CHEMICAL ENGINEERING TRANSACTIONS
VOL. 56, 2017
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Jiří Jaromír Klemeš, Peng Yen Liew, Wai Shin Ho, Jeng Shiun Lim

ISBN 978-88-95608-47-1; **ISSN** 2283-9216
DOI: 10.3303/CET1756007

Spent Coffee Grounds as a Valuable Source of Bioactive Compounds and Bioenergy

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Spent coffee grounds (SCG) are abundant, low-cost and versatile feedstocks for a wide range of high-valued end products. With a goal to achieve zero waste, this study aims to further broaden the diversity by using the residue for bioactive components, biodiesel production, as well as for the manufactures of activated carbon and fuel pellet. The analyzed SCG oil was rich in palmitic, oleic and linoleic acids. Polyunsaturated fatty acids accounted for more than 50 % of the oil composition. Among different extraction methods, microwave-assisted extraction (MAE) was found to be recommended for maximal yields of SCG's oil (17.00 %) and total flavonoid content (TFC) (31.15 mg quercetin/g); while ultrasound-assisted extraction (UAE) was more efficient toward the recovery of lipid hydroperoxide (LP) (0.0191 mM) and total phenolic content (TPC) (13.500 mg AG/g). Optimal SCG-over-solvent ratio was another studied parameter. The research also confirmed the antioxidant capability of the coffee grounds. The production of SCG's biodiesel followed the conventional esterification and transesterification processes. The assessment of the fuel complied with the American Standard for Testing Material (ASTM 6751); and most of the analyzed values satisfied the standards. The activated carbon (AC) generated from SCG demonstrated a comparable purification capacity. The BET surface area and total pore volume were 1,547 m^2/g and 0.225 cm^3/g. For optimal area's value, a chemical activation by KOH, at 800 °C and 1:1-impregnation ratio was advisable. The solid waste after the oil extraction was used to produce fuel pellet with a high measured heating value (22 MJ/kg). The study underlined spent coffee grounds as a promising feedstock for biodiesel production. The residue offered not only a cut in raw material's cost, but also an increase in net profit through the commercialization of other value-added by-products.

1. Introduction

Annually, the world consumes around 9 million tons of coffee; and a ton of green coffee can generate about 650 kg of Spent coffee grounds (SCG) (Mussatto et al., 2011). Without fully understanding the economical and environmental benefits of reusing the waste, disposing a highly valuable feedstock becomes the current practice. Biodiesel and fuel pellet production from SCG helped to solve not only environmental pollution but also energy shortage. In recent years, bioenergy production from SCG have attracted many researchers from around the world, especially in coffee exporting countries (Caetano et al., 2012).

Vietnam, as the world second-largest coffee producing nation, is most suitable as a nurturing environment for research and development of SCG-based products. According to Scientific and Technological Information (STINFO, 2016) magazine, in 2014, the total coffee growing area in Vietnam was 653,000 ha. In addition, the coffee consumption is also high. In recent years, the rapid growth of new coffee shops and chains has never ceased to stop, and opening a coffee shop has become a popular business trend in Vietnam. The total number of registered coffee shops has jumped from 19,166 (in 2009) to 23,450 (in 2014) (Vietnam Trade Promotion Agency, 2015). That number, if including several street vendors, would be significantly higher. Coffee, since long, is a part of modern culture and a highly commercial exported specialty of Vietnam. The success of SCG recycling would enhance the competitive strength of Vietnamese coffee-based products; and more importantly, the innovation would help to raise the income level of Vietnamese farmers who grow coffee. This paper is a preliminary study to construct an economical SCG recycling. The oil from SCG could be either go through

Please cite this article as: Le P.T.K., Vu Q.T.H., Nguyen Q.T.V., Tran K.A., Le K.A., 2017, Spent coffee grounds as a valuable source of bioactive compounds and bioenergy, Chemical Engineering Transactions, 56, 37-42 DOI:10.3303/CET1756007

additional extraction for bioactive compounds or being converted into biodiesel. The de-fatted part could be utilized as the precursor for activated carbon and fuel pellet. Such a process achieves not only no waste left, but also the generation of valuable products. Fuel pellet has been popular due to its low moisture, high energy density, easy storage and transportation. Activated carbon is also a high-demand product, with a wide range of applications in dyeing, separation, purification, catalytic and especially waste water treatment (Haile, 2014). But most importantly, SCG, as an abundant waste source, help to solve two core problems in the commercialization of biodiesel: high cost of feedstock and food-or-fuel dilemma.

