Purification of 3-hydroxypropionitrile by wiped molecular distillation

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Abstract A new separation method, wiped molecular distillation (WMD), was applied and experimental work was carried out to study the effect of operation parameters such as distillation temperature, pressure, feed flow rate, wiped speed and the separation stages on purifying the raw material containing 95% 3-hydroxypropionitrile (HPN). It was an excellent result that the mass concentration of HPN in the final product can be more than 99.5% under the optimistic operation conditions. The high purity cannot be achieved with normal separating method including rectification and extraction in practice. As for the raw material, a function of HPN purity in distillate was plotted with distillation temperature and pressure in experiment ranges. According to the experiment data obtained and the theory in molecular distillation, the distillation speed of HPN and separation efficiency were computed. It was concluded that the distillation speed of HPN and the separation efficiency were satisfying for industrial production.

Keywords: purification, molecular distillation, wiped, 3-hydroxypropionitrile, efficiency.

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3-hydroxypropionitrile (HPN) is widely used as materials in many organic reactions such as synthesizing medicine, pesticide and polymeric compound. Since the 1970s, HPN has mostly been synthesized with the reaction of acrylonitrile and H_2O catalyzed by NaOH aqueous solution, and the mole yield of HPN is above 85%. However, the HPN must be separated from the acrylonitrile hydration mixture and get rid of water, salt and other side products.

The traditional separation method is evaporation-extraction technology[1], in which water is evaporated in vacuum, then the HPN is extracted into the extractive phase by an organic extractant, and further purified by conventional vacuum rectifying distillation, the final product with a purity of 95% HPN can be attained. However, the traditional separation method should be improved because of the heat decomposition of HPN at 50℃ and the atmospheric pressure, and the high price of extractive solvent.

Another separation method is using macroporous adsorption resin. When the acrylonitrile hydration mixture is adsorbed by NKA-II resin, the yield of HPN can be more than 90%. The advantage of this method is that it omits the two traditional evaporating and extracting steps, reduces the equipment investment, facilitates the operation and avoids the heat decomposition of HPN[1,2]. However, a high purity of 99.5% HPN in product could not be attained in this technology.

There isn't any literature available about the puri-

fication of HPN by molecular distillation to get a high purity of more than 99.5% HPN. Compared with the conventional vacuum distillation, the molecular distillation has the advantages that the crude feed can be separated at much lower operation temperature and the residence time of heating is shorter, which can effectively avoid the heat decomposition of various components[3—7].

In this experiment, the wiped molecular distillation (WMD) equipment was applied and the raw material was 95.0% HPN. The effects of various parameters such as operation temperature and pressure, feed flow rate, rotating speed and number of separation steps were studied.

Finally, the basic mechanism of molecular distillation and advantages of wiped molecular distillation compared with other kinds of molecular distillation methods were discussed[8,9]. According to the data obtained in this experiment, the speed of distilling HPN and the separation efficiency of WMD were evaluated.

1. Experiments

1.1 Raw material

The raw material is 95.0% HPN which was provided by Fushun MeiJing Petrochemical Additive Co., Ltd (China). The chromatomap and concentrations of each component also provided by the company are showed in fig. 1 and table 1 respectively.

According to the data in fig. 1 and table 1, HPN is a middle component in the raw material represented by peak 9. In order to further purify the raw material to obtain more than 99.5% HPN product, both of the heavy components and the light components should be mostly removed. It can be realized through the following way. Firstly, HPN is regarded as a light component and mostly distilled out with other light com ponents. Then in the distillate mixture, HPN is

