Study on the Separation of M-Xdi Products by Non-Phosgene Pyrolysis System

Peilin Zhou[1,a], Peng He[2,b,*], Yan Cao[2,c], and Liguo Wang[2,d]

[1]China Academy of Science & Technology Development, Guangxi Branch, Nanning 530022, China;

[2]CAS Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, China.

[a]Zhou11030334@sina.com, [*,b]phe@home.ipe.ac.cn, [c]ycao@ipe.ac.cn, [d]lgwang@ipe.ac.cn

Abstract. m-Xylylene diisocyanate (m-XDI) is a raw material wildly used in the manufacture of high value-added polyurethane products and others. m-XDI is a heat-sensitive and easily polymerized substance, and obtaining high-purity m-XDI in industry is challenging, difficult and costly. In this paper, a coupling process of crystallization distillation was proposed to meet the challenge. First, an experiment was carried out to produce a simulated liquid close to the actual pyrolysis liquid components by the reaction of XDI and ethanol. Secondly, two key factors, the final crystallization temperature and the concentration of the m-XDI reaction liquid, which have great effect on the crystallization process of the m-XDI reaction liquid, are studied. Combined with m-XDI saturated vapor pressure and m-XDI-TLB VLE data, the process of m-XDI separation by crystallization distillation coupling was simulated (as shown in the Figure 1), and the process was compared with that of m-XDI separation by distillation alone. The purity of 99.1% m-XDI was obtained by the coupled process of crystal distillation.

Keywords: m-Xylylene diisocyanate; crystal distillation; process simulation.

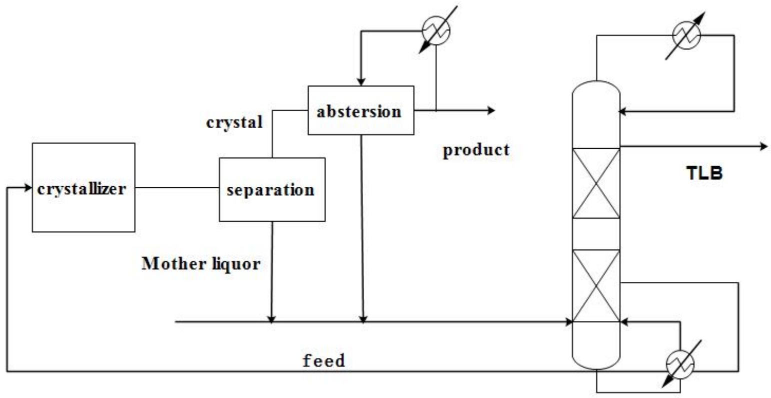

Figure 1. The process flow of crystallization distillation coupling

1. Introduction

m-Xylylene diisocyanate (m-XDI) is a raw chemical feedstock, for which the global and the domestic demand is about, 2000 ~ 3000 t/a and 200 ~ 300 t/a respectively. m-XDI is mainly used in the form of XDI-TMP adduct in China in high-end coatings, photoelectric materials, medical polyurethane materials, high-end polyurethane eye lenses and others, and its performance is superior [1]. m-XDI is difficult to be obtained as monomer because of its heat sensitive property, and its price is too high, which limits the market application and development [2,3]. According to the related VLE data for the measurement and analysis of m-XDI, m-XDI products can be separated by distillation [4]. However, due to the large solvent content used in the pyrolysis of carbamate, a long heating time is required to separate m-XDI products only by distillation operation. When the solvent is gradually separated, the obtained high-concentration m-XDI is very easy to polymerize, and the operation requirements are high, resulting in high energy consumption cost. Considering the nature of m-XDI and the cost and energy consumption of the equipment, the separation process should be selected under suitable pressure and mild conditions. The more common mild separation methods include: chromatographic separation, extraction and crystallization. The supercritical extraction method can separate the product well at low temperature, while the disadvantages are that the separation efficiency is very low and the cost is high, and therefore it is not suitable for the industrial production of m-XDI. Chromatography has a high separation efficiency, but the separation amount is small, and the separation solvent would be introduced to form another mixture, which again needs to be separated. In addition, heat-sensitive substances are not suitable for long-term treatment. Crystallization is the of choice method for many separations, but only a few substances can obtain as high-purity products through one-time crystallization, and most substances usually have the problem of wrapping solvents, hence, multiple crystallization processes are always required for the production of high-purity products, which require a series of cyclic operations and increase the system load and causes huge energy consumption [5]. Moreover, it is difficult to separate m-XDI products by crystallization alone. In addition, the separation of most heat-sensitive substances is usually processed by high vacuum distillation, which can reduce the boiling point temperature of the system and realize large-scale continuous production, etc. Therefore, the coupling process of crystal distillation is proposed to separate m-XDI.

