

Preparation of Sorbitan Stearate

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Abstract

The present paper relates to an improved method for making surfactant esters, especially sorbitan monostearate and tristearate. Sorbitan esters of fatty acid, stearate are derived from a reaction between sorbitan and fatty acid. Method of sorbitan ester production needs addition of catalyst. Sorbitan stearate production was studied using chemical catalyst. Two steps process leading sorbitan production under atmospheric and vacuum pressure with acid catalyst resulted dehydrated product at optimal residence time of 195 min at 180°C for atmospheric conditions and optimal residence time of 150 min at the same temperature respectively. Sorbitan stearate production was studied by utilizing sorbitan and stearic acid with alkaline catalyst at atmospheric pressure in an inert gas climate which resulted after 5 hrs of reaction.

Keywords: sorbitan; monostearate; tristearate; surfactant; fatty acid

1. Introduction

Sorbitan fatty acid ester called sorbitan ester, are surfactants highly safe to use on human body and are widely used as a food additive in the production process as emulsifiers. Sorbitan esters are well known emulsifiers suitable for use in food, pharmaceutical products as well as many other applications. Despite its simple

name, sorbitan ester is complex mixture of molecules [1-11]. One such technique involves direct esterification of sorbitol or an intramolecular condensate of sorbitol with fatty acids in the presence of acid or alkali catalysts in one step process [11]. In two step process, sorbitol is first dehydrated to sorbitan and then esterified with acid or alkaline catalysis [8]. Sorbitol for use may be D-sorbitol in the form of white powder. The fatty acid for use may be any fatty acid, Specific example stearic acid. The esterification of sorbitol condensate with fatty acid may be carried out with or without acid or alkali catalysts. The use of alkali catalysts is particularly preferred [8]. Examples of acid catalysts include concentrated sulfuric acid and p-toluenesulfonic acid. Examples of alkali catalysts include potassium hydroxide, sodium hydroxide, potassium carbonate, and sodium carbonate. Purification of sorbitan esters is the next step for removal of impurities from sorbitan esters [5].

The popular method for producing sorbitan esters (Fig.1)[12] is the direct esterification of sorbitol with fatty acids. Method of production sorbitan ester needs addition of catalyst. The reaction mixture may also be analyzed by HPLC. The final product must meet tight values for hydroxyl value and saponification number. Step one: Intramolecular dehydration of sorbitol is preferably carried out by heating sorbitol in the presence of a catalyst (e.g. acid catalyst,

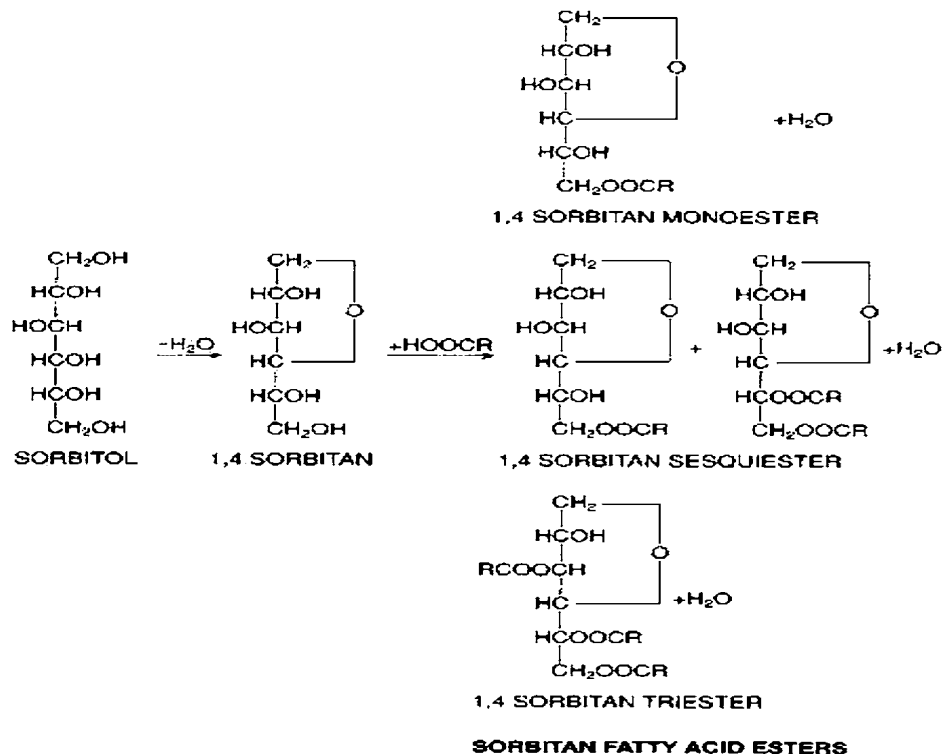


Fig.1 Direct fatty acid esterification of sorbitol with fatty acids [12].

