Research Report

(Yufeng Hui)

20240403

In these two days, I have conducted a data search, analysis and evaluation of the three companies of Synose, Gaotong, Adana, and have a more comprehensive understanding of the three companies **（Part1. And Part2.）**. At the same time, I looked up all the patents of these three companies in China, totaling 61. Among them, there are 10 items related to the synthesis of sucrose esters. Finally, I studied the three patents of Synose and expressed some of my views **（Part3.）**.

In the next two days, I am going to study and analyze other 7 patents of Gaotong and Adana (expected to be completed by Friday afternoon), while looking for other domestic company information related to sucrose ester synthesis.

Part 1. Company Overview:

Gaotong: produces sucrose fatty acid esters for food additives. The product line is relatively single

Synose: production of all types of sucrose fatty acid esters and upstream and downstream products.

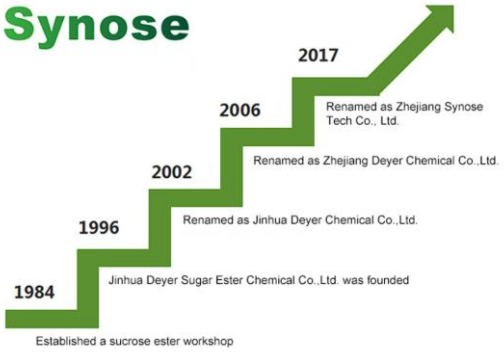
Adana: sucrose fatty acid ester series products have passed Halal certification; at present, the main products are milk fat products.

Company	Company size	Product quality	Related patent
Gaotong	small	average	3
Synose	large	best	3
Adana	medium	average	4

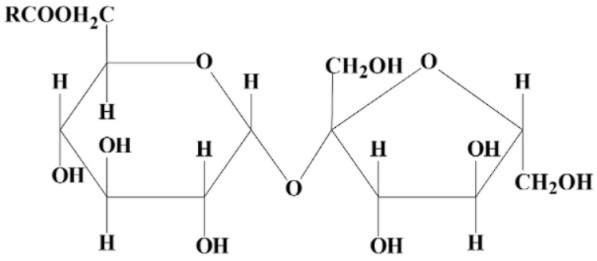
Part 2. Detailed analysis:

Synose:

At present, it is a sucrose ester manufacturer with the largest production scale and the most complete variety in China.



Main products: sucrose stearate, sucrose palmitate sucrose. Fatty acid esters are made from natural sucrose and fatty acids, which come from vegetable oils. It was synthesized by solvent-free method and refined by purification process. Sucrose molecules contain eight hydroxyl groups that can combine with fatty acids to form sucrose esters ranging from mono-fatty acids to eight-fatty acids.

