# Effect of the membrane operating parameters on the separation of oxygen and hydrogen disulphide 

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The processes of separating oxygen in air and $\mathrm{H}_{2} \mathrm{~S}$ in the acid gas feed using a membrane process are based on the relative permeability of components in the feed and are done due to the pressure difference between membrane sides. The mathematical modeling and simulations of the membrane separation processes is solved using EES software without the need for programming outside of the simulator. Passing flow through the membrane is considered counter current and the simulation is done according to the characteristics of hollow fibre membranes. In this study, using this simulator, the percentage of separating components (oxygen and $\mathrm{H}_{2} \mathrm{~S}$ ) of the air and sour gas in the two output flow of the membrane and effect of different parameters on the separation percentage of these components is reviewed. With increasing the feed flow (air and acid gas feed), oxygen and $\mathrm{H}_{2} \mathrm{~S}$ concentration output of the membrane is decreased. However, concentrations of these components have direct correlation with the selectivity and membrane surface area. In addition, the effect of the feed pressure on the oxygen and $\mathrm{H}_{2} \mathrm{~S}$ percentage output of the membrane is a function of the permeate pressure.

Keywords: Oxygen membrane separation, Membrane separation of $\mathrm{H}_{2} \mathrm{~S}$, EES software, Counter-current, Sulfur recovery unit.

Study of membrane was done in the early of $18^{\text {th }}$ Century ${ }^{1}$. Finally by the attempts of Elfred, Zsigmondy, Bachmann and Ferry in early 1930, microporosity nitrocellulose membranes was produced commercially and supplied to the market ${ }^{1-5}$. During the years 1930 to 1950, membrane technology was developed to other polymers such as Cellulose Acetate and the separation of gases with the help of membrane during recent 20 years found many industrial applications ${ }^{5}$. Graham's research on porous membranes led to the diffusion law of Graham. During the years 1943 to 1945, Graham's diffusion law was used in the uranium enrichment process for the first time. In this process the metallic membranes was used in the uranium enrichment process. In the
process, metal membranes for gas separation using membranes as the first industrial-scale membrane separation unit was used that had the greatest record of 40 years in the separation process ${ }^{6-8}$. With the development of asymmetric membranes, membrane units with increasing availability surface and resulting of the high flux were provided ${ }^{9}$.

In this study, all simulations and modeling was done with the help of EES software. EES is the abbreviation of Engineering Equation Solver ${ }^{10}$. The feature simplest of EES is solving the system of algebraic equations (including nonlinear equations). This program is very convenient especially for computing the effect of one or more variables to be analyzed ${ }^{10}$.

In this paper, EES software has been used to investigate the effect of operating parameters such as feed pressure, permeate pressure (outflow from the membrane), permeation flow rate, feed flow rate, membrane surface area and selectivity of the desired components (oxygen and $\mathrm{H}_{2} \mathrm{~S}$ ) relative to other components on the separation percent of desired components.

## Mathematical modeling

At the time being the simulations of the process, are not able to analyze non-ideal systems. In contrast a very comprehensive database of physical properties with high computational features of this simulator is very important. Therefore utilizing a tool to do the parallel mathematical simulation is essential.

To simulate of the membrane separation process, gas or liquid diffusion model through the membrane is used ${ }^{11,12}$. Figure 1 shows a membrane pattern of counter current plug flow.

The diffusion rate of the membrane components are defined as follows ${ }^{13}$ :

$$
\begin{equation*}
y_{p} n_{p}=x_{F} n_{F}-x_{R} n_{R}=Q \overline{(x P-y p)} A_{m} \tag{1}
\end{equation*}
$$

where $Q$ is Permeability, $A_{m}$ is the Surface of the membrane, $x$ and $y$ are mole fraction, $p$ and $P$ are the pressure of the permeable and feed streams. $\overline{(x P-y p)}$ is the partial pressure logarithmic mean of the membrane that is calculated from the following equation ${ }^{14}$ :

$$
\begin{equation*}
\overline{(x P-y p)}=\frac{\left(x_{F} P-y_{p} p\right)-\left(x_{R} P-y_{i} p\right)}{\operatorname{Ln}\left(\frac{x_{F} P-y_{p} p}{x_{R} P-y_{i} p}\right)} \tag{2}
\end{equation*}
$$

where $y_{i}$ is the permeate composition at the retentate end of the membrane that is calculated by equation (3) ${ }^{14}$ :

$$
\begin{align*}
y_{i}= & \frac{\left(\alpha^{*}-1\right)\left(r x_{R}-1\right)+r}{2\left(\alpha^{*}-1\right)} \\
& -\frac{\sqrt{\left[\left(\alpha^{*}-1\right)\left(r x_{R}+1\right)+r\right]^{2}-4\left(\alpha^{*}-1\right) \alpha^{*} r x_{R}}}{2\left(\alpha^{*}-1\right)} \tag{3}
\end{align*}
$$

In this relation, $\alpha^{*}$ is the selectivity, which is the component permeability ratio that was passed faster than other component that slowly diffuses, and $r$ is the ratio of feed (or retentate) pressure to the permeate pressure.

