International Journal of Chemical and Process Engineering Research
2025 Vol. 12, No. 1, pp. 12-28
ISSN(e): 2313-0776
ISSN(p): 2313-2558
DOI: 10.18488/65.v12i1.4681

Enhanced bio-oil production and fatty acid extraction from pyrolyzed spent coffee ground using Box-Behnken design optimization

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Article History
Received: 17 November 2025
Revised: 20 December 2025
Accepted: 23 December 2025
Published: 31 December 2025

Keywords
Bio-based chemical
Bio-oil
Box-Behnken design
Fatty acid
Oleic acid
Pyrolysis
Spent coffee grounds.

ABSTRACT

The disposal of spent coffee grounds (SCG), a biomass waste generated from coffee brewing, poses a significant environmental concern due to its high organic content and large volume. To address this issue, a valorization approach was undertaken that involved the production of bio-oil from SCG through pyrolysis and the subsequent extraction of oleic acid, the most abundant fatty acid in SCG. A Box-Behnken experimental design was employed to optimize pyrolysis yields using three process parameters: SCG particle size (<0.25, 0.25 – 0.70, 0.70 – 1.70 mm), pyrolysis temperature (500 – 600 °C), and nitrogen flow rate (0.5 – 1.5 L/min). Pyrolysis was conducted in a fixed-bed reactor, and the resulting bio-oil was characterized using gas chromatography. Statistical analysis indicated that all three parameters significantly influenced the bio-oil yield, with temperature and spent coffee grounds (SCG) particle size being the primary factors affecting fatty acid concentration. The optimal conditions identified included an SCG particle size of less than 0.25 mm, a temperature of 550°C, and a nitrogen flow rate of 0.5 L/min, which yielded a bio-oil production of 34.13%. Oleic acid was successfully extracted from the pyrolyzed bio-oil through liquid-liquid extraction using hexane, demonstrating its potential for further chemical processing. These findings illustrate a dual valorization pathway for SCG, enabling the production of both renewable bio-oil and oleic acid as platform bio-based chemicals.

Contribution/Originality: This study contributes to the existing literature by optimizing the pyrolysis of spent coffee grounds to maximize bio-oil yield and fatty acid content using a Box–Behnken design, while enabling post-pyrolysis recovery of oleic acid. The study documents a dual valorization pathway, producing renewable bio-oil fuel and value-added oleic acid as bio-based chemicals.

1. INTRODUCTION

The increasing need to reduce greenhouse gas emissions and shift away from fossil fuels has heightened interest in renewable and carbon-neutral energy sources [1]. Among these, biomass valorization, particularly through thermochemical routes, has attracted significant attention for its ability to generate biofuels from organic waste materials [2, 3]. However, the production cost of biofuels remains higher than that of fossil fuels. To address this issue, the co-production of value-added bio-based chemicals and biofuels through thermochemical or biochemical conversions, which are both sustainable and economical, is necessary [4].

Bio-oil, a primary product of pyrolysis, contains a complex mixture of oxygenated hydrocarbons and phenolics [5]. It has attracted increasing attention not only as a fuel precursor but also as a source of extractable fine chemicals. Extraction and fractionation techniques, especially solvent-based extractions, have emerged as promising approaches for upgrading bio-oil by separating it into chemically enriched fractions. Organic solvent extraction, in particular, is considered one of the most effective methods for targeting valuable compounds such as fatty acids. However, challenges remain due to the chemical complexity of bio-oil, which requires optimized processes for selective recovery [6]. In this context, spent coffee grounds (SCG), a byproduct generated in large quantities from global coffee consumption, present a promising feedstock due to their high organic content and availability [7-9].

SCG has been investigated for various value-added applications, including the production of biofuels such as bio-oil, biodiesel, biobutanol, and bio-hydrogen [10]. Additionally, it has been explored for the extraction of valuable chemicals, adsorption materials, and textile functionalization Kelkar, et al. [11]; Atabani, et al. [12] and Chen, et al. [13]. Ktori, et al. [7] examined the pyrolysis of wet SCG in a batch reactor, achieving a maximum bio-oil yield of approximately 40% Ktori, et al. [7]. Primaz, et al. [10] analyzed the chemical compounds present in pyrolyzed bio-oil and identified fatty acids, hydrocarbons, ketones, and phenolic compounds [14]. Krause, et al. [15] studied the fast pyrolysis of SCG and found that fatty acids were the most abundant chemicals in the bio-oil [15]. Among these, oleic acid is particularly attractive due to its applications in the pharmaceutical, cosmetic, and polymer industries [16, 17]. However, most previous studies primarily focus on using bio-oil as a fuel and do not investigate the downstream extraction or recovery of specific chemical compounds from pyrolysis bio-oil, indicating a potential area for further research and development. Although various process parameters influence the pyrolysis outcome, such as particle size, temperature, residence time, type of biomass, and carrier gas flow rate, few studies have systematically optimized these factors for spent coffee grounds (SCG). Moreover, the combined effects of particle size, pyrolysis temperature, and nitrogen flow rate using a statistically structured method like the Box–Behnken Design (BBD) remain underexplored. BBD allows for efficient multi-variable optimization without requiring an excessive number of experiments and has proven useful in biomass pyrolysis studies [18, 19].

In evaluating the variables influencing pyrolysis, the parameters most frequently examined are particle size, operating temperature, heating rate, residence time, and carrier gas flow rate. Among these, temperature is most often emphasized due to its critical role in pyrolysis, which is a thermochemical process that relies on heat to decompose lignocellulosic biomass [20]. While previous studies have explored SCG pyrolysis, the combined effects of particle size, temperature, and nitrogen flow rate as experimental factors using BBD have not been comprehensively investigated.

Furthermore, there is a lack of studies investigating the extraction of oleic acid from spent coffee grounds (SCG)-derived bio-oil as a value-added chemical product [16, 17, 21]. For instance, Vardon et al. reported the pyrolysis of defatted SCG (DSCG), a process in which lipids were removed prior to pyrolysis, resulting in lower bio-oil yields and reduced higher heating value (HHV) compared to non-defatted SCG [22]. Similar findings were reported by Krause, et al. [15]. These studies, however, did not explore post-pyrolysis chemical recovery from the bio-oil. Therefore, in the present study, spent coffee grounds (SCG) were valorized through pyrolysis using Box-Behnken Design (BBD) to optimize three key process parameters: particle size, temperature, and nitrogen flow rate. The goal was to maximize bio-oil yield and fatty acid content. Additionally, a post-pyrolysis solvent extraction of bio-oil using hexane was performed to recover oleic acid, providing a pathway to convert SCG into dual-purpose products: bio-oil as a renewable fuel and oleic acid as a value-added bio-based chemical.

2. MATERIALS AND METHODS

2.1. Materials

The wet SCG was obtained from a single source at a 7-Eleven convenience store located within the Institute of Science Tokyo (formerly Tokyo Institute of Technology), Ookayama Campus, Tokyo, Japan. The collected wet SCG

was first dried at 45°C for at least 24 hours to reduce moisture content. The samples were handled uniformly throughout all experiments. After drying, the SCG was milled using a coffee grinder and sieved to produce three particle size ranges: <0.25 mm, 0.25 - 0.7 mm, and 0.7 - 1.7 mm. Hexane was used as a solvent to extract chemicals from pyrolyzed bio-oil derived from SCG.

