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Effects of different alcoholic extraction conditions on soybean oil yield, fatty acid composition and protein solubility of defatted meal

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ABSTRACT

The aim of this work was to evaluate the feasibility of replacing hexane with ethanol in the soybean oil extraction process. The use of ethanol has very attractive advantages, including a low toxicity, good operational security, as well as being obtained from a biorenewable source. Thus, in this study solid–liquid extractions were performed under equilibrium conditions in which the variables evaluated were temperature (ranging from 40 to 90 °C) and solvent hydration (0 to 12 mass % of water). Results showed that an increase in water content of the solvent strongly suppressed the extraction of oil, whereas an increase in temperature increased the extraction of oil. For proteins, the opposite behavior was observed, where an increase in the water content of the solvent increased the extraction of such compounds, and an increase in temperature decreased the protein content in the extracted phase. The evaluation of the chemical profile and fatty acid composition of the oils obtained via ethanol showed that they had a composition typical of soybean oil, regardless of the extraction condition. The quality of the protein fraction from the oil extraction was evaluated by nitrogen solubility and thermal analysis. The evaluation indicated that the protein fraction is strongly influenced by the presence of water in the solvent and by temperature. These results indicate that it is technically feasible to use ethanol in the soybean oil extraction process; however, the hydration conditions of the solvent and the process temperature must be controlled due to their influences on the protein fraction characteristics of the defatted meal.

1. Introduction

Vegetable oils are generally obtained through mechanical pressing or solvent extraction. Hexane is the solvent most traditionally used by oil processing industries because it is low cost and highly solubilizing (Hammond, Johnson, Su, Wang, & White, 2005). However, the use of this solvent has many disadvantages and negative consequences due to its non-renewable fossil origin and high flammability, leading to concerns for environmental and public health (Johnson & Lusas, 1983; Lanska, 1999; L'Hocine, Boye, & Arcand, 2006; Li, Pordesimo, & Weiss, 2004; Oliveira, Barros, & Gimenes, 2013; Tabtabaei & Diosady, 2013).

The extraction of soybean oil with ethanol is an attractive alternative to petroleum solvents, such as hexane. Ethanol displays interesting characteristics that makes it environmentally attractive: This solvent is produced by a biotechnological process that does not generate toxic wastes and is considered safe for human health. Economically, the advantages of ethanol are also evident because it is produced at a large scale in Brazil and can be easily recovered for subsequent reuse (Oliveira, Garavazo, & Rodrigues, 2012). The use of this type of solvent can subsidize the production of more nutritious "green seal"-labeled vegetable oils, which are free of harmful chemicals and can be safely used in processed foods (L'Hocine et al., 2006; Oliveira, Oliveira, Aracava, & Rodrigues, 2012; Oliveira et al., 2013; Rodrigues, Aracava, & Abreu, 2010; Rodrigues & Oliveira, 2010).

In recent decades, soybean production has shown significant growth (SoyStats, 2013). This can be attributed to several factors, but the main driving force is the increased use of the oilseed as an important source of vegetable protein (Bader, Oviedo, Pickardt, & Eisner, 2011). Soybean is a food rich in protein, fiber and oil, in addition to being an important source of minerals and vitamins. Its nutritional value depends on the high content of easily digestible proteins, which are rich in essential amino acids and are sources of good quality oil (Corley, Woldeghebriel, Corley, & Murphy, 1999; Lynch, Berger, & Fahey, 1986; Lynch, Berger, Merchen, Fahey, & Baker, 1987).

The need for proteins with specific functional properties is due to increasing demands for its use as an ingredient in food product formulations. Many properties are governed by the physical and chemical behavior of these molecules in liquids. Among these functional properties, protein solubility is of great importance because of its influence on other features of proteins in emulsification, gelation and foaming (Heywood, Myers, Bailey, & Johnson, 2002; L'Hocine et al., 2006; Sorgentini, Wagner, & Añón, 1995; Vojdani, 1996).

The measurement of nitrogen solubility in soybean meal is important because it reflects the intensity of protein denaturation indicating the magnitude of heat treatment received by the defatted material.

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Such measurements can be used as controls as references for uniform operating procedures to improve nutritional values and can also be used to characterize the product quality (Heywood et al., 2002; Liu et al., 2008; Smith, Rackis, Isnardi, Cartter, & Krober, 1966; Vishwanathan, Singh, & Subramanian, 2011).

The aim of this study was to evaluate the technical feasibility of using ethanol as a solvent to obtain soybean oil. In this context, the extraction yield and the fatty acid composition of oils obtained under different experimental conditions were evaluated.

In addition, the behavior of the soy protein fraction was assessed. The solid materials (raffinate phase) resulting from soybean oil extraction experiments using ethanol as the solvent with different levels of hydration (i.e., 0%, 6% and 12% by mass), in temperatures ranging from 40 to 90 °C, were evaluated by the nitrogen solubility index and DSC. In terms of solubility and thermal behavior, the protein fractions obtained via alcohol extraction were compared with soybeans from different stages of vegetable oil production using the conventional solvent hexane.

2. Materials and Methods

2.1. Materials

Absolute ethanol (purity greater than 99.8%), purchased from Merck (Darmstadt, Germany), and aqueous solvents with water contents of 5.91 ± 0.27 and 11.92 ± 0.58 mass %, prepared by diluting absolute ethanol with deionized water (Millipore, Milli-Q, Bedford, MA, USA), were used as solvents. These solvents were coded and are hereafter referred to as etw0 (absolute ethanol), etw6 and etw12, aqueous solvents with approximately 6 and 12 mass % of water, respectively.