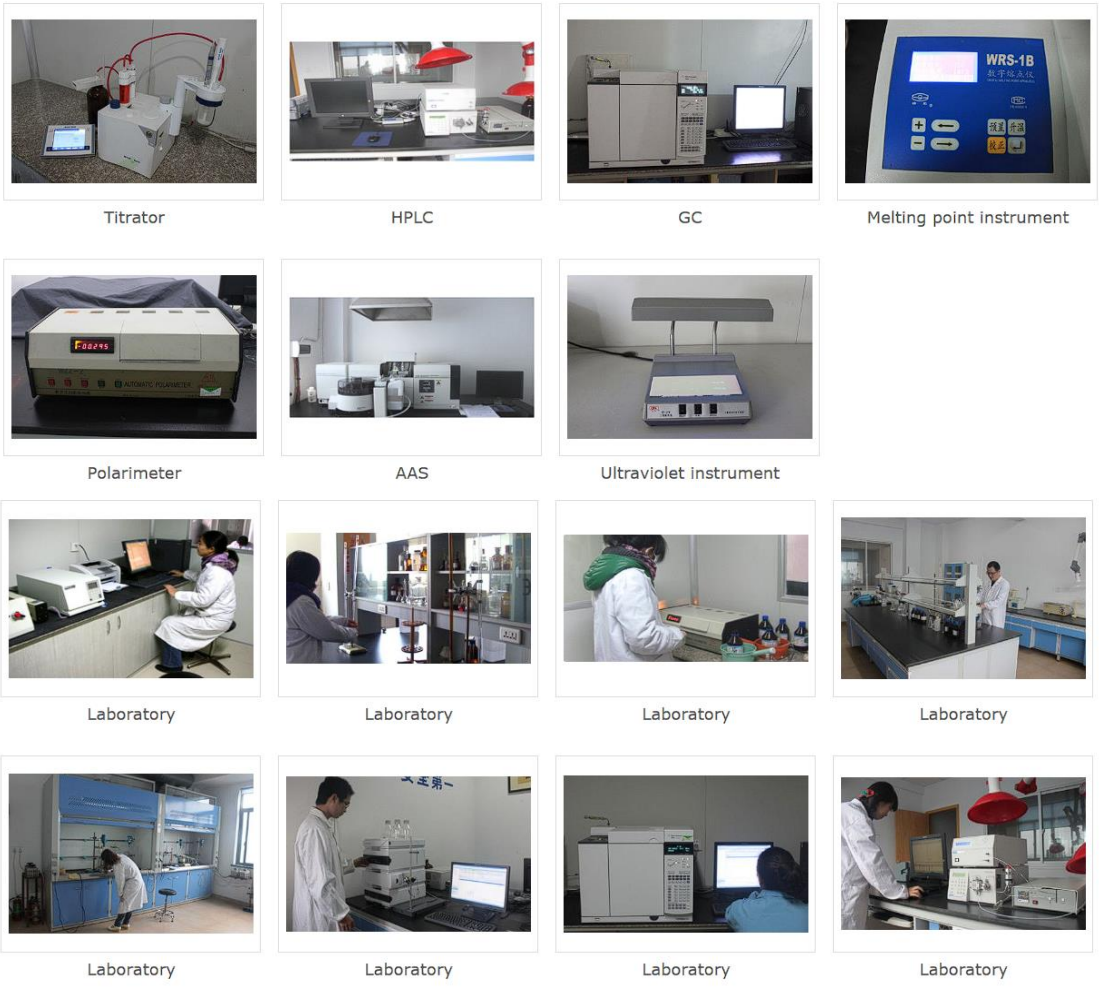


Product indicators: with high product quality, the world's leading level

ITEM	INTERNAL CONTROL STANDARD	China	JAPAN	EU	JECFA	CP	USP	EP
Assay,% ≥	80	—	—	80	80	—	—	—
Acid value(mg KOH/g)≤	5.0	6.0	6.0	—	6.0	5.0	6.0	6.0
Free fatty acid,%≤	—	—	—	3.0	—	—	—	—
Free Sucrose, %≤	5.0	10.0	5.0	5.0	5.0	4.0	4.0	4.0
Water, %≤	3.0	4.0	4.0	—	—	3.0	4.0	4.0
Ignition residue, % ≤	1.5	4.0	2.0	2.0	2.0	1.5	1.5	1.5
Arsenic, mg/kg ≤	1	1	3	3	—	1	—	—
Heavy metals(as Pb), mg/kg ≤	—	—	—	—	—	20	—	—
Lead, mg/kg≤	2	2	2	2	2	—	—	—
Dimethylformamide, mg/kg ≤	—	—	1.0	1.0	1.0	—	—	—

Cooperative institutions: Zhejiang University, Zhejiang normal University

Research and development: the laboratory is relatively simple and the equipment is relatively old. I guess the company has focused on production and R & D in recent years.



