Kinetics of soybean oil extraction using ethanol as solvent: Experimental data and modeling

Tatiane Akemi Toda, Mirian Megumi Sawada, Christianne E.C. Rodrigues *

*Separation Engineering Laboratory (LES), Food Engineering Department (ZEA/FZEA), University of São Paulo (USP),
PO Box 23, 13635-900 Pirassununga, SP, Brazil*

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ABSTRACT

The main aim of this work was to obtain experimental data of the extraction kinetics of soybean oil and free fatty acids (FFA) for systems containing an expanded mass of soybean (collets) and ethanol with different hydration levels (0 and 5.98 mass% of water) at temperatures of 40, 50 and 60 °C. Through the obtained experimental data it can be seen that increasing the hydration level of ethanol suppresses the soybean oil extraction but increases the FFA extraction, while the temperature favors the solubility of both fatty compounds. The experimental data were correlated using a model proposed by So and Macdonald (1986. Can. J. Chem. Eng. 64, 80–86), which enables determination of the mass transfer coefficients in the washing and diffusion steps, and a model proposed by Perez et al. (2011. J. Food Eng. 105, 180–185) that enables the estimation of diffusivity coefficients. High values of the coefficient of determination ($R^2 \geq 0.9961$) and low values of the average relative deviation ($ARD \leq 4.74\%$) were obtained, showing that the models used were suitable to describe the kinetics of extraction of the oil and minor compounds present in soybean. The value of the diffusivity coefficient for soybean oil increased with increasing temperature and with decreasing hydration level in the solvent, presenting values of 3.61 to $5.36 \times 10^{-11} \, \text{m}^2 \, \text{s}^{-1}$.
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1. Introduction

According to the United States Department of Agriculture (USDA, 2014), during the period of 2008 to 2013 soybean oil represented 27 to 28% of global vegetable oil production, which means about 44 million metric tons of this oil were consumed worldwide, becoming the second most consumed oil in the world, just behind palm oil (63 million metric tons or 35% of the consumption) (SoyStats, 2015).

The recovery of the oil contained in the soybean is accomplished by extraction using solvents due to the low oil content in the oleaginous material (15 to 20%). The most widely used solvent for the extraction of oil in the oily matrix is a petroleum distillate containing a mixture of *n*-hexane isomers (boiling range of 65 to 71 °C) industrially known as hexane.

Hexane is a nonpolar solvent that enables prompt dissolution of the oil and water immiscibility. This solvent presents a low latent heat of vaporization, high stability, low corrosion and enables obtaining the defatted meal with an acceptable odor and low residual oil content, properties that are considered desirable in vegetable oil extraction (Johnson and Lusas, 1983). However, hexane also presents considerable disadvantages including high toxicity, since the mixture can present 45 to 70% *n*-hexane, a compound considered a neurotoxin in the USA due to its proven toxicity at high concentrations (Hammond et al., 2005). In addition, this solvent is highly flammable and is considered a dangerous air pollutant, apart from being obtained from a nonrenewable source of raw material that carries with it the misfortunes linked to the oil market (Russin et al., 2011).

Such disadvantages of hexane have challenged researchers to establish substitute solvents for the vegetable oil extraction (Johnson and Lusas, 1983; Kuk and Hron, 1998; Russin et al., 2011). The most cited substitutes are: water with or without enzyme addition (Campbell et al., 2011; Rosenthal et al., 1996), terpenic hydrocarbons (limonene, α-pinene, p-cymene) (Li et al., 2014), supercritical fluids (carbon dioxide) (Ayas and Yilmaz, 2014; Rebolleda et al., 2012, 2014), and short chain alcohols, especially ethanol and isopropanol (Hu et al., 1996; Li et al., 2014; Martins and Peluzio, 2015; Oliveira et al., 2012a,b, 2013; Rodrigues and Oliveira, 2010; Rodrigues et al., 2010; Sawada et al., 2014; Sinichi and Diosady, 2014), among others.

Among the advantages of using ethanol as a hexane substitute can be cited its good operational safety and low toxicity. In addition, this alternative solvent can be obtained from renewable sources. This solvent allows the production of high quality oil with low levels of free fatty acids, besides enabling the removal of anti-nutritional factors such as gossypol, aflatoxins and chlorogenic acids (Hron et al., 1982). Beyond the good quality of the extracted oil, studies report that, generally, vegetable oil extraction with ethanol enables a larger extraction of sugars, phospholipids, pigments, waxes, compounds that gives bitterness to the defatted meal, etc., allowing a better quality meal to be obtained in relation to that obtained with hexane (Johnson and Lusas, 1983).

