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Original Research Article

Dehydration of Natural Gas Using Polyether Sulfone (PES) Membrane and Its Nanocomposite with Silica Particles and Nitrogen Sweeping Gas

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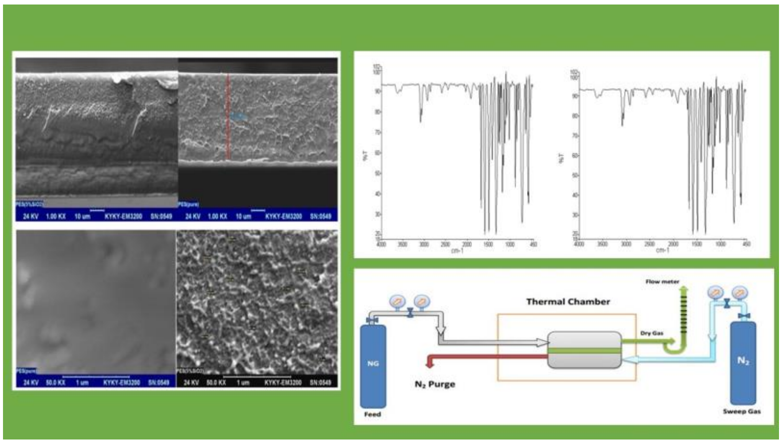
ABSTRACT

Natural gas must be dehydrated before being sent to the distribution network to control corrosion and prevent the formation of solid hydrates. Membrane technology is a viable alternative to conventional glycol absorbents and adsorbent solids. This study was performed to evaluate the dehydration of crude natural gas by membrane separation process. Various operating conditions such as the effect of silica nanoparticles, pressure and sweeping gas on the removal of water vapor dissolved in natural gas were investigated using PES membrane and its nanocomposite. PES membranes and their nanocomposites with silica was made by solution mixing method in solvent dimethyl formamide. The properties of silica nanoparticles and fabricated nanocomposite membranes were evaluated by Fourier transfer spectroscopy and scanning electron microscopy. The dehydration rate was from natural gas in the pressure range of 2 to 10 bar and temperature of 30 °C in the presence of nitrogen sweeping gas. The addition of silica nanoparticles to the Polyether Sulfone membrane significantly reduced the moisture content of natural gas. Also, with increasing feed pressure, the amount of water permeation from the membrane improved. The use of nitrogen sweeping gas reduced the amount of water in natural gas in pure Polyether Sulfone membranes by more than 80% and in nanocomposite membranes by more than 100%.

GRAPHICAL ABSTRACT



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Introduction

Separating water vapor from natural gas is called dehydration. The purpose of dehydration of natural gas is to prevent the formation of gas hydrates during the process, gas transmission network, to reach the standard amount of water in the gas sold and to prevent corrosion [1-3].

The widespread use of membrane processes for gas separation is due to its advantages, which include low investment cost, ease of separation, low energy consumption, cost-effectiveness even with small amounts of gas feed, low weight and lack of placement [3-5].

In recent years, the use of polymer membranes in various studies, especially the separation of natural gas impurities, has been increasing rapidly. While the use of polymer membranes to separate carbon dioxide from natural gas has reached industrial scale in some countries, the use of membranes to remove water moisture is still under study, experimentation and trial and error to achieve a membrane with exudation and selectivity are high. Considering the abundant gas reserves in the country and the necessity of dehydration from it, it seems necessary to replace the membrane separation process with conventional dehydration methods due to disadvantages of traditional methods [6-8].

Penn et al. 2020) have compared the removal of gas moisture by the membrane process with the Tri-ethylene glycol process in tray towers. The economics of the membrane process with the correct choice of membrane type and its high selectivity have been mentioned [8]. Baker and his colleagues have stated in their research that by choosing the right membrane, 90% of water vapor can be extracted from natural gas [7-9].

