Development of a volatile organic compounds cryogenic condensation recovery system cooled by liquid nitrogen

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Abstract: Volatile organic compounds (VOCs) are important precursors of ozone and PM2.5, and the reduction of VOCs emission is a key to control ozone and PM2.5 pollutions. For high-value VOCs such as oil gas, the cryogenic condensation method based on liquid nitrogen cooling is an effective way to recover VOCs. This method can achieve a refrigeration temperature of \(-170^\circ\text{C}\) or even lower so that the treated exhaust gas concentration can satisfy the emission standard. In this paper, a thermodynamic model is established to calculate and analyze a designed three-stage condensation recovery VOCs system process based on liquid nitrogen cooling. A set of experimental equipment was further developed and tested. And the system process, calculation results, and experimental results are introduced.

1. Introduction
Volatile organic compounds (VOCs) are key precursors of ozone and PM2.5, which play a vital role in atmospheric chemistry [1]. Its emission control directly affects the ecosystem [2], human health [3], and economic development [4]. Therefore, it is of great significance to take measures to reduce the emission of VOCs. The treatment technology of VOCs is mainly divided into two categories: destruction technology and recovery technology [5]. The former mainly includes thermal oxidation, catalytic oxidation, and so on; the latter mainly contains absorption, adsorption, membrane separation, and condensation [6]. As for high-value VOCs, such as oil gas emitted from the petrochemical industries due to oil evaporation, the cryogenic condensation method based on liquid nitrogen cooling is an effective way to recover VOCs. This method can achieve a refrigeration temperature of \(-170^\circ\text{C}\) or even lower so that the treated exhaust gas concentration can satisfy the strict emission standard [7]. In addition, the oil gas emission concentration is usually higher than 10000 ppm, so the method of
condensation has a good economy [8].

At present, there are not so many studies on the cryogenic condensation for VOCs recovery. In this paper, a thermodynamic model for a three-stage cryogenic condensation recovery VOCs system process based on liquid nitrogen cooling is established and the effects of season, water molar fraction, inlet VOCs concentration, and system stage on the system performance has been analyzed. A set of experimental equipment was further developed and tested.

2. System description

2.1. Basic process

As shown in Fig.1, a three-stage condensation recovery VOCs system process based on liquid nitrogen (LN$_2$) cooling was proposed and developed. The inlet VOCs gas from the petrochemical plant flows into the system and is cooled by the HEX1-3. The cooling power was supplied by the LN$_2$. And the liquefied VOCs and the remaining gas were separated in the GLS1-3 after the HEX1-3 respectively. When the cold carried by the purified gas from the GLS3 was recovered by the HEX1-2, the purified gas was emitted into the atmosphere satisfying the emission limitation standards.

![Fig.1 A three-stage condensation recovery VOCs system process based on LN$_2$ cooling](image)

Fig.2 shows that a set of experimental equipment was developed and tested in an application. As shown in Fig.3, a typical temperature distribution in the test was maintained during the VOCs abatement. The precooling temperature is around -5 °C, and the intercooling temperature is around -60 °C, and the cryogenic temperature is about -105--115 °C.

![Fig.2 A set of experimental equipment was developed and tested in application](image)
2.2. Basic assumptions and mathematic model

2.2.1 Basic assumptions. Some assumptions for the convenience of calculation are expressed as follows:
(1) The heat leakage of the heat exchanger is ignored in the calculation of the heat transfer between the LN2 and VOCs gas;
(2) The components of the VOCs gas stream were analyzed by a petrochemical plant listed in Table 1. And the physical parameters of each component are obtained from reference [9].
(3) The VOCs gas in Table 1 is chosen as a basic one in the subsequent calculation of several variables.

