EFFECTS OF DIFFERENT REACTION CONDITIONS ON THE SYNTHESIS OF ISOAMYL BENZOATE

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Effects of the different reaction conditions on the synthetic method of isoamyl benzoate have been reviewed in the present article. Different catalysts that consist of p-toluenesulfonic acid (PTSA), $Zr(SO_4)_2 \cdot 4H_2O$, $NaHSO_4 \cdot H_2O$ and $Ti(SO_4)_2/TiO_2$ have also been introduced. The reaction conditions include the reaction time, the molar ratio of benzoic acid to isoamyl alcohol, the amount of the catalyst, the microwave heating method and the Ti loading amount, etc. The optimum reaction time, the molar ratio of benzoic acid to isoamyl alcohol, the amount of the catalyst, the microwave heating method and the Ti loading amount are beneficial to improve the yield of the product, isoamyl benzoate.

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INTRODUCTION

Isoamyl benzoate is not only a colourless liquid with fruit aroma but also one of the important chemical products.[1] Further, due to its floral fragrance, it is widely used in different daily use chemical essence as a mobilizing agent for fragrance in different types of fixative spices and fruit/food derivatives etc. [2] It is also used as a solvent for fats or resins. Benzoic acid in the presence of concentrated sulphuric acid as catalyst is reacted with isoamyl alcohol to produce isoamyl benzoate at industrial scale process. This method has a lot of disadvantages also such as poor quality of products, serious equipment corrosion, complicated operating system and pollution environmental issues, etc. [3]

In the present paper, different catalysts such as p-toluenesulfonic acid (PTSA) which refers an organic compound with the formula $CH_3C_6H_4SO_3H$, $Zr(SO_4)_2 \cdot 4H_2O$, $NaHSO_4 \cdot H_2O$ and $Ti(SO_4)_2/TiO_2$ have been discussed. Effects of different reaction conditions, such as the reaction time, the molar ratio of benzoic acid to isoamyl alcohol, the amount of the catalyst, the microwave heating method and the Ti loading amount, on the synthetic method of isoamyl benzoate have also been reviewed. Further, a few the optimum reaction conditions are also discussed.

DISCUSSION

Effects of the reaction time on the yield of isoamyl benzoate by the addition of p-toluenesulfonic acid (PTSA) as a catalyst

Li Xiuyu [4] introduced the synthetic method of isoamyl benzoate and studied that the different conditions had an effect on the yield of isoamyl benzoate. To synthesise isoamyl benzoate, PTSA was used as a catalyst whereas benzoic acid and isoamyl alcohol were used as feedstocks respectively. The molar ratio of benzoic acid to isoamyl alcohol (1.0:2.0) and the weight ratio of PTSA to benzoic acid (3%) kept at constants. Effects of the reaction time on the yield of isoamyl benzoate had also been discussed. Table 1 showed effects of the reaction time on the yield of isoamyl benzoate. The experimental results showed that the yield of isoamyl benzoate first increased and then decreased with an increase with the reaction time. It was observed that when the reaction time was 3.0 hours, the maximum yield of isoamyl benzoate (98.75%) was obtained. Therefore, the optimum reaction time to be considered was 3.0 hours.

Table 1. The effect of the reaction time on the yield of isoamyl benzoate

Reaction time , h	1.0	2.0	3.0	4.0	5.0
Yield , %	95.24	98.35	98.75	97.42	97.00

Effects of the molar ratio of benzoic acid to isoamyl alcohol on the yield of isoamyl benzoate by the addition of $Zr(SO_4)_2 \cdot 4H_2O$ as a catalyst

Zhang Fuxing [5] used $Zr(SO_4)_2 \cdot 4H_2O$ as a catalyst and benzoic acid and isoamyl alcohol as feedstocks to synthesise isoamyl benzoate. The reaction time and the weight ratio of $Zr(SO_4)_2 \cdot 4H_2O$ to benzoic acid kept at constants were 2.5 hours and 6.56%, respectively. Effects of the molar ratio of benzoic acid to isoamyl alcohol on the yield of isoamyl benzoate had been discussed. Table 2 showed effects of the molar ratio of benzoic acid to isoamyl alcohol on the yield of isoamyl benzoate. The yield of isoamyl benzoate first increased and then decreased with an increase in the molar ratio of benzoic acid to isoamyl alcohol. When the molar ratio of benzoic acid to isoamyl alcohol was 1.0:2.5, the maximum yield of isoamyl benzoate attained was 96.3%.

