



Valorization of Coffee Husk Waste into a Sulfonated Activated Carbon Catalyst for Enhanced Glycerol Acetylation Toward Triacetin Production

Heny Dewajani*, Lintang Alivia Anggerta, Ernia Novika Dewi, Ulfiana Ihda Afifa, Luchis Rubianto, Listiyana Candra Dewi, Risky Elinaningtyas

Department of Chemical Engineering, Politeknik Negeri Malang, Jl. Soekarno Hatta No. 9, Malang 65141, Indonesia

ABSTRACT

Coffee husk, a lignocellulosic by-product of the coffee processing industry, remains largely underutilized despite its substantial carbon content and potential as a renewable catalyst precursor. This study investigated the combined effects of carbonization temperature (250–350°C) and H₂SO₄ concentration (4–10 N) on sulfonated activated carbon prepared from coffee husk and evaluated its application in glycerol acetylation. FTIR, BET, and XRD analyses of the best-performing catalyst supported successful sulfonation, a mesoporous texture, and an amorphous turbostratic carbon structure, while GC-MS confirmed the formation of monoacetin and triacetin. Two-way ANOVA showed that carbonization temperature, H₂SO₄ concentration, and their interaction significantly affected glycerol conversion (all $p < 0.0001$). Within the investigated range, the best-performing condition was 300°C carbonization and 10 N H₂SO₄, giving a mean glycerol conversion of $56.49 \pm 0.00\%$ and a triacetin selectivity of 14.38%. Reusability testing showed a marked decline in conversion from 56.49% in cycle 1 to 22.43% in cycle 2 and 12.71% in cycle 3, indicating that stabilization of sulfonic acid sites remains necessary. These findings establish coffee husk waste as a promising precursor for sulfonated activated carbon catalysts for sustainable glycerol valorization.

Keywords: activated carbon, coffee husk, glycerol acetylation, sulfonated carbon, triacetin.

1. INTRODUCTION

Indonesia is among the world's largest coffee-producing nations, generating increasing volumes of processing residues as plantation output expands [1,2]. Among the processing residues generated, coffee husk accounts for 40–45% of the total cherry weight, and most is incinerated or landfilled without recovering its intrinsic material value [1,2]. As a lignocellulosic biomass rich in cellulose, hemicellulose, and aromatic lignin, coffee husk is a promising precursor for the thermochemical synthesis of activated carbon, enabling valorization of this abundant agricultural waste stream within a circular bioeconomy framework [3–6]. Chemical activation of coffee husk with phosphoric acid (H₃PO₄) or potassium hydroxide (KOH) yields porous carbon materials with well-developed surface area

and tunable surface functional groups, suitable for both adsorption and catalytic applications [3–6]. A crucial step in heterogeneous acid catalysis is sulfonation, in which concentrated H₂SO₄ introduces covalent –SO₃H groups onto the carbon surface through electrophilic aromatic substitution (EAS). Sulfonated carbon-based solid acid catalysts have been widely reported for esterification and transesterification-related reactions, including biodiesel production and biomass-derived fuel upgrading [7–10]. The resulting Brønsted acid sites are proton-donating –SO₃H groups anchored to the carbon framework and act as primary active sites responsible for acid-catalyzed reactions, including esterification and acetylation [7–10].

The application of sulfonated activated carbon catalysts to glycerol acetylation is

*Corresponding author:

E-mail: heny.dewajani@polinema.ac.id (Heny Dewajani)

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industrially relevant because glycerol is produced as a by-product (10 wt%) of biodiesel transesterification and commands low market value [11,12]. Its sequential acetylation with acetic acid via Fischer esterification yields three value-added acetins: monoacetin (1- or 2-acetyl glycerol), diacetin, and triacetin [11]. Triacetin is the most commercially valuable acetin, used as a fuel additive, food-grade plasticizer, and pharmaceutical excipient. To achieve high triacetin selectivity, a catalyst with sufficient Brønsted acid-site density and optimized reaction conditions are required to favor esterification equilibrium [11,13,14].