caustic catalyst and tin salts catalyst) at approximately 110 to 150°C, and preferably at approximately 140°C, and removing the generated water under a reduced pressure of, for example, approximately 2kPa [3,7].

Step two: Anhydro sorbitol reaction with fatty acid (stearic acid) is effected by heating in the presence of an alkali catalyst (e.g., potassium hydroxide, sodium hydroxide, potassium carbonate, and sodium carbonate, and so on) at approximately 210 to 250°C, and preferably at approximately 220°C, and in the presence of inert gas.

The esterification is generally carried out in a common reaction vessel that is equipped with a stirrer, a heating jacket, a baffle, an inert gas inlet, a thermometer and a condenser-equipped moisture separator. Sorbitol or sorbitol intramolecular condensates, fatty acids, and catalysts are fed to the reaction vessel and are mixed and stirred [7, 13].

The aim of this investigation is the preparation of sorbitan and esterification of sorbitan with stearic acid and sorbitan estearate formation.

2. Experimental

2-1. Materials

A four-neck flask, provided with a control thermometer, an inert gas, a sampler and condenser was placed in a heater and magnetic stirrer. A vacuum pump supply required pressure in system. The entire chemicals were obtained from Merck Co. They were of analytical grades.

2-2. Method

Sorbitan esters preparation was studied by two stages method. At the first stage, production of sorbitan was studied and in the second stage esterification of sorbitan with fatty acid and sorbitan ester production.

2-2-1. First stage: Dehydrated sorbitol preparation

91g (0.5 mol) sorbitol was fed to the flask and melting (100°C) for 6 min. Addition the catalyst with the amount of 0.072 ml phosphoric acid 85%, or sodium hydroxide solution 36N. The experimental conditions are presented in Table 1.

Table 1. The experimental conditions for sorbitan production.

No	temperature (°C)	pressure (bar)	catalyst
1	120	0.05	H3PO4
2	170	1	H3PO4
3	180	1	H3PO4
4	180	0.05	H3PO4
5	180	0.05	NaOH
6	180	1	NaOH
7	220	0.05	H3PO4

2-2-2. Second stage: Esterification of sorbitan

356g (approximately 2.5mol/mol sorbitol) Stearic acids were added to the system along with 0.144cc sodium hydroxide solution (36N) to serve as a catalyst. Esterification was then carried out at 210°C under normal pressure in a nitrogen gas stream.

2-3. Analytical

The acid value, hydroxyl value was determined by ASTM standard method [14] and dehydration of sorbitol was studied by gravimetric method.

3. Results and discussion

3.1 Preparation of sorbitan

The preparation of sorbitan was effected in the first stage. Dehydration was studied under atmospheric and reduced pressure according to Table one. Dehydration was catalysed by phosphoric acid and sodium hydroxide separately under prescribed conditions for pressure and temperature. As the reaction rate for alkaline catalytic treatment is slow, so this catalyst was not suitable for this reaction according to Table 1, only acid catalyst was selected for sorbitol dehydration. Fig. 2 presents sorbitol dehydration under atmospheric pressure for two temperatures 170 and 180 °C.

According to Fig. 2, higher temperature resulted lower dehydration time from 395 to 355 min. At atmospheric pressure increasing temperature more than 180 °C results the dehydration product mostly of a dark color.

