



Highly effective organic draw solutions for renewable power generation by closed-loop pressure retarded osmosis

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ABSTRACT

An appropriate draw solution selection is a key to successful implementation of closed-loop pressure retarded osmosis (PRO) process for sustainable energy generation. In this study, the organic compounds potassium citrate, calcium acetate, potassium oxalate, potassium acetate, ammonium acetate, ammonium carbamate, ammonium formate, potassium formate, sodium glycolate, sodium propionate and calcium propionate were identified for the first time as highly effective draw solutions (except for NaP) using an easy desk-top screening method. This method identified these organic compounds by considering physical state at ambient condition, water solubility and osmotic pressure. The draw solutions were comprehensively evaluated for water flux, power density, and reverse salt flux through a laboratory-based investigation of the PRO process. The peak power densities achieved for the identified draw solutions were 5.32–6.73 W/m² at 2.8 MPa osmotic pressure. These peak power densities increased from 109% to 118% (11.1–14.64 W/m²) when increasing the osmotic pressure of the draw solutions by 50% (4.2 MPa). A significant increase in the peak power density was obtained due to the very low reverse salt flux for the organic draw solutions (0.029–0.0699 mol m⁻² h⁻¹ and 0.0325–0.0854 mol m⁻² h⁻¹ at osmotic pressures of 2.8 MPa and 4.2 MPa, respectively). The identified organic draw solutions were also analyzed as distillable and thermolytic through gravimetric method, for the identification of potential downstream recovery methods to recycle the draw solutions in the closed-loop PRO process. Membrane distillation could be used as a downstream separator technique for the distillable organic draw solutions; however, only the ammonium carbamate among the thermolytic compounds could be separated downstream by using a low-temperature thermal distillation process.

1. Introduction

Increasing rates of global energy use are diminishing the existing fossil fuel reserves. To secure a sustainable future for ourselves and generations to follow, it is widely accepted that we must act now to produce renewable energy. In light of this challenge, a massive amount of research is being conducted about the use of clean, renewable energy sources [1–9]. Pressure retarded osmosis is known as an emerging technology for renewable energy [10]. PRO is an osmotically driven membrane-based process that harnesses the energy gradient between high and low salinity streams to produce mechanical energy [11]. The primary concept behind this process is the osmotic transport of water through a semi-permeable membrane from a low salinity feed solution into a high salinity draw solution. This approach utilizes the natural process of osmosis, which is the diffusion of salt due to different salinities on either side of a semi-permeable membrane. During the PRO process, a pressure that is lower than the osmotic pressure is applied to the draw solution side to generate electricity via a turbine-generator,

which is set by releasing a portion of the pressured water that permeates across the membrane from the low salinity solution [12–16]. PRO processes can be classified into two types: open-loop PRO and closed-loop PRO processes. The diluted draw solution is discharged during the open-loop PRO process, whereas the draw solution with osmotic potential is regenerated instead of discharged during the closed-loop PRO process [17]. The closed-loop PRO process consists of three sections, that is, the PRO filtration unit, hydro turbine, and draw solution regeneration system. A schematic representation of a closed-loop PRO is shown in Fig. 1.

A closed-loop PRO process can be economically viable when the minimum peak power density value is approximately 5.0 W/m² [18–21]. Low-grade industrial heat can be used to regenerate the draw solution within the closed-loop PRO process [22]. During the industrial processes, 20–50% of the consumed energy is lost as waste heat in the form of hot exhaust gasses, cooling water, and radiant heat from hot equipment surfaces and other heated products [23]. Therefore, the closed-loop PRO process can be co-located with existing power plants,

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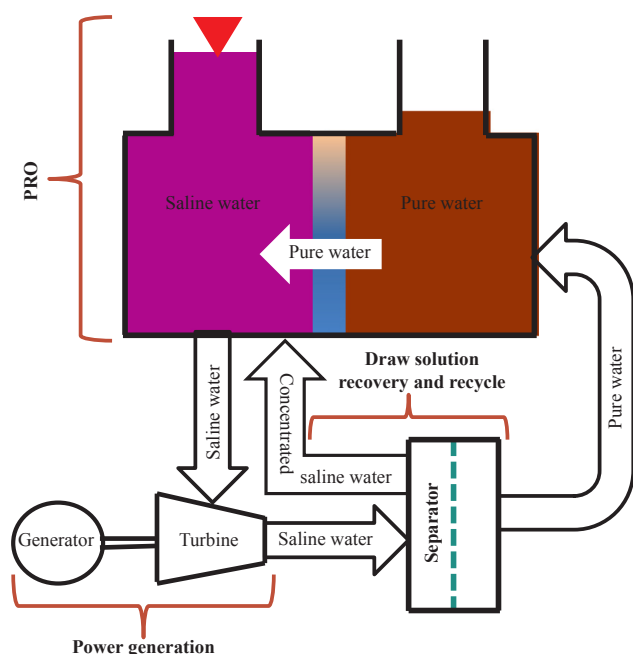


Fig. 1. A schematic representation of the closed-loop PRO process.

such as traditional and geothermal power plants or other industrial processes that emit low-grade heat, such as chemical processing plants, cement plants, and breweries. During the closed-loop PRO process, thermal and membrane distillation processes can be used to regenerate thermolytic and distillable draw solutes, respectively, using industrial waste heat [22–24]. The above context makes the closed-loop PRO process an appropriate emerging technology for the production of renewable energy from the salinity gradient of two solutions that are separated by a semi-permeable membrane [22–26].

