准差
实施例1	1:1	36.3%	0.2%	21.1%	0.1%	10.7%	0.6%	7.4%	0.5%
实施例13	3:2	18.7%	0.3%	8.8%	0.2%	30.0%	3.8%	8.5%	0.4%

[0074]

实施例14	2:3	19.7%	1.5%	15.9%	0.8%	17.7%	2.0%	11.3%	0.6%
实施例15	1:2	15.5%	0.3%	22.6%	0.4%	7.6%	0%	6.3%	0.2%
实施例16	2:5	10.7%	0.7%	18.3%	1.7%	4.3%	0.2%	8.3%	0.4%

[0075] from the results of Table 4, the molar ratio of sucrose to higher fatty acid esters in this application method is preferably 1:1.

[0076] As can be seen Table 5

[0077]

组别	添加量	蔗糖单酯	标准差	蔗糖二酯	标准差	蔗糖	标准差	硬脂酸甲酯含量	标准差
实施例1	10%	36.3%	0.2%	21.1%	0.1%	10.7%	0.6%	7.4%	0.5%
实施例17	5%	16.1%	0.5%	30.6%	0.2%	28.2%	2.7%	6.7%	0.5%
实施例18	15%	24.8%	0.7%	32.3%	0.2%	19.4%	6.5%	4.7%	0.4%
实施例19	20%	24.3%	0.2%	36.1%	0.4%	15.9%	4.0%	4.9%	0.8%
对比例1	0	4.3%	0.2%	8.8%	1.9%	27.2%	0.2%	14.5%	0.5%

[0073] As can be seen from the results of Table 5, the yield of sucrose mono-ester can be greatly improved by adding higher fatty acid salt to the synthesis method involved in this application. A better synthesis effect can be obtained if the specific quality of higher fatty acid salt is 10-25% of the total weight of sucrose and higher fatty acid ester, and 10% is further preferred.

[0079] Table 6

[0080]

组别	摩尔比	蔗糖单酯	标准差	蔗糖二酯	标准差	蔗糖	标准差	硬脂酸甲酯含量	标准差
实施例1	2:5	36.3%	0.2%	21.1%	0.1%	10.7%	0.6%	7.4%	0.5%
实施例20	1:5	14.4%	0.9%	15.6%	0.4%	19.0%	4.1%	12.0%	0.9%
实施例21	3:10	11.2%	0.3%	19.6%	0.2%	24.0%	1.6%	10.1%	1.8%

[0081]

实施例22	1:2	19.4%	0.4%	17.4%	0.1%	24.4%	3.0%	11.1%	1.7%
实施例23	3:5	22.5%	0.9%	15.3%	0.3%	26.3%	1.8%	10.6%	0.5%

[0082] It can be seen from the results of Table 6 that the amount of catalyst used in the synthesis method involved in this application is measured by the molar ratio of potassium ion to sucrose, and more sucrose monoester and sucrose diester can be obtained under the condition of 1: (1.5-2.5), and 2:5 is further preferred.

[0083] Table 7

[0084]

组别	温度	蔗糖单酯	标准差	蔗糖二酯	标准差	蔗糖	标准差	硬脂酸甲酯含量	标准差
实施例1	135℃	36.3%	0.2%	21.1%	0.1%	10.7%	0.6%	7.4%	0.5%
实施例24	120℃	<1%	/	<1%	/	47.4%	2.4%	18.1%	0.5%
实施例25	125℃	6.3%	1.1%	5.2%	1.7%	24.2%	0.1%	17.2%	0.3%
实施例26	130℃	19.1%	0.3%	27.9%	0.1%	20.6%	3.4%	6.2%	0.9%
实施例27	140℃	20.7%	0.1%	22.8%	0.4%	17.9%	1.5%	5.5%	0.1%

[0085] As can be seen from the results of Table 7, the choice of reaction temperature also has a very important influence on the synthesis method involved in this application, and the best effect can be obtained when the reaction is carried out at about 135°C.

[0086] Table 8

[0087]

组别	时间	蔗糖单酯	标准差	蔗糖二酯	标准差	蔗糖	标准差	硬脂酸甲酯含量	标准差
实施例1	4 h	36.3%	0.2%	21.1%	0.1%	10.7%	0.6%	7.4%	0.5%
实施例28	0.5 h	10.3%	0.2%	5.2%	0.0%	38.8%	5.7%	17.0%	0.5%
实施例29	2.5 h	22.3%	0.5%	31.7%	0.9%	23.3%	0.7%	2.0%	0.3%
实施例30	3.5 h	28.3%	0.7%	34.1%	0.8%	22.6%	1.7%	<1%	/
实施例31	6 h	30.9%	0.1%	31.7%	2.7%	20.0%	2.3%	<1%	/

[0088] As can be seen from the results of Table 8, the choice of reaction time also has a very important impact on the synthesis effect involved in this application, and the reaction time of 3.5-6h can obtain a better effect.

[0089] Purification embodiments 1

[0090] This purification embodiment provides a method for the synthesis of sucrose ester in the following steps:

[0091] Take 10g of the product prepared in Embodiment 1, place it in 200mL beek, add 25mL water and 50mL butanone, stir at a slight temperature until all dissolved, adjust pH to 6.5 with 96% phosphoric acid, then add CaC1,0.7g, stir at 55℃ for 40min, white precipitate appears, filter out the precipitate, and then vacuum dry the filtrate to obtain white solid After the filtrate was recrystallized with 95% ethanol, purified sucrose ester was obtained after drying.

[0092] Purification embodiments 2-4

[0093] Purified embodiments 2-4 provide four synthesis methods of sucrose esters. The difference between the method and purified embodiments 1 is only that "1.6kPa" in Embodiments 1 is replaced by 1000pa, 500pa, 200pa in turn. Other conditions refer to Embodiments 1 and purified Embodiments 1.

[0094] Evaluation of the purity of the product obtained after purification in Example 2:

[0095] The purified products from Embodiments 1-4 were ground to powder and the content of sucrose monester in the products was detected by WATERS UPC-sQ detector 2. The results were shown in Table 9.

[0096] Table 9

[0097]

组别	压力	蔗糖单酯纯度	标准差
纯化实施例1	1.6kPa	70.8	0.8%
纯化实施例2	1000pa	73.6	0.9%
纯化实施例3	500pa	75.5	0.8%
纯化实施例4	200pa	74.3	0.6%

[0098] The results showed that when the pressure was too large, the reactants could not react completely, resulting in the ideal purification result unable to be achieved by simple purification steps, which brought trouble to the purification steps. When the pressure is 200-1000pa, the reactants can react completely. Therefore, the purity of sucrose monoester can be improved by simple purification steps.

[0099] Applicant, the present application describes a solvent-free synthesis method of sucrose ester with high monoester content through the above embodiments and purification embodiments, but the present application is not limited to the above embodiments and purification embodiments, that is, it does not mean that the present application must rely on the above embodiments to be implemented. The technical personnel in the technical field of the application shall understand the present application

Any improvement, the equivalent replacement of the raw materials of the applied products and the addition of auxiliary ingredients, the choice of specific methods, etc., all fall within the scope of protection and disclosure of this application.

[0100] The above describes in detail the preferred implementation of this application, however, this application is not limited to the specific details of the above implementation, within the scope of the technical concept of this application, a variety of simple variations of the technical scheme of this application can be carried out, and these simple variations belong to the scope of protection of this application.

[0101] In addition, it should be noted that each specific technical feature described in the above specific embodiments can be combined in any suitable way without contradiction. In order to avoid unnecessary duplication, this application will not specify the various possible combinations separately.