In the field of membrane dehydration work, Hiking et al. 2020) state that in order to control corrosion and prevent the formation of gas hydrates, gas pipes must be free of water. The researchers examined different laboratory operating conditions, such as feed composition, feed flow, and sweeping gas flow, from the Pubax membrane, which is a hydrophilic membrane. Their best results were selectivity of more than 1500 for H_2O/CH_4 [10-13].

In this research, after selecting and synthesizing hydrophilic membrane of PES and its nanocomposite with silica particles in the form of industrial thin films, as well as designing and synthesizing suitable membrane contactors, to investigate the operational parameters such as the effect of nanoparticles Silica, pressure and sweeping gas at 30 °C on the separation of water from natural gas were studied [14-17]. The effect of pressure was performed in the range of 2 to 10 bar. The effect of the presence or absence of nitrogen sweeping gas on the rate of moisture removal from natural gas was investigated [18-21].

Material and methods

Dimethyl formamide solvent (DMF) was purchased from Merck, Germany. PES was used by average molecular weight of 232.25 g/mol. Also, silica nanoparticles with an average size of less than 50 nanometers, made in Spain, were used.

Membrane Synthesis

PES membranes were synthesized by solution mixing, casting and solvent evaporation. A 10 wt% solution of PES in DMF solvent was prepared at 65 °C and by casting it on a glass vessel and the solvent evaporation vessel in an atmospheric oven for 24 hours, 50-micron film membranes were obtained. PES nanocomposite was prepared by adding nano silica particles to a solution of poly ethersulfone-dimethylformamide with a ratio of 5% by weight of silica at 80 °C and vigorous stirring with an ultrasonic mixer.

Fourier Transform Infra-red spectroscopy test (FTIR)

To study the structure of membranes prepared by fourier transform Infra-red spectroscopy method. The Infra-red metering spectrum is widely used to identify organic compounds [16-18].

The pure and synthetic poly ether sulfone membrane and the nanocomposites with silica are presented in Figure 1.

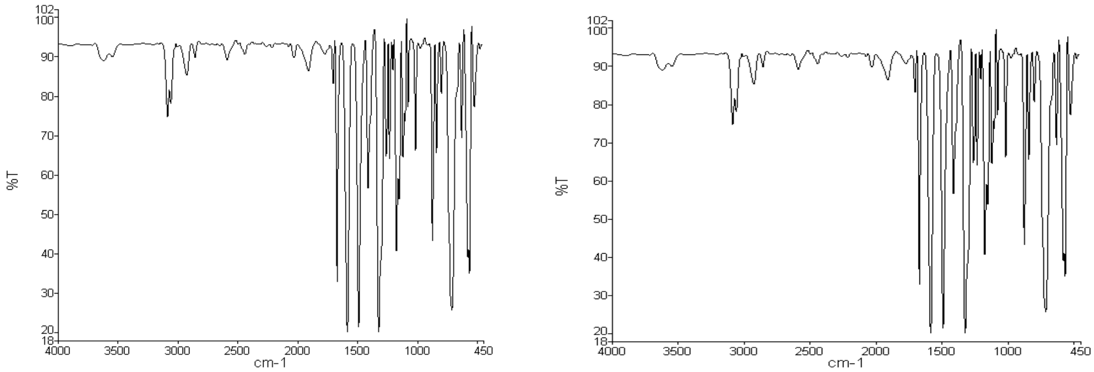

Figure 1: Infra-red spectrum of pure PES membrane (right) and 5% silica nanocomposite membrane (left)

Scanning Electron Microscopy (SEM)

Scanning electron microscopy was used to observe the morphology of silica particles in polymer by scanning electron microscopy. To prevent destroying morphology of the membrane, its samples first were broken at the liquid nitrogen at a cross section and then a very thin film of gold metal was coated on the studied surface [19].

