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Lipid-dense and pre-functionalized post-hydrolysis spent coffee grounds as raw material for the production of fatty acid methyl ester

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ABSTRACT

In this study, lipid-dense post-hydrolysis spent coffee grounds (PHSCG), containing ~23 wt% lipid, was utilized as feedstock in the production of fatty acid methyl esters (FAME) via in-situ (trans)esterification (ISTE). The collected PHSCG were pre-functionalized (~0.86 mmol H^+/g dried, lipid-free PHSCG) after sufficient drying of wet residues obtained from the dilute acid hydrolysis (DAH) of spent coffee grounds (SCG). Taguchi method and regression analysis were adopted in the optimization of the ISTE, with temperature, solvent-to-solid ratio (SSR), and reaction time, as the main factors investigated. An optimum yield of 19.47 ± 2.44 g FAME/100 g PHSCG, corresponding to ~96% conversion, could be achieved during ISTE in a batch reactor system. The ISTE of lipids in PHSCG were carried out without catalyst addition due to the inherent catalytic activity of the pre-functionalized PHSCG. Elemental and FT-IR analyses were conducted to determine the extent of the functionalization. The strong acid density of the material increased 21.5 times upon sufficient drying after DAH. Although, some of the functionalized material were solubilized during ISTE, the post-ISTE residue still had significant a strong acid site, 2.47 times of the native SCG, and exhibited appreciable activity when used as solid acid catalyst for the esterification of oleic acid and methanol while having good stability. The DAH and subsequent drying to induce simultaneous carbonization and sulfonation, may be adopted as a means of generating raw materials for biodiesel production from lipid-containing lignocellulosic residues like SCG.

1. Introduction

Spent coffee grounds (SCG) is a unique residue left after brewing of ground coffee beans. Such agricultural residue is generated both industrially (instant coffee production) and domestically (e.g. coffee shops and households). Like other oilseed coffee beans accumulate storage lipids as it matures with the fruit (coffee cherry). However, coffee cherries are harvested at different maturity and often times before ripening, rending the beans to have low lipid contents. Two most widely harvested, roasted and brewed coffee beans are those of the Arabica and Robusta species with lipid contents ranging from 15 to 18 wt%, and 8 – 12 wt%, respectively [1]. During roasting and brewing, these lipids generally remain intact in the beans, whereby the resulting in SCG with relatively higher lipid contents. In the study done by Ratnayake et al. [2], only about ~10% of the available lipids are extracted during brewing. Depending on the extent of brewing, the resulting SCG have lipid contents ranging from 18 to 30 wt% for industrially generated SCG [3-5], and 9 – 17 wt% for those generated using commercial espresso machines [4,6,7]. With SCG continuously generated in an industrial and commercial scale, it may well serve as a renewable resource or feedstock for various applications including biogas production [8], biopolymers and biocatalyst production [9], and biofuels [10].

Lipids from SCG have been previously found to be suitable for biodiesel production in the form of fatty acid methyl esters (FAME) [11]. Moreover, such non-edible source of lipids may be favorable as feedstock due to the lower-cost and would not compete with the food supply

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[12]. However, two main hindrances to its practical use is it difficulty to recover the lipids via mechanical extraction owing to its relatively small particle size [5] and tendency to have lipids less than 20 wt% [13], and its high moisture content of >60 wt% [6,14,15]. One strategy towards the effective recovery and use of the lipids found in SCG is through *in-situ* (trans)esterification (ISTE) to simultaneously convert and extract out the lipids as biodiesel. Considering that the recovery of lipids from SCG would require the use of solvents, the effective use of certain solvents to simultaneously carryout the conversion of the lipids to biodiesel and its subsequent extraction would be desirable. Several researches adopting ISTE have been successfully carried out employing either a base [16,17] or acid [18,19] catalysts. Although, base-catalyzed ISTE is possible and often preferred owing to its relatively short reaction time (1.5 to 3 h) [16,17], the content of free fatty acid (FFA) should be less than 0.5, and would often times entail a certain deacidification step [16]. With the inherent nature of biomass like SCG to be hygroscopic, it will tend to contain significant amount of water even after drying and the cost of drying would in effect translate to additional cost. This then limits the effective and practical use of base as catalyst for ISTE of SCG. In cases where FFA and moisture is unavoidable, acid-catalyzed ISTE would a suitable alternative [20]. Acid-catalyzed ISTE of SCG have been adopted for processing wet SCG, while achieving high yields of ~15 g FAME/100 g dry SCG in a short reaction time of 2 h, but would require the use of chloroform as a co-solvent and employs high solvent-to-solid ratio (SSR) of up to 12.5 mL/g and high amounts of catalyst (~230 wt% H_2SO_4 with respect of the dry solid) [19]. The use of switchable-solvent like diazabicycloundecene have also been explored to serve as reusable co-solvent and catalysts, achieving a conversion of ~97% in 0.48 h, but would require a methanol loading of 13 mL/g and an overall SSR of 33 mL/g [21]. Despite the relatively shorter time required for the reactions employing co-solvents, the high SSR also translates to lower productivity and additional cost in later solvent recovery. In principle, the direct conversion of SCG lipids to FAME could be achieved using different ISTE strategies but would require considerations for an easier process and maximize the use of SCG for later practical application. Moreover, the tendency of SCG to contain lipids <20 wt% requires further consideration to ensure its competitiveness with other oleaginous biomass used for ISTE [20].

In response to the above concerns, two related approaches have been explored at about the same time. In 2016, Go et al. [6] introduced the idea of directly hydrolyzing collected SCG. Through the dilute acid hydrolysis (DAH) of non-delipidated SCG, it was in several occasions proven to enable the production of sugar-rich hydrolysates containing sugar at 30 – 40 g/L and lipid-dense post-hydrolysis residues containing 24 – 26 wt% [6,14,15]. The advantage of this approach apart from the generation of sugar-rich and lipid dense (PHR) during the pretreatment is the lesser amount of wet residue to be dried after hydrolysis, which saves 27 – 48% of the energy required for drying the native wet SCG [14,15]. Further DAH treatment of SCG ensures that the lipid content in the resulting post-hydrolysis SCG (PHSCG) is over 20 wt% and would be favorable for ISTE. Another approach was proposed by Liu et al. [18] in 2017, where sulfuric acid was first impregnated into the wet SCG prior to drying. Although not explicitly discussed impregnation of H_2SO_4 prior to drying may have resulted in attachment of the acid onto the solid matrix of SCG after undergoing the drying process, which then serves as catalyst during the ISTE carried out in a Soxhlet extractor. Adopting such strategy allowed the use of lesser acid (~20 wt% H_2SO_4 with respect of the dry solid) and SSR (5 mL/g). Unfortunately, the use Soxhlet extractor to carry out ISTE limits its later practical industrial application in view of scaling-up the process equipment involved. These two approaches allow the possibility of processing and ensuring SCG with higher lipid content, and the possibility of minimizing amount of catalyst to be removed from the product.

In a different instance, the above two concepts have been combined in the processing of rice bran. Sutanto et al. [22,23] adopted DAH in the processing of non-delipidated rice bran to produce lipid-dense PHR, which upon drying to remove the water, facilitated the concentration of the available H_2SO_4 and subsequently incurring partial carbonization and sulfonation. The resulting PHR from hydrolyzing RB was functionalized with strong acid sites after drying, and was found to facilitate the conversion (94 – 98%) of the available lipids into FAME during ISTE without having to add any catalyst under subcritical conditions (165 – 195 °C). In a more recent work on the direct hydrolysis of non-delipidated SCG, it was also found that lipids were more easily extracted from the resulting PHSCG and could save ~ 40% of the required solvent when extracting the lipids from the native SCG [11]. Currently, no studies have been carried out in the further use of lipid from PHSCG. Further, new means to sustainably synthesize catalyst for biodiesel production is also of importance and interest [24]. In line with the above developments and research gaps, this study is aimed to utilize PHSCG as a feedstock in biodiesel production through ISTE. The specific objectives of this study are to (i) Investigate the effects of temperature, SSR, and reaction time on FAME conversion and yield during in-situ (trans) esterification at ambient pressure conditions without the addition of catalyst; and (ii) Evaluate the catalytic activity of PHSCG, and its residues through the determination of acid sites, and influence in the reaction rate during (trans)esterification.

2. Materials and methods

Fresh spent coffee grounds (~10 kg) samples were collected from a branch of global chain coffee shop located in Taipei, Taiwan. The chemical reagents used in the experiment include: analytical grade ethyl acetate 99.9 vol% (Echo Chemical Co., Ltd, Taiwan), sulfuric acid 95 vol % (Scharlau, Spain), methanol 99.99 vol% (Aencore, Australia) and sodium chloride 99.9 wt% (Showa, Japan); technical grade hexane (Echo Chemical Co., Ltd, Taiwan) with at least 95 wt% n-hexane; potassium hydroxide 85 wt% (Acros organics, USA); FAME 37-mix and boron trifluoride methanol complex solution (13–15% BF_3) (Sigma, Aldrich, Germany).

2.1. Characterization of SCG and PHSCG

Collected fresh SCG having a moisture content of ~ 61% were dried to a moisture content of less than 10 wt% to avoid bacterial or fungal growth. Drying of SCG was done by placing collected wet SCG in stainless steel trays or pans and placed in an electric convective oven operated at 50 ± 5 °C for 5 to 6 days or until the desired moisture was reached. Dried SCG are stored in air-tight polypropylene bottles at ambient conditions for later use.

