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Research Progress in Synthesis of Itaconic Esters

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Abstract: To prepare high-quality dimethyl itaconate, this analysis focuses on the synthesis of itaconate esters. Through the test preparation analysis, the optimal reaction temperature is 120 °C, the reaction time is 9 hours, and the reaction pressure is 163 kPa. In addition, the resin is selected as the catalyst in the synthesis test, which not only effectively solves the problem of corrosion of reaction equipment, but also improves the catalytic activity, physical stability, and chemical stability of the synthesis test process, which is more conducive to absorption and separation, to provide some reference for the synthesis and preparation of dimethyl itaconate in the future.

Keywords: Itaconic acid; Methanol; Dimethyl itaconate; Resin

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1. Introduction

Itaconic acid (methylene succinic acid) is a very important raw material in chemical production. The more common are polymer materials, non-toxic packaging materials, etc. The more conventional raw material of itaconic acid is glucose. According to the itaconic acid industry development report, the market size of itaconic acid in the world and China will reach 797 million yuan (RMB) and 206 million yuan in 2024. It is predicted that the compound annual growth rate of the global itaconic acid market will reach 6.67%, and the total size of the global itaconic acid market may reach 1.174 billion yuan by 2030. It can be seen that the domestic production of itaconic acid has a good prospect. Referring to the current synthesis experience of itaconic acid, the rotary tube condenser is more used in the synthesis process. Methanol is added dropwise in the reaction process. The time required for this link is about 9h, and the reaction temperature also needs to be maintained between 100–120 °C. The actual water and methanol reach the outside of the reaction system after distillation. On the whole, this process is cumbersome and difficult to control. In this paper, the synthesis of itaconic acid esters is the object, using itaconic acid and methanol to synthesize dimethyl itaconic acid, to simplify the synthesis process.

2. Test materials and equipment

2.1. Raw materials and reagents

The raw materials and reagents selected for the synthesis of itaconic acid esters are: 99% industrial itaconic acid, produced by Hubei Chenghai Chemical Co., Ltd.; 98% sulfuric acid; 85% phosphoric acid; Methanol and other analytes; The catalyst is mainly resin.

2.2. Instrument equipment and test conditions

Synthetic test instruments and equipment mainly include gas chromatograph, infrared spectrometer, etc., specifically: Agilent 7890b gas chromatograph produced by Agilent; 8% DEGC column; Hydrogen flame ion detector; Amd Ryzen 9950x data processor; Bruker alpha Fourier transform infrared spectrometer. **Table 1** shows the test conditions.

Table 1. Synthetic test conditions

Conditions	Parameter
Temperature rise requirements	Temperature programmed
Column temperature	140 °C
Gasification temperature	200 °C
Flow rate	50 mL/min
carrier gas	Nitrogen
Injection volume	0.3 μL
Test method	Liquid membrane method

2.3. Comparison of synthetic processes

To compare the synthesis effect of itaconic acid esters, the atmospheric pressure method and pressure method were selected for this test [1]. For the operation of the atmospheric pressure method, itaconic acid, methanol, and resin catalyst should be added into a three port flask with a capacity of 250 ml. The container contains an electric stirrer, thermometer, and reflux condensing pipe at the same time, and is heated, stirred and reflux treated for 9h [2]. The reaction time is observed. After the reaction is over, the tester needs to replace the equipment with a distillation unit and complete methanol recovery after frequent pressure distillation. The recovered methanol is cooled to room temperature, and the remaining material is transferred to the separation funnel. The solution with w NaOH (10%) is mainly used for neutralization treatment, which reaches neutral after water washing [3]. Determine the separation of the water layer, and treat the formed organic layer with a vacuum distillation process to obtain a fraction of 122 °C/5.35kPa. This is the product obtained after atmospheric pressure treatment. The tester needs to calculate the yield after weighing.

The pressurization method is applied in synthesis. The initial operation is the same as that of the atmospheric pressure method. Add a series of solutions into a 1 L autoclave container, set the reaction temperature at 120 °C, and the reaction time at 10h. The reaction material is cooled to room temperature, and then methanol is recovered by atmospheric distillation. The remaining substances are neutralized with w NaOH (10%) solution, and treated to neutral by water washing process. After separating the effluent layer, the organic layer was distilled under reduced pressure to obtain a fraction of about 122 °C/5.35kPa. Finally, the yield was obtained by weighing and calculating.

