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Simulation and Practice of Condensation Recovery of Nitrogen Tetroxide Based on HYSYS

Liqing Zhang, ZiwenHou, Lingzhi Huang, Pengcheng Gu and Zelong Xu

Jiuquan Satellite Launch Centre, Jiuquan732750, China

zlq0428@163.com

Abstract. The theoretical calculation results of the condensation recovery rate and the required cooling power of an engineering application unit shown that condensation recovery of N_2O_4 in the waste gas is feasible and valuable in engineering applications.A simulation model was performed by using HYSYS and according to condensate-recovery process flow. Thus two important engineering parameters were simulated which included the thermal load of condensation system and the flow of glycol-water solution. The test results of an engineering application device based on these parameters at Jiuquan Satellite Launch Center indicated that the recovery efficiency can be above 90.0%, the purity of N_2O_4 recovered can be up to 99.6%.

1. Introduction

As a rocket propellant, N_2O_4 (nitrogen tetroxide) is widely applied in scientific research and experiment fields like weapon experiment and space launch due to its good cooling and burning performances [1]. However, large amounts of waste gas containing N_2O_4vapor is produced during the storage, conveying and fueling processes. The waste gas mainly includes N_2O_4, nitrogen dioxide (NO_2) and nitrogen (N_2). Attention should be paid to the waste gas for nitrogen oxides are highly toxic [2]. The volume of waste gas produced during each rocket mission is above $1000m^3$, in which the concentration of hazards is up to $1555g/m^3$. But the allowable concentration specified in government standard is only 420 mg/m^3[3]. That means the concentration of hazards in the waste gas is thousands times higher than that set forth in the standard. For a long time, N_2O_4 waste gas has been disposed by incinerating, discharging through tall vent stack, solution absorption and other methods [1] [4-10]. Pollution can't be completely avoided in these ways and the cost is high. Besides, a large amount of resource is wasted.

Condensation method has the following advantages over the traditional ways in disposing N_2O_4 waste gas. On one hand, the condensation product can be recycled to save resources. On the other hand, the condensation unit removes the greater part of N_2O_4 from the waste gas, thus greatly reducing the load on the subsequent disposing unit to improve its work efficiency. For rather a long time, researchers at home and abroad put the ideas of condensation recovery N_2O_4 from the waste gas. But there is not any successful engineering application project except some laboratory experiment cases. How to acquire high condensation recovery efficiency in uncompressed condition and condensation product to meet the application requirements of rocket propellants and so on, all these make it difficult to put this technology into engineering application.

It is therefore necessary to conduct studies on the new recovery technology of N_2O_4 from waste gas through condescension method. Based on HYSYS, a calculation model was built and optimized to acquire the condensation recovery process technical conditions. In the engineering application test, the

key quality control requirements as well as the crucial process technologies necessary to achieve high efficient condensation recovery and stable system operation were found. These results help to lay a solid foundation for the wide application of this technology.

2. Teoretical Calculation

2.1. Composition of N_2O_4 waste gas
Nitrogen tetroxide refers to the mixture of nitrogen dioxide (NO_2) and N_2O_4 especially in space field, both of which do exist in the status of vapor-liquid phase equilibrium at measurable molar ratios. The ratio of N_2O_4 to NO_2 is 84:16 at its normal boiling point. As the temperature rises, the content of NO_2 increases.

Nitrogen is generally used to maintain the pressure to prevent moisture from entering N_2O_4 during the storage, transportation and filling processes of N_2O_4 [8-9]. So, N_2O_4 waste gas produced during the operation process is the saturated vapor of the mixture that contains N_2O_4, NO_2 and N_2 etc.[10].

2.2. Calculation parameters selection
The calculation parameters were selected according to the properties of N_2O_4 and they are shown in Table 1.

Table 1. The calculated parameters selected.

