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PURIFICATION OF HIGH-PURITY 2-MERCAPTOBENZOTHIAZOLE BY TWO-STEPS

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Abstract – High-purity 2-mercaptobenzothiazole (2-MBT) is prepared from crude 2-MBT by aniline method under high pressure by solvent crystallization and deep impurity removal. For the first step of toluene purification, the semi-finished 2-MBT with excellent purity and yield can be obtained when the temperature of toluene solution reaches 100 ^{o}C and the content of toluene is about 1.5 times of that of crude 2-MBT. For the second step of deep purification, the by-products of semi-finished 2-MBT could be further removed by Na_2SO_3 when the mass ratio of water, the 2-MBT and Na_2SO_3 is 2: 1: 0.12 and the reaction condition is under 100 ^{o}C for 0.75 h. As a result, the purity and yield of 2-MBT can reach 99.9% and 97.3%, respectively. The preparation of high-purity 2-MBT would further optimize the market demand and meet the quality standard requirements for the development of other pharmaceutical intermediates or fine chemicals. This strategy solves the current problem of purification 2-MBT, and develops a new process technology route for the production of high-purity 2-MBT.

INTRODUCTION

The 2-mercaptobenzothiazole (2-MBT) heterocyclic compound was first prepared by Hofmann in 1887, and has been widely used as an accelerator and plasticizer, respectively, in the vulcanization process and the rubber industry.[1-3] For example, its output is around 200,000 tons per year in China. In addition, 2-MBT, as an intermediate, also plays an important role in organic synthesis and pharmaceutical chemistry.[4] Thus, the preparation and purification of high-purity 2-MBT are still fascinating in academia and industry.

The preparation of 2-MBT by the reaction of carbon disulfide with *o*-haloaniline, *o*-aminothiophenols, or disulfides have been widely reported.[5-8] However, these approaches often suffer from high temperatures, long reaction times, toxic solvents, and metal catalysts. Furthermore, some of the raw materials could not be obtained directly. Therefore, 2-MBT is papered by the reaction of aniline, carbon disulfide, and sulfur at high temperatures (240-260 ^{o}C) and high pressures (9-10 MPa) in industry practice. However, the crude 2-MBT usually needs to be further purified to meet the purity requirements of the downstream industry, because the product is a mixture of 2-MBT (80-90%), raw materials, and byproducts such as, benzothiazole (BT) and heterocyclic compound resins.[9]

Up to now, extensive methods about 2-MBT purification have been reported. Among these, the acid-base method and the solvent method are commonly used in industry. For the former, although high-purity products can be obtained, the wastewater produced in this process will cause great damage to the environment. In comparison, the solvent method is relative simplicity and non-pollution because the separation process is achieved by utilizing the different solubility between 2-MBT and impurities in solvents. The main solvents reported in the literature are as follows: toluene, or toluene with ethanol, acetone or aniline, and toluene and acetone.[10-12] For instance, Hronec et al. utilized various solvents and their mixtures to purify the crude 2-MBT and realized a high purity of 99%. Whereas, it is difficult to achieve a higher purity by solvent extraction method, due to the inherent solubility of solvent.[10]

In this study, we propose a two-steps purification method based on solvent crystallization and deep impurity removal. And a high-purity 2-MBT with purity of 99.9% is achieved, which is higher than that of 2-MBT obtained by solvent extraction method.

RESULTS AND DISCUSSION

Effect of precipitation temperature of 2-MBT in toluene

According to the literature reports, toluene is selected as the extraction solvent due to excellent performance on the purification of crude 2-MBT. The effect of precipitation temperature on the purification of raw materials is investigated after the crude 2-MBT is dissolved in toluene at 200 ^{o}C. Figure 1 shows that, as temperature increases, the purity of 2-MBT elevates while the yield shows conspicuous reduction, and it will further decline at a higher precipitation temperature. Therefore, the precipitation temperature of 20 ^{o}C is the optimal choice for the relatively high purity and yield in the following experiments.