Although biomass-derived sulfonated carbon catalysts have been investigated for glycerol acetylation [7,9,12–14], the effects of precursor selection and mild carbonization conditions on catalyst preparation and performance remain insufficiently characterized. Nda-Umar et al. [7] studied biomass carbons carbonized at 400 and 800°C, whereas most coffee-derived activated carbons are prepared at substantially higher temperatures to maximize porosity [3–5]. Investigating the temperature range of 250–350°C is crucial because it encompasses the decomposition of hemicellulose and the initial stages of cellulose dehydration and lignin aromatization [4,5]. This range also preserves a greater number of oxygen-containing edge groups compared to materials that have undergone strong carbonization [7,9]. These groups can promote subsequent $-\text{SO}_3\text{H}$ anchoring, though the resulting carbon may exhibit lower surface area and hydrothermal stability [7,9]. Therefore, the sub-400°C temperature range represents a careful balance between maintaining chemically reactive surface sites and creating a more condensed, porous, and stable carbon framework [4,5,7,9]. To date, no previous study has systematically investigated coffee husk as a dedicated precursor for glycerol acetylation or quantified the combined effects of carbonization temperature and H_2SO_4 concentration within this mild carbonization process.

To address these gaps, this study synthesized sulfonated activated carbon catalysts from coffee husk waste through furnace carbonization (250, 300, and 350°C), H_3PO_4 chemical activation, and H_2SO_4 sulfonation (4, 6, 8, and 10 N). The objectives were: (1) to characterize the physicochemical properties of the prepared catalysts by FTIR, BET, and XRD and identify acetylation products by GC-MS; (2) to quantify the main and interaction effects of the two preparation factors on glycerol conversion; and (3) to evaluate the reusability of the best-performing catalyst over successive glycerol acetylation cycles.

2. RESEARCH METHODS

2.1. Materials

Coffee husks were obtained from PTPN XII Bangelan (East Java, Indonesia). The reagents were phosphoric acid (85%, Smart Lab), glycerol (99.5%, Smart Lab), acetic acid (99.8%, Smart Lab), sulfuric acid (97%, Merck), and sodium hydroxide (>99%, Merck), along with distilled water for washing and solution preparation. All reagents were used as received without further purification. The 85% analytical-grade H_3PO_4 was deliberately selected as a standard concentrated reagent for chemical activation and was diluted to the required 2 N concentration. In this study, H_3PO_4 served only as a pore-development agent, while catalytic activity and triacetin selectivity were governed by the subsequently grafted $-\text{SO}_3\text{H}$ groups. FTIR and XRD results further indicated that phosphate-derived species were removed during sulfonation. Therefore, using >98% H_3PO_4 was not expected to significantly improve the process performance or triacetin selectivity.

2.2. Catalyst Preparation

The catalyst preparation comprised five sequential stages: (1) proximate characterization of raw coffee husk, (2) drying pretreatment, (3) carbonization, (4) H_3PO_4 activation, and (5) H_2SO_4 sulfonation. Raw coffee husk, with an initial moisture content of 9.20% determined by proximate

analysis, was oven-dried at 105°C for 1 h before carbonization. As the final moisture content was not determined, this step was defined as a controlled drying pretreatment rather than drying to equilibrium moisture content. Dried material in a 500 mL porcelain crucible was carbonized in a muffle furnace at 250, 300, or 350°C for 1 h, ground with a mortar, and sieved to 100 mesh. The 100-mesh fraction was impregnated with 2 N H₃PO₄ for 24 h, filtered through Whatman No. 42 paper under vacuum, and washed with distilled water to neutral pH. For sulfonation, 10 g of activated carbon was combined with 150 mL of H₂SO₄ at 4, 6, 8, or 10 N, stirred continuously at 115°C for 5 h, filtered, washed with distilled water to neutral pH, dried at 105°C for 1 h, and cooled in a desiccator for 15 min [15].