2.2. Pre-Analysis of SCG

The SCG was analyzed using two processes: elemental analysis and thermogravimetry differential thermal analysis (TG/DTA). The elemental analysis was conducted with the Vario EL cube (ELEMENTAR) to determine the total content of carbon, nitrogen, and hydrogen in the SCG, while oxygen was assumed to be the remaining element. TG/DTA analysis was performed using the Thermo plus EVO2 (RIGAKU) instrument to investigate the thermal properties of the SCG. The sample was heated at a rate of 20 °C/min under an inert nitrogen atmosphere, covering a temperature range of 40°C to 600°C. To ensure the accuracy and reproducibility of the results, the measurements were repeated at least twice.

2.3. Experiment

The dried SCG was pyrolyzed to obtain three main products: bio-oil, char, and gas. For each experiment, a fixed amount of 20 g of dried SCG was used. The reactor was the same as reported in the previous study by the authors [23], which is a fixed-bed reactor as shown in Figure 1a. The dried spent coffee grounds (SCG) were placed in a basket inside a tube furnace equipped with a temperature controller. The reactor was connected to a water-cooled condenser, which was linked to a flask submerged in a water bath to collect bio-oil. An additional tube was connected to the flask to vent incondensable gases. Nitrogen gas was flowed into the reactor for 10 minutes to purge oxygen and establish an inert environment. The heating rate was set at 35°C per minute. The total reaction time was 10 minutes, commencing once the reactor reached the target temperature. Three parameters SCG particle size, temperature, and nitrogen flow rate were varied to optimize bio-oil yield. After each experiment, the bio-oil and residual SCG (biochar) were collected for weighing and yield calculation. The gas phase yield was determined by subtracting the combined yields of bio-oil and biochar from the total. All experiments were conducted at least twice under each set of conditions to ensure the reliability of the results.

Figure 1b shows the additional three impingers connected to the reactor for mass balance analysis. It was performed to understand the true mass balance of the experiments since some condensable gases might not be condensed in the condenser and flask. Three impingers were added to the reactor used in the pyrolysis experiment. The first impinger was filled with 50 mL of ethanol and placed in a water bath at 40°C. At this temperature, ethanol vaporizes during the reaction and dissolves the tar in gaseous form, increasing the efficiency of the tar trap because the dissolution of tars at higher temperatures is faster than at lower temperatures [24]. The second impinger was filled with 50 mL of ethanol and equipped with a glass frit as a filter. The glass frit acted as a filter that facilitated the trapping process of tars. Additionally, the glass frit reduced the size of gas bubbles, thereby enhancing the dissolution of tar in ethanol. The third impinger was empty but also equipped with a glass frit. It served as a condenser for ethanol from the second impinger. Both the second and third impingers were placed in an ice bath to trap all tar in aerosol form and vaporized solvent. The yield of tar trapped in the impinger was determined by subtracting the mass of the impinger after the experiment from its mass before the experiment.

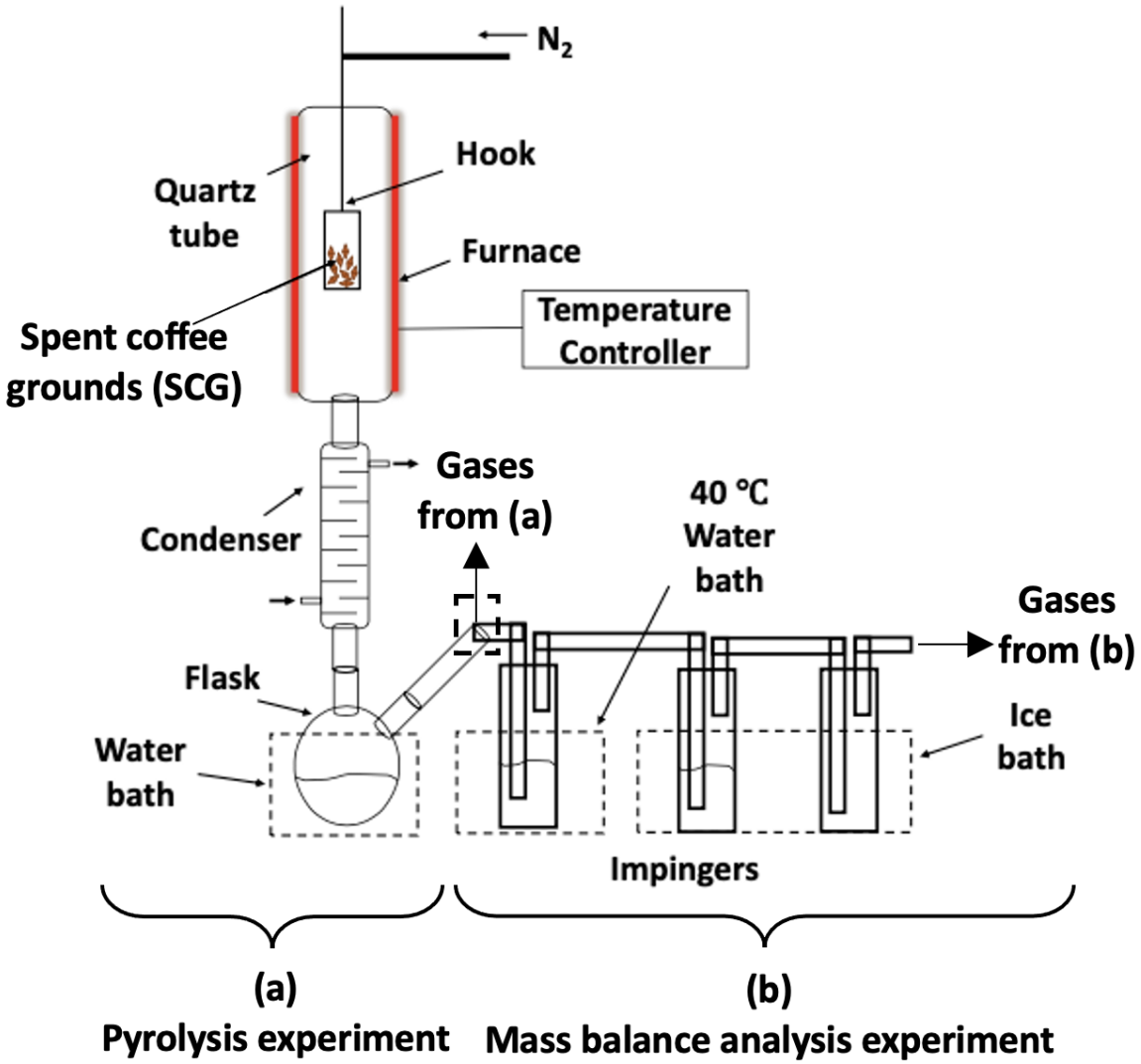

Figure 1. (a) Experimental setup of a fixed-bed reactor for pyrolysis experiments as described by Yasser et al. (2021), and (b) the additional part connected to the flask with three impingers for mass balance analysis.