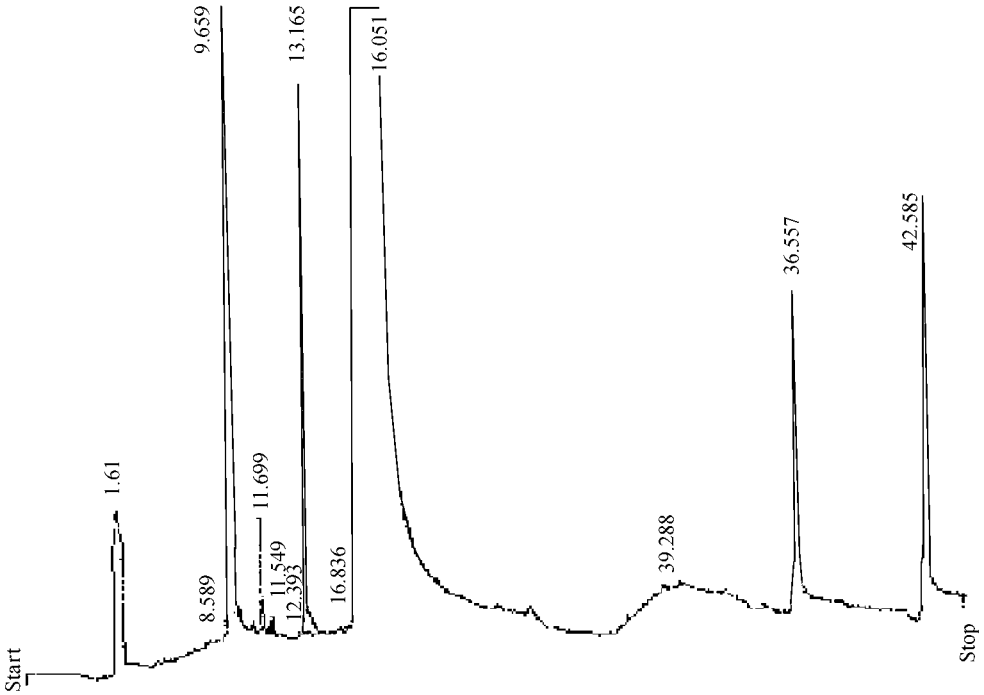

Fig. 1. The chromatomap of raw material in this experiment.

Table 1 Concentration distribution of the raw material.

Peak No.	1	2	3	4	5	6	7	8	9	10	11	12
Ret.Time/min	2.77	3.15	4.58	8.98	9.31	10.45	10.82	12.40	15.04	15.77	23.20	25.34
Concentration (%)	0.00	1.13	0.31	0.33	0.26	0.10	0.13	0.09	95.02	0.08	1.08	1.47

regarded as a heavy component. This is the most appropriate way in which cleaning apparatus can be avoided when the separation changes to the following stages.

1.2 Apparatus and procedures

The apparatus used in this study is the VKL70 wiped molecular distillation (Verfahrens-Technische Anlagen GmbH(VTA), Germany). The schematic diagram for this equipment is showed in fig. 2[10].

This apparatus, as one kind of several molecular distillation equipments, is widely applied in industry, in which, the wiper renews the evaporating liquid film continuously, and so the local overheating of the materials is avoided and the internal mass and heat transfer process at the same time are enforced[11]. After measuring the volume quantity, the feed is poured into the dosing vessel by which the feed flow speed can be controlled. Then the cold trap is filled with liquid nitrogen to protect the vacuum system, and at the same time the cooling water is switched on. In this experiment, the vacuum condition is realized by rotary vane vacuum pump together with diffusion pump. When the vacuum has been established, the compact thermostat; which is used to provide evaporating energy, is switched on, and meanwhile the proper distillation temperature is set up. When the temperature is close to the setup value, the motor drive is switched on and adjusted to the proper rotating speed. Then the feed flows to the hot zone through a needle valve. On reaching the evaporating surface, the distilland, depending on operation temperature and pressure, can split into distillate and residue, which are delivered separately out of the still to different receivers. At the end of the process, in case of the feed thermal decomposition and protection of the apparatus system, the heating temperature should be decreased to the safe range, and then the feed was turned off, followed by other shutdown procedures.