2.1.1. Determination of moisture, particle size, and lipid content

Moisture content of SCG and PHSCG were determined gravimetrically by freeze drying. Representative samples (~2 g) accurately weighed to the nearest 0.1 mg and placed in pre-dried and pre-weighed glass tubes. The weight loss was taken to be the moisture content of sample analyzed. The samples were allowed to dry until constant weight. The mean particle size was determined by the ANSI (American National Standards Institute Method) S319.4 [25]. Lipid content (C_L) was also determined gravimetrically following the AACC Method 30–25 [26], via Soxhlet extraction for 6 h with n-hexane as solvent.

Lipid profile of the extracted crude lipids were determined via gas chromatographic (GC) analysis using Shimadzu GC-2010 Plus equipped with a split injector, Rxi-5HT column (15 m × 0.32 mm × 0.1 μm), and flame ionization detector, to quantify the amount of free fatty acids, monoglycerides, diglycerides, and triglycerides. Lipid samples (125 mg) were dissolved in ethyl acetate (5 mL), and passed through 0.20-μm PTFE membrane filters (13-mm syringe filters) before subjecting to gas chromatography analysis [11,27]. The identified peaks from the chromatograms were converted to mass percentages using calibration curves established with lipid standards purchased from Sigma-Aldrich (Supleco 37 Component FAME mix CRM47885, and Lipid standard Mono-, Di-, &

Triglyceride Mix) and other reference material such as commercial soybean oil (triglyceride reference), and pure free fatty (lauric, palmitic, stearic, oleic, and linoleic) acids from Acros Organics USA. The unsaponifiable matter content and total fatty acid content (C_{TFA}) in the lipid samples were determined adopting the procedures described in the work of Loyao et al. [13]. The saponified fraction was further acidified to recover the total fatty acid to serve as a reference for the maximum FAME that could be produced, by multiplying the C_{TFA} with a factor of 1.05 to account for the methyl group attached during esterification [28], and to determine the fatty acid profile using methanol with ~ 14% BF_3 as the esterification agent prior to GC analysis.

2.1.2. Determination of acid sites

The total acid density (TAD), and strong acid density (SAD) of SCG and the later PHSCG was determined via titration as describe by Ezebor et. al [29]. In brief, for the TAD, 30 mL of standardized 0.1 M NaOH solution was added to 0.5 g of lipid-free, dried sample, accurately weighed to the nearest 0.1 mg, and placed in pre-dried 50 mL glass bottles and stirred for 6 h. Liquid was separated through vacuum filtration, and an aliquot of 10 mL was sampled for titration with a 0.1 M standardized HCl solution until equivalence point. The SAD was carried out using 30 mL of 2 M NaCl solution added to a 0.5-g lipid-free, dried sample, accurately weighed to the nearest 0.1 mg, in 50-mL glass bottles and stirred for 6 h to facilitate ion-exchange. Liquid was separated through vacuum filtration, and an aliquot of 10 mL was sampled for titration with a 0.1 M standardized NaOH solution until equivalence point. The difference between TAD and SAD is taken to be the weak acid density (WAD). All analyses were carried out in duplicates and the acid densities are reported as mmol H^+/ g of lipid free dried biomass.

2.1.3. Surface characterization and elemental analysis

To determine and validate the acid groups found in the solid matrix of SCG and PHSCG, dried lipid-free samples were ground using mortar and pestle and mixed with pre-dried and ground KBr, which was then pressed into pellets at ~6 tons of force using a mechanical press. FT-IR analysis was carried out using Shimadzu IRTracer-100. For the elemental analysis, dried lipid-free samples were sent to Precision Instrumentation Center, National Taiwan Univeristy for CHONS determination using an elemental analyzer (Elementar Vario EL cube, Germany) with sulfanilic acid and benzoic acid used as reference standards.

2.2. Dilute acid hydrolysis of SCG and subsequent functionalization

Dilute acid hydrolysis (DAH) was carried out according to an optimized procedure by Go et al. [14]. On a dry and lipid-free basis, an SSR of 8 mL/g was adopted for the DAH, with sulfuric acid solution at 4 vol% made by diluting concentrated sulfuric acid. The DAH was carried out for 3 h with intermittent shaking at 30-minute intervals. The mixture after DAH was then subjected to filtration to recover the residual solids and separate it from the hydrolysate. The solids collected after vacuum filtration were then dried at 50 ± 5 °C until constant weight (~5 – 7 days).

2.3. In-situ transesterification optimized via Taguchi method and regression analysis

In-situ (trans)esterification was carried out in a 100-mL glass bottle with Teflon lined screw caps. Appropriate amount of PHSCG was weighed, following an SSR of 6 – 10 mL/g, and placed in the glass bottles with 80 mL of methanol and stirred at 200 rpm for 4, 8 and 12 h at reaction temperatures 55, 65, and 75 °C. After the desired reaction time, the reaction mixture was filtered to separate the solid residues. Methanol (30 mL) was used to wash the solids to maximize the recovery of the products entrained on the surface of the residual solids. The filtrate was then transferred into a pre-weighed and pre-dried flask for product concentration using a rotary evaporator until constant weight. The resulting concentrate was suspended in n-hexane with the aid of an ultrasonic bath to recover the hexane soluble components. The suspension of the concentrated crude methanol extracts in hexane (~15 mL) was done for at least 4 times. The pooled extract was placed in a separation funnel (250 mL) and washed with salt solution (~15 mL) for 4 times to maximize the removal of hydrophilic components. The hexane layer was then recovered into a pre-weighed flask and concentrated in a rotary evaporator until constant weight with the collected hexane soluble material referred to as the crude product (m_{crude}). The crude product was analyzed of its FAME content or purity (C_{AE}) using the GC following a procedure previously mentioned, to calculate yields (Y_S) relative to the mass of PHSCG processed (m_{PHSCG}) and conversions (Y_P) based on the fraction of the maximum attainable FAME (Y_{S_max}) using Eq. (1) and (2), accordingly.

$$Y_S = \frac{m_{crude} \times C_{AE}}{m_{PHSCG}} \times 100 \tag{1}$$

$$Y_P = \frac{Y_S}{Y_{S\_max}} \times 100 = \frac{Y_S}{C_L \times C_{TFA} \times 1.05} \times 100 \tag{2}$$

In-situ (trans)esterification experiments were carried out adopting Taguchi method and using the L_9 orthogonal array with each run carried out duplicates. Resulting yields are processed as signal-to-noise (S/N) ratios using "the-higher-the-better" function (3) and are used as responses for subsequent optimization and statistical analysis. The experimental design and obtained responses are summarized in Table 1, with the experiments carried out in random order.

$$\frac{S}{N} = -10 \times \log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right) \tag{3}$$

The resulting S/N ratios for each experimental run were processed to determine the overall average S/N ratio (S/N_{ave}) and to obtain the mean S/N ratio for a given variable at a specified level (S/N_i) to generate the response chart to identify the corresponding level of each variable with the greatest influence, which are then taken to be the optimum for that factor. Data was also analyzed using analysis of variance (ANOVA) to objectively assess the contribution of each factor to the resulting yield. Response graphs and Pareto-ANOVA analysis was carried out with the aid of MS Excel®. For the optimum conditions selected, and with an assumption that the effect on the response is additive, a predicted S/N (S/N_{pred}), and therefore yield was also calculated using Eqs. (4) and (3), respectively.

$$\frac{S}{N_{pred}} = \frac{S}{N_{ave}} + \sum_{i=1}^{q}\left(\frac{\overline{S}}{N_i} - \frac{S}{N_{ave}}\right) \tag{4}$$

To further aid interpretation of the influence of the variables investigated, regression analysis was carried out for the gathered data. Prior to regression analysis, with the levels having equally spaced intervals, the different levels were normalized with the lowest level being −1, the middle level 0, and the highest level 1, and was regressed with Eq. (5) using data analysis tool pack of MS Excel®. Statistical and regression coefficients were looked into for the significance of each term.

$$\frac{S}{N} = \beta_0 + \beta_1 A^2 + \beta_2 B^2 + \beta_3 C^2 + \beta_4 AB + \beta_5 BC + \beta_6 AC + \beta_7 A + \beta_8 B + \beta_9 C + SEE \tag{5}$$

2.4. Catalytic activity of PHSCG residues after ISTE

After in-situ (trans)esterification (ISTE) of the best conditions with the highest FAME yield, the remaining solids after filtration was collected, dried in the convective oven overnight, and extracted using a Soxhlet extractor with hexane as solvent to determine the amount of hexane-soluble components entrained. The resulting solids from the Soxhlet extraction, was again dried before subjecting to FT-IR analysis,

Table 1
Summary of coded experiments and responses for L_9 (3^3) orthogonal array experiments on in-situ (trans)esterification of post-hydrolysis spent coffee grounds obtained after dilute acid treatment.

