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Counter-current carbon dioxide extraction of fat from soy skim☆

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ABSTRACT

This research aims to investigate the use of counter-current carbon dioxide extraction method as a means to reduce residual fat in soy skim after the enzyme-assisted aqueous extraction of soybeans. Extractions with liquid CO_2 at 25 °C and 10.34 MPa and supercritical CO_2 at 50 °C and 25.16 MPa are compared. The effects of solvent-to-feed ratio (2.5–10), addition of ethanol as a modifier (5% w/w) and introductions of packing in the column are also analyzed. Results show that the highest reduction of fat content is obtained without modifier and with packing in the column at 50 °C and 25.16 MPa. At these conditions, the total fat content present in soy skim was reduced from 4.4 to 0.7%, with the protein content practically unaffected. ANOVA was applied to determine effects on fat and protein in soy skim, being the addition of packing in the column the most significant one. The fatty acid profile was also analyzed, with C18:2 being the predominant fatty acid present in all the soy skim samples. Gel electrophoresis indicated that supercritical CO_2 settings did not affect the polypeptide band patterns; however, higher pressure, temperature, and CO_2 flow significantly increased protein solubility in aqueous media (pH 2–10) compared with un-treated samples.

1. Introduction

Soybean oil is typically produced by direct solvent extraction with a petroleum distillate containing about two-thirds of *n*-hexane [1]. However, the increasing concern about safety and environmental emissions produced by organic solvents makes it essential to search for other extraction and separation techniques. Enzyme-assisted aqueous extraction is one of the potential alternatives that are increasingly considered for processing soybean oil. This method uses water and enzymes to recover free and emulsified oil [2,3], based on the insolubility of oil in water instead of the dissolution of oil [4]. The advantage of enzyme-assisted aqueous extraction, in addition to safety and environmental benefits, are that oil and protein are extracted simultaneously [1,5]. In addition, the oil requires less refining because of its low content of phospholipids [2,4] and also protein damage is less [1]. Moreover, the capital investment of enzyme-assisted extraction is lower with respect to conventional solvent extraction [1].

The enzyme-assisted extraction method is typically performed in two steps. First, oil and protein are extracted from the high-fiber solids. Then, the extracted mixture is centrifuged to produce oil-rich fraction (free oil and cream emulsion), oil- and protein-lean spent solids, and a protein- and sugar-rich aqueous phase (skim) [6]. The skim is a valuable co-product that is not produced in other extraction processes [5]. A typical soy skim contains about 11% of dry matter, of which 56–60% is partially hydrolyzed proteins and a small amount is oil [1,3]. The content of oil for skim is typically around 13% of the total oil recovery from extruded soybean flaks in enzyme-assisted aqueous extraction process [7].

The presence of oil and the nature of the hydrolysis not only make it difficult to purify the skim protein, but also cause a substantial loss of oil product. Indeed, process economic analysis demonstrated that creating value from the skim fraction is essential to the economic feasibility of enzyme-assisted extraction processes of soybeans [5]. So far, the simplest and most economical method to purify soy proteins is isoelectric precipitation. Nevertheless, the oil has a high binding capacity for soybean protein, which limits purity that can be achieved [5].

An alternative method was used in this study to purify the soybean proteins, which involves separating the oil from the skim

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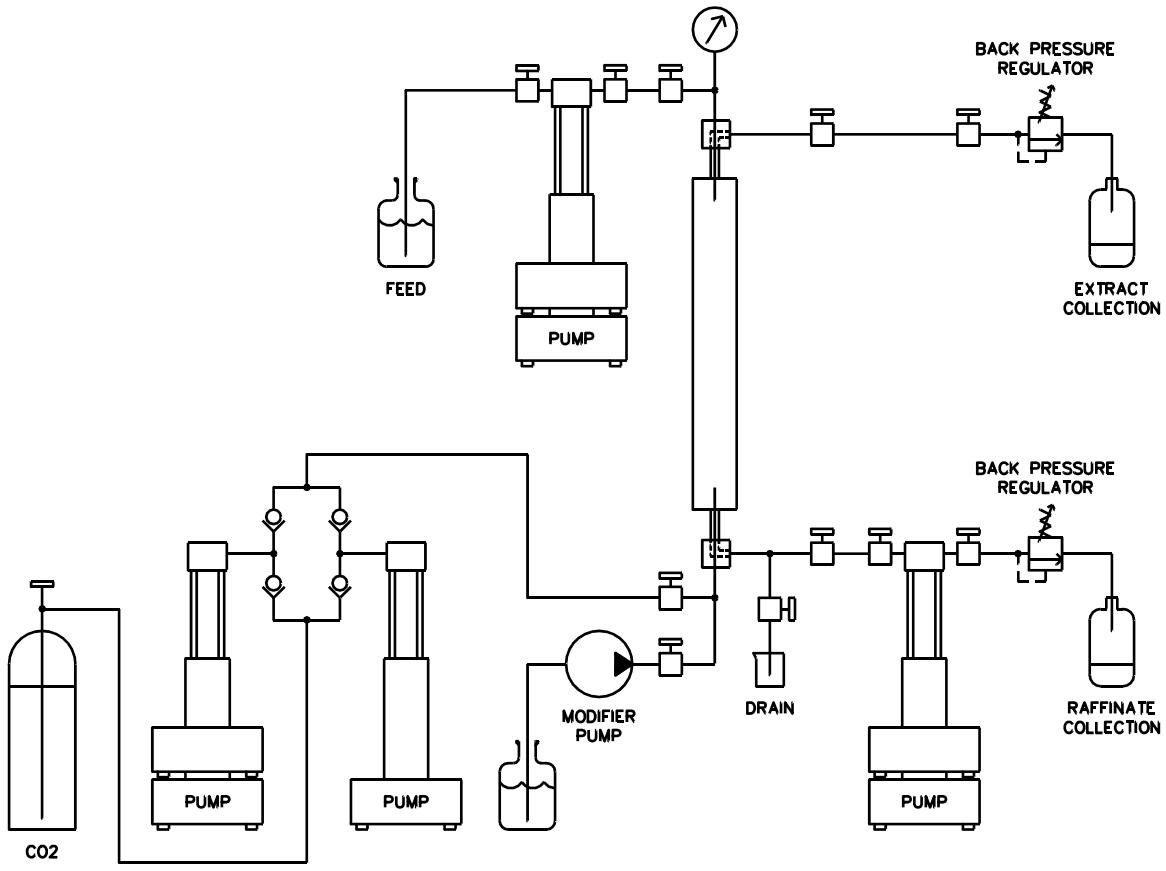

