Improvement of adsorption-thermal nitrogen cycle-shunt condensation organic gas recovery technology

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Abstract. Based on the adsorption-thermal nitrogen cycle-shunt condensation organic gas recovery technology, this paper investigates the existing adsorption theories and engineering practices and studies the desorption part of this recovery process using a combination of theory and experiment so as to propose suggestions for improvements from the viewpoint of desorption rate and desorption effect. Based on the experimental conditions of this paper, when the cyclic desorption turndown ratio (the ratio of clean gas to total circulation gas) \( \lambda \) equals 0.5, it is more advantageous to increase the desorption rate of volatile organic compounds. Continuing to increase \( \lambda \) will increase energy consumption in actual engineering, but has no significant effect on either the desorption rate of activated carbon in the adsorption tank or the desorption effect. This provides reliable data and methods for efficient operation of this technology and energy saving.

1. Introduction
The research on the desorption technology of activated carbon starts from steam desorption, nitrogen desorption to emerging desorption techniques such as nitrogen cycle desorption and microwave desorption. The major problem in application of steam desorption technology is that the high moisture content of activated carbon after desorption needs further drying treatment, and the drying effect also directly affects the adsorption effect of activated carbon [1, 2]. This shortcoming of steam desorption led to the emergence of nitrogen desorption. On the one hand, it solved the abovementioned problem; on the other hand, it solved the problem of combustibility of activated carbon under high temperature with the protection of nitrogen, which further improves the desorption effect. The main problem faced in the application of nitrogen desorption is large nitrogen consumption and low energy utilization efficiency. This technology requires to heat the activated carbon can after heating the nitrogen gas to the desorption temperature through the heat exchanger, and then cool the gas after desorption to condensation temperature, which is a waste of energy. In order to solve the above problems, the nitrogen-circulation desorption shunt -condensation technique was proposed, which is called the adsorption-thermal nitrogen cycle-shunt condensation organic gas recovery process [3]. In the desorption stage, it uses nitrogen cycle desorption to replace the original steam desorption. The process is shown in Figure 1. There are still few reports on the rapid improvement and development of this technology, except Guo Yan’s [4] study on the process of desorption and recovery of VOCs using thermal nitrogen method. Therefore, although the activated carbon adsorption-recovery technology has been widely used in the industry, many practical problems remain without the theoretical support of relevant research for practical engineering design and application.
This study, based on the investigation of existing adsorption theories and engineering practices, combining theory with experiment, establishes a laboratory thermal gas circulation desorption-shunt condensation technology to simulate different shunt-condensation adjustment processes. Under the condition of constant air volume of total desorption cycle, this study measures the corresponding VOCs concentration, desorption weight loss, and backflush use of the activated carbon after desorption by controlling the VOCs concentration turndown ratio of the system. A desorption curve was drawn to compare the technology’s effects on desorption and its improved effect. This paper further studies the desorption part of adsorption-thermal nitrogen cycle-shunt condensation organic gas recovery technology and proposes suggestions for improvement from the perspective of desorption rate and desorption effect. By studying the variation of desorption rate during thermal gas circulation desorption process and the improvement of the shunt condensation recovery process, the appropriate cycle desorption turndown ratio was proposed to further improve the desorption effect of activated carbon.

2. Material Transfer Process of the Technology

Material transfer of the thermal gas circulation desorption regeneration process is mainly divided into two steps. The first step is desorption, during which the adsorption tank to be desorbed is heated by the circulating thermal gas of the heater, and the heat and mass transfer between the hot gas and the activated carbon is performed. When the activated carbon is heated, the VOCs adsorbed in the activated carbon are removed. The second step is shunt condensation. When the VOCs in desorption cycle rise to a certain high concentration Ct, the fan in the condensing system will shunt part of the gas in the main desorption cycle and some VOCs are liquefied and separated by a heat exchanger for desorption purposes. The gas with the concentration of C1 after condensation is returned to the desorption main circulation system to obtain Ct' and partial material transfer from the adsorption tank to the recovered liquid is completed. Ideally, when the second step reaches equilibrium, i.e. Ct=Ct'=C1=CVOCs saturation (CVOCs saturation is the saturated VOCs vapor concentration at the condensing temperature after passing through the heat exchanger), the residual activity of activated carbon is the adsorption capacity of activated carbon to VOCs under the heating temperature and the saturation condition of CVOCs, and meantime, Ct is saturated to CVOCs saturation and will not continue to have VOCs condensed and shunt from the system. Thus, the entire system reaches an equilibrium state of material transfer.

It can be seen from the process of material transfer mentioned above that the heating process temperature in the main circulation system and the condensation working temperature in the shunt condensation system are the determinant factors of the final state of desorption in the original
technology. In practical engineering application, it is often the case that the heating and condensing temperature depend on the equipment. If a certain set value is reached, it will bring additional problems in terms of safety and economy to continue to increase the heating temperature (or reduce the cold condensing temperature). On the other hand, it will also demand better equipment pipelines and so on [5]. Therefore, this paper will study the desorption process of cyclic desorption and the desorption effect of the improved technology.