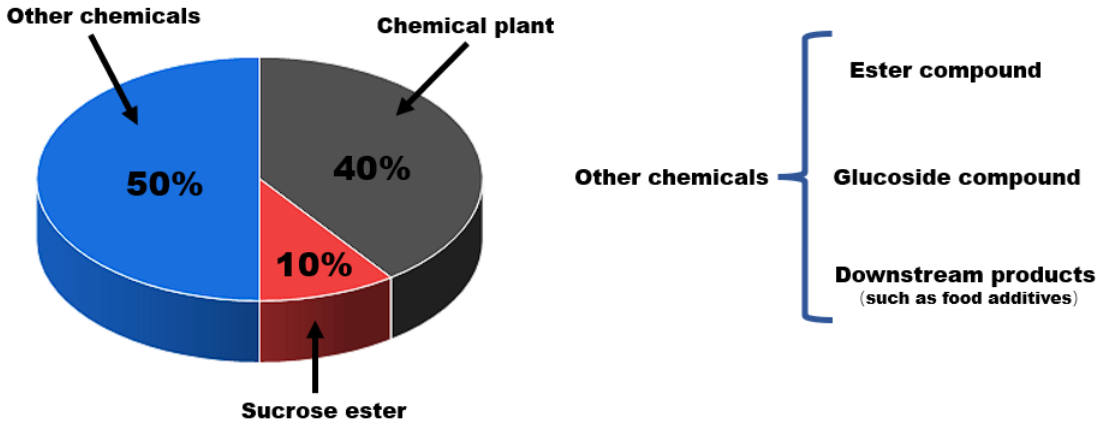
Titrator | HPLC | GC | Melting point instrument

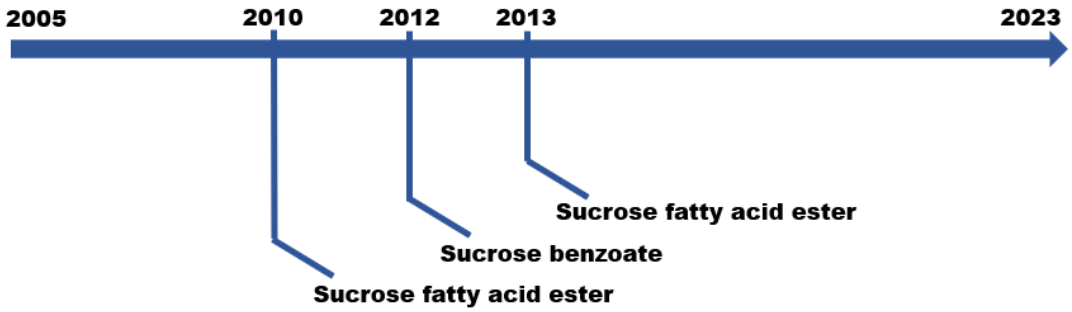
Polarimeter | AAS | Ultraviolet instrument

Laboratory | Laboratory | Laboratory | Laboratory

Laboratory | Laboratory | Laboratory | Laboratory

Patents (2005-2023): A total of 30 items. Among them, there are 12 patents related to device design, 3 patents related to sucrose ester and 15 patents related to other chemicals.





Gaotong：

Product: the product line is relatively single

Sucrose Fatty Acid Ester

High-content Sucrose Fatty Acid Ester

Sucrose fatty acid esters as raw materials…

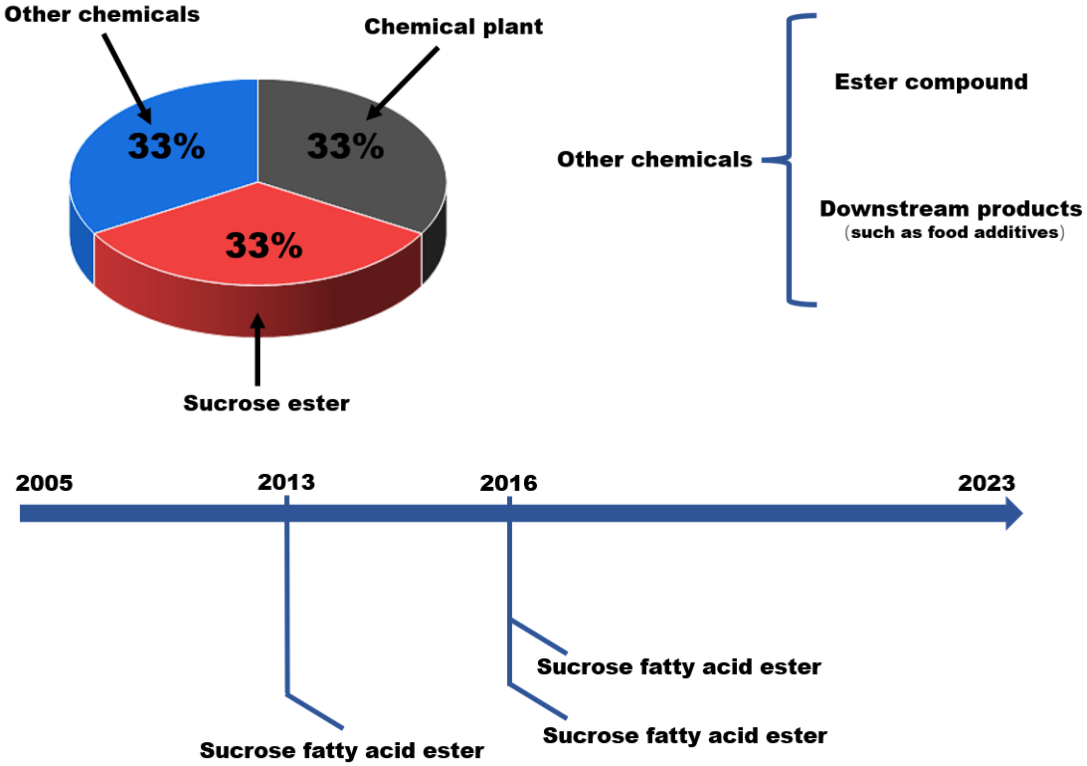
Product index: the quality is lower than Synose, consistent with Chinese standard (GB1886.27-2015)

