Grand Challenge in Membrane Simulation for Gas Separation

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ABSTRACT

This article presents various gas separation membrane simulation techniques based on typical engineering and design techniques for membrane process description. Modelling and design processes are tasks that use different tools to simulate the profile of the process. Given some initial data, such as flow, temperature, concentration and pressure, the correlations presented can be used to perform simulations. After selecting the flow configuration, types of membrane element and settings, it can be determined whether the process is working as expected. The design process, on the other hand, involves the specific results to be obtained, namely the material and geometry estimation of the membrane itself. This paper presents the challenges faced in the membrane simulation study for gas separation, which is important to predict and design the industry scale of gas separation process. At the same time, attainment of accurate results at non-ideal conditions remains challenging. More experimental data and research are needed to support and validate the results.

Keywords: Challenges, membrane simulation, gas separation, CO_2, membrane technology

1.0 INTRODUCTION

The emission of greenhouse gas such as CH_4, CO_2, CFCs, and N_2O have led to global warming and attracted extraordinary attention in recent years. After decades of development, scientists have explored a variety of materials for membrane development. According to the characteristics of these materials, membrane can generally be classified into four types: inorganic membrane, polymeric membranes, mixed matrix membranes, and other membranes [7]. Membrane processes for gas separation have gained greater acceptance in the industries. It has also been used to capture CO_2 from flue gases [3, 18]. An accurate and reliable mathematical model plays a key role in the design of membrane systems. Process simulators have proven successful in modeling, simulating, and optimizing a variety of industrial processes. Most of the commercial simulators are available in solving mathematical models based on membrane applications, such as Ansys Fluent, Aspen, COMSOL, PRO/II etc. This article introduces various gas

separation membrane simulation techniques based on typical engineering and design techniques, proposes practical applications to modern gas separation membranes, and compares common simulators for CO_2 capture simulation studies.

2.0 SIMULATION APPROACHES FOR GAS SEPARATION USING MEMBRANE TECHNOLOGY

As reported by Castel *et al.* (2018) [2], simulation of a complete gas separation process for membrane technology involves several steps, including problem definition, process simulation, process design, techno-economic analysis and process selection based on the simulation results. The potential bottlenecks can be indicated through the function computations. Typically, problem definition is limited to the availability of the membrane permeance data, which is affected by the operating conditions and membrane properties such as the membrane thickness. At this stage, significant error might occur which can affect the membrane actual performance. Process simulation will be depended on the simulation methods used to design the process. Process design requires the knowledge on the cost and lifetime of the membranes. It is noted that realistic cost functions are often confidential, and the techno-economic studies are often limited to one process. The limitation might affect the comparison on the cost functions for various competing technologies for techno-economic analysis. The following sections discuss the steps involved in the membrane simulation using different approaches.

2.1 Dynamics Simulation

The structural and transport properties of the membrane from a microscopic aspect can be simulated via molecular dynamics simulation. Separation properties are often considered in the simulation, including permeability, selectivity, diffusivity, absorptivity and etc. Monte Carlo (MC) is a stochastic approach in which demonstrative configuration can be built by using statistical methods. It includes a list of ensembles including canonical, isothermal-isobaric, isentalpic-isobaric and micro-GCMC [12]. Grand Canonical Monte Carlo (GCMC) was used to simulate the constructed material when the realistic and physical unnatural trial moves are involved, such as the rotation, translation, displacement and regrowth. Vieira-Linhares and Seaton (2003) [17] used GCMC to conduct non-equilibrium molecular dynamics simulation for gas separation across microporous carbon membrane. The temperature, volume and chemical potential of all species are kept constant by changing the total number of molecules during simulation. Assumptions made for the simulation include: (i) the adsorbed molecules are in equilibrium with the bulk phase and (ii) the Peng-Robinson Equation of state is used to relate the chemical potential to the pressure and composition of the bulk gas phase. Dual Control Volume Grand Canonical Molecular Dynamics (DCV-GCMD) simulation was used to consider non-equilibrium states. Periodic boundary conditions are stated in the x and y directions. The simulation box consists of two reservoirs. The reservoirs are found to be linked with diffusion that depends on the chemical potential of the species.

2.2 Fluid Dynamics Simulation

Computational fluid dynamics (CFD) is a branch of fluid mechanics that uses

numerical analysis and data structures to analyse and solve problems that involve fluid flows [19]. Computers are used to perform the calculations required to simulate the free-stream flow of the fluid, and the interaction of the fluid (liquids and gases) with surfaces defined by boundary conditions. Typically, the general workflow of CFD simulation includes three main stages, which can be categorized as pre-processing, solver, and post-processing [16]. During pre-processing stage, two- or three-dimensional fluid flow system will be created using ANSYS Design Modeler. Then, the CFD simulation of the membrane geometry will be conducted using ANSYS FLUENT Solver [13]. For post-processing, a completely defined fluid flow system consisted of geometry, computational mesh, CFD setup setting, solution, and results will be presented [11].

The numerical simulations were also performed using the COMSOL Multiphysics® package [8]. S Qadir *et al*. (2019) [10] reported the application of COMSOL on different membrane modules to study gas transport through membranes and to separate binary gas mixtures. It was concluded that in the membrane module, as the feed pressure increases, the pressure gradient also increases, resulting in higher flux, higher gas permeation and highest permeate purity. The simulation result computed using COMSOL is validated by comparing with values available in the literature.

