International Journal of Design & Nature and Ecodynamics
Vol. 20, No. 9, September, 2025, pp. 2147-2156
Journal homepage: http://iieta.org/journals/ijdne

Recirculated Process-Derived Liquid as an In-Situ Modifier for Fabricating Acidic Coffee Parchment Hydrochar as a Potential Biodiesel Catalyst

Raudah[1,2], Rosdanelli Hasibuan[1*], Irvan[1], Erni Misran[1]

[1] Department of Chemical Engineering, Faculty of Engineering, Universitas Sumatera Utara, Medan 20155, Indonesia
[2] Department of Chemical Engineering, Politeknik Negeri Lhokseumawe, Lhokseumawe 24301, Indonesia

Corresponding Author Email: rosdanelli@usu.ac.id

https://doi.org/10.18280/ijdne.200918

Received: 22 August 2025
Revised: 22 September 2025
Accepted: 26 September 2025
Available online: 30 September 2025

Keywords:
biodiesel catalyst, hydrochar functionalization, liquid fraction recirculation, microwave-assisted hydrothermal carbonization, sustainable catalyst production

ABSTRACT

Sustainable biodiesel production requires the development of eco-friendly heterogeneous acid catalysts. Conventional sulfonation methods rely on hazardous chemicals, which undermine the environmental benefits. This study explores the use of self-derived liquid fraction (LF) from microwave-assisted hydrothermal carbonization (MA-HTC) of coffee parchment as a green in-situ functionalization agent for hydrochar, eliminating the need for external sulfonating agents. Coffee parchment underwent MA-HTC at 100℃ for 2 hours under a biomass-to-water ratio of 1:10, with up to three LF recirculation cycles. The chemical evolution of LF was monitored through Fourier Transform Infrared (FTIR) spectroscopy, total organic carbon (TOC) analysis, and high-performance liquid chromatography (HPLC). The resulting hydrochar was characterized for acid density (using Boehm titration) and porosity (via nitrogen adsorption–desorption analysis). The aqueous medium, rich in acetic and lactic acids, aromatic compounds, and nitrogen-containing species, correlated with an increase in strong acid density and altered weak acid content. The hydrochar's surface showed enrichment of both Brønsted (–COOH) and Lewis (N-groups) acid sites. FTIR analysis suggests the possible presence of sulfonic acid groups ($–SO_3H$), though this remains speculative. XPS analysis is recommended for further confirmation of these functional groups in future studies. Optimal recirculation (one cycle) preserved mesoporosity (3.91 nm pore diameter), which is critical for reactant diffusion. Further recirculation cycles led to an expansion of pores (12.48 nm) but a reduction in surface area from 0.658 to 0.263 m^2/g. Recirculated LF acts as a self-sustaining functionalization medium, successfully anchoring these acid sites onto hydrochar. This strategy not only replaces hazardous sulfonation but also valorizes waste liquor, aligning with circular economy principles and contributing to the development of green biodiesel catalysts.

1. INTRODUCTION

The global shift from fossil fuels to renewable energy sources has positioned biodiesel as a key sustainable transportation fuel. Produced via esterification and transesterification of biological lipids, biodiesel offers biodegradability, low toxicity, and a significant reduction in greenhouse gases compared to petroleum diesel [1]. To enhance process sustainability, recent research has focused on developing heterogeneous acid catalysts derived from biomass. These catalysts are favored for their reusability, easy separation, and reduced environmental footprint [2]. Among these, sulfonated carbon-based catalysts have demonstrated exceptional efficiency in converting free fatty acids (FFAs) and triglycerides into biodiesel [3, 4].

However, conventional sulfonation methods rely on the use of hazardous mineral acids (e.g., H_2SO_4) to introduce Brønsted acid sites ($–SO_3H$), generating toxic effluents and compromising the environmental advantages of biomass-derived catalysts [5, 6]. This creates a critical need for greener functionalization strategies that eliminate chemical additives and simultaneously valorize waste streams. A promising solution lies in utilizing by-products from biomass processing, particularly the aqueous hydrothermal liquor produced during hydrothermal carbonization (HTC).

Biomass-derived heterogeneous catalysts, especially those functionalized with sulfonic acid groups, have garnered significant attention in biodiesel production due to their high catalytic efficiency and renewable origin [4]. Sulfonated carbon-based catalysts have demonstrated excellent performance in esterification of FFAs and transesterification of triglycerides, yielding competitive biodiesel amounts and maintaining activity over multiple cycles [3, 6-10]. Comprehensive reviews indicate that crucial physicochemical properties—including acid density, strength, and type—are essential factors influencing catalyst performance and recyclability [11]. As the global biodiesel industry continues to embrace sustainable, waste-derived materials, there is a pressing need to explore alternative methods of functionalizing biomass-based catalysts that do not rely on hazardous chemicals.

Despite their catalytic efficiency, the synthesis of sulfonated carbon materials traditionally involves chemical sulfonation using strong mineral acids such as H_2SO_4 or ammonium sulfate. While effective in introducing $–SO_3H$ groups, these processes require handling hazardous reagents, generating acidic effluents, and incur additional operational costs. As a result, they undermine the environmental and safety benefits of the final product [3, 5, 6]. From a process sustainability perspective, a key research challenge is the development of in-situ functionalization methods that minimize or eliminate the use of such chemicals. Achieving this goal would not only reduce the ecological footprint of catalyst production but also facilitate decentralized biodiesel manufacturing in regions with limited infrastructure for chemical handling and waste treatment.