Measuring the amount of Dehydration of Natural Gas in the Membrane Contactor Device

After synthesis of PES membranes as well as polymer-silica composite membranes, they were subjected to permeability to water vapor dissolved in natural gas in the presence of nitrogen sweeping gas [20-22]. In membrane contactors, the gas phase entering the system is called the feed. Also, the gas passing through the membrane is the permeable phase and the exhaust gas from the membrane surface is called the residual phase. In this study, the aim was to reduce the amount of water in the residual phase or the exhaust gas from the membrane surface. According to figure 2, after making a membrane contactor with a useful membrane area of 17 cm^2, the feed was continuously put into the system under different operating conditions. By accurate hydrometer, the amount of water in the exhaust gas from the membrane surface was calculated.

In these experiments, nitrogen sweeping gas was used continuously in the counter current with the feed, below the membrane surface to eliminate concentration polarization and as a result, water vapor permeated better [2].

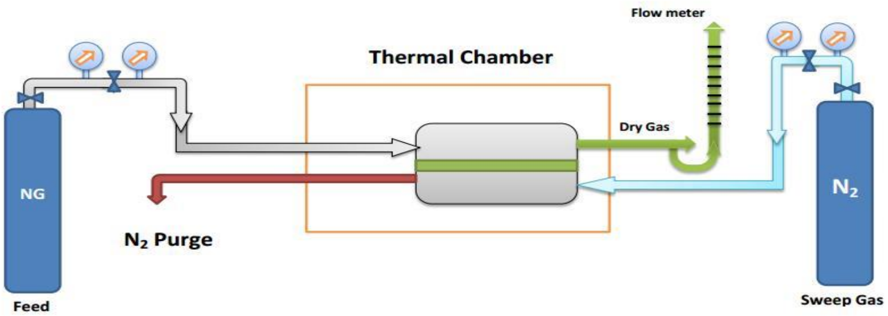

Figure 2: Schematic of the built membrane contactor for testing natural gas dehydration

The following principles were observed in performing the above tests:

- Contact between feed and sweeping gas was continuous and counter current.
- The amount of water in the feed was 910 mg per standard cubic meter (mg/sm^3).

- The standard feed flow rate was 1000 cubic centimeters per minute and the sweeping gas to feed ratio was set to 1.

Result and Dissection

The Results of the Fourier Transform Infra-red Spectroscopy Test

As can be seen in Figure 1, the presence of strong absorption peaks in the wavelength range of 1070 cm^{-1} indicates asymmetric Si-O-Si tensile bonds forming silica particles. In the Infra-red spectra diagrams of sulfonated polyether membranes and their nanocomposites with silica, the strong symmetric peak S = O corresponds to the sulphones in the range of 1150 cm^{-1}, the strong peak S = O corresponds to the sulphones in the range of 1300 cm^{-1} and also the bond peaks C = C. The aromatic ring is visible in the range of 1500 cm^{-1}.

Results of the Test

In Figure 3 the scanning electron microscope test images are presented.

