Succession of States Mathematical Algorithm for Incorporation of Unit Operation in iCON® Process Simulator Applied in Natural Gas Purification

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Abstract
Over recent years, incorporation of unit operation in industrial process simulators remains an intriguing area of research. This is especially applicable to natural gas plant aimed for CO₂ gas removal in offshore platform that is often accompanied with a number of unit operations, complicated configurations, non-standard operating conditions and high impurities content. In addition, it is highly desirable to link the natural gas purification unit with other pretreatment, dehydration and auxiliary equipments already implemented in the process simulators to constitute the entire process plant. Although research work has arisen in this area, the incorporation is particularly challenging for iCON® process simulator since it does not inherit the intrinsic capability to incorporate standalone models of additional unit operations. Nonetheless, the incorporation is of exceptional importance since the intrinsic physical property and thermodynamic databases of iCON® process simulator can be employed conveniently to determine heating value of the product streams. Therefore, in current research work, a mathematical model has been developed to describe the countercurrent hollow fiber membrane module, which has been integrated as an extension in iCON® through utilization of the export/import functions embedded within the Excel unit operation of the process simulator. Validity of the simulation model has been demonstrated through good accordance with published literature. It is found that by determining the separation mechanism via adaptation of the mathematical model, heating value of the purified product stream can be reflected directly in iCON® to evaluate feasibility of the entire process design in offshore natural gas purification platform.

Keywords: Heating Value, iCON, Natural Gas, Process Simulation, Succession of States

1. Introduction
It is highly sought after to implement membrane mathematical models in industrial process simulator. The incorporation enables membrane unit to be linked with any other unit operations that are readily available within the process simulators (such as pretreatment, dehydration, heat exchangers and compressors) to study the performance of design configuration in industrial application as a whole. Of particular importance is it allows the physical properties and thermodynamic databases that are inherent within the process simulators to be conveniently and fully utilized, which is typically crucial in CO₂/CH₄ separation applied in natural gas sweetening. The intrinsic thermodynamic calculation can be adopted to determine heating value of the purified streams, which is a direct quantification of product quality to evaluate feasibility of the design process.

A simple crossflow membrane model has been developed by Rautenbach et al. within Aspen Plus without incorporating any pressure effects. Chowdhury et al. incorporated a multi-component gas separation that is applicable to high-flux asymmetric membrane for cocurrent and countercurrent flow in Aspen Plus. Tessendorf et al. included their model that characterizes the cocurrent, countercurrent and crossflow single permeator
membrane module within external process simulator OPTISM by adapting the equation oriented approach. Davis implemented mathematical model for crossflow and countercurrent flow configurations, which are applicable to the spiral wound and hollow fiber membrane, by assuming negligible pressure drop and logarithmic mean partial pressure driving force within Aspen HYSYS. A One Dimensional (1-D) membrane model for hollow fiber gas separation has been incorporated in Aspen HYSYS by Hussain and Hagg while ignoring thermodynamic effect in order to elucidate feasibility of CO2 capture from flue gas through employment of a facilitated transport membrane. Later, a comparison analysis has been conducted by Peter et al. in Aspen HYSYS to determine the technological advantages of a gas separation process using adsorption and membrane respectively. In our previous publications, a hollow fiber membrane model has been developed and subsequently interfaced in Aspen HYSYS adapting the revised succession of states approach originally proposed by Thundyil and Koros to describe the separation mechanism.

iCON® is a software developed by the Malaysian Oil Company, PETRONAS (Petroleum Nasional Berhad) together with Virtual Material Group from Canada. In industry, this software is often used to predict behaviour of the upstream and downstream for oil and gas processes and has been widely adopted throughout PETRONAS operational performance units in Malaysia. Nonetheless, unlike other commercial software that allows incorporation of the hollow fiber membrane models as an embedded extension to hinder the constraint of scarcely available membrane unit, iCON® does not inherit the intrinsic capability to incorporate standalone models of additional unit operations. The limitation curbs the simulation of hollow fiber membrane unit operation in iCON®, which presents a prevailing research gap to overcome this limitation.

