

Article

A Comparative Study on Thermochemical Valorization Routes for Spent Coffee Grounds

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Abstract: Extracting oil from spent coffee grounds (SCG) for biodiesel production has recently attracted much research interest. Large amounts of organic solvents are involved for oil extraction and biodiesel synthesis. Hydrothermal liquefaction (HTL) is an emerging thermochemical technology with great potential for biocrude production from a broad range of feedstocks. This study attempted to compare two SCG valorization options: route 1, oil extraction for biodiesel production followed by HTL of defatted SCG; and route 2, direct HTL of raw SCG. The microwave-assisted extraction conditions were optimized to effectively remove oil from SCG using response surface methodology. Under optimal conditions, an SCG oil yield of 8.4 wt.% could be achieved. HTL of defatted SCG generated less biocrude (18.9 wt.%) than that of raw SCG (28.1 wt.%). The biochemical compositions of resultant biocrudes were largely different from each other. The life cycle assessment was conducted on each of the SCG valorization routes and showed that the greenhouse gas emissions from direct HTL of raw SCG were only 35% of the other valorization route, suggesting that direct HTL is a favorable valorization route for SCG within this study's scope.

Keywords: hydrothermal liquefaction; biocrude; biodiesel; life cycle assessment; spent coffee grounds; extraction



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1. Introduction

Coffee is one of the most popular beverages worldwide. Approximately 9.9 billion kilograms of coffee were consumed globally in 2019 according to the International Coffee Organization [1]. Enormous amounts of spent coffee grounds (SCG) are generated after coffee brewing, and most of them are underutilized and disposed of in landfills as opposed to being used as compost, mainly because SCG are high in several compounds that are detrimental to the environment [2]. Although the direct combustion of dried SCG generates a higher heating value than wood pellets at the same moisture content, the emission of nitrogen oxides in the flue gas needs to be largely reduced [3]. Recently, the incorporation of biorefinery concepts into SCG valorization has gained much research attention [2,4]; in particular, extracting oil from SCG for biodiesel production has been well investigated. Rocha et al. reported that about 12 wt.% SCG oil was obtained from ultrasound-assisted extraction of SCG (using hexane as the organic solvent), along with an oil-to-biodiesel conversion efficiency of 97% [5]. Caetano et al. used a pilot-scale Soxhlet system to extract oil from SCG, and ~6 wt.% SCG oil was recovered; the conversion efficiency of SCG oil into biodiesel ranged from 47.4% to 86.0%, depending on the applied extraction solvents and biodiesel synthesis procedures [6]. Liu et al. attempted to directly trans-esterify oil in SCG into biodiesel, and a conversion efficiency of 98.6% was reported [7].

Much research effort has been dedicated to SCG biodiesel production, but the processes in these efforts have often relied on organic solvents and acidic/basic catalysts. Additionally, these studies primarily focused on extracting and converting lipid into biodiesel without reutilizing the secondary waste (defatted SCG). This does not align well with the

intended final goal of a green SCG biorefinery. In contrast, hydrothermal liquefaction (HTL) is an emerging thermochemical conversion technology which uses water as the processing media to convert biomasses into crude bio-oil at moderate to high temperature (250–400 °C) and high pressure (5–30 MPa) [8–10]. HTL takes advantage of the physicochemical properties (e.g., low dielectric constant) of subcritical water that serves as a reactant, solvent, and catalyst during biocrude formation [9]. Various biomass feedstocks have been tested for biocrude production through HTL, such as agriculture/forest wastes [11], food processing wastes [12], micro/macroalgae [13], and raw digestate biomass [14]. Moreover, HTL has been used as a post-resource recovery step after biomethane production using co-digestion technologies [15].

Biomass feedstocks usually consist of lipids, carbohydrates, and proteins [16], and HTL biocrudes' yields and qualities were highly associated with feedstocks' biochemical compositions [17]. Recently, a few attempts have been made to better understand the biocrude formation pathways using biomass model components [12]. The lipid content of feedstock was demonstrated to be a crucial factor for biocrude yield and quality [18], and lipids were proved to synergistically interact with carbohydrates, leading to a higher biocrude yield [19]. Yang et al. illustrated that when a high lipid content was present in the feedstock, more biocrude was produced from the HTL process [19]. These observations raise a significant question: how does the oil removal from SCG influence the biocrude yield and quality? Therefore, two SCG valorization routes were proposed in the study as shown in Figure 1. Within route #1, SCG oil was extracted for biodiesel production followed by HTL of defatted SCG to produce biocrude. For route #2, biocrude was generated through direct HTL of raw SCG.