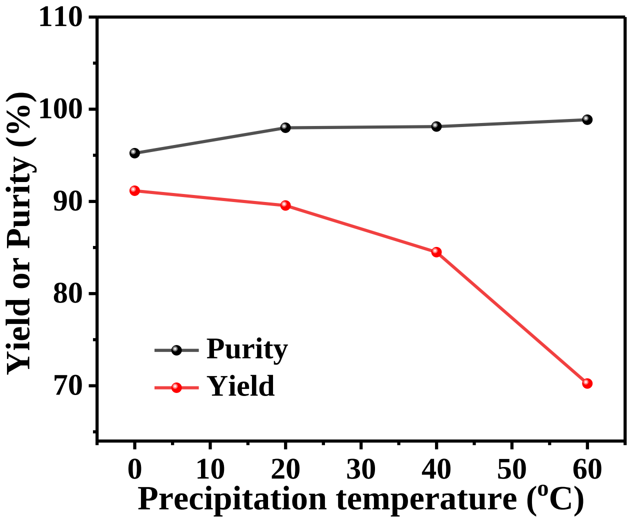


Figure 1. Effect of precipitation temperature on the purification of crude 2-MBT in toluene

Effect of solution temperature of 2-MBT in toluene

In addition to the precipitation temperature, the influence of solution temperature on the purification of raw materials is also examined at 20 °C precipitation temperature. As shown in Figure 2, the purity and yield of 2-MBT have no significant change with the increase of solution temperature from 100 °C to 200 °C. Therefore, the dissolution temperature is set at 100 °C.

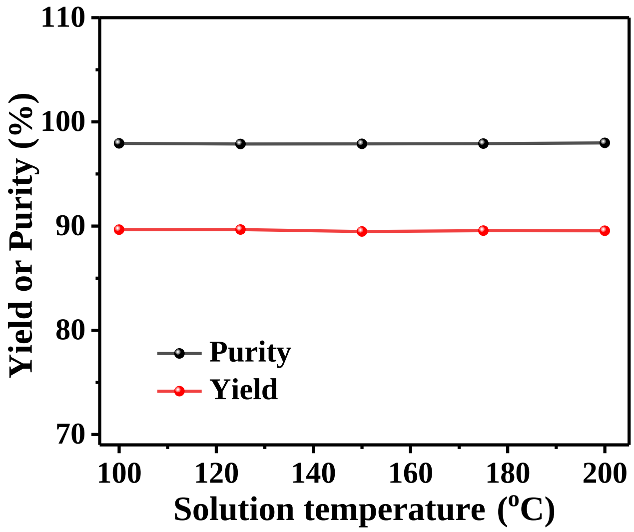


Figure 2. Effect of solution temperature on the purification of crude 2-MBT in toluene

Effect of the content of toluene

Apart from the precipitation temperature, the content of toluene is another important parameter for the purification, which directly affects the purity and yield of crude 2-MBT. As shown in Figure 3, the purity of 2-MBT increases slightly with the increasing of the toluene amount, while the yield of 2-MBT has no significant change until the ratio of toluene and 2-MBT reaches 2.5. Therefore, when the content of toluene is about 1.5 times of that of the crude 2-MBT, the purity and yield of 2-MBT can achieve 98.0% and 89.9% respectively.

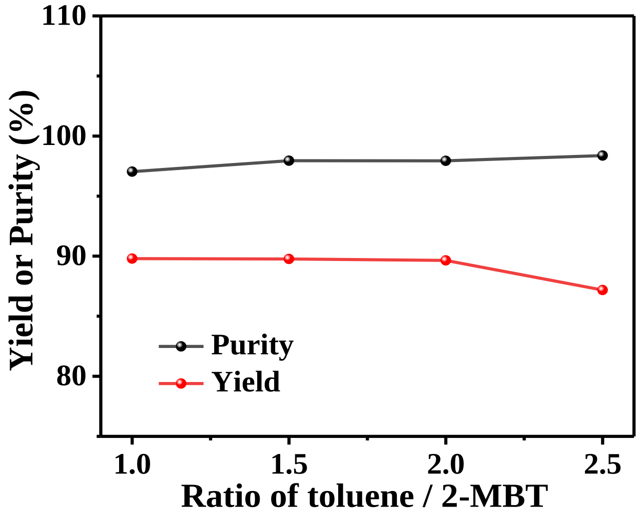


Figure 3. Effect of the amount of toluene on the purification of crude 2-MBT

Effect of toluene after used

Considering the impact on the environment, the recovery of toluene is a significant indicator in industrial application. In the following experiments, the toluene is reused after being obtained through a filter and without any treatment. Figure 4 reveals that the purity of 2-MBT decreases when the toluene is used in the second time. Consequently, other treatment methods, such as distillation, should also be considered to realize the reuse of toluene.