2.4. Chemical Composition Analysis

Bio-oil, one of the products from each pyrolysis experiment, was analyzed using (GC-MS). The collected bio-oil was diluted by mixing with ethanol to achieve a concentration of 5% (v/v). The analysis was performed using a GC-2010 Plus equipped with a mass detector (GCMS-QP2010 SE) (Shimadzu, Japan). The column used was an Rxi-5sil MS with specifications of 30 m × 0.255 mm and a film thickness of 0.25 µm. The oven temperature program was as follows: (1) 80 °C held for 5 minutes, (2) increased at 5 °C/min to 240 °C and held for 5 minutes, (3) increased at 2.5 °C/min to 320 °C and held for 5 minutes, and (4) increased at 1 °C/min to 350 °C and held for 5 minutes. Each chemical component in the bio-oil was identified by comparing the mass spectra with the NIST 11 MS library available in the GC-MS software. The top 100 peaks with similarities above 80% were used to ensure data validity. The GC analysis of the bio-oil was conducted in two parts: one focusing on chemical group classification and the other on individual compound identification. The results were expressed as relative content, calculated by dividing the peak area of each chemical group or individual compound by the total peak area of all detected compounds.

2.5. Box-Behnken Design (BBD)

Design of Experiments (DoE) is a systematic and efficient approach that enables the evaluation of multiple input variables and their interactions to understand their effects on output responses. Among various DoE methodologies, the Box–Behnken Design (BBD) is a widely used response surface methodology based on a three-level factorial design [18]. This method has been applied in numerous studies because it effectively reduces the number of required experiments while avoiding extreme combinations of factor levels, which may lead to impractical or unsafe operating conditions. It has been used with various types of biomass in pyrolysis processes [19].

The BBD was chosen as the DoE to optimize the pyrolysis and chemical composition analysis results. The parameters used in pyrolysis were the SCG particle size, temperature, and nitrogen flow rate. Each parameter has three levels, which can be represented geometrically as -1, 0, and 1, corresponding to low, medium, and high values, respectively (Figure 2). The dots in the figure represent the combination of parameters. The central point (0, 0, 0) was repeated three times in each batch to obtain the experimental error. All values are listed in Table 1, and the full experimental list with 13 combinations is shown in Table 2.

Bio-oil production from pyrolysis typically occurs at elevated temperatures between 300 and 1000 °C under limited oxygen conditions. Based on prior studies using various types of biomass, a temperature range of 500–600 °C and a particle size of 0.25–1 mm have been found to be optimal for maximizing bio-oil yield. This temperature range allows the majority of biomass components cellulose, hemicellulose, and lignin to be efficiently converted into condensable vapors that form bio-oil, without excessive cracking into gases [12, 20, 25]. Therefore, the temperature and SCG particle size ranges selected for this study were 500 – 600 °C and <0.25, 0.25 – 0.70, and 0.70 – 1.75 mm, respectively. Regarding the nitrogen flow rate, most previous studies have employed relatively low flow rates (< 0.5 L/min) [25]. However, a more detailed investigation into higher flow rates is necessary to understand their impact more fully. Thus, this study adopts a flow rate range of 0.5–1.5 L/min, which is consistent with studies on beech wood pyrolysis [26].

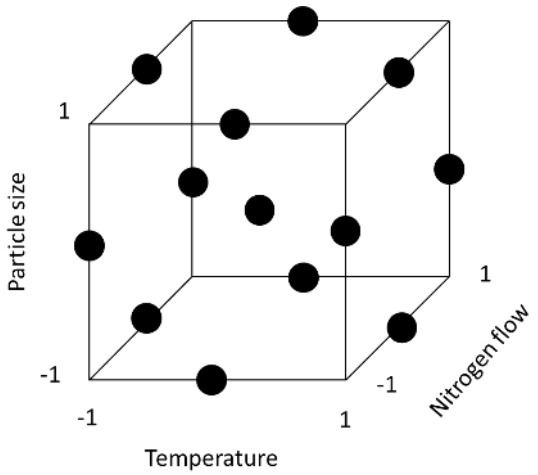

Figure 2. Box-Behnken design in geometric representation.

Table 1. Levels of variables in the Box-Behnken experimental design for pyrolysis.

Variables	Range and levels		
	Low (-1)	Medium (0)	High (1)
SCG particle size, X_1 [mm]	< 0.25	0.25 – 0.7	0.7 – 1.7
Temperature, X_2 [°C]	500	550	600
Nitrogen flow rate, X_3 [L/min]	0.5	1	1.5

Table 2. Box-Behnken design for three parameters with three levels.

Run	Particle size	Temperature	Nitrogen flow rate
1	-1	-1	0
2	1	-1	0
3	-1	1	0
4	1	1	0
5	-1	0	-1
6	1	0	-1
7	1	0	1
8	0	0	1
9	0	-1	-1
10	0	1	-1
11	0	-1	1
12	0	1	1
13	0	0	0
14	0	0	0
15	0	0	0

2.6. Statistical Analysis

The results of the pyrolysis experiment and GC-MS analysis were further examined using a statistical approach to understand the effects of various parameters on target outcomes, including bio-oil, char, and gas yields, as well as fatty acid concentrations. Polynomial regression was employed to determine the P-value, which helps assess the significance of each parameter in influencing these target values. The second-order polynomial model used in this analysis was explained by Equation 1, where γ is the response variable (bio-oil yield, char yield, gas yield, fatty acids, N-containing compounds, oleic acid, and caffeine); $\beta_0, \beta_i, \beta_{ii}$, and β_{ij} are the regression coefficients for intercept, linear, quadratic, and interaction terms, respectively; X_i and X_j represent the independent variables. The SCG particle size (X_1), temperature (X_2), and nitrogen flow rate (X_3), were the independent variables in this research. Pearson's correlation analysis was performed to understand the relationships between parameters and between parameters and target values. The calculations were conducted using R-Studio software.

$$\gamma = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1} \beta_{ii} X_i^2 + \sum_{i=1}^{n} \sum_{j=i+1}^{n} \beta_{ij} X_i X_j \quad (1)$$

2.7. Fatty Acid Extraction

The obtained bio-oil from pyrolysis experiments consisted of two phases: an aqueous phase, which is a light-brown liquid, and an organic phase, which is a very dense, black, tar-like liquid. These two phases were separated immediately after production using a separatory funnel. Hexane was selected as the solvent for this liquid-liquid extraction process. Various volume ratios of hexane were tested to determine the optimal solvent volume. The ratios of bio-oil to hexane examined included 1:2.5, 1:5, 1:7.5, and 1:10 (v/v). A fixed volume of 0.5 mL of the aqueous phase and corresponding amounts of hexane (1.25, 2.5, 3.75, and 5 mL) were measured and added to small sample bottles. The bottles were then stirred vigorously for at least 12 hours to facilitate extraction. Following the extraction, the aqueous phase and the solvent were separated again using a separatory funnel and subsequently analyzed by (GC-MS). All procedures were conducted at room temperature throughout the separation and extraction processes.

