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Thermodynamic analysis of energy density in pressure retarded osmosis: The impact of solution volumes and costs

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ABSTRACT

A general method was developed for estimating the volumetric energy efficiency of pressure retarded osmosis via pressure-volume analysis of a membrane process. The resulting model requires only the osmotic pressure, π, and mass fraction, w, of water in the concentrated and dilute feed solutions to estimate the maximum achievable specific energy density, u, as a function of operating pressure. The model is independent of any membrane or module properties. This method utilizes equilibrium analysis to specify the volumetric mixing fraction of concentrated and dilute solution as a function of operating pressure, and provides results for the total volumetric energy density of similar order to more complex models for the mixing of seawater and riverwater. Within the framework of this analysis, the total volumetric energy density is maximized, for an idealized case, when the operating pressure is $\pi/(1+\sqrt{w}^{-1})$, which is lower than the maximum power density operating pressure, $\Delta\pi/2$, derived elsewhere, and is a function of the solute osmotic pressure at a given mass fraction. It was also found that a minimum 1.45 kmol of ideal solute is required to produce 1 kWh of energy while a system operating at “maximum power density operating pressure” requires at least 2.9 kmol. Utilizing this methodology, it is possible to examine the effects of volumetric solution cost, operation of a module at various pressure, and operation of a constant pressure module with various feed.

1. Introduction

Pressure retarded osmosis is a method of generating energy from a potential energy gradient between two solutions [1–27]. In PRO, a volume of water is passed up a pressure gradient by a chemical potential gradient generated by dissolved solutes. The volume passed and its energy density are interdependent: operating at high pressures will limit the relative volume that can be passed but the volume will have a high energy density, while operating at low pressures will allow a larger relative volume of water to transfer with a lower energy density. There have been a number of papers which consider the energy that can be extracted in a PRO process; this energy is inversely related to the minimum energy of desalination [28–30]. Previous characterizations of volumetric energy density of PRO processes have defined a frame of reference to dictate the resulting value based on the stream perceived to be more expensive or limiting; two previous analyses of a commonly proposed osmotic energy source, the mixing of seawater and riverwater, resulted in different analyses by selecting opposite bases for normalization. Veerman et al investigate the “fuel efficiency” of a seawater–riverwater reverse electrodialysis (RED) process and concluded that if the pretreatment cost of riverwater is substantial [31], operating at high transfer by fully diluting the concentrated solution will be more efficient. Yip and Elimelech [14,15], however, arrive at an energy density of approximately 0.75 kWh/m^3 of dilute feed solution for a seawater–riverwater PRO process by assuming the dilute feed solution will be the limiting resource. As the energy of mixing is a thermodynamic property, is has been shown that the maximum extractable energy for RED and PRO processes are identical for identical feed conditions [32]. More recently, Lin et al analyze the specific energy density of PRO process accounting for both feed and draw solution but ignoring, to an extent, dimensional parameters such as membrane area and module length [33]. By this type of analysis, the volumetric energy density of either or both streams may be specified to yield a more practical result for process design. A more general analysis of the “cost” per unit volume of PRO working solutions, such as pretreatment and pumping costs, allows extension of the concept of specific energy density to specific energy “cost”, which allows the minimization of the total cost, per total volume of input solution.

Analyses of seawater and riverwater PRO processes have implied that the volumetric energy density of the process, which has a maximum value of approximately 0.192 kWh/m^3 of seawater

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and riverwater combined, is too low, especially when considering pretreatment costs for seawater and riverwater, to be a practical source of renewable energy [33]. PRO has also been proposed and evaluated as an energy recovery process for reverse osmosis (RO), by which riverwater or treated wastewater is mixed with RO brine to recover a portion of the energy spent on desalination [32,34,35]. Both of these processes are open-loop, in that the feed streams are not manually regenerated. Osmotic heat engines (OHE) have been proposed which utilize continually regenerated (closed-loop) streams of concentrated and dilute solutions [33,36]. While such a system is feasible in a number of forms, OHE are typically contrived to utilize low-grade heat and are proposed as add-on energy recovery systems, not as primary energy generation technologies, as the thermal efficiencies are typically low and temperatures are restricted to those which polymeric membranes can withstand [37]. These engines are proposed as alternatives to Organic Rankine Cycle engines (ORC) for recovering waste heat from industrial processes and power production. A third form of PRO may be envisioned in which an external, natural source of feedwater, e.g. seawater or riverwater, is combined with a stored solution, e.g. rainwater or an specialized draw solute, to produce power. Such a system must only store one of the solutions of a traditional closed-loop PRO process. Like closed-loop systems, such “semi-open” systems must regenerate the initial stored solution and external solution for re-use and discharge.