No.	Parameter	Numerical
1	Temperature of N_2O_4/T_1	15°C（298K）
2	Degree of dissociation/α	0.10
3	Pressure of N_2O_4/p_1	0.10 MPa
4	Standard pressure/p_0	0.10 MPa
5	Temperature of condensation/T_2	-10°C（263K）
6	Specific heat of N_2O_4/C_{PN2O4}	5.471kJ/(kg·K)
7	Heat of vaporization of N_2O_4/$C_{gaseousN2O4}$	413.8 kJ/kg
8	Specific heat of N_2/C_{pN2}	1.038 kJ/(kg·K)
9	Ratio of saturation vapor pressure in 15°C/-10°C(p_2/p_3)	0.075MPa/0.020MPa

2.3. Calculation of material parameters
At 15°C, the average molecular weight of N_2O_4 and NO_2 mixture in the waste gas is 83.6. When the gage pressure of the waste gas is 0.10MPa, the content respectively of N_2O_4 and NO_2 mixture, N_2 in the 1.0m³ waste gas are calculated through the formulas below.

m_1, the content of the N_2O_4 and NO_2 mixture:

$$m_1 = \frac{1.0 \times \dfrac{p_2}{p_0 + p_1} \times M_0}{22.4 \times \dfrac{298}{273}} \approx 1.33kg \tag{1}$$

m_2, the content of nitrogen:

$$m_2 = \frac{1.0 \times \dfrac{(p_0 + p_1 - p_2)}{p_0 + p_1} \times M_{N2}}{22.4 \times \dfrac{298}{273}} \approx 0.74kg \tag{2}$$

A cubic meter of N_2O_4 is cooled to -10°Cfrom the temperature of 15°C. That leads to the decrease in the statured vapor pressure and part of the mixture will become liquid. So, the content of N_2O_4 mixture in the gas, the amount of N_2O_4 recovered and the recovery rate are determined respectively through the following formulas.

m_3, the content of N_2O_4 mixture in the gas after condensation:

$$m_3 = \frac{1.0 \times \dfrac{p_3}{p_0 + p_1} \times M_0}{22.4 \times \dfrac{263}{273}} \approx 0.39kg \tag{3}$$

m_4, the amount of N_2O_4 recovered:

$$m_4 = m_1 - m_3 = 0.94kg \tag{4}$$

η, the recovery rate:

$$\eta = \frac{m_4}{m_1} \times 100\% \approx 70.6\% \tag{5}$$

If the flow of waste gas to be disposed in engineering application is 300m³/h, the cooling power P needed shall be:

$$P = \frac{300 \times (m_1 \times C_{PN_2O_4} \times \Delta T + m_2 \times C_{pN_2} \times \Delta T + m_4 \times C_{gaseousN_2O_4})}{3600} \approx 49.2kW \tag{6}$$

3. Engineering Application Process and HYSYS Simulation

3.1. Condensate Recovery Process Flow of N_2O_4

The condensation process flowofN_2O_4 is shown in Figure 1.

Process flow: Glycol-water solution at a desired temperature provided by the cooling water unit flows into the heat exchanger to cool N_2O_4.The newly formed mixture contains gas and liquid and it flows into the separator. Later, the liquid is separated from the gas which is then delivered to the waste gas disposal system. The liquid is collected in the tank. Glycol-water solution used in this process is not only the intermediate heat transfer medium but also the cool storage medium. That's how the system operates stably. There are totally two medium lines.

(1) Condensation recovery line: The waste gas flowing into this system is cooled to -10°C～-5°C in the heat exchanger and then becomes a mixture of gas and liquid. Later, the liquid is separated from the gas which is then delivered to the waste gas disposal system. The liquid is collected in the tank.

(2) Circulating line of glycol-water solution: Glycol-water solution (the ratio of glycol to water=1:1) is transferred through the circulating pump to the cooling water unit to be cooled. This solution will be delivered to the heat exchanger when it reaches -10°C to absorb the heat of the waste gas. After that, the solution will flow into the buffer tank as glycol-water solution has already expanded. Driven by a circulating pump, the glycol-water solution flows back into the cooling water unit where it is cooled again. These steps above form a complete circulation.

3.2. HYSYS Simulation

HYSYS calculation model was built for the condensate recovery process of N_2O_4 is shown in Figure 2. It mainly contains two parts: the cooling circulation of cooling medium and the liquidation path of N_2O_4.

