Interferometric study on the mass transfer in cryogenic distillation under magnetic field

S R Bao, R P Zhang, Y Y Rong, X Q Zhi and L M Qiu*
Institute of Refrigeration and Cryogenics, Zhejiang University, Hangzhou 310027, China
E-mail: Limin.Qiu@zju.edu.cn

Abstract. Cryogenic distillation has long been used for the mass production of industrial gases because of its features of high efficiency, high purity, and capability to produce noble gases. It is of great theoretical and practical significance to explore methods to improve the mass transfer efficiency in cryogenic distillation. The negative correlation between the susceptibility of paramagnetic oxygen and temperature provides a new possibility of comprehensive utilization of boiling point and susceptibility differences in cryogenic distillation. Starting from this concept, we proposed a novel distillation intensifying method by using gradient magnetic field, in which the magnetic forces enhance the transport of the oxygen molecules to the liquid phase in the distillation. In this study, a cryogenic testbed was designed and fabricated to study the diffusion between oxygen and nitrogen under magnetic field. A Mach-Zehnder interferometer was used to visualize the concentration distribution during the diffusion process. The mass transfer characteristics with and without magnetic field, in the chamber filled with the magnetized medium, were systematically studied. The concentration redistribution of oxygen was observed, and the stable stratified diffusion between liquid oxygen and nitrogen was prolonged by the non-uniform magnetic field. The experimental results show that the magnetic field can efficiently influence the mass transfer in cryogenic distillation, which can provide a new mechanism for the optimization of air separation process.

1. Introduction
The metallurgical, coal chemical, and electronic industries need massive quantities of industrial gases, which impels the development of improved air separation technologies. Air separation techniques depend on the physical property differences of the substances, i.e. boiling point difference in distillation method, molecular size difference in membrane method [1]. Containing two unpaired electrons, an oxygen molecule is paramagnetic, and the susceptibility of oxygen is much larger than that of nitrogen. This unique property has been used to measure the concentration of oxygen, control the air flow and produce oxygen-enriched air [2]. Asako et al. simulated the distribution of oxygen concentration of air in a capsule under a strong magnetic field gradient [3]. Cai et al. designed a ‘Magnetic-Sieve’ structure, the maximum degree of single stage oxygen enrichment in their experiment reached 0.65% [4]. The magnetic method is particularly suited to produce oxygen-enriched air, but the large-scale production of highly purified product only through this method at normal temperature is impractical.

The negative correlation between the susceptibility of paramagnetic gases and temperature [5] provides a new possibility for utilizing susceptibility differences in the cryogenic air separation. For example, the magnetic force acting on liquid oxygen reaches 120.3 N/kg, that is, 12 times gravity,
under 0.5 T magnetic field with a gradient of 100 T/m. Starting from this concept, we proposed a novel distillation intensifying method by using gradient magnetic field [6], in which the magnetic forces acting on the oxygen molecules affect the two-phase flow, heat transfer and mass transfer in the distillation process. In our previous work, we studied the involved free-surface flow [7] and convective heat transfer [8] phenomenon numerically. However, to the best of the authors' knowledge, there is no report about the effect of magnetic field on the mass transfer between oxygen and nitrogen at cryogenic temperatures, which is the research object of this study.

The basic mass transfer model is single-phase diffusion. The laser interference technique is an effective non-contact method for measuring the concentration field in the study of diffusion. Some researchers have attempted to use this technique at cryogenic conditions [9]. In this research, a cryogenic testbed was designed and fabricated to study the diffusion between liquid oxygen and nitrogen under magnetic field. A Mach-Zehnder interferometer was applied to visualize the concentration distribution during the diffusion process. The mass transfer characteristics with and without magnetic field in the chamber filled with magnetized medium were investigated.

2. Experimental techniques

2.1. Cryostat system

![Figure 1. Schematic diagram of the experimental system.](image)

The experimental apparatus mainly consists of a cryostat system and an optical measurement system, as shown in Figure 1. The cryostat is mounted on a damping isolation optical platform to reduce the vibration caused by the vacuum pump. A vacuum multi-layer insulated rectangular chamber is placed inside the vacuum chamber of the cryostat. Two optical glass-to-Kovar flanges are installed in central position of the inner chamber, and two optical quartz glass windows are installed on the vacuum chamber to let the laser beam pass through. Liquid nitrogen and oxygen are charged into the rectangular chamber from bottom. To improve the stability of liquid charging during the experiment, a gas-liquid separator and a low temperature needle valve are added to the inlet pipe.
The evaporated vapor comes out from the top of the cavity. A small amount of vapor is pumped to the gas chromatograph by the sampling pump to analyze the volume fraction of oxygen. The temperature at the exterior surfaces of the entry and exit conical expanding sections of the chamber are measured by two calibrated temperature sensors (PT100) with an uncertainty of ±0.1 K. The total heat leakage of the cryostat is estimated to be 2.8 W.