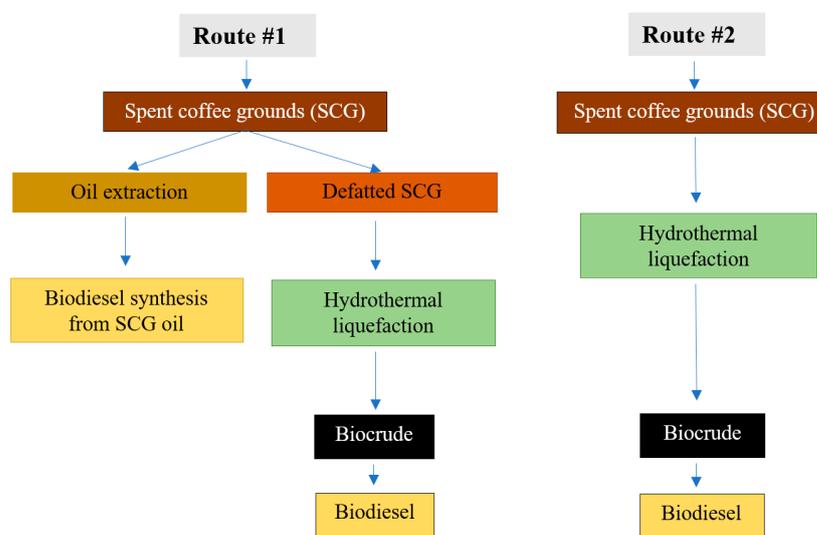


Figure 1. Spent coffee grounds valorization routes for biodiesel production.

The study aims to compare two thermochemical routes for SCG. The effect of microwave power, solvent/solid ratio, and time on SCG oil extraction was investigated to obtain the optimal extraction conditions through response surface analysis. Detailed characterization of defatted and raw SCG was carried out prior to conducting HTL for biocrude production. The resultant yields and qualities of the biocrudes were quantified to assess whether oil removal exhibited significant influence. Life cycle assessment was also carried out for each SCG valorization route to determine which is favorable from an environmental impact perspective. This is the first attempt at evaluation of two different SCG valorization routes for biodiesel production, shedding light on how to effectively utilize SCG from a clean and sustainable production perspective.

2. Materials and Methods

2.1. Materials

Wet SCG were collected from Tim Hortons, Truro, Nova Scotia, Canada, and oven dried at 105 °C for 24 h. Reagent grade hexane and dichloromethane were purchased from Fisher Scientific and Sigma-Aldrich, respectively. All chemicals were used as received.

2.2. SCG Oil Extraction

SCG oil was extracted by hexane in a microwave reactor (Multi-wave Pro, Anton Parr). In a typical run, 5 g of dried SCG was weighed and transferred to a reaction vessel containing a magnetic stirring rod with a mixing speed of 200 rpm. A pre-calculated amount of hexane based on the ratio of solvent and SCG was added into the vessel, which was then sealed and placed in the microwave reactor. The hexane and SCG were exposed to microwave radiation at powers of 200, 350, or 500 W for 5, 10, or 15 min according to the experimental design as shown in Table 1. The selection of microwave power level and extraction time was based on the relevant literature and instrument capacity (maximum microwave power of 900 W when four vessels are loaded) [20,21]. Once the pre-set extraction time was reached, the vessel was cooled down by a built-in fan in the microwave cavity. The contents of the vessel were then transferred to a centrifuge tube and centrifuged for 6 min at 3000 rpm. The supernatant in the centrifuge tube was poured into a syringe with a 0.45 µm filter attached to the end and filtered into a round-bottom flask. The hexane was then vacuum evaporated at 70 °C and −0.5 bar, the SCG oil was obtained, and the yield was calculated by the following Equation (1). The residual SCG after oil extraction are termed as defatted SCG.

$$\text{SCG oil yield (wt.\%)} = \frac{\text{Mass of SCG oil}}{\text{Mass of SCG}} \times 100\% \quad (1)$$

Table 1. Independent factors and levels used for the central composition design.