Therefore, in current work, a validated mathematical model charactering CO2/CH4 gas separation in hollow fiber membrane has been developed. Later, the open architecture and built-in linkage of iCON® process simulator with Microsoft Excel has been utilized to incorporate the hollow fiber membrane for countercurrent flow. The hollow fiber membrane unit has been implemented as an Excel unit operation through the import/export functions. By determining separation mechanism of the hollow fiber membrane, it has been demonstrated that heating value of the product streams can be reflected directly in iCON® process simulator to evaluate feasibility of the natural gas processing plant.

2. Methodology

The first subsection describes the succession of states methodology adapted to develop mathematical model that characterizes the binary CO2/CH4 separation within a countercurrent flow hollow fiber membrane. Later, the simulation interface approach is discussed, which provides the information regarding the incorporation of the hollow fiber membrane unit as user defined Excel unit operation in iCON® process simulator.

2.1 Succession of States

The succession of states approach has been employed in current work, which involves resolving the problem through division of the membrane module into predefined finite number of cells, x. In each cell, assumption of constant mass transfer rate has been employed consistently, which enables the computation to be performed independently on each entity without being affected by one another. The independent mass balance implies that outlet specification of each cell will be determined upon the provided inlet condition, while the computed value will be subsequently utilized as input parameter to the neighboring cell. Hence, from a single cell, the calculation can be carried on to the subsequent one and finally proceeds to completion over the entire membrane module.

In order to simplify the computation procedure so that the governing equations can be resolved as a quick design solution, several assumptions have been adopted throughout the work, which are highlighted as the following:

- Gas configuration within the hollow fiber membrane can be adequately characterized through plug flow, whereby strictly no mixing in the inner and outer sides of the hollow fibers has been assumed.
- The same properties (e.g. outer diameter, inner diameter and active membrane layer thickness) have been assumed for all hollow fibers.
- Pressure variations in the lumen and shell sides of hollow fiber membranes are minor and can be sufficiently neglected.
- Any thermodynamic effects within the membrane module are negligible.
Figure 1 show the shell side feed countercurrent hollow fiber membrane module employed in gas separation, while Figure 2 depicts implementation of the membrane within the One Dimensional (1-D) succession of states methodology.

**Figure 1.** Schematic illustration of the shell side feed hollow fiber membrane module with countercurrent flow mechanism, adapted from Rautenbach and Albrecht work.

**Figure 2.** Schematic representation of cells within the 1-D succession of states for mathematical modeling of countercurrent hollow fiber membrane module with reference to Figure 1.

As shown in Figure 1, the hollow fiber membranes are exposed to feed gas containing mixture of components that flows in the longitudinal direction to the retentate end. The retentate stream, which is depleted with the more permeable component, exits the membrane module through the retentate outlet. On the other hand, the permeable component that diffuses across the membrane into the hollow fiber lumen flows in the opposite direction as compared to the feed stream.

From Figure 2, it is found that volume of each membrane element, $V$, which is defined as a disc with radius, $R$ and axial thickness, $\Delta z = L / x$ can be computed according to (1), while the effective membrane area, $A_w$, is calculated from $\frac{\pi R^2 \Delta z}{L}$.\(^{21,23}\)

\[
V = \pi R^2 \Delta z
\]

\[
A_w = 4\pi R^2 \Delta z (1 - \epsilon) / d_o
\]

Nonetheless, it is long recognized that mathematical model associated to the countercurrent flow mechanism is relatively complicated in comparison to its counterpart in the cocurrent manner. The complexity can be rationalized through the fact that permeation at each stage is reliant upon composition of each gas component that has permeated, which is unknown in the beginning of the computational procedure. Hence, the problem has been counterfeited through assumption of cross flow configuration that proceeds with much simplicity from the feed to retentate end as initial guesses in order to reduce computational time. The schematic representation of the cross flow initial guess has been proposed in Figure 3. Comparable approach has been adopted by Coker et al.\(^{13}\) to kick start the solution algorithm pertaining to countercurrent flow membrane in their work.

