Experimental study on emission of VOCs from tanker using hollow fiber membrane absorption method with different absorbents

J Y Zhou, B F Wang, L H Nie, J X Lu, Y J Hao and R R Xu

School of Petrochemical and Energetic Engineering, Zhejiang Ocean University, Zhoushan 316000, China

1 E-mail: 646522786@qq.com

Abstract. China's oil dependence is getting higher and higher, 90% of oil import is transported by sea. Tankers will produce a lot of VOCs during loading and unloading, so the prevention of such pollution has become increasingly urgent. The hollow fiber membrane absorption method combined the characteristics of the absorption method for the treatment of high concentration and large flow of VOCs and the advantage of low energy consumption of membrane method. At present, the research on the recovery of oil and gas is relatively few. In this paper, the effect of membrane absorption on the recovery of oil and gas was investigated. The different absorbent affected the oil vapor recovery, the experimental results showed that the performance of absorbent of AbsFOV-97 was better than that of heat conductive oil.

1. Introduction

In 2015, China's apparent consumption of oil was estimated at 5.43 tons, up slightly by 25 million tons from a year earlier [1]. China's net imports of foreign crude oil reached 328 million tons in 2015, up 6.4 percent from the previous year, the growth rate was up 0.6 percentage points from 2014. China's oil consumption continued to grow at a moderate and low speed, and its foreign dependence exceeded 60% and make for the first time in history, reaching 60.6% [2]. 90% of China's imported oil is completed by sea shipping. Oil is a complex mixture of thousand of hydrocarbon compounds. Some volatile organic vapors (VOCs) will evaporate from the oil during the loading and unloading of tankers, the lower the boiling point of the oil, the more the times of loading and unloading, the greater the changes of temperature and pressure, the more the loss of oil evaporation [3]. At present, the various VOCs program both at home and abroad includes resource non-recyclable and recyclable, the former such as direct combustion, catalytic combustion, photocatalysis, nano-materials self-catalyzed, the latter such as absorption, adsorption, condensation and membrane recovery technology, etc [4]. Conventional absorption methods had the advantages of being able to treat the VOCs of high concentration and high flux, while the membrane separation method had the characteristics of low energy consumption, simple process, high recovery rate, high operational flexibility, high degree of automation, no need for maintenance, no secondary pollution, environmental protection, energy saving, safe and reliable [5], the contrast of several traditional techniques is shown in table 1. Therefore, the combination of this two methods, membrane-based absorption coupling technology, was of great concern because of its characteristics of large gas-liquid contact area, large mass transfer rate, high operational flexibility, no flooding, no fog entrainment and simple equipment etc [6]. The selection of absorbent was the key point of membrane absorption technique, because the absorbent
was acted as a primary selective action on membrane absorption [7]. That is to say, the adsorbent has a direct effect on the selectivity and absorption rate of hydrocarbon components. Hollow fiber membrane absorption technology has been widely studied for the removal of CO$_2$ and SO$_2$ in flue gas [8-11]. But the case of recycling VOCs with hollow fiber membranes has not yet appeared, this paper studied the recovery process and effect of the emission of VOCs during loading and unloading in tankers in the application of hollow fiber membranes with different absorbents. In the mid-1980s, scientists developed a new composite membrane, nanofiltration (UF) membrane, which has a higher permeation flux [12] but we chose to use PVDF membrane was because that its characteristic of heat resistance, corrosion resistance, radiation resistance, chemical stability, mechanical high strength and good toughness was more suitable for the production of hollow fiber membrane.