2. Materials and Methods

2.1 SCG's bioactive contents

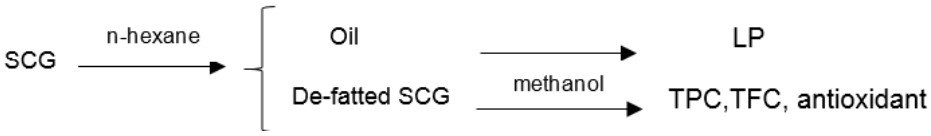

Figure 1: The extraction sequence

Figure 1 describes the procedure to extract bioactive compounds from SCG. The complete extraction sequence was triplicated. In each run, the starting material was 10 g of SCG. The amount of the solvent, n-hexane, depended on SCG/solvent ratio of 1:10, 1:15, 1:20 and 1:25 w/v. For Soxhlet, the solvent was boiled and refluxed in the Soxhlet extractor at 65 ± 5 ^{o}C. For the other three methods, Maceration, UAE and MAE, the experiments were set at room temperature. The extract was repeatedly dissolved in the fresh solvent, and the extraction ended when the extract became colourless. After filtration and evaporation, SCG's oil was collected, weighed, re-dissolved in methanol and stored at -18 ^{o}C until the analysis for the content of LP. The de-fatted SCG was processed in a similar extraction procedure as the raw SCG with only the change in solvent used, methanol instead of n-hexane. The collected extract, phenolic phase, was also stored at -18 ^{o}C until the analysis of TPC, TFC and antioxidant. Table 1 below provides the analysis methods employed to measure the contents of the bioactive compounds.

Table 1: Analysis methods

Compound	Analysis Method
LP	Complex formation between Fe^{3+} and SCN^{-}
TPC	Folin-Ciocalteu
TFC	Aluminium chloride colorimetric
Antioxidant	DPPH

2.2 SCG's activated carbon

2.2.1 Chemical activation

First, to study the effect of impregnation ratio (IR), 20 g of dried SCG were impregnated in KOH 5 N with four ratios, 0.25, 0.5, 0.75 and 1.25 of KOH (90 %)/SCG (w/w) for 1 h; then dried at 105 ^{o}C for 8 h. The dried SCG was heated to 700 ^{o}C for an hour. The heat rate was 10 ^{o}C/min and nitrogen flow rate was 50 L/h. After cooling, AC were crushed, washed sequentially with HCl 0.1 N, deionized water until pH value reached 6–7. Finally, they were dried in a vacuum oven at 105 ^{o}C for 4 h then stored in a desiccator until use.
Second test is on the effect of activation temperature. The activation was conducted at different temperatures, 600 ^{o}C to 900 ^{o}C, with a 100 ^{o}C-step in an hour with the optimum IR found in the first part of the experiment. Heating rate and N_2 flow rate were stable at 10 ^{o}C/min and 50 L/h respectively.

2.2.2 Physical activation

20 g of dried SCG was heated to 400 ^{o}C for 30 min to remove organic contents. The next step was the carbonization at 600 ^{o}C for 2 h, at the same heating and flow rate as in the above chemical process. The activation had two variables: heating temperatures (700 ^{o}C, 800 ^{o}C, 900 ^{o}C) and time (1 h, 2 h, 3 h). The heating and flow rate were same as in chemical process, but CO_2 was substituted for N_2.
As for mathematical models, Langmuir adsorption isotherm model was employed for the methylene blue (MB) adsorption test and Brunauer-Emmett-Teller (BET) theory was used to calculate the AC's surface area.

