Energy Proceedings
Vol 27, 2022
ISSN 2004-2965

Hydrophobic modification of ceramic membrane and its application in CO_2 capture

Hongming Fu[1], Kaili Xue[1], Heng Zhang[1,*], Haiping Chen[1]

1 School of Energy, Power and Mechanical Engineering, North China Electric Power University, Beijing 102206, China

* Corresponding author

ABSTRACT

In order to improve CO_2 flux of ceramic membrane in membrane absorption, the micro Al_2O_3 ceramic membrane is modified from hydrophilic to hydrophobic, and its surface morphology, wettability and water flux are characterized. The CO_2 capture performance of CM before and after modification is studied experimentally. The surface morphology of ceramic membrane has no obvious difference before and after modification. After modification, contact angle increased from 47° to 130.9° with critical breakthrough pressure 1 bar, and its pure water flux decreased significantly. The mass transfer rate of CO_2 at interface of ceramic membrane increases with increase of both absorbent flow rate and flue gas flow rate, and the mass transfer rate of modified ceramic membrane is always higher than that of unmodified ceramic membrane, which means a better CO_2 capture performance. We believe this study will provide technical references for industrial CO_2 capture applications.

Keywords: Ceramic membrane, Hydrophobic, CO_2 capture, Mass transfer rate

NONMENCLATURE

Abbreviations	
MEA	Monoethanolamine
NaOH	Sodium hydroxide
Symbols	
Q	gas flow rate
φ	volume fraction
P	density
m	mass
J	mass transfer rate
S	contact area

1. INTRODUCTION

The over exploitation and utilization of fossil fuel has caused excessive CO_2 emission. According to the National Bureau of Statistics, China's coal, oil and natural gas consumption accounted for 84.1% of the total energy consumption in 2020. For a long time, fossil energy will still occupy a dominant position in the energy consumption structure. The amount of flue gas emitted by thermal power plants is huge, which is one of the main sources of CO_2 emission. Carbon capture, utilization and storage (CCUS) is an effective way means to reduce carbon emissions and suppress greenhouse effect[1]. Before CO_2 is used and sealed, it needs to be captured first. At present, carbon capture technologies mainly include pre-combustion capture, post-combustion capture and oxygen-enriched combustion technologies. Due to the advantages of easy coupling with current equipment, small reformation of power plant equipment, etc., post-combustion capture technology is widely used in the actual industrial production process[2]. Post-combustion capture technologies mainly include chemical absorption, adsorption and membrane separation. Among them, membrane absorption method combines chemical absorption with membrane separation method, and has the advantages of high selectivity of chemical absorption, high specific surface area of membrane separation, small equipment occupation and low investment cost, which attracts the interest of researchers [3].

In the process of membrane absorption, liquid phase and gas phase are separated on both sides of membrane. Gas and liquid phases usually flow in the form of convection, and gas phase permeates through the membrane by diffusion, and is selectively absorbed by absorbent at the liquid-membrane interface[4]. According to the principle of membrane absorption, in order to avoid leakage of absorbent in the membrane, the membrane used in this process must be hydrophobic. The most commonly used membranes in industry are organic fiber membrane and ceramic membrane, which has been widely used in wastewater treatment, gas separation, pharmaceutical and food industries. Organic fiber membrane is widely concerned in CO_2 capture because of its natural hydrophobicity. However, due to low mechanical strength, organic membrane is easy to swell when contacted with water, and surface morphology is easy to change, which disable the membrane performance. At the same time, low high temperature resistance and corrosion resistance of organic membrane are not conducive to capture CO_2 from flue gas in thermal power plant. Ceramic membrane, on the other hand, has high mechanical strength, good high temperature resistance and corrosion resistance, so it is suitable for working in the tail flue of thermal power plant. However, ceramic membranes are mostly made of Al_2O_3, MgO, TiO_2 and their mixture. Because of the existence of hydroxyl groups (-OH) on the surface, it usually shows high hydrophilicity. It needs to be hydrophobically modified to avoid leakage of absorbent and decrease of CO_2 mass transfer rate.