3. RESULTS AND DISCUSSION

3.1. Elemental Analysis Result

The results of the elemental analysis of spent coffee grounds (SCG) revealed that it contained 51.83% carbon, 6.99% hydrogen, and 2.6% nitrogen. The sulfur content was not directly measured, as the value was referenced from other studies reporting a narrow range between 0 and 0.24% in SCG [27-29]. Variations in sulfur content could be attributed to differences in coffee types. Since SCG is a biological feedstock, its composition is highly variable, depending on factors such as brewing method, coffee variety, and growing conditions [30]. The oxygen content was

then estimated as the remaining percentage, ranging from 38.34% to 38.58%. The nitrogen content in SCG was higher than that of typical woody biomass, which is approximately 0.1% [31]. This elevated nitrogen level is likely due to the presence of caffeine, a compound with the chemical formula $C_8H_{10}N_4O_2$, which contains nitrogen atoms. Consequently, a significant amount of nitrogen-containing compounds is expected in SCG, reflecting its chemical composition and potential applications in various fields such as bioenergy and material science.

3.2. TG/DTA Analysis Result

The TG/DTA result curve of SCG can be seen in Figure 3. Since SCG is a lignocellulosic biomass that contains cellulose, hemicellulose, and lignin, three stages of thermal decomposition can be clearly observed. The first stage occurs around 100 - 200 °C and can be attributed to the release of water, with approximately 1 wt% of its mass decomposed. The second stage begins from 250 - 400 °C. During this stage, approximately 77 wt% of the mass is lost, indicating the decomposition of cellulose and hemicellulose, as more than half of SCG consists of cellulose and hemicellulose [11]. Lignin also decomposes at this stage, as lignin degradation occurs over a broader temperature range of 200 - 500 °C [32]. Finally, the third stage occurs at approximately 400 °C, indicating the decomposition of the SCG structure, which contributes to the biochar mass. This stage proceeds at a very slow rate with minimal weight loss, similar to the results presented by Primaz et al [14]. Based on this result, to maximize the production of bio-oil, a temperature of approximately 400°C should be used. Furthermore, many studies indicate that the temperature range of 450°C to 550°C is optimal for the pyrolysis of spent coffee grounds (SCG) [11, 15, 31, 33]. Therefore, the temperature range of 500–600°C was chosen as the optimal range for further research and optimization.

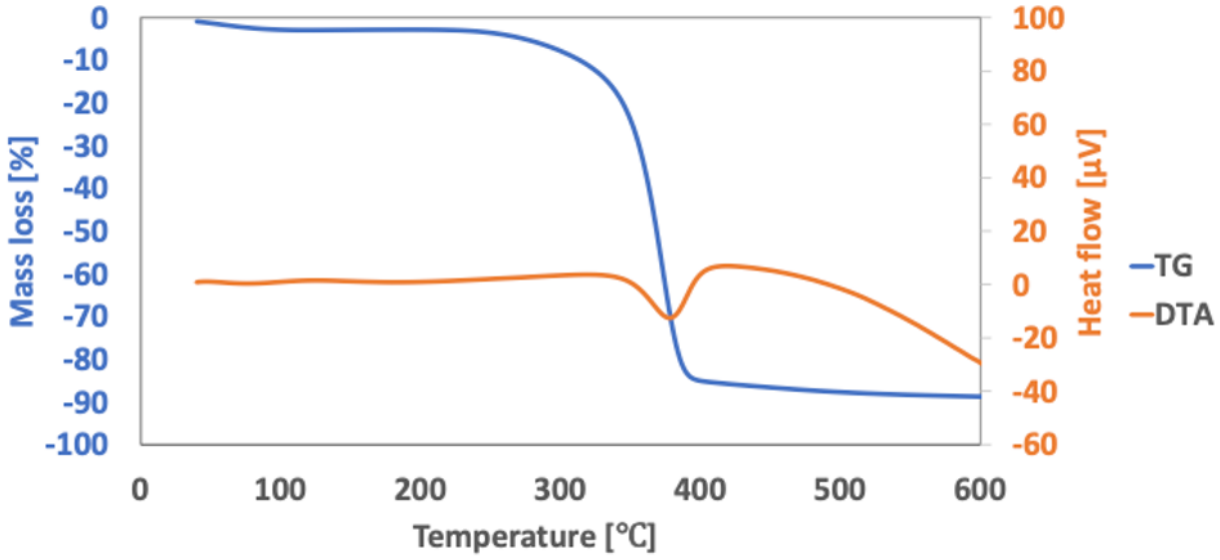

Figure 3. TG/DTA analysis result of SCG.

3.3. Pyrolysis Result

The pyrolysis experiments were conducted using three key parameters: SCG particle size, temperature, and nitrogen flow rate. Each parameter was tested at three levels in accordance with the Box-Behnken Design (BBD) and subsequently analyzed using statistical methods. Each experiment was performed in duplicate, and the average values are reported. Figure 4 presents the yields of pyrolysis products: bio-oil, biochar, and bio-gas. The gas yield was calculated by subtracting the mass yields of bio-oil and biochar. In this study, the gas yield was assumed to represent non-condensable gases.

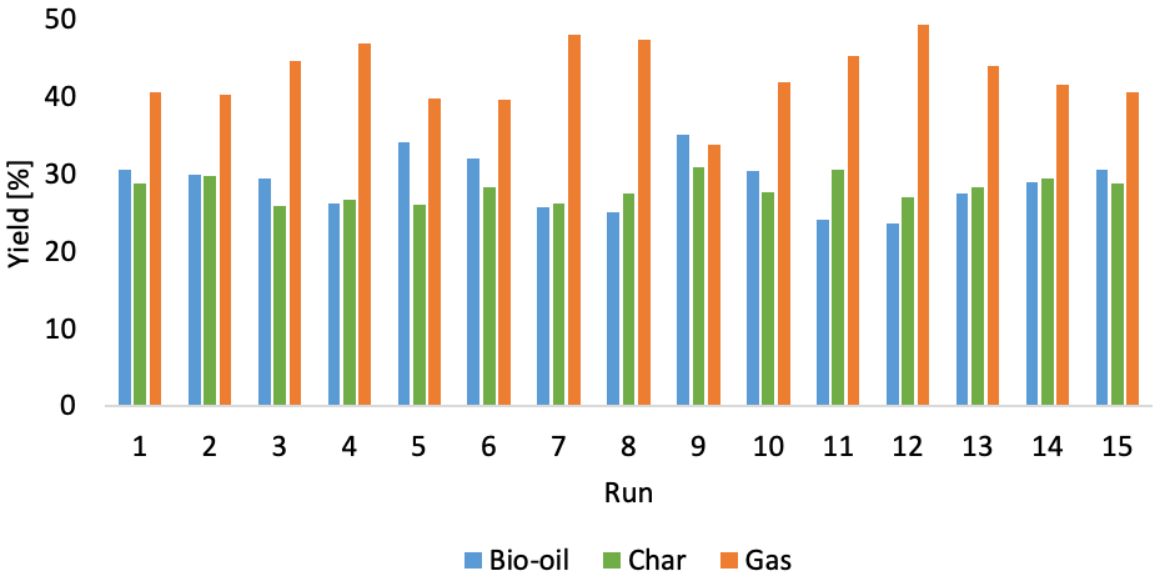

Figure 4. Yield of bio-oil, char, and gas from pyrolysis of SCG.