A promising approach to achieving this goal is the use of by-products generated during biomass processing—specifically, the aqueous phase produced during hydrothermal carbonization (HTC). HTC, which converts wet biomass into hydrochar under subcritical water conditions, produces two primary products: a carbon-rich hydrochar and a liquid fraction (LF) containing a mixture of organic compounds. These compounds—such as volatile fatty acids (VFAs), phenolic compounds, furans, and other oxygenated species—are by-products of the hydrolysis, dehydration, and depolymerization of biomass components [12]. While HTC has traditionally been investigated for hydrochar use as a solid fuel [13-15], adsorbent [16], or in biochemical and energy recovery processes, its use as a functionalizing agent for catalyst production remains largely unexplored.

The LF produced during HTC contains organic acids and aromatics, such as acetic acid, furfural, and phenolics, which could impart catalytic functionalities to hydrochar surfaces without requiring externally added chemicals. However, previous research has largely focused on optimizing HTC process parameters for hydrochar yield and composition rather than investigating LF chemistry for direct catalyst functionalization. To the best of the authors' knowledge, there have been limited publications that specifically discuss using liquid fraction (LF) as a functionalization agent, especially for catalyst functionalization intended for biodiesel production. There is a clear gap in studies examining how LF composition influences the formation of acid sites on hydrochar, which is crucial for understanding its catalytic potential.

Although hydrothermal carbonization (HTC) has been extensively studied for producing biochar and for energy recovery, the use of liquid fraction (LF) as an in-situ functionalization agent for hydrochar has not been widely explored in the literature. While most research has focused on optimizing HTC process parameters for biochar yield or energy applications, the potential of LF to functionalize catalysts, particularly for biodiesel production, remains largely underexplored. This gap in the literature presents an opportunity for this study, which aims to investigate the use of LF derived from HTC of coffee parchment as a green, in-situ functionalization agent for hydrochar. By utilizing this approach, this research intends to fill the existing void and provide new insights into the development of sustainable, biomass-derived catalysts for biodiesel production, offering an environmentally friendly alternative to traditional sulfonation methods.

Biochar modification generally focuses on introducing acid functional groups, such as $–SO_3H$ or –COOH, through a variety of methods [17-19]. These methods typically include: (i) using the inherent weak acid groups in biochar, (ii) adding acid sites through sulfonation or copolymerization with acid-functionalized monomers, and (iii) immobilizing solid acids on the biochar surface. This research seeks to leverage the organic compounds present in LF to achieve autogenous functionalization of hydrochar, thereby creating acid sites, such as –COOH, without relying on external chemical reagents. By doing so, this study aims to fill the gap in existing research on using LF for functionalizing catalysts intended for biodiesel production, contributing to more sustainable and efficient catalyst development.

Studies suggest that certain biomass-derived organics naturally present in the LF can perform similar roles to externally added chemicals in introducing catalytic functionalities to carbon surfaces. For example, organic acids and phenolic compounds derived from biomass have been shown to anchor $–SO_3H$ and –COOH groups onto carbon supports, generating both Brønsted and Lewis acid sites [6, 17]. A notable example is the one-pot carbonization–sulfonation of orange peel bio-waste, which yielded carbon-based catalysts with high $–SO_3H$ density (~1.96 mmol/g) and high biodiesel yields [20]. These findings suggest that leveraging organics inherently generated during HTC, such as acetic and lactic acids, could provide an environmentally friendly route to catalyst functionalization without the need for hazardous reagents.

Microwave-assisted hydrothermal carbonization (MA-HTC) offers additional advantages for implementing this strategy. Unlike conventional HTC, MA-HTC provides rapid and uniform heating, reduced reaction times, and better control over product properties [19, 21]. These benefits could enhance the interactions between LF-derived organics and hydrochar, improving the efficiency of functional group grafting. Recent studies have also demonstrated that recirculating LF in HTC processes can progressively enrich it with VFAs, phenolics, and nitrogenous compounds [20, 22], potentially increasing its ability to impart catalytic functionalities in situ. However, systematic investigations linking LF recirculation to chemical evolution and measurable changes in catalyst acidity and porosity remain scarce.

While several studies have explored LF recirculation for purposes such as nutrient recovery, chemical concentration, or enhanced hydrochar yields [23-25], limited attention has been given to its role as a self-sustaining functionalization medium for catalyst production. Moreover, there is a notable lack of research correlating changes in LF composition—such as total organic carbon (TOC), organic acid profiles, and functional group spectra—with the hydrochar’s acid site density, porosity, and catalytic properties. This represents a critical knowledge gap, as these surface properties are directly linked to the catalytic performance of biomass-derived materials in biodiesel synthesis [6, 11].

This study aims to fill this identified research gap by proposing and investigating a circular and autogenous functionalization strategy. The research utilizes the liquid fraction from microwave-assisted HTC (MA-HTC) of coffee parchment, an abundant and underutilized agro-industrial residue, as a green, in-situ functionalization medium. We hypothesize that the recirculation of this self-derived LF will progressively enrich it with reactive organic species (e.g., acetic acid, lactic acid, and phenolics), which in turn will enable the functionalization of the co-produced hydrochar with acid sites, eliminating the need for external sulfonating agents. The primary objectives of this work are to: (1) characterize the chemical evolution of the LF across multiple recirculation cycles using Fourier Transform Infrared (FTIR) spectroscopy, total organic carbon (TOC) analysis, and high-performance liquid chromatography (HPLC); (2) quantify the resulting changes in the hydrochar's surface acidity (total, strong, and weak acid density) via Boehm titration; and (3) analyze the alterations in the hydrochar's textural properties (surface area, pore volume, and pore size distribution) via nitrogen physisorption. By correlating LF chemistry with hydrochar properties, this study seeks to validate the role of recirculated LF as a self-sustaining functionalization medium, thereby contributing to the development of a more sustainable and circular pathway for producing biodiesel catalysts.

