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THEORETICAL INVESTIGATION ON CONDENSING CHARACTERISTICS OF AIR AND OIL VAPOR MIXTURES

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ABSTRACT

The condensation process of the volatilized oil-vapor is calculated for certain given constituents of air and oil-vapor mixtures by using finite difference method. The results indicated that there are three distinct temperature regions in the whole cooling process; each corresponds with special refrigeration processes. The temperature region from 308.15 K to 276.15 K is the prepared cooling for removing the water vapor by condensation which will effects the later condensing of the oil-vapor, the temperature region from 276.15 K to 238.15 K is the condensation process of high carbon organic substances, and the temperature region from 238.15 K to 198.15 K is the condensation region for relative low carbon organic substances. According to the calculation results, some key problems were discussed in the condensing recovery apparatus and system design.

Key Words: oil-vapor, condensation recovery, convective heat transfer

INTRODUCTION

Refrigeration condensation of volatilized oil-vapor is one method of oil vapor recovery (Zhao *et al.* 2001; Li *et al.* 2006; Tang *et al.* 2007). Such a method includes a complex condensation process with mixtures of several kinds of condensable vapors and mixtures of dry air and water vapor. The volatilized oil-vapors are harmful to the environment (Wang, 2007; Chen, 2007). Besides, they badly affect qualities of oil and gasoline and induce danger of fire and blast. The condensable oil vapors are main light alkyls and alkenes. The number of carbon atoms in such a molecule is among 4~6. In air and oil-vapor mixtures, factors of light hydrocarbons with different partial pressure and physical characteristics, such as saturated pressure, saturated temperature and triple points, are destined to complex condensing processes. Condensation of water vapor (Kang and Kim, 1994), which plays a main role in the primary cooling process before temperature decreases to water freezing point, should be non a neglectable factor, because of its relative humidity of about 60%. And pre-removing of water vapor is a necessary step for the refrigeration used for oil vapor recovery. Condensation of light hydrocarbons is a typical multi-mixtures process with the feasibility of Marangoni condensation for small fractions of kinds of hydrocarbon vapors and their different boiling points. And the immiscible solution, because of the existence of water liquid, leads to the possibility of dropwise condensation. Complex heat transfer and enhancement mechanism have been discussed (Ma *et al.*, 2008), while few investigations aimed at the air and oil-vapor mixtures condensation (Peng, 2000).

The purpose of this paper is to discuss condensation process of the volatilized oil-vapor, in view of theoretical investigation.

CALCULATION METHOD

The petroleum or oil constitutes of the complicated organic hydrocarbons. Every hydrocarbon holds different fraction, which is attributed to exploitation location in the world and the exploiting stage. And the volatilized oil

components could be different relative to the local temperature, measurement to sun radiation and value of octane for gasoline. One case shows in table 1.

Table 1. volume fraction of a certain air and oil vapor mixtures

component	n-C ₄	i-C ₄	c-C ₄	n-C ₄ ⁼	i-C ₄ ⁼	n-C ₅	i-C ₅	n-C ₆	hydrocarbons fraction
vol (%)	2.420	2.894	3.724	2.944	3.24	0.434	6.156	6.884	28.696

The oil vapor is actually a mixture consisted of kinds hydrocarbons, the reason only considering certain components is that the revelation from oil refineries and gasoline indicates that only parts of the hydrocarbons can volatilize easily. Date measured from (Peng, 2000) declares that 34.3vol% hydrocarbons components exist in air and oil-vapor mixtures in LuoYang Petroleum and Chemical Plant. And the main components are C₄, C₅ and C₆.

Three Parameters Method steam pressure equation (Hatsopoulous and Keenan, 1891) is adopted and verified by the date from software NIST as following

$$\ln p_r = f^{(0)}(T_r) + \omega f^{(1)}(T_r) \tag{1}$$

where

$$f^{(0)} = 5.92714 - 6.09648/T_r - 1.28862 \ln T_r + 0.169347 T_r^6$$

$$f^{(1)} = 15.2518 - 15.6875/T_r - 13.472 \ln T_r + 0.43577 T_r^6$$

$$\omega = (-\ln p_c - 5.92714 + 6.09648\theta^{-1} + 1.28862 \ln \theta - 0.1697347\theta^6) / (15.2518 - 15.6875\theta^{-1} - 13.472 \ln \theta + 0.43577\theta^6)$$

The θ values and eccentricity factor ω for calculated hydrocarbons showed in table 2.

Table 2. values of θ parameter and eccentricity factor

component	θ	ω	component	θ	ω
n-C ₄	0.6413	0.1966	i-C ₄ ⁼	0.6320	0.1898
i-C ₄	0.6405	0.1811	n-C ₅	0.6584	0.2492
c-C ₄	0.6210	0.1833	i-C ₅	0.6538	0.2260
n-C ₄ ⁼	0.6400	0.2429	n-C ₆	0.6737	0.3008

Software Nist employed to validate the Three Parameters Method is plotted in Figure 1. The calculated and compared component is butane. Results indicate that departure of the calculated date by Three Parameter Method is no more than 2% from the Nist one, so that the method can be acceptable.