The highest bio-oil yield (35.20%) was obtained from Experiment number 9, which used a middle value of particle size (0.25–0.7 mm), a low temperature (500 °C), and a middle value of nitrogen flow rate (1 L/min). The second-highest bio-oil yield was 34.13% in Experiment number 5, which employed a low particle size (< 0.25 mm), a middle temperature (550 °C), and a low nitrogen flow rate (0.5 L/min). In contrast, the highest gas yield (49.39%) was observed in Experiment number 12, which used a middle particle size (0.25–0.7 mm), high temperature (600 °C), and a high nitrogen flow rate (1.5 L/min). Interestingly, Experiment number 9 had the lowest gas yield among all experimental conditions, while Experiment number 12 produced the lowest bio-oil yield (23.59%). The primary differences between Experiments 9 and 12 were the temperature and nitrogen flow rate levels. Higher temperatures promote secondary cracking reactions, resulting in increased gas yield [34]. Additionally, a high nitrogen flow rate can lead to greater gas yield due to insufficient residence time for condensable vapors to fully condense in the condenser or flask. The two highest char yields were obtained in Experiments 9 (30.96%) and 11 (30.65%), both of which employed a middle particle size and a low temperature. The key differences were in the nitrogen flow rates, with a high value in Experiment 9 and a low value in Experiment 11. The middle particle size appears optimal for char production. If the particle size is too small, rapid decomposition may reduce char yield and promote secondary vapor-phase reactions, lowering the bio-oil yield. Conversely, a larger particle size may hinder decomposition, also reducing bio-oil yield. The experimental error was calculated to be 5.39%, based on values from Experiments 13–15, which used the same experimental variables at the central point of the Box–Behnken Design (BBD).

3.4. GC-MS Result of Bio-Oil from Pyrolysis of SCG

GC-MS analysis was performed on the bio-oil obtained from each set of experimental conditions in the pyrolysis experiments. The results were organized into two sections: analysis by groups of chemicals and analysis by individual chemicals.

First, the analysis of chemicals by the group was performed. The compounds were classified into seven categories: alcohols, fatty acids, hydrocarbons, ketones, N-containing compounds, phenols, and others. Fatty acids consistently represented the highest composition among the chemical groups in nearly all experiments, as shown in Figure 5, followed by hydrocarbons and N-containing compounds. The highest concentration of fatty acids was observed in Experiment number 1 (44.67 relative concentration %), followed by Experiments number 2 and 5.

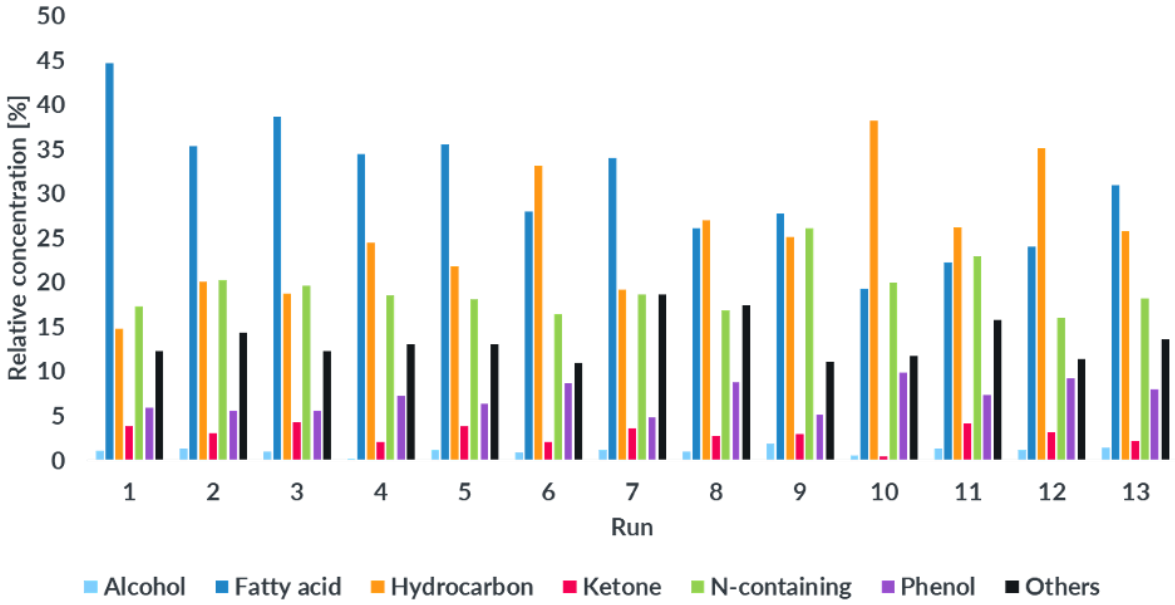

Figure 5. GC-MS results of group of chemicals in pyrolyzed bio-oil from SCG.

In the analysis of individual chemical compounds, the most abundant compounds from the top three groups of chemicals namely fatty acids, hydrocarbons, and nitrogen-containing compounds were identified and reported. Oleic acid, a fatty acid, consistently exhibited the highest concentration in spent coffee grounds (SCG)-derived pyrolyzed bio-oil across all experiments, followed by caffeine, a nitrogen-containing compound, and pentadecane, a hydrocarbon, as shown in Figure 6. Oleic acid is a valuable fatty acid with applications in the chemical and pharmaceutical industries, including its use as a stabilizer and emulsifier, in the reduction of cancer cell development, and in the improvement of blood pressure [35, 36]. Due to its prevalence and industrial significance, oleic acid was selected as the target value-added bio-based chemical in this study. The highest relative concentration of oleic acid was observed in Experiment 1, with 28 relative concentration percentage, followed by Experiments 4 and 3, with 26.33 and 26.15 relative concentration percentages, respectively. Experiment 1 employed low values of both SCG particle size and pyrolysis temperature, while Experiments 3 and 4 used middle values of temperature and nitrogen flow rate.