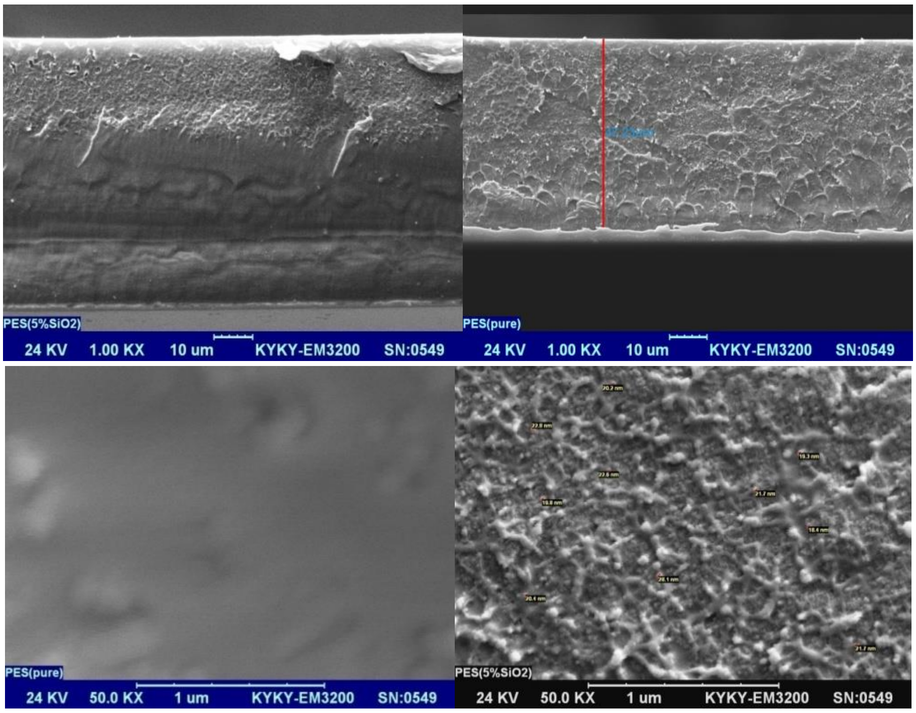

Figure 3: SEM images of cross section of PES and nanocomposite membranes

As the pictures show, the prepared membranes are dense and symmetrical. Scanning electron microscopy (SEM) images show that with increasing silica in the membranes, the cross-sectional roughness has increased. With the use of silica nanoparticles in PES membranes, the accumulation of particles in the polymer matrix increases. In all SEM images, the presence and distribution of nanometers of silica particles can be seen, which confirms the optimal dissolution of silica particles in the polymer.

Results of the Study of the effect of Operational Parameters on the Rate of Dehydration of Natural Gas

In this section, the results of increasing the silica nanoparticles on reducing the moisture content of natural gas passing through the surface of the PES membrane, called the residual phase in industry, gas sales or gas dehydration, are presented [22]. Also, the effects of sweeping gas and pressure on the dehydration rate of natural gas using PES membrane and its nanocomposite with silica have been investigated.

The effect of adding silica Nanoparticles on PES Membrane in the Dehydration Process of Natural gas

Figure 4 compares the changes in the amount of water in the residual phase in the PES membrane and its 5% nanocomposite with silica particles at a temperature of 30°C and different pressures.

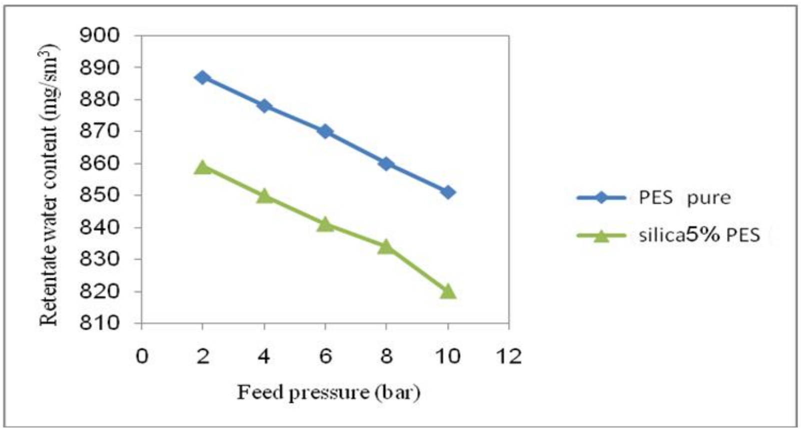

Figure 4: Changes in the amount of water in the residual phase at 30 °C and different pressures in PES and PES-Silica membranes

According to figure 4, it is clear that with the increase of silica nanoparticles in the PES membrane, the amount of water in the residual phase decreases and this indicates an increase in the permeability of water molecules from the PES nanocomposite membrane with the increase of silica particles. For example, in Figure 4 at a temperature of 30 °C and a pressure of 10 bar, the pure PES membrane reduces 50 mg/sm^3 of feed moisture while 5% by weight silica nanocomposite reduces 90 mg / sm^3 of feed moisture under the same conditions, this means a nearly 2-fold increase in feed dehydration rate with 5% w/w silica nanocomposite compared to pure PES membrane.

