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Effects of different reaction conditions on the synthesis of tributyl citrate

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ABSTRACT

The main properties of tributyl citrate have been introduced. Different catalysts that consist of solid superacid SO_4^{2-} /ZnO-TiO_2, carbon-based solid acid, modified silica gel supported phosphotungstic acid and phosphotungstic acid have also been introduced. Effects of different reaction conditions such as the amount of catalyst, the molar ratio of citric acid to butanol, the reaction temperature and the reaction time are discussed. The optimum amount of catalyst, the molar ratio of citric acid to butanol, the reaction temperature and the reaction time are beneficial to improve the yield of tributyl citrate.

KEYWORDS

Overview;
Reaction conditions;
Tributyl citrate.

INTRODUCTION

Tributyl citrate is one of nontoxic and biodegradable plasticizers. It also is widely used in polyethylene, polyvinyl chloride, polypropylene, celluosic resin, etc. There are a lot of advantages listed as follows: good intermiscibility with resin, high plasticizing efficiency, no poison and low volatility, etc. 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 tributyl citrate, 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[1].

In the present paper, different catalysts such as solid superacid SO_4^{2-} /ZnO-TiO_2, carbon-based solid acid, modified silica gel supported phosphotungstic acid and phosphotungstic acid have been evaluated in the synthesis of tributyl citrate. Effects of different reaction conditions, such as the amount of catalyst, the molar ratio of citric acid to butanol, the reaction temperature and the reaction time, on the synthetic method of tributyl citrate have been reviewed. Furthermore, the optimized reaction conditions are also pointed out.

RESULTS AND DISCUSSION

Effects of the amount of catalyst on yields of tributyl citrate (TBC)

Feng Xilan[2] studied effects of the amount of solid superacid SO_4^{2-}/ZnO-TiO_2 on yields of tributyl citrate by keeping the reaction time (3 hours), the molar ratio of citric acid to n-butanol (1.0 : 4.0) and the reaction temperature (130 °C - 138 °C). The experimental results, TABLE 1, showed that the yield of tributyl citrate increased with an increase in the amount solid superacid SO_4^{2-}/ZnO-TiO_2. It was observed that the maximum yield of tributyl citrate 98.9 % was attained when the amount of solid superacid SO_4^{2-}/ZnO-TiO_2 was 1.0 % of total reactant. Since then, the yield of tributyl citrate was decreased with the amount of solid superacid SO_4^{2-} /ZnO-TiO_2 addition.

TABLE 1 : Effects of the amount of catalyst on yields of tributyl citrate

Reaction time, h	Molar ratio of citric acid to n-butanol	Reaction Temperature, °C	Amount of catalyst, %	Yield of Tributyl citrate, %
3	1.0:4.0	130-138	0.3	72.5
3	1.0:4.0	130-138	0.5	80.5
3	1.0:4.0	130-138	0.7	92.3
3	1.0:4.0	130-138	1.0	98.9
3	1.0:4.0	130-138	1.5	98.6
3	1.0:4.0	130-138	2.0	98.0

Effects of the molar ratio of citric acid to butanol on yields of tributyl citrate

Hu Renguo[3] used carbon-based solid acid as a catalyst and citric acid and butanol as feedstocks to synthesize tributyl citrate. The reaction time and the amount of carbon-based solid acid kept at constants were 4.0 hours and 0.3 g per 0.1 mol of citric acid of total reactant, respectively. Effects of the molar ratio of citric acid to butanol on yields of tributyl citrate had been discussed. TABLE 2 showed effects of the molar ratio of citric acid to butanol on yields of tributyl citrate. The yield of tributyl citrate increased with an increase in the molar ratio of citric acid to butanol. When the molar ratio of citric acid to butanol was 1.0 : 4.5, the maximum yield of tributyl citrate attained was 99.1 %. After that, even if the amount of butanol was increased, the yield of tributyl citrate wasn't increased. Otherwise, it had trend to be decreased.