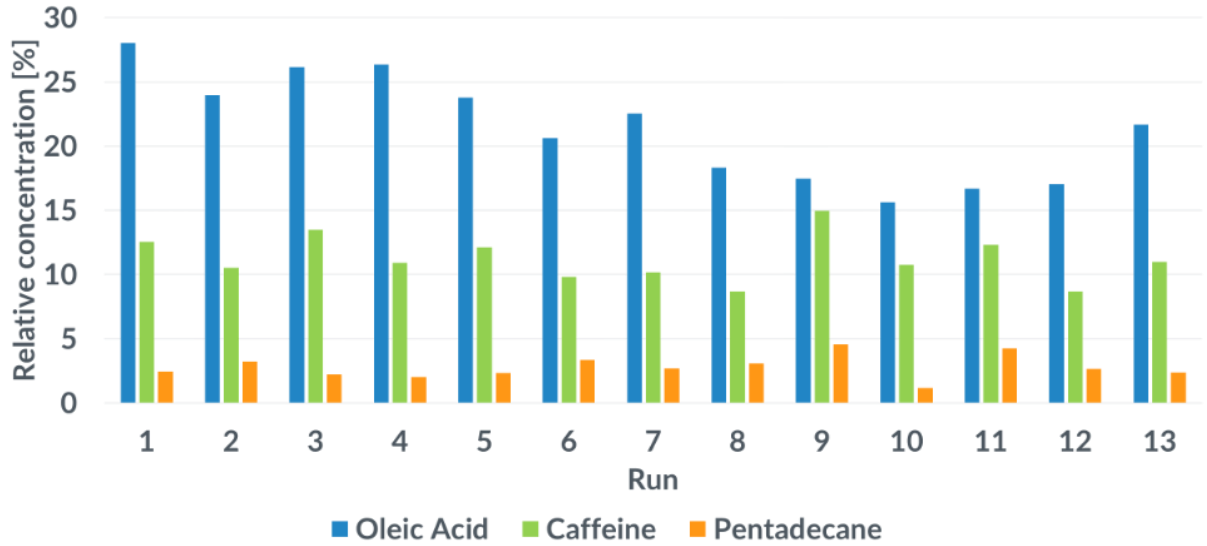

Figure 6. GC-MS results of abundant chemicals in SCG bio-oil.

GC-MS analysis revealed that fatty acids constituted the highest proportion of compounds in the pyrolyzed bio-oil derived from spent coffee grounds (SCG), with oleic acid identified as the most abundant individual compound. However, the specific process parameters influencing the yields of bio-oil, fatty acids, and oleic acid remained unclear. Therefore, statistical analyses were conducted to identify and evaluate the effects of these parameters.

3.5. Statistical Analysis Result

Polynomial regression analyses were conducted for both the pyrolysis results (yields of bio-oil, biochar, and bio-gas) and the GC-MS results (groups of chemicals and individual chemicals) to identify the statistically significant parameters influencing the response variables. For the pyrolysis experiments, the response variables included the yields of bio-oil, biochar, and bio-gas. Using multiple regression analysis, the predicted responses (γ) for each yield were modeled using second-order polynomial equations (Equations 2-4), where $X1$ (SCG particle size), $X2$ (temperature), and $X3$ (nitrogen flow rate) represent the coded values of the independent variables. The P-values for each response variable were calculated using RStudio software and are presented in Table 3.

$$\gamma_{Oil} = 27.53 - 0.81X_1 - 1.25X_2 - 4.16X_3 - 0.61X_1X_2 + 0.38X_1X_3 + 1.05X_2X_3 + 1.22{X_1}^2 + 0.32{X_2}^2 + 0.49{X_3}^2 \quad (2)$$

$$\gamma_{Char} = 28.41 - 0.65X_1 - 1.60X_2 - 0.19X_3 - 0.01X_1X_2 - 0.26X_1X_3 - 0.07X_2X_3 - 1.30{X_1}^2 + 0.72{X_2}^2 - 0.07{X_3}^2 \quad (3)$$

$$\gamma_{Gas} = 44.06 + 0.16X_1 + 2.85X_2 + 4.36X_3 + 0.62X_1X_2 - 0.12X_1X_3 - 0.97X_2X_3 + 0.09{X_1}^2 - 1.04{X_2}^2 - 0.43{X_3}^2 \quad (4)$$

Table 3. P-values of pyrolysis experiment products.

Product	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	${X_1}^2$	${X_2}^2$	${X_3}^2$
Oil	0.032	0.010	0.000	0.136	0.298	0.041	0.056	0.486	0.301
Char	0.019	0.001	0.253	0.962	0.287	0.733	0.016	0.072	0.803
Gas	0.636	0.002	0.000	0.247	0.797	0.111	0.888	0.167	0.511

Generally, P-values below 0.05 are considered statistically significant. As shown in Table 3, all independent variables were statistically significant with respect to bio-oil yield. According to Equation 2, each variable had a negative relationship with bio-oil yield, indicating that higher values of these parameters led to a decrease in bio-oil yield. However, the interaction between temperature and nitrogen flow rate (X_2X_3) had a positive effect, suggesting that their combined influence could enhance bio-oil yield. For bio-char yield, particle size (X_1) and temperature (X_2) were statistically significant, both showing a negative relationship. Additionally, the significance of the second-order term for particle size (X_1^2) suggests a non-linear relationship between particle size and bio-char yield. In the case of bio-gas yield, temperature (X_2) and nitrogen flow rate (X_3) were significant parameters, both exhibiting a positive correlation with bio-gas yield. To further assess the strength and the direction of the relationships between process parameters and response variables, Pearson's correlation analysis was conducted.

Pearson's correlation is a useful statistical tool for assessing both the strength and direction of relationships between variables. The correlation coefficient ranges from -1 to 1, where 0 indicates no correlation, 1 represents a perfect positive correlation, and -1 signifies a perfect negative correlation [37]. A positive correlation means that as variable X increases, variable Y also increases; conversely, a negative correlation indicates that an increase in X leads to a decrease in Y. Based on the Pearson's correlation coefficients of the pyrolysis products shown in Table 4, nitrogen flow rate exhibited a strong negative correlation with bio-oil yield, while particle size and temperature showed weak to moderate negative correlations. Therefore, to maximize bio-oil yield, the results suggest using a small to medium particle size, a low to moderate temperature, and a very low nitrogen flow rate.

Table 4. Pearson's correlation coefficient of pyrolysis products.

Variable	Particle size	Temp.	Nitrogen flow rate	Bio-oil yield	Char yield	Gas yield
Particle size	1	0	0	-0.18	0.32	0.03
Temperature		1	0	-0.27	-0.78	0.53
Nitrogen flow rate			1	-0.91	-0.1	0.82
Bio-oil yield				1	0.18	-0.93
Char yield					1	-0.54
Gas yield						1

Based on the GC-MS results, the response variables were the concentration of oleic acid, caffeine, fatty acids, and N-containing compounds. The predicted response (γ) could be obtained via the second-order polynomial (Equations 5-8), with the same variables as the pyrolysis results.

$$\gamma Oleic\ acid = 28.94 + 0.14X_1 + 3.81X_2 - 1.91X_3 + 4.23X_1X_2 - 2.77X_1X_3 + 0.60X_2X_3 + 1.07{X_1}^2 - 1.49{X_2}^2 - 1.49{X_3}^2 \quad (5)$$

$$\gamma Caffeine = 8.2 - 0.26X_1 - 0.46X_2 - 0.60X_3 + 0.49X_1X_2 - 0.25X_1X_3 - 0.06X_2X_3 + 1.01{X_1}^2 + 3.06{X_2}^2 + 0.05{X_3}^2 \quad (6)$$

$$\gamma Fattyacids = 30.91 - 3.62X_1 - 1.70X_2 - 0.51X_3 + 1.29X_1X_2 - 0.09X_1X_3 + 2.57X_2X_3 + 7.46{X_1}^2 - 0.09{X_2}^2 - 7.46{X_3}^2 \quad (7)$$

$$\gamma N\_containing\ compounds = 18.18 - 0.19X_1 - 1.58X_2 - 0.77X_3 - 0.99X_1X_2 + 0.004X_1X_3 - 0.21X_2X_3 - 1.48{X_1}^2 + 2.26{X_2}^2 + 0.81{X_3}^2 \quad (8)$$

