Optimizing Synthetic Process of Epoxysuccinic Acid

Zhenfa Liu[1,2,a] , Haihua Li[1,2,b], Yuhua Gao[1,2,c], Lihui Zhang[1,2,d]

[1] Institute of Energy Resources, Hebei Academy of Sciences Shijiazhuang, China

[2] Hebei Engineering Research Center for Water Saving in Industry

[a]email: lzf63@sohu.com, [b]email: c.t.0205@sina.com, [c]email: gaoyuhua77@163.com, [d]email: zlhkxy@sohu.com

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Abstract. Epoxysuccinic acid (ESA) was synthesized using maleic anhydride (MA) as the raw material, NaOH as the initiator and 30% H_2O_2 as the oxidizing agent, and three kinds of agents as catalysts, and the effects of different catalysts on the yield of ESA were investigated. The results showed that the optimal composite catalyst was composed of sodium tungstate（Na_2WO_4）and sodium molybdate（Na_2MoO_4）. The optimal synthetic conditions of ESA were as follows: the molar ratio of MA to NaOH was 1:2, the mass ratio of 30% H_2O_2 to MA was 7:10, the epoxidation temperature and time were 65 ^oC and 0.5 h, and the dosage of the catalyst was 4% of MA. Under the optimal synthetic condition, the yield of ESA can reach 95.68%. The structure of ESA was characterized by Fourier transform infrared spectrometry (FT-IR).

Introduction

Polyepoxysuccinic acid (PESA) is originally developed as a scale and corrosion inhibitor. It has strong chelating ability for calcium ion, magnesium ion and iron ion, which makes it suitable for water treatment with high hardness and high alkalinity, and PESA without phosphorus and nitrogen is recognized as a green water treatment agent [1-5]. Epoxysuccinic acid (ESA) is the intermediate product in the synthesis of PESA [6-9]. Its yield has a great influence on the yield, the cost, and the performance of PESA. Thus, the research about the optimal synthetic condition of ESA was meaningful.

In this research, sodium tungstate (Na_2WO_4), sodium molybdate (Na_2MoO_4) and sodium vanadate (Na_3VO_4) were investigated as catalysts for the synthesis of ESA. Synthesis conditions such as molar ratio of MA to NaOH, reaction temperature and time were investigated to obtain the higher yield of ESA. The structure of the product was characterized by FT-IR.

Experimental

Agents and instrument

Agents used in the present research included the analytical grade NaOH, H_2O_2, Na_2WO_4, Na_2MoO_4, and Na_3VO_4, and the technical grade maleic anhydride (MA).

The instrument used in the present research was Fourier transform infrared spectrometry (USA, Perkin-Elmer, Spectrum 100).

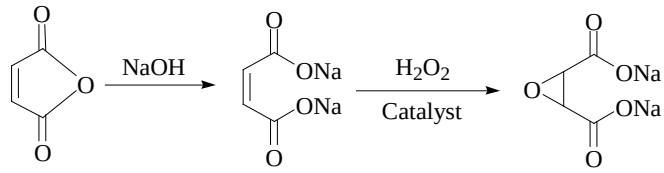
Synthesis of ESA

24.5 g MA and 40 mL deionized water were added into a four-neck round bottom flask with stirring at normal temperature till the solution completely transparent. 0.5 mol NaOH dissolved in 50 mL distilled water (the molar rate of MA to NaOH was 1:2) was slowly dropped into the solution below 55 ^oC. Then the solution was heated to 55 ^oC, 0.5 g catalyst was dissolved in the solution. Three kinds of compound agents were used in the experiments. The numbers and the compositions of the catalysts were listed in table 1. For convenience, the catalyst was represented by the number in table 1 in the post text.