3. Results and analysis

3.1. Catalyst

This time, dimethyl itaconate was synthesized from itaconic acid and methanol. The resin was selected as the catalyst, and the effects of other catalysts on the yield of synthetic substances were compared. The results are shown in **Table 2**.

According to the data in **Table 2**, it can be recognized that the selection of catalyst will affect the synthesis yield of dimethyl itaconate to a certain extent. The yields of the three catalysts in **Table 2** are all above 75%, but the resin yield is the highest. In addition, resin is more applicable in industrial production, so the synthesis test mainly uses resin as a catalyst.

Table 2. Effect of catalyst on synthesis yield

	Catalyzer			
	Nothing	**Resin**	**P-toluenesulfonic acid**	**w(H_3PO_4)=85%**
Yield	41.5%	85.7%	80.3%	78.1%

Note: The reaction conditions for sorting out the data in **Table 2** are itaconic acid: methanol=1:10, resin: itaconic acid=1:100, and the reaction temperature, pressure, and time are set at 120 °C, 163 kPa, and 9 h respectively

3.2. Acid alcohol

During the test, the effect of acid alcohol on the formation of the final synthesis yield of dimethyl itaconate was observed, and the data are summarized in **Table 3**. According to the data in **Table 3**, it is found that the initial reaction temperature and yield begin to increase after the alcohol content decreases. Generally, if the amount of alcohol decreases, the yield will also decrease; If the temperature is increased, the yield will also increase. Therefore, the setting of reaction temperature during the synthesis test directly affects the yield of the final synthesis, and the degree of influence is significantly greater than that of the decrease of alcohol content. Based on this finding, the synthesis of dimethyl itaconate can be carried out by the atmospheric pressure method, which is an important prerequisite for raising the reaction temperature. During this period, observe the change in the yield of the final product. **Table 4** shows the sorted data. According to the data in **Table 4**, when the amount of alcohol increases, the yield of dimethyl itaconate is positively proportional to it, showing an increasing trend. When the amount of acid and alcohol is adjusted to 1:10, any adjustment thereafter will not have a direct impact on the yield. Therefore, when the amount of acid and alcohol is 1:10, the yield can exceed 87%.

Table 3. Effect of acid alcohol on synthesis yield

	Acid: alcohol			
	1:8	**1:5**	**1:3**	**1:2.2**
t	71–75 °C	80–87 °C	85–93 °C	95–113 °C
Yield	35.1%	46.8%	70.3%	55.2%

Note: The reaction conditions for sorting out the data in **Table 3** are itaconic acid 66 g, resin 0.8 g, and reaction time 9 h

Table 4. Effect of acid-alcohol ratio synthesis yield after pressurization

	Acid: alcohol				
	1:3	**1:5**	**1:8**	**1:10**	**1:12**
Yield	70.2%	77.0%	83.2%	87.5%	87.1%

3.3. Reaction temperature

The effect of reaction temperature was observed during the test. **Table 5** shows the sorted data. According to the data in **Table 5**, it is found that the yield of dimethyl itaconate will also increase with the increase in reaction temperature. The reaction temperature reached about 120 °C, and then the reaction temperature continued to rise, but the yield decreased. When the reaction temperature was 130 °C, the discharge was observed, and it was found that the color of the reactants actually obtained was darker. After vacuum distillation, there were more viscous substances at the bottom of the reaction tank. The reason was that the polymerization of itaconic acid/ itaconic acid ester occurred after the temperature increased. Therefore, the high reaction temperature is not conducive to the improvement of yield, and the optimal reaction temperature is 120 °C.

