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Extraction of lipids from spent coffee grounds with non-polar renewable solvents as alternative

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ABSTRACT

Spent coffee grounds (SCG) contain significant amounts of lipids (~16%w/w), which could potentially be utilized as feedstock in biodiesel production. Together with other lipids are tocopherols, which can be taken advantage of to improve the oxidation stability of the biodiesel. Lipids from SCG are preferably extracted with the aid of a solvent (*n*-hexane). Alternative non-polar solvents have been explored, but discrepancies exist between the yield and recovery values reported. In this study, a washing step, with saline solution as wash agent, after lipid extraction is introduced to determine the actual amount of available crude lipid extracted. The effects of extraction time on lipid yield from spent coffee grounds using different solvents (ethyl acetate, ethanol, isopropanol, and *n*-propanol) as an alternative were investigated. The use of ethyl acetate and *n*-propanol as extracting solvents enabled the complete recovery of the available lipids from the SCG. Moreover, the washing step introduced allowed a more objective assessment of the crude lipid extracted by alternative solvents. Furthermore, the tocopherol content in SCG (19.35 mg/100 g dry SCG) found in the lipid extracts was also determined. It was found that ethyl acetate and *n*-propanol were able to simultaneously extract about 93 and 87% of the available tocopherol in SCG, respectively, after an extraction time of 6 h.

1. Introduction

Coffee is considered as one of the most widely traded commodities in the world, with an annual production of ~9 million tons of green coffee beans (International Coffee Organization, 2017). The residue left after brewing is referred to as spent coffee grounds (SCG). About 65% w/w of the green coffee bean ends up as SCG in the production of instant coffee (Murthy and Madhava Naidu, 2012). Spent coffee grounds contains a number of organic compounds such as carbohydrates, lipids and proteins which requires high amounts of oxygen for degradation (Silva et al., 1998). It contains compounds such as caffeine and polyphenols. Caffeine, for instance, may act as a natural pesticide in plants. Moreover, at certain concentrations, it can cause organ failure in animals (Gartrell and Reid, 2007). Even though it contains compounds which may be harmful to the environment, most of the SCG still ends up in landfills. Spent coffee grounds are also known to have been used as fuel in industrial boilers of coffee processing industries (Silva et al., 1998), because of the high calorific value (~25 kJ/g dry SCG), owing to the appreciable quantity of lipids present, which could be as high as ~16%w/w (Wang, 2012). Instead of direct burning, these lipids may be recovered and converted to biodiesel. Conventional sources of biodiesel such as animal fats and vegetable oils, pose issues on food prices and the conversion of forests for farms. Thus, SCG has also been considered as a potential feedstock for biodiesel (Al-Hamamre et al., 2012; Kondamudi et al., 2008; Vardon et al., 2013).

The extraction of lipids from plant-based sources is usually achieved by two means, either through mechanical or solvent extraction. Mechanical extraction is preferable for biomass having lipid contents of > 20%w/w (Koubaa et al., 2016), while solvent extraction is more efficient for sources with lower lipid content (< 20%w/w). Soxhlet extraction is one of few solvent extraction techniques employed for solid-liquid extraction and is a convenient method for carrying out exhaustive extraction of lipids from solid samples for determination of total crude lipid content (Manirakiza et al., 2001). As a well-established method of total crude lipid extraction and determination, there is a significant number of studies, information and data for comparison. A summary of SCG crude lipid extraction results employing Soxhlet extraction involving different solvents or a combination of solvents is shown in Table 1

Solvent extraction of lipids in industry usually employs the use of hexane as the main solvent. Owing to increased public health and environmental concerns about its usage, and also its non-renewability (Puértolas et al., 2016), the use of alternative solvents has been investigated. A number of studies explored alternative solvents, a

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Table 1
Lipid yields and extraction efficiency (recovery) by different solvents using Soxhlet extraction.

Extraction Solvent		Time (min)	Lipid Yield[a]	Efficiency/Recovery[b]	References
Hydrocarbons	Pentane	30	15.18	99.35	Al-Hamamre et al. (2012)
	n-Heptane	n.s.[c]	18.6	116.98	Caetano et al. (2012)
	n-Octane	n.s.	26.5	166.67	
	Benzene	360	16.6	99.4	Ahangari and Sargolzaei (2013)
	Toluene	30	14.32	93.72	Al-Hamamre et al. (2012)
Alcohols	Methanol	1200	6.8	55.74	Cholakov et al. (2013)
	Ethanol	n.s.	15.8	99.37	Caetano et al. (2012)
	Ethanol	70	11.43	74.8	Al-Hamamre et al. (2012)
	Ethanol	360	15	125	Andrade et al. (2012)
	Isopropanol	n.s.	21.0	132.02	Caetano et al. (2012)
	Isopropanol	50	11.43	71.47	Al-Hamamre et al. (2012)
Ketones	Acetone	40	12.3	80.5	Al-Hamamre et al. (2012)
	Dichloromethane	360	10.8	90	
Halides	Chloroform	50	10.98	71.86	Andrade et al. (2012)
	Dichloromethane	360	10.8	90	
Ester	Ethyl acetate	360	11.8	98.33	Andrade et al. (2012)
Mix-Solvents	Hexane: Isopropanol (1:1/v:v)	n.s.	21.6	135.85	Caetano et al. (2012)
	Hexane:Methanol (4:1/v:v)	1200	8.8	72.13	Cholakov et al. (2013)
	Hexane:Methanol(with 2% water) (4:1/v:v)	1200	8.3	68.03	

