A simulation study for the treatment of Kuwait sour gas by membranes

Yousef Alqaheem *

Petroleum Research Center, Kuwait Institute for Scientific Research, Kuwait

1. Introduction

Natural gas is considered as the cleanest fossil fuel because the combustion generates lower emissions (Srinivasan, 2006). Kuwait produces around 14 million m$^3$ of natural gas, annually, and most of the gas is produced during oil extraction (associated gas) (CEIC Data, 2020). Almost half of natural gas in Kuwait is used for power generation and water desalination. The other half of natural gas is for liquefied petroleum gas (LPG) production (cooking gas and petrochemicals) and for producing hydrogen for the treatment of fuels.

The associated gas needs processing since it contains impurities of carbon dioxide and hydrogen sulfide. It is stated that natural gas should have no more than 2 mol% of carbon dioxide and 4 ppm of hydrogen sulfide because these gases can form corrosive acids that damage pipelines (Poe and Mokhatab, 2017). It is reported that associated gas of west Kuwait fields is sour and can have 12 mol% of carbon dioxide and 4 mol% of hydrogen sulfide (Ashkanani, 2018). The gas is first collected at the gathering center of Kuwait Oil Company (KOC) and after that, it is sent to Kuwait National Petroleum Company (KNPC) to remove the acid gas. Thereafter, the gas is sent to the LPG plant to produce lean gas, ethane, propane, LPG, and natural gasoline as shown in Figure 1.

In case of an unexpected shutdown of the acid gas removal facility at KNPC, the associated gas might be flared. But because this practice negatively affects the environment, KOC decided to install two on-site units at the gathering center of the west fields to treat the sour gas. The first unit removes carbon dioxide and hydrogen sulfide using amine solvent. The process is based on chemical absorption and the solvent is regenerated back to the process by heating. The second unit removes water since it can react with the hydrocarbons to form ice-like hydrates that can cause freezing and blockage of pipes (Carroll, 2009). Therefore, water content should be maintained below 64 mg/m$^3$ (Hyne, 1991). For this purpose, ethylene glycol unit has been installed to remove water by physical absorption. The gas is then sent to the KNPC LPG plant for further processing.

It is known that both the amine and ethylene glycol units are energy-intensive and suffer from issues such as flooding and solvent disposal. Alternatively, polymeric membranes are commercially available and they are energy-efficient because no solvents nor mechanical parts are needed. The units are also compact and have a reporting life of more than 3 years (Mustafa et al., 2016). The membranes are also capable of removing carbon dioxide, hydrogen sulfide, and water in one step (Chen et al., 2015). Furthermore, a significant saving in the gas processing cost is expected when the membranes system is used instead of amine and ethylene glycol units. For example, it is reported that the membranes system can reduce the gas processing costs by 20% compared to the amine unit for treating a gas containing 30 mol% carbon dioxide and 1 mol% hydrogen sulfide (Bhide and Stern, 1993).

For sour gas treatment, membranes units are usually made from cellulose acetate due to the high stability and good permeation (Crespo and Böddeker, 2013; Freeman and Yampolskii, 2011). The material is also commercialized and has been installed in many refineries worldwide (Iulianelli and Drioli, 2020). The membrane
works based on the solution-diffusion model in which the gas dis-
solves and diffuses through the dense membrane (Wijmans and
Baker, 1995). Each gas has different solubility and diffusivity values
and this creates the separation mechanism. The driving force for
mass transport across the membranes is based on the pressure dif-
fERENCE. The objective of this study is to investigate the possibility of
using the membranes for treating Kuwait sour gas. A simulation
study using UniSim had been performed to see if the membranes can
reduce carbon dioxide and hydrogen sul-
fi
de contents from 12 mol% and 4 mol%
to the pipeline gas speci-
fi
ca
tions of 2 mol% carbon
dioxide and 4 ppm hydrogen sul-
fi
de. The dominant industrial pro-
cess for acid gas removal is still the amine scrubber because the
membranes suffer from the tradeoff between the product purity and
fl
ow recovery due to the change in the membrane area (Alkatheri
et al., 2016). In this paper, the simulation was also run to optimize
the membrane performance by alternating the feed composition and
calculating the recovery to achieve the pipeline gas specifications.