**Figure 3.** Schematic representation of cross flow module for x number of cells.

For a binary gas separation system, permeate composition of the more permeable component, which is $CO_2$, $y_{\alpha, [j]}$, can be calculated using (3)\(^{11}\). In (3), $\alpha$ is the ideal selectivity, which is defined as ratio of $CO_2$ to $CH_4$ permeability, $\beta$ is ratio of the high to low side pressure ($p_h / p_l$) while $x_{\alpha, [j]}$ is feed side composition of the faster permeating component.

\[
y_{\alpha, [j]} = \frac{(x_{\alpha, [j]} + \beta y_{\beta, [j]})^\alpha - \beta y_{\beta, [j]}^\alpha}{(x_{\alpha, [j]} + \beta y_{\beta, [j]})^\beta - \beta y_{\beta, [j]}^\beta} \]

Via employment of the solution diffusion model, the total amount of gas permeated, $\Delta V'$, as well as the quantity of each gas component, $\Delta V_{\alpha}$, can be conveniently computed based on (4) and (5). According to the solution diffusion model, at the high pressure region of the membrane, components that can potentially sorb in the membrane material dissolve within it, which are subsequently subjected to diffusion through a driving force imposed by pressure difference between the high and low pressure ends and finally evaporate from the low pressure side of the membrane.\(^{22}\) In these equations, $Q_{\alpha}$ is the permeance of each component, $x_{\alpha, [j]}$ is the feed composition entering each cell and $y_{\alpha, [j]}$ is the permeate composition leaving each element.

\[
\Delta V = \sum_{\alpha} Q_{\alpha} \left( x_{\alpha, [j]} - p_h y_{\alpha, [j]} \right)
\]

\[
\Delta V_{\alpha} = Q_{\alpha} x_{\alpha, [j]} - p_h y_{\alpha, [j]}, n = 1, 2
\]

Adopting the succession of states methodology, the flow rates in the retentate end, $V_{\alpha, [j]}$, flow rate in the permeate side, $V_{\alpha, [j]}$, and retentate composition, $x_{\alpha, [j]}$, leaving each element of the membrane can be determined employing (6), (7) and (8) respectively.

\[
V_{\alpha, [j]} = V_{\alpha, [j-1]} - \Delta V
\]

\[
V_{\alpha, [j]} = \Delta V
\]

\[
x_{\alpha, [j]} = (x_{\alpha, [j-1]} x_{\alpha, [j]} - \Delta V_{\alpha}) / V_{\alpha, [j]}
\]

With the crossflow solution as an initial guess, $y_{\alpha, [j]}$ is estimated and improved based on (9), which has been derived from the cell mass balance as depicted in Figure 2.
as developed in Section 2.1. An example of the Excel unit operation interface to define the module specification and to import characteristic of the feed streams from iCON® process simulator, such as that highlighted in yellow cells is shown in Figure 5, while the interface to display computed values of the retentate and permeate streams and to export the calculated product properties to iCON®, such as that provided in the green cells is provided in Figure 6.

### 3. Results and Discussion

This section is divided into two subsections, whereby the first is the model validation to describe validity of the developed hollow fiber membrane mathematical model and the second is simulation results for incorporation of the hollow fiber membrane Excel unit operation within iCON® process simulator to determine heating value of the product streams.

#### 3.1 Validation of Simulation Model

Accuracy of the succession of states methodology describing separation performance of the hollow fiber membrane has been verified through published data by Sidhoum et al. as provided in Table 1, whereby a small percentage error has been observed between the simulated and experimental results.

**Table 1.** Model validation with published experimental results of Sidhoum et al. for countercurrent flow hollow fiber membrane $P_h / P_l = 404 / 101$ kPa; $\frac{x_{CO_h}}{x_{CO_l}} = 0.60 / 0.40$; $P_{co_h} / P_{co_l} = 3.66 / 3.06$; $\mu = 0.3$; $d_0 = 230 \mu m$; $(1-\varepsilon) = 0.50$; $R = 0.136$ cm

| Stage Cut | Simulated Result | Experimental Result | Percentage Error (%) |
|-----------|------------------|---------------------|----------------------|
| 0.080     | 0.8498           | 0.850               | 0.02353              |
| 0.190     | 0.8153           | 0.815               | -0.03681             |
| 0.340     | 0.7880           | 0.790               | 0.25316              |
| 0.525     | 0.7225           | 0.725               | 0.34483              |
3.2 Process Simulation in iCON® to Determine Heating Value of Product Streams

