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Influence of solvent selection and extraction temperature on yield and composition of lipids extracted from spent coffee grounds

Ioannis Efthymiopoulos[a,*], Paul Hellier[a], Nicos Ladommatos[a], Alessandro Russo-Profili[a], Aaron Eveleigh[a], Abil Aliev[b], Arthur Kay[c], Ben Mills-Lamptey[c]

[a] Department of Mechanical Engineering, University College London, Torrington Place, London WC1E 7JE, United Kingdom
[b] Department of Chemistry, University College London, 20 Gordon St., Bloomsbury, London WC1H 0AJ, United Kingdom
[c] Bio-Bean Ltd., 6-8 Cole St., London SE1 4YH, United Kingdom

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ABSTRACT

Spent coffee grounds (SCG) are a potentially sustainable source of C16-C18 triglycerides. This study investigates known solvent extraction technologies with a wide range of solvents for lipid extraction from SCGs, and determines the effect of solvent selection and process temperature on the extraction efficiency and composition of the obtained oil. A correlation between increasing solvent boiling point, and therefore process temperature, and improved oil extraction efficiency was observed in Soxhlet extractions with a wide range of solvents. Experiments at elevated temperatures (up to 200 °C) were performed through Accelerated Solvent Extraction (ASE) and temperature increase initially improved the oil extraction efficiency when non-polar solvents were used, before decreasing it at higher temperatures. Utilization of ethanol resulted in the highest oil extraction ratio by ASE (at 165 °C), suggesting that temperature increase is more beneficial to the extraction efficiency of polar solvents. In addition, analysis of the oils was carried out to evaluate the composition of the oils extracted from SCGs using different solvents and extraction parameters. The Nuclear Magnetic Resonance (NMR) results were in agreement with the values obtained from the titrimetric determination of the free fatty acid content (FFA) of the oils in terms of the comparative trends, and also tentatively suggest that some differences in the composition of the extracted oils might be related to the type of extraction solvent used.

1. Introduction

Coffee is a crop cultivated in 80 countries and one of the most popular beverages worldwide (Campos-Vega et al., 2015; Murthy and Madhava Naidu, 2012). According to International Coffee Association, (2016), 9.1 million tonnes of coffee were produced globally between October 2015 and September 2016 with a 1.8% increase in global coffee production compared to 2014/15. There are ~80 coffee species, however, only two are economically significant, *Coffea arabica* and *Coffea canephora* (Robusta) (Murthy and Madhava Naidu, 2012). Specifically, of the total worldwide coffee production in 2015, Arabica and Robusta varieties accounted for ~5.3 and ~3.8 million tonnes representing 58.2% and 41.8% of the overall respectively (International Coffee Association, 2016). Worldwide coffee consumption between October 2015 and September 2016 was 9.3 million tonnes, with the deficit between production and consumption covered by stocks accumulated in previous years, while an average annual growth rate of 1.9% has been observed in global coffee consumption since 2012/13 (International Coffee Association, 2016).

Spent coffee grounds (SCG) are the residues obtained during coffee brewing and represent the main coffee industry residual material (Campos-Vega et al., 2015). On average, 650 kg of roasted coffee are generated from one ton of green coffee and approximately 2 kg of wet SCGs are obtained for each kilogram of soluble coffee produced (Murthy and Madhava Naidu, 2012). Consequently, a significant amount of SCGs is generated annually and a waste management plan consistent with existing regulations is required. SCGs are used for various purposes such as composting, sugar production, mushroom growth and bioenergy production (Campos-Vega et al., 2015). However, much recent attention has been given to the potential use of SCGs oil as a biodiesel feedstock (Kondamudi et al., 2008; Oliveira et al., 2008).

Coffee seeds contain lipids stored in the endosperm tissue as energy reserve for germination and post-germination growth (Crisafulli et al., 2014). Coffee oil is mainly comprised of triglycerides and small amounts of diglycerides, monoglycerides and FFAs with the glyceride

Abbreviations: SCG, Spent coffee ground; ASE, accelerated solvent extraction; NMR, nuclear magnetic resonance; FFA, free fatty acid

* Corresponding author.
E-mail address: i.efthymiopoulos@ucl.ac.uk (I. Efthymiopoulos).