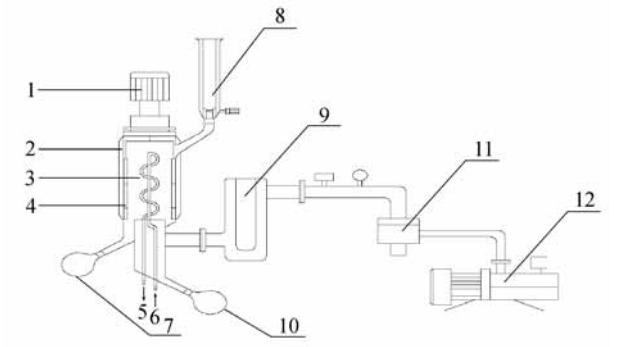

Fig. 2. Apparatus diagram of the VKL70 short-path distillation. 1, Motor drive; 2, heating jacket; 3, condenser; 4, wiper; 5, cooling water outlet; 6, cooling water inlet; 7, residue receiver; 8, dosing vessel; 9, cold trap; 10, distillate receiver; 11, diffusion pump; 12, rotary vane vacuum pump

1.3 Analysis methodology

The analysis method for HPN is gas chromatograph. The analysis parameter values and conditions are listed in table 2[12].

2 Theory related

Nowadays, there are three forms of molecular distillatory: falling film, centrifugal and wiped film. The falling film molecular distillatory depends on the liquid gravity to develop the liquid film, and now it is less applied because of the no uniformity of the liquid film and its stratified flow status. As for the centrifugal molecular distiller, the rotated conic heating plane makes the liquid film uniformly distributed. However, the thickness of liquid film in falling film molecular distiller limits the distillation speed of desired component and the distillation area in centrifugal molecular distiller is not used as efficiently as in wiped molecular distiller[13,14]. So, the wiped molecular distillatory has been most widely used now for its best separation effect.

Traditional theory of molecular distillation is based on mean free-path theory of gas molecule, and an equation given by Langmuir[15] is as follows:

$$\lambda_{\mathrm{m}} = \frac{k}{\sqrt{2}\pi} \cdot \frac{T}{d^2 P}. \quad (1)$$

Table 2 Part of the HP GC analysis parameters and conditions

Column		Detector (FID)	
Capillary column		Temperature:	250℃
Nominal length:	30.0 m	Hydrogen flow:	40.0 mL/min
Nominal diameter:	250.0 μm	Air flow:	450.0 mL/min
Initial flow:	1.2 mL/min		
Nominal init pressure:	14.95 psi		

It shows mean free path λ_m is related to temperature T (K), pressure P (Pa) and size of molecule d (m). k, the Boltzman constant, is 1.380×10^{-23} J • K^{-1}.

During the molecular distillation process, phases between gas and liquid are not balanced. The distilling speed was given by Langmuir-Knudsen as follows[16]:

$$G = 1580 \bullet P \bullet \frac{M}{T}. \quad (2)$$

The distilling speed G (kg • m^{-2} • h^{-1}) depends on the distillation temperature T (K), and pressure P (mbar) and molecular weight m.

It should be emphasized that the separation efficiency in molecular distillation is always less than in conventional vacuum distillation. The separation efficiency demonstrates difficulty of separation process and is expressed by separation factor (α) in molecular distillation. According to the conception of relative volatility in distillation computation, separation factor is first developed by Langmuir[15] to estimate the relative ability of liquid molecule evaporating into gas to liquid surface capturing gas molecule. An equation of computing separation factor has been developed[17]:

$$\alpha = 1 + \frac{\ln\dfrac{\omega_W(1-\omega_F)}{\omega_F(1-\omega_W)}}{\ln\dfrac{W(1-\omega_W)}{F((1-\omega_F)}}, \quad (3)$$

where ω_W and ω_F respectively represent the mass fraction of the more volatile component in the residue and the feed if the distillate is desirable, and W and F(kg/h) respectively represent the mass flow rate of the residue and the feed.