Variables	Symbol Code	Levels		
		−1	0	1
Power (W)	X ₁	200	350	500
Solvent/solid ratio (mL/g)	X ₂	4	6	8
Time (min)	X ₃	5	10	15

2.3. Feedstock Characterization

The feedstock characterization on the raw SCG and defatted SCG was conducted by SGS Lab (Guelph) at Ontario, Canada. AOAC and NFTA methods were used to measure the moisture, ash, lipid, protein, lignin, acid detergent fiber, and neutral detergent fiber [22]. The average values are reported, and the measurement error is less than 5% of reported values.

2.4. Hydrothermal Liquefaction Processes

Advanced models were developed to predict the yields of biocrude and char based on feedstocks' biochemical compositions and process variables in our previous work [23], and the optimal HTL conditions for dried, raw SCG were determined to be a temperature of 295 °C, a reaction time of 12.5 min, and a feedstock concentration of 10 wt.%. A 4590 micro-reactor (100 mL, Parr Instrument) was used to hydrothermally liquefy feedstocks into biocrude. In a typical run, 3 g of dried, defatted SCG along with 27 g of distilled water were loaded into the reaction vessel. The reaction vessel was then sealed and mounted on the support stand, purged with high purity nitrogen gas, and re-pressurized to 1 MPa. The magnetic stirrer with 120 rpm speed was started, and the reaction vessel was heated to 295 °C with a heating rate of 10 °C/min and kept at 295 °C for 12.5 min. Once the reaction was completed, the reactor was cooled down to 25 °C by quenching with a cold-water bath

within 5 min. The stirrer was stopped, and the gaseous phase was vented into a fume hood. The aqueous phase containing certain amounts of solids was then centrifuged at 3000 rpm for 5 min to separate aqueous phase and solids. The aqueous phase was discharged, and the remaining solids were collected in a beaker for downstream biocrude recovery processes. The detailed downstream processing procedures for recovering biocrude and separating biochar can be found in our previous work [23,24]. Briefly, dichloromethane (DCM) was used as a recovery solvent for biocrude. About 120 mL DCM was utilized to wash reactor, stirrer, and solid remaining on filter paper. DCM was then evaporated under vacuum to obtain biocrude and DCM-insoluble solid was referred to as hydrochar and dried at 105 °C for 12 h. The yield of biocrude and char was calculated using the following Equations (2) and (3), respectively.

$$\text{Biocrude yield (wt.\%)} = \frac{\text{Mass of biocrude}}{\text{Mass of feedstock}} \times 100\% \quad (2)$$

$$\text{Char yield (wt.\%)} = \frac{\text{Mass of char}}{\text{Mass of feedstock}} \times 100\% \quad (3)$$

2.5. Biocrude Characterization

The higher heating values (HHV) of obtained biocrudes were evaluated using an oxygen bomb calorimeter (Parr 6300 Calorimeter, IL, USA). The chemical composition of biocrude was identified via gas chromatography–mass spectroscopy (GC–MS) [14,25]. The GC–MS analysis was achieved using a PerkinElmer SQ8 MS and Clarus 680 GC equipped with an Rxi-5ms column (30 m × 0.25 mm × 0.25 μm). The GC injection temperature was 280 °C, and the splitless mode was applied. High-purity helium gas was utilized as the carrier gas at a flow rate of 1 mL/min. The injection volume was 1 μL. The GC oven temperature programming was as follows: initial oven temperature at 50 °C for 2 min, then increasing to 280 °C at a heating rate of 10 °C/min. A solvent delay of 3.8 min was applied to protect MS from solvent shock. The MS source and GC–MS transfer line temperatures were 150 °C and 200 °C, respectively. Data were acquired in 45–400 *m/z* scan mode. The peaks in total ion chromatogram (TIC) were tentatively identified by using NIST library.

2.6. Life Cycle Assessment

A well-known software for life cycle assessment, openLCA, was used to estimate the greenhouse gas (GHG) emissions from the SCG valorization routes proposed in this study. The assessment was carried out based on the Ecoinvent 3.5 database. A tool for the reduction and assessment of chemical and other environmental impacts (TRACI) was applied as the assessment method. The initial input of SCG was set to be 1000 kg, in which biodiesel production from SCG was assumed to be on pilot scale.

2.7. Experimental Design and Data Analysis

Face-centered response surface methodology (RSM) was utilized to optimize the conditions for microwave-assisted SCG oil extraction [26]. The Minitab 18 software was used. Table 1 presents the RSM coded symbols and levels. The response optimizer was used to obtain the optimal conditions for SCG oil extraction. More detailed information for RSM analysis can be found in our previous study [27].