2. MATERIAL AND METHOD

2.1 Materials

Coffee parchment (CP), a lignocellulosic waste material sourced from CV. Nutrisi Aceh (Takengon, Indonesia) was used as the feedstock for hydrothermal carbonization (HTC). The raw CP was ground and sieved to a particle size range of 0.15–0.42 mm to ensure uniform heat and mass transfer during hydrothermal processing. The sieved CP was stored in moisture-proof polyethylene bags at room temperature until further use.

2.2 Microwave-assisted hydrothermal carbonization (MA-HTC)

MA-HTC was carried out using a modified conventional microwave (MW) operating at 2450 MHz. In the initial cycle (Cycle 0), 30 g of CP was added to 300 g of distilled water, maintaining a biomass-to-water ratio of 1:10. The mixture was heated to 100℃ at a ramp rate of 5℃ per minute and held at this temperature for 2 hours. After the reaction, the system was allowed to cool naturally to 25℃. The resulting solid hydrochar and liquid fraction were separated via vacuum filtration using Grade 4 filter paper with 20–25 µm pores. The solid hydrochar (CPH-R0) was oven-dried at 105℃ for 24 hours, while the liquid fraction (LF-R0) was collected and reserved for characterization and recirculation in subsequent cycles.

2.3 Liquid fraction recirculation protocol

The aqueous liquid fraction (LF) generated during the initial MA-HTC cycle was collected and reused for subsequent recirculated HTC experiments. Recirculation was performed to evaluate the effects of cumulative enrichment of organic compounds in the LF on hydrochar surface chemistry and catalytic properties. For each recirculation cycle, the LF from the previous cycle was collected and reused, maintaining a total liquid mass of 300 g per cycle, without adding distilled water. This method ensures that the LF undergoes repeated cycles, progressively increasing the concentration of volatile fatty acids (VFAs) and phenolic compounds, which could potentially enhance the self-functionalization of hydrochar. Four recirculation cycles were performed: the first cycle (LF-R0) used no recirculated LF, the second cycle (LF-R1) used one recirculation of LF, the third cycle (LF-R2) used two recirculations, and the fourth cycle (LF-R3) involved three recirculations. After each cycle, the LF was collected, characterized, and reused in the next cycle, following the procedure outlined in Figure 1.

2.4 Liquid fraction characterization

The evolution of the liquid fraction (LF) was analyzed to monitor changes in its visual appearance and to quantify its enrichment with functionalizing agents. Total Organic Carbon (TOC) analysis was performed using combustion catalytic oxidation (Shimadzu TOC-L) at 680℃. The visual color change of the LF was also monitored throughout the recirculation cycles [12, 26]. Organic acids, including acetic and lactic acids, were quantified using high-performance liquid chromatography (HPLC) (Hitachi Primaide) with an Aminex HPX-87H column, using 0.1% H_3PO_4 as the mobile phase (1.0 mL/min) at 60℃ and detection at 210 nm. Calibration was performed using standard acetic and lactic acid solutions. The functional groups in the LF were identified using Fourier Transform Infrared (FTIR) spectroscopy (Shimadzu IRPrestige-21), where freeze-dried LF was mixed with KBr (1:100 ratio) and analyzed across a wavelength range of 4000–400 cm^{-1}.

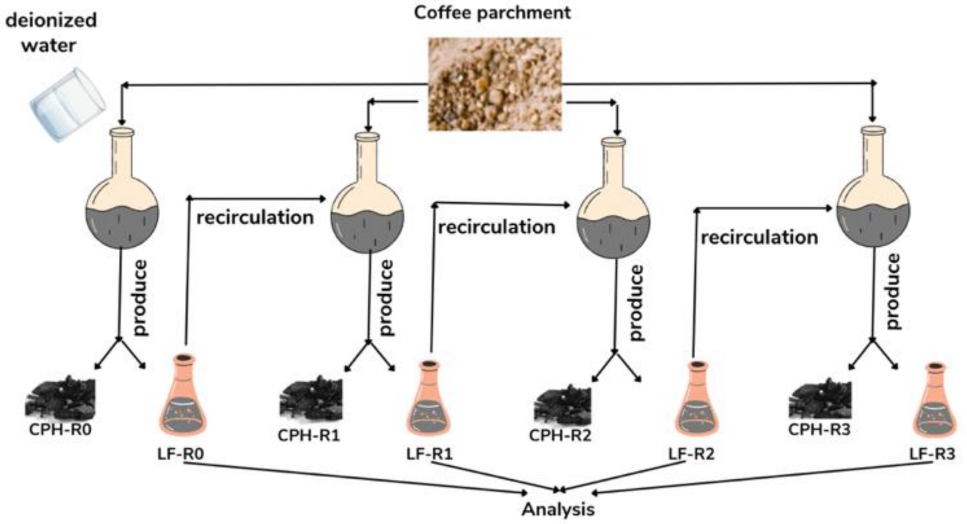

Figure 1. Schematic diagram of LF recirculation in microwave-assisted hydrothermal carbonization of coffee parchment

2.5 Hydrochar characterization

The yield of hydrothermal carbon (hydrochar) at each recirculation stage was determined by measuring the mass of the solid hydrochar after filtration and drying. The measurement was performed three times for each recirculation stage (LF-R0, LF-R1, LF-R2, LF-R3) to ensure consistency. The average mass of hydrochar produced was recorded in grams, and the yield was calculated as the mass of hydrochar obtained relative to the initial amount of CP used in each cycle. This procedure was performed at each stage of recirculation to monitor the effects of repeated LF use on hydrochar yield.