According to eq. (1), the mean free path of HPN was calculated to be 0.105 mm at 0.1 Pa and 25℃. The value is far less than the distance between evaporation surface and condensation surface in the molecular distillery, which is not accurately identical with the original definition of molecular distillation. So, molecular distillation in this paper owns comprehensive meaning as many other papers pointed out.

3 Results and discussion

3.1 Effect of evaporating temperature and pressure

HPN in the raw material is neither a light component nor a heavy component. So we firstly distilled it out as part of light components and regarded the distillate as middle product. Then the middle was distilled and the product with high purity of HPN in residue could be obtained. When distilling the raw material, we considered the effects of evaporating temperature and pressure, which are showed in figs. 3 and 4.

Both in fig. 3 and fig. 4, the wiped speed and feeding speed were fixed at 130 r/min and 2.0 mL/min on the basis of the reported experimental data[4]. The volume ratio of distillate to feed varied largely when the temperature increased from 20℃ to 50℃. However, the effect of pressure was not very obvious. From the experiment data it was found that, to obtain a reasonable volume ratio, the evaporation temperature

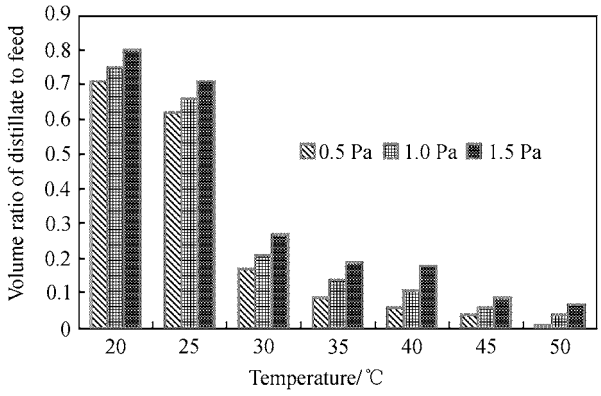

Fig. 3. Effect of distillation temperature and pressure on yield.

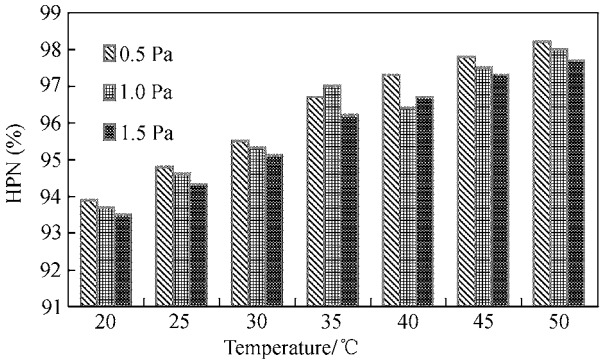

Fig. 4. Effect of distillation temperature and pressure on purity.

should be above 30℃ if the HPN is distilled out as product and should be less than 25℃ if the HPN is obtained in residue as product. Fig. 4 shows the same information as fig. 3 because the HPN concentration in raw material is as high as 95%. Meanwhile, fig. 4 also apparently shows us that the purity of HPN in distillate just increases slightly with the increase of temperature above 40℃. It is reasonable from figs. 3 and 4 to specify the distillation temperature and pressure at 35 ℃ and 0.5 Pa when the distillate is regarded as product, and 20℃ and 1.5 Pa when residue is desirable.

According to the above experiment data, purity of HPN in distillate can be plotted as a function of temperature and pressure as follows[18]:

$$y = 10.799T^{0.0999}P^{-0.0114}, \quad (4)$$

Where y presents HPN purity in feed (%), T is distillation temperature (℃) and P is pressure (mPa). Corresponding to the function, HPN concentration in feed is 95.02%, distillation temperature ranges from 25℃ to 35℃ and P from 500 to 1500 mPa.

3.2 Effect of feed flow rate

The effects of feed flow rate on volume ratio of distillate to raw material and on HPN purity in distillate were studied with the distillation temperature and pressure fixed at the above specified values, and the results are showed in figs. 5 and 6.

