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Concentration of glycerol from dilute glycerol wastewater using sweeping gas membrane distillation

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ABSTRACT

In this work, experimental results for the concentration of dilute glycerol wastewater using membrane distillation (MD) with a microporous hydrophobic flat-sheet PTFE membrane are reported. Experiments were performed using the sweeping gas mode of the MD (SGMD) process. The effects of various operating variables, such as feed temperature, glycerol concentration in aqueous phase, feed flow rate and sweeping gas flow rate were studied. A Taguchi analysis has been performed on the experimental results which determined the effects and contribution of each of the factors on the distillate flux and the interactions between the operating variables. Results showed that the most influential factor was feed temperature. The second significant contribution was observed for the sweeping gas flow rate. Feed concentration had a negative effect on the distillate flux. At optimum conditions (i.e. 65 °C, 400 mL/min, 1 mass%, and 0.453 Nm^3/h), the Taguchi model predicted the value of the response (the distillate flux) as 20.93 L/m^2 h, which had good agreement with the experimental results.

1. Introduction

Most membrane separation processes (MSPs) are isothermal that depend on the difference in hydrostatic pressure, concentration or electrical potential as a driving force. These isothermal membrane processes are reverse osmosis (RO), microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), electrodialysis (ED) and gas separation, which have been developed for various applications [1–6]. A relatively new hybrid non-isothermal membrane separation process was introduced that is a combination of a traditional distillation process and membrane technique, called the “membrane distillation” process [7–12]. Membrane distillation (MD) is a versatile and under-developing non-isothermal membrane process for separations that is mainly suited for applications in which water is the major component present in the feed stream to be treated. MD refers to a *thermal driven transport* of vapor molecules through a microporous hydrophobic membrane. The driving force is the vapor pressure difference between each side of the membrane's pores [13]. MD was first conceived as a separation process that could operate with a minimum external energy requirement and the least capital and land for the operating plant. The large vapor space required by a conventional distillation column is replaced in MD by pores' volume of a microporous membrane, which is generally on the order of 100–250 μm [14]. However, conventional distillation relies on high vapor velocity to provide intimate vapor–liquid contact, and MD uses a microporous hydrophobic membrane to support the vapor–liquid interface. Therefore, the required equipment for the MD process can be much smaller, which translates to a savings in terms of real state; and operating temperature is much lower, because it is not necessary to heat the process liquid above its boiling temperature [15]. These benefits result in less heat lost to the environment through the equipment body. Feed temperatures in MD typically ranged from 40 to 80 °C [16]. Therefore, low-grade waste and/or alternative energy sources such as solar, wind or geothermal energies, and waste thermal energy sources in industrial plants can be coupled with MD systems for a cost and energy efficient separation [17]. Indeed, MD plants powered by solar energy have been shown

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Table 1
Some physicochemical properties of glycerol [31].

Chemical formula	$C_3H_5(OH)_3$
Molecular mass	92.093 g mol^{-1}
Viscosity at 20 °C	~1.5 Pa s
Density at 20 °C	~1.26 g cm^{-3}
Melting point	~18 °C
Boiling point	~290 °C
Flash point	~160 °C
Surface tension at 20 °C	~64 mN m^{-1}

to be cost competitive with RO in remote areas [18]. Also, easier operating conditions, lower operating pressure (usually environmental pressure which increased safety); and less fouling problems are some other benefits of the MD process. MD has been used for a wide range of applications such as desalination [19], food processing [20], bioethanol processing [21,22], and wastewater treatment [23].

In fact, nearly all of membrane processes are within the scope of process intensification. This is because the membrane systems are very compact systems that falls within the criteria introduced in 1995 by Ramshaw, one of the pioneers in the field of process intensification. He defined the process intensification as a strategy for performing dramatically reduction in the size of a chemical plant for attaining a given production objective [24,25].

Membrane distillation is probably the best-known hybrid system that is being investigated worldwide. The MD process is a powerful alternative to reverse osmosis and evaporation that being widely considered. Four basic advantages of membrane distillation over traditional processes are:

- The rejection value for ions, macromolecules, colloids, cells, and other non-volatiles is nearly 100%.
- The trans-membrane pressure is very lower than the pressure driven processes.
- The fouling of the membrane is less because of larger pores and hydrophobic nature of the membrane.
- The operating temperatures are lower in comparison to the conventional evaporation or distillation processes and this makes the MD process ideal for processing of temperature-sensitive materials.