Table 2. The effect of the molar ratio of benzoic acid to isoamyl alcohol on the yield of isoamyl benzoate

Molar ratio	1.0:1.0	1.0:1.5	1.0:2.0	1.0:2.5	1.0:3.0
Yield, %	75.8	86.4	92.7	96.3	94.8

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Effect of the amount of $NaHSO_4 \cdot H_2O$ on the yield of isoamyl benzoate by the addition of $NaHSO_4 \cdot H_2O$ as a catalyst

Guang Shibin [6] replaced concentrated sulfuric acid with $NaHSO_4 \cdot H_2O$ as a catalyst to synthesise isoamyl benzoate. The reaction time and the molar ratio of benzoic acid to isopropanol kept at constants were 2.0 hours and 1.0:1.4, respectively. The effect of the amount of $NaHSO_4 \cdot H_2O$ on the yield of isoamyl benzoate had also been discussed. Table 3 presented effects of the amount of $NaHSO_4 \cdot H_2O$ on the yield of isoamyl benzoate. The yield of isoamyl benzoate first increased and then decreased with an increase in the amount of $NaHSO_4 \cdot H_2O$. It was noticed that when the amount of $NaHSO_4 \cdot H_2O$ was 24.59% of benzoic acid weight, the maximum yield of isoamyl benzoate attained was 83.3%.

Table 3. The effect of the amount of $NaHSO_4 \cdot H_2O$ on the yield of isoamyl benzoate

Weight ratio of $NaHSO_4 \cdot H_2O$ to PhCOOH, %	4.10	8.20	16.39	24.59	32.78
Yield (%)	75.0	77.1	81.3	83.3	79.2

Effect of microwave heating method on the yield of isoamyl benzoate by the addition of p-toluenesulfonic acid (PTSA) as a catalyst

Shi Lei [7] also studied the effect of the reaction conditions on the yield of isoamyl benzoate. He synthesised it by using PTSA as a catalyst and benzoic acid and isoamyl alcohol as feedstocks produced isoamyl benzoate. It was observed that the molar ratio of benzoic acid to isopropanol and the amount of PTSA kept at constants at 1.0:3.0 and 14.88% of benzoic acid weight, respectively. Table 4 showed that different heating methods had a different effect on the yield of isoamyl benzoate. The experimental results revealed that two types of methods had almost the same yield, but they applied the different reaction time. The yield of isoamyl benzoate in the microwave heating methods reached 95.0% in 0.5 hour; however the yield in the oil bath heating methods attained at 94.8% in 2 hours.

Table 4. the effect of heating method on the yield of isoamyl benzoate

Conditions	**Microwave heating method**	**Oil bath heating method**
Temperature, °C	120 - 136	136 – 148
Yield, %	95.0	94.8
Reaction time, h	0.5	2.0

Effect of Ti loading amount on the yield of isoamyl benzoate by the addition of $Ti(SO_4)_2/TiO_2$ as a catalyst

Zhang Fujuan [8] used $Ti(SO_4)_2/TiO_2$ as a catalyst to synthesise isoamyl benzoate. The effect of Ti loading amount on the yield of isoamyl benzoate had been discussed. It was observed that the reaction time, the molar ratio of benzoic acid to isopropanol and the amount of $Ti(SO_4)_2/TiO_2$ kept at constants were 1.5 hours, 1.0:4.0 and 40.98% of benzoic acid weight, respectively. Table 5 showed effects of different Ti loading amount on the yield of isoamyl benzoate. The yield of isoamyl benzoate firstly increased and then decreased with an increase in the Ti loading amount. When the Ti loading amount was 10%, the maximum yield of isoamyl benzoate was found to be 92.7%.

Table 5. The effect of different Ti loading amount on the yield of isoamyl benzoate

Ti loading amount, %	6	8	10	12	14
Yield, %	70.2	78.2	92.7	89.9	89.9

CONCLUSION

Based on the above mentioned results, discussion and review, using benzoic acid and isopropanol as feedstocks and p-toluenesulfonic acid (PTSA), $Zr(SO_4)_2 \cdot 4H_2O$, $NaHSO_4 \cdot H_2O$ and $Ti(SO_4)_2/TiO_2$ as catalysts, effects of he reaction time, the molar ratio of benzoic acid to isoamyl alcohol, the amount of the catalyst, the microwave heating method and the Ti loading amount on the yield of isoamyl benzoate, the experimental observations obtained are as follows:

(1) The maximum yield of isoamyl benzoate attained 98.75% in 3 hours by the addition of PTSA.

(2) The maximum yield of isoamyl benzoate attained 96.3% under the condition of benzoic acid/isopropanol ratio (1.0:2.5) when $Zr(SO_4)_2 \cdot 4H_2O$ as the catalyst was added into this reaction system.

(3) The maximum yield of isoamyl benzoate was 83.3% when the amount of $NaHSO_4 \cdot H_2O$ was 24.59% of benzoic acid weight.

(4) The maximum yield of isoamyl benzoate got 95.0% under the condition of the microwave heating method (0.5 hour) and the molar ratio of benzoic acid to isopropanol (1.0:3.0) and the weight ratio of PTSA to benzoic acid (14.88%).

(5) The maximum yield of isoamyl benzoate reached 92.7% under the condition of the Ti loading amount (10%), the reaction time (1.5 hours), the molar ratio of benzoic acid to isopropanol (1.0:4.0) and the weight ratio of $Ti(SO_4)_2/TiO_2$ to benzoic acid (40.98%) .

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