The surface acidity of the hydrochar samples was evaluated by measuring acid site density (sites/g). Total Acid Density (TAD) was determined by ion exchange with 2 M NaCl, followed by titration with 0.01 M NaOH. Strong Acid Density (SAD), attributed to $-SO_3H$ groups, was measured using a modified Boehm titration method with 0.1 M NaOH. Weak Acid Density (WAD) was calculated as the difference between TAD and SAD, as described by Flores et al. [26]. Acid densities, initially expressed in mmol/g, were converted to sites/g using Avogadro's constant (6.022×10^{23} mol^{-1}).

The textural properties of the hydrochar samples were characterized by nitrogen adsorption-desorption isotherms at 77 K using a QuadraSorb SI analyzer (Quantachrome, USA). Specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method, while pore volume and pore diameter were determined using the Barrett–Joyner–Halenda (BJH) model. Before analysis, the samples were degassed at 125℃ under vacuum ($<10^{-2}$ Pa) for 12 hours to remove adsorbed moisture and gases. Special attention was given to mesoporosity, as pores in the 2–50 nm range facilitate the diffusion of larger reactants, such as free fatty acids (FFAs), in esterification reactions.

3. RESULTS AND DISCUSSION

3.1 Liquid fraction characterization: Self-enrichment of functionalizing agents

The recirculation strategy progressively concentrated reactive organics in the liquid fraction (LF), facilitating the in-situ functionalization of hydrochar. Hydrothermal carbonization of coffee parchment (CP) under microwave-assisted conditions consistently produced an LF mass ranging from 227 to 235 g across all recirculation cycles, indicating minimal change in volumetric yield. This observation is consistent with reports suggesting that LF yield in low-temperature hydrothermal carbonization (HTC) stabilizes due to equilibrium between solubilization and condensation reactions in the aqueous phase [12].

3.2 TOC accumulation and visual changes

Analysis of total organic carbon (TOC) in the LF demonstrated a consistent increase in dissolved organic matter with each recirculation cycle. The initial LF (LF-R0) contained approximately 1.245 g L^{-1} TOC, which steadily increased with each subsequent cycle (Figure 2). This trend reflects the continuous generation and retention of water-soluble organics such as volatile fatty acids (VFAs) and sugars. Despite minimal changes in volumetric yield (227–235 g LF across cycles), compositional enrichment rather than volumetric changes enhanced the functionalization potential. The enrichment in organic content, especially VFAs and sugars, remained stable under hydrothermal conditions [12]. The constant volume of LF across recirculation cycles, despite higher TOC, indicates that compositional changes, rather than volume shifts, drive the potential for functionalization.

Moderate TOC enrichment (e.g., LF-R1) correlated with favorable hydrochar properties. However, excessive accumulation of TOC (e.g., in LF-R2 and LF-R3) posed risks such as pore blockage due to non-catalytic carbonaceous residues, which reduced the accessible surface area of hydrochar.

Visually, the LF transitioned from yellowish-brown (LF-R0) to dark brown (LF-R3), as shown in Figure 3, indicating the accumulation of furfural and polymerization products resulting from the dehydration reactions of pentoses and hexoses [27-29]. These soluble organics act as precursors for acid site grafting, highlighting a trade-off between chemical enrichment and textural preservation.

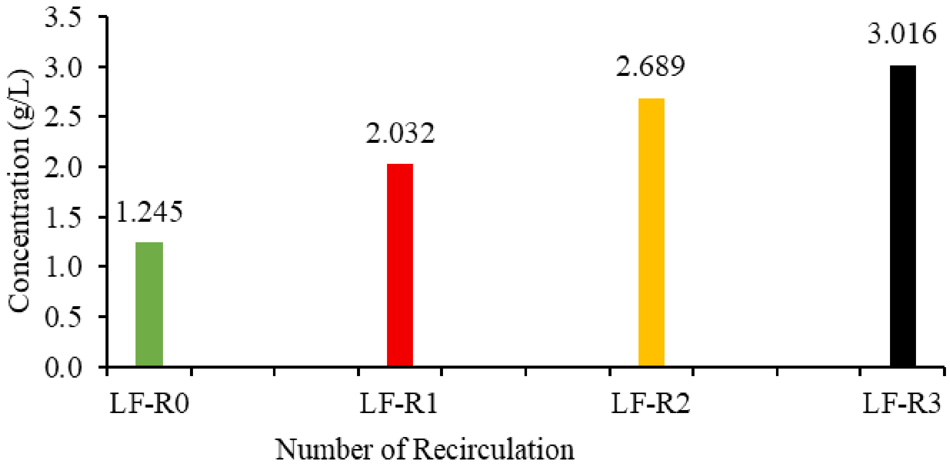

Figure 2. Total organic carbon (TOC) concentration in LF across recirculation cycles

