ISSN : 0974 - 7443 Volume 9 Issue 4

CHEMICAL TECHNOLOGY

An Indian Journal

Review

CTAIJ 9(4) 2014 [154-157]

Effects of different reaction conditions on the synthesis of terpinyl acetate

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ABSTRACT

The main properties of terpinyl acetate have been introduced. Different catalysts that consist of solid superacid SO_4^{2-} /ZnO-TiO_2, $SnCl_4 \cdot 5\ H_2\ O$, H_3PO_4/[C_4 mim]BF_4, functional polyether ionic liquid (1-(3-sulfonic group)propyl -3 -polyoxyethyleneimi - dazole dihydrogen phosphate ([$HS0_3$ - $(CH_2)_3$ - im - $(CH_2CH_2O)_n$ H] H_2PO_4)) and $SO^{2-}{}_4$ /SnO_2 - CeO_2 have also been introduced. Effects of different reaction conditions such as the amount of catalyst, the molar ratio of terpineol to acetic anhydridel, the reaction temperature, the reaction time and reusable catalyst times are discussed. The optimum amount of catalyst, the molar ratio of terpineol to acetic anhydridel, the reaction temperature, the reaction time and reusable catalyst times are beneficial to improve the yield of terpinyl acetate.

KEYWORDS

Overview;
Reaction conditions;
Terpinyl acetate.

INTRODUCTION

Terpinyl acetate is one type of perfumes and the colorless liquids. It is widely used as a synthetic flavouring agent[1]. There are two steps to synthesize terpinyl acetate. The first step is that terpilenol is gotten by using turpentine as a feedstock. The second step is that terpineol and acetic anhydridel react to produce terpinyl acetate. Concentrated sulphuric acid is one of the main catalysts, but apart from several advantages, such as more secondary reaction taking place, low yield and purity of terpinyl acetate, it has a lot of disadvantages also. Lot of waste water is discharged during the process causing severe environmental pollution problem and at the same time equipments are corroded[2].

In the present paper, different catalysts such as solid superacid SO_4^{2-} /ZnO-TiO_2, $SnCl_4 \cdot 5\ H_2\ O$, H_3PO_4/[C_4mim]BF_4, functional polyether ionic liquid (1-(3-sulfonic group)propyl -3 -polyoxyethyleneimi - dazole dihydrogen phosphate ([$HS0_3$ - $(CH_2)_3$ - im - $(CH_2CH_2O)_n$ H] H_2PO_4)) and $SO^{2-}{}_4$ /SnO_2 - CeO_2 have been evaluated in the synthesis of terpinyl acetate. Effects of different reaction conditions, such as the amount of catalyst, the molar ratio of terpineol to acetic anhydridel, the reaction temperature, the reaction time and reusable catalyst times, on the synthetic method of terpinyl acetate have been reviewed. Furthermore, the optimized reaction conditions are also pointed out.

RESULTS AND DISCUSSION

Effects of the amount of catalyst on yields of terpinyl acetate

Yu Shitao[3] described effects of the amount of solid superacid SO_4^{2-}/TiO_2 on yields of terpinyl acetate by keeping the reaction time (6 hours), the molar ratio of terpineol to acetic anhydridel (1.0 : 1.3) and the reaction temperature (40 °C). The experimental results, TABLE 1, showed that the yield of terpinyl acetate in-

TABLE 1 : Effects of the amount of catalyst on yields of terpinyl acetate

Reaction time, h	Molar ratio of terpineol to acetic anhydridel	Reaction Temperature, °C	Amount of catalyst, %	Yield of terpinyl acetate, %
6	1.0:1.3	40	0.5	64.0
6	1.0:1.3	40	1.0	70.4
6	1.0:1.3	40	1.5	80.7
6	1.0:1.3	40	2.0	83.9
6	1.0:1.3	40	2.5	82.8

creased with an increase in the amount solid superacid SO_4^{2-}/TiO_2. It was observed that the maximum yield of terpinyl acetate 83.9 % was attained when the amount of solid superacid SO_4^{2-}/TiO_2 was 2.0 g. Since then, the yield of terpinyl acetate was decreased with the amount of solid superacid SO_4^{2-}/TiO_2 addition.

Effects of the molar ratio of terpineol to acetic anhydridel on yields of terpinyl acetate

Zhao Qianrong[4] explained the synthetic method of terpinyl acetate by using $SnCl_4 \cdot 5H_2O$ as a catalyst. The reaction time, the amount of $SnCl_4 \cdot 5H_2O$, and the reaction temperature kept at constants were 4.0 hours, 2% of total reactant and 30 °C, respectively. Effects of the molar ratio of terpineol to acetic anhydridel on yields of terpinyl acetate had been discussed. TABLE 2 showed effects of the molar ratio of terpineol to acetic anhydridel on yields of terpinyl acetate. The yield of terpinyl acetate increased with an increase in the molar ratio of terpineol to acetic anhydridel. When the molar ratio of terpineol to acetic anhydridel was 1.0 : 1.4, the maximum yield of terpinyl acetate attained was 91.3 %. After that, the yield of terpinyl acetate was decreased with the amount of acetic anhydridel addition.

Effects of the reaction temperature on yields of terpinyl acetate

Liu Shiwei[5] used phosphoric acid/ionic liquid composite, that is $H_3PO_4/[C_4mim]BF_4$, as a catalyst to synthesize terpinyl acetate. The experiment was conducted by keeping $H_3PO_4/[C_4mim]BF_4$ catalyst (0.03 g), the reaction time (10 hours) and the ratio of terpineol to acetic anhydride (1.0 : 1.5). Effects of the reaction temperature on yields of terpinyl acetate had been discussed. TABLE 3 presented effects of the reaction temperature on yields of terpinyl acetate. The yield of terpinyl acetate increased with an increase in the reaction temperature. It was noticed that when the reaction temperature was 40 °C, the maximum yield of terpinyl acetate attained was 86.5 %. When the temperature reached above 40 °C, the yield of terpinyl acetate was decreased.