Table 5. Effect of different reaction temperature on product yield

	Reaction temperature				
	50°C	**70°C**	**90°C**	**120°C**	**130°C**
Yield	28.7%	60.2%	69.5%	79.8%	78.4%

Note: The reaction conditions for sorting out the data in **Table 5** are 130 g itaconic acid and 320 g resin, and the reaction temperature, pressure, and time are set at 120 °C, 163 kPa, and 9 h respectively

3.4. Reaction time

The acid-base titration analysis method is mainly used in the test and analysis process. The standard solution is C (KOH)=0.1mol/l, and the indicator is phenolphthalein. The reaction mixture obtained is tracked and observed at four time points of 1 h, 8 h, 9 h, and 12 h respectively. 5 ml of the sample was taken once to observe the amount of KOH solution consumed, and the test data was sorted out in **Table 6**. By analyzing the data in **Table 6**, it is found that after 10 h of the test, the fluctuation of KOH solution consumption is not obvious. It can be seen that 9 h has reached the reaction equilibrium point. If the reaction time of the test continues to be extended, it will not have a direct impact on the conversion rate. Therefore, the optimal reaction time for the synthesis of dimethyl itaconate is 10 h.

Table 6. Effect of different reaction times on test progress

	Reaction time			
	1 h	**8 h**	**9 h**	**12 h**
KOH solution consumption	45.9 mL	21.4 mL	14.3 mL	12.6 mL

Note: The reaction conditions of the data in the table are resin 1.3 g, acid: alcohol=1:10, and the reaction temperature and pressure are set at 120 °C and 163 kPa respectively

3.5. Content test and analysis of dimethyl itaconate

3.5.1. Chemical method

The tester accurately weighed about 2.5 g of dimethyl itaconate sample and tested the ester content by acid-base titration analysis. The test was carried out 3 times, and the average ester mass fraction calculated by numerical method was 98.28%. Calculation formula:

$$Ester\ mass\ fraction = [M \times (V_0 - V_1)/(20 \times m) - M \times A/130] \times 100\% \quad (1)$$

In Formula 1, M represents the molar mass of dimethyl itaconate, V_0 and V_1 represent the volume of HCl standard solution used for blank sample and the volume of HCl standard solution consumed by KOH that is still unreacted after saponification of the sample, A represents the acidity, and M represents the mass of the sample.

3.5.2. Gas chromatography

The gas chromatograph was used in this test, and the tester determined the ester content in dimethyl itaconate by gas chromatography. The experimental results showed that the final mass fraction of dimethyl itaconate was 99.15%, which was close to the data obtained by the chemical method (98.26%), indicating that the final mass fraction of dimethyl itaconate was more than 98%.

3.5.3. Fourier transform infrared spectroscopy

To verify the validity of the data related to the synthesis of dimethyl itaconate determined in this test, the final test also needs to determine the product by Fourier transform infrared spectroscopy. The absorption peaks of the synthesized dimethyl itaconate and the dimethyl itaconate stored in the infrared spectrum library were consistent, which also verified that the product prepared in this test was dimethyl itaconate.

4. Conclusions

Combined with the test process and results of the synthesis of dimethyl itaconate from itaconic acid and methanol, the resin was selected as the catalyst, and the test conclusions are as follows.

Dimethyl itaconate was synthesized after the experiment. The infrared spectrum and standard spectrum were compared, and it was confirmed that they were the same. According to the results of gas chromatography analysis, the synthetic product is dimethyl itaconate, and the purity is as high as 98%.

The optimal synthesis conditions of dimethyl itaconate synthesized in the test are summarized in **Table 7**. Based on this condition, dimethyl itaconate can be synthesized, and the yield of the product is more than 85%.

Table 7. Optimum conditions for the synthesis of dimethyl itaconate

Condition	Parameter
Itaconic acid: methanol	1:10
Catalyst (resin): itaconic acid	1:100
Reaction temperature	120 °C
Reaction time	9 h
Reaction pressure	163 kPa

5. Suggestions

5.1. Basic reaction conditions

5.1.1. Raw material ratio

Based on the experience of synthesis and preparation of dimethyl itaconic acid in the industry and combined with the results of this synthesis test, it is suggested that the molar ratio should be set between 1:6 and 1:10 in the synthesis test of itaconic acid and methanol in the future. If methanol is excessive, the equilibrium

conversion of the esterification reaction in the synthesis process can be effectively improved. In addition, the catalyst selected for this synthesis test is resin. In addition, it is recommended to use a chitosan sulfate catalyst, and the appropriate acid-alcohol ratio is 7:1 and 4.