The liquid oxygen-nitrogen mass transfer around a single permanent magnet has already been studied previously [10]. To enhance the effect of magnetic field, we designed a magnetic system that can be filled into the inner chamber, as shown in Figure 2. The magnetic space is constructed with two cuboids neodymium-iron-boron permanent magnets of the same size (60×40×10 mm). Opposite magnetic poles of the permanent magnets face each other with steel wools filled in the gaps between the poles. The magnetic conductive steel wools, which are widely used in magnetic separation of minerals, can produce a high gradient magnetic space around their surfaces. The magnetic conductive shell around the magnets serves as magnetic yoke. A similar structure with stainless steel 304 filling blocks is arranged in the upper part of the chamber, thus to make the interior space symmetric in the vertical direction. The distribution of magnetic flux density along the centerline is measured by a gauss meter, as shown in Figure 3. For the magnets without steel wools between them, the maximum magnetic flux density is 0.33 T.

Before the experiments, the vacuum chamber is evacuated, and the vacuum pump is kept working during the experiments. Liquid nitrogen is first charged into the inner chamber to cool down the device. After the magnet system as well as the inner chamber are cooled sufficiently, liquid nitrogen is removed from the chamber by the gaseous nitrogen until the fluid level is flush against the top edge of the window. Then, liquid oxygen is slowly charged into the chamber until the interface between oxygen and nitrogen reaches the central position of the window, at which point the inlet valve is closed and the vent valve is opened to maintain a stable pressure in the chamber. The mass transfer process between liquid oxygen and nitrogen in the field of view is visualized by the optical measurement system.

2.2. Optical measurement system
The experimental setup of the optical measurement system is shown in Figure 4. A Mach–Zehnder interferometer is employed to record the line-of-sight images of the concentration field. A single longitudinal mode solid-state laser with a wavelength of 532 nm and output power of 10 mW is chosen as the coherent light source, considering the absorption spectrum of liquid oxygen has a
relatively small value around this wavelength. The laser beam is enlarged to a diameter of 35 mm by a beam expander. The beam is then split into two beams, a reference wave and an object wave by a beam splitter. A neutral density filter is added to the reference wave to keep the interference pattern clear in case of the decreasing of object wave intensity. The beam that carries the mass transfer information in the cryostat is then combined with the reference wave by a second beam splitter. A CCD camera (MV-E1600M) is used to record the interferograms with the solution of 4896×3264 pixels at a frame rate of 5 fps.

Figure 4. Schematic of the optical system for interference measurement.

3. Results and discussion
The mixing mass transfer process of liquid oxygen and nitrogen was measured by the laser interferometry technology in real-time. Permanent magnetic field together with magnetic conducting medium were used in the experiment to provide sufficient magnetic forces on oxygen molecules. The diffusion characteristics with and without high gradient magnetic field were tested, respectively. The temperatures at the bottom and top position of the inner chamber, and the oxygen concentrations in the evaporated gas were also measured and analyzed.

3.1. Mass transfer process with magnetic field
Figure 5 shows the interference patterns during the mixing, diffusion and evaporating process of liquid oxygen and nitrogen under gradient magnetic field. Two rectangular permanent magnets and 3 g magnetic conductive steel wools filled in the gap between them were used in the experiment. According to the feature of the fringe patterns, we divide the mass transfer between oxygen and nitrogen components into four different phases: liquid oxygen charging phase, stable stratified diffusion phase, bubble rising phase, and stable evaporating phase. In Figure 5(a), the liquid level of nitrogen just reached the upper edge of the window. The fringes in the field of view were irregular and the interval between fringes was relatively wide. The liquid oxygen charging phase is shown in Figure 5(a-b). Many dense and horizontal fringes appeared and raised from the bottom, and the densified area went dark due to light-absorbing property of oxygen component. The liquid charging stopped after the boundary between the wide and dense fringes approached the central position, which typically takes 5 minutes. The dense and horizontal fringes reflect a high concentration gradient in vertical direction. Besides, the fringes were quite clear and stable at a time after the charging was finished, indicating that the liquid in the field of view is subcooled and no bubbles are generated.