TABLE 2 : Effects of the molar ratio of citric acid to butanol on yields of tributyl citrate

Amount of catalyst, g per 0.1 mol of citric acid	Reaction time, h	Molar ratio of citric acid to butanol	Yield of Methyl oleate, %
0.3	4	1.0:3.5	95.0
0.3	4	1.0:4.0	97.9
0.3	4	1.0:4.5	99.1
0.3	4	1.0:5.0	98.9
0.3	4	1.0:6.0	98.6

Effects of the reaction temperature on yields of tributyl citrate

Nie Lijuan[4] described modified silica gel supported phosphotungstic acid as a catalyst to synthesize tributyl citrate. The experiment was conducted by keeping modified silica supported phosphotungstic acid catalyst (2.5 g), phosphotungstic acid loading amount (43.5 %), the reaction time (4 hours) and the ratio of citric acid to n-butanol (4.0 : 1.0). Effects of the reaction temperature on yields of tributyl citrate had been discussed. TABLE 3 presented effects of the reaction temperature on yields of tributyl citrate. The yield of tributyl citrate gradually increased with an increase in the reaction temperature. It was noticed that when the reaction temperature was 140 °C, the maximum yield of methyl oleate attained was 92.2 %. When the temperature reached above 140 °C, the yield of methyl oleate was decreased.

TABLE 3 : Effects of the reaction temperature on yields of of tributyl citrate

Amount of catalyst, %	Phosphotungstic acid loading amount, %	Reaction time, h	Molar ratio of citric acid to n-butanol	Reaction Temperature, °C	Yield of Tributyl citrate, %
2.5	43.5	4	1.0:4.0	120	85.3
2.5	43.5	4	1.0:4.0	130	89.5
2.5	43.5	4	1.0:4.0	140	92.2
2.5	43.5	4	1.0:4.0	150	90.2
2.5	43.5	4	1.0:4.0	155	87.9

Effects of the reaction time on yields of tributyl citrate

Li Hongchao[5] used phosphotungstic acid as the catalyst while the molar ratio of citric acid to butanol (1.0 : 4.0), the reaction temperature (150 °C) and the amount of phosphotungstic acid (3 % of butanol acid total mass). Effects of the reaction time, Figure 1, indi-

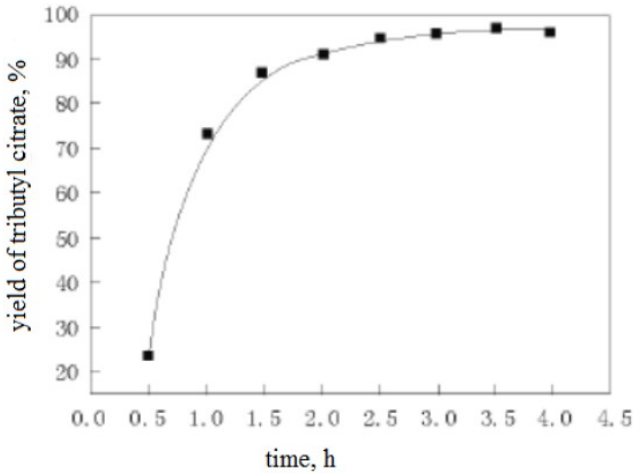

Figure 1 : Effects of the reaction temperature on yields of tributyl citrate

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cated that the yield of increased with an increase in the reaction time. When the reaction time was 3.5 hours, the maximum yield of methyl oleate was 97.96 %. When the reaction time was more than 3.5 hours, the yield of tributyl citrate did not increase.

CONCLUSION

Based on the above discussion and review, using citric acid and butanol as feedstocks and solid superacid SO_4^{2-}/ZnO-TiO_2, carbon-based solid acid, modified silica gel supported phosphotungstic acid and phosphotungstic acid as catalysts, effects of the amount of catalyst, the molar ratio of citric acid to butanol, the reaction temperature and the reaction time have been discussed. The experimental results obtained are the following:

(1) The maximum yield of tributyl citrate 98.9 % was attained when the amount of solid superacid SO42-/ZnO-TiO2 was 1.0 % of total reactant.
(2) When the molar ratio of citric acid to butanol was 1.0 : 4.5, the maximum yield of tributyl citrate attained was 99.1 %.
(3) When the reaction temperature was 140 °C, the maximum yield of methyl oleate attained was 92.2 %.
(4) When the reaction time was 3.5 hours, the maximum yield of methyl oleate was 97.96 %.

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