2.3 SCG's biodiesel and fuel pellet

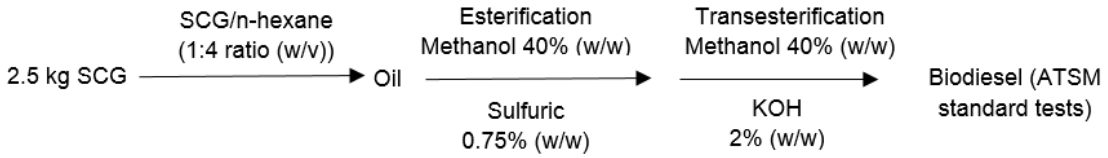

Figure 2: SCG-to-Biodiesel procedure

Figure 2 provides the guideline to produce biodiesel from SCG. The compositions of fatty acid in SCG oil and methyl ester in biodiesel were determined by Gas Chromatography Mass Spectrometry (GC-MS). American Society for Testing and Materials (ASTM) standard methods, ASTM D445, were employed for the biodiesel fuel properties, such as gross heating value, specific density, kinematic viscosity, cloud point, iodine and acid value. The evaluation of copper corrosion was followed ASTM D130. In addition, the carbon residue was measured by ASTM D4530.
SCG and its de-fatted residue were compressed into fuel pellets. Parr 6400 calorimeter was used to measure the heating values of the pellets, as well as SCG's oil and biodiesel.

3. Results and discussion

3.1 SCG's bioactive contents

Table 2: Optimal measurements and conditions

Compound	Optimal measurement	Method	Solvent	Ratio
Oil	16.99 % yield	MAE	n-hexane	1:15
LP	0.0191 mM	UAE	n-hexane	1:20
TPC	13.466 mg AG*/g dry weight	UAE	methanol	1:20
TFC	31.15 mg quercetin**/g dry weight	MAE	methanol	1:20
Antioxidant	The indicator changed its color from purple (DPPH) to yellow (DPPHH)			

$$\text{Equivalent content A} = \frac{V \times m_1 \times C \times F}{m_2 \times 1000} \quad (1)$$

In Eq(1), m_1 (mg) and m_2 (mg) were total weight of sample and weight of analyzed sample respectively. For (*), A was equivalent to AG; F was a dilution factor; and C was the concentration of gallic acid from the calibration curve. For (**), A was equivalent to quercetin; F was a dilution factor; and C was the concentration of quercetin from the standard curve.

3.2 SCG's activated carbon

The study indicated the superiority of physical activation in optimizing AC's carbon yield. Nonetheless, between KOH and CO_2 activations, only the first method qualified the standards of activated carbon. Its BET value was greater than 900 m^2/g, the volume pore was over 0.2 cm^3/g and the adsorption capacity was around 200 mg MB/g.

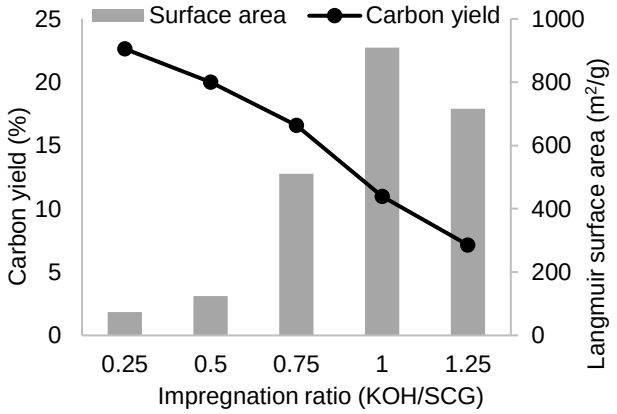

Figure 3: The effect of impregnation ratio (IR) on carbon yield and surface area

In Figure 3, the dependence of the surface area on the ratio was closely comparable to a negative quadratic relationship, with its vertex, or peak, at IR equalled 1. Basta et al. (2009) explained that the phenomenon was happened due to the reaction in Eq(2).

$$6\ KOH + 2\ C \rightarrow 2\ K + 3\ H_2 + 2\ K_2CO_3 \quad (2)$$

The formed potassium was assumed to diffuse into the char internal structure, widening current pores and also generating new ones. Hence, a raise in KOH/char ratio, within a certain extent, increased the surface area. Nonetheless, after a peak point, a counter effect happened, when the expansion was unrestrained, burning off pores and consequentially, lowering the surface area.