The component of flue gas thermal power plants is complex and containing water vapor, SOx, NOx, fine particles and other pollutants. When membrane absorption system is used to capture CO2 in the flue gas, water vapor in the flue gas will first condense on membrane surface, forming a thin liquid film, which will hinder non-condensable gas from entering the membrane pores. At the same time, due to hydrophilicity of ceramic membrane, the absorbent will enter pores and block membrane. The combined effect of the above two factors inhibited transport of CO_2, resulting in decrease of gas flux and deterioration of CO_2 capture performance[5]. To solve this problem, Zhang et al. [6] studied the effect of negative pressure operation on the CO_2 capture performance of hydrophilic Al_2O_3 ceramic membrane. The negative pressure operation can avoid the leakage of absorbent, and the CO_2 capture efficiency can reach more than 98% by adjusting the operation parameters. In addition, the hydrophobic modification of ceramic membrane is also an important method to solve the leakage of absorbent and the blockage of membrane pores. Yu et al. [7] modified Al_2O_3 ceramic membrane with ZnO_2 coating by triethoxy-1H, 1H, 2H, 2H-tridecafluoro-n-octylsilane solution. After modification, the contact angle was 153°, and the CO_2 capture efficiency was above 90%. Abdulhameed et al. [8] grafted alumina hollow fiber ceramic membrane with 1H, 1H, 2H, 2H-perfluodecyltriethoxysilane, the contact angle reached 143°, and the absorption flux of CO_2 reached 0.18 $mol \cdot m^{-2} \cdot s^{-1}$. Although hydrophobic modification of ceramic membrane can improve its wetting resistance and mass transfer flux, the pore diameter of modified membrane is usually in nanometer level, and small pore diameter leads to higher resistance and lower flux of gas passing through ceramic membrane. However, micron ceramic membrane usually has high gas flux and water flux because of its larger pore size. Flux can be improved through hydrophobic modification, but at present, there is little research on hydrophobic modification of micron ceramic membrane for CO_2 capture.

In this paper, Al_2O_3 ceramic membrane is hydrophobically modified by fluorosilane solution, and its performance in carbon capture is studied. The performance of the ceramic membrane before and after modification is characterized, and the operating factors affecting the CO2 mass transfer rate are analyzed, which has theoretical guiding significance for CO_2 capture after combustion in thermal power plants.

2. EXPERIMENTAL

2.1 Materials

Tubular Al_2O_3 ceramic membrane with an average pore size of 1μm is purchased from Xinyuan membrane industry Co.,Ltd (Ningbo, China), and absolute ethanol (99%), acetone (99%), 1H,1H,2H,2H-perfluorosilyl triethoxysilane (96%) and monoethanolamine (MEA, 99%) were purchased from Aladdin Company(Shanghai, China). Deionized water (conductivity<5μS/cm) is prepared from the laboratory. All of the above inorganic and organic materials were used without further purification.

2.2 Preparation of hydrophobic Al2O3 ceramic membrane

The modification process of ceramic membrane is shown in Figure 1. Before chemical modification, it is necessary to pretreat. The Al_2O_3 ceramic membrane was cleaned with deionized water, acetone and ethanol respectively for 30 min, and then dried at 80℃ for 12 h, thus increasing the hydroxyl (-OH) concentration on the surface of membrane. 1H,1H,2H,2H-perfluorodecyl triethoxysilane was mixed with ethanol to prepare 0.1mol/L graft solution. Immerse Al_2O_3 ceramic membrane in grafting solution at room temperature, and keep for 12 hours. Finally, take out the ceramic membrane, clean it with deionized water and dry it at 80 ℃ for 2 hours to obtain the hydrophobic Al_2O_3 ceramic membrane.