Table 1 Numbers and compositions of the catalysts

Number	1#	2#	3#
Composition	Na_2WO_4	Na_2WO_4+Na_2MoO_4	Na_2WO_4+Na_2MoO_4+Na_3VO_4
Mass ratio	/	1:1	2:1:1

Then 10 mL 30% H_2O_2 was added in the solution in 0.5 h and then the solution was heated at 65 ^oC for 0.5 h. After the reaction was finished, the light yellow solution was obtained, which was the target produce of ESA. The synthesis route of ESA is given in scheme 1.



Scheme 1. Synthesis route of ESA.

Measurement of the yield of ESA [9]

The epoxy group in ESA molecule can react with HCl to generate chlorinated alcohol with $MgCl_2$ saturated solution. After the reaction, the rest of HCl was titrated by NaOH standard solution. The yield of ESA was calculated according to equation (1).

$$X = \frac{[V_0 - (V_1 - V_2 \times m)] \times C \times M}{10 \times m} \times 100\% \quad (1)$$

Where V_0 (mL) is the consumption of NaOH standard solution volume for the blank sample; V_1 (mL) is the consumption of NaOH standard solution volume for the sample with $MgCl_2$ at 60 ^oC for 0.75 h; C (mol/L) is the concentration of NaOH standard solution; m (g) is the mass of the sample; V_2 (mL) is the consumption of NaOH standard solution volume for per gram sample with $MgCl_2$ at normal temperature for 0.75 h; M (mol/g) is the molecular weight of ESA.

Results and discussion

Effect of the mole ratio of MA to NaOH on the yield of ESA

The synthetic conditions of ESA were as follows: the contant of H_2O_2 was 50% (w/w), the epoxidation temperature was 65 ^oC, the epoxidation time was 2 h, and the contant of the composite catalyst was 2% (w/w). Fig.1 shows the effect of the molar ratio of MA to NaOH on the yield of ESA with different composit catalysts. As shown in Fig.2, the yield of ESA was the maximum when the molar ratio of MA to NaOH was 1:2. It was because when the molar ratio of MA to NaOH was less than 1:2, the ESA was hydrolyzed to tartaric acid at the acid environment, while that was larger than 1:2, H_2O_2 decomposed with the dosage of NaOH increasing.

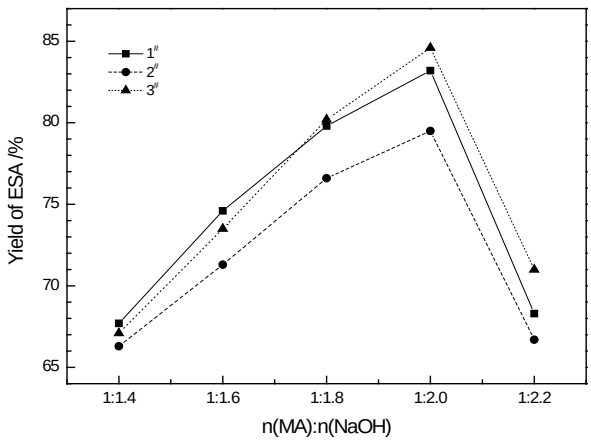


Fig.1. Influence of the mole ratio of MA to NaOH on the yield of ESA

Effect of H_2O_2 dosage on the yield of ESA

The synthetic conditions of ESA were as follows: the molar ratio of MA to NaOH was 1:2, the epoxidation temperature was 65 ^oC, the epoxidation time was 2 h, and the contant of the composite catalyst was 2% (w/w). Fig.2 shows the effect of H_2O_2 dosage on the yield of ESA with different composit catalysts. The optimal dosages of H_2O_2 were 90% (w/w), 70% (w/w) and 50% (w/w), respectively, for Na_2WO_4, the compound of Na_2WO_4 and Na_2MoO_4, and the compound of Na_2WO_4, Na_2MoO_4 and Na_3VO_4 used as the catalysts. When the dosage of H_2O_2 was less than the best, MA was epoxidated to ESA, thus the yields of ESA increased with the dosage of H_2O_2 increasing. While when the dosage of H_2O_2 was higher than the best, adding the dosage would increase the ESA hydrolysis reaction, which would lead to a drop in the yield of ESA. With different catalyst combinations in the same mass, the dosage of H_2O_2 for obtaining the maximum yield of ESA could be ranked as follows: $1^{\#}>2^{\#}>3^{\#}$.