3. Results and Discussion

3.1. Microwave-Assisted SCG Oil Extraction

The conditions for microwave-assisted oil extraction from SCG were optimized using response surface methodology. There were three studied process variables, including microwave power (W), solvent to solid ratio (mL hexane/g SCG), and extraction time (min). The detailed experimental design and data are provided in the Supplementary Materials, Table S1. The developed mathematical equation based on obtained data is presented in Table 2. An Adj R² of 83.4% implies a moderate to strong correlation between

experimental data and predicted data. Analysis of variance (ANOVA) is presented in Table 3. Microwave power and extraction time appear to be insignificant factors for the SCG oil yield as indicated by their p -values (>0.05), while changing solvent/solid ratio substantially affects SCG oil yield. Rocha et al. conducted the extraction of SCG oil using an organic solvent (hexane) and ultrasound assistance, and they also observed that solvent/solid ratio was a more important factor than extraction temperature and time [5].

Table 2. The coded mathematical equation for the oil yield from microwave-assisted extraction of spent coffee grounds (SCG).

Mathematical Equation	R ² (Adj)
SCG oil yield (wt.%) = $7.376 + 0.116X_1 + 1.269X_2 - 0.214X_3 - 0.312X_1X_2 + 0.345X_1X_3 + 0.36X_2X_3 - 0.350X_1^2 - 0.565X_2^2 + 0.300X_3^2$	83.5%

Note: X1 = microwave power; X2 = ratio; X3 = extraction time.

Table 3. Analysis of variance (ANOVA) for the oil yield from microwave-assisted extraction of spent coffee grounds.

Source	F-Value	p-Value
Linear	27.05	0.000
Power	0.65	0.438
Ratio	78.26	0.000
Time	2.23	0.167
2-Way Interaction	4.49	0.031
Power*Ratio	3.80	0.080
Power*Time	4.63	0.057
Ratio*Time	5.04	0.049
Square	3.56	0.055
Power*Power	1.64	0.230
Ratio*Ratio	4.27	0.066
Time*Time	1.20	0.298

As illustrated in Table 3, the effect of solvent/solid ratio was also dependent on the extraction time (ratio*time p -value = 0.049 $<$ 0.05). The ratio*time interaction was demonstrated by a contour plot as shown in Figure 2. Using a solvent/solid ratio of ~6.3 mL/g at an extraction time of 5 min was able to achieve ~8 wt.% SCG oil yield, whereas a solvent/solid ratio of 7.5 mL/g was required to obtain a comparable SCG oil yield for an extraction time of 10 min.

The developed equation was then used to determine the optimal conditions for the maximum SCG oil yield. A microwave power of 200 W, a solvent/solid ratio of 8 mL/g, and an extraction time of 5 min were suggested to be the optimal conditions, and under such conditions, the SCG oil yield could reach 8.4 wt.%.

3.2. Biochemical Compositions of Defatted and Raw SCG

The biochemical composition of raw SCG without oil extraction was presented in Table 4. The raw SCG mainly comprised carbohydrates (hemicellulose, cellulose, and lignin) along with 14.2 wt.% protein and 9.5 wt.% lipid. The biochemical composition of defatted SCG generated under optimal extraction conditions was also assessed and is listed in Table 4. The defatted SCG contained 3.6 wt.% lipid compared to 9.7 wt.% in the raw SCG, resulting in a difference of 6.1 wt.% between them, even though it was suggested that 8.4 wt.% SCG oil could be obtained under optimal conditions. The inconsistent percentage of extracted oil was likely due to model prediction error and experimental error from lipid content testing. Caetano et al. used a pilot-scale Soxhlet extractor to extract SCG oil and obtained about 6 wt.% SCG oil, which was in agreement with our result [6].