2. Methodology

The composition of the sour gas used in this study is given in Table 1.
The gas contains 65 mol% methane, 12 mol% carbon dioxide, and 4 mol
% hydrogen sulfide. The gas also contains ethane, propane, butane, ni-
trogen, and water. The membrane module is assumed to have a spiral-
wound structure and hence the flow can be assumed as a cross-
flow (Figure 2). Mole balance across the membrane can be applied since
there is no reaction (neglecting accumulation):

\[ x_F n_F = y_P n_P + x_R n_R \]  
(1)

where \( n \) is the number of moles (kmol), \( x_F \) is the mole fraction of
component i in the feed, \( x_R \) is the mole fraction in the retentate, and \( y_P \) is
the mole fraction in the permeate. Rearranging the equation gives:

\[ y_P n_P = x_F n_F - x_R n_R = Q A \left( \frac{x_P - x_R}{y_P} \right) \]  
(2)

where \( Q \) is the permeance (in kmol m\(^{-2}\) h\(^{-1}\) kPa\(^{-1}\)), \( A \) is the membrane
surface area (m\(^2\)), and the last term is the average trans-membrane
pressure difference (kPa). \( P_F \) and \( P_P \) are the feed and permeate pres-
sures, respectively. The average trans-membrane pressure difference can
be then approximated by the logarithmic mean:

\[ \frac{P_F - y_P P_P}{\ln \frac{y_P}{x_P}} = \frac{x_P - x_R}{\ln \frac{x_P}{x_R}} \]  
(3)

For faster calculations and avoiding the division by zero, the previous
equation is estimated by (J. Chen, 1987):

\[ \frac{x_F - x_R}{\ln \left( \frac{x_P}{x_R} \right) \left( \frac{x_F + x_R}{2} \right)^{1/3}} \]  
(4)

The calculations are performed by first guessing the stage-cut (\( \theta \)) of
the components in the permeate using:

\[ \theta_\text{Guess} = \frac{y_P n_P}{x_F n_F} \]  
(5)

After that, \( x_R \) and \( y_P \) are solved simultaneously using the following
equations:

\[ y_P n_P = x_F n_F - x_R n_R \]  
(6)

\[ \sum_{i=1}^{n} x_F = 1 \]  
(7)

\[ \sum_{i=1}^{n} x_R = 1 \]  
(8)

\[ \sum_{i=1}^{n} y_P = 1 \]  
(9)

Afterward, the calculated \( x_R \) and \( y_P \) are used to calculate the stage-cut
using permeance data:

\[ \theta_\text{Calc} = \frac{Q A (x_F P_F - y_P P_P)}{x_F P_F} \]  
(10)

The guessed stage-cut is then changed until the calculated \( y_P \) gives the
same stage-cut as the guessed one. For the data to be converged, the
square difference between the guessed and the calculated stage-cut
should be less than 0.0001.

| Component               | Mole Fraction (%) |
|-------------------------|-------------------|
| Methane (CH\(_4\))      | 65.0              |
| Carbon dioxide (CO\(_2\))| 12.0              |
| Hydrogen sulfide (H\(_2\)S)| 4.0              |
| Nitrogen (N\(_2\))      | 0.5               |
| Ethane (C\(_2\)H\(_6\)) | 10.0              |
| Propane (C\(_3\)H\(_8\))| 5.0               |
| Butane (C\(_4\)H\(_10\))| 2.5               |
| Water (H\(_2\)O)        | 1.0               |

Table 1. Composition of the sour gas used in this study.