| component   | molar fraction | molar weight (kg/kmol) | normal boiling temperature (K) |
|-------------|----------------|------------------------|-------------------------------|
| Methane     | 4.920e-004     | 16.043                 | 111.67                        |
| Ethylene    | 3.600e-005     | 28.054                 | 169.38                        |
| Ethane      | 4.510e-004     | 30.069                 | 184.57                        |
| Propane     | 4.034e-003     | 44.096                 | 231.04                        |
| n-Butane    | 1.430e-002     | 58.122                 | 272.66                        |
| i-Butane    | 1.920e-002     | 58.122                 | 261.40                        |
| tr2-Butene  | 3.600e-005     | 56.106                 | 274.03                        |
| Nitrogen    | 9.614e-001     | 28.013                 | 77.35                         |

2.2.2 Mathematic model. In this section, the thermodynamic model was established mainly including several equations. Firstly, the Peng-Robinson equation [10] is applied for physical property calculation [11]. The basic state equation is equation (1) and its detailed expression is illustrated in reference [12]. As for the system process calculation and analysis, the mass conservation equation (2), molar fraction summations equations (3)-(4), thermodynamic phase equilibrium equation (5), and energy
conservation equation (6) were employed. And the equations (7)-(10) were applied for the heat transfer. Finally, the system performance was evaluated by $\theta$ (the ratio of the mass flowrate of liquefied VOCs to the liquid nitrogen), which was expressed in equation (11) in detail.

(1) State equation

$$ P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} $$

(1)

(2) Mass conservation equation

$$ X_iL_{ij} + Y_iG_{ij} = X_oL_{o,j} + Y_oG_{o,j} $$

(2)

where

$$ X_i, Y_i $$ — inlet flowrate of liquid and gas phase, respectively;

$$ X_o, Y_o $$ — outlet flowrate of liquid and gas phase, respectively;

$$ L_{ij}, G_{ij} $$ — inlet molar fraction of component $j$ in liquid and gas phase, respectively;

$$ L_{o,j}, G_{o,j} $$ — outlet molar fraction of component $j$ in liquid and gas phase, respectively.

(3) Molar fraction summations

$$ \sum L_j = 1 $$

(3)

$$ \sum G_j = 1 $$

(4)

where

$$ L_j, G_j $$ — a molar fraction of the liquid and gas, respectively.

(4) Thermodynamic phase equilibrium

$$ G_j = \varphi_j L_j $$

(5)

where

$$ \varphi_j $$ — phase equilibrium constant of component $j$.

(5) Energy conservation equation

$$ X_iH_{iX} + Y_iH_{iY} + Q = X_oH_{o,X} + Y_oH_{o,Y} $$

(6)

where

$$ H_{iX}, H_{iY} $$ — enthalpy of inlet mass flowrate of liquid and gas phase, respectively, kJ/kg;

$$ H_{o,X}, H_{o,Y} $$ — enthalpy of outlet mass flowrate of liquid and gas phase, respectively, kJ/kg;

$$ Q $$ — cooling power, kW.

(6) Cooling power required by the system

$$ Q_R = UA \cdot \Delta T $$

(7)

where

$$ Q_R $$ — cooling power required by the system, kW;

$$ U $$ — heat transfer coefficient, kW/(m$^2 \cdot$ K);
A – heat transfer area, m²;
\( \Delta T \) – heat transfer temperature difference, K.

(7) Cooling power supplied by the LN₂

\[
Q_{LN₂} = Q_L + Q_S = Q_R
\]

\[
Q_L = \dot{M}_{LN₂} \times L_{LN₂}
\]

\[
Q_S = \dot{M}_{LN₂} \times (H_{N1} - H_{N2})
\]

where

\( Q_{LN₂} \) – cooling power supplied by the LN₂, kW;
\( Q_L \) – cooling power supplied by latent heat of the LN₂, kW;
\( Q_S \) – cooling power supplied by sensible heat of the LN₂, kW;
\( \dot{M}_{LN₂} \) – mass flowrate of LN₂ for consumption, kg/h;
\( L_{LN₂} \) – latent heat of LN₂, kJ/kg;
\( H_{N1}, H_{N2} \) – specific enthalpy of nitrogen corresponding to temperature, kJ/kg.