As described in Figure 4, the study also showed that a raise in temperature enhanced the expansion of surface area, but reduced the carbon yield value. Hence, for optimal mass production of AC, the proposal conditions were KOH activating agent, 800 ^{o}C, IR = 1 and one-hour activation time.

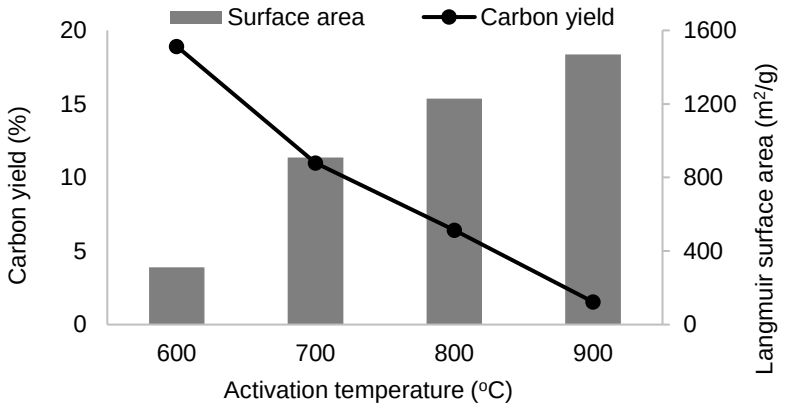

Figure 4: The effect of activation temperature on carbon yield and surface area

3.3 SCG's biodiesel

The composition of fatty acid in SCG reported using C-MS, highlighted cis-9,12 octadecadienoic acid (34.36 %), hexadecanoic acid (27.81 %) and cis-9 octadecanoic acid (27.31 %) as the major components of the extracted oil. Polyunsaturated fatty acids accounted for more than 50 % of the composition. Because of this fact, SCG oil could get oxidized easily. In determination of the composition of methyl ester in biodiesel fuel, most of fatty acids in SCG oil were converted into methyl esters. The top constituents were methyl linoleate (30.93 %), methyl palmitate (27.96 %) and methyl oleate (23.96 %).

As for optimal molar ratios, Figure 5 (a) and (b) show that m_0, m_1 and m_2 respectively stood for the amount of SCG oil, of product obtained after the first stage and of biodiesel collected in the second stage. For maximal biodiesel production, the recommended conditions were 40 % of methanol/oil and 2 % of KOH/oil (w/w) ratios.