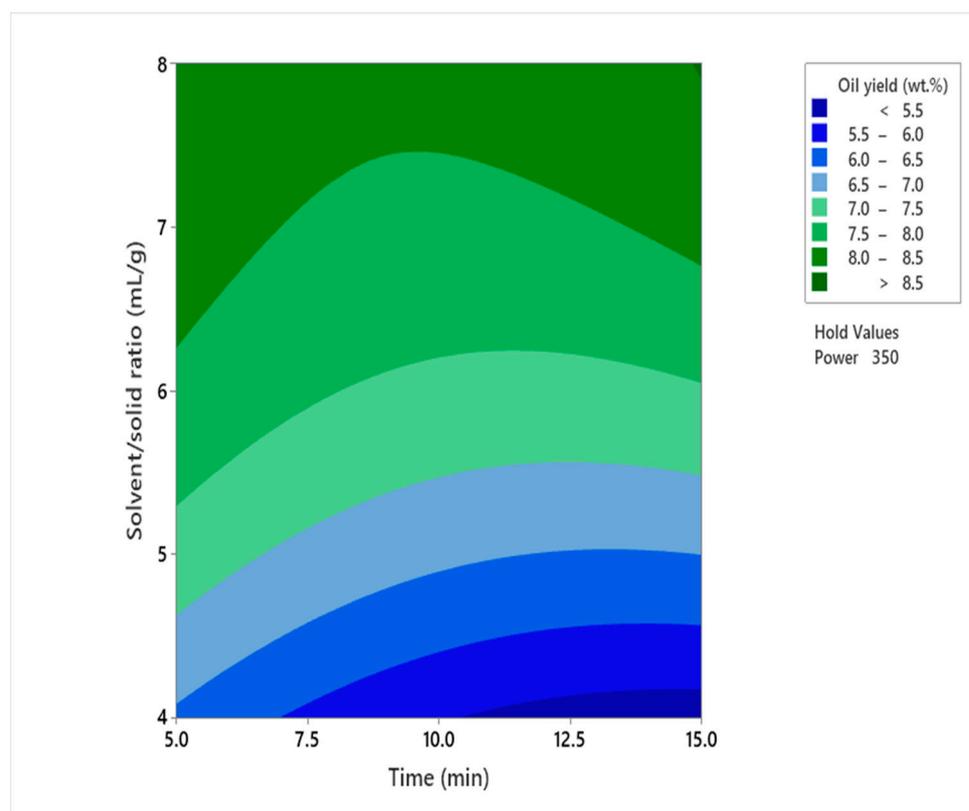


Figure 2. The contour plot for the interaction between solvent/solid ratio and extraction time.

Table 4. The biochemical composition (dry weight basis) of spent coffee grounds (SCG) before and after oil extraction.

	Raw SCG	Defatted SCG
Protein (wt.%)	14.4	16.8
Hemicellulose (wt.%)	22.9	26.9
Cellulose (wt.%)	27.3	23.5
Lignin (wt.%)	24.4	27.1
Lipid (wt.%)	9.7	3.6
Ash (wt.%)	1.3	2.0

3.3. HTL of Defatted and Raw SCG

3.3.1. Optimal HTL Conditions

Knowing the biochemical composition of defatted SCG (Table 4), the developed models were utilized to generate contour plots (Figure S1) to find out the optimal HTL conditions for defatted SCG. Interestingly, the removal of lipid did not largely alter the pattern of contour plots compared to that of raw SCG in our previous work [23]. The optimal HTL conditions for defatted SCG were, therefore, determined to be identical to those of raw SCG, and the resultant biocrude yields and char yields are presented in Table 5.

Biocrude yields of 28.1 wt.% and 18.9 wt.% were obtained for HTL of raw SCG and defatted SCG, respectively (Table 5), giving a difference of 9.2 wt.% between them. A 9.2 wt.% decline in biocrude yield was slightly higher than that of the 6.1% oil removal (Section 3.1). HTL of pure lipid revealed that the majority of lipid (>95%) can be converted into biocrude [19,28]; thus, the reason for a 9.2 wt.% decline in biocrude yield was likely to be that the removal of oil diminished the interactions between the oil and the other constituents, in particular, the lipid and saccharide interaction that was proved to synergistically promote the biocrude yield [19].

Table 5. The yield/properties of biocrude derived from defatted and raw spent coffee grounds (SCG).

	Defatted SCG	Raw SCG [23]
Biocrude yield (wt.%)	18.9 ± 1.0	28.1 ± 1.0
Char yield (wt.%)	23.3 ± 0.9	25.0 ± 0.2
Biocrude chemical composition (peak area percentage)		
acids	12.9 ± 0.6	6.1 ± 1.4
alcohols	-	11.1 ± 2.5
amides	5.0 ± 0.2	4.0 ± 0.1
amines	19.5 ± 2.2	12.1 ± 0.6
N-containing heterocycles	21.7 ± 1.4	3.6 ± 0.9
esters	11.3 ± 0.3	35.4 ± 2.6
furans	1.3 ± NA	-
hydrocarbons	8.8 ± 1.4	8.7 ± 1.3
ketones	3.9 ± 0.1	6.0 ± 0.5
phenolics	16.2 ± 1.2	13.0 ± 1.2
Biocrude HHV (MJ/kg)	29.7 ± 0.9	33.5 ± 0.2

Note: HHV = higher heating value; ± sign indicates the standard deviation.