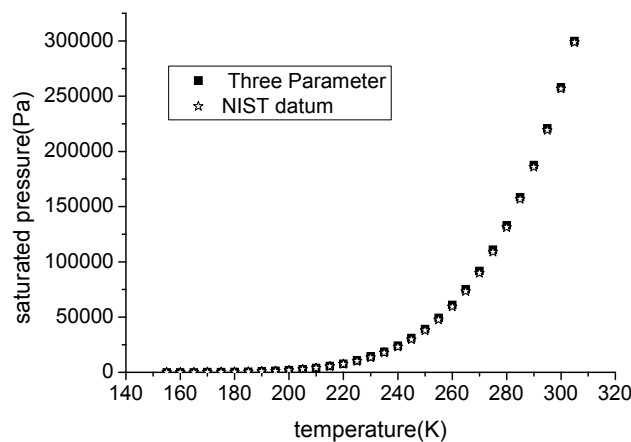


Figure 1: Saturated temperature and pressure relation of butane steam

The gas and oil-vapor mixtures listed in table 1 are considered as ideal gas mixtures. So every component in the gas phase satisfies the ideal gas state equation

$$p_i V = n_i RT_i \quad (2)$$

which can be supported by data from Table 4, with the calculating temperature 293.15 K. Compressibility factors of components in Table 2 are more close to 1, which indicates that the gas and oil-vapor mixtures can be considered as ideal gas mixtures. Especially, volume fractions of components listed in Table 1 is less than 8%, which means every hydrocarbon shares no more than 8% of the total pressure. Therefore, the ideal gas mixture assumption is reasonable.

Table 2 compressibility factors (Z) of hydrocarbons in 20 degrees centigrade and 1 atm.

component	methane	ethane	propane	butane	pentane	hexane
Z	0.9981	0.9920	0.9834	0.9682	0.9450	0.9190

The condensation of one component did not effected by others for ideal gas mixtures, so that when analyzing a certain component hydrocarbon condensation, the others could be treated as a certain ideal gas, the state equations of the analyzed component in two different points would be as

$$p_1 V_1 = n_1 RT_1$$

$$p_2 V_2 = n_2 RT_2$$

When temperature drop is tiny enough in the cooling process so that there is a little difference between T_2 and T_1 , considering T_2 equals T_1 , the error can be accepted. So the condensation quantity can be easily expressed as follows with the overall pressure p constant:

$$\Delta n = n_1 - n_2 = \frac{V}{RT_1} (p_1 - p_2 \times \frac{p - p_2}{p - p_2}) \quad (3)$$

Where, Δn is the condensation quantity of the analyzed component with its saturated partial pressure. And the assumption above can clearly be true if the temperature drop is small enough. Therefore, in any temperature drop from the above three intersected temperature intervals, a certain component condensation can be calculated accordingly, with the saturated temperature judged by the Three Parameters Method state equation described above.

CALCULATION RESULTS AND DISCUSSION

According to equation (3), the condensation process is plotted in Figure 2 for the case showed in Table 2 with calculating temperature step 0.5°C in every step and the condensation of water vapor is not included. It is seen from Figure 2 that only $n-C_6$ condenses in the first intervals with temperature drop from 276.15 K to 238.15 K. The reasons are $n-C_6$ has a relative high boiling point and the high fraction in the mixture. In fact, more than 80% water vapor condensed when the air and oil-vapor mixtures reach 276.15 K. So in an oil-vapors recovery system, the first interval is important. Because the water condensate could solidified to additive on the heat exchanger surfaces, it will affect the process of heat transfer. Therefore, the pre-cooling is important, which is the so called first region.

When the temperature decreases from 276.15 K to 238.15 K, nearly 80% $n-C_6$ has changed to liquid and $i-C_5$ condenses a lot also. But other components just begin condensation. In this temperature drop region, the remnant water vapor condenses almost and become frost, which brings lots troubles to the actual heat exchangers and the ability to be provided with the frost remove measurement should be considered further.

All the hydrocarbon components happen to condense in the third region, i.e. temperature drop from 238.15 K to 198.15 K. There exists a large phase-change heat load in the third region, which is great consumption to the refrigerating load as cost will be more if the same heat load stands at much lower temperature point than the environment one. In this interval, more than 80% hydrocarbon components can be effectively reclaimed. And almost 99% components are reclaimed, if the lowest cooling temperature reaches minus 90°C .

In the whole condensation process, the condensation rate could be quite different. The temperature interval between 233 K~190 K shares a high condensation rate for hydrocarbons C_4 and C_5 . Every hydrocarbon condenses faster at its condensation beginning. Oil-vapors recovery efficiency is 82%, when setting the lowest temperature as 198.15. and 96% can obtain, when the lowest temperature is 183.15K.