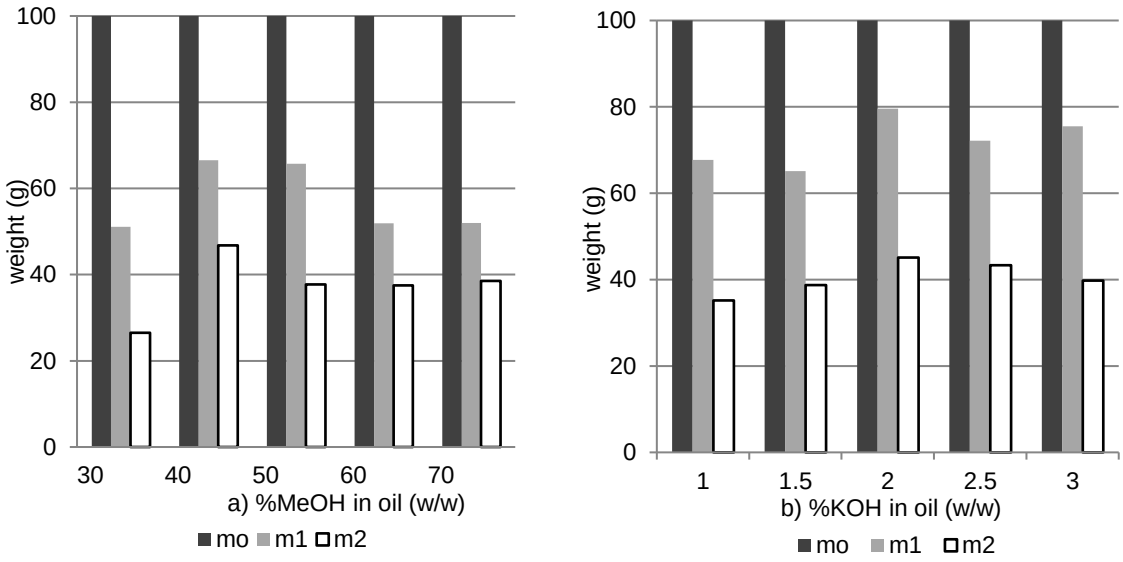

Figure 5: (a) Effects of methanol/oil ratio and (b) of KOH/oil ratio

Table 3: Biodiesel fuel properties

Properties	Heating Value, MJ/kg	Specific Density, (40 °C), kg/m^3	Flash Point, °C		Kinematic Viscosity, (40 °C), mm^2/s	Cloud point, °C	Acid value, mmg KOH/ g oil	Iodine value, g iodine/ 100 g oil	Copper Corrosion, (50 °C and 100 °C)	Carbon residue, %w
			closed cup	opened cup						
Biodiesel-standard ASTM D6751	-	860 - 900	≥ 93	130	1.9 - 6	-3-12	≤ 0.8	120 (EN14111)	≥ No.3	≤ 0.05
Biodiesel from SCG oil	39.35	865	147	80	4.94	8	0.88	120	1	0.1

According to Table 3 (Konthe, 2006), most of the SCG oil's physical and chemical properties complied with ASTM D6751. Nonetheless, the acid and carbon residue values of the SCG biodiesel slightly exceeded the ASTM standards due to the high content of unsaturated fatty acids in the extracted oil. In Table 4, the carbon residue in SCG oil was roughly half of the diesel's value. Hence, SCG biodiesel can be used directly or blended with diesel fuel in diesel engines without any further modification.

Table 4: Fuel properties of SCG oil methyl ester, RSO methyl ester and diesel fuel

	Heating Value (MJ/kg)	Specific Density (kg/m^3)	Viscosity (mm^2/s)	Carbon Residue (w %)	References
CG biodiesel	39.35	865	4.94	0.1	This study
RSO	36.5	874	5.81	--	(Ramadhas et al., 2005)
Diesel fuel	42	850	2.6	0.17	(Balat, 2011)

3.4 Fuel pellet and heating value

Table 5 records the heating values of different SCG's products. Energy content of biomass pellets is typically from 19.3 to 21.6 MJ/kg (Haile, 2014); the heating value of SCG's pellet obtained in this study was in the high end of the referred range. According to Weger et al. (2014), mechanical pre-treatment is proved to enhance the energy efficiency of solid biofuel produced from brewer's spent grain (BSG) by transferring most of the nitrogen

content into the liquid phase of the spent grains. Similar pre-treatment would be considered as an experimental parameter in future research on this topic.

Table 5: Heating value

Type	Heating value (MJ/kg)
SCG (pellet)	22
De-fatted SCG (pellet)	20
SCG's oil	39.3
SCG's biodiesel	39.35

4. Conclusions

The study indicated the effectiveness of MAE and UAE methods in providing high yields of the bioactive compounds (LP, TPC, TFC) extracted from SCG. The coffee residue was also highlighted for its antioxidant capability. In the production of activated carbon, compared to physical activation, activation by KOH was superior; and its optimal conditions included a 800 ^{o}C temperature, an IR equalled 1 and an hour process. From mass spectrometry analysis, SCG was proved to be rich in linoleic (34 %), palmitic (28 %) and oleic acid (27 %), which were subsequently converted into corresponding methyl esters. Biodiesel produced from SCG complied with most of the ASTM D6751 standards; and 40 % (w/w) of methanol/oil and 2 % (w/w) of KOH/oil were recommended for the production. The recorded heating value of SCG's pellet was 22 MJ/kg. The yields of biodiesel and activated carbon by KOH were 17 % and 10.98-22.63 %. The findings are corner-stones for the commercialization of multiple valuable products from SCG.

Acknowledgements

This research was funded by JICA Project for AUN/SEED-Net under grant number HCMUT CRC 1501.

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