Industrial Crops and Products 74 (2015) 69–75

Contents lists available at ScienceDirect

Industrial Crops and Products

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

Extraction of soybean oil using ethanol and mixtures with alkyl esters (biodiesel) as co-solvent: Kinetics and thermodynamics

João Luiz Andreotti Dagostin, Danielle Carpiné, Marcos L. Corazza*

Department of Chemical Engineering, Federal University of Paraná, 81531-990 Curitiba, PR, Brazil

ARTICLE INFO

Article history:
Received 7 January 2015
Received in revised form 9 March 2015
Accepted 27 April 2015
Available online 20 May 2015

Keywords:
Soybean oil
Extraction
Kinetic
Ethanol
Biodiesel

ABSTRACT

The kinetics and thermodynamics of soybean extraction using ethanol and ethanol + alkyl esters mixtures (biodiesel) as co-solvent were investigated. The extraction parameters investigated were temperature (25, 40 and 55 °C) and biodiesel to ethanol mass ratio. The extractions were carried out in batch mode at a fixed solvent to soybean mass ratio (4:1). Three different kinetic models were used to correlate the overall extraction curves, namely a first-order, second-order, and a mass transfer model based on Fick's Law. The mass transfer model presented a mean absolute relative deviation of 4.7%, while de first and second-order models showed values around 10.1% and 4.4%, respectively. From the experimental results obtained, it was observed that higher temperatures affected positively the extraction yields. Furthermore, higher mass ratio of biodiesel to anhydrous ethanol provide higher extraction yields, at temperatures of 25 and 40 °C. At 55 °C, the extraction yields were not improved when adding the biodiesel as co-solvent to the anhydrous ethanol. On the other hand, using hydrated ethanol as solvent resulted in lower extraction yields, so higher amounts of biodiesel were necessary to reach the same levels of extractions performed using anhydrous ethanol. The thermodynamic analyses showed that both ΔH° and ΔS° are positive for this process, while negative values of ΔG° were found, that means the process evaluated is characterized as endothermic, irreversible and occurs spontaneously.

1. Introduction

Soybean (*Glycine max* L.) is the most cultivated oilseed crop in the world, mainly because it combines moderate oil content and high amount of protein, which represents approximately 20–40% of its total mass, respectively (Shukla et al., 1992). Data from the United States Department of Agriculture indicate an estimated global soybean production in 2013/14 of 283.95 million metric tons. This estimate shows US ranking as first in world on soybean production, followed by Brazil and Argentina, representing 31.52%, 30.82% and 19.05% of global production, respectively (USDA, 2014).

The extraction is the most important process applied in soybean oil production, occurring after the grains preparation steps, as dehulling, cracking and flaking. Most widely studied methods for the oil extraction from plants involve either mechanical pressing (Subroto et al., 2015; Patil and Ali, 2006) or solvent extraction (Kostić et al., 2014); the last may be accomplished using solvent at both thermodynamic conditions: at room temperature and pressure or under subcritical (Liu et al., 2014; Ndlela et al., 2013) and supercritical (Jokić et al., 2010) conditions. Commonly, soybeans are solvent-extracted using commercial "hexane", a mixture of hydrocarbons with a boiling point around 65–69 °C that contains about 65% *n*-hexane and 35% of cyclopentane and hexane isomers (Kemper, 2005). This solvent presents several advantages, as low latent heat of vaporization, complete solubility with oil, low corrosiveness, easy recovery and water immiscibility. However, there are also disadvantages associated, mainly concerning environmental, safety and health issues. The US Environmental Protection Agency (EPA) has published online, through the Integrated Risk Information System (IRIS), a complete toxicological review about the *n*-hexane (Benedict et al., 2005). This review states that individuals exposed to *n*-hexane vapor may exhibit injuries in the nervous system, besides other symptoms as irritation of the respiratory tract and eyes. Another problem associated with hexane is that its vapor is heavier than air, forming a highly explosive mixture with the last, even when small amounts are dispersed (Kemper, 2005).

Several alternative solvents have been proposed to replace hexane in vegetable oil extraction including the use of trichlorethylene, *n*-heptane, ethanol, isopropanol and *n*-propanol (Arnold and

* Corresponding author at: Department of Chemical Engineering, Federal University of Paraná, PO Box 19011, Polytechnic Center, Curitiba 81531-980, PR, Brazil. Tel.: +55 41 33613190.
E-mail address: corazza@ufpr.br (M.L. Corazza).

http://dx.doi.org/10.1016/j.indcrop.2015.04.054
0926-6690/

Choudhury, 1962; Seth et al., 2007; Gandhi et al., 2003). Among these, the ethanol seems to be a promising solvent for soybean oil extraction in the US and Brazilian industries. Both countries are pioneers in the production of ethanol and soybean, ranking first and second for both commodities, respectively. According to the Renewable Fuels Association (RFA), the US and Brazil produced 13,300 and 6267 millions of gallons of ethanol in 2013, respectively, corresponding to 83.52% of the total ethanol produced in the world. Despite the lower total production, Brazilian ethanol has the advantage of lower cost of production and higher productivity per acre due to the use of sugarcane as feedstock (Budny, 2007). With regard to health and safety, ethanol presents lower risk than hydrocarbons. There is no evidence of toxicity by inhalation of ethanol (Nadeau et al., 2003; Clayton and Clayton, 1994), and it presents lower flammability compared to hexane (Anderson, 2005).