Addition of silica particles to the polymer has changed the permeability of water vapor for the following reasons [21]:

- The presence of silica nanoparticles increases the average distance between polymer chains. The changes achieved by adding silica nanoparticles to the polymer structure increase the permeability of water vapor from the membrane by limiting the compression of the chains as well as tightening the membrane structure.
- Interactions between OH groups excess silica nanoparticles and polar bond gases such as H_2O change the morphology of the membrane, resulting in increased solubility. Increasing solubility also means increasing the permeability of water vapor.
- Weak interactions between silica and polymer particles lead to the formation of voids at the boundary between the two phases of polymer and silica, which significantly increases water seepage. The amount of these joints and voids can be controlled by controlling the interaction between the polymer and the silica particles.

The effect of Pressure on the amount of Water Removal from natural gas

The effect of pressure changes on the amount of water in the residual phase of the output of pure PES membrane nanocomposite and its nanocomposite at 30 °C is presented in Figure 5 and Figure 6, respectively.

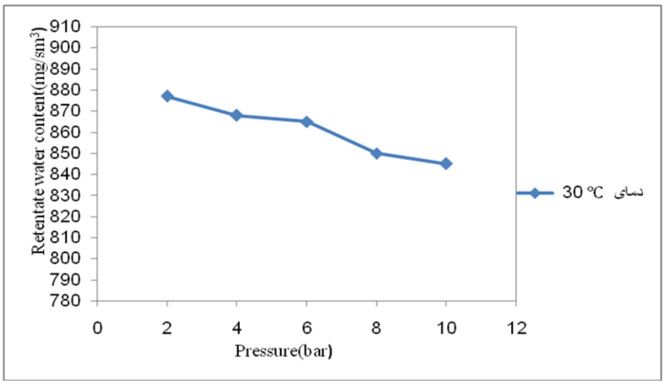

Figure 5: Changes in the amount of water in the residual phase at 30 °C relative to pressure changes in the PES membrane

As can be seen in Figure 5, the graph displays changes in the amount of water in terms of increasing pressure due to the increase in driving force, the difference in the partial pressure of water on both the feed and permeable sides, the permeability of water vapor increases and as a result, the amount of water in the remaining phase decreases. The increase in permeability at higher pressures is due to the increased interaction between water molecules and PES agents. In other words, with increasing pressure, water solubility is expected to increase, condensability to increase, and permeability to increase.

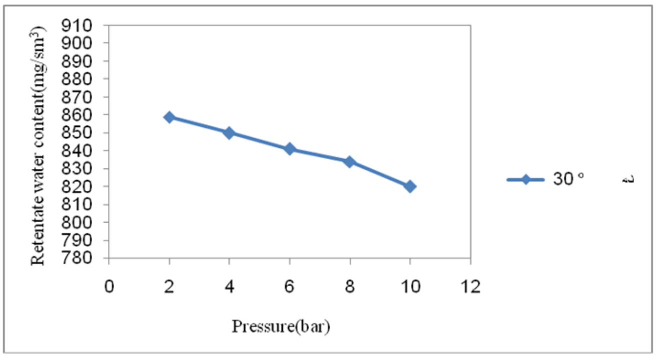

Figure 6: Changes in the amount of water in the residual phase in the 5 wt % PES-Silica nanocomposite membrane at 30 °C temperature relative to pressure changes

As can be seen in Figure 6, the graph shows water volume changes in terms of pressure changes for PES-Silica membrane is also decreasing, with increasing pressure, the permeability of water vapor from the membrane increases and the rate of dehydration increases. For example, at feed pressure 2 bar and temperature 30 °C, 50 mg/sm^3 of feed moisture is reduced, while at constant conditions, with increasing feed pressure to 10 bar, the amount of water reduced from the output phase is equal to 90 mg / sm^3, which was measured and showed a nearly double increase.

The effect of Sweeping Gas on the Removal of Water from Natural Gas

Table 1 compares the use of Sweeping Gas and its non-use in the amount of water passing through the pure PES membrane at a temperature of 30°C and different pressures. Also, this comparison and the percentage of increase in the amount of water passing through the membrane using a sweeping gas for the sulfone-silica composite membrane is shown in table 2.