As shown in Figure 2, the waste gas mixture (15℃, 1.200bar) enters the the condensing heat exchanger through the inlet pipe. The temperature of mixture 6-2 (-5℃, 1.050bar) is lowered by the heat exchanger at the gas outlet. Mixture 10 (-5.134℃, 1.036bar) is separated in the gas-liquid

separator V-0101 while the end gas 7-2 (-5.134℃, 1.036bar) is discharged through the outlet pipe for waste gas. The glycol-water solution is pumped to the cooling unit for cooling 12 (-10.00℃, 2.700bar) . Then glycol-water solution 2-2 (-9.978℃, 1.643bar) is heated by the heat exchanger to be the fluid 3-2 (-6.937℃, 1.493bar) and enters the next circle through the outlet pipe of glycol.
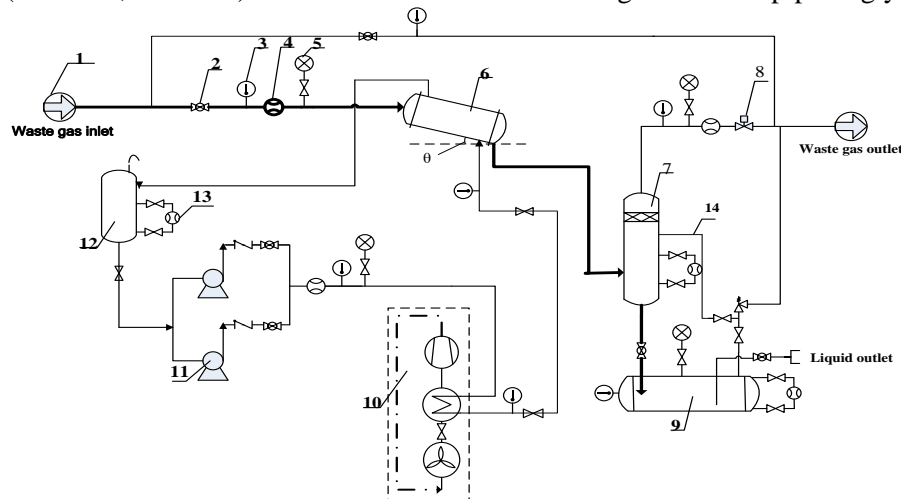

Figure 1. The condensation process flow chart of N_2O_4.

1-gas inlet and outlet2-electric ball valve3-temperature sensor 4-flowmeter 5-pressure gauge and sensor 6-condensing heat exchanger 7-gas-liquid separator 8-flow adjusting valve9-collection tank of condensate liquid 10- water chilling unit 11-circulating pump of glycol-water solution 12-buffer tank for glycol expansion 13-content gauge 14-communicating pipe
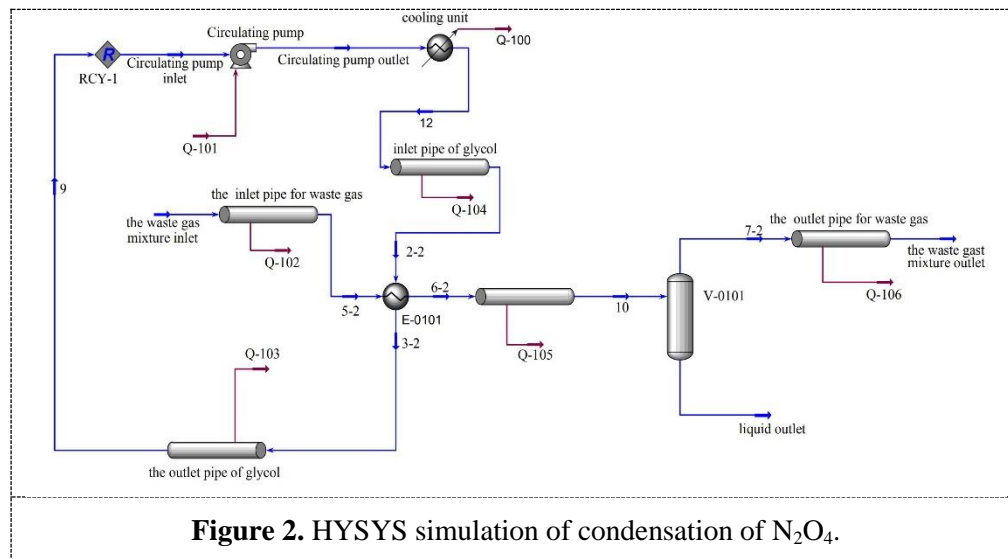

Figure 2. HYSYS simulation of condensation of N_2O_4.