Table 1. The comparison of several traditional technologies.

| Recovery method       | Advantages                                      | Disadvantages                                      |
|-----------------------|-------------------------------------------------|---------------------------------------------------|
| absorption            | The method is simple and can handle mixed gases. | Low efficiency; high performance and equipment selection conditions |
| adsorption            | Its operation is simple and the efficiency is high. | The adsorption of activated carbon will release heat, so there are security risks; the activated carbon need to replaced regularly; high operating costs. |
| condensation          | The quality of recycled products is pure.       | Large energy consumption; it cannot deal with low concentration of VOCs; high technical requirements. |
| membrane separation   | Easy to use; service life long; small occupied area. | Large investment; high technical requirements. |

2. Experimental

2.1. Experimental apparatus and materials
GC9720 gas chromatograph was supplied by Zhejiang Fuli Analytical Instruments Co. Ltd. PVDF hollow fiber membrane module was made in laboratory, its specifications was L50cm × D10cm, table 2 lists the solution composition, AbsFOV-97 absorbent was supplied by Changzhou university.

Table 2. Solution composition of PVDF hollow fiber membrane.

| Spinning dope | Content (%) |
|---------------|-------------|
| PVDF          | 17%         |
| DMAC          | 78%         |
| PVP           | 5%          |

2.2. Experimental methods
The experimental process is shown in figure 1, the VOCs that needed for the experiment was produced by the way of nitrogen bubbling in the gasoline, the VOCs flowed from the inside of the hollow fiber membrane, and the outside was filled with absorbent. Then, the absorbent was evacuated and regenerated by a vacuum pump in the side of the shell. As a result, the raw gas was obtained from 1 # sampling port, the purified gas was obtained from 2 # sampling port, the condensed gas after absorbed
was obtained from 3 # sampling port, and then these gas was sampled by gas sampling bag for gas chromatography analysis. Set the flow rate to 500 mL / min.

3. Results and discussions

3.1. Gas chromatographic analysis of raw VOCs before absorption

When the absorber was heat conductive oil, the results of gas chromatography analysis of 1# raw VOCs before absorption is shown in figure 2. From figure 2, it could be seen that the content of n-butane was 1.6099%, the content of propylene was 0.0010%, the content of isobutene was 0.3057%, the content of cis -2- butene was 0.2403%, the content of 1,3- butadiene was 1.9331%, and the content of 2- methyl -2- butene was 0.0006%, thus, it could be calculated that the concentration of the raw gas VOCs before absorbed was 4.0906%.

When the absorber was AbsFOV-97, the results of gas chromatography analysis of 1# raw VOCs before absorption is shown in figure 3. From figure 3, it could be seen that the content of propane was 0.3257%, the content of propylene was 0.2599%, the content of n-butane was 0.4988%, the content of allene was 0.0009%, the content of anti -2- butene was 0.0002%, the content of cis-2-butene was 0.2277%, the content of 1,3-butadiene was 0.8923%, the content of 2- methyl -2- butene was 0.8773%, thus, it could be calculated that the concentration of the raw gas VOCs before absorbed was 3.0828%.

![Figure 1. Experimental process.](image1)

![Figure 2. Gas chromatography of 1# raw VOCs before absorption (absorbent for heat conduction oil).](image2)
Figure 3. Gas chromatography of 1# raw VOCs before absorption (absorbent for AbsFOV-97).

3.2. Gas chromatographic analysis of purified VOCs after absorption

When the absorber was heat conductive oil, the results of gas chromatography analysis of 2# purified VOCs after absorption is shown in figure 4. From figure 4, it could be seen that the content of methane was 0.2297%, the content of ethane was 0.1724%, the content of ethylene was 0.0185%, the content of propylene was 0.0171%, the content of n-butane was 0.3341%, the content of trans-2-butene was 1.4695% The content of isobutene was 0.0274%, the content of cis-2-butene was 0.1056%, the content of 1,3-butadiene was 1.0798%, and the content of 2-methyl-2-butene was 2.1188%, thus, it could be calculated that the concentration of purified VOCs after absorption was 5.5729%.