The efficacy of the PRO process is highly dependent on the membrane, the draw solution, the recovery system chosen, and the power density obtained for electricity generation [12–14,16,17,22–26,27]. In recent years, various inorganic salts have been used as draw solutions in membrane-based osmotic processes where high reverse salt fluxes were observed [27–31]. Draw solutions with high solubility and high osmotic pressure, yet lower reverse salt flux are most effective for membrane-based osmotic processes [27–31]. Previously, Hickenbottom et al., Bowden et al., and Corzo et al. used organic draw solutions in membrane-based osmotic processes [23,32,33]. Compared to inorganic draw solutions, some of these organic draw solutions exhibited high solubility and high osmotic pressure, but more importantly, all of the organic draw solutions tested possessed lower reverse salt fluxes [28–33]. This low reverse salt flux of draw solutions can decrease concentration polarization, and allow for achievement of higher water fluxes in membrane-based osmotic processes [23,27–34], which can contribute to high power density in PRO [23–27]. Therefore, in the search for effective organic draw solutions for renewable power generation via PRO, we—for the first time—report eleven organic draw solutions (potassium citrate, calcium acetate, potassium oxalate, potassium acetate, ammonium acetate, ammonium carbamate, ammonium formate, potassium formate, sodium glycolate, sodium propionate, and calcium propionate) with high solubility, high osmotic pressure, feasibility for recovery by low temperature thermal distillation/membrane distillation, very low reverse salt flux, and true viability for power generation.

2. Selection of organic draw solutions

Fig. 2 represents the method used to select the organic draw solutions. Initially, 550 organic compounds were screened as potential draw solutions. The compounds that were not solid at normal temperature

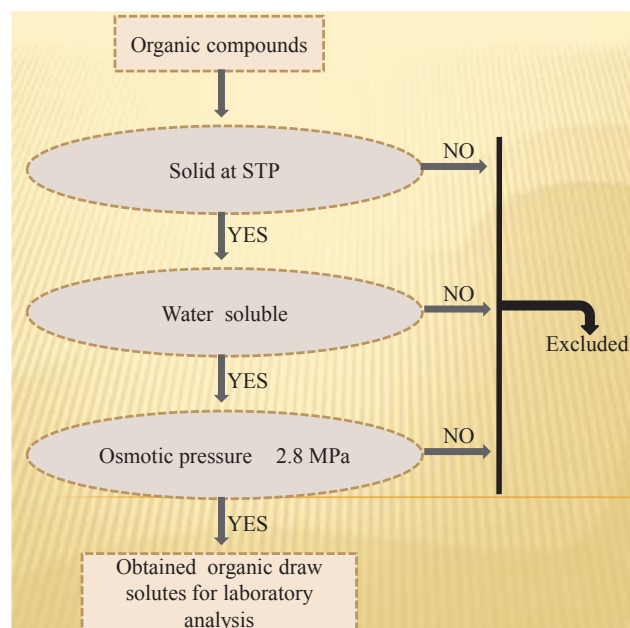


Fig. 2. Flow chart for the selection of the organic draw solutes.

and pressure and not soluble in water were eliminated by the database-driven screening method to create a shortlist of potential chemicals. The osmotic pressures of the draw solutions as a function of the concentration were then determined using the OLI Stream Analyzer™ (OLI Systems, Inc.). Draw solutions with an osmotic pressure lower than 2.8 MPa (the osmotic pressure of sea water [29]) at the saturation concentration were excluded to obtain the desired draw solutes. At the end of the selection process, the following eleven organic compounds were identified as desirable organic draw solutes: potassium citrate, calcium acetate, potassium oxalate, potassium acetate, ammonium acetate, ammonium carbamate, ammonium formate, potassium formate, sodium glycolate, sodium propionate and calcium propionate.

3. Materials and experimental methods

3.1. Solution of the draw solutes

Certified ACS-grade sodium glycolate was obtained from Alfa Aesar by Thermo Fisher Scientific, USA, and all other organic compounds were obtained from Sigma-Aldrich, USA, to produce all the draw solutions. These draw solutions are all provided in Table 1. De-ionized (DI) water (Millipore, Billerica, MA) was used as the feed stream in all of the experiments. The concentrations of each draw solution at 2.8 and 4.2 MPa osmotic pressure were determined using the OLI Stream Analyzer™ (OLI Systems, Inc.) (Table 1). The OLI Stream Analyzer™ was also used to find the mutual diffusivity (D), viscosity, and solubility for each draw solution (Table 1).

3.2. Membrane performance evaluation

A flat-sheet of thin-film composite (TFC) forward osmosis membrane (Hydration Technology Innovations, HTI, Albany, OR) was used to conduct all the PRO experiments. The water permeability coefficient (A) and salt permeability coefficient (B) for the TFC membrane was investigated using a flat-sheet bench-scale cross-flow RO test system. A coupon of the membrane with an effective surface area of 19.94 cm² was placed in a stainless steel test cell with active surface of the membrane facing the feed stream. The membrane coupon was also placed in the stainless steel test cell with support surface of the membrane facing the feed stream in order to investigate water permeability

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