# EFFECTS OF DIFFERENT REACTION CONDITIONS ON THE SYNTHESIS OF BENZYL ACETATE

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Effects of different reaction conditions such as different water carrying agents, the amount of water carrying agent, the calcination temperature, the calcination time and the amount of catalysts, the reaction time, the molar ratio of acetic acid to benzyl alcohol, the reaction temperature, the amount and type of catalyst (tris(trimethylsilylmethyl)tin chloride, $S_2O_8^{2-}$-$Fe_2O_3$-CoO, N-methylpyrrolidone hydrosulfate, $FeCl_3$(46 %)/carbon, $SO_4^{2-}$-$ZrO_2$-$Nd_2O_3$, strong acid cation exchange resin loaded $Fe^{3+}$ and the catalyst drying temperature) on the synthesis of benzyl acetate from benzyl alcohol and acetic acid are discussed.

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## INTRODUCTION

Benzyl acetate is a colourless oily liquid. It is naturally found in many flowers such as jasmine, ylang-ylang and tobira. Its molecular formula, melting point, boiling point, relative density (16 °C), refractive index $n_D^{20}$ and flash point are $C_9H_{10}O_2$, 50 °C, 213 °C, 1.057, 1.5232 and 102 °C, respectively. Benzyl acetate is hard to dissolve in water, but it is completely miscible in organic solvents. [1]

Due to floral fragrance and low price, it is widely used in different areas such as soap class essence and other industrial essence, etc. [2] Benzyl alcohol with concentrated sulphuric acid as a catalyst reacts with acetic acid to synthesise benzyl acetate. Concentrated sulphuric acid has a lot of disadvantages also except several advantages, such as long reaction time, low yield and purity of benzyl acetate.

Large amount of waste water is discharged to cause the problem of environmental pollution and equipments are seriously corroded at the same time. [3]

The overview of its synthetic methods has just been reviewed. [4] In the present paper, usability of different catalysts such as tris(trimethylsilylmethyl) tin chloride, $S_2O_8^{2-}$ - $Fe_2O_3$ – CoO, N-methylpyrrolidone hydrosulfate, 46% $FeCl_3$/carbon, $SO_4^{2-}$-$ZrO_2$-$Nd_2O_3$ and strong acid cation exchange resin loaded $Fe^{3+}$ have been discussed. The effects of different reaction conditions, such as different water carrying agents, the amount of water carrying agent, the calcination temperature, the calcination time, the amount of catalysts, the reaction time, the molar ratio of acetic acid to benzyl alcohol, the reaction temperature, the amount of $Fe^{3+}$ loaded and the catalyst drying temperature have also been reviewed.

## DISCUSSION

### Effect of different water carrying agents on the yield of benzyl acetate by addition of tris(trimethylsilylmethyl)tin chloride as the catalyst.

Chen Fushan[5] described the synthesis of tris(trimethylsilyl methyl) tin chloride and benzyl acetate and studied the effects of different reaction conditions on the yield of benzyl acetate using tris(trimethylsilylmethyl) tin chloride as the catalyst. The molar ratio of acetic acid and benzyl alcohol (2.0 : 1.0) and the weight ratio of tris(trimethylsilylmethyl) tin chloride to benzyl alcohol (1.0 %) and the reaction time (2.5 hr) were kept constants while studying the effects of different water carrying agents on the yield of benzyl acetate. Table 1 showed that toluene was one of the best water carrying agents. The reaction time decreased and the yield of benzyl acetate improved because the esterification reaction was a reversible reaction and reactive balance was beneficial to the esterification reaction with addition of water carrying agents. Furthermore, the boiling point of toluene (110 °C) was more than that of water (100 °C), so it effectively improved the yield of benzyl acetate.

**Table 1.** Effects of different water carrying agents on the yield of benzyl acetate

| **Water carrying agents** | Cyclohexane | Benzene | Toluene |
|---|---|---|---|
| **Yield of BzOAc, %** | 75.3 | 81.6 | 87.8 |

### Effect of the amount of water carrying agents on the yield of benzyl acetate by addition of tris(trimethyl-silylmethyl) tin chloride as the catalyst

Chen Fushan[5] described effects of the amount of water carrying agents (toluene) on the yield of benzyl acetate under the condition. When the molar ratio of acetic acid and benzyl alcohol (2.0 : 1.0) and the weight ratio of tris(trimethylsilyl methyl) tin chloride to benzyl alcohol (1.0 %) and the reaction time (2.5 hr) were kept constants. The experimental results presented in Table 2 show that the yield of benzyl acetate first increased and then decreased with an increase in the amount of toluene. It was noticed that the maximum yield of benzyl acetate 87.8 % was attained when the amount of toluene was 80 % of benzyl alcohol weight.