The closed-loop and semi-open loop PRO processes allow for the storage of energy through the storage of the unmixed working fluids. A plant may operate as a load-leveling battery, generating concentrated and dilute solutions at night and mixing them during the day, or as a battery for peak demand or intermittent power production. For the application of an osmotic battery, the specific energy density allows the comparison between competing forms of stored energy which have better defined specific energy densities; this includes solid-state batteries, flow-cell battery working fluid, fuel cell fuels, and combustion fuels. The specific energy density, here defined only in terms of the process working fluids, may then be weighed in combination with other concerns, membrane power density, in W/m^2, the related module power density, in W/m^3, and the system cost in USD/W. By analyzing the specific energy density of osmotic agents as well as the limits on energy extraction by reasonable operating conditions, it is possible to compare PRO systems to competing technologies such as chemical heat pumps, thermal storage, pumped hydro gravity storage, solid-state batteries, flow cell batteries, and compressed air storage.

In this paper a general method is developed for estimating the volumetric energy efficiency of pressure retarded osmosis via pressure-volume analysis of a membrane process. The resulting model requires only the osmotic pressure, π, and mass fraction, w, of water in the concentrated and dilute feed solutions to estimate the maximum achievable specific energy density, u, as a function of operating pressure. This method utilizes equilibrium analysis to specify the volumetric mixing fraction of concentrated and dilute solution as a function of operating pressure, and provides results

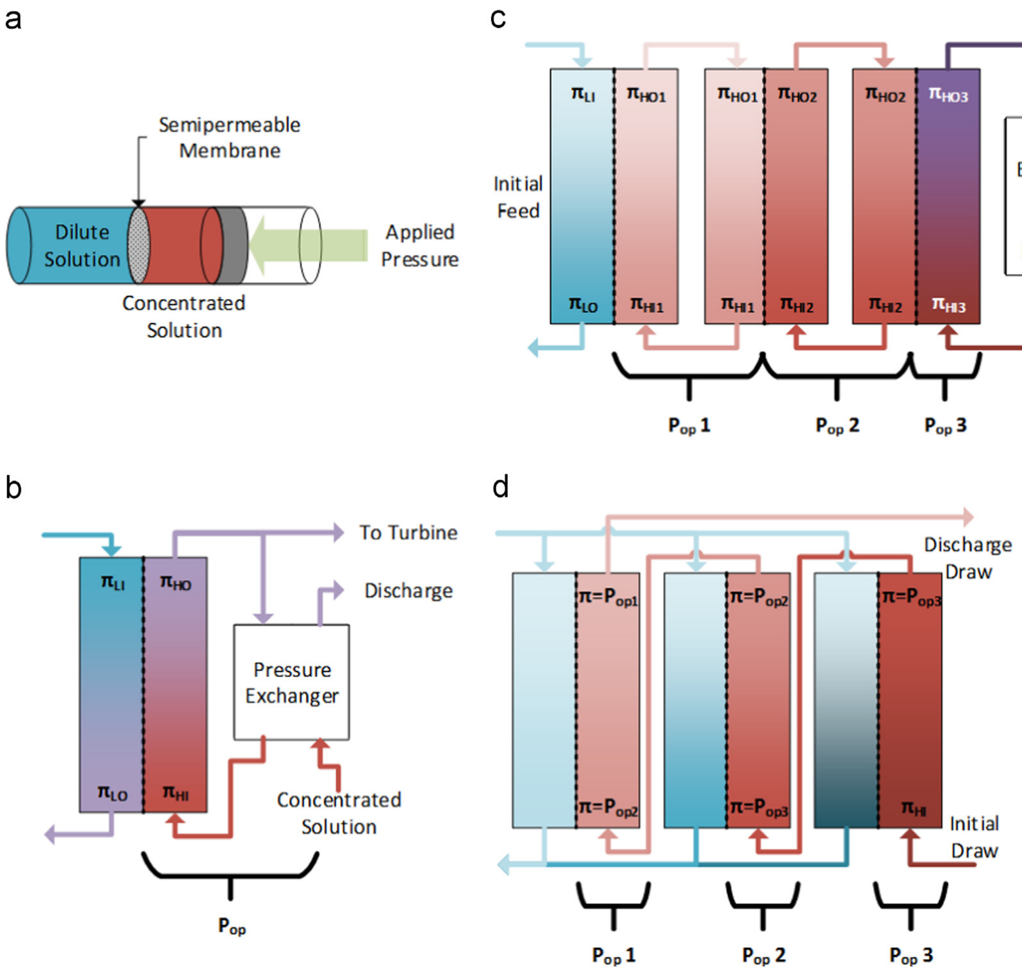

Fig. 1. Four schemes of PRO operation. a) variable pressure (“piston-type”) PRO. b) typical open-loop counter-current flow PRO process. c) A “series” PRO process with one dilute solution and staged concentrated solutions to access high osmotic pressures. d) A “parallel” PRO process with multiple dilute inlets and consecutive concentrated solution steps to approximate variable pressure operation, assuming each stage achieves equilibrium.