Item	Index
Acid value (KOH)/(mg/g) ≤	6.0
Free sucrose, w/% ≤	10.0
Water, w/% ≤	4.0
Ignition residue, w/% ≤	4.0
Total arsenic (As), (mg/kg) ≤	1.0
Lead (Pb), (mg/kg) ≤	2.0

Business model: OEM contract manufacturing, including packaging products. OEM drinks, food, etc.

Research and development: it is not found that the company has its own R & D center.

Patents (2013-2023): a total of 9 items. Among them, there are 3 patents related to device design, 3 patents related to sucrose ester and 3 patents related to other chemicals.



Adana:

Products: the product line is very rich. According to news reports, now the company's main products are dairy products (cheese) and cream products.

FIC2024圆满收官，柳爱科技展后回顾，期待与您来年再见

第二十七届中国国际食品添加剂和配料展览会暨第三十三届全国食品添加剂生产应用技术展示会（FIC2024）完美落下帷幕。**Enzymatic cream, enzymatic butter, enzymatic cheese**

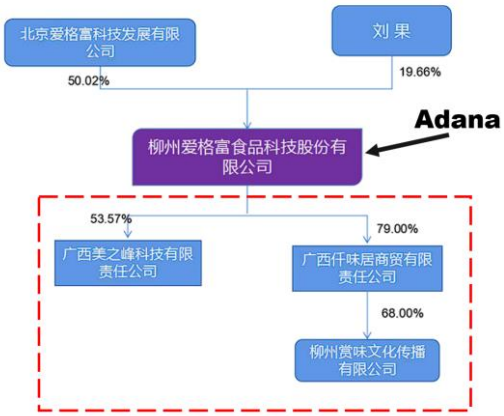
本次展会，柳爱科技团队携酶解奶油、酶解黄油、酶解奶酪三大酶解乳品系列产品再次亮相，通过丰富多样的应用案例展示了EMI 酶解乳品—浓缩天然风味定制、差异化方案。

展会现场客人络绎不绝、热闹非凡，众多国内外客户及行业专业人士纷纷驻足交流，并与柳爱科技团队深入洽谈合作事宜。

Product index: the quality is lower than Synose, consistent with Chinese standard (GB1886.27-2015)