In this experiment, XMI content, crystallization rate and purification capacity in crystals were selected as evaluation indexes, which were defined as:

$$\text{Crystallization rate：Kc} = \frac{\text{Crystal quality}}{\text{Raw material quality}} \times 100\%$$

$$\text{Product refining capacity：Gp} = \frac{\text{Product purity} - \text{Feed purity}}{1 - \text{Feed purity}} \times 100\%$$

2. Study on the separation of m-XDI products from non-phosgene pyrolysis system by crystal-coupled distillation

2.1.Effect of final temperature on crystallization of m-XDI reaction solution

The crystallization temperature, a critical element in the purity of crystals [6], was investigated in this paper. The range of m-XDI liquid crystallization temperatures from minus 10 to above 1 degree Celsius was explored, with the results depicted in Figure 2. When the temperature rises, the crystallization rate shows a downward trend, and -5.0℃ is the obvious point of the downward trend. The XMI content increases with the decrease of the crystallization final temperature, especially at -5~-1℃. When the final crystallization temperature exceeds -3 degrees Celsius, the purification capacity of m-XDI decreases with the increase of temperature.

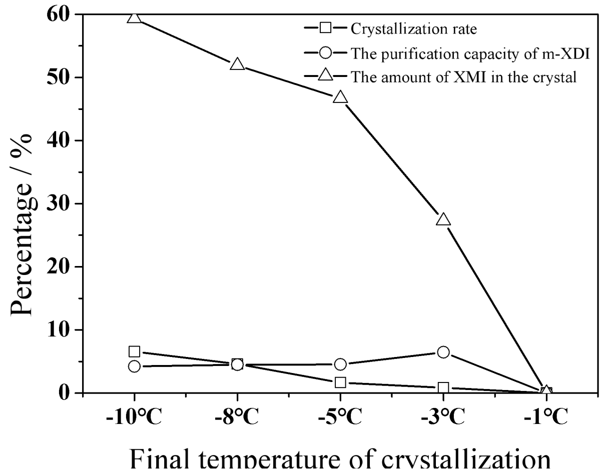

Figure 2. The crystal purity is affected by the varying crystallization temperature

2.2.Effect of different m-XDI concentrations on the crystallization of simulated liquid

Substrate concentration is another key factor affecting the crystallization rate and purity, so the crystallizations of m-XDI with 50-90% concentrations were subsequently investigated（Figure 3）. The purity of XMI is directly proportional to the concentration of m-XDI reaction solution, and then changes slowly with the increase rate of m-XDI crystal content after 60% concentration, indicating that 60% m-XDI reaction liquid concentration is the best crystallization concentration.

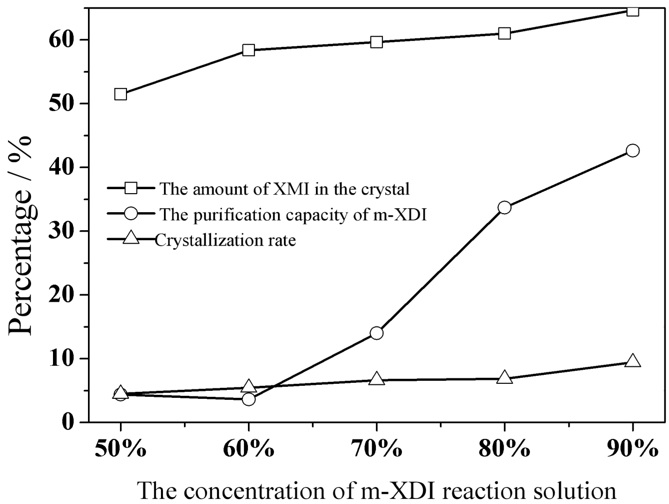

Figure 3. The effect of different m-XDI reaction concentration on the crystallization of simulated liquid

2.3.Design and simulation of m-XDI process for distillation separation

The process simulation and comparison of m-XDI products separated from non-phosgene pyrolysis by crystal distillation coupling method and distillation method were carried out.

The distillation separation of m-XDI is designed, and the process is shown in Figure 4. The feed rate of raw material XDC pyrolysis liquid (mainly composed of TLB, m-XDI and XMI) is 1000 kg/h, the feed pressure is 1 bar, and the feed temperature is 25°C. From the position of 25 theoretical plates, the m-XDI reaction liquid enters the rectification column; when the number of plates is 50 the distillation column is the optimal solution. The top of the tower can be extracted with a purity of 96.3% m-XDI, including 1.2% XMI and 2.5% TLB, and the rectification tower requires 3353.25 kW for heating.