Expt. Run	Trial	Variables Varied (Taguchi Levels)			Coded Variables and Normalized Levels			Yield, g FAME/100 g PHSCG	Average Yield ± SD	S/N
		T, °C	SSR, $cm^3 \cdot g^{-1}$	T, h	A	B	C			
1	1	55	6	4	−1	−1	−1	8.84	8.99 ± 0.22	19.07
	2	(1)	(1)	(1)				9.14		
2	1	55	8	8	−1	0	0	13.86	14.53 ± 0.96	23.22
	2	(1)	(2)	(2)				15.21		
3	1	55	10	12	−1	1	1	17.75	15.48 ± 3.21	23.51
	2	(1)	(3)	(3)				13.20		
4	1	65	6	8	0	−1	0	18.80	17.03 ± 2.49	24.49
	2	(2)	(1)	(2)				15.27		
5	1	65	8	12	0	0	1	15.80	16.66 ± 1.22	24.39
	2	(2)	(2)	(3)				17.52		
6	1	65	10	4	0	1	−1	15.68	15.12 ± 0.79	23.57
	2	(2)	(3)	(1)				14.55		
7	1	75	6	12	1	−1	1	15.37	13.96 ± 1.99	22.76
	2	(3)	(1)	(3)				12.55		
8	1	75	8	4	1	0	−1	16.69	16.56 ± 0.19	24.38
	2	(3)	(2)	(1)				16.42		
9	1	75	10	8	1	1	0	18.65	18.39 ± 0.37	25.29
	2	(3)	(3)	(2)				18.13		
10*	1	65	10	8	0	1	0	19.25	19.21 ± 0.08	25.67
	2	(2)	(3)	(2)				19.11		
	3							19.26		
11*	1	70	9.4	8	0.5	0.7	0	18.70	18.96 ± 0.25	25.56
	2							18.99		
	3							19.21		

* Confirmatory test runs based on Taguchi method (Run 10) and that from the regression analysis (Run 11)

and SAD determination for remaining catalytic sites as previously described. Finally, the post-ISTE PHSCG is used as a catalyst for the esterification of oleic acid with methanol at a 10 wt% catalyst loading with respect to the fatty acid. Oleic acid (~5 g) was added to a 50-mL glass bottle with 20:1 M ratio of methanol to FFA, continuously stirred (200 rpm) for 24 h at 60 °C. A volume of 100-μL aliquot was sampled at predetermined time intervals. Aliquots were centrifuged to remove the solids and the supernatant was removed of the unreacted methanol by drying the collected supernatant in a convective oven until constant weight. The collected product free of methanol was then dissolved in ethyl acetate for GC analysis and subsequent FAME content determination.

3. Results and discussions

Provided in Table 2 is a summary of the characteristics of the gathered SCG and prepared PHSCG. As could be observed, the moisture content of the generated PHSCG is similar to that of the collected SCG, but upon hydrolysis ~20 wt% of the moisture-free material was dissolved into the hydrolyzing medium. This implies lesser solids to be subsequently dried and lesser quantity of water to be removed, as previously established [14,15]. With most of the lipids being hydrophobic in nature, these are less likely solubilized, and with the dissolution of part of the SCG the lipid is expected to be densified in the resulting PHSCG [6,11]. Similar to previous works done on the DAH of SCG without prior lipid extraction, the lipid content of the resulting PHSCG (23.1 wt%) is higher than the collected SCG (16.6 wt%). The increase is attributed not only due to densification but also to the release of bound lipids, which were not originally extractable as supported by the increase in the total fatty acid content. The fatty acid profile of lipids from PHSCG were comparable to that of lipids obtained from SCG, with estimated fuel properties of corresponding FAME conforming to standards (Table 3). Aside from these, the FFA was also observed to increase from 9.3 to 16.4 wt%, which may have resulted from either the release of the bound fatty acids from the solid matrix, or those from the acylglycerides. Regardless if the starting material is SCG or PHSCG, the presence of FFA in the lipids implies the need to use catalysts other than alkali to convert the lipids into FAME-based biodiesel. Interestingly, obtained PHSCG was analyzed to contain higher amounts of sulfur (3.95 wt%) as compared to that of the native SCG (0.18 wt%). The increase in sulfur may be attributed to the sulfuric acid that is left behind upon drying and could well serve as catalyst for the (trans)esterification reaction, whether in bound or free form.

Preliminary extraction experiments have been carried out with the

Table 2
Characteristics of collected spent coffee grounds (SCG) and post-hydrolysis SCG (PHSCG) and lipid profile.

Biomass	SCG	PHSCG*
Particle size (μm)	365.17 ± 34.97	385.54 ± 11.39
Composition (wt.%)		
Moisture	61.78 ± 1.64[a]	63.34 ± 0.75[a]
	(5.87 ± 0.01)[b]	(6.11 ± 0.24)[b]
Lipids[c]	16.60 ± 0.13	23.10 ± 0.93
	(16.60 ± 0.13)[d]	(18.41 ± 1.13)[d]
Free fatty acid[e]	9.28 ± 0.19	16.36 ± 0.04
Monoglyceride[e]	7.13 ± 0.06	3.94 ± 0.10
Diglyceride[e]	11.66 ± 0.16	8.92 ± 0.43
Triglyceride[e]	67.55 ± 2.75	65.63 ± 1.49
Unsaponifiable Matter[e]	3.97 ± 1.15	3.52 ± 0.94
Total Fatty Acid Content	84.28 ± 0.77[e]	85.23 ± 1.55[e]
	(13.99 ± 0.17)[d]	(15.69 ± 1.00)[d]
Theoretical Maximum FAME Yield[f]	~88.49	~89.49
	(~14.69)[c,d]	(~20.67[c]/~16.16[d])
Sulfur Content[c]	~0.1761	~3.9536
	(~0.1761)[d]	(3.1519)[d]

* Obtained after subjecting SCG to dilute acid hydrolysis with 4 %v/v acid (95% H_2SO_4) at an SSR of 8 mL/g (based on dry-lipid-free biomass) for 3 h at 95 °C with intermittent shaking (30 min interval); [a]Moisture as received or obtained (expressed in wet basis). [b]Moisture content determined after oven drying (expressed in wet basis); [c]Expressed in dry basis (moisture-free); [d]Expressed relative to the native dry biomass and in dry basis (dry matter yield after hydrolysis = 79.72 ± 3.66 wt%); [e]Expressed relative to the extracted lipids; [f]Theoretical maximum FAME estimated by multiplying a factor of 1.05 to the determined total fatty acid content in order to account for the incorporated methyl group.

Table 3
Fatty acid profile of lipids obtained from SCG and PHSCG, and their estimated FAME properties.

Fatty Acid Profile[a]	SCG	PHSCG	Literature[b]	
Lauric (C12:0)	0.02 ± 0.01	0.02 ± 0.01	0.1–3.3	
Myristic (C14:0)	0.08 ± 0.00	0.08 ± 0.01	0.28–1.0	
Palmitic (C16:0)	32.70 ± 0.08	32.73 ± 0.37	11.2–26.5	
Palmitoleic (C16:1)	0.09 ± 0.00	0.09 ± 0.00	0.1–0.3	
Stearic (C18:0)	7.55 ± 0.02	7.27 ± 0.09	1.0–2.6	
Oleic (C18:1)	10.11 ± 2.53	12.45 ± 1.08	6.7 – 24	
Linoleic (C18:2)	44.06 ± 2.67	42.03 ± 0.68	22 – 49.9	
Arachidic (C20:0)	2.64 ± 0.02	2.62 ± 0.23	1.1–4.7	
Behenic (C22:0)	0.10 ± 0.02	0.09 ± 0.03	0.1–4.3	
Lignocergic (C24:0)	0.02 ± 0.1	0.01 ± 0.00	0.1–0.5	
Others	3.74 ± 0.44	0.99 ± 0.10	-	
Biodiesel Properties[c]	**SCG FAME**	**PHSCG FAME**	**ASTM[d]**	**EN[d]**
Saturated Fatty Acids, SFA	43.11	42.82	n.a.	n.a.
Monounsaturated FA, MUFA	10.20	12.54	n.a.	n.a.
Polyunsaturated FA, PUFA	44.0.06	42.03	n.a.	n.a.
Degree of Unsaturation, DU	98.32	96.60	n.s.[c]	n.s.
Iodine Value, IV (g I_2 per 100 g)	88.99	87.42	n.s.	$\leq$ 120
Saponification Value, SV ($mg \cdot g^{-1}$)	199.80	199.83	n.s.	n.s.
Cetane Number, CN	53.59	53.94	$\geq$ 47	$\geq$ 51
Density ($kg \cdot m^{-3}$)	853	853	n.s.	860 – 890
Kinematic Viscosity ($mm^2 \cdot s$)	3.61	3.63	1.9 – 6.0	3.5 – 5.0
Higher Heating Value ($MJ \cdot kg^{-1}$)	38.36	38.38	n.s.	n.s.
Long-Chain Saturated Factor	9.88	13.94	n.a.	n.a.
Cloud Point, CP (C)	12.21	12.22	n.s.	n.s.
Pour Point, PP (C)	6.43	6.45	n.s.	n.s.
Cold Filter Plugging Point, CFPP (C)	14.54	13.94	n.s.	n.s.
Allylic Position Equivalents, APE	98.23	96.51	n.a.	n.a.
Bis-Allylic Position Equivalents, BAPE	49.34	47.27	n.a.	n.a.
Oxidation Stability Index, OSI (h)	5.27	5.40	$\geq$ 3	$\geq$ 6