3.3.2. Biocrude Yield and Properties

The chemical compositions of obtained biocrudes are presented in Table 5. Biocrude derived from defatted SCG had a much lower ester content than raw SCG biocrude (11.3% vs. 35.4%, respectively), as a reduced oil content in defatted SCG led to fewer oil hydrolysis products (esters). The percentage of N-containing heterocycles (21.7%) in biocrude derived from defatted SCG was significantly higher than that of 3.6% in raw SCG biocrude. This suggests that the Maillard reaction that is known to generate N-containing heterocycles through protein and carbohydrate interaction outcompeted the oil hydrolysis (ester formation) during HTL of defatted SCG. The oil hydrolysis and Maillard reaction during HTL biocrude formation have been widely reported [29,30]. Biocrude derived from raw SCG contained 11.1% alcohols (Table 5), of which 6.1% was E,E,Z-1,3,12-Nonadecatriene-5,14-diol (fatty acid-like alcohol), as presented in Tables S2 and S3. However, no alcohol was detected in defatted SCG biocrude. A relatively high content of acids (mainly fatty acids) was detected in defatted SCG biocrude compared to raw SCG (12.9% vs. 6.1%). These results suggest that HTL of low-lipid content feedstock could favor the formation of acids over alcohols. In terms of biocrude higher heating value (HHV), defatted SCG biocrude exhibited a relatively low HHV (29.7 MJ/kg) when compared to raw SCG biocrude (33.5 MJ/kg). This is consistent with other studies that have shown HTL of lipid-rich feedstocks can lead to biocrudes with high HHV.

3.4. Life Cycle Assessment on SCG Valorization Routes

A life cycle assessment was carried out for each SCG valorization route that aims to produce biodiesel (route #1 and route #2 as shown in Figure 1), and the corresponding greenhouse gas (GHG) emissions are presented in Figure 3. The detailed parameters used in the life cycle assessment are provided in Table 6. As illustrated in Table 6, in route # 1, biodiesel synthesis from SCG oil only generated 12 g CO₂ eq/MJ GHG emission, while SCG oil extraction resulted in ten times more GHG emissions (120 g CO₂ eq/MJ). Indeed, the majority (84.5%) came from the use of hexane in the SCG oil extraction process. Following the oil extraction, the defatted SCG were hydrothermally liquefied into biocrude, which produced GHG emissions of 154.5 g CO₂ eq/MJ. It is interesting to note that the direct HTL of raw SCG for biocrude production only generated GHG emissions of 92.2 g CO₂ eq/MJ. This observed difference was mainly due to HTL of defatted SCG leading to a lower yield of biocrude with a lower heating value compared to that of direct HTL of raw SCG. The overall GHG emissions for route #1 and route #2 were 297.6 g CO₂ eq/MJ and 103.3 g CO₂ eq/MJ, respectively, and these results were consistent with previous studies [31–33]. For instance, Chan et al. conducted a life cycle assessment on HTL biocrude production

from oil palm biomass and reported GHG emissions of 100 g CO₂ eq/MJ [31]. Due to the much higher GHG emissions from route #1, it is obvious that valorizing SCG into biodiesel through route #2 is favorable in this study.