![Figure 1. Gas production and processing in Kuwait.](image1)

![Figure 2. The cross-flow pattern in spiral-wound cellulose acetate membranes.](image2)
Unfortunately, UniSim does not have an integrated membrane unit. Therefore, the unit was modeled using a component splitter and an integrated spreadsheet (Davis, 2002). Feed, retentate, and permeate data are first linked to the spreadsheet and then the equations were added. Solving for \( x_R \) and \( y_p \) were performed using the “adjust function” in which the lower and upper limits were set to 0 and 1, respectively. The tolerance was set to 0.00001 and all the functions were solved simultaneously. The associated gas enters the first membrane and then the permeate enters the second unit. The retentate of the second unit is recycled back with the associated gas and enters the first membrane as demonstrated in Figure 3. This setup is widely used in the industry because it gives a balanced performance between product purity and recovery. Hydrocarbons recovery was calculated by summing the number of moles of methane, ethane, propane, and butane in the product (retentate of the first membrane) to their moles in the feed:

\[
\text{HCs Recovery (\%)} = \left( \frac{n_{C1} + n_{C2} + n_{C3} + n_{C4}}{n_{C1} + n_{C2} + n_{C3} + n_{C4}} \right)_\text{feed} \times 100
\]  

(11)

The associated gas was fed at 60 bar at a temperature of 60 °C with a flowrate of 70,000 m³ h⁻¹ (60 MMSCFD). The retentate pressure was set at 58 bar and the permeate pressure was 2 bar. The operating conditions are given in Table 2. The permeability and selectivity data used in the simulation study are given in Table 3. In this study, it is assumed the system is completely mixed, no mass-transfer resistance across the membrane, and permeability values are constant.

To run the simulation, the membrane area should be defined. The starting total area was set to 10,000 m² (distributed equally between the two membranes) and the product composition was monitored. The area was then changed accordingly until the pipeline gas specifications were achieved.

3. Results and discussion

UniSim flowsheet and the spreadsheet are given in Figures 4 and 5. It should be noted that the permeate of the first membrane was sent to a compressor to raise the pressure back to 60 bar. This increase in pressure resulted in a rise in temperature to 463 °C and therefore a cooler was used to reduce the temperature to 60 °C. Using membranes area of 10,000 m² gives product composition of 6.7 mol% of carbon dioxide and 88 ppm of hydrogen sulfide which does not meet the pipeline requirements. Therefore, the area was increased to 20,000 m² and 30,000 m². An area of 40,000 m² gives a product composition of 2 mol% carbon dioxide and 4 ppm of hydrogen sulfide which meets the standards. However, hydrocarbons recovery was only 57% due to the large membrane area that increased the flow of hydrocarbons through the membranes. Accordingly, it can be stated the cellulose acetate membranes cannot be used for treating a sour gas containing up to 3.5 mol% carbon dioxide and 0.15 mol% hydrogen sulfide due to the uneconomical hydrocarbons recovery. The results are shown in Table 4.

The second step of this study was to determine the maximum carbon dioxide and hydrogen sulfide composition that the membrane can handle and the corresponding hydrocarbons recovery. The simulation was run by changing the feed mole fraction of methane, carbon dioxide, and hydrogen sulfide. The mole fraction of other components were kept constant. The total membrane area was changed from 10,000 to 14,000 m². Results are shown in Table 5 and it is found that the membranes can treat a sour gas containing up to 3.5 mol% carbon dioxide and 0.15 mol% hydrogen sulfide for a hydrocarbons recovery of 97%. To tradeoff the hydrocarbons recovery for a higher acid gas removal capacity, the

Table 3. Permeability and selectivity data used in the simulation study (Cooley and Coady, 1978; Qi and Henson, 2000).

| Component                  | Permeability (GPU) | Selectivity to Methane |
|----------------------------|-------------------|------------------------|
| Methane (CH₄)              | 13                | —                      |
| Carbon dioxide (CO₂)       | 67                | 5.1                    |
| Hydrogen sulfide (H₂S)     | 169               | 13.0                   |
| Nitrogen (N₂)              | 12                | 0.9                    |
| Ethane (C₂H₆)              | 9                 | 0.7                    |
| Propane (C₃H₈)             | 6                 | 0.5                    |
| Butane (C₄H₁₀)             | 4.5               | 0.4                    |
| Water (H₂O)                | 750               | 57.7                   |

\*1 GPU = 1.21 × 10⁻⁶ kmol m⁻² h⁻¹ kPa⁻¹; ± assumed values.
Figure 4. UniSim flow sheet of the two-stage membranes for sour gas treatment.