TABLE 2 : Effects of the molar ratio of terpineol to acetic anhydridel on yields of terpinyl acetate

Reaction time, h	Amount of catalyst, % of total reactant	Reaction temperature, °C	Molar ratio of terpineol to acetic anhydridel	Yield of terpinyl acetate, %
4	2	30	1.0:1.2	89.8
4	2	30	1.0:1.4	91.3
4	2	30	1.0:1.6	85.5
4	2	30	1.0:1.8	82.2
4	2	30	1.0:2.0	72.3

TABLE 3 : Effects of the reaction temperature on yields of terpinyl acetate

Amount of catalyst, % of terpineol mass	Reaction time, h	Molar ratio of terpineol to acetic anhydride	Reaction Temperature, °C	Yield of terpinyl acetate, %
3	10	1.0:1.5	20	73.0
3	10	1.0:1.5	30	84.7
3	10	1.0:1.5	40	86.5
3	10	1.0:1.5	50	76.1
3	10	1.0:1.5	60	46.0

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Effects of the reaction time on yields of terpinyl acetate

Liu Shiwei[6] studied functional polyether ionic liquid (1-(3-sulfonic group)propyl -3 -polyoxyethyleneimi - dazole dihydrogen phosphate ([HS0$_3$ - (CH$_2$)$_3$ - im - (CH$_2$CH$_2$O)$_n$ H] H$_2$PO$_4$)), as a catalyst to synthesize terpinyl acetate. The experiment was conducted by keeping the molar ratio of terpineol to acetic anhydridel (1.0 : 1.5), the reaction temperature (40 °C) and the amount of acidic functional polyether ionic liquid (1.5 g). Effects of the reaction time on yields of terpinyl acetate had been discussed. TABLE 4 presented effects of the reaction time on yields of terpinyl acetate. The yield of terpinyl acetate gradually increased with an increase in the reaction time. It was indicated that when the reaction time was 8 hours, the maximum yield of terpinyl acetate attained was 87.8 %. When the time was over 8 hours, the yield of terpinyl acetate was decreased.

Effects of reusable catalyst times on yields of terpinyl acetate

Guo Haifu[7] discussed reusable SO^{2-}_4 /SnO_2 - CeO_2 times on yields of terpinyl acetate. The experiment was conducted by keeping the molar ratio of terpineol to acetic anhydridel (1.0 : 1.2), the reaction temperature (50 °C), the reaction time (3.5 hours) and the amount of SO^{2-}_4 /SnO_2 - CeO_2 (3 % of terpineol mass). TABLE 5 presented effects of reusable SO^{2-}_4 /SnO_2 - CeO_2 times on yields of terpinyl acetate. After SO^{2-}_4 / SnO_2 - CeO_2 was reused 5 times, the yield of terpinyl acetate still reached 77.5 %.

TABLE 4 : Effects of the reaction time on yields of of terpinyl acetate

Amount of catalyst, g	Reaction temperature, °C	Molar ratio of terpineol to acetic anhydridel	Reaction Time, h	Yield of terpinyl acetate, %
1.5	40	1.0:1.5	6	83.7
1.5	40	1.0:1.5	8	87.8
1.5	40	1.0:1.5	10	87.3
1.5	40	1.0:1.5	12	87.1

TABLE 5 : Effects of the reusable catalyst on yields of terpinyl acetate

Molar ratio of terpineol to acetic anhydridel	Reaction temperature, °C	Reaction Time, h	Amount of catalyst, % of terpineol mass	Reusable catalyst times	Yield of terpinyl acetate, %
1.0:1.2	50	3.5	3	1	82.4
1.0:1.2	50	3.5	3	2	81.6
1.0:1.2	50	3.5	3	3	79.1
1.0:1.2	50	3.5	3	4	76.8
1.0:1.2	50	3.5	3	5	77.5

CONCLUSION

Based on the above discussion and review, using terpineol and acetic anhydridel as feedstocks and solid superacid SO_4^{2-} /ZnO-TiO_2, $SnCl_4 \cdot 5 H_2O$, H_3PO_4/ [C_4mim]BF_4, functional polyether ionic liquid (1-(3-sulfonic group)propyl -3 -polyoxyethyleneimi - dazole dihydrogen phosphate ([HS0$_3$ - (CH$_2$)$_3$ - im - (CH$_2$CH$_2$O)$_n$ H] H$_2$PO$_4$))and SO^{2-}_4 /SnO_2 - CeO_2 as catalysts, effects of the amount of catalyst, the molar ratio of terpineol to acetic anhydridel, the reaction temperature, the reaction time and reusable catalyst times have been discussed. The experimental results obtained are the following:

(1) The maximum yield of terpinyl acetate 83.9 % was attained when the amount of solid superacid SO_4^{2-} /TiO_2 was 2.0 g.

(2) When the molar ratio of terpineol to acetic anhydridel was 1.0 : 1.4, the maximum yield of terpinyl acetate attained was 91.3 %.

(3) When the reaction temperature was 40 °C, the maximum yield of terpinyl acetate attained was 86.5 %.

(4) The reaction time was 8 hours, the maximum yield of terpinyl acetate attained was 87.8 %.

(5) After SO^{2-}_4 /SnO_2 - CeO_2 was reused 5 times, the yield of terpinyl acetate still reached 77.5 %.

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