With the specified flow rate and feed composition, the initial guess for the minor component in the feed, that is entered to permeate, was considered to be shown with $\theta$. Then quantities of $x_{F}$ and $y_{p}$ are calculated with mass balance equations of the inlet and outlet flow of the membrane. Using values of $x_{F}$ and $y_{p}$, the new value of equation (4) is obtained.

$$
\begin{equation*}
\theta=\frac{y_{p} n_{p}}{x_{F} n_{F}}=\frac{Q \overline{(x P-y p)} A_{m}}{x_{F} n_{F}} \tag{4}
\end{equation*}
$$

The above steps are repeated until the answers converge. The solution method of presented in above is speculation, so to speed up the convergence, the algorithm of the Fletcher-Reeves can be used to minimize the objective function given in equation (5) to increase the convergence speed of answer ${ }^{15,16}$.


Fig. 1 - Membrane pattern of counter current plug flow ${ }^{2}$

However, to the counter current state and the plug flow, it is assumed that the permeate stream is well mixed and the following equation for the average partial pressure in the guess-and-error process can be used ${ }^{16}$ :
$\overline{(x P-y p)} \cong\left[\frac{x_{F}-x_{R}}{L N\left(x_{F} / x_{R}\right)}\right] P-y_{p} p$
The membrane models for gas permeation are based on species mole balances in addition to the local rates of permeation in Eq. (1):
$x_{F} n_{F}=x_{R} n_{R}+y_{p} n_{p}$
where $x_{F}, x_{R}$ and $y_{p}$ are the feed, retentate, and permeate mole fractions, respectively, $n_{F}$ and $n_{p}$ are the feed and permeate molar flow rates, respectively. The pressures and temperatures are typically assumed to be constant in gas permeation. Eqs. (1) and (7) are required for each species in the feed stream. In addition, the mole fraction in each stream must to one:
$\sum x_{F}=1 ; \sum x_{R}=1 ; \sum y_{p}=1$
For simulation and modeling of membrane separation processes involving oxygen and $\mathrm{H}_{2} \mathrm{~S}$, the feed conditions to membrane units must be specified that for both processes given in Table 1. Also polyethylene methacrylate and Zeolite Polymeric membranes are used for the membrane units of air and acid gas feed, respectively ${ }^{15}$.

## Results and Discussion

The main work of the oxygen in the Claus unit is to partially oxidize $\mathrm{H}_{2} \mathrm{~S}$ in the acid gas feed to $\mathrm{SO}_{2}$ and it will also convert to significant amount of the sulfur in the sulfur recovery unit (SRU) ${ }^{15}$.
\(\left.\begin{array}{lll}Table 1 - Conditions of the acid gas feed and air input to <br>

membrane module\end{array}\right]\)| Composition/mol (\%) | Acid gas feed | Input air |
| :--- | :--- | :--- |
| $\mathrm{O}_{2}$ | 0 | 21 |
| $\mathrm{~N}_{2}$ | 0 | 79 |
| $\mathrm{CO}_{2}$ | 67.73 | 0 |
| $\mathrm{H}_{2} \mathrm{~S}$ | 31.26 | 0 |
| $\mathrm{CH}_{4}$ | 1.01 | 0 |
| Total | 100 | 100 |
| Temperature $\left({ }^{\circ} \mathrm{C}\right)$ | 120 | 70 |
| Pressure/Psia | 30 | 14.7 |

$\mathrm{H}_{2} \mathrm{~S}$ is the main source of sulfur in the sulfur recovery unit and its concentration in the feed can have a large impact on the sulfur recovery. Based on the Le Chatelier's principle, with increasing concentrations of $\mathrm{H}_{2} \mathrm{~S}$ in the acid gas feed, the amount of produced sulfur by the Claus reactions (equations 9 and 10) increases ${ }^{5}$.
$\mathrm{H}_{2} \mathrm{~S}+3 / 2 \mathrm{O}_{2} \leftrightarrow \mathrm{SO}_{2}+\mathrm{H}_{2} \mathrm{O}$
$2 \mathrm{H}_{2} \mathrm{~S}+\mathrm{SO}_{2} \leftrightarrow 3 / \mathrm{nS}_{\mathrm{n}}+2 \mathrm{H}_{2} \mathrm{O}$
Therefore, in this paper, using two membranes in the path of air and acid gas feed inlet to the sulfur recovery unit, the changes of oxygen concentration and $\mathrm{H}_{2} \mathrm{~S}$ (With respect to changes in the key parameters of membrane units) will be investigated.

## Oxygen enrichment

Figure 2 shows the effect of air flow rate (in the different pressures of the feed to the sulfur recovery unit) on the oxygen concentration in the permeate. As can be seen in the figure, with the increase of feed flow rate in the constant pressure, oxygen concentration has dropped out of the membrane. Also by increasing the pressure of feed, the diagrams slope of oxygen concentration becomes steeper. This means that at higher pressures, the concentration of the permeable has been further reduced. So if the feed rate is at its minimum, it is better that to work on the possible maximum pressure, to obtain maximum oxygen concentration in the membrane output.