Next, m-XDI coupling separation by crystallization distillation is designed, and the process is shown in Figure 5. The feed conditions are consistent with the rectification conditions mentioned above. From the position where the theoretical number of plates is 20 into the distillation tower with the theoretical number of plates 40, the top of the tower is extracted to obtain 99.1% purity m-XDI, containing 0.2% XMI and 0.5% TLB, and the heating power of the crystallization distillation coupling process is 440.92 kW (without adding crystallization energy consumption). Therefore, the simulation results show that the crystal distillation coupling process is more suitable for separating m-XDI mixture.

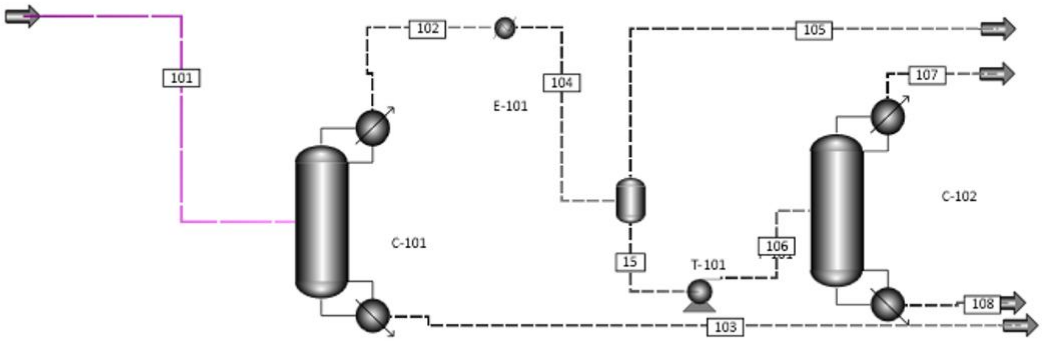

Figure 4. The process of distillation separation XDI. C-101, C-102—rectifying column；101—mixture Raw material；102, 106, 107—overhead；103, 108—Tank distillate；105—Atmospheric connection pipe

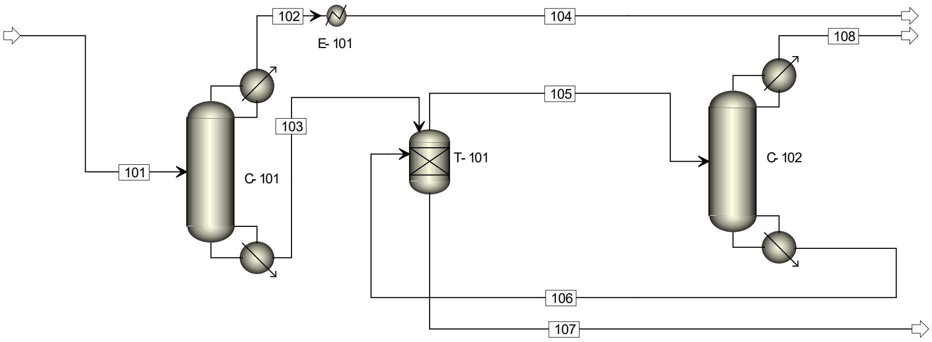

Figure 5. C-101、C-102—rectifying column；T-101—crystallizer；101—mixture Raw material；102、108—overhead；103—Tank distillate；105—Crystalline filtrate；106—Tower kettle production；107—Crystal production； 108—Top distillate

3. Summary

In conclusion, the coupled process of crystallization distillation proposed in this paper can effectively solve the problems of high concentration heat sensitive m-XDI which is easy to polymerize, difficult to separate and high energy consumption. The influence of temperature and concentration of reaction liquid on the crystallization process was investigated. The separation process of m-XDI reaction liquid by coupled crystallization distillation was simulated and compared. The results showed that -5.0°C is the best crystallization temperature of m-XDI, and 60% m-XDI reaction solution is the best crystallization concentration. The separation process of m-XDI products from non-phosgene pyrolysis system by crystal distillation coupled process was simulated and compared with m-XDI products by distillation. Compared with the distillation process, the coupling process of crystal distillation can separate m-XDI reaction liquid to obtain higher purity m-XDI with lower energy consumption. Therefore, the coupled crystal distillation process is suitable for the separation of m-XDI products in non-phosgene pyrolysis system.

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