Table 1: Comparison of residual phase water for pure PES membrane at a temperature of 30 °C and different pressures

Pressure (Bar)	The amount of water remaining in the residual phase with No sweeping gas (mg/sm^3)	The amount of water remaining in the residual phase With Sweeping Gas (mg/sm^3)	Increasing percentage of water passing through the Membrane
2	897	887	76
4	895	878	113
6	889	869	95
8	884	860	92
10	879	851	90

The data in the table above show that the use of sweeping gas has almost doubled the dehydration rate of natural gas.

Table 2: Percentage increase of water passing through nanocomposite membrane 5% by weight Polyether sulfone - silica at a temperature of 30 °C in different pressures

Pressure (Bar)	The amount of water remaining in the phase No Sweeping gas (mg/sm^3)	The amount of water remaining in the residual phase With sweeping gas (mg/sm^3)	Increasing percentage of water passing through the Membrane
2	886	859	112
4	883	850	122
6	878	841	116
8	875	834	92
10	869	820	120

For example, according to Table 2 the rate of dehydration in the nanocomposite membrane of 5% PES silica at a pressure of 2 bar and a temperature of 30 °C and without the use of sweeping gas from 910 mg/sm^3 feed humidity, reached to 886 mg/sm^3, this means the amount of water passing through the membrane without the use of sweeping gas was 24 mg/sm^3, which reached 51 mg/sm^3 in the presence of nitrogen sweeping gas. Therefore, the amount of water passing through the membrane using a sweeping gas increased by 112%. Baker (2019) stated that in membrane separation of gases, the gas mixture passes over the surface of the membrane, under the membrane, becoming reach in one component of the gas mixture that has the most permeation. Because the components of the gas mixture penetrate at different speeds, a concentration gradient is created in the fluid on both sides of the membrane, which is called concentration polarization. Concentrated polarization in gases is due to the greater penetration of gas mixture particles from liquids. In his studies, he introduced turbulence as one of the ways to eliminate concentration polarization in the feed side and the use of inert gases such as helium and nitrogen in the counter current to the feed in the membrane permeation side.

Conclusion

In this research, using the solution mixing method, dense and hydrophilic PES membrane and its nanocomposite 5% by weight with silica particles in the form of flat films with a thickness of less than 50 microns were synthesized and the characteristics of synthesized membranes were checked by using FTIR and SEM. The results of the above tests confirmed the proper distribution and the presence of nanometers of silica particles in the polymer network. Crude natural gas dehydration experiments were performed using nitrogen sweeping gas at an operating pressure of 2 to10 bar and at a temperature of 30 °C. With the addition of silica nanoparticles to the PES membrane, the dehydration rate of natural gas increased significantly. This increase was due to the interaction between the polymer chain and nano particles and the reduction of polymer compaction.

The process of removing water from natural gas by PES membrane and its nanocomposites with silica, with pressure changes from 2 to 10 bar is upward. The increase in water vapor permeability at higher pressures is due to the increased interaction between water molecules and PES agents. In other words, water solubility and permeability are expected to increase. Also, the use of nitrogen sweeping gas improved the dehydration rate of natural gas in pure PES membrane by more than 80% and in its nanocomposites by more than 100%. According to the results of the experiments, we can be optimistic about the membrane process of gas separation in dehydration from natural gas.

By making and using a membrane contactor with higher pressures and close to operating conditions, as well as changing the membrane module and Turning into tubular membranes or hollow fibers, we can approach an industrial process. In the near future, by examining and conducting membrane separation experiments with PES and its nanocomposites to simultaneously remove water with other natural gas impurities such as carbon dioxide, nitrogen, hydrogen sulfide and helium, this process can replace the conventional costly processes of gas refineries.

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Authors' contributions

All authors contributed toward data analysis, drafting and revising the paper and agreed to be responsible for all the aspects of this work.

Conflict of Interest

We have no conflicts of interest to disclose.

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