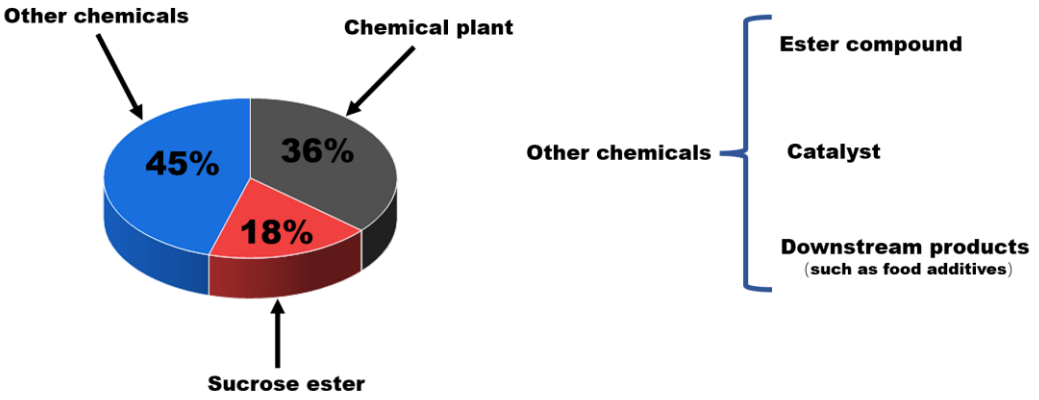
Item		Parameter
Acidity / (as of KOH mg/g)	≤	6.0
Free sucrose / (%)	≤	10.0
Loss on drying / (%)	≤	4.0
Burning residue / (%)	≤	4.0
As / (%)	≤	1.0
Pb / (%)	≤	2.0

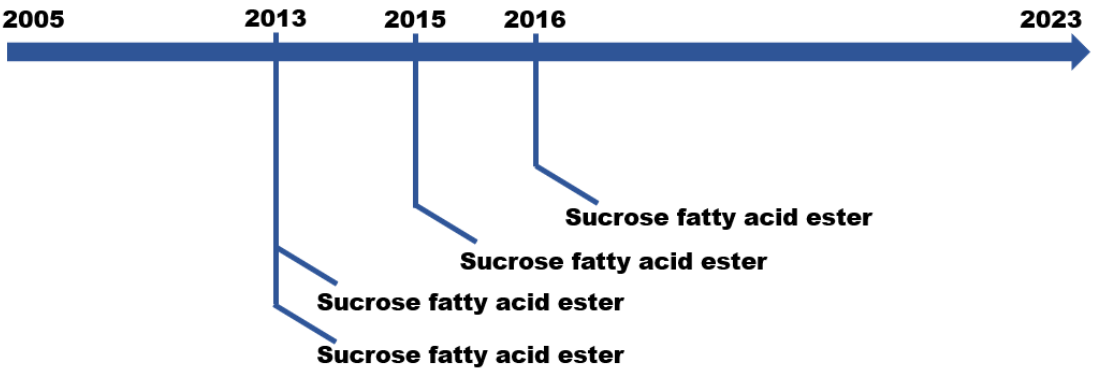
Business model: according to Adana's annual report, the company is the main company with three subsidiaries. In the follow-up, I am going to study the operating products of three subsidiaries.



Research and development: has its own independent laboratory for product research and development, a number of product certificates. Adana's product is the only one of the three companies that has passed halal certification.

Patents (2005-2023): A total of 22 patents. Among them, there are 8 patents related to device design, 4 patents related to sucrose ester and 10 patents related to other chemicals.





Part 3. Abstract of related patent（Synose）:

1. A method for purification and separation of sucrose fatty acid esters CN 104004033 B (Link to ***Synose01***)

The traditional purification method of sucrose esters is to saponify sucrose esters, then precipitate them in sodium chloride solution to get solution and precipitation, and then get different sucrose esters after post-treatment. However, the traditional purification methods are easy to hydrolyze sucrose esters and produce a lot of chlorine-containing wastewater. The sub-patent provides an efficient and environment-friendly method for purification and separation of sucrose fatty acid esters, which has the advantages of simple process, few side reactions, high product content and recovery, and can simultaneously complete purification and separation of sucrose monoester and diester to obtain products with different sucrose monoester content, and the sucrose in the crude sucrose ester can be recovered and applied, and the amount of waste is less and easy to be treated.