**Table 2**. The relationship between the amount of toluene and the yield of benzyl acetate

| **Weight ratio of toluene to benzyl alcohol, %** | 40 | 60 | 80 | 100 | 120 |
|---|---|---|---|---|---|
| **Yield of BzOAc, %** | 65.7 | 73.5 | 87.8 | 85.1 | 81.9 |

## Effect of the calcination temperature on the yield of benzyl acetate by addition of $S_2O_8^{2-}$ - $Fe_2O_3$ - CoO as the catalyst

Zhang Yingjun[6] used $S_2O_8^{2-}$ - $Fe_2O_3$ - CoO as the catalyst while the molar ratio of acetic acid : benzyl alcohol : water carrying (cyclohexane) (2.0 : 3.0 : 0.093) and the reaction time (2.5 hr) were kept constants. Effects of the calcination temperature, Table 3, indicated that the yield of benzyl acetate first increased and then decreased with an increase in the calcination temperature. When the calcination temperature was lower than 500 °C, it was not enough to get rid of water and $(NH_4)_2S_2O_8$ from this reaction system, so $S_2O_8^{2-}$ on the surface of the catalyst did not combine with metallic oxides to become a strong acid centre. On the other hand, when the calcination temperature was higher than 500 °C, $(NH_4)_2S_2O_8$ decomposed to release $SO_2$. The catalytic activity decreased due to loss of $S_2O_8^{2-}$ from the surface of the catalyst and the specific surface area decreased. It was observed that the maximum yield of benzyl acetate reached 94.1 % when the calcination temperature was 500 °C.

**Table 3.** Effects of the calcination temperature on the yield of benzyl acetate.

| **Calcination temp., °C** | 300 | 400 | 500 | 600 |
|---|---|---|---|---|
| **Yield of BzOAc, %** | 76.8 | 88.9 | 94.1 | 89.0 |

## Effect of the calcination time on the yield of benzyl acetate by addition of $S_2O_8^{2-}$-$Fe_2O_3$-CoO as the catalyst

Zhang Yingjun[6] also studied the effects of the calcination time on the yield of benzyl acetate by keeping the molar ratio of acetic acid to benzyl alcohol to water carrying (cyclohexane) at 2.0:3.0:0.093 and the reaction time, 2.5 hr, constant. The experimental results, Table 4, show that the yield of benzyl acetate first increased and then decreased with an increase in the calcination time. The reason is that when the calcination time was less than 2.5 hr, the catalyst had no time to become the superacid. On the other hand, when the calcination time was more than 2.5 hr, its catalyst construction may have collapsed and its specific surface area had decreased. It was noticed that the maximum yield of benzyl acetate was 95.7 % when the calcination time was 2.5 hr.

**Table 4.** The effect of the calcination time on the yield of benzyl acetate

| **Calcination time, h** | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
|---|---|---|---|---|---|
| **Yield of BzOAc, %** | 70.1 | 78.9 | 87.9 | 95.7 | 94.3 |

## Effect of the added amount of N-methylpyrrolidone hydrosulfate as the catalyst on the yield of benzyl acetate

Zhou Beilei[7] replaced concentrated sulfuric acid with ionic liquids (N-methylpyrrolidone hydrosulfate) as catalysts to synthesise benzyl acetate. The reaction time (1 hr), the reaction temperature (110 ℃) and the molar ratio of acetic acid to benzyl alcohol (1.4 : 1.0) were kept constants. The results, Table 5, show that the yield of benzyl acetate increased with increasing amount of N-methylpyrrolidone hydrosulfate. When the amount of N-methylpyrrolidone hydrosulfate was 5.0 % of benzyl alcohol molar, the yield of benzyl acetate was maximum at 63.8 %.