2.3. Glycerol Acetylation

Glycerol was reacted with acetic acid at a glycerol-to-acetic-acid molar ratio of 1:8 in a round-bottom flask equipped with a reflux condenser. Catalyst loading was 5 wt% relative to the initial glycerol mass, and the reaction was conducted at 115°C for 120 min under continuous stirring. Residual acetic acid was quantified by back-titration with standardized 0.1 N NaOH to a phenolphthalein endpoint. The reported conversion value was calculated from the decrease in titratable acetic acid relative to its initial amount [16,17] and was used as an indirect measure of glycerol acetylation under the stated stoichiometric assumptions. All experimental conditions were tested in triplicate (n = 3).

2.4. Catalyst Characterization

Proximate analysis (moisture, ash, volatile matter, fixed carbon) was performed gravimetrically on raw coffee husk. The best-performing catalyst within the investigated range was characterized by FTIR spectroscopy (400–4500 cm⁻¹), BET surface-area, pore-diameter, and pore-volume analysis, and XRD using Cu-K α radiation (2 θ = 5–100°).

2.5. Product Analysis by GC-MS

The acetylation product mixture obtained using the best-performing catalyst preparation condition (300°C carbonization and 10 N H₂SO₄ sulfonation) was analyzed by GC-MS to identify the acetin products and determine their relative chromatographic peak areas.

2.6. Catalyst Reusability Test

The best-performing catalyst prepared at 300°C and sulfonated with 10 N H₂SO₄ was evaluated over three consecutive glycerol acetylation cycles under the same reaction conditions described in Section 2.3. After each cycle, the catalyst was recovered by filtration, washed with distilled water, dried at 105°C, and reused in the subsequent cycle without additional regeneration. Glycerol conversion was determined after each cycle.

2.7. Statistical Analysis

A fully crossed 3 × 4 factorial design was employed to evaluate the effects of carbonization temperature (250, 300, and 350°C) and H₂SO₄ concentration (4, 6, 8, and 10 N) on glycerol conversion. Each treatment combination was performed in triplicate (n = 3). The main effects and their interaction were evaluated using a two-way factorial ANOVA model, expressed in Equation (1). This formulation is appropriate for hypothesis testing across the discrete factor levels used in the experimental design, rather than for continuous response-surface optimization.

$$Y_{ijk} = \mu + \alpha_i + \beta_j + (\alpha\beta)_{ij} + \varepsilon_{ijk} \dots\dots\dots (1)$$

In Equation (1), Y_{ijk} is the observed glycerol conversion, μ is the overall mean, α_i is the effect of the i th carbonization-temperature level, β_j is the effect of the j th H₂SO₄-concentration level, $(\alpha\beta)_{ij}$ is the interaction between the two factors, and ε_{ijk} is the residual error [18]. Statistical significance was evaluated at a 95% confidence level (α = 0.05). When significant differences were detected, a post hoc multiple-comparison test was applied to compare treatment means.

Data are reported as mean $\pm$ standard deviation. Because the design did not include the center or axial points required for quadratic response-surface modeling, statistical inference was restricted to the tested factor levels. The analysis was not used to estimate a stationary point or extrapolate beyond 250–350°C and 4–10 N H₂SO₄.

3. RESULTS AND DISCUSSION

3.1. Proximate Characterization of Coffee Husk Waste

Proximate analysis of the raw coffee husk yielded the values shown in Table 1. The moisture content of 9.20% is within the acceptable range for lignocellulosic biomass feedstocks. Pre-drying before carbonization is crucial because excess moisture consumes part of the supplied thermal energy for water evaporation, thereby reducing the energy available for hemicellulose dehydration and depolymerization, which begin at approximately 200°C. The diversion of thermal energy reduces both char yield and the structural quality of the resulting carbon precursor [1,4].