5.1.2. Catalyst

Given the previous use of acid catalysts in the industry, such as sulfuric acid and molybdenum nickel catalysts, the amount of catalyst needs to reach about 1%–3% of the total mass of reaction materials [4]. Considering the importance of environmental protection in industrial production, environmental protection catalysts, such as resin and chitosan sulfate, should also be given priority in the selection of catalysts in the future. The specific dosage should reach 2% of the total material. This environmental protection catalyst supports recycling, and the yield of the final product can exceed 80% [5].

5.1.3. Reaction temperature and time

Compared with the parameters of the traditional catalyst used in the synthesis of dimethyl itaconate in the past, such as the reaction temperature of 120 °C, the reaction time of the synthesis test of about 6–10h, and the yield of 80%. When the catalyst is changed to resin, the reaction time can be increased to about 9 h [6]. In the future, it is suggested to choose glycan sulfate as the catalyst for the synthesis of dimethyl itaconate, which is conducive to raising the reaction temperature, shortening the reaction time and increasing the yield.

5.2. Optimization of synthesis process

5.2.1. Pressure control

The sulfuric acid catalytic system was constructed during the synthesis test. It is suggested to adjust the reaction pressure to about 163 kPa. This data is conducive to accelerating the reaction rate.

5.2.2. Post treatment and purification

The tester observed that the reaction was over, and the non-reactive methanol was recovered by the fractionation process. If there was residual product, the purification was completed by vacuum distillation. The purity of the product obtained by this process was greater than 98%, which was conducive to saving production costs [7].

5.3. Precautions

5.3.1. Corrosion resistance of synthetic equipment

Considering that the strong acid catalyst may cause corrosion to the equipment, it is necessary to optimize the corrosion resistance of the reactor, for example, glass lining or Hastelloy material is preferred.

5.3.2. Timely identification of synthetic products

For the final synthetic product, the tester needs to determine the purity of dimethyl itaconate by using Fourier transform infrared spectroscopy, comparing the standard spectrum, gas chromatography quantitative analysis, and other procedures.

5.3.3. Recommended process

The catalyst selected for synthesis is resin, which can maintain high activity, stability, and environmental protection, and has high recovery efficiency. It can prevent the erosion of different chemicals and can reflect

good adaptability in different chemical reaction environments. It is one of the key measures for the realization of green and environmental protection in the chemical industry.

Disclosure statement

The authors declare no conflict of interest.

References

[1] State Intellectual Property Office, 2024, A Bio-Based Itaconate Rubber Sole Material and its Preparation Method. Rubber Technology, 22(7): 414.

[2] Wang JL, Yang C, Chen SS, et al., 2024, Effects of Dimethyl Itaconate on the Secretion of Proinflammatory Cytokines by Dendritic Cells and Helper T Cell 17 in Mice with Experimental Autoimmune Uveitis. New Progress in Ophthalmology, 44(5): 346–349.

[3] Yan WY, Zhang R, Ma HT, 2024, Regulation of Dimethyl Itaconate on H2O2 Induced Mitochondrial Dysfunction in AML-12 Cells and its Mechanism. Journal of Nanjing Agricultural University, 47(1): 28–35.

[4] Ji HJ, Yang H, Wang X, et al., 2022, Design, Development and Industrial Application of Bio-Based Itaconic Acid Ester Rubber. Journal of Beijing University of Chemical Technology (Natural Science Edition), 49(5): 13–21.

[5] Bian JN, Chen J, Yang ZZ, et al., 2022, Preparation and Properties of Polysiloxane Modified Epoxy Itaconate Waterborne UV Curable Resin. Forest Products Chemistry and Industry, 42(4): 9–15.

[6] Bian JN, Chen J, Yang ZZ, et al., 2022, Synthesis and Characterization of Isocyanate Modified Epoxy Itaconate Waterborne UV Curable Resin. Forest Chemistry and Industry, 42(2): 101–109.

[7] Han JY, Chen JY, Wang K, et al., 2021, Effect of Dimethyl Itaconate on Insulitis in Non-obese Diabetic Mice. Fujian Medical Journal, 43(6): 122–125.