**Table 5.** The effect of the amount of N-methylpyrrolidone hydrosulfate on the yield of benzyl acetate

| **Molar ratio of N-methylpyrrolidone hydrosulfate to benzyl alcohol (%)** | **Yields of BzOAc (%)** |
|---|---|
| 0.1 | 53.2 |
| 0.5 | 60.5 |
| 1.0 | 62.8 |
| 1.5 | 63.0 |
| 2.0 | 63.3 |
| 2.5 | 63.5 |
| 5.0 | 63.8 |

## Effect of the reaction time on the yield of benzyl acetate by addition of the weight ratio of $FeCl_3$ to carbon (46 %) as the catalyst

Yu Junfeng[8] described the synthesis of benzyl acetate and studied the effects of different reaction conditions on the yield of benzyl acetate using $FeCl_3$/carbon as the catalyst. The molar ratio of acetic acid and benzyl alcohol (1.0 : 1.8) and the weight ratio of $FeCl_3$/carbon to benzyl alcohol (10.29 %) and the reaction time (2.0 hr) were kept constants while studying the effects of the reaction time on the yield of benzyl acetate. Table 6 showed that the yield of benzyl acetate first increased and then decreased with an increase in the reaction time. It was observed that the maximum yield of benzyl acetate 87.8 % was attained when the reaction time was 2 hr.

**Table 6.** The effect of the reaction time on the yield of BzOAc

| **Reaction time, h** | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 |
|---|---|---|---|---|---|
| **Yield of BzOAc, %** | 68.3 | 77.4 | 84.2 | 89.1 | 88.6 |

**Effect of the molar ratio of acetic acid to benzyl alcohol on the yield of benzyl acetate by addition of $SO_4^{2-}$-$ZrO_2$-$Nd_2O_3$ as the catalyst**

Yang Yiwen[9] described the effects of the molar ratio of acetic acid to benzyl alcohol on the yield of benzyl acetate under the condition when the reaction temperature (120 °C) and the weight ratio of $SO_4^{2-}$ - $ZrO_2$ - $Nd_2O_3$ to benzyl alcohol (1.0 %) and the reaction time (5.0 hr) were kept constants. The experimental results presented in Table 7 show that the yield of benzyl acetate first increased and then decreased with an increase in the molar ratio of acetic acid to benzyl alcohol. It was noticed that the maximum yield of benzyl acetate 92.0 % was attained when the molar ratio of acetic acid to benzyl alcohol was 5.0 : 1.0.

**Table 7.** The relationship between the molar ratio of acetic acid to benzyl alcohol and the yield of benzyl acetate

| **AcOH/BzOH molar ratio** | 1.0 | 2. | 3 | 4 | 50 | 6 |
|---|---|---|---|---|---|---|
| **Yield of BzOAc, %** | 68.9 | 86.7 | 87.2 | 90.1 | 92.0 | 90.1 |

**Effects of the reaction temperature on the yield of benzyl acetate by addition of $SO_4^{2-}$ - $ZrO_2$ - $Nd_2O_3$ as the catalyst**

Yang Yiwen[9] used $SO_4^{2-}$ - $ZrO_2$ - $Nd_2O_3$ as a catalyst while the molar ratio of acetic acid to benzyl alcohol (5.0:1.0), the reaction time (5 hr) and the weight ratio of $SO_4^{2-}$-$ZrO_2$-$Nd_2O_3$ to benzyl alcohol (6 %) were kept constants. Effects of the reaction temperature on the yields of benzyl acetate, Table 8, indicated that the yield of benzyl acetate first increased and then decreased with an increase in the reaction temperature. It was observed that the maximum yield of benzyl acetate reached 86.7 % when the reaction temperature was 120 °C.

**Table 8.** The effects of the reaction temperature on the yield of benzyl acetate

| **T, °C** | 100 | 110 | 120 | 130 | 140 | 150 |
|---|---|---|---|---|---|---|
| **Yield of BzOAc, %** | 71.5 | 83.8 | 86.7 | 81.5 | 86.0 | 82.8 |

**Effect of the amount of $Fe^{3+}$ loaded on the yield of benzyl acetate by addition of strong acid cation exchange resin loaded $Fe^{3+}$ as the catalyst**

Jiang Hongzhi[10] studied effects of the amount of $Fe^{3+}$ loaded on the yield of benzyl acetate by keeping the molar ratio of acetic acid to benzyl alcohol (1.0 : 1.0), the reaction time (3.3 hr), the reaction temperature (80 °C) and the weight ratio of strong acid cation exchange resin loaded $Fe^{3+}$ to benzyl alcohol constant (10.0 %). The experimental results, Table 9, show that the yield of benzyl acetate first increased and then decreased with an increase in the amount of $Fe^{3+}$ loaded. It was observed that the maximum yield of benzyl acetate 52.52 % was attained when the amount of $Fe^{3+}$ loaded was 0.3656.