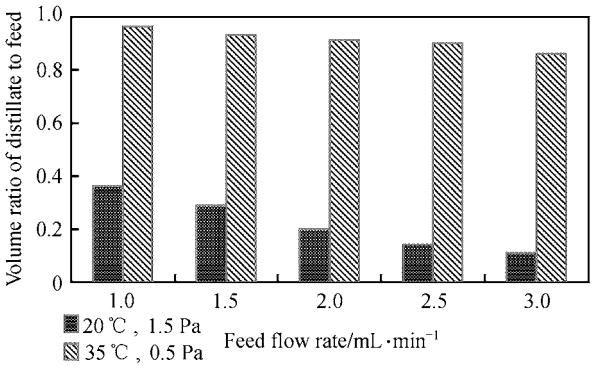

Fig. 5. The effect of feed flow rate on yield.

Both from figs. 5 and 6, it showed that when the residue is desired, the purity of HPN and the volume ratio both decrease with increase of the flow rate, and

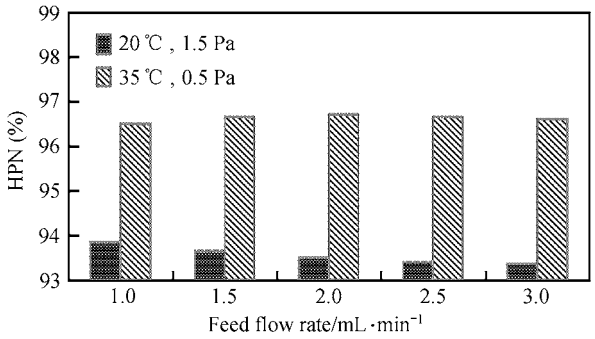

Fig. 6. The effect of feed flow rate on purity.

so the feed flow rate should be lower to distill more undesired components out. Contrarily, when the distillate mixture is desired, the purity increases at first but decreases slightly with flow rate above 2.0 mL/min, and the ratio decreases slightly with increase of feed flow rate, so the feed flow rate should be properly high to prevent more undesired components distilling out. The fact is that more undesired components will be distilled out and the heat decomposition of HPN will happen in some degree if the feed flow rate is too low, or the volume ratio of the distillate to the feed will be unreasonably small if the feed flow rate was too large. According to the above results and demonstrations, it is proper to fix the feed flow rate at 1.5 mL/min when the residue is desired and at 2.5 mL/min when the distillate is desired.

3.3 Effect of rotating speed

The effect of rotating speed of the wiper had been studied by distilling the raw material at distillation temperature 35℃, pressure 0.5 Pa and feed flow rate 2.5 mL/min. Either on the volume ratio of the distillate mixture to the raw material feed or on the HPN purity in distillate mixture the effect of rotating speed was not very obvious as showed in figs. 7 and 8.

From the data in fig. 7 it was found that the yield of desired product increases apparently with increase of rotating speed in the range of low values. This implies that the distillation speed increases when the liquid film in the internal surface of the evaporator continuously becomes more and more uniform with the increase in rotating speed. However, such effect can be out of consideration when the rotating speed is more

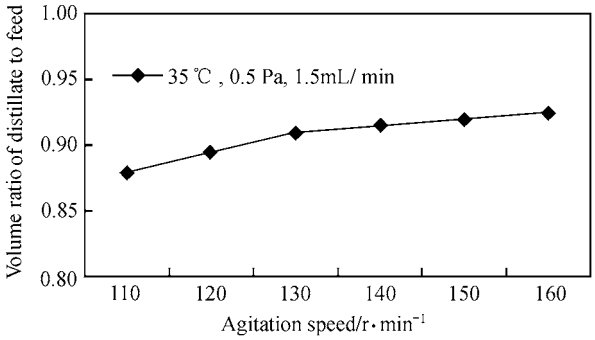

Fig. 7. The effect of wiped speed on yield.