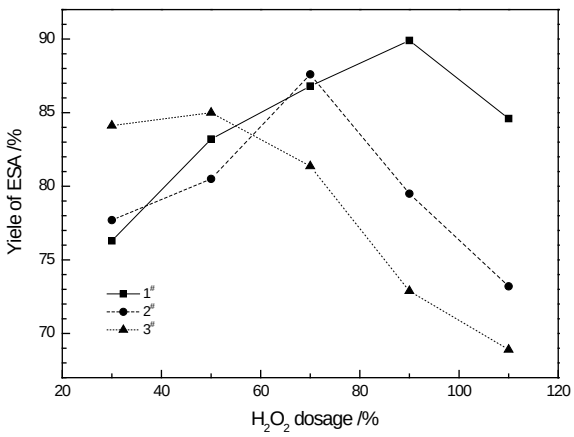


Fig.2. Influence of H_2O_2 dosage on the yield of ESA

Effect of epoxidation temperature on the yield of ESA

The synthetic conditions of ESA were as follows: the molar ratio of MA to NaOH was 1:2, the

contant of H_2O_2 was 50% (w/w, percentage of MA), the epoxidation time was 2 h, and the contant of the composite catalyst was 2% (w/w). Fig.3 shows the effect of temperature on the yield of ESA with different composit catalysts. While this reaction is a consecutive reaction, the ESA is easily hydrolyzed to tartaric acid in an acid condition. In Fig.1, the yields of ESA increase with temperature increasing between 55-65 ^{o}C. This was because the rate of epoxidation reation was accelerated with temperature increasing and was greater than that of ESA hydrolysis. When the temperature is higher than 70 ^{o}C, the yields of ESA decrease observably. This was because H_2O_2 decomposed at high temperature, which led to the ESA epoxidating rate decreasing, while, at the high temperature range, the hydrolysis rate of ESA increased. Therefore, the maximum yield of ESA was obtained at 65 ^{o}C.

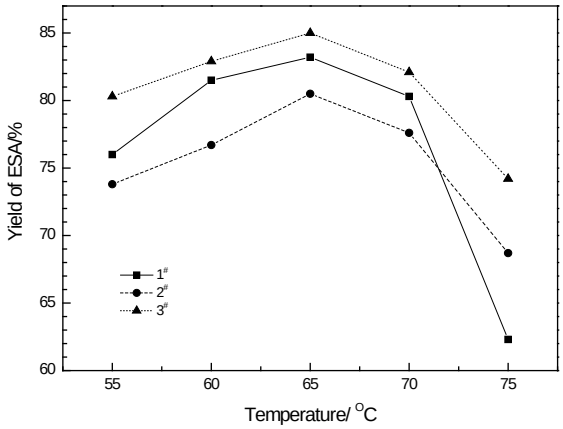


Fig.3. Influence of epoxidation temperature on the yield of ESA

Effect of epoxidation time on the yield of ESA

The synthetic conditions of ESA were as follows: the molar ratio of MA to NaOH was 1:2, the contant of H_2O_2 were the optimal dosages with different catalysts, respectively, the epoxidation temperature was 65 ^{o}C, the contant of the composite catalyst was 2% (w/w). Fig.4 shows the effect of epoxidation time on the yield of ESA with different composit catalysts. It costs 1.5 h to obtain the maximum yield 93.15% when 1$^{\#}$ used as catalyst. It cost 0.5 h to obtain the maximum yield of 93.27% with 2$^{\#}$ and 92.73% with 3$^{\#}$. It showed that using composite catalysts could save 1 h comparing with Na_2WO_4 as the catalyst for obtaining the maximum yield. For the yield using Na_2WO_4, Na_2MoO_4 and Na_3VO_4 ternary compound as catalyst was slightly higher than that of Na_2WO_4 and Na_2MoO_4 dual compound. Considering the price of the catalyst and the practical energy consumption in industrial production, choosing 2$^{\#}$ as catalyst is more reasonable.