[a] Fatty acid profile expressed as percent relative abundance (%w/w) based on chromatographic areas of detected fatty acid methyl esters; [b]Literature data obtained from previously published work by Jenkins et. Al. [30]; [c]Biodiesel properties were estimated using "Biodiesel Analyzer© Ver. 2.2″ (available on "http://www.brteam.ir/biodieselanalyzer") with empirical correlations based on related literature [31,32]; [d]ASTM and EN prescribed limits were referenced from the summary provided in a review by Wieselburg et. al. [33]

use of methanol to understand the extent of methanol's extracting power when it comes to removing the available lipids from SCG or PHSCG. At an SSR of 6 mL/g, SCG and PHSCG samples were suspended in methanol with continuous stirring (200 RPM) for 6 h at 65 °C. Upon separation and recovery, it was observed that methanol was able to dissolve and/or extract 12.19 ± 0.1 wt% and 50.4 ± 0.1 wt% of the SCG's and PHSCG's mass, respectively. Further fractionation with hexane revealed that methanol extraction for 6 h had a hexane soluble material yield of 3.71 ± 1.57 g per 100 g SCG and 17.28 ± 2.38 g per 100 g PHSCG processed. These are indicative of the ease of solubilizing PHSCG components, allowing the recovery of lipids from PHSCG with methanol as solvent and using less amount of solvent as compared to recovering of lipids from SCG. These results are consistent with previous observations on the recovery of lipids from PHSCG with n-hexane as solvent, where extraction occurred at a much faster rate (~90% extracted in less than 1 h) and the solvent required was 40% less as compared to systems involving SCG [11]. In addition, the resulting hexane soluble fraction with the use of methanol as solvent PHSCG-system contained significant amount of FAME (~98.5 wt%) which is not observed from extracts obtained from SCG. This results further indicate the possibility of implementing ISTE and avoiding the addition of catalyst in the production of FAME with PHSCG as the raw material. The following section details the influence of temperature, SSR, and time on the FAME yield during ISTE of lipids in PHSCG and analysis to elucidate the catalytic activity of the resulting PHSCG as a catalyst.

3.1. Yield of FAME from PHSCG during ISTE

In-situ (trans)esterification of lipids found in PHSCG was carried out adopting L_9 orthogonal array with resulting yields converted into S/N ratio and summarized in Table 1. The responses of a given variable and level were pooled and their means presented in a response graph (Fig. 1). As could be observed, the S/N ratio and correspondingly the yield increases as the temperature (A) is increased from 55 to 65 °C but have tendency to decrease as the temperature was further increased to 75 °C. For SSR (B), increase in SSR generally resulted in increase in yield but approaches a limit as SSR was increased to 10 mL/g. In view of reaction time (C), a certain optimum is reached at about 8 h, with prolonged reaction time resulting in decrease in the yield. In the Taguchi design of experiments, the main effect is determined via a Pareto analysis by taking the difference (Δ_i) between the maximum and minimum S/N_i of a given variable. In the ISTE of PHSCG within the levels of the variables investigated, Temperature (A) was found to be the primary factor influencing the obtained FAME yield, followed by SSR (B), and Time (C). However, the determined Δ_i of each variable were not very much different from one another (Table 4).

To have a more objective assessment, analysis of variance (ANOVA) was carried out and results are summarized in Table 4. Despite all three variables having been statistically found to have insignificant ($p > 0.05$) influence within the level investigated, the contribution of temperature (A), SSR (B), and time (C), were found to be 28.54%, 20.29%, and 14.04% respectively. From ANOVA the unaccounted contribution (error) is 37.13%, which may be owing to interaction effects and other variables unaccounted in the current experimental design. Although the adopted experimental design does not enable the determination of interaction effects, its main advantage is its optimization process solely based on the main effects. From the response graph (Fig. 1), an improved or optimized response is expected when combining variables at levels with highest S/N_i, which in this case are A2, B3, and C2. Using Eqs. (3) and (4), the predicted optimum S/N is 25.79 ± 1.32 dB, corresponding to an optimum yield of 19.47 ± 2.44 g FAME/100 g PHSCG at 95% confidence interval. These predicted values for S/N and yield are within bound of the theoretical maximum of 25.76 dB and 19.41 g FAME/100 g PHSCG, respectively. Actual validation experiment carried out in triplicates achieved an S/N of 25.67 with a yield of 19.21 ± 0.08, which coincides well with the predicted value. Thus, through the use of Taguchi L_9 orthogonal design, the variables contributing to the FAME yield during the ISTE of PHSCG could be easily determined and maximum yield could be well predicted.

3.2. Regression analysis and influences of reaction parameters

In aid of better understanding the influence of the different variables and interaction effects, regression analysis was further employed, with the gathered responses in terms of S/N. Summarized in Table 5 are the results of fitting different multivariate linear and quadratic models. Although linear contribution of the variables is often assumed in Taguchi's optimization principle, it could be observed from Table 5 that

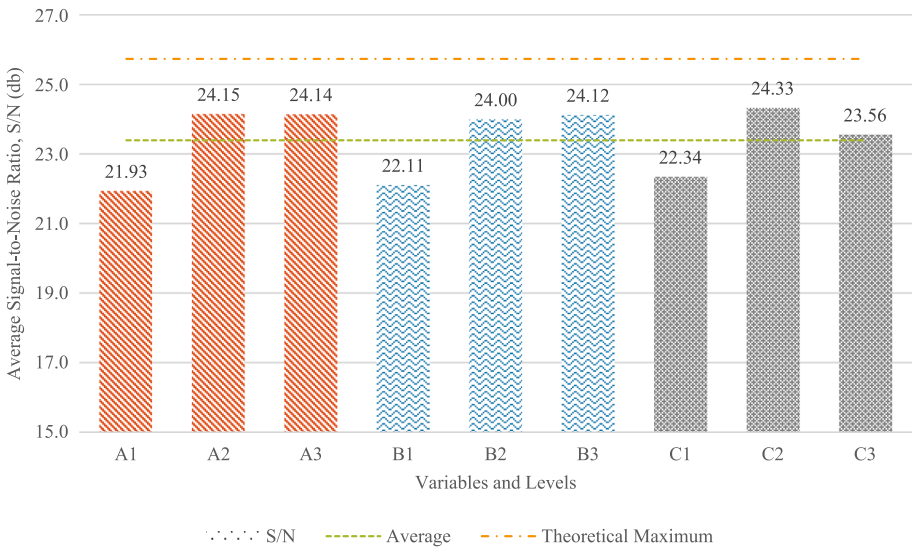

Fig. 1. Response graph of the-higher-the-better S/N ratios of FAME yield (S/N_{ave} = 23.41). A: temperature (55, 65, 76 °C); B: solvent-to- solid ratio (SSR: 6, 8, 10 mL/g); C: time (4, 8, 12 h).

Table 4
Summary of Pareto analysis and analysis of variance for the FAME yields expressed in terms of signal-to-noise ratios obtained from employing Taguchi L_9 (3^3) orthogonal array design of experiment.

Parameters	Average Signal-to-Noise Ratio (S/N_i)			Error	Total
Variables and Levels	Temperature (A)	Solvent-to-solid Ratio (B)	Time (C)		
1	21.9331	22.1060	22.3397	–	–
2	24.1515	23.9981	24.3315	–	–
3	24.1438	24.1243	23.5571	–	–
Average	23.4094	23.4094	23.4094	–	–
Δ_i	2.2184	2.0183	1.9918	–	–
Rank	1	2	3	–	–
DOF	2	2	2	2	8
SS	9.8090	7.6697	6.0493	2.4076	25.9356
MS	7.4013	5.2621	3.6416	9.6306	
F	0.7685	0.5464	0.3781		
p-value	0.5654	0.6467	0.7256		
Contribution (%)	28.54	20.29	14.04	37.13	100.0

DOF: degrees of freedom; SS: sum of squares; MS: sum of square error; F: F-ratio; p: p value (F_{crit} = 19 at p = 0.05)

the main effects also involved quadratic terms, whereby improving the overall fit of the model when quadratic terms are included. Apart from the main effects, interaction terms also play a significant role with temperature and time interaction found to be the most significant ($p < 0.05$). Two truncated models, model K1 and K2, were found to adequately fit the responses obtained, with the main difference in the quadratic term involving the SSR (B). Both models were found to have R^2 of at least 0.99 and adjusted-R^2 of at least 0.95. Further, lack of fit test was carried out for both models, with both models K1 (F-value = 0.18, F-critical = 4.26) and K2 (F-value = 0.13, F-critical = 5.12) having no lack of fit with its F-value less than the critical F-values at 95% confidence level. Moreover, the parity plot (Fig. 2a) of the predicted and actual responses observed also falls along the 45-degree line while indicates a good fit. Taking into considerations the coefficients of each term in the generated models the positive coefficients in the linear terms indicate the possible main effect of all three variables to FAME yield. However, with the negative coefficients in the quadratic terms these indicates that extremely high temperatures, excessive amounts of methanol, and ISTE reactions carried out at extended reaction times will have detrimental influences to the FAME yield.

The increase in temperature generally brings about faster reaction and extraction rates and generally shifts the equilibrium forward for endothermic processes like ISTE. However, higher temperatures may result in unwanted side reactions causing losses in the FAME during ISTE. In the direct (trans)esterification of SCG lipids in H_2SO_4 impregnated SCG by Liu et al. [18], an increase in FAME yield from 16.19 to 17.08 g/100 g SCG was observed when the temperature was increased from 60 to 70 °C, but a further increase resulted in a slight decrease to 16.86 g/100 g SCG, but such decrease was found to be statistically insignificant. In a separate work by Park et al. [19] involving the acid-catalyzed (H_2SO_4) ISTE of wet SCG with chloroform as a co-solvent, it was found that FAME yields decreased as the temperature was increased beyond 95 °C, attributing the lower yields to the vaporization of methanol at higher temperatures, and or other side reactions.