The thermal load of condensation system and the required glycol solution flow are vital to the engineering equipment design.According to the simulation data of Table 2, they are calculated as follows:

(1) The thermal load of condensation is about 55.1kW and it is basically the same with the theoretical value.

(2) The flow of glycol-water solution is nearly 19.0m³/h.

Table 2. Material stream parameter of HYSYS.

Parameter	Materials				
	The waste gas mixture inlet	6-2	12	2-2	3-2
Vapor fraction	1.0000	0.6979	0.000	0.0000	0.0000
Temperature/°C	15.20	-5.000	-10.00	-9.978	-6.937
Pressure/bar	1.200	1.050	2.700	1.643	1.493
Molar flow(Nm^3/h)	300.0	300.0	1.561×10^{-4}	1.561×10^{-4}	1.561×10^{-4}
Liquid volume flow(m^3/h)	0.6062	0.6062	19.00	19.00	19.00
Heat flow/kW	10.75	-44.33	-6.379×10^{-4}	-6.379×10^{-4}	-6.373×10^{-4}

4. Engineering Application Experiments

4.1. Design of the heat exchanger

The heat exchanger is the most important equipment in the condensing recovery engineering unit.During the condensation process of the mixture of N_2O_4 and N_2, the gas phase and liquid phase keep changing and so does the equilibrium between N_2O_4 and N_2. Therefore, HTRI, a piece of software for heat transfer calculation is used to do the computation. Under the condition that the heat exchange power is not less than 60kw, the calculation results of heat exchanger related data are shown in Table 3.

Table 3. The heat exchanger data.

No.	Parameter	Numerical
1	Heat ex-changer form	Tube and shell
2	Molar flow	0.1936kg/s(697kg/h)
3	Ethylene solution inlet/outlet temperature	-10℃/-5℃
4	Tube outer diameter/thickness of heat ex-changer	16mm/2mm
5	Tube length of heat ex-changer	2.1m
6	Inner diameter of heat ex-changer	600mm
7	Tilt angle heat ex-changer	30°
8	Total area of heat ex-changer	60m^2
9	Number of heat ex-change tube	600

4.2. Main Design Parameters of the Engineering Device

Based on the calculation results above and relevant experiment requirements of engineering application, the main parameters of the engineering device were designed and they are shown in Table 4.

Table 4. Main design parameters of the engineering device.

No.	Parameter	Numerical
1	Maximum gas flow	300m^3/h
2	Temperature of gas import/export	15°C/-5°C
3	Temperature of ethylene solution inlet/outlet	-10°C/-5°C
4	Heat transfer power	60kW
5	Refrigeration power	80kW
6	Volume of ethylene solution	1.0 m^3
7	Circulating pump flow rate	25.0 m^3/h

4.3. Experiment

Two experiments were conducted separately under different waste gas inlet temperature conditions. The glycol-water solution temperature in condensation process was maintained between -10°C and -5°C. Titration was used to test the purity of the product [11]. The experiment results are shown in Table 5.

Table 5. The condensation recovery experiments data.

Parameter	Normal temperature	Lower temperature
Waste gas inlet temperature	18°C	3°C
Processing	$210m^3$	$520m^3$
Collection	278L	294L
Recovery efficiency	90.1%	95.6%
Purityof N_2O_4	99.6%	99.6%

5. Conclusions

  (1) An engineering device applying the process flow technology mentioned in this article was used to recover N_2O_4 from waste gas. The recovery efficiency can be above 90.0%.

    (2) The impact of parameters like the waste gas flow, the condensate temperature and the pressure of the system outlet on the condensation recovery rate of N_2O_4 were studied.Results show these parameters should be adjusted and controlled within the optimization range to achieve high recovery rate.

    (3) The purity of N_2O_4 recovered was higher than 99.6% to meet the application requirements of rocket propellant [7]. It is also found that this value is even higher than the purity of N_2O_4 stored in the tank.

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