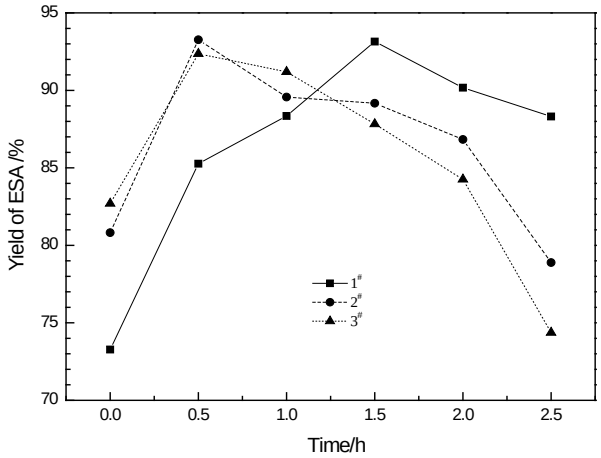


Fig.4. Influence of epoxidation time on the yield of ESA

Purification and IR analysis of ESA

Putting HCl into the light yellow solution obtained in the synthetic reaction to adjust pH to 2, there was a lot of white powder precipitated. Then the powder was filtered and washed by a large amount of ethanol and methanol. The white powder was dried at 60 ^{o}C and the structure was characterized by FT-IR. The strong peak at 3520 cm^{-1} in Fig. 5 aroses from the deformation vibration of O–H bond bending in –COOH, the absorption peak at 3037 cm^{-1} is attributed to the C-H stretching in epoxy group, the absorption peak at 1636 cm^{-1} is C=O stretching in –COOH, the peak at 1456 cm^{-1} is C–H deformation vibration peak of epoxy group, the peaks at 1270cm^{-1} and 1068cm^{-1} are C–O stretching in –COOH, and the peaks at 1134 cm^{-1} and 951 cm^{-1} are the vibration absorption peak of epoxy group, which indicate that the product was ESA.

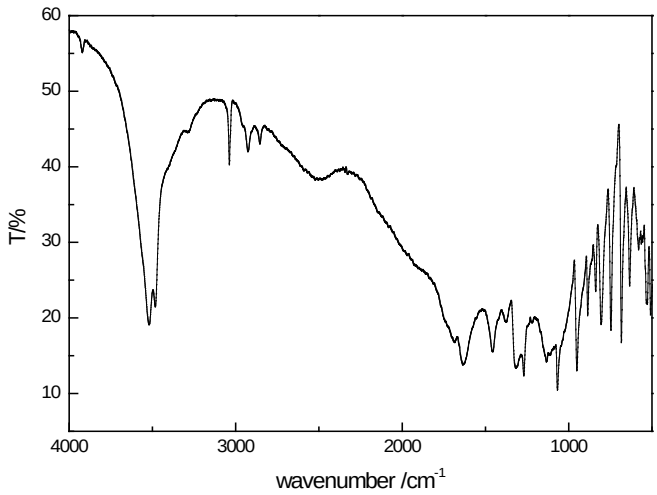


Fig.5. IR spectrum of ESA

Conclusions

ESA was successfully synthesized using MA as raw material. The optimum conditions for the synthesis of ESA were as follows: the molar ratio of MA to NaOH was 1:2, the contant of H_2O_2 was 70% (w/w), the epoxidation temperature was 65 ^{o}C, the epoxidation time was 0.5 h, the mass ratio of Na_2WO_4 to Na_2MoO_4 was 1:1, and the contant of the composite catalyst was 2.5% (w/w).

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