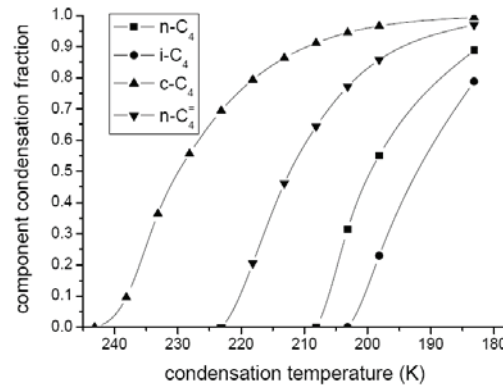


Figure 2(a): Relations of cooling temperature and component condensation fraction

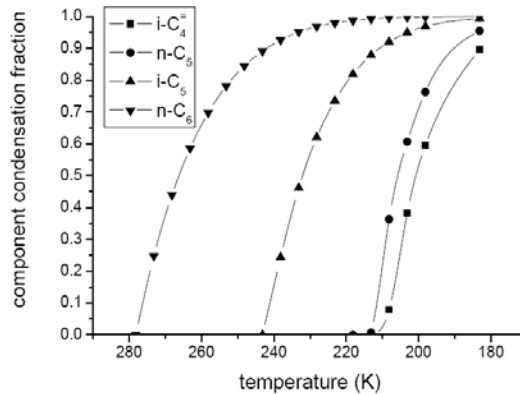


Figure 2(b): Relations of cooling temperature and component condensation fraction

According to the calculation results, the important factors should be considered for the design of an oil vapor recovery refrigeration system as following.

The first, pre-cooling should be adapted to gas and oil-vapor mixtures so as to minimize the energy consumption.

The second, the third region refrigerating machine occupies the position with characteristics of relative low temperature (lower than the terminal temperature of the treated gas mixture) and relative big refrigerating loads, which is contributed to the main hydrocarbon phase-change course. If the overall refrigerating machines are self-governed three cycles, the third intervals power consumption of compressor will be amazed big, due to the relative high environment temperature compared to that of the refrigerant temperature in the entry to the compressor. Such a big potential difference for heat transfer is not proposed. And huge power consumption in compressor is at the expense of potential difference. To solve the problem, the cascaded refrigeration cycle is advised in the second and the third parts, which means refrigeration load of the second cycle respectively serve the second class refrigeration load and the third class condenser. Table 4 below gives contrast between the unattached cycle and the cascaded refrigeration one. It is clear that the cascaded refrigeration cycle can obviously improve the overall refrigeration Cop for our problem.

Table 4 Cop comparison between unattached and overlap coupled refrigerating system

case	unattached	cascaded refrigeration one and export air pre-cooling
Cop	0.604	1.56

And the third, the tube and shell heat exchanger is prevalently advised (e.g. Song, 2007; Tan, 2008). For the finned tube heat exchanger, to avoid the relative bad heat transfer capacity of gas-gas heat exchanger, secondary refrigerant can be a considerable scheme in the heat load transport between gas and oil-vapor mixtures and refrigerant. Therefore, the gas velocity could not be big enough, which further worsens the heat transfer coefficient of gas mixtures. So heat transfer enhancement and optimization could be very important.

CONCLUSIONS

Gas and oil-vapor mixtures condensing with the purpose of recovery oil-vapor is a very complex process. This paper pays main attention to the condensation recovery of kinds of hydrocarbon components and their relations with temperature points. Every component in the gas mixture, including the condensable gas and the non-condensable, is a resistance to other components diffusion. Based on the calculation results, some conclusions could be obtained as followings.

- Condensation rate in different temperature point could be quite different, with the relative low temperature region existing big condensation rate for every condensable component and a large phase-change heat load.
- Dehumidification process from 308.15 K to 276.15 K is important and to decrease the frost effects to next further refrigerating process. And The relative high boiling point and the high fractions (such as C_6 in present work) condensate in the first region.
- The temperature region from 276.15 K to 238.15 K is the condensation process of high carbon organic substances, and the temperature region from 238.15 K to 198.15 K is the condensation region for relative low carbon organic substances.
- The temperature interval between 233 K~190 K shares a high condensation velocity for hydrocarbons C_4 and C_5 . And cascaded refrigeration one is a rational strategy to improve overall Cop, because of the relative large heat load.

NOMENCLATURE

P_r	contrast pressure, $P_r = P/P_c$	(-)	Subscripts
P	total pressure	(Pa)	i a vapor component
T_r	contrast temperature, $T_r = T/T_c$	(-)	1 condition before condensation
Z	compressibility factor	(-)	2 condition after condensation
R	molar gas constant	(J/mol·K ⁻¹)	c critical point
ω	eccentricity factor	(-)	b ordinary boiling point
θ	dimensionless temperature, $\theta = T_b/T_c$	(-)	
n	molar rate	(mol s ⁻¹)	
Δn	molar condensation rate	(mol s ⁻¹)	
COP	coefficient of performance,	(W/W)	

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