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Supercritical carbon dioxide-based integrated continuous extraction of oil from chicken feather meal, and its conversion to biodiesel in a packed-bed enzymatic reactor, at pilot scale

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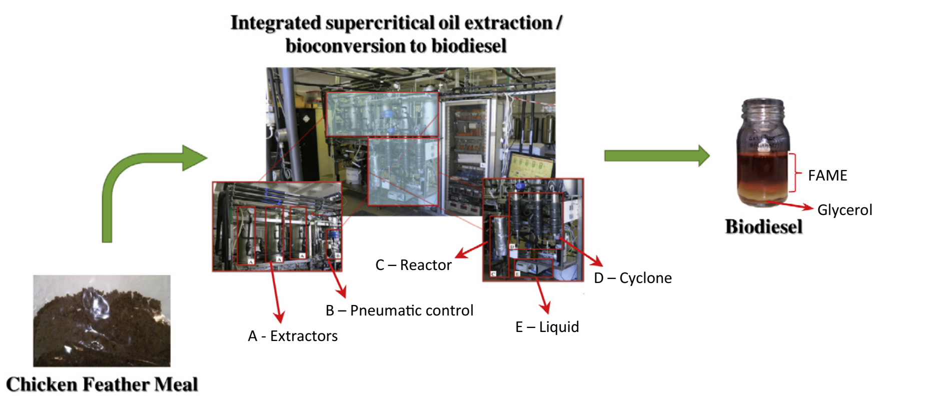
HIGHLIGHTS

- Continuous biocatalytic production of biodiesel from chicken feather meal in $scCO_2$.
- Integration of extraction and reaction processes at pilot scale.
- Over 90% of the oil available in CFM was extracted by sc-CO_2 in 60 min.
- Yields of biodiesel over 96.7% were obtained using Lipozyme TL RM®.

GRAPHICAL ABSTRACT



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ABSTRACT

The continuous production of biodiesel (fatty acid methyl esters; FAME) from chicken feather meal (CFM) was carried out in supercritical carbon dioxide (sc-CO_2), in a process combining extraction of oil from CFM followed by transesterification of the CFM oil with methanol. First, extraction experiments were carried out at different pressure, temperature and solvent flow rate conditions to assess the influence of these process parameters on the extraction rate and composition of extracted oil. Over 90% of the oil available in CFM was extracted by sc-CO_2 in 60 min. Oleic acid (C18:1), palmitic acid (C16:0) and linoleic acid (C18:2) were the major components of the oil extracted, accounting for ca. 84% w/w. The integrated extraction and enzymatic transesterification of CFM oil was then carried out at 40 °C and 250 bar, at solvent flow rates in the range 30–150 g/min, for oil:methanol molar ratios of 1:6–1:24, using Lipozyme RM IM® as biocatalyst, in a pilot plant unit. The lowest FAME yield obtained was 96.7%. Both the extraction and reaction steps were modeled, based on a broken and intact cells approach and the consideration of three consecutive steps, respectively, and a good agreement with experimental data was obtained.

1. Introduction

Biodiesel is a biodegradable, nontoxic and eco-friendly alternative biofuel, obtained through the transesterification of triacylglycerols with an alcohol in the presence of a catalyst [1,2]. One of the drawbacks of biodiesel is the cost of feedstock, which accounts for

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75–80% of the total operating cost [3]. This has driven research into the conversion of waste or recycled oil and animal fats into biodiesel, which additionally does not compete directly with food production and allows the integration of waste management operations with a variety of other industries [4–11].

Over the years world meat production has increased, and is forecast to reach over 260 million tons in 2014, of which 22.6% as beef, 42.5% as pork and 34.9% as poultry, respectively [12]. This has been accompanied by an increase in the amounts of by-products generated, such as chicken feather meal (CFM). According to the U.S. Census Bureau, "Feather meal (hydrolysed poultry feathers) is the product resulting from the treatment under pressure of clean, undecomposed feathers from slaughtered poultry" [13]. The U.S. poultry industry produces nearly 9 billion broiler chickens each year. The inedible by-products of chicken slaughtering account for about one third of the total mass of the broiler chicken, resulting in an annual production of 2 million ton of feather meal [14]. This feedstock contains a significant amount of fat, varying from 2% to 12% [9], which can be converted to biodiesel [4,8–11,15].

Organic solvents, such as *n*-hexane, are widely used for oil extraction when applying protocols for the determination of fat content in foodstuffs [16]. However, long extraction times, low selectivity, the accumulation of large amounts of waste solvent and its inherent toxicity are perceived drawbacks [17]. These can be overcome by using supercritical carbon dioxide (sc-CO_2) as extraction solvent. The physico-chemical properties of sc-CO_2, such as density, diffusivity and viscosity, can be easily controlled by changing the pressure and/or the temperature [18]. The possibility to easily adjust the solvation ability of sc-CO_2 has led to many applications of this solvent not only for extraction, but also for reaction and downstream processing [19].