3. Analysis of the concentration curve of cyclic desorption

Under the experimental conditions, the ratio of the amount of clean gas to the total circulating gas after concentration adjustment is recorded as $\lambda$. This experiment studies desorption of activated carbon at 150 °C under three turndown ratios and two extreme cases. Different turndown ratios are set to simulate the process of condensing and removing VOCs from cyclic desorption at a certain rate in actual engineering. The change in the concentration of the dichloromethane $C_t$ and the concentration after mixing $C_t'$ of the desorbed circulation outlet at different turndown ratios with time are shown in Figures 2(a) and (b).

![Desorption curves for different turndown ratios](image)

Figure 2. Desorption curves for different turndown ratios

It can be clearly seen from the figures that when the turndown ratio $\lambda=0$, dichloromethane concentration in the desorption cycle is always quite high, which also indicates the concentration of the circulating gas and that of condensed VOCs are related when the cyclic desorption condensation reaches a certain stage. After reaching equilibrium of concentration and desorption, there is no additional driving force in dynamics to continue to desorb VOCs from the activated carbon or condense and liquefy it from the circulation gas path. In the experiment, the actual device volume is relatively small compared with the actual project, causing material loss in the circulating gas path during the sampling and other operation processes. Therefore, the desorption outlet concentration curve has been declining in the later stage. When the complete removal of methylene chloride is adjusted to $\lambda=1$, the dichloromethane concentration in the circulating gas path is nearly reduced to zero, which is equivalent to the open circuit thermal gas purge desorption. In the process of cyclic desorption, it is significant to compare the desorption effect with or without adjustment. Additional concentration adjustment system simulates the different condensation effects in the actual project to remove VOCs from the circulation gas path, which can further promote the material transfer equilibrium of the whole system, significantly reduce the balance concentration of the circulating gas path, and reduce the desorption residual amount of the activated carbon so as to enhance the desorption effect; on the other hand, reducing the concentration of the circulating gas path can also increase desorption rate, accelerating desorption and shortening the desorption time.

The main characteristic of the three desorption curves of different turndown ratios is that as the $\lambda$
increases, the peak concentration of the condensed outlet methylene chloride decreases, and the concentration of methylene chloride after emptying and mixing also decreases. When the outlet methylene chloride concentration is less than 0.5 g/m³, the timing of the desorption process ends; according to Figure 2, when \( \lambda \) changes from 0.25 to 1, the desorption end times are 80 min, 40 min, 30 min, and 30 min respectively. That is, as the \( \lambda \) increases, the cycle desorption time decreases.

4. The effect of turndown ratio in cyclic desorption

4.1. Analysis of the effect of turndown ratio on cyclic desorption

Under the cyclic desorption shunt condensation system, the actual desorption concentration of the activated carbon in the tank is the difference between the concentration of the outlet VOCs and the concentration of the desorption tank inlet (i.e., the concentration of the mixed VOCs). Based on the concentration curve of Figure 2, the variation of the weight loss accumulation of desorbed activated carbon with time under the different turndown ratios as shown in Figure 3 is obtained. Calculate the tangent slope for each sampling point in Figure 3, thereby the instantaneous desorption rate (g/min) at each sampling time point under different turndown ratios is obtained, as is shown in Table 1.

![Figure 3. Desorption rate curves for different turndown ratios](image)

| The turndown ratio | Instantaneous desorption rate g/min |
|--------------------|-----------------------------------|
|                    | 1min     | 5min     | 10min    | 15min    |
| \( \lambda = 0.25 \) | 1.7744   | 1.9744   | 1.6963   | 0.94076  |
| \( \lambda = 0.50 \) | 3.0616   | 2.6611   | 1.7076   | 0.74169  |
| \( \lambda = 0.75 \) | 3.1837   | 2.6931   | 1.6680   | 0.7267   |
| \( \lambda = 1 \)   | 3.0155   | 2.4840   | 1.4281   | 0.60496  |

From Figure 3 and Table 1, when the \( \lambda \geq 0.5 \), the instantaneous desorption rate is not much different. When the desorption is performed for 1 min, the instantaneous desorption rate is 3.0-3.2 g/min; when it comes to 5 min, the rate is 2.5-2.7 g/min. At the two sampling time points, the maximum instantaneous desorption rate is \( \lambda = 0.75 \). According to the theoretical analysis, when the
temperature of the cyclic desorption process is the same, as the concentration of the imported VOCs increases, and the concentration of the exported activated carbon increases accordingly, but the actual maximum instantaneous desorption rate decreases; in the process of shunt condensation, in which the main material transfer is from the desorption cycle system to the liquid phase, the increase of λ means the increase of methylene chloride condensed by the simulation, but as λ increases after desorption condensation adjustment, the desorption outlet concentration decreased in turn, so the instantaneous rate (g/min) of methylene chloride entering the regulator can be measured by the air volume and the corresponding desorption outlet, as shown in Table 2.