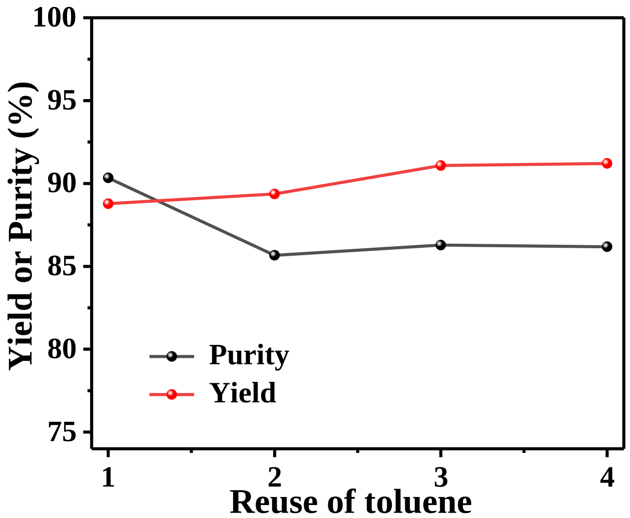


Figure 4. Effect of toluene after used on the purification of crude 2-MBT

Effect of the amount of sodium sulfite

The Na_2SO_3 solution is used to further purify the product 2-MBT recovered by toluene in the following experiments, because some byproducts, such as sulfur, cannot be completely removed by toluene. Figure 5 indicates that the enhanced purity and reduced yield of 2-MBT with the increase of Na_2SO_3 usage from 8.0 g to 12.0 g. However, when the usage of Na_2SO_3 increases to more than 12.0 g, both purity and yield does not change and keep at 99.9% and 97.4%, respectively. Thus, the amount of sodium sulfite is chosen to be 12.0 g.

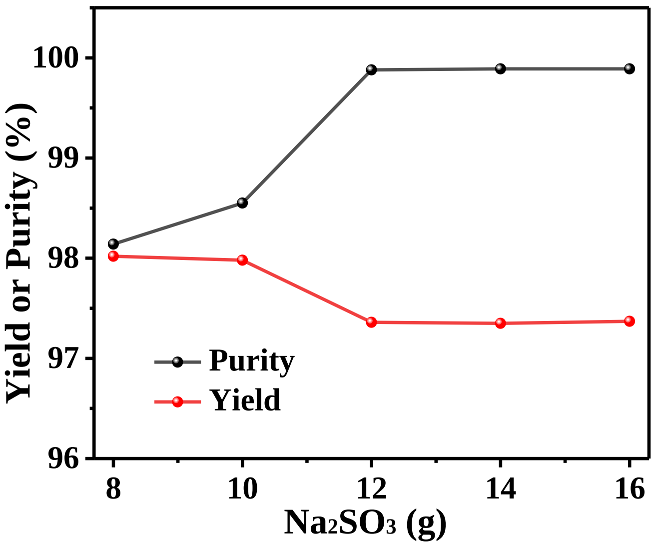


Figure 5. Effect of the amount of Na_2SO_3 on the purification of crude 2-MBT

Effect of the amount of H_2O in Na_2SO_3

In addition, the amount of H_2O is another important parameter for the purification, which also affects the purity and yield of 2-MBT. The influence of the amount of H_2O is investigated and the results are shown in Figure 6. The purity increases to 99.9% and the yield decreases to 97.4% when the water is added from 100.0 g to 200.0 g, while the degree of improved purity and the reduced yield are negligible with the further increase of water. More importantly, the generated wastewater will do great damage to the environment and bring more troubles to the follow-up treatment process. Therefore, the excellent yield and purity of 2-MBT can be obtained when the amount of water is controlled at 200.0 g.