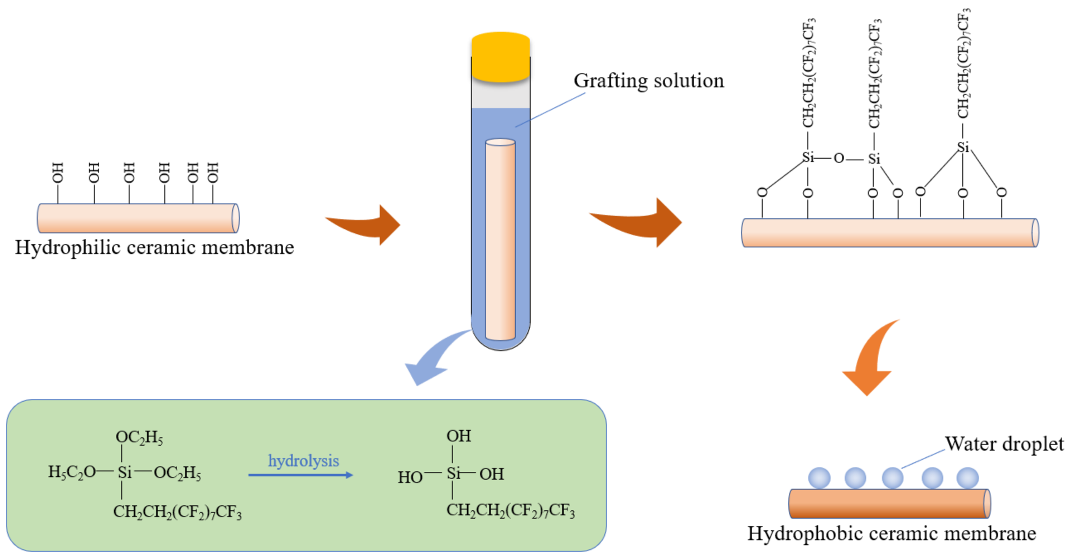


Fig. 1. Schematic diagram of ceramic membrane hydrophobic modification

2.3 Characterization

Scanning electron microscope (SEM, S-4800, Hitachi, Japan) is used to observe the surface microstructure and morphology of Al_2O_3 ceramic membrane before and after modification. Before the experiment, all samples are treated with gold spraying. Pure water flux of Al_2O_3 ceramic membrane was measured by self-made equipment. The hydrophobicity of modified Al_2O_3 was measured by contact angle meter (DSA25, KRUSS, Germen).

2.4 Experiment on CO_2 capture performance of Al_2O_3 ceramic membrane in the laboratory scale

In order to verify the CO_2 capture performance of hydrophobic membrane, a laboratory-scale CO_2 absorption experiment is carried out in this paper. The experimental system is shown in Fig.2: the whole experimental system takes a single tube hydrophobic Al_2O_3 ceramic membrane contactor as core, divided into two parts: the flue gas side and the absorbent side. Flue gas and absorbent cross-flow on both sides of the membrane, respectively. On the flue gas side, CO_2 in the mixed gas is transported across the membrane and absorbed by absorbent. The rest of gas is introduced into NaOH solution through the pipeline and finally discharged into the atmosphere. 5wt.% MEA absorbent on the absorbent side is circulated between the membrane contactor and the absorption tank by a circulation pump, and its flow rate is measured by a flowmeter. Hydrophobic Al_2O_3 ceramic membrane itself does not participate in the reaction in the process of CO_2 absorption, but only acts as a barrier for the reaction between absorbent and CO_2, making gas and liquid flow on both sides of the membrane respectively.

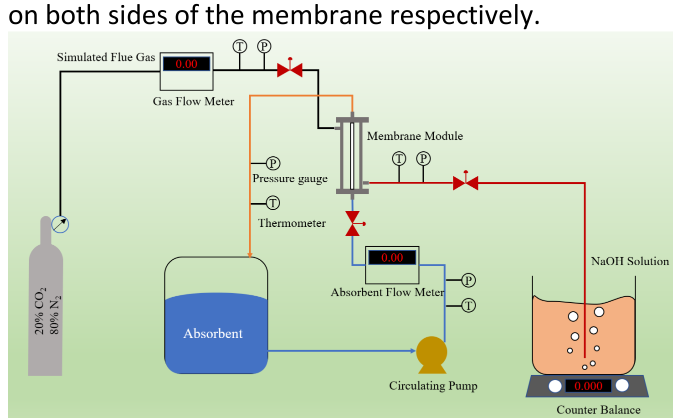


Fig.2. CO_2 absorption setup combined with a membrane contactor

2.5 Evaluation of CO_2 capture performance of ceramic membrane

The CO_2 capture performance of ceramic membrane is mainly evaluated by CO_2 mass transfer rate, which is calculated as follows[9]:

