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Experimental and mass transfer modelling of oil extraction from salmon processing waste using SC-CO_2

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ABSTRACT

In this study, supercritical carbon dioxide extraction (SC-CO_2) was studied as a method to recover oil from salmon waste. Experiments at pressures of 15, 25, and 35 MPa, temperatures of 313, 333, and 353 K, and CO_2 flow rates of 0.18–0.48 kg/h were conducted and the yield compared. The yields at 35 MPa, temperatures of 313, 333, and 353 K, and CO_2 flow rates of 0.18 kg/h were approximately 39, 46, and 41 (wt.%). A process model based on intra-particle diffusion (D_e) and external mass transfer of fish oil (k_f) is presented for the supercritical extraction process. The adsorption equilibrium constant (K) is determined by fitting the theoretical extraction curve to the experimental data. The model using the best fit of theoretical extraction curve correlated the experimental data satisfactorily with AAD (%) ranged from 2.4 to 10.6%.

1. Introduction

Supercritical fluid extraction (SFE) is an alternative to conventional separation processes in the recovery of essential oils from plants and animal tissue. SFE using CO_2 (SC-CO_2) typically results in a high purity product and free of toxic solvent compared to conventional solvent extraction processes [1–3]. SC-CO_2 has a high organic diffusivity, is a relatively inexpensive solvent, and is nonflammable. In the SFE process, the fluid is at its critical temperature and pressure, where it exhibits gas like viscosities and liquid like densities. Several investigators have explored SFE using carbon dioxide (CO_2) for the extraction of edible/nutraceutical oils from plant and animal products (e.g., peach almond seed [4,5], sunflower seed [6,7], canola [8], spearmint leaf [9], sesame seed [10], peppermint [11], aromatic plant [12], vetiver root [13], hazelnut [3], ginger [14], and fish [15–21]).

Fish processing facilities generate a significant amount of fish by-products that could be an important source of energy, food, or industrial feedstock. Fish oil is a natural source of omega-3 polyunsaturated fatty acids (PUFA) (mostly eicosapentaenoic acid (EPA), and docosahexaenoic acid (DHA)) used in nutritional supplements. PUFA occurs as triacylglycerides (TAG) in fish oil with a mass fraction between 10% and 25%. These fatty acids are used in the prevention and treatment of coronary heart disease, blood platelet aggregation, hypertension, arthritis, abnormal cholesterol levels, mental illness, and autoimmune disorders [22]. Fish oil is also a rich source of vitamins including vitamin A, D, E, and K. However, the ability to extract, refine, and get to market may be challenging at processing facilities where there is limited infrastructure and plants are remotely located. Fish oil (edible and non-edible) can be recovered through several methods. Typically the recovery method selected attempts to minimize oil decomposition or denaturization of the products. The most common process employed in fish oil production is wet reduction (fishmeal process), which enables recovery of a high volume of fish oil and may require subsequent refining steps in order to make the fish oil edible [22]. Other conventional fish oil recovery processes include hydraulic pressing, vacuum distillation, urea crystallization, hexane/solvent extraction, and conventional crystallization. Each of these processes incorporate either high temperatures and/or the use of flammable or toxic solvents, which could result in loss of functional properties, denaturization of fish protein, and deterioration of oil quality and nutrition value (e.g., PUFA oxidation) [22].

Mathematical modelling of separation processes is critical in predicting process behavior, design of the process, and subsequent scale up [16,23]. In large scale SFE processes, the solute concentration profiles in the solid and fluid phase are difficult to measure due to cost and the issues associated with sampling continuously in a high pressure system [23]. A process model based on experimental data could be used as a tool in scale-up and optimization of a SC-

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Nomenclature

AAD	Average absolute deviation
CASD	Center for aquaculture and seafood development
CO_2	Carbon dioxide
DHA	Docosahexaenoic acid
EPA	Eicosapentaenoic acid
EOS	Equation of states
Re	Dimensionless Reynolds number
Sc	Dimensionless Schmidt number
SCE	Supercritical carbon dioxide extraction
SC-CO_2	Supercritical carbon dioxide
SFE	Supercritical fluid extraction
Sh	Dimensionless Sherwood number