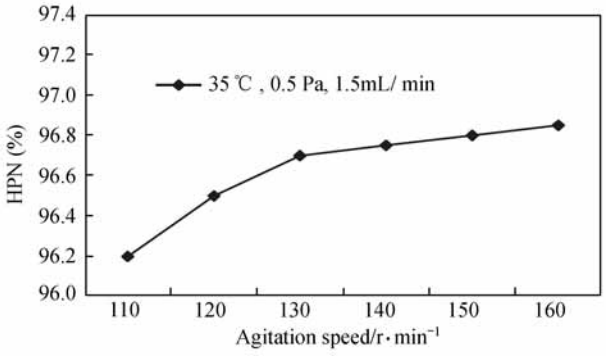

Fig. 8. The effect of wiped speed on purity.

than 130 r/min. The data in fig. 8 also showed the same information that the rotating speed 130 r/min was desirable in the experiments.

3.4 Separation stages to obtain desired HPN purity

In this experiment, two stages to eliminate most heavy components were carried out firstly and the purity of HPN in distillate could be as high as 97.955%. Then other two stages to eliminate most light components were processed to obtain higher than 99.5% HPN product in the form of residue. It is reasonable that HPN is firstly regarded as part of light component in the first two stages and then as a heavy component in the following stages. Part of the proper operation parameter values and the HPN purity in the desired product obtained in each stage are shown in table 3.

Table 3 The variation of HPN purity with separation stages

Appellation	Temperature/℃	Pressure/Pa	HPN (%)
HPN purity in raw material	–	–	95.02
One stage	35	0.5	96.70
Two stages	35	0.5	97.95
Three stages	25	1.5	98.80
Four stages	25	1.5	99.65

3.5 Evaluation of distillation speed and separation efficiency

According to eq. (2), the distillation speed of HPN in this experiment was calculated and shown in table 4. Based on eq. (3), the overall efficiency under the specified conditions in this experiment was evaluated and also showed in table 4.

In this experiment, the residue is desirable at the last two stages, so ω_W should be substituted with ω_L and W with L (the distillate mass flow rate, kg • h^{-1}) when the α is calculated. Also the component mass balance of HPN is carried out to obtain the value of ω_W at the end of the first two stages and the value of ω_L at the end of the last two stages[19]. The data in table 4 showed that the distillation speed of HPN and the separation efficiency are reasonable for industrial production.

4 Concluding remarks

A new separation method was successfully applied to get high purity of HPN. According to the experiment, several conclusions can be made as follows.

(i) It is really feasible to separate HPN from 95% raw material to obtain more than 99.5% HPN high purity product. At the same time, the separation process is relatively simple for the parameters, such as distillation temperature and pressure, feed flow rate and rotating speed are easy to set up and control. Also, the heat decomposition of feed components can

Table 4 Distillation speed of HPN and separation efficiency [a)]

T/℃	P/Pa	G/kg • m^{-2} • h^{-1})	ω_W	ω_F	ω_L	α
35	0.5	1796	0.8836	0.9500	0.9795	3.75
25	1.5	5570	0.9965	0.9795	0.954	8.72

a) ω_F, ω_W and ω_L respectively represent the mass fraction of HPN in the feed, residue and distillate.

be easily avoided by choosing proper operation conditions.

(ii) According to the previous analysis of the raw material chromatomap and concentrations, the feed temperature should be fixed at atmospherical temperature. The distillation temperature, pressure and feed flow rate, when distillate mixture is desired, should be respectively fixed at 35℃, 1.5 Pa and 2.5 mL/min, or 20℃, 0.5 Pa and 1.5 mL/min when residue is desired, and the rotating speed is set up at 130 rpm in either case. To attain more than 99.5% HPN purity, four separation stages are enough, which include two stages reserving most HPN in distillate mixture firstly and the other two stages obtaining product from the residue.

(iii) As the desired component is in the middle position in the chromatomap of every feed, it should be distilled out as a light or heavy components. To avoid washing equipment at each time when the separation is switched to the following stages, it is reasonable that HPN is regarded as a light component in the first two stages and then as a heavy component in the last stages to be separated.

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