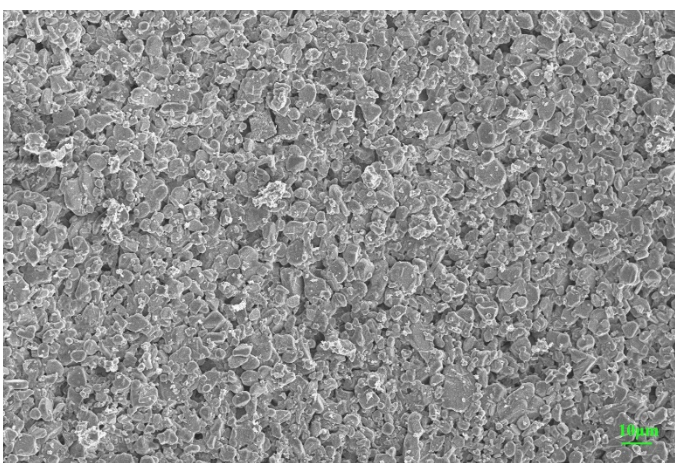
$$J = \frac{Q_{g,in}\varphi\rho - (m_1 - m_0)}{44S} \cdot 60 \quad (1)$$

Where $Q_{g,in}$ is gas flow rate (L/min), φ is volume fraction (%) of CO_2 in the mixed gas, ρ is density (g/L) of CO_2, m_0 is the mass (g) of NaOH solution before the experiment, m_1 is the mass (g) of NaOH solution after experiment, and J is the mass transfer rate of CO_2 (mol/(m^2·h)). S is contact area(m^2).

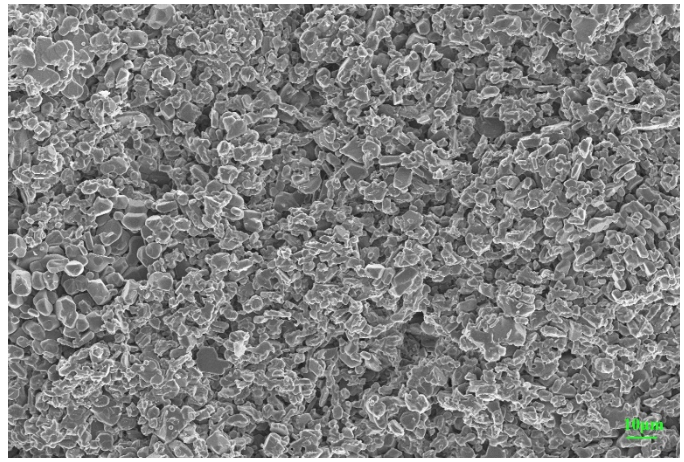
3. EXPERIMENTAL

3.1 Surface morphology

Fig.3 shows surface morphology of ceramic membrane before and after modification. Surface morphology of ceramic membrane has not changed obviously before and after modification, and basically remains unchanged. At the same time, it can be seen that the pores of the modified ceramic membrane are not blocked. This is because fluorosilane molecule is grafted on surface of ceramic membrane at the molecular level, the influence on surface can be neglected, thus greatly reducing the mass transfer resistance of gas in the ceramic membrane and ensuring a larger gas flux.



(a)