Fig. 1. Schematic of CO_2 counter-current extraction apparatus.

fraction through counter-current CO_2 extraction. Previous research demonstrated that CO_2 can effectively solubilize soybean oil [8]. At liquid state, the use of CO_2 to remove hexane from soybean oil was tested [9,10]. At supercritical state, Fang et al. [11] showed that CO_2 is effective to extract fatty acids methyl esters from soybean oil (16 MPa, 313–348 K). The phase behaviour of soybean fatty acid ethyl esters in CO_2 at high pressures was also reported [12].

CO_2 is an ideal solvent to be used for food applications since is inert and non-toxic, and does not require high temperatures that could damage thermo-labile compounds. Besides, CO_2 counter-current fractionation is an environmentally friendly process in which CO_2 can be safely recycled after product separation.

List [13] investigated the degumming and physical refining of hexane-extracted soybean oil by counter-current CO_2, reducing its phosphorous content from 620 ppm to less than 5 ppm at 55 MPa and 70 °C. Moreover, supercritical countercurrent CO_2 has been carried out in aqueous solutions [14]. Other applications of CO_2 counter-current separation method applied to oils that have been reported include purification of raffinate rice oil from rice bran [15], fractionation of fish oils [16] and extraction of olive oil [17]. The advantages of using the counter-current mode of operation are the reduction of solvent consumption, an increased throughput, higher oil extract concentrations in the solvent and lower residual concentration in the raffinate [18]. In addition, counter-current fractionation of a feed mixture can be implemented in a continuous mode [19].

In this study, the influence of the main operating variables (pressure, temperature, solvent-to-feed ratio, modifier and packing) affecting the extraction of fat from soy skim by counter-current CO_2 separation is investigated. The amounts, electrophoretic patterns, and solubility behaviour of proteins in the soy skim samples before and after extraction were determined, in order to detect any alterations due to the CO_2 treatment. The results reported herein can support the development of an environmentally-friendly and safe process to achieve oil/protein separation from soy skim.

2. Materials and methods

2.1. Materials

Soy skim was provided by Center for Crops Utilization Research, Iowa State University, Ames, IA. Carbon dioxide was provided by ILL-MO products Co. (Jacksonville, IL). Absolute ethanol was supplied by Fisher scientific (Fair Lawn, NJ).

C11 triacylglycerol (TAG), chloroform, hydrochloric acid, diethyl eter, hexane, toluene, methanol, boron trifluoride (BF3) in methanol, sodium hydroxide, and sodium sulphate were supplied by Fisher scientific (Fair Lawn, NJ, USA).

2.2. Counter-current extraction apparatus

The basic design of the counter-current CO_2 plant was previously published [20,21]. The stainless steel column is 1.22 m and has an internal diameter of 1.75 cm. The original system was modified for this study to include ethanol supplementation. The gas booster pump was substituted with a syringe pump. Fig. 1 shows a schematic of the complete apparatus. The function of the raffinate pump was to remove the raffinate from the bottom of the column while maintaining constant pressure with the fractionation column. The CO_2 flow rate was measured under pressurized conditions using the Isco syringe pump. In some experiments, the column was packed with seventy-six vertically-stacked packing pieces, 316-stainless steel Pall Ring, of 0.016 m (AMACS Process Tower Internals. Houston, TX).