Journal of Food Engineering 224 (2018) 71–79

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Progressive stirred freeze-concentration of ethanol-water solutions

M. Osorio [a], F.L. Moreno [b], M. Raventós [c], E. Hernández [c], Y. Ruiz [b, *]

[a] Master in Design and Process Management, Universidad de La Sabana, Campus Universitario del Puente del Común, Km 7 Autopista Norte de Bogotá, Chía, Cundinamarca, Colombia
[b] Agroindustrial Process Engineering, Universidad de La Sabana, Campus Universitario del Puente del Común, Km 7 Autopista Norte de Bogotá, Chía, Cundinamarca, Colombia
[c] Agri-Food Engineering and Biotechnology Department, Universidad Politécnica de Cataluña (UPC) C/Esteve, Terradas, 8, 08860, Castelldefels, Barcelona, Spain

ARTICLE INFO

Article history:
Received 6 October 2017
Received in revised form
14 December 2017
Accepted 28 December 2017
Available online 2 January 2018

Keywords:
Freeze concentration
Ethanol
Response surface
Dimensionless analysis

ABSTRACT

Progressive freeze-concentration is a technology to separate water from solutions by freezing. In the present investigation, ethanol-water solutions were freeze-concentrated by the progressive stirred technique. The freezing stage was carried out in a stirring vessel. Solute recovery by the fractionated thawing of ice was also studied. The effects of stirring speed (500, 1000, and 2000 rpm), initial concentration of the solution (3%, 5%, and 8% ethanol), and temperature of the thawing stage (0, 10, and 20 °C) on the solute yield and average distribution coefficient were determined using response surface analysis. The ethanol concentration was found to have increased by 1.3 and 2.1 times at the end of the freeze concentration process. It was found that the initial concentration had a significant effect on the distribution coefficient. In addition, the average yield was increased by 28% by fractionated thawing. Subsequently, a non-dimensional analysis of the distribution coefficient was developed to yield a model to predict the distribution coefficient as a function of the Reynolds number, the relationship between the average ice growth rate and the stirring speed, the agitator diameter, and the liquid fraction. This technique proved to be valid with respect to the concentration of ethanol-water solutions, with better yields being obtained at low initial concentrations. This model is the first of its kind to describe the ethanol-water interaction in agitated freeze-concentration systems.

1. Introduction

Freeze-concentration (FC) is a technique defined as a method to remove water from solutions by freezing until the formation and separation of ice crystals occurs. In this way, it is possible to obtain a product of greater concentration than the initial solution while preserving its quality (Sánchez et al., 2009). In general, there are three types of FC: suspension, block and film FC. The first is the most used in the industry for its high efficiencies, although it is associated with high operating and investment costs (Miyawaki et al., 2005; Auleda et al., 2011); which is why the researchers have looked for ways to make other techniques improve their performance (Moreno et al., 2014a; Moreno et al., 2014b).

Film freeze-concentration is an FC method, in which unidirectional crystallization of the water present in the solution takes place. In this technique, a single layer grows while being adhered to the walls of the heat exchange surface. The solution is concentrated as it is circulated on the surface of the formed ice, which grows layer by layer. Due to the formation of a single ice layer, separation of the concentrated solution is facilitated (Liu et al., 1997; Miyawaki et al., 2016a; Miyawaki et al., 2016b; Miyawaki et al., 2005; Sánchez et al., 2009). Film FC can be classified into two types: plate FC (also called falling film) and progressive FC, as proposed by (Sánchez et al., 2009, 2011). The main difference between the two techniques is the geometry of the equipment used for the formation of crystals; the falling film FC uses a plate whereas in the progressive FC, concentration of the solute occurs at the bottom or on the walls of a tank or pipe (Sánchez et al., 2009). Further, the progressive FC equipment can be classified into two types based on their design — vertical progressive FC and tubular progressive FC (Miyawaki et al. 2005, 2015; Miyawaki and Kitano, 2015; Miyawaki et al., 2016a,b).

Agitated tanks are used for vertical progressive FC; the growth of a single ice crystal occurs at the base of the tank while it is submerged at a specific velocity in the refrigerant (Miyawaki et al., 2012). On the other hand, a tubular progressive FC consists of two

---

* Corresponding author.
E-mail address: ruth.ruiz@unisabana.edu.co (Y. Ruiz).