When the absorber was AbsFOV-97, the results of gas chromatography analysis of 2# purified VOCs after absorption is shown in figure 5. From figure 5, it could be seen that the content of ethane was 0.0323%, the content of ethylene was 0.2426%, the content of propylene was 0.5685%, the content of n-butane was 0.0776%, the content of butene-1 was 1.2046%, the content of cis-2-butene was 0.0956%, the content of 1,3-butadiene was 1.0198%, thus, it could be calculated that the concentration of purified VOCs after absorption was 3.241%.

Figure 4. Gas chromatography of 2# purified VOCs after absorption (absorbent for heat conduction oil).
3.3. Gas chromatographic analysis of concentrated gas VOCs after absorption

When the absorber was heat conductive oil, the results of gas chromatography analysis of 3# concentrated VOCs after absorption is shown in Figure 6. From figure 6, it could be seen that the content of propylene was 0.0471%, the content of n-butane was 0.0005%, the content of propylene was 0.0022%, the content of isobutene was 0.2771%, the content of cis-2-butene was 0.2207%, the content of 1,3-butadiene was 0.0021% and the content of 2-methyl-2-butene was 0.0024%, thus, it could be calculated that the concentration of concentrated VOCs after absorption was 0.5521%.

When the absorber was AbsFOV-97, the results of gas chromatography analysis of 3# concentrated VOCs after absorption is shown in Figure 7. From figure 7, it could be seen that the content of propane was 0.0002%, the content of n-butane was 0.2930%, the content of propadiene was 0.0005%, the content of cis-2-butene was 0.0010%, and the content of 1,3-butadiene was 0.0001%, thus, it could be calculated that the concentration of concentrated VOCs after absorption was 0.2948%.
4. Conclusion
When we used heat conductive oil as absorbant, we can respectively obtained that the content of VOCs of raw gas, purified and concentrated gas was 4.0906%, 5.5729% and 0.5521% from figure 2, figure 4 and figure 6. When we used AbsFOV-97 as absorbant, we can respectively obtained that the content of VOCs of raw gas, purified and concentrated gas was 3.0828%, 3.241% and 0.2948% from figure 3, figure 5 and figure 7. It can be seen from the above experimental results that the removal rate with the absorbent of heat conductive oil was 86.50%, the removal rate with the absorbent of AbsFOV-97 was 90.44%. The performance of AbsFOV-97 was better than that of heat conductive oil, and the smaller the gas flow rate, the better the oil and gas recovery effect of the membrane absorption device, then when the gas flow rate was below 50mL/min, the removal rate of hydrocarbons should be about 99.50%.

References
[1] Chai J, Wang S B, Wang S Y and Guo J 2012 J. Energies 5 577-598
[2] CNPC economic & technology research institute 2016 Development report on domestic and foreign oil and gas industry in 2015 (Beijing: CNPC economic&technology research institute)
[3] Huang W Q 2011 Basic theory and application of oil and gas recovery (Beijing:China Petrochemical Press) pp 7-10
[4] Huang W Q, Wang D L, Li F and Wang H N 2012 J. Oil and Gas Storage and Transportation 31 641-646
[5] Strathmann H 2001 J. AIChE 47 1077-87
[6] Gabelman A and Huang S T 1999 J. Journal of Membrane Scicence 159 61-106
[7] Shelekhina A B and Beckmanb I N 1992 J. Journal of Membrane Science 73 73-85
[8] S Boributh, R Jiraratananon and K Li 2013 J. Journal of Membrane Science 429 459-472
[9] Lai C F, Yang B, Zhang G L, Wen C S, Cao R and Wu R R 2012 J. Journal of Chemical Industry and Engineering(China) 63 500-507
[10] Luis P, Garea A and Irabien A 2012 J. Chemical Engineering and Processing: Process Intensification 52 151-154
[11] Cui Z D, Hou C N, Chen Y and Guan Y P 2012 J. Membrane Science and Technology 31 84-88
[12] Miao J, Zhang L C and Lin H C 2013 J. Chemical Engineering Science 87 152-159