In view of SSR, the presence of adequate amount of methanol ensures its availability for the (trans)esterification reaction and its capacity to extract the lipids and/or the FAME formed within the solid matrix during the ISTE process. However, excess methanol or solvent in general may also result decrease in the FAME yields, owing to either difficulty in separation from the glycerol phase or as a result of slower reaction rates owing to dilution of the system. Park et al. [19] observed a decrease in FAME yield when the amount of methanol to dry SCG exceeded 8.33 mL/g or at an overall SSR of 12.5 mL/g (chloroform to methanol volume ratio of 1:2) during the acid-catalyzed ISTE of wet SCG. The observed decrease was attributed to decrease in separation yield between the FAME and glycerol phases. However, in the current study, methanol was first removed after the reaction, minimizing such concern. Thus, the negative influence of excess SSR may be attributed to the dilution [20], whether in the bulk system or within the solid matrix. In another instance, Nguyen et al. [21] observed that a methanol to dry SCG beyond ~13 mL/g resulted in decrease in the observed FAME yield, attributing this to the dilution of the catalyst in the system. Similarly, in the ISTE of PHSCG, no additional catalyst is added apart from the residual acid present after hydrolysis and subsequent drying, thus an increase in SSR inevitably dilutes the effective concentration of catalyst in the system. Considering the magnitude of the coefficient of the quadratic term in model K2, it is less than that of the linear term, thus resulting in an overall positive influence of SSR on the FAME yield.

As for reaction time, longer reaction times are generally preferred as this would ensure that the reaction approaches completion or reaches the equilibrium. For SCG impregnated with H_2SO_4 prepared by Liu et al. [18] and the reaction carried out in a Soxhlet extractor, the required

Table 5
Summary of regression analysis of the FAME yields expressed in terms of signal-to-noise ratios obtained from employing Taguchi L_9 (3^3) orthogonal array design of experiment.

Parameters	Regression Models									
	Linear		Linear + Quadratic		Linear + Interaction		Truncated 1 (K1)		Truncated 2 (K2)	
Predictors	Coefficient	p-value	Coefficient	p-value	Coefficient	p-value	Coefficient	p-value	Coefficient	p-value
Intercept	23.4094	$6.69x10^{-08}$	25.6623	0.0014	23.40945	0.0001	25.0736	0.0001	25.3047	0.0075
Linear										
A	1.1054	0.1175	1.1054	0.1323	0.0772	0.8799	1.1054	0.0197	1.1054	0.7618
B	1.0091	0.1452	1.0091	0.1530	−0.3890	0.4793	0.4034	0.1804	0.4728	0.2267
C	0.6087	0.3459	0.6087	0.3071	1.5616	0.0742	0.6087	0.0610	0.6087	0.1368
Quadratic										
A2			−1.1131	0.2878			−1.1131	0.0524	−1.1131	0.1298
B2			−0.8830	0.3730					−0.3466	0.4065
C2			−1.3831	0.2165			−1.3831	0.0368	−1.3831	0.1049
Interaction										
AB					1.9057	0.1063				
BC					−2.0564	0.0933				
AC					−2.7963	0.0538	−1.2114	0.0383	−1.0728	0.1346
Standard Error of Estimate	1.4332	–	1.0972	–	0.7307	–	0.3861	–	0.3255	–
Model (n = 9)	–	0.1699	–	0.2534	–	0.1185	–	0.0341	–	0.1298
Regression										
DOF	3	–	6	–	6	–	6	–	7	–
SS	15.6646	–	23.5279	–	24.8677	–	25.6374	–	25.8296	–
MS	5.2215	–	3.9213	–	4.1446	–	4.2729	–	3.6899	–
Residual										
DOF	5	–	2	–	2	–	2	–	1	–
SS	10.2710	–	2.4076	–	1.0679	–	0.2982	–	0.1060	–
MS	2.0542	–	1.2038	–	0.5339	–	0.1491	–	0.1060	–
R^2	**0.6040**	**–**	**0.9072**	**–**	**0.9588**	**–**	**0.9885**	**–**	**0.9959**	**–**
R^2-adjusted	**0.3664**	**–**	**0.6287**	**–**	**0.8353**	**–**	**0.9540**	**–**	**0.9671**	**–**

time to reach the highest FAME yield and conversion was 12 h and prolonged reaction time up to 17 h did not result changes in the yield with the reaction carried out at 70 °C. In the current study, a reaction time of around 8 h was found favorable, with extended periods having tendencies to result in lower yields. This could be attributed to side reactions, considering that the extracted lipids and/or FAME generated are continuously in contact with the solids and other materials, unlike in a Soxhlet extractor where products are continuously separated from the solids. Apart from the main effects, the interaction effect of temperature and time was found to be negative as well, which indicates that increasing both temperature and time will be detrimental to the overall FAME yield, with reactions employing high temperatures favorably carried out with shorter reaction time and lower temperatures having to be carried out at longer reaction times. To better visualize these, contour plots are generated based on model K1 as presented in Fig. 2b-d.

Considering that models K1 and K2 have quadratic terms, and as could be observed from the contour plots a local optimum is expected. Optimization of both models resulted in the following optimized combination of variables, A = 69.95 °C, and C = 8.01 h for model K1, and A = 69.80 °C, B = 9.36 mL/g, and C = 8.13 h for model K2. The calculated optimum parameters are very similar, but with model K1 not having a specified SSR (B) since there is no quadratic term, which could be taken as 10 mL/g to achieve the highest yield. For practicality, confirmatory runs were carried out based on both optimizations by Taguchi (A = 65 °C, B = 10 mL/g, and C = 8.0 h) and at A = 70 °C, B = 9.4 mL/g, and C = 8.0 h, with considerations to the possibly of reducing the SSR. A summary of the results from the confirmatory runs and corresponding predicted values are presented in Table 6.

Yields from both conditions adopted for validation can be well predicted using model K1 with results falling within 95% confidence of the predicted values (Fig. 2a). Both conditions tested resulted in yields of ~19 g/100 g PHSCG (~20 g/100 g moisture-free PHSCG), which translates to a conversion of ~98% with FAME content or purity meeting of the generally required 96.5%. Optimization by either Taguchi's method or by regression analysis of the results obtained from the L_9 orthogonal array design of experiments, both allows the determination of the optimum combination of the factors and their levels, which at the same time adequately predicts the yields.

3.3. Surface characterization and catalytic activity of Functionalized-PHSCG

During DAH, H_2SO_4 generally acts as the catalyst for the hydrolysis of the different SCG components but may well have also reacted with these. Upon separation, it is unavoidable that part (~20%) of the hydrolysate or the initial hydrolyzing medium is adsorbed or entrained in the PHR. During the drying process to remove the water from the PHR, H_2SO_4 becomes concentrated and may have resulted in the subsequent partial carbonization and sulfonation likening the process of direct sulfonation of cellulosic biomass in the synthesis of sulfonic based solid acid catalyst [34,35]. This is evident in observed darkening of the PHR as they were dried and the increase in the sulfur content of PHSCG (4.84 ± 0.04 wt%), which is 23 times higher than the native SCG (0.21 ± 0.29 wt%). Coincidentally, the SAD also increased 21 times (Table 7), which can be attributed to the attachment of acidic sulfur containing groups to the biomass surface as sulfonic acid groups and the increase in carboxylic acid croups in the resulting material. Further analysis using FT-IR revealed that the characteristic peak attributed to C–H axial deformation of CH_2 and CH_3 which may be of the lignocellulosic materials (cellulose, hemicellulose, and lignin) in the 2900 cm^{-1} region [36] from SCG (Fig. 3a) has disappeared or shifted, and PHSCG now have characteristics peaks of sulfonic acid groups as observed at 1221 and 1057 cm^{-1}. This is in agreement with Ngaosuwan et al. [37] and the SO_2 bands they have detected in the SCG-derived solid acid catalyst with wavelengths 1000, and 1100 cm^{-1}. The differences in the observed spectra may be owing to the differences on how the catalytic material was prepared. In their study, SCG was sulfonated after partial carbonization (600 °C), where concentrated H_2SO_4 (20 mL) was mixed with 1 g of carbonized SCG and sulfonated at various temperatures (140 – 200 °C), which resulted in a catalyst having a sulfonic acid density of 0.4 – 0.7 mmol H^+/g. In this work, much higher acid density is achieved, while requiring less severe process conditions, and allows recovery of the available sugars as previously demonstrated [6,14,15].