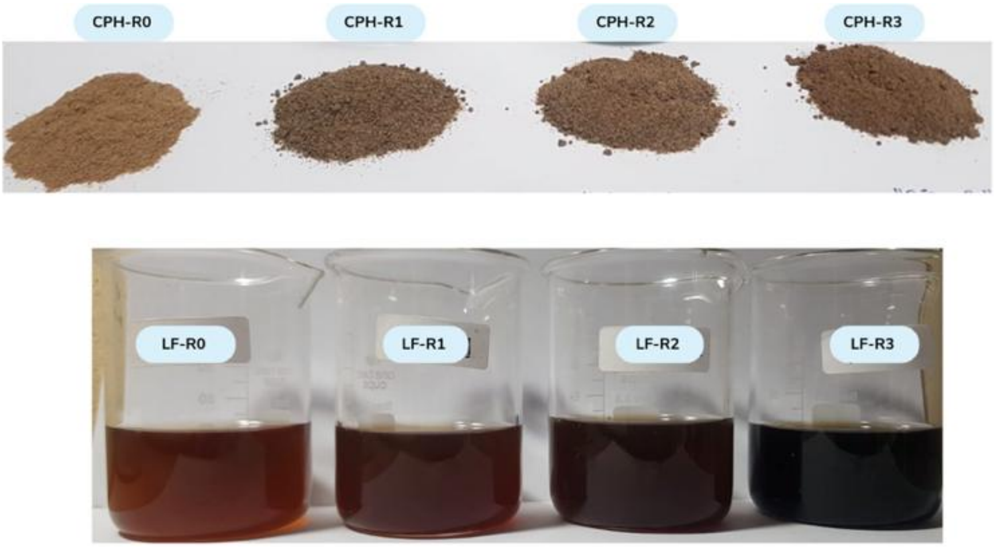

Figure 3. Appearance of coffee parchment hydrochar (CPH) and liquid fraction (LF) at each recirculation stage

3.3 Organic acid accumulation

HPLC analysis revealed a monotonic increase in acetic acid and lactic acid concentrations across LF recirculation cycles (Figure 4). Acetic acid remained the dominant organic acid, consistent with its stability under hydrothermal conditions and its continual production from hemicellulose and lignin degradation [20, 22, 25, 26]. Lactic acid levels also rose, likely due to retro-aldol and dehydration pathways converting sugars into hydroxy acids. Both acids play critical roles in functionalization: acetic acid esterifies hydrochar hydroxyl groups to create acid sites, while lactic acid's bifunctional linkages enhance surface polarity [3, 4].

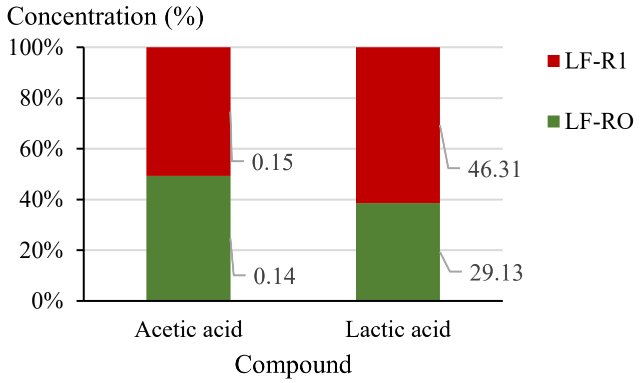

Figure 4. HPLC results for acetic acid and lactic acid concentrations in LF across recirculation cycles

Similar results have been reported for lactic acid-treated activated carbons, which demonstrated enhanced Brønsted acidity without the use of mineral acids [30]. However, excessive concentrations of phenolics and furans in the LF could promote polymerization during thermal treatment, potentially clogging pores [27, 28]. Therefore, process optimization may require controlling LF composition to balance beneficial acid incorporation with minimal structural damage.

3.4 Functional groups analysis using FTIR

Fourier Transform Infrared (FTIR) spectroscopy spectra confirmed the progressive enrichment of oxygenated and nitrogenous functionalities in the LF with recirculation. All LF samples exhibited a broad absorption band around 3400 cm^{-1}, corresponding to hydroxyl (–OH) stretching in alcohols, phenols, and bound water, as shown in Figure 5. Strong absorptions near 1700 cm^{-1} indicated carbonyl (C=O) groups, including aldehydes, ketones, and carboxylic acids—functionalities with known catalytic significance when immobilized on carbon surfaces [3, 4]. With increasing recirculation cycles, peaks in the 1200–1300 cm^{-1} range intensified, indicating the growing presence of C–O stretching in ethers, esters, and alcohols. Aromatic C=C stretching bands near 1595 cm^{-1} became more prominent in LF-R1 to LF-R3, suggesting lignin-derived aromatic compounds that could serve as anchoring points for sulfonic groups during functionalization [20]. Additionally, a distinct peak near 3307 cm^{-1} appeared in recirculated samples, indicating nitrogen-containing functionalities, possibly from protein degradation, which may contribute to Lewis acidity.