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portion accounting for 80–95%, while the rest of the oil consists of terpenes, sterols and tocopherols (Jenkins et al., 2014). Previous studies that investigated the extraction of lipids from SCGs through the Soxhlet method reported oil yields ranging from 7 to 30.4% w/w on a dry weight basis, with most researchers reporting values between 11 and 20% w/w (Al-Hamamre et al., 2012; Caetano et al., 2012; Deligiannis et al., 2011; Efthymiopoulos et al., 2017; Haile, 2014; Jenkins et al., 2014; Pichai and Krit, 2015).

Other researchers have used solvent extraction variations for extraction of SCG oil including microwave-assisted extraction with extraction ratios reported to range between 77.25 and 82.63% w/w of the total available oil (Ahangari and Sargolzaei, 2013), and ultrasound-assisted extraction with extraction ratios of 83–98% w/w of the total available oil (Abdullah and Bulent Koc, 2013; Ahangari and Sargolzaei, 2013; Rocha et al., 2014). Supercritical fluid extraction has also been used previously used for oil extraction from SCGs with extraction ratios ranging from 82.6 to 98.1% w/w (Ahangari and Sargolzaei, 2013; Akgün et al., 2014; Couto et al., 2009). In all the studies where an oil extraction ratio is stated, a Soxhlet method was utilised to determine reference oil content.

The wide range of oil yields obtained in previous studies can be attributed to the different blends of coffee varieties used in the samples, the origin of coffee (cultivation, climate, time of picking) and the upstream processing (wet or dry processing and roasting) (Al-Hamamre et al., 2012; Jenkins et al., 2014; Oliveira et al., 2008). The different methods of coffee brewing generally do not significantly affect the lipid content of SCGs (Campos-Vega et al., 2015). Other parameters that affect the oil extraction efficiency of solvent extraction are related to the extraction procedure including moisture content, particle size, coffee to solvent ratio, type of solvent, extraction method and extraction duration (Al-Hamamre et al., 2012; Caetano et al., 2012; Efthymiopoulos et al., 2017; Pichai and Krit, 2015). With the exception of supercritical fluid extraction where lipids are removed by a supercritical fluid (e.g. CO_2), all the methods use organic solvents for lipid extraction.

The effect of solvent selection on the SCG oil extraction efficiency is a research objective that has been addressed by very few studies, with only Al-Hamamre et al. (2012) and Caetano et al. (2012) examining more than 3 different solvents. In particular, Caetano et al. (2012) performed Soxhlet experiments with hexane, heptane, octane, ethanol, isopropanol and mixtures of hexane and isopropanol ranging from 50:50 vol/vol to 80:20 vol/vol for durations of 2.5–9 h and found that the greatest oil yield was obtained with octane (26.5% w/w) and the lowest with hexane and ethanol (16% w/w). Al-Hamamre et al. (2012) used pentane, hexane, toluene, chloroform, acetone, isopropanol and ethanol in Soxhlet extractions for durations of 15–70 min and found that hexane resulted in the highest oil yield (15.28% w/w) and chloroform in the lowest (8.6% w/w).

Generally, non-polar solvents are better suited to oil extraction than polar ones, because the low presence or complete absence of charges allows penetration into the low polar matrix of SCGs (Al-Hamamre et al., 2012; Pujol et al., 2013). Polar solvents like alcohols are known to extract higher amounts of FFAs and undesired products such as proteins, carbohydrates, Maillard reaction products, phosphatides and other compounds (Al-Hamamre et al., 2012; Johnson and Lusas, 1983; Kondamudi et al., 2008).