The steps of purification and separation of sucrose fatty acid esters are as follows:

A, the crude sucrose ester is dissolved and dispersed in the organic solvent A, and the crude sucrose ester solution is obtained after filtering and recovering sucrose; the crude sucrose ester mainly contains sucrose ester, sucrose and fatty acid potassium salt or sodium salt; the organic solvent An is selected from one or any of the following combinations: ethyl acetate, butanone, n-butanol. B, the crude sucrose ester solution was mixed with alkaline earth metal salts at 25-80 ℃ for re-decomposition, and then filtrate *A* and solid *B* were obtained by solid-liquid separation at 5-80 ℃. C. Sucrose ester product *A* was obtained from filtrate *A* by washing, distillation and drying. D, solid *B* and organic solvent *B* were extracted at 50-80 ℃. The extract was washed, distilled and dried to obtain sucrose ester product *B*.

In my opinion, **step B is more critical**. Alkaline earth metal salts were added to the crude solution of sucrose esters and reacted with fatty acid salts (potassium or sodium fatty acids) to form insoluble fatty acid alkaline earth metal salts and another alkali metal salts (potassium or sodium salts). They form coprecipitates with sucrose esters, while sucrose monoesters form coprecipitates more easily than sucrose diesters. Therefore, sucrose monoesters are enriched in the coprecipitate to achieve the purpose of separating sucrose monoesters and sucrose diesters. Further, the alkaline earth metal salt can be selected from one or any of the following combinations: magnesium sulfate, calcium chloride and barium chloride, and the amount of the alkaline earth metal salt is 1-1.05 times the amount required to fully react with fatty acid salts in crude sucrose esters. The reaction time of re-decomposition is preferably 10-100 minutes. The solid-liquid separation is preferably carried out at 30-65 ℃.

100g
Crude products of sucrose fatty acids,
500ml three-neck bottle

↓ EA 250ml
70℃, Stir, 30min

↓ 60℃
15g Magnesium sulfate aqueous solution
(5g $MgSO_4$, 10gH_2O)
Stir, 1h

Get liquid A and solid B

A

↓ Wash by water
(60ml X 3)
Spin drying

Sucrose fatty acids A
18.5g (W=94.2%)
The content of sucrose monoester is 28.5%.

B

↓ EA 300ml
60℃, extract
Wash by water (60ml X 3)
Spin drying

Sucrose fatty acids B
27.8g (W=96.1%)
The content of sucrose monoester is 58.2%.