According to Aguilera (2003), solid–liquid extraction is a separation process involving contact between a fluid phase and a solid phase that allows the transfer of solute from the solid matrix to the solvent. Specifically in the case of oily solid matrices, during the extraction process the concentration of oil in the solid matrix varies with time, making it possible to visualize a series of stages during the contact period between the solvent and the solid such as: solid involvement by the solvent; a stage of internal diffusion that comprises solvent penetration and diffusion through the oily matrix cell wall until it reaches the lipid bodies; solubilization of lipid compounds by the solvent; a stage of internal diffusion that includes transport of the extract solution (oil/solvent) to the outside of the solid matrix through the cell wall; and the external diffusion that comprises transport of the solute from the surface of the solid matrix to the bulk solution (Kemper, 2005).

In the process stages that involve molecular diffusion, characterized by molecular random movements caused by a gradient of concentration, this phenomenon can be described by Fick's laws, enabling us to estimate the diffusion coefficient or diffusivity that is an important transport property useful in equipment design involving mass transfer (Perez et al., 2011). Fick's first law is useful under conditions of a stationary state and Fick's second law is applicable to non-stationary systems and short periods of time, conditions in which changes in solute concentration with time and position within the solid matrix are observed (Aguilera, 2003; Chan et al., 2014; Lloyd and Wyk, 2011).

In fact, an extraction kinetic study is a very important tool in the delineation of the process, which allows the knowledge of the process' variable effects such as solid/solvent ratio, temperature and hydration level of the solvent on the rate of extraction of the compound of interest.

The main objective of modeling the kinetic curves is to define parameters for process design. These parameters are then used to predict the total curve of extraction and, in this way, to estimate the viability of the process on an industrial scale. A model must be a mathematical tool that reflects the physical behavior of the actual structure and experimental observations. Thereby it can be used as a simulation tool and then in industrial applications of this process.

Different mathematical models have been suggested to analyze the extraction kinetics of vegetable oils from different oily matrices and solvents such as: pressed, flaked or ground canola seed using hexane as solvent (Fernández et al., 2012; So and Macdonald, 1986), ground green coffee using hexane (Dibert et al., 1989), ground corn grains and ethanol as solvent (Chien et al., 1990), jojoba seeds and hexane (Allawzi et al., 2005), olive cake and hexane or azeotropic ethanol (Meziane et al., 2006; Meziane and Kadi, 2008), ground *Rosa rubiginosa* seeds and ethanol (Franco et al., 2007), hazelnut seeds and ethanol (Franco et al., 2009), expanded mass of sunflower seeds (collets) and hexane (Baümler et al., 2010, 2011), ground sunflower seeds and hexane (Perez et al., 2011), solid coconut waste and hexane (Sulaiman et al., 2013), ground hemp seeds and hexane (Kostic et al., 2014), castor bean seed cake and ethanol (Amarante et al., 2014), and flaked soybean and ethanol or mixtures of ethanol and alkyl esters (Dagostin et al., 2015).

It can be inferred that in most published studies about the kinetic extraction of oil using solvents, the main focus was determination of the diffusivity of the total material extracted without differentiation of the classes of compounds.

In fact, while the kinetics of extraction of oils has been widely studied, only a few studies have been published monitoring the kinetics of extraction of the minor compounds: chlorogenic acids (Dibert et al., 1989), tocopherols, phospholipids and waxes (Baümler et al., 2010, 2011; Fernández et al., 2012) and gossypol (Saxena et al., 2012). This monitoring is, however, of great importance for the delineation of the process.

Free fatty acids are compounds that impact negatively on the quality of an extracted oil. Thus, it can be inferred that knowledge of the extraction rate of this minor compound class under determined conditions of temperature and type of solvent can enable the production of crude oils with lower acidity levels. In fact, crude oils with a lower level of free fatty acids lead to an exemption from further steps of refining which the oil must undergo in order to be labeled as edible.

Based on the aforementioned information, in this work, experimental data were determined on the kinetics of extraction of oil and free fatty acid from an expanded soybean mass (collets) using ethanol as solvent, under absolute and azeotropic degrees, at three temperature levels, 40, 50 and 60 °C. Mathematical models suggested by Perez et al. (2011) and So and Macdonald (1986) were used to describe the experimental data, enabling calculation of the mass transfer coefficients of the washing and diffusion steps and also the diffusivity coefficient.

2.   Materials and methods

2.1.   *Materials*

The expanded soybean mass (collets) was kindly supplied by the Brazilian company Granol S/A (Bebedouro, SP, Brazil). The soybean was cracked industrially, dehulled, cooked, flaked and expanded to form collets. The soybean collets were then stockpiled at −20 °C to prevent enzymatic degradation until submitted to the extraction process.