2.3 Process Simulation/Techno-Economic Analysis

Separation performance of the membrane is possible to be affected by various factors, such as the concentration of the feed gas, pressure of the feed stream to the membrane module, recycle ratio that indicates the amount of second stage retentate which recycle to the feed of the first stage, gas permeance and selectivity of the membrane, recovery ratio and flow rate of sweep gas. Hence, process simulation is required to predict the performance of the membrane simulation for gas separation. Techno-economic analysis is important to estimate the minimal overall cost of the unit including the operating (OPEX) plus capital (CAPEX) expenses by combining materials and process engineering considerations, energy requirement and the size of installation. It can be used to estimate a minimum total cost for each strategy with an optimal recovery ratio [1]. Instead, it is also possible to provide different design options for the strategy. Sublet *et al*. (2012) [15] reported the techno-economical assessment of MFI-type of zeolite membrane for CO_2 capture from post combustion process of flue gases. The analysis was conducted on a membrane cascade configuration. An overall CO_2 removal target of at least 75% of the inlet value and a CO_2 purity of at least 95% in the downstream permeate flow was attained. It is reported that high effective surface is required for high purification and high unit cost, and thus, causing infeasibility of the membrane technology as compared to the conventional chemical absorption or polymeric membrane.

2.4 Others

PRO/II (Schneider Electric) is another powerful steady-state process simulator aimed for process design and operational analysis for process engineers in the chemical, petroleum, natural gas, solids processing, and polymer industries [4]. Elke Goos *et al*. (2011) [5] reported the CO_2 compression process using gas separation membranes in post-

combustion capture was simulated using Pro/II software. Using several different equations of state, phase diagrams for different CO_2-N_2 gas mixtures (e.g. 5 mol%-10 mol% N_2) were calculated and compared with the precise thermodynamic and transport properties. The specific energies of the compression process for each gas mixture were analyzed. The energy consumption and the state of the compressed compound are strongly influenced by the N_2 composition in the mixture.

3.0 CHALLENGES IN MEMBRANE SIMULATION

3.1 Molecular Dynamics Simulation

Simulation of gas separation via membranes is designed to solve Navier-Stokes equations in discrete form. The advantage of this method is that it can use various discretization schemes suitable for geometric and process requirements. However, it is difficult to achieve high accuracy due to the computational error of the fitting equation, especially when complex geometric shapes are involved. Most of the assumptions are made based on ideal conditions. Actual operating conditions such as the aging or fouling rate of membrane, pore plugging by the impurities, plasticization at high pressure, concentration polarization, and others are ignored in the simulation. Therefore, it is also difficult to identify the factors that lead to the poor performance of the membrane. It is also difficult to identify the factors that lead to the poor performance of the membrane as the assumptions were mostly made based on the ideal conditions. A Mokrane *et al.* (2018) [9] report the modelling, simulation and validation aspects that are essential for the selective laser sintering (SLS) process of polymer powders. The parametric analysis was

finally proposed to test the reliability of the model in representing real physical phenomena and the thermal history that the material experiences in the process. However, the accuracy of the analysis results requires further verification due to the complexity of the geometry.

3.2 Fluid Dynamics Simulation

Due to the limited experimental data reported, hypothetical data and formulas are required, and it must be compared with the real results as a reference and cannot be directly used as the actual measurement results. S Shirazian *et al.* (2012) [14] discussed mathematical modeling and numerical simulation of gas separation using polymer membrane contactors. COMSOL Multiphysics was used for the simulation. The velocity distribution of the gas flow in the contactor was obtained from the Happel model. Due to the limited experimental data available, the parameters for the simulation were mostly assumed. By comparing the predicted values with the experimental values for CO_2 removal from CO_2/N_2 in the literature, the model predictions agree with the experimental data.

3.3 Process Simulation/Techno-Economic Analysis

The validated membrane simulation results can predict the performance and the cost of the membrane after been scaling up. The process can even be optimized by varying the operating parameters, such as flow rate, temperature, concentration, and pressure, based on the theoretical basis and benchmark for industrial application. For complex structures and changing conditions in the process, synthetic routes can be preset and feasibility can be tested through

process simulation. This is especially essential for the process system designers. Nevertheless, there are some challenges to be addressed in getting reliable simulation results, such as the actual material and operating costs required to run the process. Some models used are also not able to suit the non-ideal conditions of the process. Table 1 summarizes the challenges faced by different simulation stages by comparing their respective advantage and limitation

Table 1 Challenges faced at different simulation stages

Simulation stages	Advantages	Limitation
Molecular dynamics simulation	Various discretization schemes suitable for geometric and process requirement can be used.	Difficult to achieve high accuracy due to the computational error of the fitting equation, especially when complex geometric shapes are involved.
Fluid dynamics simulation	Able to save cost before scaling up for real working condition.	Hypothetical data and formulas are required, and it must be compared with the real results as a reference and cannot be directly used as the actual measurement results.
Process simulation/techno-economic analysis	The validated membrane simulation results can predict the performance and the cost of the membrane after been scaling up.	Reliability of the results is limited by the actual costs and built-in models in the simulators.

4.0 CONCLUSION AND PERSPECTIVE

Although the simulation methods for different membrane technologies vary, they can be combined for the modeling and simulation of integrated membrane systems. The results obtained from these calculations can also be used to demonstrate the potential of the materials in an increasing number of potential gas separation membranes. Discretization dependent on grid structure is always a source of error, which can be minimized by appropriately adjusting element size, shape and type. However, the formulations of this fluid dynamics approach cannot predict the thermodynamics of the simulated environment. With various gas separation membrane simulation methods, the design and modelling cost can be reduced. Griffin and Hammond (2019) [6] reported that by combining membranes with traditional purification processes such as distillation, solvent extraction, production processes for gas absorption, these processes can be passed in simulators to study alternative processes. Possible problems can be inferred in advance, and simulated data can be considered as the reference for industrial applications.

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