According to the results in Table 5, no parameters were statistically significant for either oleic acid or caffeine. The R^2 values of the fitted models were 65% for oleic acid and 55% for caffeine, indicating a limited fit of the models to the response variables and, consequently, a lack of statistically significant predictors. Although these R^2 values are moderate, they are within an acceptable range for exploratory studies using Box-Behnken Design (BBD), particularly in systems with inherent biological variability. Similar low R^2 values have been reported in previous BBD-based optimization studies on food sensory attributes, where values above 0.6 were still considered indicative of valid models when variability is high and the number of experimental points is limited [38]. While R^2 values above 0.8 are generally preferred, values exceeding 0.6 have also been deemed acceptable for modeling complex systems under constrained experimental conditions [39]. The observed R^2 values in this study are therefore considered sufficient to identify general process trends and support subsequent optimization efforts. Future studies with larger datasets and broader parameter ranges may facilitate the application of hybrid machine learning-based modeling frameworks to more accurately capture the underlying system complexity.

Table 5. P-values of GC/MS-identified chemical groups.

Chemical groups	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	X_1^2	X_2^2	X_3^2
Oleic acid	0.975	0.218	0.493	0.309	0.483	0.873	0.830	0.766	0.766
Caffeine	0.071	0.696	0.609	0.764	0.876	0.971	0.645	0.220	0.982
Fatty acid	0.000	0.005	0.123	0.031	0.791	0.005	0.000	0.851	0.000
N-containing compound	0.881	0.283	0.567	0.600	0.998	0.909	0.559	0.392	0.744

Conversely, the R^2 values for the chemical group models were approximately 99%, indicating that second-order polynomial regression analysis was suitable for predicting chemical groups but not for individual compounds. Among the process parameters, particle size (X_1) and temperature (X_2) were identified as significant factors influencing fatty acid production. According to Equation 7, both parameters demonstrated a negative relationship with fatty acid concentration. However, their interaction term (X_1X_2) showed a positive effect, suggesting that a specific combination

of particle size and temperature could enhance fatty acid content in the bio-oil. Additionally, the interaction between temperature and nitrogen flow rate (X_2X_3) was also significant and positively correlated with fatty acid concentration. Both particle size and nitrogen flow rate exhibited nonlinear effects on fatty acid concentration.

Pearson's correlation analysis was conducted to evaluate the strength of the relationship between process parameters and each chemical concentration. As shown in Table 6, both particle size and temperature exhibited a fair negative correlation with fatty acid concentration, while nitrogen flow rate showed almost no correlation. These results suggest that using a small to medium SCG particle size and a moderate temperature is favorable for achieving a higher concentration of fatty acids.

Table 6. Pearson's correlation coefficient of GC/MS results.

Variable	Particle size	Temperature	Nitrogen flow rate	Oleic acid	Caffeine	Fatty acid	N-containing compound
Particle size	1	0	0	0.02	-0.1	-0.41	-0.06
Temperature		1	0	0.53	-0.17	-0.67	-0.46
Nitrogen flow rate			1	-0.27	-0.22	0.05	-0.23
Oleic acid				1	0.38	0.13	-0.18
Caffeine					1	0.25	0.63
Fatty acid						1	-0.2
N-containing compound							1

Based on the actual yield results and statistical analysis, the optimal conditions for maximizing both bio-oil and fatty acid yields were identified as a small particle size (< 0.25 mm), a temperature of 550°C, and a nitrogen flow rate of 0.5 L/min. Therefore, experiment number 5 (-1, 0, -1) was selected as the optimal condition in this study.

3.6. Mass Balance Analysis Result

In the pyrolysis experiment, it was observed that a high nitrogen flow rate could reduce bio-oil yield, as condensable gases may not have sufficient residence time to fully condense in the condenser or collection flask. Consequently, some condensable gases might escape as non-condensable gases during the condensation process. To clarify the actual mass distribution, a mass balance analysis experiment was conducted using the setup illustrated in Figure 1b. The experiment was performed using the sample from Experiment number 5, which had been identified as the optimal condition in this study. The experiment was conducted twice to ensure data validity.

During the experiment, a thick white mist was observed in the first impinger, indicating the presence of tar in aerosol form. The mist was not observed in the second or third impingers, likely because some of the tar was dissolved in ethanol in its gaseous form and subsequently condensed in the second impinger due to the lower temperature. Additionally, a small amount of black liquid was observed in the hose connecting the first and second impingers. This may have been tar-laden ethanol that condensed before reaching the second impinger. These observations serve as useful indicators of the effectiveness of the tar-trapping system.

After the experiment, a dirty glass frit was observed in the second impinger, whereas the glass frit in the third impinger remained clean. This observation suggests that all the tar produced during the pyrolysis process was effectively trapped in the first and second impingers, as no residue reached the third. As summarized in Table 7, the bio-oil yield increased by approximately 4%, from 34.13% to 37.68%, while the gas yield decreased by approximately 5%, from 39.78% to 34.40%. This indicates that the gas yield in the original pyrolysis experiment included both condensable and non-condensable gases. The additional trapping step enabled a more accurate quantification of the condensable fraction, thereby allowing for a more precise mass balance of the pyrolysis process.

Table 7. Results of the mass balance experiment.

Run	Without impinger			3 impingers + glass frits		
	Bio-oil yield [%]	Char yield [%]	Gas yield [%]	Bio-oil yield [%]	Char yield [%]	Gas yield [%]
5	34.13	26.09	39.78	37.68	27.92	34.40

3.7. Fatty Acid Extraction Result

The bio-oil produced from Experiment number 5 was selected for liquid-liquid extraction because it represented the optimal conditions for maximizing both bio-oil and fatty acid yields. The pyrolyzed bio-oil was separated into two distinct phases: an aqueous phase and an organic phase. These phases were separated using a separatory funnel. Only the aqueous phase was subjected to liquid-liquid extraction experiments, as the organic phase was dissolved in the solvent, making it unsuitable for liquid-liquid extraction with solvent. The chemical compositions of both phases were analyzed using GC-MS. Nearly half of the aqueous phase consisted of fatty acids, with oleic acid identified as the most abundant compound. Conversely, a smaller amount of oleic acid was detected in the organic phase. Additionally, nitrogen-containing compounds, particularly caffeine, were found in high concentrations in the aqueous phase. Hydrocarbons were not detected in the aqueous phase but were prominently present in the organic phase.