https://doi.org/10.1016/j.jfoodeng.2017.12.026
0260-8774/

Nomenclature

$X_{s\ 0}$	Ethanol mass fraction in the initial solution (w/w)
$X_{s\ ice}$	Ethanol mass fraction in ice (w/w)
$X_{s\ liq}$	Ethanol mass fraction in the freeze-concentrated liquid fraction (w/w)
$m_{s\ liq}$	Solute mass in the liquid fraction (kg)
$m_{s\ 0}$	Solute mass in the initial solution (kg)
m_{ice}	Mass of the ice sheet (kg)
m_{liq}	Collected liquid mass (kg)
m_0	Initial mass (kg)
ρ_{ice}	Ice density (kg/m^3)
ρ_w	Water density (kg/m^3)
ρ_{et}	Ethanol density (kg/m^3)
ρ	Solution density (kg/m^3)
μ_w	Water viscosity (kg/ms)
μ_{et}	Ethanol viscosity (kg/ms)
μ	Solution viscosity (kg/ms)
$\overline{K}_{app}$	Average distribution coefficient (dimensionless)
Y	Solute yield (dimensionless)
CI	Concentration index (dimensionless)
$\overline{v}_{ice}$	Average ice growth rate (μm/s)
f	Liquid fraction (dimensionless)
Ac	Area under the Y vs. f curve (dimensionless)
D_a	Diameter of the agitator (m)
N	Stirring speed (rps)
r	Vessel radius (m)
t	Time of freezing (h)
h	Ice layer height (m)
T_H	Heating temperature (°C)
C_o	Initial concentration (w/w)
V_a	Stirring speed (rpm)

connected tubes; the solution circulates inside the tube while the refrigerant circulates outside, thus generating a solid phase on the inner walls and the concentrated solution flows through the ring that has not yet frozen (Miyawaki et al., 2005). Both techniques have delivered promising results using which it has been possible to demonstrate that both geometries are efficient. In the case of tubular progressive FCs, their high efficiency and ease of scaling is emphasized while in the case of vertical progressive FCs, it has been possible to obtain crystals of high purity (Miyawaki et al., 2016a,b). Recently, there was a report on hybrid equipment (Ojeda et al., 2017), which functions as a vertical progressive FC but manages to generate the ice film not only at the bottom but also on the inner walls of the tank, similar to a progressive tubular FC. One of the most important challenges faced by progressive FCs is in increasing the solute recovery (increased separation efficiency) as ice tends to grow with impurities. One strategy to increase the recovered amount is to apply controlled thawing to ice after the FC process, similar to what was is done during block FC, also known as freeze-thaw process (Robles et al., 2016). Controlled thawing is usually performed on other equipment than those used to make the progressive FC (Miyawaki et al., 2012; Moreno et al., 2014b). Therefore, research is being conducted to design hybrid equipment that allows high separation efficiencies, easy scalability, and allows the controlled recovery of solutes within the same unit.

Progressive FC has been used to recover solutes from products such as wine must (Miyawaki et al., 2016a,b; Hernández et al., 2010), ethanol–water solutions (Haizum et al., 2015), juices (Miyawaki et al., 2016a,b), and coffee extracts (Gunathilake et al., 2014). The comprehension of ethanol – water solutions is useful for the application of FC to alcohol-containing matrices, such as wines or beers, which present concentration difficulties due to the loss of ethanol and volatile components related to the flavor of the drinks. A water ethanol mixture has a crystallizing line and a melting line that are separated, and thus it can exist together both liquid and solid phases (Kuwahara and Ohkubo, 2010). This condition makes the ethanol water mixtures favorable to be separated by freeze concentration techniques, in a temperature range between 0 and -70 °C, according to the phase diagram proposed by (Ohkubo et al., 1997).

The objective of this work was to evaluate a progressive FC technique that combines elements of vertical and tubular progressive FCs and allows us to recover ice in the same equipment; this process will be called progressive stirred freeze-concentration (PSFC) assisted by fractionated thawing. Ethanol-water model solutions were used to study the technique and the effect of initial concentration and stirring speed during the PSFC process on the average distribution coefficient and solute yield were determined. At the same time, a non-dimensional analysis was performed to propose an empirical mathematical model that allows us to calculate the classic variables of the FC in the proposed technique.

2. Materials and methods

2.1. Materials

Ethanol-water solutions were prepared from distilled water and commercial grade ethanol (Quimics Dalmau, Barcelona, Spain) with an initial concentration of 93.3% (w/w) ethanol.

2.2. Methods

The effect of stirring speed (V_A) and initial concentration (C_O) on the concentration of ethanol in the PSFC equipment was studied. Similarly, the effect of thawing temperature (T_H) on the recovery of solutes was also studied. A freezing temperature of −15 °C was defined for the initial concentration interval studied. This condition avoids a fast freezing that can lead to the occlusion of solutes, and also allows a desirable average freezing rate, according to those reported in literature (Nakagawa et al., 2010; Moreno et al., 2014b; Petzold et al., 2016). All the FC tests were performed for 1 h.

The concentration of ethanol in each of the samples was analyzed using an electronic densimeter (DMA 35, Anton Paar) capable of reading ethanol concentration data in terms of percentage weight/weight, percentage volume/volume, density, and degrees Brix.

2.2.1. Freeze-concentration protocol

The tests were performed in the freeze-concentration equipment, similar to the one shown in Fig. 1. In the receiving tank (1), 1400 g of a previously refrigerated sample was placed; the sample was held until it reached a temperature of approximately 0 °C in a cooler. The tank, which has a total height of 24 cm and diameter of 11 cm is made of AISI 304 stainless steel, and has an outer jacket (3) to allow the cooling liquid to flow; the cooling liquid is composed of a mixture of ethylene glycol and water (53% w/w) circulating in the thermostatic bath (4) equipped with a temperature controller (6).