**Table 9.** The effect of the amount of $Fe^{3+}$ loaded on the yield of benzyl acetate

| **$Fe^{3+}$ amount before loading mmol $L^{-1}$** | **Loading time, h** | **The amount of $Fe^{3+}$ loaded, mmol $L^{-1}$** | **Yields of BzOAc, %** |
|---|---|---|---|
| 13.44 | 0.083 | 0.2222 | 50.57 |
| 22.30 | 0.083 | 0.3656 | 52.52 |
| 23.61 | 0.083 | 0.4233 | 51.70 |
| 52.73 | 0.083 | 0.7198 | 47.55 |
| 78.13 | 0.083 | 0.8344 | 43.53 |
| 150.08 | 0.083 | 1.006 | 43.36 |

**Effects of the catalyst drying temperature on the yield of benzyl acetate by addition of strong acid cation exchange resin loaded $Fe^{3+}$ as the catalyst**

Jiang Hongzhi[10] also studied the effects of the catalyst drying temperature on the yield of benzyl acetate while the molar ratio of acetic acid to benzyl alcohol (1.0:1.0), the reaction time (3.3 hr), the reaction temperature (80 °C) and the weight ratio of strong acid cation exchange resins loaded $Fe^{3+}$ to benzyl alcohol (10.0 %) were kept constants. Effects of the catalyst drying temperature on the yields of benzyl acetate, Table 10, indicated that the yield of benzyl acetate first increased and then decreased with an increase in the catalyst drying temperature. It was observed that the maximum yield of benzyl acetate 58.37 % was attained when the catalyst drying temperature was 55 °C.

**Table 10.** The effect of the catalyst drying temperature on the yield of benzyl acetate

| **Catalyst drying temperature, °C** | 45 | 55 | 65 | 75 | 90 |
|---|---|---|---|---|---|
| **Yield of BzOAc %** | 49.36 | 58.37 | 51.21 | 48.12 | 47.98 |

## CONCLUSION

Effects of different reaction conditions such as different water carrying agents, the amount of water carrying agent, the catalyst calcination temperature, the calcination time and the amount of catalysts, the reaction time, the molar ratio of acetic acid to benzyl alcohol, the reaction temperature, the amount of $Fe^{3+}$ loaded and the catalyst drying temperature, tris(trimethylsilylmethyl) tin chloride, $S_2O_8^{2-}$-$Fe_2O_3$–CoO, N-methylpyrrolidone hydrosulfate, the weight ratio of $FeCl_3$ to carbon (46 %), $SO_4^{2-}$-$ZrO_2$-$Nd_2O_3$ and strong acid cation exchange resin loaded $Fe^{3+}$, on the synthesis of benzyl acetate from benzyl alcohol and acetic acid were studied, and these are summarised as follows:

(1) The maximum yield was 81.6 % by using tris(trimethylsilylmethyl) tin chloride as the catalyst and toluene as the water carrying agent.

(2) The maximum yield was 87.8 % under the condition of toluene/benzyl alcohol weight ratio (80 %).

(3) The maximum yield was 94.1 % at 500 °C (the calcination temperature) when $S_2O_8^{2-}$ - $Fe_2O_3$ - CoO was used as the catalyst.

(4) The maximum yield was 95.7 % in 2.5 hr (the calcination time) when $S_2O_8^{2-}$-$Fe_2O_3$-CoO was the catalyst.

(5) The maximum yield was 63.8 % when N-methylpyrrolidone hydrosulfate was the catalyst and the amount of N-methylpyrrolidone hydrosulfate was 5.0 % of molar benzyl alcohol**.**

(6) The maximum yield was 87.8 % in 2.0 h when $FeCl_3$/carbon was the catalyst.

(7) The maximum yield was 92.0 % when $SO_4^{2-}$-$ZrO_2$-$Nd_2O_3$ was the catalyst and the molar ratio of acetic acid to benzyl alcohol was 5.0 : 1.0.

(8) The maximum yield was 86.71 % at 120 °C (the reaction temperature) when $SO_4^{2-}$-$ZrO_2$-$Nd_2O_3$ was the catalyst.

(9) The maximum yield was 52.52 % when strong acid cation exchange resin loaded $Fe^{3+}$ was the catalyst and the amount of $Fe^{3+}$ loaded was 0.3656.

(10) The maximum yield was 58.37 % at 55 °C (the catalyst drying temperature) when strong acid cation exchange resins loaded $Fe^{3+}$ was the catalyst**.**

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