



Evolution of polymeric hollow fibers as sustainable technologies: Past, present, and future

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ABSTRACT

Energy, water, affordable healthcare and global warming are four major global concerns resulting from resource depletion, record high oil prices, clean water shortages, high costs of pharmaceuticals, and changing climate conditions. Among many potential solutions, advances in membrane technology afford direct, effective and feasible approaches to solve these sophisticated issues. Membrane technology encompasses numerous technology areas including materials science and engineering, chemistry and chemical engineering, separation and purification phenomena, molecular simulation, as well as process and product design. Currently, polymeric hollow fiber membranes made using a non-solvent-induced phase inversion process are the dominant products because polymers offer a broad spectrum of materials chemistry and result in membranes with desirable physicochemical properties for diverse applications. Their low cost and ease of fabrication make polymeric membranes superior to inorganic membranes. Therefore, this review focuses on state-of-the-art polymeric hollow fiber membranes made from non-solvent-induced phase inversion and the potential of membrane processes for sustainable water and energy production. The specific topics include: (i) basic principles of hollow fiber membrane formation and the phase inversion process; (ii) membranes for energy (natural gas, H₂, and biofuel) production; (iii) membranes for CO₂ capture; and (iv) emerging desalination technologies (forward osmosis and membrane distillation) for water production. Finally, future opportunities and challenges for the development of advanced membrane structures are discussed.

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1. Introduction

Since Loeb and Sourirajan [1] invented asymmetric cellulose acetate reverse osmosis (RO) membranes via phase inversion in the late 1950s, membranes with different materials and designs have been progressively developed for diverse applications in reverse osmosis (RO), micro/nano/ultra-filtration (MF,NF,UF), dialysis, gas separation, and pervaporation. At present, there are many types of membrane configurations available in the market, such as flat sheet composite membranes, polymeric hollow fibers, and inorganic tubular membranes. Hollow fiber membranes made of polymeric materials, first patented by Mahon [2] five decades ago, are highly competitive with flat and inorganic membranes because they possess several beneficial features. Compared to other membrane configurations, the hollow fiber geometry offers a larger effective membrane area per unit volume of the separation device (i.e., membrane module) which results in greater process intensification. Additionally, the hollow fiber form provides good self mechanical support and ease of handling during module fabrication and process operation.

A rich literature on membrane formation mechanisms and applications of hollow fiber membranes has been established during the past five decades [2–12]. Most efforts focused on innovative approaches for the formation of hollow fibers with an ultra-thin selective layer and physicochemical properties that improve dramatically separation performance. The membrane community has tried to adopt casting conditions used for flat-sheet membranes to spin comparable hollow fiber membranes. However, the formation mechanism for hollow fiber membranes via phase inversion is considerably more complex than that for flat-sheet membranes, and the factors controlling hollow fiber structure are distinctly different from those for flat sheets. One essential difference is the dope formulation: a sufficiently high polymer dope concentration is required for hollow fiber spinning. This usually results in much more complicated phase inversion properties and

non-Newtonian rheological behavior. Moreover, in flat-sheet membrane formation, the phase inversion usually starts from the top surface of the as-cast film upon immersion in a coagulation bath, whereas hollow fiber fabrication involves two coagulants (internal and external coagulants). The internal coagulant controls the inner skin morphology, while the external coagulant controls the outer skin morphology. Other factors such as spinneret design, rheology within the spinneret, air-gap distance, moisture, die swell and elongational stresses also can impact final membrane morphology and performance.

The majority of the innovations and developments in hollow fiber membrane manufacture have been made through trial and error aided by past experience, empirical data, and qualitative scientific understanding. The potential for membrane technology to provide sustainable solutions to global demand for clean energy, water and health care has spurred membrane research and development to identify new polymeric materials with desirable properties and the advanced manufacturing technologies required to transform them into membranes. To transform these new materials into useful hollow fiber membranes and fully utilize their separation potential, researchers must understand the intrinsic physicochemical properties of these new materials, manipulate phase inversion processes, and control dope rheological responses during membrane formation to produce the desired membrane macro- and micro-structure.

Fabrication of hollow fiber membranes with both desirable morphology and separation performance is challenging. Macrovoids and irregular shapes are often observed in hollow fibers and they are considered as defects because they could lead to membrane mechanical failure if the membrane is operated under high pressure or subject to vibration for extended periods of time. Changes in polymer molecular structure to improve separation performance are limited by the well-known trade-off between permeability and selectivity—an increase in permeability usually is accompanied by a decrease in selectivity and vice

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