Due to its polar nature, however, ethanol is a weaker oil solubilizing agent than the hexane. Ethanol presents a limited solubility with triacylglycerols and is capable of solubilizing not only the oil present in the matrix but also water and other polar components. If hydrated ethanol is applied as solvent, its ability of solubilizing triglycerides is further decreased, gradually limiting the process efficiency (Dagostin et al., 2015). In order to increase the solubility of a component into another some thermodynamic artifices can be used, as increasing the pressure and temperature or adding a co-solvent to the mixture. By definition, a co-solvent is a substance that presents complete solubility in both solute and solvent and improves the overall solubility of the system.

Studies have shown that biodiesel is able to solubilize oils and alcohols at adequate proportions and operational temperatures (Dagostin et al., 2015; Silva et al., 2013). Thus, biodiesel could be a feasible co-solvent to be used together with ethanol in oil extraction processes.

Biodiesel is a mixture of alkyl esters commonly produced by a transesterification reaction between triglycerides (such as soybean oil) and an alcohol (usually short chain alcohols as methanol or ethanol) in the presence of a catalyst yielding the alkyl esters and glycerol as by-product (Fukuda et al., 2001). Taking into account the integration between the oil extraction plant and biodiesel production unit, the biodiesel (ethyl esters) application as co-solvent for soybean oil extraction is a promising strategy. In this context, the main subject of this study was to evaluate the kinetics and thermodynamics aspects of soybean oil extraction using (ethanol + biodiesel) mixtures in batch systems. The experimental variables studied were time, temperature and solvent-to-solids ratio for the soybean oil extraction.

2. Experimental procedure

2.1. Material

Soybean flakes (*G. max*) were gently supplied by IMCOPA (Araucária, Brazil). These were vacuum-packed in high-density polyethylene bags, which were stored under refrigeration (−12 °C) before analyses. Fatty acid ethyl esters (ethylic biodiesel) containing 97.6% esters content (wt%) were produced as previously reported (Dagostin et al., 2015). The anhydrous (>99.8% v/v) and hydrated ethanol (96% v/v) of analytical grade were purchased from PANREAC (Barcelona, Spain). The chemicals were used as received, without further purification.

2.2. Methods

2.2.1. Extraction apparatus and experimental procedure

Batch extractions were performed with weighed portions of soybean and pre-determined amounts of solvent in Erlenmeyer flasks (50 mL). The solvents used were anhydrous ethanol or hydrated ethanol 96% (v/v) and their mixtures with biodiesel, at different solvent to biodiesel mass ratios. Sample and solvent were previously heated/cooled to the extraction temperature prior to extraction. Just after mixing the solvent with the soybean, these were immediately sealed with Parafilm M™ and covered with PVC film to avoid solvent loss. The temperature of extraction was controlled by a Dubnoff reciprocal shaker (Ethik Technology, model 304-TPA) at 25, 40 or 55 °C applying vigorous shaking. At the end of a predetermined extraction time (1, 2, 5, 10, 15, 30, 60, 90, 120 and 180 min), the bulk phase was immediately collected using a syringe fitted with a paper membrane (14 μm) and transferred to tubes. Each experiment was carried out at least in duplicate. The oily extract was determined gravimetrically by evaporating the collected samples (60 °C, 24 h). The volatile fraction was considered as ethanol, while the heavier fraction was composed by soybean oil and fatty acid ethyl esters. Mass balance was made to calculate the amount of oil extracted. Extraction yields are expressed as amount of extract (mass) per 100 g of soybean.

Total oily extract was obtained by two Soxhlet exhaustive types of extraction following the AOCS Ac 3–44 method (AOCS, 2001). The first exhaustive extraction used petroleum ether (5 h) and the last anhydrous ethanol (7 h).

2.2.2. Kinetic modeling

Although power law models are used extensively in adsorption processes, they are also able to describe well solid–liquid extraction processes (Man et al., 2012; Sayyar et al., 2009). An equation in the form of power law is a relationship of $Y = kX^n$, where X and Y are the variables of interest, n is called the exponent of the power law and k is a constant. For an extraction kinetic, it becomes as described by Eq. (1).

$$\frac{dC}{dt} = k(\Delta C)^n = k(C_\infty - C)^n \quad (1)$$

where k is the constant of extraction rate (min^{-1}), $C\infty$ is the solute concentration at equilibrium (g solute g^{-1} soybean), C is the concentration of solute extracted at a given time (also in terms of g solute g^{-1} soybean) and n is the order of the equation.

2.3. First-order model

If at the beginning of the process $t = 0$, the concentration of solute in the solvent is $C = 0$; therefore, Eq. (1) takes the form:

$$C = C_\infty(1 - exp^{-kt}) \quad (2)$$

2.3.1. Second-order model

With the initial conditions at $t = 0$ with $C = 0$, the following equation is obtained from Eq. (1) after integration and rearranging:

$$C = \frac{t}{\frac{1}{kC_\infty^2} + \frac{t}{C_\infty}} \quad (3)$$

2.3.2. Mass transfer kinetic model (MTKM)

The mass transfer kinetic model used in this work was derived from the Fick's law of diffusion for an infinite slab in a well stirred solvent of infinite volume, according to Chan et al. (2014) and Crank (1975). The basic assumptions used in this work to simplify the problems of mass transfer were

(a) The soybean flakes are symmetrical, in the form of infinite plates measuring 2*L*.
(b) The solid particles are considered a porous pseudo-homogeneous medium. The concentration of solute in the solid particle depends on time and thickness.