A mentioned earlier, the catalytic activity of PHSCG was initially

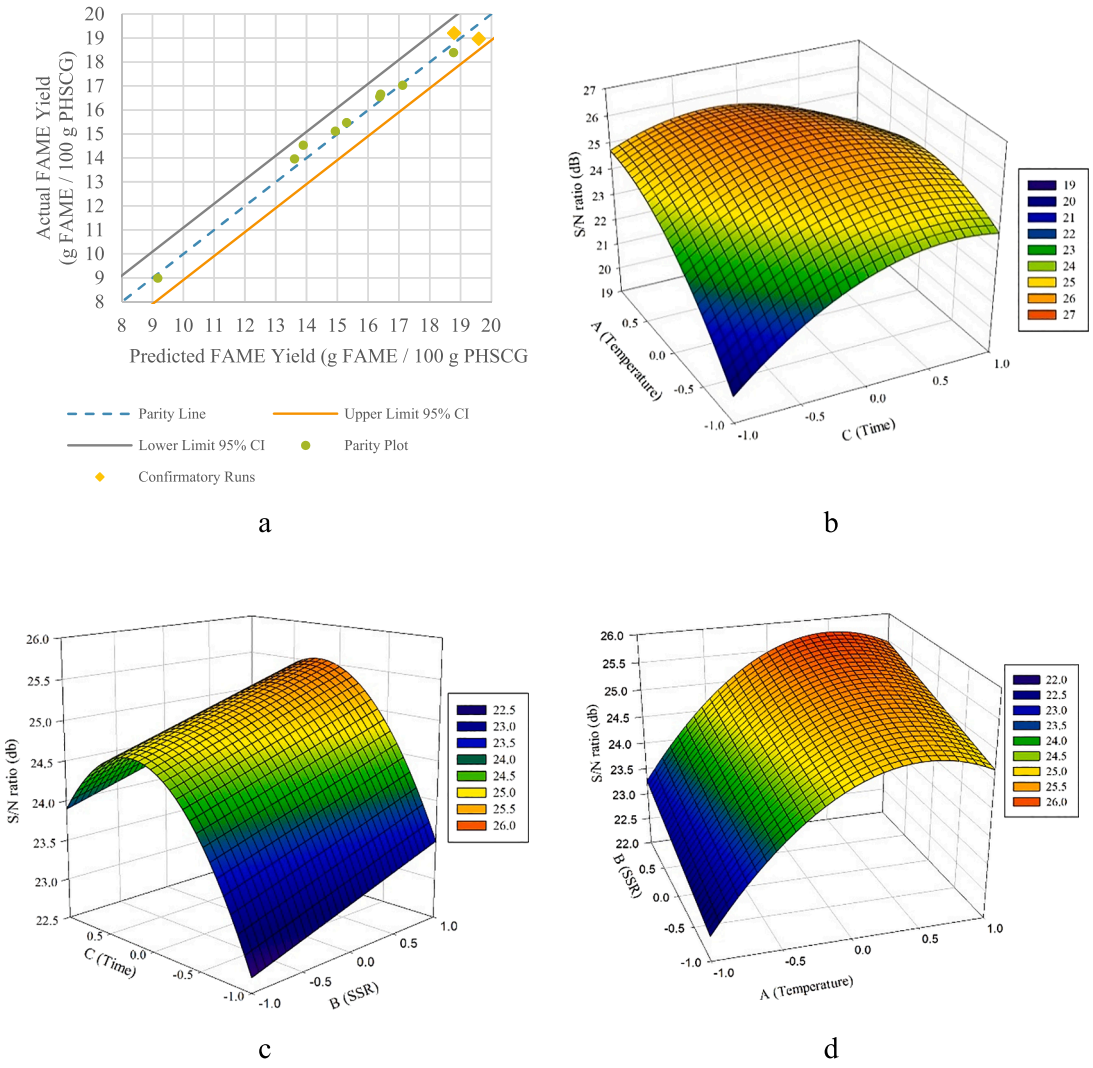

Fig. 2. Parity plot (a) based on truncated regression model K1, response surface plot at a fixed SSR of 10 mL/g (b), fixed temperature of 65 °C (c), and fixed reaction time of 8 h (d).

Table 6
Summary of confirmatory runs based on predicted local optimum conditions.

Expt. Run	Reaction Condition T,°C	SSR, $cm^3 \cdot g^{-1}$	T, h	FAME Yield ± SD	Predicted Yield ± SD	S/N	Predicted S/N ± SD	FAME Content (%)	Conversion (%)
10	65	10	8	19.21 ± 0.08 (20.46 ± 0.82)[a]	19.47 ± 2.44[b] 18.78 ± 1.05[c]	25.67	25.79 ± 1.32[b] 25.47 ± 0.39[c]	96.92 ± 0.48	98.98[d]
11	70	9.4	8	18.96 ± 0.25 (20.20 ± 0.85)[a]	19.59 ± 1.05[c]	25.56	25.84 ± 0.39[c]	95.64 ± 1.21	97.75[d]

[a] Moisture-free basis; [b] Predicted using Taguchi optimization model; [c] Predicted using truncated regression model K1; [d] relative to optimum FAME yield of 20.67 ± 0.91 g FAME/100 g moisture-free PHSCG (moisture content ~6.11 ± 0.24 g H_2O / 100 g PHSCG).

observed in the during the extraction of lipids from SCG and PHSCG using a batch reactor initially intended to evaluate the solvent's extracting power. For PHSCG, the lipid profile of the hexane soluble fraction of the methanol extractives revealed significant amount of FAME (~98.5 wt%), which was not detected in the methanol extracts of SCG. This gives rise to the notion that PHSCG, not only served as a lipid source, but also a catalyst in the (trans)esterification of the available fatty acid chains to FAME, thus even during the optimization experiments and validation runs no additional catalyst was added to the system. However, after ISTE, the SAD in the remaining residue dropped by approximately 80% (Fig. 3b). This could mean that the substances which contain sulfonic and/or carboxylic groups may have solubilized during ISTE. Considering that the resulting crude extract was further subjected to ~70 °C for methanol removal using a rotary evaporator for 1 h, the observed conversion remained a wide range from 46 to 98% in the set of experiments carried out even when the crude methanol extract was in a narrow range of 43 to 54 g/100 g PHSCG. Thus, the dissolved components may not entirely contain sulfonic groups having significant catalytic activity.

Despite the decrease in SAD after ISTE, the remaining strong acid sites in the post-ISTE residue is still roughly 3 times higher than that of native SCG. In Fig. 3a, asymmetric and symmetric SO_2 were still detected as 1159 and 1058 cm^{-1}. To further evaluate the catalytic activity of the remaining residues with strong acid sites, the residues

Table 7
Elemental composition and acid densities of lipid-free spent coffee grounds (SCG) and post-hydrolysis SCG (PHSCG).

Material	%C[a]	%H[a]	%O[a]	%N[a]	%S[a]	Sulfur Content[b] (mmol S/g solid)	SAD[c], (mmol H^+/g solid)	TAD[d], (mmol H^+/g solid)	WAD[e], (mmol –OH/g solid)
SCG	51.25 ± 0.19	6.59 ± 0.03	42.38 ± 1.88	2.82 ± 0.04	0.21 ± 0.29	0.06 ± 0.09[f] (0.0500)[g]	0.04 ± 0.00[f] (0.0334)[g]	2.21 ± 0.17[f] (1.8431)[g]	2.16 ± 0.17[f] (1.8014)[g]
PHSCG	49.59 ± 0.17	5.15 ± 0.13	39.05 ± 0.06	3.30 ± 0.00	4.84 ± 0.04	1.51 ± 0.01 (1.1612)	0.86 ± 0.04 (0.6613)	5.10 ± 0.31 (3.9219)	4.24 ± 0.31[f] (3.2606)

[a] Results obtained from elemental analysis of pre-dried, lipid- free samples; [b] Calculated from sulfur weight percentage from elemental analysis; [c] Strong Acid Density (SAD) determined from a 6 h reaction time of 0.5 g of pre-dried lipid- free samples with 2 M NaCl solution; [d] Total Acid Density (TAD) determined from a 6 h reaction time of 0.5 g of pre-dried lipid- free samples with 0.1 M NaOH solution; [e] Weak Acid Density (WAD) calculated as the difference between TAD and SAD; [f] Values expressed in terms lipid-free solids and in dry or moisture-free basis; [g] Values expressed in termed of solid samples containing lipids and in dry or moisture-free basis.

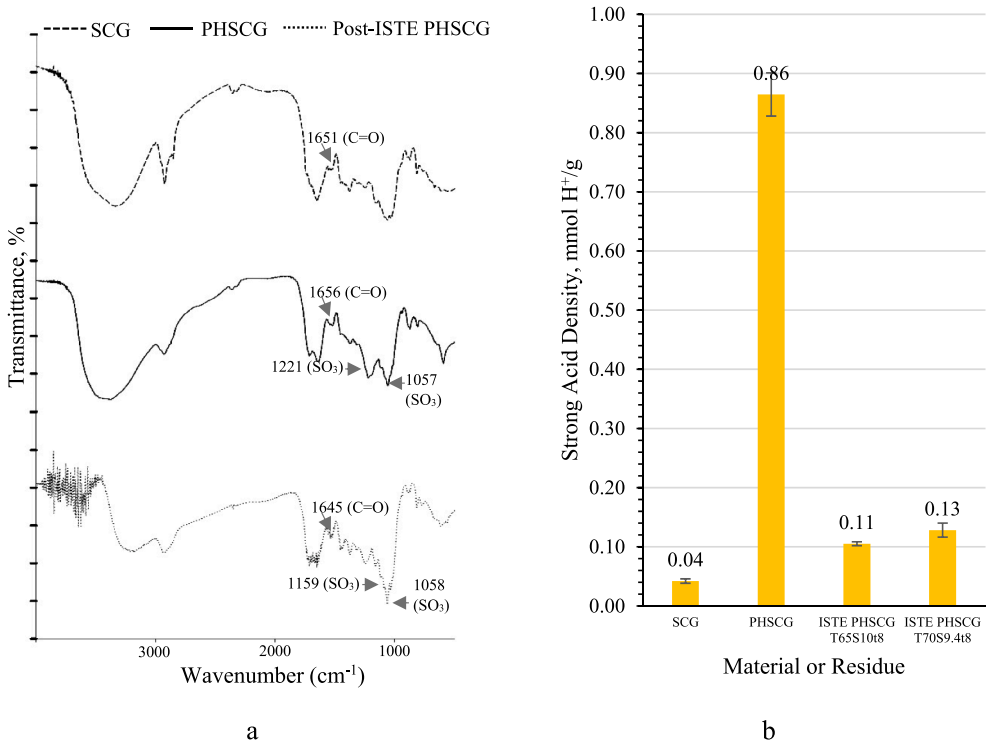

Fig. 3. Fourier transform infrared spectra (a) and strong acid cites (b) of delipidated SCG, PHSCG and residual PHSCG.