Figure 5. Snapshot of the spreadsheet used for calculation of the product composition of the sour gas using a membrane area of 10,000 m².

Table 4. Product composition of the two-stage cellulose acetate membranes for treating 70,000 m³/h of sour gas (65 mol% CH₄, 12 mol% CO₂, 4 mol% H₂S, 1 mol% H₂O).  

| Membranes area (m²) | Product gas composition | Concentrated acid gas | Hydrocarbons Recovery (%) |
|---------------------|-------------------------|-----------------------|---------------------------|
|                     | CH₄ (mol%)   | CO₂ (mol%) | H₂S (ppm) | H₂O (mg/m³) | CH₄ (mol%) | CO₂ (mol%) | H₂S (mol%) |
|---------------------|--------------|------------|-----------|-----------|------------|------------|-----------|
| 10,000              | 71.9         | 6.7        | 88        | 0.15      | 17.3       | 48.1       | 25.4      | 97        |
| 20,000              | 72.9         | 3.3        | 22        | 0.05      | 43.9       | 34.8       | 14.3      | 85        |
| 30,000              | 71.6         | 1.7        | 9         | 0.04      | 56.9       | 24.5       | 8.7       | 65        |
| 40,000              | 73.9         | 0.8        | 4         | 0.01      | 56.7       | 22.3       | 7.6       | 57        |

a 4 mol% H₂S = 40,000 ppm.
b 1 mol% H₂O = 7,359 mg/m³.
membranes can handle a sour gas containing 5 mol% carbon dioxide and 0.25 mol% hydrogen sulfide with a drop in hydrocarbons recovery to 91%.

### 4. Conclusions

The majority of Kuwait natural gas is produced from the associated gas during oil extraction. All of the natural gas is consumed locally mainly for power generation and water desalination. Natural gas needs processing before usage and this is done by the acid gas removal unit and LPG plant at KNPC. In case of an unexpected shutdown in the KNPC acid gas facility, KOC installed on-site amine and ethylene glycol units in the west fields of Kuwait to avoid flaring. It is known that amine and ethylene glycol units require high energy and have some problems related to flooding and solvent disposal. The membrane technology provides another solution for acid gas removal along with gas dehydration. In this study, cellulose acetate membranes were simulated using UniSim for sour gas treatment containing 12 mol% carbon dioxide and 4 mol% hydrogen sulfide at a flowrate of 70,000 m$^3$ h$^{-1}$. Results show that the membranes can achieve the pipeline gas specifications of 2 mol% carbon dioxide and 4 ppm hydrogen sulfide but the hydrocarbons recovery was very low. This was explained by the large membrane area which caused a tradeoff between product purity and hydrocarbons recovery. The simulation was used again to determine the maximum concentration of the acid gas that the membranes can process and it was found that the associated gas should contain no more than 3.5 mol% carbon dioxide and 0.15 mol% hydrogen sulfide to achieve a hydrocarbons recovery of 97%. Nevertheless, the results can still vary depending on the membrane design such as the membrane structure and the number of stages.

### Declarations

#### Author contribution statement

Yousef Alqaheem: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

### Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

### Data availability statement

Data included in article/supp. material/referenced in article.

### Declaration of interests statement

The authors declare no conflict of interest.

### Additional information

No additional information is available for this paper.