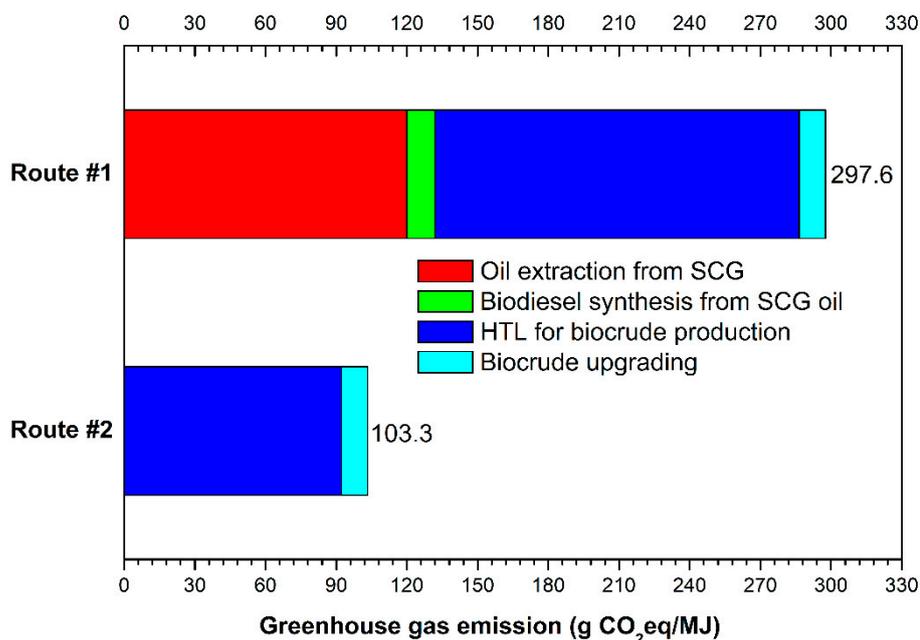


Figure 3. Greenhouse gas emission (g CO₂ eq/MJ) for two spent coffee grounds (SCG) valorization routes.

Table 6. The detailed parameters for life cycle assessment on valorization routes for spent coffee grounds.

	Route #1	Route #2
SCG oil extraction		
Electricity	0.2125 kWh	-
Heat	6.83 MJ/kg SCG oil	-
Hexane	1.4 kg/kg SCG	-
Biodiesel synthesis		
Electricity	0.0375 kWh	-
Heat	1.7 MJ/kg biodiesel	-
Methanol	0.348 kg/kg SCG oil	-
Hydrochloric acid	0.085 kg/kg biodiesel	-
Potassium hydroxide	1.5 wt.% SCG oil	-
HTL for biocrude production		
Heat	0.72 MJ/kg water	0.72 MJ/kg water
Biocrude yield	18.9 wt.% of SCG	28.1 wt.% of SCG
Biocrude heating value	29.7 MJ/kg	33.5 MJ/kg
Biocrude upgrading into diesel		
Efficiency	0.75 kg/kg biocrude	0.75 kg/kg biocrude
Biodiesel heating value	45 MJ/kg	45 MJ/kg
Process embedded in ecoinvent 3.5	Petroleum Refinery operation-diesel	

4. Conclusions

Two thermochemical valorization routes for spent coffee grounds (SCG) were thoroughly compared in this study. In route #1, SCG oil was extracted for biodiesel production followed by hydrothermal liquefaction (HTL) of defatted SCG for biocrude production, while raw SCG was directly liquefied into biocrude in route #2 as conducted in our previ-

ous study. The optimized microwave-assisted extraction conditions to effectively remove oil from SCG were determined using response surface methodology. It was found that solvent/solid ratio was the most influential factor for SCG oil extraction, and an SCG oil yield of 8.4 wt.% could be obtained with a solvent/solid ratio of 8 mL/g under a microwave power of 200 W for 5 min. HTL of both defatted and raw SCG revealed that the defatted SCG gave a much lower biocrude yield (18.9 wt.%) than the raw SCG (28.1 wt.%). The removal of oil from SCG also resulted in a decrease in higher heating value (29.7 vs. 33.5 MJ/kg). Biocrude derived from defatted SCG had fewer esters but more nitrogen-containing heterocycles compared to raw SCG biocrude. Life cycle assessment on the two SCG valorization routes for biodiesel production found that the greenhouse gas (GHG) emissions from route #1 and route #2 were 297.6 CO₂ eq/MJ and 103.3 CO₂ eq/MJ, respectively, and thus, route #2 was identified as the favorable approach to valorizing SCG into biodiesel in this study. The techno-economic analysis for the proposed routes is recommended in future work.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/en14133840/s1>, Table S1. Raw data for microwave-assisted extraction of spent coffee grounds oil; Figure S1. Contour plots for biocrude yield and solid residue from hydrothermal liquefaction of post-extracted spent coffee grounds; Table S2. Chemical composition for biocrude derived from raw spent coffee grounds; Table S3. Chemical composition for biocrude derived from defatted spent coffee grounds.

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Conflicts of Interest: The authors declare no conflict of interest.

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