collected and delipidated after ISTE of PHSCG at the optimum conditions was used as a catalyst in the esterification of oleic acid with methanol. It can be observed that at 12 h reaction time, ~92% FAME content in the reaction product was achieved and reached ~95% at 24 h (Fig. 4). Comparing with the performance of the SCG-derived solid acid catalyst (SAC) (71.5%) in the study by Ngaosuwan [37], post-ISTE

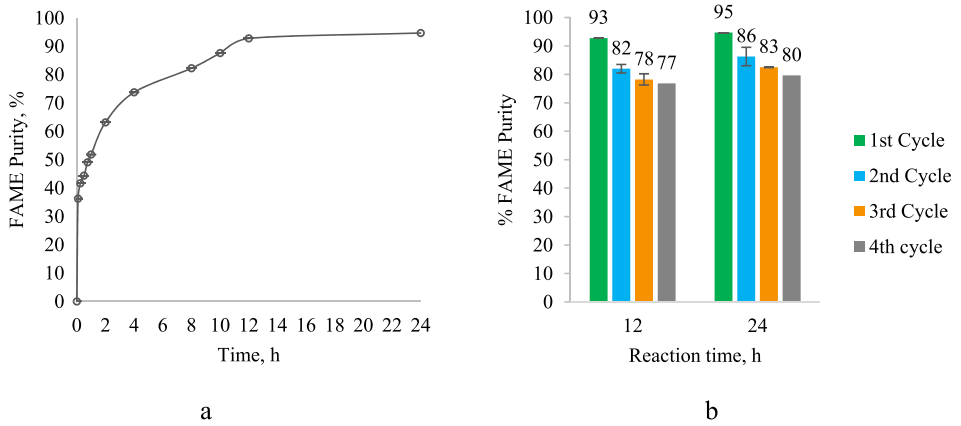

Fig. 4. Esterification of oleic acid with methanol at solvent-to-fatty acid ratio of 20 mol/mol for 24 h at 60 °C with constant stirring at 200 rpm (a) and reusability of PHSCG residues after ISTE as catalyst (b).

residue gave a comparable conversion (~74%) at 4 h, without the need of preparing the catalyst at high temperatures. In addition, the post-ISTE residue also exhibits catalytic activity when used in the transesterification of soybean oil with methanol under the same methanol to fatty acid ratio and reaction condition, achieving at least 5.28 ± 0.08 wt % FAME in the product. Although the attained conversion is not high, the results still indicate that the partially carbonized and sulfonated material exhibits catalytic activity during transesterification, apart from esterification.

From the above results it is evident that PHSCG does have catalytic activity and served catalyst in the (trans)esterification of its lipids to FAME avoiding the need for the addition of an external catalyst. Furthermore, despite the decrease in acid sites, post-ISTE residue could be used as catalyst for esterification (Fig. 4a). In terms of stability of the catalytic activity of the post-ISTE residue, it can be reused up to three times while retaining at least 85% of its activity after 4 cycles (Fig. 4b). Although a decrease in the activity is observed, the post-ISTE residue retained much higher activity as compared to the SCG-derived SAC synthesized through partial carbonization and subsequent sulfonation, which was reported to retain only ~70% of its original activity, despite using $ZnCl_2$ as an activation agent [37]. In addition, the post-ISTE residue also have better stability in its activity when compared to sulfonated partially carbonized SCG without any activation agent, which was recent reported by Agapay et al. [38] to retain only ~26% of its original activity after the 3rd reuse. Although a decrease in activity is observed the magnitude of the decrease is less after each cycle and tends to become stable afterwards. A similar observation was also made in related works of carbon-based SAC, when loosely bound or soluble components bearing the active or catalytic moiety has been removed, leaving behind the stable active sites beyond the 3rd cycle [35,39,40]. The good stability of the catalytic activity can be supported by the better retention of the strong acid sites with the catalyst still retaining an acid density of 0.1020 mmol H^+/g, at least ~90% of its initial density, after the 4th cycle. With this, the resulting post-ISTE residue from PHSCG could be further explored in the future as a potential green heterogeneous acid catalyst to replace homogeneous H_2SO_4 in systems favoring an acid catalyst, such as high FFA containing lipids.

3.4. Process comparison and evaluation

Native SCG has a lipid content of less than 20% by wt. and the employment of dilute acid as a pretreatment densified the lipid content to >20% by wt. increasing its competitiveness with current lipid containing feedstock or even when compared to native SCG. The FFA content (~16 wt%) in PHSCG is also higher than the usual SCG lipid (<15 wt%), and while this is a disadvantage for a base-catalyzed reaction, in view of the acid-catalyzed (trans)esterification, this is advantageous. Another characteristic of PHSCG is the incorporation of sulfonic sites which is then serves as catalyst in the conversion of its lipids to FAME and eliminates the need for sulfuric acid addition. From Table 8, H_2SO_4 is required at a loading of 20 – 230 wt% relative to the amount of SCG to achieve good conversions (>95%). With respect to this, the use of PHSCG can be considered a greener alternative and maximizes the use of sulfuric acid which was initially only intended for the hydrolysis process. Moreover, the time required for the reaction (8 h) is competitive with other ISTE systems for SCG without the need to use high SSR or catalyst.

In view of the SSR, the optimum SSR for PHSCG (10 mL/g) is considerably less for when compared to other acid-catalyzed ISTE of lipids from SCG. It must be noted that despite higher lipid content in PHSCG the required SSR was not much higher. In principle the added methanol at the given SSR is more than enough to theoretical convert all the available fatty acid chains at a solvent-to-fatty acid molar ratio (SFR) of ~293. The relatively lower SSR required for ISTE of PHRB is indicative of the ease of mass transport of reactants and products to and from the solid matrix of PHSCG. However, in the study by Liu et al. [18] where a Soxhlet extractor was used to carry out the direct (trans)esterification of lipids in sulfuric acid-impregnated SCG, an apparent SSR of only 5 mL/g was required to achieve a conversion of 98.6%. For a Soxhlet extractor, the apparent SSR is simply based on the amount of solvent charged into the boiling flask relative to the amount of solid placed in the extraction thimble. Unfortunately, the actual volume of solvent that comes in contact with the solids over time may be more than the volume charged to the system depending on the actual number of cycles the extraction process has undergone. Thus, its effective SSR could actually be much higher than 5 mL/g.

In addition, systems likening the Soxhlet extractor enables fresh solvent to come in contact with the packed SCG and is therefore not limited by equilibrium. Despite this advantage, Soxhlet extractor system is challenged in terms of scalability. For comparison purposes, the best catalyst loading condition obtained in the study by Liu et al. [18] was replicated in a batch reactor system using SCG. It can be observed from Table 8 that only a conversion of 23.43% could be achieved despite 20 wt% of acid loaded and the higher amount of methanol added. In this system, the two mechanisms of the ISTE process, extraction and reaction could have been limited by mass transfer. Another experimental run was carried out, by adding an equivalent concentration of H_2SO_4 with the acid sites of PHSCG. This system achieved a FAME conversion of only 2.26%. Even though higher acid loading resulted in higher conversions, these conversions are relatively low. Thus apart from the amount of acid loaded, the lower conversions achieved by both systems can be attributed to the hindrance provided by the solid matrix. This was not a challenge when using PHSCG as part of the biomass was already solubilized during DAH pretreatment of the native SCG. Without the use of a Soxhlet extractor equilibrium and mass transfer limitations during ISTE could be addressed through the use of lipid-dense PHSCG. Thus, the use of PHSCG over SCG decreases the mass transfer limitations brought about by the solid matrix, which is yet another advantage apart from the inherent catalytic activity.

At the best conditions determined in this study, an apparent conversion of ~96% was achieved based on the FAME yield from the products after separating the solid and liquid fraction of the reaction mixture, with the product containing ~96.9 wt% FAME. The solid fraction accounts for ~53% of the initial PHSCG used in the reaction, with the solid residue still containing ~7% hexane soluble material or equivalent to 0.5 g of hexane soluble components per 100 g of PHSCG processed. The hexane soluble material contained ~ 35% FAME, along with unreacted monoglycerides (~36 wt%), and diglycerides (~21 wt %). Accounting for all the FAME produced from the ISTE, this results in an overall conversion of ~ 99%. With unreacted acylglycerides still detected in the hexane soluble fraction of the post-ISTE residue, it is possible that over all reaction yields and conversion could go beyond 100%, which is expected from ISTE of lipid-containing biomass owing to the release and conversion of bound fatty acids [20]. Although not all product and unreacted lipids are extracted during the ISTE of PHSCG under the optimum conditions determined in this study, owing to extraction and/or reaction equilibriums, the resulting product have higher purity which meets the requirements for biodiesel (~96.5 wt%).

