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Supercritical extraction of sunflower oil: A central composite design for extraction variables

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ABSTRACT

Supercritical carbon dioxide (SC-CO_2) extraction of sunflower seed for the production of vegetable oil is investigated and compared to conventional methods. The effects of extracting variables, namely pressure, temperatures, particle size, SC-CO_2 flow rate and co-solvent, on SC-CO_2 extraction are investigated. The maximum yield for sunflower oil is found to be about 54.37 wt%, and is obtained when SC-CO_2 extraction is carried out at 80 °C, 400 bar, 0.75 mm particle and 10 g/min solvent flow with 5% co-solvent. A central composite design is used to develop the model and also to predict the optimum conditions. At optimum conditions obtained based on desirability function, 80.54 °C, 345 bar, 1.00 mm, 10.50 g/min and 7.58% ethanol, SC-CO_2 extraction has performed and found that extraction yield dropped by 2.88% from the predicted value. Fatty acid composition of SC-CO_2 and hexane extracted oil shows negligible difference and found high source of linoleic acid.

1. Introduction

The sunflower oil is a major source of monounsaturated fatty acids for nutrition products (Salgin, Doker, & Calmli, 2006) and is also suitable emollient due to its good oxidation stability, moisturizing properties, excellent skin feel with good absorbity. Sunflower oil is also used in sun care products because it exhibits a resistance to rancidity over time compared to other available oils due to the presence of low polyunsaturated fatty acids and high natural tocopherol content (Nimet et al., 2011). Further, sunflower have a high oil content (~50 wt%) with large amount of protein (50–60%) and hence have an excellent potential for their use in the production of edible oil and food formulation products (Salgin et al., 2006). Also, sunflower oil has a high content of the natural antioxidant such as tocopherols, which make it superior as compared to other vegetable oils. Sunflower oil have high amount of unsaturated fatty acids (77–82%) like linoleic acid (59–67.5%) and oleic acid (14.0–18.1%). It is mostly used as cooking oil as well as food additive in Western and Asian countries (Shahidi, 2005).

Supercritical fluid extraction (SFE) with supercritical carbon dioxide as a solvent, is widely used as an alternative to traditional techniques like mechanical pressing, organic solvent extraction. The supercritical carbon dioxide most common solvent because of its unique properties such as, non-flammable, non-toxic, non-explosive, cost efficient, non-polar, easy to remove and also offers a higher extraction rate (Mukhopadhyay, 2000).

Due to the above advantages, the present work is focus on experimental study of supercritical extraction of oil from sunflower seeds from northern part of India. The main objective of the present work is to develop the statistical model to evaluate the cumulative extraction yield. Response surface methodology with centered composite design has been used to interpretation of extraction yield obtained by suggested experimental runs in terms of recovered mass. Some important properties of seed material such as, structure of seed particles, functional groups and thermal degradation are evaluated by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy and thermo gravimetric analysis (TGA) respectively. The vegetable oil composition has been analyzed by gas chromatography for all experimental runs.

2. Experimental

2.1. Materials

The shelled and dried sunflower seeds have been purchased from local market at Roorkee and unshelled manually. After drying under sunlight and without any pre-treatment, all the seeds have been chopped in domestic mixer grinder (Bajaj, India). The

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chopped seed particles have been sieved and fractionated according to their particle size by certified test sieves (Endecotts Ltd., London, England) with a vibratory sieve shaker (octagon 200, Endecotts Ltd., London, England) and stored at 4 °C in sealed plastic jars. Three different sized particles (1) $-1.180 + 0.850 \approx 1.00$ mm (2) $-0.850 + 0.600 \approx 0.75$ mm (3) $-0.600 + 0.425 \approx 0.50$ mm, have been used for SFE and for convenience, mean particle diameter, based on sieve openings, has been assigned to a fraction between two successive sieves.

Liquefied CO_2 of purity 99.9% is supplied by Sigma gases, India in pressurized deep tube cylinders. All the solutions are prepared with ultrapure water obtained from Milli-Q system supplied by Millipore, Bedford, MA, USA. The entire standard chemicals such as *n*-hexane, anhydrous sodium sulfate in the form of powder, sulfuric acid (98.5%), potassium bicarbonate, toluene, methanol, sodium chloride, analytical and HPLC grade, have been obtained from Merck Ltd. (Mumbai, India). Standard solution of fatty acid methyl esters (FAMEs) FAME 37 Mix is obtained from Sigma Chemicals (St. Louis, MO, U.S.A.). Ethanol is purchased from Merck Ltd. (Darmstadt, Germany).

2.2. Supercritical fluid extraction

Supercritical carbon dioxide extraction has been carried out in a 1 l extraction vessel using supercritical fluid extraction system (SFE 1000F) supplied by Thar Technologies Inc., Pittsburgh. The system included a high pressure pump, co-solvent pump, heat exchangers, chiller, two separators and an extractor of 1 l capacity. The detailed description and working of SFE unit are given in author's previous work (Rai, Mohanty, & Bhargava, 2015). The precision of temperature and pressure of the extraction system were ±0.5 °C and ±1 bar, respectively.