To the best of our knowledge, the application of MD processes for separation of glycerol–water solutions has not yet been reported.

Glycerol is a simple polyol compound. It is a colorless, odorless, viscose liquid with a sweet taste that is widely used in pharmaceutical, food, detergent, and chemical industries [26,27]. It is completely soluble in water and alcohols, and is slightly soluble in many solvents such as ether and dioxane, but is insoluble in hydrocarbons such biodiesel. It is worth quoting that glycerol is the main co-product of trans-estrification biodiesel production [2,27]. Glycerol contains three hydrophilic alcoholic hydroxyl groups (Fig. 1), which are responsible for its high solubility in water. Table 1 shows the general properties of glycerol. Traditionally, glycerol has been used, either directly as an additive or as a raw material, ranging from its use as a food and drug additive to the synthesis of acrolein, acrylic acid, and acrylonitrile, and other valuable chemicals [28–30]. In the food industry, glycerol is used as a solvent, sweetener, and humectant. It is also used as filler in commercially prepared low-fat foods such as cookies, and as a thickening agent in liqueurs. Therefore, glycerol in dilute aqueous form could be found in a wide range of industrial wastewater streams [28–37].

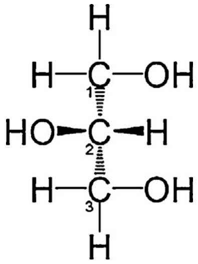

Fig. 1. Chemical structure of glycerol.

Removal of water is one of the important steps in the production of pure glycerol, either in the fat-splitting process or glycerol separation from detergent production wastewater streams. Conventionally, evaporation and distillation were used for water removal from glycerol solutions. The high boiling point of glycerol (Table 1), alone with its low decomposition temperature (~190 °C), necessitates the use of vacuum pressure to lower temperature requirements. Therefore, such a kind of separation process which can achieve dewatering at much lower operating temperatures is an attractive alternative. One choice could be the pervaporation (PV) process. Burshe et al. [38] studied the dehydration of glycerol water mixture using Nafion®, cellulose triacetate, polyimide, carboxylated polyvinyl chloride, and polyethersulfone membranes through PV. The feed sample contained 95% glycerol and 5% water, by mass. Using 30 °C operating temperature, the highest distillate flux was 0.2–1.45 kg/m^2 h when the Nafion membrane was applied. Khairnar and Pangarkar [39] investigated the homo and copolymer membranes for dehydration of glycerin–water mixture using PV. Results indicated that all applied membranes were highly water selective, and homo-polymers gave better distillate flux than copolymers. Moreover, in their work, no effect on selectivity of the membranes was observed by changing the operating variables. It is worth quoting that PV has a relatively low permeation rate and is useful when highly concentrated glycerol mixture needs to be processed. However, an alternative with a higher permeation rate is necessary when dilute glycerol solutions should be processed.

In this work, sweeping gas membrane distillation (SGMD) was used for water removal from dilute glycerol–water solutions (a simulated wastewater sample). A commercial hydrophobic polymeric membrane was used for the experiments. The effect of operating variables on the distillate flux was investigated. Taguchi optimization and sensitivity analysis were carried out for the studied factors. To the best of our knowledge, in the open literature this was the first attempt to use the MD process for dewatering the dilute glycerol wastewater sample.

2. Materials and methods

2.1. Materials

Feed samples (synthesized wastewater samples) were prepared by dissolving the analytical grade glycerol (ultra-pure, Fluka, Switzerland) in distilled water with various concentrations, 1, 3 and 5 mass%. A commercial hydrophobic membrane made of PTFE with 0.22 μm pore size was used for the experiments. The specifications of the applied membrane are presented in Table 2.

2.2. Experimental apparatus and procedure

A SGMD experimental apparatus was used in this work. The setup consisted of a plate and frame module made of Plexiglas^{TM}, a

Table 2
Specifications of applied membrane in this work.

Material	Pore size (μm)	Thickness (μm)	Porosity (%)	Manufacturer
PTFE	0.22	175	70	Millipore