As shown in Figure 5(c-f), stable stratified diffusion was maintained between 5-76 minutes. During this process, the magnetic field produced a resistance force to the natural convection in liquid oxygen at the bottom, and the mass transfer in the oxygen enriched area was mainly through diffusion. At the same time, the magnetic field near the edge of the magnets were stronger than that near the center line, which made the boundary between the wide and dense fringes cave downward and the curvature of the
boundary increase as the boundary moved toward the upper surface of the magnets. However, a slight increase of the boundary and a densification of fringes in the nitrogen enriched area were found from 45-60 minutes, which is probably because of the pressure rising inside the liquid caused by the accumulated bubbles in the porous steel wools.

Figure 5. Dynamic diffusion between liquid oxygen and nitrogen with magnets and steel wools.

At 76 minutes, the fluid in the chamber lost its stability, and a large amount of bubbles passed through the liquid with the assistance of buoyance and caused violent mixing of the components, as shown in Figure 5(g). Such violent mixing in the fluid thoroughly broke the oxygen layer maintained by the magnetic field, so the interference patterns became wide fringes between those of pure liquid nitrogen and oxygen again, after the fluid returned to a stable state. The mixture liquid was boiled away gradually thereafter, as shown in Figure 5(h-j).

3.2. Mass transfer process without magnetic field

Figure 6. Dynamic diffusion between liquid oxygen and nitrogen without magnetic field.
Figure 6 shows the interference patterns during the mixing and evaporating process of liquid oxygen and nitrogen without magnetic field, by replacing the permanent magnets with same sized stainless steel 304 blocks and keeping the same filling content of steel wools. The fluid charging finished at 5 minutes. After a short time, a sudden increase of the liquid level occurred, and this phenomenon repeated in many experiments, as shown in Figure 6(c). The probable reason is that the residual liquid oxygen in the inlet pipe suddenly flowed into the chamber without the blockage of magnetic field. Figure 6(b) and Figure 6(d) shows that the boundary between the wide and dense fringes was maintained horizontal by gravity, and the fluctuation near the boundary is more violent than that in Figure 5 without the constraint of magnetic force. The appearance of a large amount of bubbles was observed at 38 minutes, and the duration of stable stratified diffusion was reduced to half of that with magnetic field. It's worth mentioning that this kind of gas blockage may cause flooding and pressure fluctuation in practical air distillation column, thus the structure of the magnetic conductive medium should be carefully designed and optimized. During the stable evaporating phase, the disturbance in the liquid was also more violent than that with magnetic field, as shown in Figure 6(f-j).

3.3. Temperature and volume fraction variations during the mass transfer

Temperature variations during the mass transfer process of liquid oxygen and nitrogen at the bottom and top position of the chamber are shown in Figure 7 and Figure 8. The stratified liquid oxygen (90 K, at bottom) and liquid nitrogen (77 K, at top) were mixed together in this experimental study. Therefore, the temperature at the bottom position increased to the liquid oxygen temperature during the first 5 minutes of liquid oxygen charging phase, while the temperature at the top position decreased slightly due to the rise of liquid level.

![Figure 7. Temperature variation with magnetic field.](image1)

![Figure 8. Temperature variation without magnetic field.](image2)

With the evaporation of the liquid, the temperature at top increased monotonically. The temperature at bottom increased slowly during the stratified diffusion process, because of the heat transfer from liquid oxygen to the chamber wall and the accumulation of blocked vapor. After the bubble rising was observed, the bottom temperature with magnetic field dropped suddenly, while that without magnetic field rose. The main reason for the different phenomenon is the blockage effect of the porous steel wools holding the oxygen bubbles is much stronger under magnetic field, thus the accumulation and pressure rise of the vapor is higher than those without magnetic field. When the blocked vapor lost its stability, a great deal of oxygen bubbles pushed the liquid oxygen to the top of the liquid directly and the bottom space was filled by liquid nitrogen. And in the case without magnetic field, the blocked vapor was too limited to generate enough buoyance to break the liquid
stratification completely, so the bottom space was still filled by the surrounding liquid oxygen after the bubble rising. Furthermore, another small temperature drops happened at about 190 minutes without magnetic field, and the phenomenon hasn’t been captured this time due to the liquid level being lower than the window.