Hexane was chosen as the solvent for extracting fatty acids from spent coffee grounds (SCG)-derived pyrolyzed bio-oil because it is one of the most widely used solvents for fatty acid and lipid extraction, owing to its low cost, high efficiency, and broad applicability across different types of biomass [40, 41]. Various bio-oil-to-hexane ratios (1:2.5, 1:5, 1:7.5, and 1:10) were tested to determine the optimal conditions for oleic acid recovery. Oleic acid was selected as the indicator compound due to its significance as a platform chemical and its abundance in SCG-derived pyrolyzed bio-oil. Following extraction, the bio-oil was analyzed using GC-MS, and the mass of oleic acid was quantified using a calibration curve. At a bio-oil-to-hexane ratio of 1:2.5, approximately 36% of the oleic acid present in the bio-oil was extracted. The yield increased to approximately 46% at a ratio of 1:5, corresponding to about 1.3 mg of oleic acid. Further increases in the solvent ratio to 1:7.5 and 1:10 did not yield significant improvements, indicating that the 1:5 ratio was optimal under the given experimental conditions. Although the absolute quantity of extracted oleic acid may appear low, it represents a considerable fraction of the recoverable fatty acids in the aqueous-phase bio-oil. This study thus serves as a proof of concept for valorizing SCG through pyrolysis and subsequent liquid-liquid extraction, with oleic acid identified as the targeted value-added compound.

Oleic acid has been reported to offer several health benefits, including the regulation of blood pressure and the inhibition of cancer cell development. Furthermore, when sufficiently purified, oleic acid can be employed as a component in drug delivery systems to enhance clinical effectiveness due to its bioactive properties [35, 36]. Previous studies have demonstrated solvent extraction of bio-oils derived from Jatropha curcas seed cake [42] and olive mill waste [40]. To the best of our knowledge, no study has reported the liquid-liquid extraction of fatty acids from pyrolyzed bio-oil derived from spent coffee grounds (SCG). The findings of this study underscore the feasibility and selectivity of this approach, supporting its potential for future scale-up and application to other biomass sources.

3.8. Comparative Analysis of SCG Pyrolysis Yields and Value-Added Components Extraction from Bio-Oil

This research focuses on producing bio-based chemicals from SCG-derived pyrolyzed bio-oil. The optimized bio-oil yields obtained in this study were benchmarked against previous SCG pyrolysis studies conducted under similar thermal conditions. A bio-oil yield of 34.13% was achieved under optimal conditions involving fine SCG particle size (< 0.25 mm), a pyrolysis temperature of 550 °C, and a nitrogen flow rate of 0.5 L/min. When impingers were employed, the yield increased to 37.68%. Comparable studies reported yields of 36% at 540 °C with a heating rate of 50 °C/s [7] and 30.51% at 500 °C in a fixed-bed reactor with a nitrogen flow rate of 0.1 L/min [14]. These comparisons demonstrate that the yields obtained in this study are within or slightly above the range of those previously reported.

Primaz, et al. [10] analyzed SCG pyrolysis bio-oil using GC×GC/TOF-MS and identified a high abundance of fatty materials, hydrocarbons, ketones, and phenols [14]. Similarly, Krause, et al. [15] investigated the fast pyrolysis of SCG and found that fatty acids were the most abundant compounds in the resulting bio-oil [15]. These findings suggest that SCG-derived bio-oil is a promising feedstock for biofuel applications due to its rich fatty acid content. However, the presence of nitrogen-containing and oxygenated compounds, such as ketones and phenols, poses challenges for direct fuel application. As a result, converting SCG-derived bio-oil into value-added chemicals may represent a more viable utilization pathway. Fatty acids (lipids), for instance, can be employed as fillers, solubilizers, and emulsifiers in the pharmaceutical industry, with their physicochemical properties tunable to enhance drug delivery and clinical efficacy [43]. While advanced pyrolysis methods, such as catalytic pyrolysis or hydrothermal liquefaction, can influence product distribution, the present study establishes baseline yields for conventional thermal pyrolysis and demonstrates the effectiveness of BBD in evaluating the effects of three key process parameters (SCG particle size, temperature, and nitrogen flow rate) on the yields of bio-oil, biochar, bio-gas, and fatty acids.

4. LIMITATIONS AND DIRECTIONS FOR FUTURE RESEARCH

Despite the approach adopted in this study to valorize spent coffee grounds (SCG) through pyrolysis and subsequent oleic acid extraction from bio-oil, several limitations should be acknowledged, providing direction for future research. The chemical analysis in this work was primarily conducted using GC-MS. While it was suitable for identifying major components, advanced characterization techniques such as FTIR, NMR, or 2D-GC could provide deeper structural insights and are recommended for future studies.

In terms of process outcomes, the absolute yield of oleic acid recovered (approximately 1.3 mg) may seem low for industrial-scale applications. Although this supports the proof-of-concept for SCG bio-oil valorization as bio-based chemicals, further research is necessary to evaluate the economic feasibility and scalability of the method. Exploring different types of solvents or adjusting experimental parameters could be effective strategies to increase the yield and optimize the process.

Lastly, the regression models used for predicting oleic acid and caffeine concentrations also showed modest R^2 values (65% and 55%, respectively), which limits the reliability of the optimization framework. Although there is no dedicated regression model for oleic acid and caffeine content from SCG pyrolysis, this work could serve as a preliminary approach to developing predictive models for optimizing oleic acid and caffeine recovery. Future research may benefit from conducting additional experiments and applying improved modeling techniques or machine learning approaches to enhance predictive performance.

5. CONCLUSION

In this study, the production of bio-oil and value-added bio-based chemicals from spent coffee grounds (SCG) was investigated. Oleic acid, a fatty acid with broad applicability in the chemical industries, was selected as the target compound due to its abundance in the pyrolyzed bio-oil. Pyrolysis experiments were conducted using three key process parameters: SCG particle size, temperature, and nitrogen flow rate. Each parameter was varied across three levels following a Box-Behnken design. Pearson's correlation analysis was used to evaluate the strength of association between each parameter and the response variables. The results indicated that the optimal conditions for maximizing both bio-oil yield and fatty acid content were a particle size of less than 0.25 mm, a temperature of 550 °C, and a nitrogen flow rate of 0.5 L/min. Additionally, oleic acid was successfully extracted from the pyrolyzed bio-oil using hexane, with the optimal bio-oil-to-hexane ratio determined to be 1:5 (v/v). It is important to note that the composition of SCG can vary significantly depending on several factors such as coffee bean variety, roasting conditions, and storage practices. In this study, SCG samples were collected from a single source and processed under consistent conditions to minimize variability. While the absolute amount of oleic acid extracted was relatively low

and alternative sources may be more economically viable, this research demonstrates an approach for the dual valorization of SCG into bio-oil as a renewable bioenergy source and oleic acid as a value-added bio-based chemical.

Funding: This study received no specific financial support.
Institutional Review Board Statement: Not applicable.
Transparency: The authors state that the manuscript is honest, truthful, and transparent, that no key aspects of the investigation have been omitted, and that any differences from the study as planned have been clarified. This study followed all writing ethics.
Competing Interests: The authors declare that they have no competing interests.
Authors' Contributions: All authors contributed equally to the conception and design of the study. All authors have read and agreed to the published version of the manuscript.
Disclosure of AI Use: The author used OpenAI's ChatGPT (GPT-4) to edit and refine the wording of the Introduction and Literature Review. All outputs were thoroughly reviewed and verified by the author.

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