Soybeans were industrially cracked, dehulled, flaked and expanded to form soybean collets, which were kindly supplied by Granol, a Brazilian company dedicated to the production and marketing of grains, bran, vegetable oils and biodiesel (Bebedouro, SP, Brazil). The soybean collets were stored at −20.0 °C to prevent enzymatic degradation until submitted to the extraction process. Soybean collets were ground prior to the extraction experiments due to the high variability of sizes and shapes. Particle sizes between 10 and 14 mesh were used in the ethanol extractions.

Soybeans in other stages (i.e., non-collets) of the industrial process (after flaking, after solvent extraction using hexane, and after meal desolventizing/toasting) were also evaluated for comparison purposes. These samples were also kindly supplied by the Granol company.

2.2. Analysis

2.2.1. Proximate Analysis

Soybean collets were submitted to proximate analysis for crude protein (AOCS Ba-4f; AOCS, 1998) (Leco, model FP-528, St. Joseph, MI, USA), moisture (AOCS Ac 2-41; AOCS, 1998), oil (AOCS Am 2-93; AOCS, 1998), ash (AOAC, 2007), and fiber content (Van Soest, Robertson, & Lewis, 1991). A nitrogen-to-protein conversion factor of 6.25 was used.

2.2.2. Oil Fatty Acid Composition

After extraction from collets according to Bligh and Dyer (1959), soybean oil was submitted to FAME gas chromatography to determine the fatty acid composition, according to the official methods AOCS Ce 2-66 and Ce 1-62 (AOCS, 1998). Under the following experimental conditions, the GC analysis was carried out on a Shimadzu 2010 AF capillary gas chromatograph (Japan), with an automatic injector (Shimadzu, model AOC 20i, Japan) and a flame ionization detector: a non-bonded poly(biscyanopropyl siloxane) phase 0.20 μm, 100 m × 0.25 mm i.d. capillary column (SP-2560, Supelco, Bellefonte, PA, USA); a helium carrier gas at a rate of 0.74 mL/min; an injection temperature of 250 °C; a column temperature of 140 °C (held for 5 min), increased to 240 °C (rate of 4 °C/min), held at 240 °C for 15 min.; a detection temperature of 260 °C; and an injection volume of 1.0 μL. The FAMEs were compared with external standards from Supelco (Bellefonte, PA, USA). Quantification was based on the area ratios of each fatty acid to the area of the internal standard, methyl tridecanoate C13:0 from Sigma-Aldrich (Bellefonte, PA, USA), using the response correction factors of the flame ionization detector and the conversion of methyl esters of fatty acids to fatty acid.

2.2.3. Nitrogen Solubility Index

The solubility was determined according to Morr et al. (1985) with minor modifications. Approximately 1.0 g of soybean meal, previously dried at 60 °C for 24 h and ground, was dispersed in 50 g of 0.1 M NaCl solution. The dispersions were adjusted to an appropriate pH (2.0, 4.0, 4.5, 5.0, 7.0 and 9.0) with 0.1 N HCl or 0.1 N NaOH, and kept under agitation with the aid of a magnetic stirrer for 2 h, at 25 °C. Then, the dispersions were transferred to centrifuge tubes and centrifuged at 5000 g for 30 min at 4 °C. The samples were filtered through a medium-flow filter paper (cellulose filter, 11 μm, Whatman qualitative filter paper, Grade 1). Aliquots of the filtrate were taken for determination of total nitrogen by a combustion method (AOCS Ba-4f; AOCS, 1998). The nitrogen solubility index (NSI) was calculated according to Eq. (1).

$$\mathrm{NSI}(\%) = \frac{Nitrogen^{Filtrate}(\%) \times NaCl\ \ solution\ \ wt\ (\mathrm{g})}{Nitrogen^{Sample}(\%) \times Sample\ \ wt\ (\mathrm{g})} 100 \quad (1)$$

2.2.4. DSC measurements

The thermal characteristics of the samples were assessed using a TA 2010 differential scanning calorimeter (DSC; TA Instruments, New Castle, DE, USA). Soybean meals, pre-dried at 60 °C for 24 h and ground, were weighed (10–15 mg) on an SA210 precision balance (Scientech, Boulder, CO, USA) in aluminum pans. Samples in open pans were kept for 48 h in an incubator with a beaker containing water, which ensured an environment with high humidity (close to 100%), at room temperature. After this conditioning period, the pans were hermetically sealed, then heated from 15 to 120 °C at a rate of 10 °C/min. A sealed empty pan was used as a reference. The denaturation enthalpy (ΔH) and the denaturation temperature (T_d) were calculated from the thermograms using the Universal Analyse V.3.9A software (TA Instruments). The equipment was calibrated using indium as a standard (TA Instruments). ΔH values were always expressed in J/g protein, using the data of the total sample in the pan and crude protein percentage in the sample. In this way, after measurement, the pans were drilled and placed in an oven at 105 °C for 48 h (AOAC, 2007) to ensure complete drying before the mass determination of protein on a dry basis. Duplicate measurements were taken.

2.3. Processing

2.3.1. Batch extraction

Soybean collets were submitted to the oil extraction process using absolute and aqueous ethanol with 6 and 12 mass % of water (etw0, etw6 and etw12) at different temperatures (40, 50, 60, 65, 70, 80 and 90 °C), at a solvent to solid mass ratio of 3 (Rodrigues et al., 2010). Batch extractions were performed in a 500 mL stainless steel isothermal cylindrical reactor, as described by Rodrigues et al. (2010) and Oliveira, Oliveira, Aracava, and Rodrigues (2012).

Soybean collets and selected solvents were weighed on an analytical balance with a readability of 0.0001 g (Adam, model PW 254, Milton Keynes, UK). The pre-set amounts of collets and solvent were transferred to the extractor and were agitated (175 rpm) for at least one hour after the temperature reached the desired level. Extraction experiments were carried out at least five times.