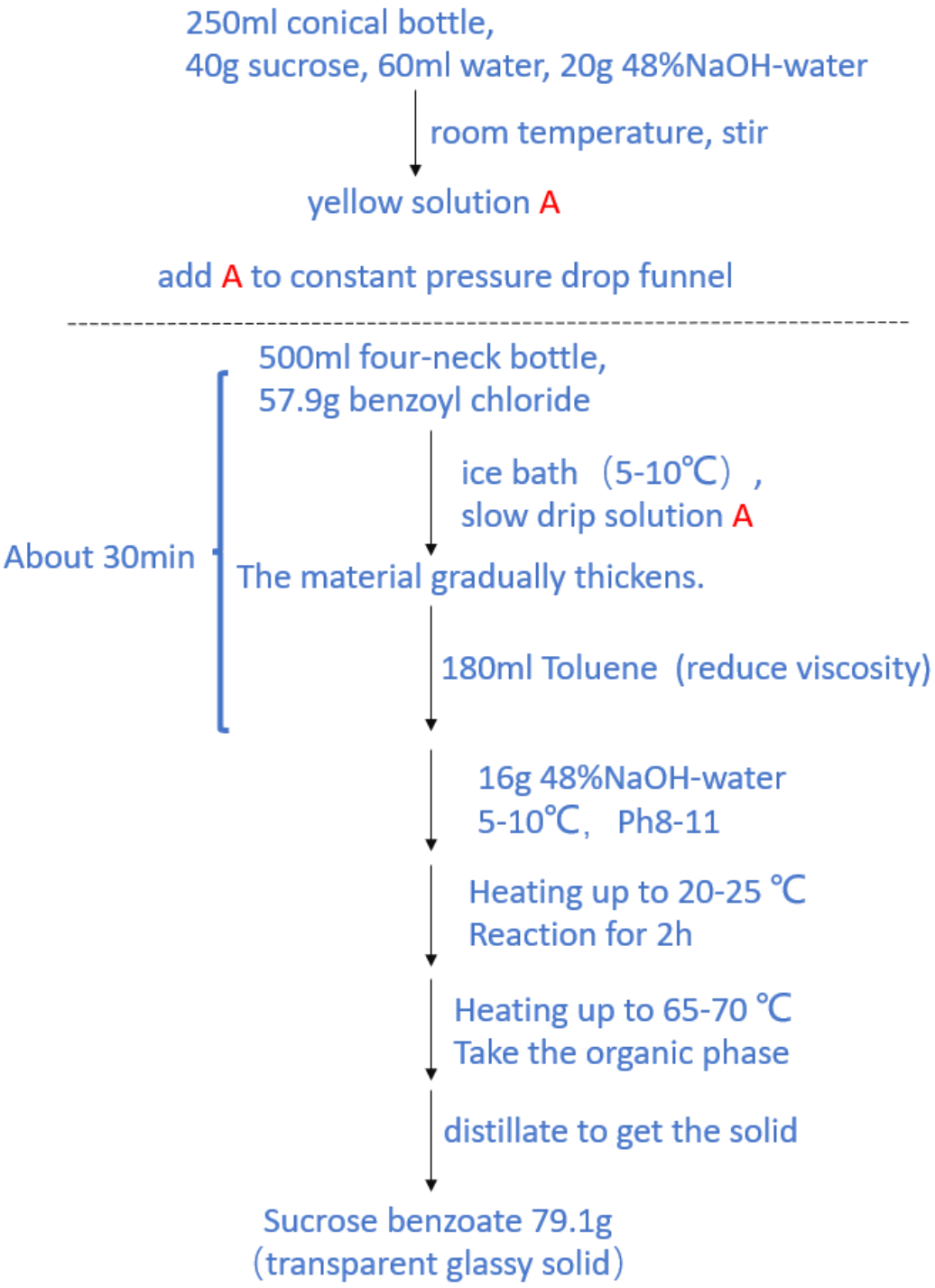
2. A method for preparing sucrose benzoate
CN 102731583 B (Link to *Synose02*)

The traditional method can only produce sucrose benzoate with an average degree of substitution of 6: 8, but not sucrose benzoate with an average degree of substitution of 3: 6. In the traditional method, the utilization rate of raw materials (sucrose and benzoyl chloride) is low, the yield of the product is low, and the COD of wastewater is high. The traditional scheme has some disadvantages such as large amount of waste water per unit product, high COD of waste water, large unit consumption of solvent and high cost.

The patent provides a simple, effective and stable method for producing sucrose benzoates with a specific degree of substitution with an average degree of substitution between 3 and 6. This method has the advantages of high yield, low unit consumption of solvent, low residual rate of solvent in waste water, less waste water per unit product and low COD of waste water, and has little impact on the environment, so it is suitable for industrial production.

The patented method: Sucrose reacts with sodium hydroxide An in water to obtain sodium sucrose alcohol aqueous solution; under continuous stirring, the sodium sucrose alcohol aqueous solution is dripped into benzoyl chloride for reaction When the temperature of the reaction solution is 0: 15 ℃, the reaction system thickens, and when the reaction system is too thick to stir, toluene is added to the reaction system to reduce the viscosity of the reaction system. After the sodium sucrose alcohol solution is added, the aqueous solution of sodium hydroxide B is added, and the temperature of the reaction solution is 0: 15 ℃, the pH value is 8: 11, the temperature of the reaction solution is 20 ~ 25 ℃, and the reaction time is 1 h (preferably 2 h). Then heat up to 65-70 ℃, separate the water layer, wash the organic layer to neutral with a small amount of water, then distillation to recover toluene, the residue is sucrose benzoate. The mass ratio of sucrose, benzoyl chloride and total sodium hydroxide is 1, 3, 6, 6 and 6.2. The average degree of substitution of the sucrose benzoate is 3-6.

In my opinion, **Stickiness is more critical**. With the continuous progress of the reaction, the viscosity of the reaction system increases. This increases the difficulty of stirring and mixing raw materials. Therefore, it is necessary to add toluene to reduce the viscosity of the reaction system, facilitate the full mixing of raw materials, and prevent excessive substitution caused by uneven dispersion of raw materials. The reaction system is monitored during the reaction process. According to the needs of the reaction system, toluene is added when the reaction system is so thick that it is difficult to stir. Usually, the amount of toluene added in the reaction system is 3 to 8 times the mass of sucrose.