### References

Alkatheri, M., Grandas, R., Betancourt-Torcat, A., Almansoori, A., 2016. Ultra-sour natural gas sweetening using membranes/amines hybrid systems for recurrent middle east conditions. In: Abu Dhabi International Petroleum Exhibition & Conference. Society of Petroleum Engineers, Abu Dhabi, UAE.

Ashkanani, M., 2018. Sulfur Free Gas Supply for Kuwait Refineries. Refining Community Conference, Valencia.

Bhude, B., Stern, S., 1993. Membrane processes for the removal of acid gases from natural gas. II. Effects of operating conditions, economic parameters, and membrane properties. J. Membr. Sci. 81, 239–252.

Carroll, J., 2009. Natural Gas Hydrates: a Guide for Engineers. Elsevier Science.

CEIC Data, 2019. Kuwait Natural Gas Production: OPEC: Marketed Production. Chen, J., 1987. Comments on improvements on a replacement for the logarithmic mean. Chem. Eng. Sci. 42, 2488–2489.

Chen, G., Kanehashi, S., Doherty, C., Hill, A., Kentish, S., 2015. Water vapor permeation through cellulose acetate membranes and its impact upon membrane separation performance for natural gas purification. J. Membr. Sci. 487, 249–255.

Cooley, T.E., Coady, A.B., 1978. Removal of H2S and/or CO2 from a light hydrocarbon stream by use of gas permeable membrane. In: Patent, U.S. (Ed.), United States.

Freeman, B., Yampolskii, Y., 2011. Membrane Gas Separation. Wiley.

Hyne, N., 1991. Dictionary of Petroleum Exploration, Drilling and Production. PennWell Publishing Company.

Iulianelli, A., Driti, E., 2020. Membrane engineering: latest advancements in gas separation and pre-treatment processes, petrochemical industry and refinery, and future perspectives in emerging applications. Fuel Process. Technol. 206, 106464.

Mustafa, J., Farhan, M., Hussain, M., 2016. CO2 separation from flue gases using different types of membranes. J. Membr. Sci. Technol. 6, 1–7.

Poe, W., Mokhtarab, S., 2017. Modeling, Control, and Optimization of Natural Gas Processing Plants. Gulf Professional Publishing, Boston.

Qi, R., Henson, M., 2000. Membrane system design for multicomponent gas mixtures via mixed-integer nonlinear programming. Comput. Chem. Eng. 24, 2719–2737.

Srinivasan, S., 2006. Fuel Cells: from Fundamentals to Applications. Springer US.

Wijmans, J., Baker, R., 1995. The solution-diffusion model: a review. J. Membr. Sci. 107, 1–21.

### Table 5.

| Feed Composition | Product gas composition | Concentrated acid gas | Hydrocarbons Recovery (%) | Membranes Area (m$^2$) |
|------------------|-------------------------|-----------------------|---------------------------|-------------------------|
| CH$_4$ (mol%) | CO$_2$ (mol%) | H$_2$S (mol%) | CH$_4$ (mol%) | CO$_2$ (mol%) | H$_2$S (mol%) | CH$_4$ | CO$_2$ | H$_2$O (mg/m$^2$) | H$_2$O | CO$_2$ | H$_2$S | Recovery (%) | Area (m$^2$) |
| 77.3 | 3.5 | 0.15 | 79.1 | 2 | 4 | 0.55 | 43.8 | 31.8 | 2.3 | 97 | 10,000 |
| 76.5 | 4.2 | 0.20 | 78.1 | 2 | 4 | 0.01 | 62.5 | 24.2 | 1.6 | 94 | 12,000 |
| 75.7 | 5.0 | 0.25 | 77.6 | 2 | 4 | 0.01 | 63.3 | 24.9 | 1.7 | 91 | 14,000 |

Feed pressure = 60 bar, permeate pressure = 2 bar, mole percentage of feed: N$_2$ = 0.05%, C$_3$H$_8$ = 10%, C$_4$H$_8$ = 5%, C$_6$H$_{10}$ = 2.5%, H$_2$O = 1% (7,359 mg/m$^2$).