The results of volume fraction of oxygen in the evaporated vapor also support the above explanation. As shown in Figure 9. After the bubble rising, the volume fraction in the experiment with magnetic field increased rapidly with the coming up vapor oxygen and the movement of liquid oxygen to the top layer. While the volume fraction in the experiment without magnetic field didn't show a significant change, which illustrated that the concentration at the top of the liquid layer is stable. It should be noted that the curves of volume fraction before bubble rising has confirmed the effectiveness of using gradient magnetic field to make oxygen molecules more likely to retain in the liquid, which may promote the distillation of air. However, the use of porous material may also cause vapor blockage and break the stability in vapor-liquid mass transfer, which apparently calls for a further investigation.

Figure 9. Volume fraction of oxygen in the evaporated vapor.

4. Conclusion
The diffusive mass transfer between liquid oxygen and nitrogen under gradient magnetic field was revealed experimentally. A Mach-Zehnder interferometer was applied to visualize the concentration distribution during the mass transfer process. The temperature and volume fraction characteristics with and without magnetic field, in the chamber filled with magnetic medium were investigated.

The experimental results indicate that the mass transfer between oxygen and nitrogen components can be divided into four different phases: liquid oxygen charging phase, stable stratified diffusion phase, bubble rising phase, and stable evaporating phase. The magnetic field maintained the stable stratification of liquid for double time as that without magnetic field and affected the shape of the mass transfer interface during the stable stratified diffusion phase. The volume fraction of oxygen in the evaporated air also revealed the effectiveness of magnetic field on retaining the oxygen molecules in the liquid layer. However, sudden bubble rising happened due to the vapor blockage by porous magnetic conducting medium, which broke the stable stratification and should be avoided.

This study preliminarily validates the possibility of using gradient magnetic field to control the mass transfer of paramagnetic oxygen in cryogenic air separation process. We expect to obtain reliable mass transfer theories and models to allow the calculation and design of the magnetically intensified air separation devices.
5. References
[1] Smith A R and Klosek J 2001 A review of air separation technologies and their integration with energy conversion processes Fuel Process. Technol. 70 115–34
[2] Bao S R, Zhang J H, Zhang X B, Tang Y, Zhang R P and Qiu L M 2015 Progress in magnetic air separation technology J. Zhejiang Univ. Eng. Sci. 49 605–15 (in Chinese)
[3] Asako Y and Suzuki Y 2006 Oxygen Separation/Enrichment From Atmospheric Air Using Magnetizing Force J. Fluids Eng. 129 438–45
[4] Cai J, Wang L, Wu P, Li Z Q, Tong L G and Sun S F 2008 Study on oxygen enrichment from air by application of the gradient magnetic field J. Magn. Magn. Mater. 320 171–181
[5] Kratky K W 1975 Explanation of the magnetic behaviour of oxygen in the liquid state Acta Phys. Acad. Sci. Hung. 39 15–21
[6] Qiu L M, Bao S R, Zhang J H and Zhang X B 2016 Method and device for cryogenic distillation separation of air assisted by gradient magnetic field Chinese Patent 201410111337X
[7] Bao S R, Zhang R P, Wang K, Zhi X Q and Qiu L M 2017 Free-surface flow of liquid oxygen under non-uniform magnetic field Cryogenics 81 76–82
[8] Bao S R, Zhang R P, Zhang Y F, Tang Y, Zhang J H and Qiu L M 2016 Enhancing the convective heat transfer in liquid oxygen using alternating magnetic fields Appl. Therm. Eng. 100 125–32
[9] Nakano A and Shiraishi M 2004 Investigation for Magnetic Separation of Oxygen from Supercritical Air Near the Maxcondentherm Point Adv. in Cryogenic Eng. 49 1923–30
[10] Zhang J H, Bao S R, Zhang R P and Qiu L M 2015 A dynamic optical measurement system for cryogenic fluids using laser interferometry IOP Conf. Ser. Mater. Sci. Eng. 101 12190

Acknowledgements
The authors greatly acknowledge the support from the National Key R&D Program of China (No. 2017YFB0603701) and Natural Science Foundation of China (Key program, No. 51636007).

The authors would like to thank Prof. Dr. A.T.A.M. de Waele and Prof. Dr. Holger Neumann for their constructive suggestions on the experimental design.