In the FTIR analysis, features consistent with the presence of $-SO_3H$ groups were observed across all recirculation stages, particularly the bands around ~1220–1100 cm^{-1} and the bending band near ~620–580 cm^{-1}. However, this interpretation cannot be considered conclusive, as these bands also strongly overlap with vibrations from C–O (carbohydrates/esters/ethers), sulfate/sulfonate esters, and other groups. To confirm the presence of $-SO_3H$ groups, complementary evidence is required. A summary of the evidence from each spectrum is as follows:

- For CPH-R0, a band in the range of 1284–1111 cm^{-1} was observed, which corresponds to C–O and C–O–C vibrations, and could also be consistent with S=O asymmetric vibrations (~1220–1140 cm^{-1}). Additionally, a weak band around ~594 cm^{-1} was detected, which could correlate with S–O bending/sulfonate, but it may also arise from other vibrations.
- In CPH-R1, bands at 1213, 1121, and 1093 cm^{-1} were found, which fall within the range commonly associated with S=O asymmetric (~1220–1170 cm^{-1}) and symmetric (~1070–1030 cm^{-1}) vibrations. However, there was no clear and exclusive S–O bending peak, though a peak at ~489 cm^{-1} was

observed.

- CPH-R2 showed a band at 1301 cm^{-1} and a range from 1078–1062 cm^{-1}, part of the range relevant for sulfonate/sulfonic groups, along with a peak at 607 cm^{-1}, which could be consistent with S–O bending.
- Finally, CPH-R3 showed the reappearance of bands at 1213, 1121, and 1093 cm^{-1}, with additional peaks at 634, 617, and 576 cm^{-1}, supporting the possibility of S–O bending vibrations around ~600–620 cm^{-1}.

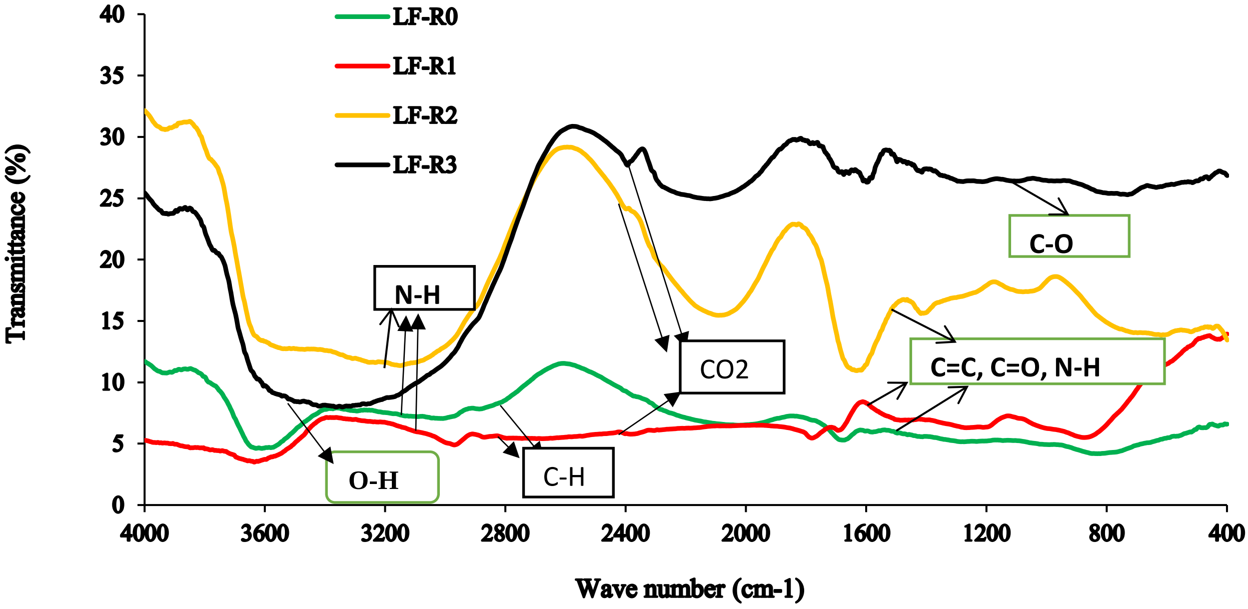

Figure 5. FTIR spectra of the liquid fraction

These FTIR trends support the hypothesis that LF recirculation increases the abundance and diversity of functional groups capable of chemically modifying hydrochar surfaces, generating both Brønsted (─SO_3H/─COOH) and Lewis acid sites. Such multifunctionality is advantageous for biodiesel synthesis from feedstocks containing both FFAs and triglycerides [11, 31, 32].

3.5 Hydrochar characterization

3.5.1 Hydrochar yield

The analysis of hydrochar product masses obtained from four samples (CPH-R0, CPH-R1, CPH-R2, and CPH-R3) with an initial material mass of 30 grams reveals consistent results across the samples. The masses of the products were calculated based on the yield percentages, resulting in the following values: 26.24 grams for CPH-R0, 27.17 grams for CPH-R1, 27.09 grams for CPH-R2, and 26.97 grams for CPH-R3. These values represent the average mass obtained across the three repetitions for each case. The results demonstrate a high degree of uniformity, with product masses varying only within a narrow range of approximately 26.24 to 27.17 grams. This indicates that the hydrothermal carbonization (HTC) process has produced stable yields under the conditions used for these experiments.