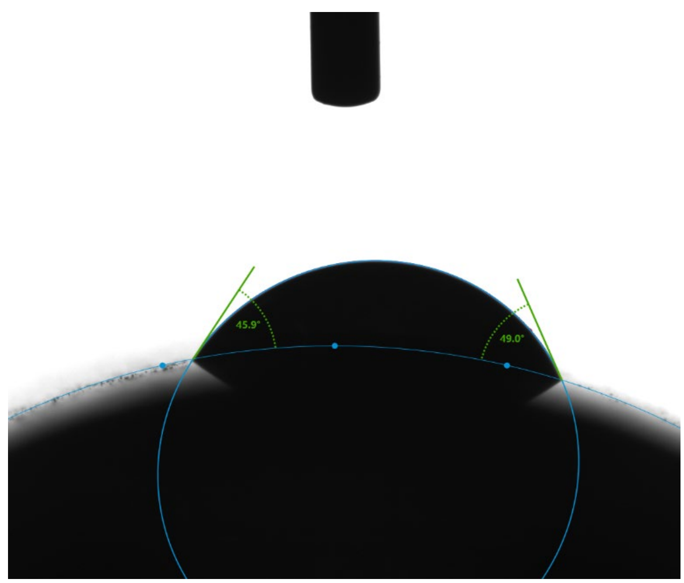


(b)

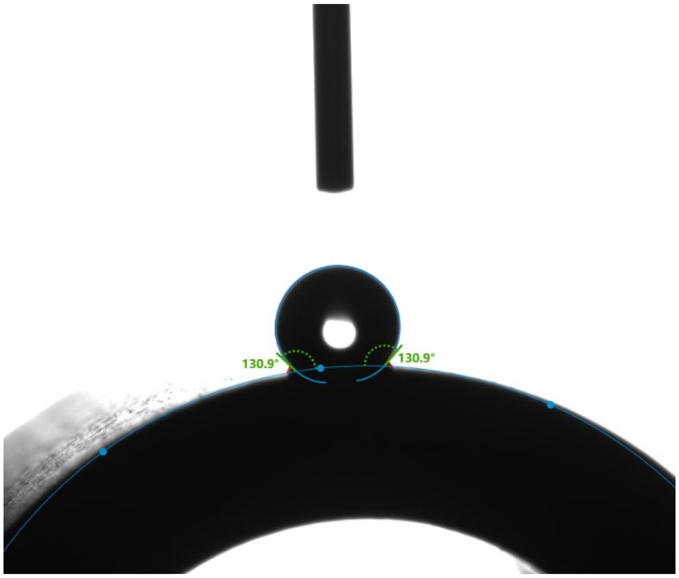
Fig.3. Surface morphology of ceramic membrane before and after modification
(a: Before modification b: After modification)

3.2 Contact angle

The change of contact angle of ceramic membrane before and after modification is shown in Fig.4. Due to the hydrophilicity and porous structure of ceramic membrane, water droplets begin to penetrate into the membrane at the moment of contact, and water contact angle of ceramic membrane rapidly decreases from the initial 49°. During the testing process, it can be seen that the contact angle of droplets on the surface of ceramic membrane decrease to 0 within 1s, and finally the liquid droplets completely penetrate into the membrane. As for hydrophobic ceramic membrane, the surface contact angle remains at 130.9°. With the increase of contact angle, the hydrophobicity of the ceramic membrane surface increases, and the droplets stay on the ceramic membrane surface without penetration.



(a)



(b)
Fig.4. Contact angle of ceramic membrane before and after modification
(a: Before modification b: After modification)

3.3 Water flux

In order to verify the influence of hydrophobic modification on the performance of ceramic membrane, water flux of ceramic membrane before and after modification is studied through experiments. As shown in Fig.5, pure water flux of ceramic membrane before and after modification both increases with increase of pressure. Once the pressure in the unmodified ceramic membrane increases slightly, water will slowly seep out from the membrane surface. However, due to the hydrophobicity of the modified ceramic membrane, water flux is zero at 0.5bar, and when the pressure was slowly increased to 1bar, water begin to seep out of the membrane surface, indicating that its breakthrough pressure is about 1bar. At the same time, it can be seen that water flux of the modified ceramic membrane is much lower than that before modification, showing that the modified ceramic membrane is not easy to be wetted, which is theoretically beneficial to mass transfer of flue gas at membrane interface.