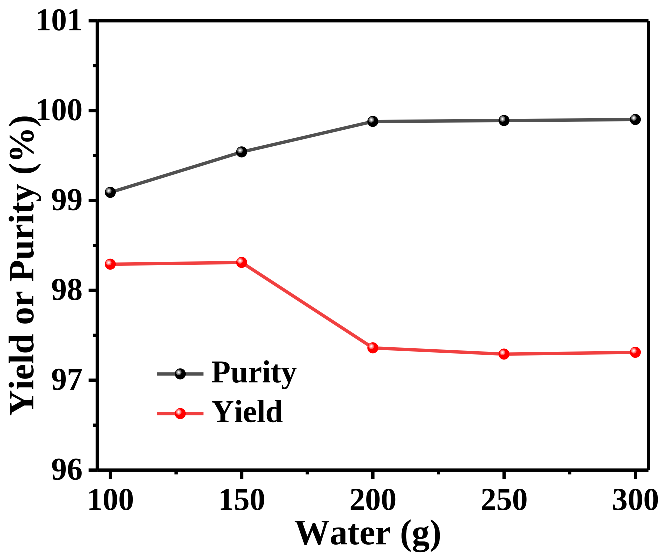


Figure 6. Effect of the amount of H_2O on the purification of crude 2-MBT

Effect of the reaction temperature

The temperature may also influence the reaction between Na_2SO_3 and the byproducts. As observed in Figure 7, the purity of 2-MBT is improved while the yield decreases sharply with temperature increasing. Particularly, when the temperature increases from 80 ^{o}C to 100 ^{o}C, the purity and yield change dramatically. Therefore, the reaction is conducted at 100 ^{o}C to obtain the 2-MBT with 99.9% purity and 97.3% yield.

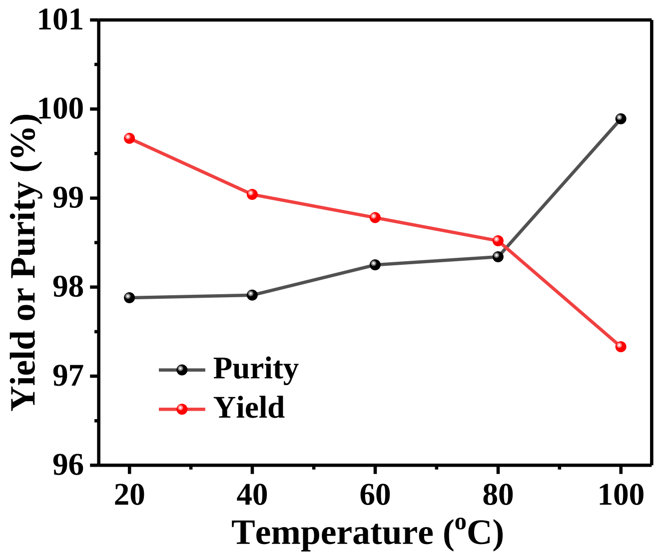


Figure 7. Effect of the reaction temperature on the purification of crude 2-MBT

Effect of the reaction time

Finally, the influence of reaction time is discussed, and the results are shown in Figure 8. The purity and yield of 2-MBT have no obvious change after reacting 0.75 h. Therefore, the reaction time is chosen to be 0.75 h.