Compared to other approaches in the ISTE of lipids in SCG, the preprocessing of SCG to PHSCG, provides a means of maximizing the use of SCG as a raw material for biofuel production. Unlike other pretreatment approaches or catalyst synthesis approaches where energy intensive steps are required as pretreatment without producing valuable side products, the case is different when it comes to DAH of SCG. Dilute acid hydrolysis as a pretreatment not only densifies the lipid-containing biomass, alongside it is the saccharification of available sugars to produce sugar-rich hydrolysates for fermentation [23,41]. Moreover, upon drying of the wet residues after hydrolysis to produce the lipids dense PHRs, consequent generation of a SAC is achieved via simultaneous carbonization and sulfonation upon sufficient drying. Thus, generating a functionalized lipid-dense material, which could be used as feedstock with inherent catalytic activities for ISTE. In addition, the post-ISTE

Table 8
Comparison of results in *In-situ* (trans)esterification of spent coffee grounds lipids with significant free fatty acids.

Feedstock Quality[a]		Alkyl Donor and Co-solvent (mL/g) [b]		Solvent Loading [b]		Catalyst Loading	Mixing/ Irradiation/ Heating	T (C)/P (MPa)/t (h) [c]		Space Loading/ Reactor Loading [d]		Yields and Purity [e]		Material [Ref.]
M:	0–60	Methanol:	8.3	SFR_n:	- [g]	H_2SO_4	n.s.	T:	95	SL:	~58 *	Y_S:	>15	SCG [19]
L:	n.s.	Chloroform:	4.2	SLR:	~83*	2.4 vol.% of solvent*		P:	Ambient	RL:	~28 *	Y_L:	-	
F:	n.s.			SSR:	12.5	230 wt.% of the solid		t:	2			Y_P:	-	
P:	n.s. [f]											C_{AE}:	-	
M:	n.s.	Methanol:	5	SFR_n:	-	H_2SO_4 *(impregnated)*	*Mixing not specified*	T:	70	SL:	-	Y_S:	17	SCG [18]
L:	17			SLR:	29	2.2 vol.% of solvent*	Heating Tapes	P:	Ambient	RL:	-	Y_L:	-	
F:	7			SSR:	5	20 wt.% of the solid	Soxhlet Apparatus	t:	12			Y_P:	98.6	
P:	n.s.											C_{AE}:	-	
M:	52	Methanol:	13	SFR_n:	-	Diazabicycloundecene	n.s.	T:	60.2	SL:	-	Y_S:	-	SCG [21]
L:	13	Diazabicycloundecene:		SLR:	~331 *	30 mL/g of dry SCG*		P:	Ambient	RL:	-	Y_L:	-	
F:	7.7		30	SSR:	43			t:	0.48			Y_P:	97.31	
P:	n.s.											C_{AE}:	-	
M:	5.87	Methanol:	7.1	SFR_n:	292.3	H_2SO_4	200 rpm	T:	65	SL:	~12	Y_S:	4.55	SCG [This
L:	15.63			SLR:	43.29	1.45 vol.% of solvent	Magnetic Stirrer	P:	Ambient	RL:	~72	Y_L:	29.1	Study]
F:	9.28			SSR:	7.1	20 wt.% of the solid	Hotplate/ Water Bath	t:	8			Y_P:	23.43	
P:	0.37											C_{AE}:	88.54	
M:	5.87	Methanol:	7.1	SFR_n:	292.3	H_2SO_4	200 rpm	T:	65	SL:	~12	Y_S:	0.44	SCG [This
L:	15.63			SLR:	43.29	0.18 vol.% of solvent	Magnetic Stirrer	P:	Ambient	RL:	~70	Y_L:	2.81	Study]
F:	9.28			SSR:	7.1	2.41 wt.% of the solid	Hotplate/ Water Bath	t:	8			Y_P:	2.26	
P:	0.37						200 rpm					C_{AE}:	25.05	
M:	6.11	Methanol:	10	SFR_n:	292.3	Strong acid Sites	200 rpm	T:	65	SL:	~15	Y_S:	19.21	PHSCG
L:	21.68			SLR:	43.29	0.86 mmol/g solid [h]	Magnetic Stirrer	P:	Ambient	RL:	~68	Y_L:	88.57	[This Study]
F:	16.36			SSR:	10	0.17 vol % H_2SO_4 – Equivalent of solvent	Hotplate/ Water Bath	t:	8			Y_P:	98.98	
P:	0.39					3.0 wt.% of the solid	200 rpm					C_{AE}:	96.92	
M:	6.11	Methanol:	9.4	SFR_n:	292.3	Strong acid Sites	200 rpm	T:	70	SL:	~14	Y_S:	18.97	PHSCG
L:	21.68			SLR:	43.29	0.86 mmol/g solid [h]	Magnetic Stirrer	P:	Ambient	RL:	~68	Y_L:	87.47	[This Study]
F:	16.36			SSR:	9.4	0.18 vol % H_2SO_4 – Equivalent of solvent	Hotplate/ Water Bath	t:	8			Y_P:	97.75	
P:	0.39					3.0 wt.% of the solid	200 rpm					C_{AE}:	95.64	

* Entries to the table are calculated based on available information to facilitate comparison; [a] Spent coffee grounds quality in terms of moisture content (M, %w/w), lipid content (L, %w/w), free fatty acid content (F, %w/w), and particle size (P, mm); [b] Alkyl donor and co-solvent relative to the mass of dry solid (mL/g), solvent loading as expressed in terms of solvent-to-total fatty acid molar ratio (SFR_n), solvent-to-lipid volume to mass ratio (SLR, mL/g), and solvent-to-solid volume to dry biomass ratio (SSR, mL/g); [c] Temperature (T), pressure (P), and time (t); [d] Space loading (expressed as the reactor volume to the amount of biomass loaded, mL/g), and reactor loading (percentage of the reactor volume occupied by the reaction mixture); [e] Yields expressed as the amount of FAAE with respect to the solid (Y_S), with respect to the total lipids (Y_L), and with respect to the theoretical maximum amount of alkyl ester (Y_P), with purity (C_{AE}) expressed as the alkyl ester content; [f] not specified (n.s.); [g] incomplete information to allow estimation; [h] moisture-free and lipid-free basis.

residues still retain significant catalytic activity, which could be adopted as catalyst in the esterification of fatty acids. Although much is still to be done to optimize the entire process, these findings, opens a new possibility for processing lipid-containing biomass to serve as raw material for biofuel production.

4. Conclusions

Post-hydrolysis spent coffee grounds were proven to be a viable feedstock for producing FAME. Employment of dilute acid hydrolysis (DAH) as pretreatment increased the lipid content 1.4 times, from ~16 to ~23% in dry basis. Alongside its lipid densification, a simultaneous functionalization via simultaneous carbonization and sulfonation occurred with sufficient drying of the wet residues from DAH. The functionalized PHSCG exhibit catalytic activity, which enabled the ISTE of PHSCG lipids into FAME, without the addition of catalyst. Taguchi method was successfully employed to determine the optimum conditions for ISTE of PHSCG lipids without catalyst addition in a batch reactor. The maximum FAME yield, 19.47 ± 2.44 g FAME/100 g PHSCG, corresponding to ~96% conversion, could be achieved at a temperature of 65 °C, SSR of 10 mL methanol/g dried PHSCG, and a reaction time of 8 h. From ANOVA, temperature was determined to have the highest contribution to the FAME yield, followed by SSR and Time. Furthermore, regression analysis revealed that higher temperature over 65 °C and at prolonged reaction time (>8h), and their interaction have a negative influence on the FAME yield. The catalytic activity of PHSCG was supported by the increase in its strong acid sites 21.5 times, when compared to the native SCG, and sulfonic groups were detected during FT-IR spectral scans. Moreover, the post-ISTE residue still exhibited appreciable catalytic activity when used as a solid acid catalyst for the

esterification of oleic acid with methanol. Post-ISTE residue from PHSCG has a good stability after 4 cycles of use, maintaining over 80% of its original activity. As the choice of pretreatment for the valorization of lipid-containing lignocellulosic biomass like SCG, DAH has proven to be beneficial in lipid densification, and subsequent functionalization of the remaining solid during drying, to produce raw materials to serve as feedstock, lipid-source, and catalyst, for biodiesel production, while maximizing and reducing the use of non-renewable mineral acid (H_2SO_4).

CRediT authorship contribution statement

Kristelle L. Quijote: Writing - original draft, Writing - review & editing, Formal analysis, Conceptualization, Methodology, Investigation, Data curation. **Alchris Woo Go:** Writing - original draft, Writing - review & editing, Supervision, Project administration, Formal analysis, Funding acquisition, Conceptualization, Methodology, Visualization. **Ramelito C. Agapay:** Conceptualization, Writing - review & editing, Formal analysis, Visualization. **Yi-Hsu Ju:** Writing - review & editing, Conceptualization, Resources, Supervision. **Artik Elisa Angkawijaya:** Writing - review & editing, Resources, Supervision. **Shella Permatasari Santoso:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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