The slight variations observed in the product masses could be attributed to factors such as small differences in experimental conditions (e.g., temperature, pressure, reaction time) or slight measurement errors. In general, such variability is typical in experimental setups, even with controlled conditions. The yield percentage, which represents the proportion of the initial biomass converted into the final product, is a crucial parameter for assessing the efficiency of the HTC process. These yields, being above 85%, suggest that the process is relatively efficient, retaining a significant portion of the original biomass. This is particularly important in applications where material retention is critical, such as in biochar production for soil amendment or energy generation.

Although minor fluctuations were observed across the repetitions, the overall stability of the results indicates that the process could be further optimized for even more consistent and potentially higher yields. Optimizing parameters such as feedstock size or better control of reaction conditions could further minimize these slight variations, making the process even more reliable and scalable for industrial applications. The relatively high yields achieved in all cases underscore the potential of HTC as an effective method for producing hydrochar from biomass with minimal loss, thus providing promising opportunities for bioenergy and environmental applications [28].

3.5.2 Surface acidity

The surface acidity, a paramount property for a catalyst, was profoundly affected by LF recirculation. Boehm titration revealed that the initial hydrochar (CPH-R0) had a Total Acid Density (TAD) of 1.73 × 10^{21} sites/g, which was predominantly composed of weak acid sites (WAD, 95.82%). These WAD sites, primarily carboxylic (─COOH) and phenolic (─OH) groups, originate from the partial depolymerization of cellulose and hemicellulose during the initial MA-HTC.

Contrary to what might be intuitively expected, recirculation progressively reduced the overall TAD, which fell to 1.16 × 10^{21} sites/g in CPH-R3. This decrease is attributed to the depletion of WAD via decarboxylation and dehydration reactions, which are promoted under the increasingly acidic environment of the recirculated LF. Such reactions remove labile oxygenated functional groups, a phenomenon consistent with biochar aging studies where aromatic condensation increases at the expense of polar, oxygen-containing groups under thermal and acidic conditions.

In stark contrast, the Strong Acid Density (SAD), associated with resilient acid sites like sulfonic groups ($-SO_3H$), remained remarkably stable across all samples, ranging only from 7.23×10^{19} to 9.64×10^{19} sites/g. Consequently, the ratio of SAD to TAD doubled from 4.18% in CPH-R0 to 8.33% in CPH-R3. This indicates a selective preservation and possible formation of strong Brønsted acid sites, even as the weaker acids were being stripped away. This selective enrichment could be aided by LF-derived aromatic sulfonates or other sulfur-containing compounds that resist degradation under hydrothermal conditions. The presence of sulfur in the original coffee parchment (0.28%, as reported by Setiawan et al. [33]), provides a plausible source for the in-situ formation of $-SO_3H$ groups, as sulfur can be incorporated into the carbon matrix during HTC.

This resulting acid profile—featuring robust, strong acid sites for the esterification of FFAs, coupled with residual weak acids that enhance hydrophilicity and polar reactant adsorption—is highly advantageous for bifunctional catalysis. Such a balance is beneficial for processing real-world, mixed oil feedstocks that contain both FFAs and triglycerides [7, 34, 35].

3.5.3 Textural properties

Textural analysis revealed low BET surface areas (< 1 m^2/g) across all hydrochars, typical for mild-temperature HTC, as shown in Table 1. CPH-R0 exhibited optimal mesoporosity (BET: 0.658 m^2/g; pore diameter: 3.91 nm), facilitating FFA diffusion [3, 4]. In contrast, CPH-R1 showed a reduced BET area (0.263 m^2/g) and an increase in pore diameter (~12.48 nm), suggesting structural expansion or partial collapse during repeated recirculation.

The recirculation process decreased BET surface area (e.g., 0.263 m^2/g for CPH-R1) and expanded pore diameters towards the macropore range (~12.48 nm). This suggests that LF organics may cause partial structural collapse, potentially due to deposition or swelling effects. CPH-R1 also showed an increase in micropore surface area (0.686 m^2/g), which could hinder liquid-phase diffusion.

The increase in micropore surface area in CPH-R1 may restrict liquid-phase esterification due to limited diffusion, although it could benefit gas-phase catalysis. The shift from mesopores to micro/macropores emphasizes the need to preserve mesoporous architecture for optimal biodiesel catalysis [36, 37]. While LF recirculation enriches chemical functionalities, excessive cycles can compromise pore accessibility, reducing the number of active sites available to reactants.

The shift from meso-to-macro pores highlights the need to balance chemical enrichment with structural integrity. Minimal recirculation (≤1 cycle) preserves mesoporosity while enhancing acid site enrichment, optimizing hydrochar for biodiesel catalysis.