| The turndown ratio | Instantaneous rate of methylene chloride entering the regulator g/min |
|--------------------|---------------------------------------------------------------|
| 1min               | 5min               | 10min              | 15min              |
| λ=0.25             | 1.058              | 1.669              | 1.500              | 0.688              |
| λ=0.50             | 2.089              | 1.745              | 0.916              | 0.422              |
| λ=0.75             | 3.304              | 2.374              | 1.499              | 0.432              |
| λ=1                | 3.468              | 2.563              | 1.342              | 0.466              |

It can be concluded from Table 2 that as the turndown ratio increases, the rate of methylene chloride entering the regulator increases. According to the definition of λ, the rate of methylene chloride shunt and condensed in stimulation from the cyclic desorption increases accordingly. When λ≥0.5 and the rate of removing methylene chloride from the system is significantly increased, the desorption rate of methylene chloride in the adsorption tank is not significantly increased. In engineering application, increasing shunt and condensation rate of VOCs requires not only a higher condensing system load, but more energy loss as it requires to cool a larger amount of gas from 150 °C to 0-20 °C and then return to 150 °C in the main desorption cycle. Therefore, under the experimental conditions, when the turndown ratio is λ=0.5, it is advantageous to increase the desorption rate of dichloromethane. At 1 min, the desorption rate of dichloromethane reaches 3.0616 g/min. Continued increase of λ increases the rate of removing methylene chloride from the system, but has no significant effect on the desorption rate of dichloromethane from the activated carbon in the canister.

4.2. Effect of the turndown ratio on the desorption effect
The relevant experimental data after changing the turndown ratio are shown in Table 3. This experiment focuses on two parameters of the desorption effect are: desorption weight loss and cooling purge concentration of the adsorption tank.

From the results of desorption weight loss, during the 2-hour cyclic desorption, the desorption weight loss after the simulated adjustment (λ>0) is significantly greater than direct desorption. Under different turndown ratios, the desorption weight loss of activated carbon differs. According to the desorption curve and the concentration of circulating gas at the end of desorption, the gas circulation concentration has dropped to 0.2 g/m3. According to the process analysis of the technology, the turndown ratio has an effect only on the desorption rate, and the equilibrium state mainly depends on the temperature of desorption and condensation. Therefore, the desorption weight loss is basically the same under different turndown ratios. There is a certain error due to the influence of the experimental batch.

According to the purge concentration analysis after cooling of adsorption tank, as the turndown ratio increases, the purge concentration of the adsorption tank gradually decreases. This means that with certain blast capacity and desorption time, the emission limits of degraded activated carbon applied to adsorption occasion decreases. Take the experiment as an example, the concentration of dichloromethane purged by only by activated carbon in circulating desorption and clean air is 0.530 g/m3, much higher than the national standard requirements. As the turndown ratio increases, purge concentration after desorption for unit time and cooling in the adsorption tank is significantly reduced. When the turndown ratio is 0.5, the concentration decreased to 0.089 g/m3.
Table 3. Desorption results of different turndown ratios

| the cyclic desorption turndown ratio $\lambda$ | Activated carbon quality $q$ g | Desorption weight loss $g$ | Gas concentration at the end of desorption g/m³ | Purge concentration of adsorption tank g/m³ |
|---------------------------------------------|-------------------------------|--------------------------|-----------------------------------------------|---------------------------------|
| $\lambda=0$                                 | 260.99                        | 22.86                    | 44.569                                        | 0.530                           |
| $\lambda=0.25$                              | 260.98                        | 31.6                     | 0.113                                         | 0.350                           |
| $\lambda=0.50$                              | 260.97                        | 32.3                     | 0.205                                         | 0.089                           |
| $\lambda=0.75$                              | 260.98                        | 31.2                     | 0.098                                         | 0.009                           |
| $\lambda=1$                                 | 260.99                        | 29.75                    | 0.095                                         | 0.005                           |

5. Conclusion

According to the desorption curve of cyclic desorption experiment, in the process of cyclic desorption, the effect of turndown ratio on desorption effect is significant. On the one hand, the equilibrium concentration of the circulating gas path is significantly reduced, the amount of desorption residual of activated carbon is reduced, and the desorption effect is improved. On the other hand, the desorption rate is increased, the desorption speed is accelerated and desorption is shortened. From the analysis of instantaneous desorption rate in the cyclic desorption experiment, the following conclusions are drawn: when the turndown ratio $\lambda \geq 0.5$, the instantaneous desorption rate is not much different; when the desorption is performed for 1 min, the instantaneous desorption rate is 3.0-3.2 g/min; the maximum desorption rate is always $\lambda=0.75$. Combined with the actual analysis, under the conditions of this experiment, when the turndown ratio is $\lambda=0.5$, it is advantageous to increase the desorption rate of dichloromethane; at 1 min, the desorption rate of dichloromethane reaches 3.0616 g/min. Continued increase of $\lambda$ will increase the energy consumption in the actual project, but it has no significant effect on the desorption rate of dichloromethane and the desorption effect of the activated carbon in the adsorption tank.

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