(8) The ratio \( \theta \) (mass flowrate of L\( _{VOCs} \) (liquefied VOCs) to LN₂)

\[
\theta = \frac{\dot{M}_{L_{VOCs}}}{\dot{M}_{LN₂}}
\]

where

\( \dot{M}_{L_{VOCs}} \) – mass flowrate of L\( _{VOCs} \), kg/h;
\( \dot{M}_{LN₂} \) – mass flowrate of LN₂ for consumption, kg/h;

3. Results and discussion

The effect of season

Fig.4 shows the influence of the season on the system performance when the inlet VOCs gas concentration and flowrate are the same at the specific cryogenic temperature. It can be seen that the \( \dot{M}_{L_{VOCs}} \) of each season is the same because the mass flowrate of VOCs can be liquefied is constant at the same cryogenic temperature. However, the ratio \( \theta \) and \( \dot{M}_{LN₂} \) in summer are the largest, followed by transition seasons, and the smallest in winter. Especially, the ratio \( \theta \) in summer is around 75% higher than that in winter. The reason is that the environment temperature in summer is higher than that in winter, which significantly affects the inlet VOCs gas temperature.
The effect of season on the system performance

Fig. 4 The effect of season on the system performance

The effect of water molar fraction

Fig. 5 shows the effect of the different water molar fractions on the system performance when the inlet VOCs gas concentration and flowrate are the same at the specific cryogenic temperature. It can be observed that the $\dot{M}_{\text{LN}_2}$ increases with the increase of water fraction. When the water fraction increases from 0 to 1.5%, the increase of ratio $\theta$ is 9.8%. It is worth mentioning that the $\dot{M}_{\text{VOCs}}$ condensed in the HX1 increase apparently and most of the substance is water.

Fig. 5 The effect of water molar fraction on the system performance

The effect of inlet VOCs concentration

The inlet VOCs concentration without abatement generally fluctuates in a wide range when the developed equipment is in the application. The effect of different inlet VOCs gas concentrations on the system performance was analyzed when the inlet VOCs gas temperature and flowrate are the same at the specific cryogenic temperature, as shown in Fig. 6. It can be seen that both the $\dot{M}_{\text{LN}_2}$ and $\dot{M}_{\text{VOCs}}$ increase with the increase of concentration. However, the ratio $\theta$ decreases with the increase of the
concentration. The ratio $\theta$ has decreased about 37% with the concentration of inlet VOCs increasing from 3.8% to 11.6%.

![Fig.6 The effect of inlet VOCs concentration on the system performance](image)

The effect of system stage

Fig. 7 shows the effect of the system stage on the system performance when the inlet VOCs gas concentration and flowrate are the same at the specific cryogenic temperature. It can be seen that the ratio $\theta$ of the system with three stages is the same as that of the system with two stages. However, the heat transfer area of all heat exchangers of the system with two stages that eliminate the pre-cooling heat exchanger is smaller than that of the system with three stages. The reason is that the selected VOCs components hardly contain high melting point substances, which accounts for that the $M_{LVOCs}$ obtained from the pre-cooling heat exchangers is little in the system with three stages. Therefore, the total heat transfer area of HX2 and HX3 in the system with three stages is almost same as the that of the system with two stages.

![Fig.7 The effect of system stage on the system performance](image)
4. Conclusion

(1) The effect of season, water molar fraction, the inlet VOCs concentration, and system stage on the system performance were analyzed.

(2) The ratio $\theta$ in summer is around 75% higher than that in winter because the environment temperature influences the inlet VOCs gas temperature.

(3) The higher the concentration of inlet VOCs gas, the lower ratio of the liquid nitrogen consumption to liquefied VOCs, which account for the better economic benefits for high concentration VOCs gas treatment.

(4) The system with two stages has a better performance when the inlet VOCs gas hardly contains high melting point substances.

5. References

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