A cylindrical stainless steel basket of height 19 cm and 7.5 cm diameter has been used for easy loading and unloading of the extraction vessel. The glass beads of diameter 5 mm has been used to pack the cylindrical basket. Initially, the 150 g glass beads of height 3.0 cm have been situated at the bottom of the basket, and then glass wool of thickness 0.5 cm is placed over it followed by 150 g of glass beads over the glass wool. This arrangement has been helpful for uniform distribution of supercritical CO_2. Above this arrangement, a layer of 50 g of seed particles is placed followed by glass beads, glass wool and again glass beads of heights 3.0, 0.5 and 3.0 cm respectively. This arrangement stops the carryover of solute particles with supercritical CO_2.

2.3. Design of experiments for extraction

There are large number of parameters like pressure, temperature, solvent flow rate, particle diameter, co-solvent (%), extraction time, bed void fraction, initial moisture content, etc. influence the supercritical extraction directly or indirectly (Rai et al., 2015). However, the study of the effect of each parameter on cumulative extraction yield at a time is a time taking and very difficult process, particularly when the large numbers of input parameters are involved. Hence, keeping view the above fact, in the present work response surface methodology (RSM) with five input parameters like pressure, temperature, CO_2 flow rate, particle size and co-solvent (%) are used to study the effects on cumulative extraction yield while, remaining parameters have been fixed at favorable conditions such as extraction experiments have been performed for 250 min with 50 g seed particle. RSM is a statistical and mathematical technique that is used for modeling and analysis of response/output variable which is influenced by several input parameters. The purpose of RSM is to simultaneously optimize the levels of selected five input parameters to obtain the maximum cumulative extraction yield.

The face central composite design (CCD) of RSM, suggested by Box and Wilson (Hinkelmann & Kempthorne, 2005), is used to examine the effect of individual and interactions of input parameters on the cumulative extraction yield. The uncoded levels of five independent input parameters for supercritical fluid extraction are listed in Table 1a. It shows the minimal (X_i, min), the mid range (X_i, mid) and the maximal (X_i, max) levels for each parameter, which corresponds to −1, 0 and +1 levels, respectively, in terms of coded variable X_i defined by Eq. (1).

$$X_i = \frac{2(X_{\text{actual}} - \overline{X})}{X_{i,\max} - X_{i,\min}} \tag{1}$$

where, $\overline{X} = \frac{X_{i,\max}+X_{i,\min}}{2}$

As discussed in our previous work, small face centered central composite design (SFCCCD) suggests 26 experiments with different combinations of five different parameters which consists of five center, ten axial and eleven factorial points (Rai et al., 2015). The sets of combination of input operating parameter as suggested by the DE7 software are shown in Table 1b. Based on the experimental results for cumulative extraction yield of supercritical fluid extraction of sunflower seed presented in Table 1b, the following second order input–output relationships (Eq. (2)), called regression or statistical models, are fitted.

$$Y = \beta_0 + \sum_{i=1}^{5}\beta_i X_i + \sum_{i=1}^{5}\beta_{ii} X_i^2 + \sum_{i=1}^{k-1}\sum_{j>i}^{k}\beta_{ij} X_i X_j \tag{2}$$

where, Y is the estimated response, X_i, X_j are independent variables, β_0 is the coefficient of intercept, β_i are the ith coefficient of linearity, β_{ii} are the quadratic coefficient and β_{ij} are linear by linear interaction coefficients.

Design Expert software (trial version 7.0.3, Stat Ease, USA) is used for RSM regression analysis and optimization of cumulative extraction yield data with input parameters. The statistical testing of the model, which includes linear, quadratic and interaction coefficient, is performed by ANOVA analysis with *F*-test to obtain the mathematical/statistical relationship between input and output parameters. To examine the goodness of fit of the model, each term of model is tested statistically and confirmed the significance of *F*-values with $p \leqslant 0.05$. The values of R^2, adjusted R^2, predicted R^2, lack of fit and adequate precision of models are obtained to check the quality of the suggested polynomial. In order to visualize the input–output relationships and also to work out the optimum

Table 1a
Coded and real levels of input parameters involved in experimental design to estimate supercritical extraction of sunflower oils.

Factors	Name	Low level $X_{i,\min} = -1$	Mid level $X_{i,\text{mid}} = 0$	High level $X_{i,\max} = +1$
X_1	Temperature (°C)	60	80	100
X_2	Pressure (bar)	200	300	400
X_3	Particle Size (mm)	0.5	0.75	1.00
X_4	CO_2 flow rate (g/min)	5	10	15
X_5	Co-solvent (% of CO_2 flow rate)	0	5	10