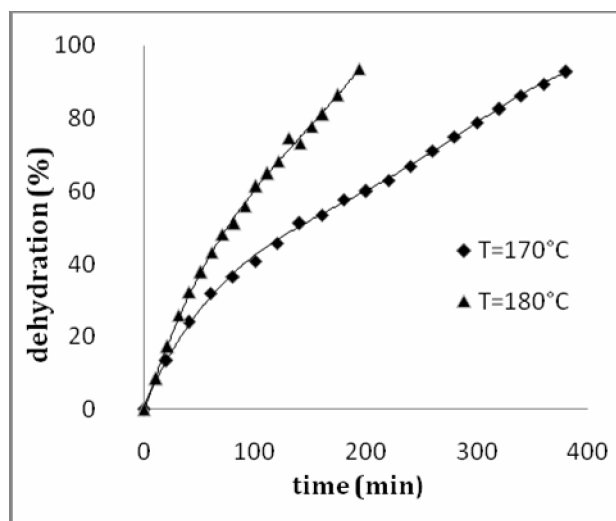


Fig. 2. Dehydration of sorbitol with acid catalyst under atmosphere pressure

Fig. 3 presents sorbitol dehydration under reduced pressure for three different temperature 120, 180 and 220 °C. Optimal dehydration was observed for 220°C and the rate of dehydration is high about 12 min.

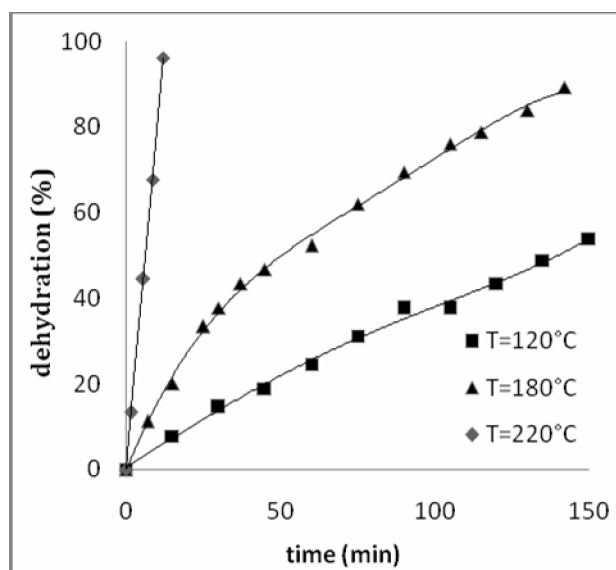


Fig. 3. Dehydration of sorbitol with acid catalyst under reduced pressure

Comparing the rate of dehydration for atmospheric and reduced pressure is shown in Fig. 4, which reduced pressure showed residence time of 150 min but for atmospheric case 195 min respectively.

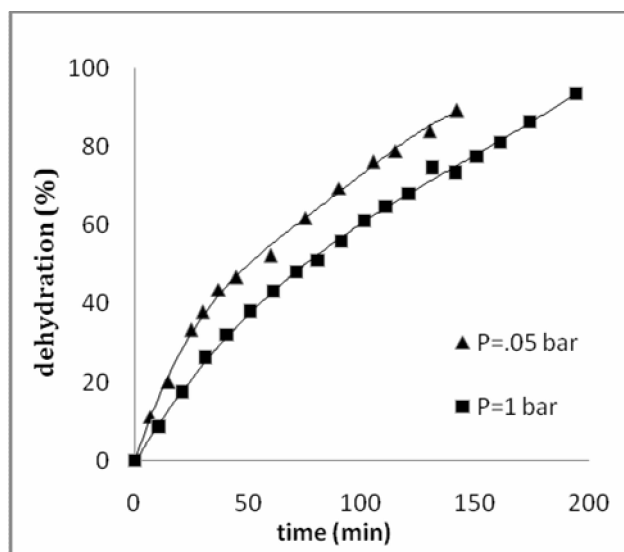


Fig. 4. Dehydration of sorbitol with acid catalyst at T=180°C

Table 2 is the optimal residence time for sorbitan preparation. The condition for this investigation is according To Table1. Dehydration process is achieved by acid catalysis, H₃PO₄ Dehydration under reduced pressure 0.05 bar resulted preferably in lower residence time of 150 hrs compared to atmospheric pressure for 195 hrs at 180 °C respectively.