Early on sc-CO_2 has been shown to efficiently extract fat from a variety of meat matrices containing 2–35% w/w of fat, as reported by King et al., who obtained yields of extraction of over 96% at 80 °C and pressures between 350 and 700 bar [20]. Orellana et al. reported similar fat extraction efficiencies from poultry meal, using both liquid and supercritical CO_2, at 50 °C and 345 bar [21]. The utility of sc-CO_2 and near critical CO_2 to perform the enzymatic conversion of oils and fats to biodiesel is also well documented [2,6,7,21–24]. Although the choice of an alkaline catalyst for the conversion of lipids into biodiesel is very common, a pre-treatment is required if the amount of free fatty acids (FFA) in the starting material exceeds a certain level, in order to avoid formation of soap that decreases the biodiesel yield. FFAs can be esterified by using an acid catalyst, but alkali-catalysed transesterification is comparatively much faster [1,25]. The use of an enzyme can overcome the problem of high FFA content of feedstocks since both triacylglycerols and FFA are converted to alkyl esters. Several lipases have been successfully used [26,27]. Methanol is a preferred alcohol in biodiesel production due to its availability and low cost [2].

Here we report on the supercritical fluid extraction (SFE) of oil from chicken feather meal (CFM) with sc-CO_2 at 40 and 65 °C, pressures from 200 to 300 bar, and solvent flow rate from 75 to 150 g/min. The use of sc-CO_2 has the additional advantage of allowing the integration of process steps. We further report on a sc-CO_2-based, continuous process, combining oil extraction from CFM with oil conversion into fatty acid methyl esters (FAME) through enzymatic transesterification catalysed by immobilized *Rhizomucor miehei* lipase (Lipozyme RM IM), carried out in a pilot scale unit.

2. Experimental

2.1. Materials

CFM was kindly supplied by Lusiaves of Lavos, Figueira da Foz. The average particle size of CFM was determined with a Malvern Morphologi® G3 particle characterization system. Lipozyme RM IM (*R. miehei* lipase immobilized on an ion exchange resin) was from Novozymes (Denmark). CO_2 (⩾99.95%) was from Air Liquide (Portugal). The FAME C_{16}–C_{18} standard was from Supelco. Methanol was from Sigma–Aldrich, *n*-heptane, *n*-hexane, pyridine and chloroform were from Carlo Erba, tricaprin was from TCI, N-methyl-n-(trimethylsilyl)trifluoroacetamide was from Alfa Caesar, ethylene glycol was from Merck, and acetone was from Valente e Ribeiro, Lda. All reagents were of PA grade.

2.2. SFE of oil from CFM

SFE experiments were carried out in a high pressure apparatus similar to that described by Couto et al. [28]. A 316SS, 55 mm internal diameter, 600 mm length extraction vessel was used, packed with ca. 0.5 kg of CFM. Samples were collected in a cyclone (Separex 4140/CY01 AS2). SFE of oil from CFM was carried out at 40 and 60 °C, in the pressure range 200–300 bar, at sc-CO_2 flow rates from 75 to 150 g/min. For reference, the extraction of oil from CFM was also carried out in a Soxhlet, with *n*-hexane at its normal boiling point (68.7 °C). 18 g of CFM and 250 mL of solvent were used in each assay and the extraction ran until the feedstock was exhausted of oil (6 h). *N*-hexane was subsequently removed in a rotary evaporator.

2.3. Pilot scale continuous oil extraction and conversion to biodiesel

The pilot plant unit is shown schematically in Fig. 1. The reaction and separation sections of this unit have been described by Lisboa et al. [7]. Gaseous CO_2 is liquefied in a cryostat (Julabo FL 2503), compressed to the desired extraction pressure by a liquid pump (Lewa EHM 1), and heated to the desired temperature in a water bath. It then flows upward through a 316SS, 64 mm internal diameter, 600 mm length extraction vessel heated by a heating tape, packed with ca. 0.5 kg of CFM. Methanol is pumped with an HPLC pump (Gilson 305) and mixed with the outlet stream of the extraction vessel. Sc-CO_2 carrying extracted oil and methanol passes through a vertically mounted 316SS, 25 mm internal diameter, 600 mm length packed-bed enzymatic reactor heated by a heating jacket, filled with 84 g of enzyme. The pressure in the reactor is controlled by an electro-pneumatic control valve (von Rohr Armaturen VEGP 700 F59). The pressure in the extraction vessel and in the reactor is measured with a pressure transducer (Wika 881.14.600). The outlet stream of the reactor is collected in a cyclone (Separex 4140/CY01 AS2, France) heated by a heating jacket. CO_2 is recycled back to the liquid pump. Temperature is controlled to ±0.5 °C and pressure to ±1 bar. Integrated, continuous extraction of CFM oil and biodiesel production was carried out at 40 °C and 250 bar, at solvent flow rates in the range 30–150 g/min, with oil to methanol molar ratio of 1:6–1:24. Available phase equilibrium data relevant for binary and ternary systems [29,30] indicate that a single-phase system exists at the pressure and temperature conditions selected for the extraction and reaction experiments.

2.4. Analysis

2.4.1. Acylglycerols, glycerol, FAME and fatty acid analysis

The methods used conform to the European Standard EN 14214/ASTM D6584-13e1. Tri-, di- and monoacylglycerols, and glycerol were measured by GC analysis performed with a Trace ULTRA Series Unicam gas chromatograph with on-column injection, equipped with a 10 m × 0.32 mm i.d. column coated with a 0.10 μm thickness film of 5% diphenyl-95% dimethylpolysiloxane, from Thermo Unicam (Thermo Biodiesel (G)). All the data was processed with software Chrom-Card. The operating conditions were