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An experimental study of membranes for capturing water vapor from flue gas

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ABSTRACT

This paper has made an active attempt on recovering water from flue gas using membranes. The properties of SPEEK/PES, a hydrophilic composite hollow fiber membrane, are studied in the present paper using experimental analyses of thermal gravimetric, differential scanning calorimetry and scanning electron micrograph. Experimental results show that SPEEK/PES composite hollow fiber membranes have excellent thermal stability and mechanical properties in flue gas. An experiment with using simulated flue gas (N_2/water vapor mixed) is carried out to study the impact of sweep gas flow rate and feed gas temperature on the membrane module properties. The results indicate that the water recovery rate increases with the temperature increasing from 40 °C to 70 °C. The application of capturing the water in flue gas is very attractive, and it will provide a new way of saving energy and alleviating the haze.

1. Introduction

Nowadays renewable and nuclear energy source have already not met the worldwide requirement of energy. Traditional fossil fuels (coal et al.) will still be the main supply of our energy in the next several decades [1]. Burning coal will produce tremendous amounts of flue gas, which mainly contains nitrogen, water vapor and carbon dioxide. The emissions not only lead to the environment pollution, but also are the main reason for the hazy weather. For coal-fired power plants, the quantity and the proportion of the component in the flue gas change with the variation of the coal and it is estimated that water vapor accounts for about 10% of the flue gas.

In China, the capacity installed of coal-fired power plants has reached 1040 million kilowatts and accounts for 66.24% in the overall capacity installed till the December of 2016 [2]. If 20% of water vapor in the flue gas of thermal power plants can be captured, the recycled pure water annually will be more than 0.2 billion tons, which means saving over 3.3 billion dollars per year. Besides that, the removal of water vapor from the flue gas stream can prevent the low-temperature corrosion, air pollution and save energy to some extent.

The removal of water vapor from flue gas is an important method in industry, which has been applied in many fields, such as the dehydration of flue gas [3], natural gas dehydration [4–6], the storage of fruits and vegetables under protective atmosphere [7].

The membrane technology for dehydration is promising and attractive, which has advantages of small footprint, less energy costs and easy operation [8]. This kind of technology has received increasing attention since the 1980s and it has already been used in different industrial fields, especially the gas–liquid mass transfer. The potential of process based on non-aqueous solvents is still unexplored [9]. So far, the membrane technology has been applied in the dehydration of natural gas [10,11], the capture of carbon dioxide [12–15], distillation for desalination of water [16], the formation of functional textile and energy storage [17]. In recent years, more and more attention has been paid to the technology of flue gas dehydration. Two potential membranes materials, SPEEK (sulfonated polyether ether ketone) and PEBAX® 1074, for flue gas dehydration were compared and the results showed that SPEEK material was superior [8]. Fourteen institutes were

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Nomenclature

y_i	volume fraction of permeation gas
m	mass of permeation gas
x_i	volume fraction of feed gas
p	pressure
J_{H_2O}	permeation flux
V	volume
T	temperature
M	molecular weight
R	gas constant
S	effective area

organized to study the technology of flue gas dehydration using polymer membranes by the EU in 2010 [18], but the technology is still in the experimental stage now. Mechanism research on flue gas dehydration using membranes was carried out by China Huadian Environmental Engineering Company [19]. A highly hydrophilic rubbery membrane which could be applied to CO_2 capture and dehydration of flue gas were introduced in 2010 [20]. All of these technologies, however, are not mature enough for commercial use.

In the present work, SPEEK/PES (polyether sulfone) composite hollow fiber membranes were prepared by coating a SPEEK top layer on PES basement membranes. The characterization of the composite membranes was studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron micrograph (SEM) and mechanical strength experiments. The composite membranes were proved to possess excellent thermal stability and mechanical properties. Furthermore, experiments were conducted to measure the performance of composite membranes, such as the water vapor permeability. This work has made an attempt to use composite hollow fiber membranes (SPEEK/PES) to recover water vapor from the mixture of nitrogen and water vapor, and prepared several different sulfonation degrees of SPEEK/PES membranes. Comparing to the literature 8, except for gas separation experiments, this paper has carried out a plenty of performance tests to evaluate these prepared membranes for exploring the possibility of using in coal-fired power plants.

2. Preparation of hydrophilic composite membranes

To capture water with high purity from the flue gas, composite membranes should have high selectivity and hydrophilic property. The flue gas from coal-fired power plants includes N_2, O_2, CO_2, SO_x and NO_x, and N_2 accounts for over 70% of the flue gas. Both SPEEK and PES have extremely-high water vapor permeability and selectivity in H_2O/N_2, and the interaction between molecules makes the two materials to connect with each other more tightly [21]. Therefore, the hydrophilic composite hollow fiber membrane with high permeability in water vapor and high selectivity in H_2O/N_2 can be obtained by coating a top layer of SPEEK on PES hollow fiber membranes for recovering water vapor from flue gas.

Hydrophilic composite hollow fiber membranes are mainly made up of two parts, SPEEK and PES. SPEEK can be gained by sulfonating PEEK, and the sulfonation mechanism is shown in Fig. 1. Fig. 2 presents the preparation of hydrophilic SPEEK/PES composite membranes.

Firstly, PES should be pretreated before being used as basement membrane of the hydrophilic composite membrane: PES should be immersed in deionized water for 24 h and then into hydrochloric acid (0.5 mol/L) for half an hour. After that, PES need to be washed by sodium hydroxide solution and deionized water successively until they become neutral. Finally, PES should be dried in a vacuum oven (the temperature is set to 30 °C) for 12 h.

Secondly, the coating liquid is produced by SPEEK and methanol. Two kinds of SPEEK are used, the sulfonation degrees of which are 59% and 68.5%, named SPEEK59 and SPEEK68.5, respectively. SPEEK should be put into methanol in a beaker, the mass fraction of which is 1%. And then the mixture should be stirred by a magnetic stirrer for 12 h while the beaker is sealed with plastic wrap for preventing methanol volatilizing. Finally, the coating liquid is gained.

The PES pretreated need to be immersed in the coating liquid mentioned above for 10–15 s and then being taken out to be dried by air. The PES continues to be dried in a vacuum oven (the temperature is set to 30 °C) for 12 h. When it finishes, the hydrophilic composite hollow fiber membranes are prepared.

3. Instrumental characterization and analysis of composite membranes

3.1. Analysis of scanning electron micrograph (SEM)

The sulfonation degree of the composite membrane (SPEEK/PES) used is 59%. The other degree is not analyzed in this part. The sectional structures of membranes are observed by the scanning electron micrograph (JSM-6510A, JEOL). Picture (a) in Fig. 3 shows that the PES has a porous structure like honeycomb in the middle part, the interspace of which is a passage for water vapor to permeate fast because of its low resistance. As is shown in Picture (b) and (c), the top layer of the PES is dense and homogeneous, and the coating SPEEK layer is nearly 1.5 μm. PES and SPEEK perform good compatibility with each other. Small amounts of SPEEK have permeated into the dense top layer of PES and are embedded in the porous structure like honeycomb of the PES.

3.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA Q500, TA Company in America) is conducted in the circumstance of nitrogen and the thermogravimetric curve of hollow fiber membranes, as is shown in Fig. 4, are produced by increasing the operational temperature at a rate of 10 °C/min.

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