250ml conical bottle,
40g sucrose, 60ml water, 20g 48%NaOH-water
room temperature, stir
yellow solution A
add A to constant pressure drop funnel
500ml four-neck bottle,
57.9g benzoyl chloride
ice bath （5-10℃）,
slow drip solution A
About 30min
The material gradually thickens.
180ml Toluene （reduce viscosity)
16g 48%NaOH-water
5-10℃, Ph8-11
Heating up to 20-25 ℃
Reaction for 2h
Heating up to 65-70 ℃
Take the organic phase
distillate to get the solid
Sucrose benzoate 79.1g
(transparent glassy solid)

3. A method for purification of Sucrose Fatty acids
CN 101781340 B (Link to *Synose03*)

Molecular distillation is a special liquid-liquid separation technology, which is different from traditional distillation by the separation principle of boiling point difference, but by the difference of the average free path of different molecules. Molecular distillation technology has incomparable advantages over other separation technologies: 1. Low operating temperature (far below boiling point), high vacuum (no load ≤ 1Pa), short heating time (seconds), high separation efficiency, etc., especially suitable for the separation of substances with high boiling point, heat sensitivity and easy oxidation; 2. It can effectively remove low molecular substances (deodorization), heavy molecular substances (decolorization) and impurities in the mixture. 3. The separation process is a physical separation process, which can well protect the separated substances from pollution, especially to maintain the original quality of the natural extract. 4. The degree of separation is high, which is higher than that of traditional distillation and ordinary thin film evaporators.
The patent provides a method for purifying sucrose fatty acid esters using molecular distillation technology. In this method, fatty acids, unreacted fatty acid methyl esters, monoglycerides and fatty acid propylene glycol esters were removed by molecular distillation to obtain sucrose esters purified by molecular distillation. The method has the advantages of good effect, simple process and convenient recovery and utilization of by-products.
The purification method described in the patent includes the following steps. The crude sucrose fatty acid ester was distilled by secondary molecular distillation. The temperature of the first stage distillation was 100 ~ 140C, the distillation pressure was 600~800Pa, and the temperature and pressure of the second stage distillation were 100-150C and 0.01-l Pa, respectively. The heavy phase obtained was the purified sucrose fatty acid ester product. In the process of molecular distillation operation, the distillation flow rate needs to be adjusted according to the production capacity of molecular distillation equipment, which is a well-known operation method for technicians in the field, and appropriate adjustments are made according to the difference of the equipment. In the embodiment of the invention, the flow rate of primary distillation is controlled in 0.05~2kg/h.
In my opinion, **Pre-treatment is more critical**. [before the purification method, it is best to acidify the crude product of sucrose fatty acid ester in the presence of organic solvent and wash it to obtain crude sucrose fatty acid ester, and then purify the crude sucrose fatty acid ester to produce sucrose fatty acid ester. The purpose of acidification here is to acidify the fatty acid soap in the mixture of sucrose fatty acid esters to fatty acids, and the purpose of washing is to remove residual sucrose, salt and water-soluble pigments.

1. **Synthesis of crude products of Sucrose Fatty Acid Esters by solvent-free method**

171g Sucrose + 150g methyl stearate + 54g potassium stearate + 22.5g potassium carbonate

↓ 140-145℃, 2000Pa, 8h

Crude products of sucrose fatty acids 372.5g

2. **Pretreatment of crude products of sucrose fatty acid esters**

300g Crude products of sucrose fatty acids

↓ 200ml EA , 200ml H2O, 50℃ Agitation dissolution

↓ 10 W% citric acid, Ph=3

The organic phase （EA） is spun dry to get the product. 176g

3. **Purification of crude products of sucrose fatty acid esters**

100g the product.

First-order distillation: 100℃ 800Pa, 0.1Kg/h

Second-order distillation: 110℃ 0.01Pa

Using Molecular distillation unit

Sucrose fatty acids 70.3g