The FFA content of oil is a major quality factor when considering transesterification to produce biodiesel, as high amounts of FFAs increase oil acidity, susceptibility to oxidation, speed up degradation and inhibit alkaline catalyzed transesterification (Al-Hamamre et al., 2012; Predojević, 2008). In general, FFA levels between ~3% and ~20% relative to oil weight are common in previous studies using hexane as the solvent (Al-Hamamre et al., 2012; Efthymiopoulos et al., 2017; Go et al., 2016; Haile, 2014; Kwon et al., 2013; Vardon et al., 2013), however values as low as 0.31% w/w (Deligiannis et al., 2011) and as high as 59% w/w (Caetano et al., 2012) have been reported, suggesting a significant variation in the composition of oil extracted from different sources with different extraction parameters. The composition of the extracted oil is an important parameter for its subsequent utilization either as a biodiesel feedstock or in the food and cosmetic industry and a number of authors have reported the use of ^{1}H NMR spectroscopy for the analysis of the composition of lipids and fats containing complex lipid mixtures (Guillén and Ruiz, 2001; Nieva-Echevarría et al., 2014; Satyarthi et al., 2009; Skiera et al., 2014), while it has also been used for the broad analysis of oils extracted from coffee grounds and SCGs (D'Amelio et al., 2013; Jenkins et al., 2014).

The effect of process temperature on the solvent extraction of oil from SCG has not been previously investigated, and only Ahangari and Sargolzaei, (2013) have extracted SCG oil through microwave-assisted solvent extraction with hexane and petroleum benzene at elevated temperatures by applying irradiation levels of 200 W and 800 W, though without specifying the achieved temperature. Generally, an increase in temperature improves the solubility of lipids, as high temperature can disrupt the cohesive and adhesive interactions between oil molecules and oil-matrix molecules respectively, thus increasing the diffusion rate of the lipids (Johnson and Lusas, 1983; Richter et al., 1996).

Previous studies that investigated the effect of extraction temperature (40 °C to 100 °C) on the accelerated solvent extraction of lipids from sources like rice bran (Jalilvand et al., 2013), pistachio seed (Sheibani and Ghaziaskar, 2008) and corn kernels and oats (Moreau et al., 2003) observed that increase of process temperature resulted in improved oil extraction efficiency. Increase of the extraction temperature decreases the strength of solvent intermolecular forces and thus its viscosity allowing better penetration into the matrix particles, and decreases surface tension allowing the solvent to better coat the feedstock and therefore increase rates of lipids extraction (Camel, 2001; Kaufmann and Christen, 2002; Richter et al., 1996). A decrease in surface tension also leads to easier formation of cavities and lipid molecules are more quickly dissolved in the solvent (Richter et al., 1996).

This paper presents results of experimental investigations into effect of solvent extraction conditions on oil extraction efficiency and composition of oils extracted from SCGs, with a comprehensive range of polar and non-polar extraction solvents investigated along with varying process temperatures. In this paper, the FFA content of the extracted SCG oil samples was determined by titration, with NMR analysis undertaken in order to make a preliminary assessment of changes in extracted oil composition when different solvents were used.

2. Materials and experimental methods

The SCG samples used were provided by bio-bean Ltd. and local coffee shops. Multiple SCG batches were used due to supply issues, and these resulted in different oil yields after Soxhlet extraction. *N*-Hexane was chosen as the baseline solvent based on previous studies which considered different solvents and found *n*-hexane to be amongst the most effective in extracting oils from SCGs (Al-Hamamre et al., 2012; Haile, 2014; Kondamudi et al., 2008), while the samples were dried prior to oil extraction at a temperature of 100 °C for 5.5 h. Information regarding the origin and upstream processing of the samples used was not available, however, it was known that three samples had been utilised for instant coffee production and will be referred to throughout as ICG1, ICG2 and ICG3, where ICG stands for instant coffee grounds, and the rest were products of the retail market used in espresso machines and will be referred to as RCG1 and RCG2, where RCG stands for retail coffee grounds. Table 1 shows the average baseline oil yields on a dry weight basis obtained after three repeats utilising *n*-hexane as the extraction solvent.

When oil extraction ratios obtained from different SCG batches are compared in the Results section, it is the extracted oil yield relative to oil yield achieved by Soxhlet with *n*-hexane (Table 1) which is presented.