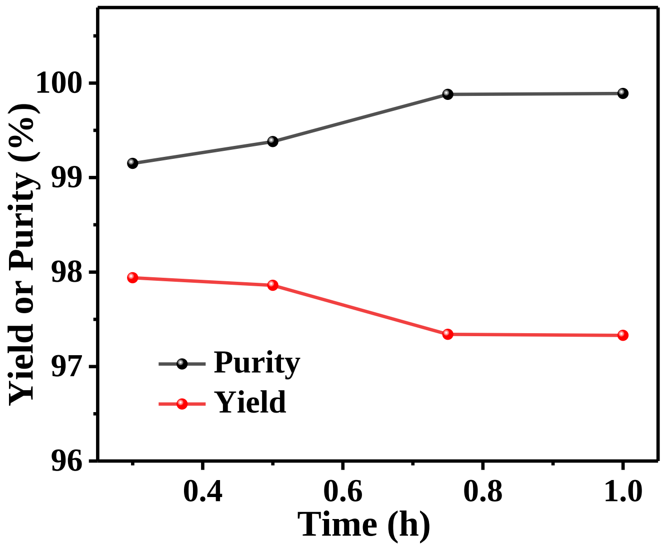


Figure 8. Effect of the reaction time on the purification of crude 2-MBT

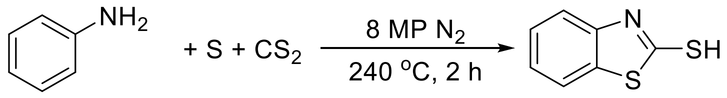
CONCLUSION

In this study, high purity of 2-MBT is obtained from the crude 2-MBT *via* two steps. The semi-finished 2-MBT with 98.0% purity and 89.9% yield is obtained through the first step of toluene purification when the solution temperature is 100 ^{o}C and the toluene content is about 1.5 times of the crude 2-MBT. Whereafter, Na_2SO_3 is used to further remove some by-products of semi-finished 2-MBT for deep impurity removal. The purity and yield of 2-MBT can reach 99.9% and 97.3%, respectively, when the mass ratio of water, 2-MBT and Na_2SO_3 is 2: 1: 0.12 and the reaction condition is under 100 ^{o}C for 0.75 h. This strategy may develop a new process technology route for the production of high-purity 2-MBT.

EXPERIMENTAL

Materials. All chemicals were purchased from Aladdin and Sinopharm Chemical Reagent Co., Ltd., and were employed with no further purification. Deionized H_2O was used in all experiments.

Preparation of crude 2-MTB. The 2-MTB was prepared according to a previous report but with some changes,[13] and were illustrated as the following reactions.

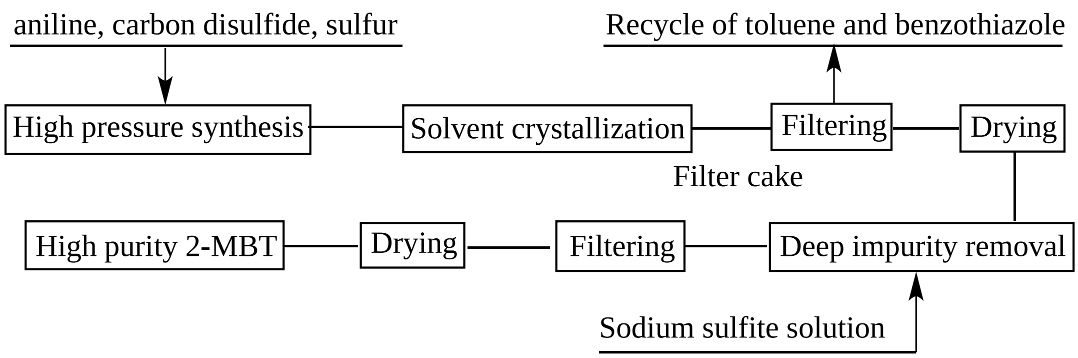


Scheme 1. The process of reactions

Briefly, aniline, carbon disulfide, and sulfur were loaded into a 100 mL stainless-steel autoclave equipped with a magnetic stirrer. After sealing and charging with N_2 (8 MPa), the autoclave was heated to the desired temperature (240 °C) and kept for 2 h. After the reaction, the autoclave was cooled. The raw MTB were collected and analyzed by HPLC.

Purification of crude 2-MBT by toluene. Typically, the crude 2-MBT (1.5 kg) and toluene (2.25 L) were added into a crystallization kettle (5 L). After dissolving the solid at 100 °C, the kettle was cooled at 20 °C. The purified semi-finished 2-MBT was separated by filtration, washed with toluene two times, dried at 100 °C for 12 h, and weighed. From the weight of the solid product, the yield of 2-MBT was determined, and the purity was calculated by HPLC.

Purification of semi-finished 2-MBT by Na_2SO_3 solution. The purification was performed in a stainless steel autoclave. After Na_2SO_3 (12 g) was dissolved in 200 g water, the semi-finished 2-MBT (100 g) was added to the solution. After refluxing 2 h, the solid was obtained by filtering, weighted, and analyzed by HPLC.



Scheme 2. Process flow diagram

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