In Figure 3 the effect of the selectivity and membrane surface area were investigated on the


Fig. 2 - Effect of air flow rate (in the different pressures of the input air to membrane) on the oxygen concentration in the permeate
permeation of oxygen concentration. It is seen that in the constant selectivity, with the increase of membrane surface area, the permeation of oxygen also increases. It is also understood by this figure that the selectivity of the membrane is directly proportional to the oxygen concentration.

## $\mathrm{H}_{2} \mathrm{~S}$ enrichment

The investigation of $\mathrm{H}_{2} \mathrm{~S}$ concentration changes in Permeable stream than the feed pressure (feed acid gas) and pressure of the permeable is performed in the Fig. 4. As shown in Fig. 4, it is observed that at permeate low pressures ( 15 and 30 KPa ), with increasing of acid gas feed pressure, concentration of $\mathrm{H}_{2} \mathrm{~S}$ with the different gradient is increased, however in the 60 KPa pressure, The concentration of permeable $\mathrm{H}_{2} \mathrm{~S}$ increased initially to a maximum value and then not much has changed.


Fig. 3 - Effect of the selectivity and membrane surface area on the oxygen concentration


Fig. 4 - Effect of feed pressure (in the different pressures of permeate) on the $\mathrm{H}_{2} \mathrm{~S}$ concentration


Fig. 5 - Effect of the feed flow rate (in the different pressures) on the $\mathrm{H}_{2} \mathrm{~S}$ concentration


Fig. 6 - Effect of the membrane surface area (in the different selectivities) on the $\mathrm{H}_{2} \mathrm{~S}$ concentration

Figure 5 shows changes of the $\mathrm{H}_{2} \mathrm{~S}$ concentration with respect to pressure and acid gas feed flow rate. With increase of acid gas feed flow rate in the 150 and 200 KPa pressures, the permeate $\mathrm{H}_{2} \mathrm{~S}$ concentration is reduced in the same gradient. But in the $200 \mathrm{KPa}, \mathrm{H}_{2} \mathrm{~S}$ concentration of become constant initially and then declined. Therefore in an acid gas feed constant pressure, flow rate should be at least possible. With the increasing of the membrane surface area, the $\mathrm{H}_{2} \mathrm{~S}$ concentration in the each three selectivity increased, that increasing is higher for the higher selectivity (Fig. 6).

## Conclusion

In this study, using EES software, the effects of membrane operating parameters such as permeate pressure, pressure and feed flow rate, surface area and selectivity of the membrane on the separation of oxygen and $\mathrm{H}_{2} \mathrm{~S}$ has been investigated.

It is concluded that with increasing the inlet air flow at a constant pressure of permeate, the permeate oxygen concentration decreases. However, the percentage of oxygen output of the membrane is directly correlated with selectivity and membrane surface.

In the high pressures of permeate, by increasing the acid gas feed pressure, permeate $\mathrm{H}_{2} \mathrm{~S}$ concentration permeation flow is increased, however in the low pressure increased initially and then remained roughly the same. Also at a constant pressure of acid gas feed, the feed flow rate should be reduced to a minimum amount to obtain maximum $\mathrm{H}_{2} \mathrm{~S}$ concentration. Moreover, with increasing of the both parameters surface area and membrane selectivity, the $\mathrm{H}_{2} \mathrm{~S}$ concentration is highly increased.

## Rreferences

1 Acharya M \& Foley H C, J Membr Sci, 161 (1999) 1.
2 Coombe H S \& Nieh S, Energy Convers Manage, 48 (2007) 1499.

3 Davis R A, Chem Eng Technol, 25 (2002) 717.
4 Domínguez-Domínguez S A, Microporous Mesoporous Mater, 115 (2008) 51.
5 Elford W J, Transact Faraday Soc, 33 (1937) 1094.
6 Ettouney H M, El-Dessouky H T \& Abou Waar W, J Membr Sci, 148 (1998) 105.
7 Güler E, Elizen R, Vermaas D A, Saakes M \& Nijmeijer K., J Membr Sci, 446 (2013) 266.
8 Lee A L, Feldkirchner H L, Stern S A, Houde A Y, Gamez J P \& Meyer H S, Gas Separa Purificat, 9 (1995) 35.
$9 \quad$ McCandless F P, J Membr Sci, 19 (1984) 101.
10 Sripathi V G P, Nijmeijer A \& Benes N E, Proceed Eng, 44 (2012) 642.
11 Tong J, Su C, Kuraoka K, Suda H \& Matsumura Y, J Membr Sci, 269 (2006) 101.
12 Zotov N, Baumann S, Meulenberg W A \& Vaßen R, J Membr Sci, 44 (2013) 119.
13 Johnson D J, Al Malek S A, Al-Rashdi B A M \& Hilal N, J Membr Sci, 389 (2012) 486.
14 Ndungu K \& Mathiasson L, Analyt Chim Acta, 404 (2000) 319.

15 Tan J, Shao H W, Xu J H, Lu Y C \& Luo G S, J Membr Sci, 385 (2011) 123.
16 Vergili I, Kaya Y, Sen U, Gönder Z B \& Aydiner C, Resourc, Conserv Recycl, 58 (2012) 25.