Table 2 the optimal residence time for sorbitan preparation

No	Optimal residence time (min)
1	355
2	395
3	195
4	150
5	No reaction
6	No reaction
7	12

3.2 Sorbitan ester formation

Esterification was studied under inert gas, nitrogen at atmospheric pressure and temperature, 210 °C. Stearic acid was selected for sorbitan ester formation. Alkaline catalyst, sodium hydroxide acts as catalyst in this stage. Residual fatty acid or fatty acid consumption with time is presented in Fig. 5.

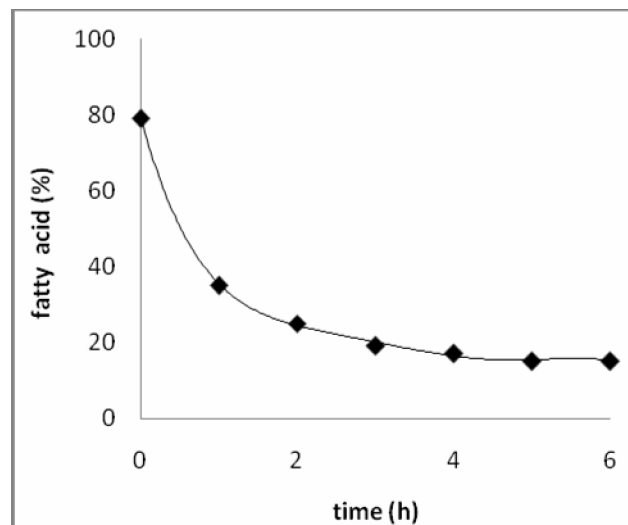


Fig. 5. Conversion fatty acid in esterification

4. Conclusion

An increase in temperature results the reduction in dehydration time or increase in the rate of dehydration.

Under pressure dehydration causes increase in rate of reaction or decrease in dehydration residence time.

Rate of sorbitan ester formation is high until three hours of catalytic reaction and after that rate is nearly constant.

5. References

[1] K.R Brown, Monoesters of Inner Ethers of Hexahydric Alcohols, U.S. Patent 2322820, 1943

- [2] J.E. Holladay, J.Hu, Y.Wang and T.A. Werpy Two-Stage Dehydration of Sugars, **U.S. Patent** 2007/0173651 A1, 2007.
- [3] G.J. Stochburger, Process For Preparing Sorbitan Esters, **U.S. Patent** 4,297,290, 1981.
- [4] Y. Kunimi, A. Tabata and Y.Fujita Process For Production of Solid Sorbitol, **U.S. Patent** 5,068,467,1991.
- [5] S. M. Beshouri and R.P. Admaski, Sorbitan Ester Purification Process, **U.S. Patent** 5,306,831, 1994.
- [6] S. Soltzberg, Sorbitan and Process for Making The Same, **U.S. Patent** 2390395, 1941.
- [7] S. Nagahiro and E. Kamiryu, Process For Producing Sorbitan Fatty Acid Ester, **EP Patent** 1,770,082 A1, 2006.
- [8] J. Smidrkal, R. Cervenkova, and V. Fillip, P. McGrane, Method for the direct Esterification of Sorbitol With Fatty Acids, **U.S. Patent** 7,151,186 B2, 2006.Eur. J. Lipid Sci. Technol. Vol.106, 2004, pp.851-855.
- [9] P. V. D. Plank and A. Rozendaal, Process for Preparing Partial Polyol Fatty Acid Esters, **U.S Patent** 5,006,648, 1991.
- [10] J. Hu, J.E. Hollady, X. Zhang and Y. Wang, Method of Performing Sugar Dehydration And Catalyst Treatment, **U.S. Patent** No. US2007/0173653 A1, 2007.
- [11] J. Giacometti, C. Milin, N. Wolf, F. Giacometti, Process for preparing nonionic surfactant sorbitan fatty esters with and without previous sorbitol cyclization, **J. Agric. Food Chem.** Vol. 44, 1996, pp.3950-3954.
- [12] R.J. Whithurst, **Emulsifiers in Food Technology**, Northampton, UK: Basic Books Inc. Pub. 2004.
- [13] H. Stuhler, Process for Preparing Carboxylic Acid Esters of Hexitols, **U.S. Patent** 4562007, 1985
- [14] **ASTM**, Standard Test Method for Acid Value of Fatty Acids and Polymerized Fatty Acids, designation: D 1980 – 87.