[a] Amount of lipid extracted relative to the amount of dry SCG (g lipids/100 g SCG) subjected to the extraction process.
[b] Amount of lipid extracted relative to the amount of *n*-hexane extractable lipids.
[c] Not specified.

combination of solvents, irradiation methods, and the use of supercritical fluids (carbon dioxide with and without co-solvents) in extracting the available lipids. Several solvents used in the extraction of SCG as presented on Table 1 include alcohols, hydrocarbons, ketones, esters, and halides. In view of lipid extraction from SCG, the extraction solvent should have a high selectivity for triglycerides, and other components in the lipid while being unreactive to SCG. Another factor considered is the toxicity of the solvent, and thus researchers have considered the use of solvents with tolerable toxicity upon ingestion or exposure. Taking into consideration such factors and the later use of its lipid extracts for possible nutraceutical applications, ethanol, *n*-propanol, isopropanol and ethyl acetate are potential alternatives as they are categorized as Class 3 solvents, which are regarded as less toxic, having a lower risk to human health and are found to have no long term carcinogenicity and negative genotoxicity (Misra et al., 2017; U.S. Department of Health and Human Services Food and Drug Administration, 2012).

As presented in Table 1, inconsistencies for the yields of polar solvents especially alcohols are observed. The study of Al-Hamamre et al. (2012) blamed the low extraction of alcohols on the inability of polar solvents to penetrate the SCG matrix which depends on Van der Waals forces. This however, may also have resulted from the short extraction time (~ 60 min) employed. The studies of Caetano et al. (2012) and Andrade et al. (2012) presented equal or higher efficiencies to that of hexane in terms of lipid recovery. Andrade et al. (2012) attributed it to the possibility of other compounds in the matrix being soluble to the medium. To have an objective comparison of the solvents, these inconsistencies must be minimized. The use of polar solvents and mixtures with non-polar solvents have long been used in the extraction of animal tissues (Bligh and Dyer, 1959; Folch et al., 1957), however, washing of the extracts with salt (NaCl, $CaCl_2$, and KCl) solution is often employed (Christie, 2003). Unfortunately, washing of lipid extracts with saline solution is not practiced when extracting lipids from agricultural sources using polar solvents.

Coffee is known to have a number of antioxidants, among these are tocopherols. A study by Alves et al. (2010) determined that only 1% of the total tocopherol present in the roasted coffee, which ranged from 32 µg/g SCG to 91 µg/g SCG (depending on species, roast degree and source), is removed during the extraction or brewing, leaving most of the tocopherol in the SCG. Extraction of lipids co-extracts the tocopherols left in the SCG. Biodiesel is known to have oxidation problems during storage and during its actual application. However, biodiesel derived from lipids with tocopherols naturally present are found to have better oxidative stability (Ingendoh, 2010), since tocopherols remain even after the esterification of oil and serve as an anti-oxidants. While synthetic antioxidants could generally be mixed with the finished biodiesel, the presence of naturally occurring antioxidants decreases the amount which needs to be added. Thus, the tocopherol content of lipids obtained through the extraction with various solvents would also be an important factor to consider.

In this study, the effects of different solvents and various extraction times on the extraction yield and efficiency of the hexane extractable crude lipids are investigated. Furthermore, the effects of incorporating a washing step on the lipid yield of the alternative solvents is also looked into. To aid in later assessment, whether the extracted lipids are suitable as biodiesel feedstock or other applications, the characteristics of the extracted lipids in terms of free and total fatty acid content, unsaponifiables, tocopherol content, and fatty acid profile were also determined.

2. Materials and methods

2.1. Materials

Spent coffee grounds were collected from a local coffee shop in Cebu City, Philippines. Samples were dried at 60 °C for 3 days or until the moisture content was below 10%. The dried SCG were then stored in a dry polypropylene container at room temperature. The dried SCG were then determined of its moisture (M) gravimetrically by drying samples (2–3 g) at 105 °C until constant weight and mean particle size (d_M) by sieving dried SCG samples (~ 50 g) through pre-weighed standard Tyler mesh (3150, 2000, 850, 250, and 180 µm) with the aid of a sieve shaker (Mod.A5911, Intertest Benelux, Netherlands). Solvents, *n*-hexane (96%), ethanol (99.9%), ethyl acetate (99.5%) and isopropanol (99.8%), were obtained from Scharlau, Spain while *n*-propanol (98%) from AJAX, New Zealand. Chemical reagents potassium hydroxide (KOH) was obtained from Merck, Germany, potassium hydrogen phthalate (KHP) from AnalaR, England, butylated hydroxytoluene (BHT) and ascorbic acid from APS Finechem, Australia, sodium chloride (NaCl) from HiMedia, India, and BF3-methanol solution (14%) and reference standard alpha-tocopherol from Sigma-Aldrich, USA.