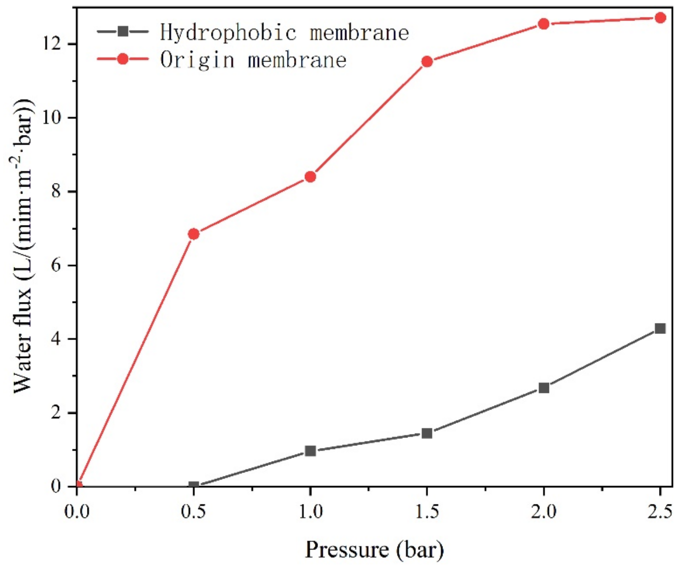


Fig.5. Water flux of ceramic membrane with pressure before and after modification

3.4 CO_2 capture performance

In order to study the effect of ceramic membrane before and after modification on CO_2 capture performance, absorbent flow rate and simulated flue gas flow rate are adjusted. As shown in Fig.6, with the increase of absorbent flow rate, mass transfer flux of CO_2 increases slowly, and mass transfer flux of modified ceramic membrane is much higher than that of unmodified ceramic membrane. It can be easily seen from Fig.7 that with the increase of simulated flue gas flow rate, the mass transfer flux of ceramic membrane before and after modification increases linearly. The flux of modified ceramic membrane is still higher than that of external modified ceramic membrane. This is because in the experimental process, the hydrophobic ceramic membrane is not wetted, but the unmodified ceramic membrane is wetted at the beginning of experiment, and the mass transfer resistance increased, so the mass transfer flux is much lower than that of the modified one.