Symbols

α_p	Specific surface area (m^{-1})
A	Constant defined by Eq. (25) (−)
b	Constant defined by Eq. (26) (−)
A_b	Bed cross sectional area (m^2)
c	Constant defined by Eq. (27) (−)
c_f	Solute concentration in the solvent phase (kg/m^3)
c_p	Solute concentration within the particle pore (kg/m^3)
c_{ps}	Solute concentration in pore space at the particle surface (kg/m^3)
c_s	Solute concentration in the particle (kg/m^3)
c_0	Solute concentration in the pore phase at $t=0$ (kg/m^3)
c_{s0}	Solute concentration in the solid phase at $t=0$ (kg/m^3)
c_{f0}	Total solute concentration (kg/m^3)
d_p	Thickness of the particle/slab (m)
D_{12}	Binary diffusion coefficient (m^2/s)
D_e	Effective intraparticle diffusion coefficient (m^2/s)
F	Cumulative fraction of solute extracted (−)
k_f	External mass transfer coefficient (m/s)
k_g	Global mass transfer coefficient (m/s)
K	Adsorption equilibrium constant (−)
L	Length of the bed (m)
Q_{CO_2}	CO_2 volumetric flow rate (m^3/s)
r	Radial position in spherical particle (m)
t	Time (s)
U_s	Superficial velocity (m/s)
x	Dimensionless solute concentration in effluent (−)
x_0	Initial solute mass ratio in the solid phase (−)
x_p	Dimensionless solute concentration in pore (−)
x_s	Dimensionless solute concentration in solid phase (−)
y	Solute mass ratio in the fluid phase (kg/kg)
z	Bed length coordinate (m)
α	Bed void fraction (−)
β	Particle porosity (−)
ϕ	Dimensionless mass transfer coefficient (−)
θ	Dimensionless time (−)
ρ_s	Solid density without void fraction of the solid matrix (kg/m^3)
ρ_{CO_2}	CO_2 density (kg/m^3)
τ	Total bed volume (m^3)/volumetric flow rate (s)
ψ	Particle geometry factor
ξ	Particle geometry parameter

CO_2 process. Several models have been proposed for the SFE of fixed bed of solid substrate based on empirical kinetic equations [24–26]. The advantages of kinetic models are their simplicity and ability to describe the kinetics of an extraction profile very precisely. Kinetic studies have been used in the SFE of biomass [8,27–29]. Del Valle et al. [24] presented a review of kinetic and equilibrium models of SFE processes. For scale up and design purposes, the kinetic models are not adequate as they fail to provide the description of underlying mass transfer phenomena and in these cases mass balance models can be used [24,26,30]. Many researchers have investigated mass balance models for SFE of a solute from fixed bed of solid substrate and Del Valle et al. [24] provides a comprehensive review. Studies relevant to this work are summarized in Table 1. As Table 1 shows, there is little work on the extraction of oil and lipids from animal muscle. In our laboratory, we are investigating SFE using CO_2 to extract fish oil from fish processing waste. There are several challenges with this type of work, predominantly in the heterogeneity of the waste material as fish species and degree of fish processing varies based on location and season. In Newfoundland and Labrador, salmon (Salmo salar Linnaeus) is harvested and processed. The high oil content and proximity to waste feedstock made this an ideal feedstock for our study. Offal (heads, trimmings, and frames) discarded during peeling; cutting and evisceration processes were obtained from local industries. This study is part of an ongoing research on alternative fish oil extraction methods beneficial for biofuel application [22], low grade biofuel process optimization [51], comparison of biofuel quality as a function of oil extraction methods (accepted – Fuel Journal), characterization of biofuel blends with petroleum fractions (currently under review – Fuel Journal), and life cycle analysis (LCA) of various extraction processes studied (currently being done).

The objective of this work was two-fold; optimize the SFE process conditions to maximize oil yield under the least intensive conditions (pressures, temperatures, and CO_2 consumption); and develop a model to predict oil extraction as a function of process conditions.

2. Mathematical modeling

Freeze-dried salmon offal is made up of protein, bone meal, and moisture and a lipid–oil mixture. The lipid–oil mixtures are the extractable components and can be treated as a single (pseudo-solute) substance. The general mass transfer equations for the SFE processes proposed by Akgerman and Madras [52], Del Valle et al. [24], and Del Valle et al. [53] are similar to mass transport operations involving solid-fluid processes, such as adsorption, desorption, and leaching. The models comprise of two differential solute mass balances on the solvent and solid phases. It also incorporates local equilibrium adsorption that describes the relationship between solute and solid [34]. The extraction model in this work is based on the model first developed by Goto et al. [11] for the prediction of essential oil extraction from peppermint leaves. Duford et al. [16] used the Goto et al. model to determine the cumulative fraction of edible oil from Atlantic mackerel at different moisture content and Mongkholkhajornsilp et al. [34] also used the model proposed by Goto et al. for the correlation of nimbin extraction from neem seeds. Rai et al. [25] compared Goto et al. model with models proposed by Reverchon, Marrone, Sovova, and Goodarznia. The local adsorption equilibrium model proposed by Goto et al. [8] was found most suitable for our process as it addresses intra-particle diffusion and external mass transfer of SFE in a fixed solid bed.

The fixed bed of salmon offal particle containing the oil is defined as the stationary (solid) phase with flowing SC-CO_2 as the mobile (fluid) phase, with assumptions that:

(i) the solid particle is porous,
(ii) axial and radial dispersions are negligible,