Table 1. Surface area, pore volume, and pore size distribution of CPH

Morphology	Method	CP	CPH-R0	CPH-R1
Surface area (m^2/g)	MultiPoint BET	5.083×10^{-1}	6.583×10^{-1}	2.633×10^{-1}
	BJH method cumulative adsorption surface area	2.847×10^{-1}	4.685×10^{-1}	2.026×10^{-1}
	BJH method cumulative desorption surface area	4.064×10^{-1}	5.596×10^{-1}	2.285×10^{-1}
	DH method cumulative adsorption surface area	2.884×10^{-1}	4.766×10^{-1}	2.057×10^{-1}
	DH method cumulative desorption surface area	4.127×10^{-1}	5.744×10^{-1}	2.345×10^{-1}
	t-method external surface area	3.775×10^{-1}	6.583×10^{-1}	-4.223×10^{-1}
	t-method micropore surface area	1.308×10^{-1}	ND	6.856×10^{-1}
	DFT cumulative surface area	2.211×10^{-1}	3.810×10^{-1}	4.596×10^{-1}
Pore volume (mL/g)	BJH method cumulative adsorption pore volume	1.701×10^{-2}	3.983×10^{-2}	1.843×10^{-2}
	BJH method cumulative desorption pore volume	1.716×10^{-2}	3.997×10^{-2}	1.823×10^{-2}
	DH method cumulative adsorption pore volume	1.633×10^{-2}	3.818×10^{-2}	1.768×10^{-2}
	DH method cumulative desorption pore volume	1.649×10^{-2}	3.832×10^{-2}	1.750×10^{-2}
	t-method micropore volume	6.230×10^{-5}	ND	3.495×10^{-4}
	HK method micropore volume	2.116×10^{-4}	2.423×10^{-4}	ND
	SF method micropore volume	1.245×10^{-4}	1.439×10^{-4}	ND
	DFT method cumulative pore volume	1.139×10^{-3}	1.107×10^{-3}	9.237×10^{-4}
Pore size (nm)	Average pore Diameter	1.345×10^{2}	2.427×10^{2}	2.784×10^{2}
	BJH method adsorption pore Diameter (Mode Dv(d))	5.660	3.915×10^{2}	1.248×10^{1}
	BJH method desorption pore Diameter (Mode Dv(d))	4.291	4.292	1.719×10^{1}
	DH method adsorption pore Diameter (Mode Dv(d))	5.660	3.915	1.248×10^{1}
	DH method desorption pore Diameter (Mode Dv(d))	4.291	4.292	1.719×10^{1}
	HK method pore Diameter (Mode)	3.675×10^{-1}	3.675×10^{-1}	1.697
	SF method pore Diameter (Mode)	4.523×10^{-1}	4.523×10^{-1}	3.027
	DFT pore Diameter (Mode)	1.068×10^{1}	5.199×10^{1}	1.688

3.6 Integration with the hypothesis and broader implications

The central hypothesis of this study—that LF recirculation enriches the reaction medium with reactive organic species capable of introducing and stabilizing Brønsted and Lewis acid sites on hydrochar—was strongly supported by the results. Combined FTIR, TOC, HPLC, and acid density analyses demonstrate that recirculated LF enhances the chemical complexity of the aqueous phase, leading to measurable increases in hydrochar surface acidity.

From a broader perspective, this approach addresses multiple sustainability goals. It reduces reliance on hazardous sulfonating agents, valorizes what is traditionally considered waste (the LF), and integrates catalyst synthesis directly into the HTC process without additional chemical steps. Additionally, using coffee parchment as feedstock contributes to waste minimization in the coffee industry, aligning with circular economy principles.

However, trade-offs between chemical enrichment and structural preservation, observed in the textural analysis, highlight the need for process optimization. Excessive recirculation could compromise mesoporosity, reducing catalytic accessibility despite higher acid density. Future process designs could incorporate partial LF recirculation or selective removal of heavy aromatic compounds to balance these effects.

In comparison, conventional sulfonation processes still offer significant advantages in achieving very high SAD levels, but at a considerable environmental and safety cost [21]. The LF recirculation method offers a greener alternative with competitive catalytic potential, especially in decentralized or small-scale biodiesel production settings where chemical handling and waste treatment infrastructure are limited.

These findings open the possibility of applying LF recirculation to other biomass feedstocks with high soluble organic yields, such as sugarcane bagasse, rice husk, or fruit peels. The mechanistic insights gained, particularly the role of VFAs and phenolics in functional group formation, can inform broader strategies for biomass-derived catalyst development.

4. CONCLUSIONS

This study demonstrated that the recirculation of the liquid fraction (LF) obtained from microwave-assisted hydrothermal carbonization (MA-HTC) of coffee parchment effectively enhanced the in-situ functionalization of hydrochar, transforming it into a promising heterogeneous acid catalyst for biodiesel synthesis. FTIR, TOC, and HPLC analyses confirmed that the LF progressively enriched with oxygenated and nitrogenous compounds, particularly acetic and lactic acids, contributed to the incorporation of both Brønsted and Lewis acid sites onto the hydrochar surface. Acid density measurements revealed a doubling of strong acid sites compared to the non-recirculated sample, while still maintaining significant levels of weak acids that enhance the adsorption of polar reactants.

Textural analysis indicated that a single recirculation cycle preserved a favorable mesoporous structure, optimal for the esterification of bulky molecules such as free fatty acids (FFAs). However, excessive recirculation led to pore enlargement and a reduction in surface area. This research contributes to the growing body of knowledge by integrating LF valorization into catalyst synthesis, minimizing the reliance on hazardous sulfonating agents, and aligning catalyst production with circular economy principles.

Future research should focus on optimizing recirculation parameters, selectively removing non-functional heavy organics from LF, and evaluating the catalytic performance in actual biodiesel production systems using waste oils. The insights gained in this study can also be applied to other biomass feedstocks, advancing the development of greener and more sustainable catalytic materials.

ACKNOWLEDGMENT

This work was supported by the Directorate of Research and Community Services (DRPM), Ministry of Research and Technology/ National Agency for Research and Innovation, Republic of Indonesia for their sponsorship under the doctoral dissertation research scheme with contract number: 093/E5/PG.02.00.PL/2024, 11th June 2024 and 57/UN5.4.10.S/PPM/KP-DRTPM/2024, 12th June 2024.

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