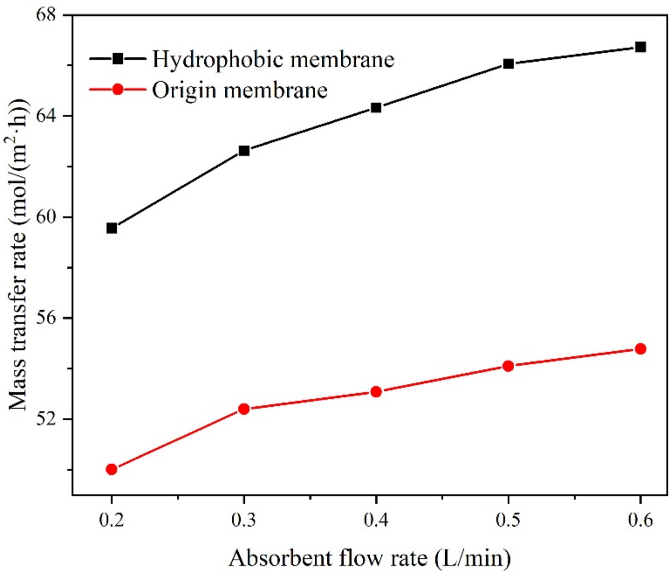


Fig.6. CO_2 absorption vs. absorbent flow rate

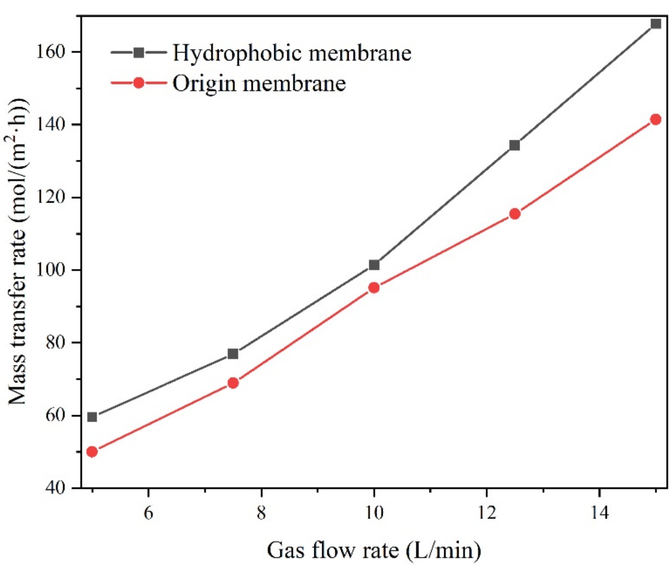


Fig.7. CO_2 absorption vs. gas flow rate

4. CONCLUSIONS

In this paper, the hydrophobic Al_2O_3 ceramic membrane is prepared by hydrophobic modification of micron alumina ceramic membrane, and the CO_2 capture performance before and after modification was studied experimentally. The conclusions are as follows:

(1) Through the modification of fluorosilane, the ceramic membrane changes from hydrophilic to hydrophobic, and the contact angle can reach 130.9°.

(2) The surface morphology of ceramic membrane has no obvious change before and after modification, and the modified ceramic membrane is not easily wetted by water with critical breakthrough pressure 1bar.

(3) Compared with the unmodified ceramic membrane, the modified hydrophobic ceramic membrane has lower mass transfer resistance and higher CO2 mass transfer flux, which can reach up to 167.76 mol/(m^2 h).

In the future, the long-term stability of hydrophobic ceramic membrane will be experimentally studied, so as to facilitate its application in practical engineering.

ACKNOWLEDGEMENT

This work is financially supported by National Key R&D Program of China (2018YFB0604302) and Key Research and Development Program of Shanxi Province (201603D312001).

REFERENCE

[1] R.A. Tufa, D. Chanda, M. Ma, D. Aili, T.B. Demissie, J. Vaes, Q. Li, S. Liu, D. Pant. Towards highly efficient electrochemical CO2 reduction: Cell designs, membranes and electrocatalysts. APPL ENERG. 277 (2020) 115557.

[2] Z. Cheng, S. Li, Y. Liu, Y. Zhang, Z. Ling, M. Yang, L. Jiang, Y. Song. Post-combustion CO2 capture and separation in flue gas based on hydrate technology:A review. Renewable and Sustainable Energy Reviews. 154 (2022).

[3] H. Wu, Q. Li, M. Sheng, Z. Wang, S. Zhao, J. Wang, S. Mao, D. Wang, B. Guo, N. Ye, G. Kang, M. Li, Y. Cao. Membrane technology for CO2 capture: From pilot-scale investigation of two-stage plant to actual system design. J MEMBRANE SCI. 624 (2021) 119137.

[4] E. Magnone, H.J. Lee, M.C. Shin, J.H. Park. A performance comparison study of five single and sixteen blended amine absorbents for CO2 capture using ceramic hollow fiber membrane contactors. J IND ENG CHEM. 100 (2021) 174-185.

[5] H. Nieminen, L. Järvinen, V. Ruuskanen, A. Laari, T. Koiranen, J. Ahola. Insights into a membrane contactor based demonstration unit for CO2 capture. SEP PURIF TECHNOL. 231 (2020) 115951.

[6] H. Zhang, K. Xue, C. Cheng, D. Gao, H. Chen. Study on the performance of CO2 capture from flue gas with ceramic membrane contactor. SEP PURIF TECHNOL. 265 (2021) 118521.

[7] X. Yu, L. An, J. Yang, S. Tu, J. Yan. CO2 capture using a superhydrophobic ceramic membrane contactor. J MEMBRANE SCI. 496 (2015) 1-12.

[8] M.A. Abdulhameed, M.H.D. Othman, A.F. Ismail, T. Matsuura, Z. Harun, M.A. Rahman, M.H. Puteh, J. Jaafar, M. Rezaei, S.K. Hubadillah. Carbon dioxide capture using a superhydrophobic ceramic hollow fibre membrane for gas-liquid contacting process. J CLEAN PROD. 140 (2017) 1731-1738.

[9] X. Yu, L. An, J. Yang, S. Tu, J. Yan. CO2 capture using a superhydrophobic ceramic membrane contactor. J MEMBRANE SCI. 496 (2015) 1-12.