To demonstrate applicability of the hollow fiber membrane Excel unit operation to determine the heating value of product streams in CO₂/CH₄ gas separation, the membrane module is simulated as a simple single stage membrane. The simulations are run under 1,000 kg mole/hr feed gas flow rate with 50 bar pressure. Feed gas containing 50% CO₂ and 50% CH₄ is simulated, which is equivalent to application of acid gas removal from natural gas with high impurities concentration. Ratio of the feed to the permeate pressure is maintained at 50, analogous to atmospheric condition for the permeate stream. The fiber bundle is assumed to be 50% packed with hollow fibers of outer diameter 250 µm. Cellulose triacetate has been adopted as material of fabrication of the membrane with permeance values as followed: $P_{\text{CO}_2} = 60$ GPU and $P_{\text{CH}_4} = 2.86$ GPU. The fiber bundle radius, $R$, is maintained at 8 in, while the active length of the hollow fibers, $L$, is altered within the range of 100-1000 cm to vary the membrane area.

The process flow diagram for simulation within iCON® process simulator is demonstrated in Figure 7. It is depicted that the built-in compressor and cooler unit operations have been utilized to simulate the feed gas of the natural gas purification plant to the desired operating conditions. The special property operation of iCON® has also been employed to determine heating values of the product streams. The minimum heating value to meet industrial specification is 800 BTU/SCF.

Since CH₄ is the mere component contributing to heating value of the stream, the higher amount of CH₄ increases the heating value of the product stream. Hydrocarbon lost is defined as the percentage of hydrocarbon that diffuses across the membrane to the permeate stream as compared to the amount of hydrocarbon contained in the feed. It is depicted that hydrocarbon lost increases with increment in the hollow fiber membrane length attributed to addition of effective membrane area that also enhances permeation of more hydrocarbon simultaneously.

It is depicted that sufficient membrane area should be provided to improve the quality and to achieve the designated heating value of product streams. Nonetheless, it is found that the improvement in heating value reduces at higher hollow fiber membrane length upon exceeding 600 cm. This is ascribed to slower decrement of the CO₂ residue composition when the amount of impurities on the shell side depleted to the extent of reducing the driving force for separation mechanism to occur. On the other hand, it is exemplified that the hydrocarbon lost continues to increase albeit a plateau of the heating value that characterizes the product quality has been achieved. This demonstrates the vitality of determining a tradeoff between product quality and hydrocarbon lost, which can be accomplished conveniently adopting process simulation tools. Therefore, the finding further emphasizes the importance of current work to incorporate hollow fiber membrane mathematical model within iCON® process simulator to assist in the design and optimization of the entire process flow in natural gas purification plant.

4. Conclusion

The separation mechanism of a countercurrent hollow fiber membrane has been modeled adopting a succession of states methodology. Subsequently, the open architecture of iCON® process simulator with Microsoft Excel has been utilized to incorporate the hollow fiber membrane mathematical model as an Excel unit operation. The built-in import/export functions embedded within Excel unit operation have been utilized to acquire operating conditions of the feed stream and to output computed properties of the retentate and permeate streams. Accuracy of the developed simulation model within iCON® process simulator has been supported through excellent accordance with published experimental results. The simulation model has been employed to demonstrate
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applicability of the membrane Excel unit operation in determining heating value of product streams applicable to CO₂/CH₄ gas separation. It is found that by computing separation mechanism of the hollow fiber membrane through employment of the simulation model, the heating value of the product streams can be reflected directly in iCON® process simulator to evaluate feasibility of the natural gas processing plant. Therefore, the developed mathematical model integrated within the Excel unit operation of iCON® process simulator can be applied in process design development by determining the favorable characteristics of various operating conditions and scale-up in industry scale. In future work, it is deemed important to apply process economics studies alongside the developed simulation model so that a tradeoff of the product quality and hydrocarbon lost can be determined under varying membrane operating parameters.

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