The low ash content (1.18%) is favorable because elevated inorganic residues occlude pore channels and reduce accessible surface area in the final activated carbon [3,4]. The high volatile matter (76.24%) reflects the substantial fraction of decomposable hemicellulose, cellulose, and lignin that is released as combustible gases and vapors during carbonization, leaving behind the fixed carbon skeleton. The fixed carbon content (13.56%) is consistent with values reported for other coffee-derived lignocellulosic biomasses and indicates an adequate carbonaceous fraction for char formation [1,4,5]. Although lower than typical values for coconut shell or rice husk carbons (20–30%), which partly explains the modest BET surface areas obtained under mild carbonization, the high aromatic lignin content of coffee husk provides anchoring sites conducive to covalent –SO₃H incorporation [9,19].

Table 1. Proximate characteristics of coffee husk waste.

Parameter	Value (%)
Moisture content	9.20
Ash content	1.18
Volatile matter	76.24
Fixed carbon	13.56

3.2. Effect of Temperature and Concentration on Carbonization and H₂SO₄ on Glycerol Conversion

Figure 1 and Table 2 show that both carbonization temperature and H₂SO₄ concentration significantly influence glycerol conversion (ANOVA: $F_{\text{temp}} = 693.93$; $F_{\text{conc}} = 866.41$; $F_{\text{interaction}} = 31.71$; all $p < 0.0001$). The highest mean conversion observed in the experimental matrix, $56.49 \pm 0.00\%$, was obtained with the catalyst prepared at 300°C and 10 N H₂SO₄ (significance group “a,” Table 3). This was the best-performing condition within the experimental range, but it cannot be regarded as a global optimum. The upper concentration boundary was set at 10 N, and the experiment did not include concentrations above this limit or use a quadratic response-surface design.

Across the investigated temperature range, catalysts carbonized at 300°C generally yielded higher glycerol conversions than their counterparts prepared at 250 and 350°C. This response may reflect differences in the extent of carbon-framework condensation and the retention of oxygen-containing surface groups. At 250°C, incomplete decomposition and aromatization may have produced a relatively less-condensed matrix with limited structural stability and a greater proportion of hydrolytically labile aliphatic C–O functionalities. Carbonization at 300°C may have promoted dehydration and partial aromatization while retaining edge-plane defects and residual –OH and –COOH groups. These surface features have been reported to facilitate electrophilic aromatic substitution and the covalent anchoring of –SO₃H groups, and may also contribute to surface Brønsted acidity [9,20,21]. At 350°C,

increased condensation and decarboxylation may have reduced the abundance of oxygen-containing anchoring sites and, consequently, the extent or accessibility of sulfonic-acid functionalities. The proposed structural differences align with the lower glycerol conversion seen in the catalyst prepared at 350°C relative to that prepared at 300°C. However, to validate this interpretation, a direct quantification of surface functional groups and acid-site density is necessary [7,9].

Glycerol conversion increased with the concentration of H_2SO_4 at all carbonization temperatures (Figure 1), consistent with enhanced sulfonating activity and a greater density of accessible Brønsted-acid sites [7,9,15,20]. However, the monotonic response up to 10 N does not establish the optimum acid concentration [15,18]. A concentration above 10 N might initially increase $-\text{SO}_3\text{H}$ loading, but it could also intensify oxidation and carbon loss, collapse or block accessible pores, increase residual sulfate and washing demand, raise solution viscosity and handling difficulty, accelerate acid-site leaching, and create greater corrosion, safety, and waste-neutralization burdens [7,9,21,22]. The statistically significant interaction term ($F = 31.71$, $p < 0.0001$) shows that the benefit of increasing acid concentration depends on the carbonization temperature.

The results obtained in the present sub-400°C range should be compared cautiously with those reported for catalysts carbonized at $\geq 400^\circ\text{C}$ because differences in feedstock characteristics, catalyst-preparation protocols, acid-site properties, and experimental conditions may also influence catalytic performance. Nda-Umar et al. [7] evaluated palm-kernel-shell-derived catalysts carbonized at 400 and 800°C at 120°C using an acetic acid: glycerol ratio of 6:1. The 800°C template-derived catalyst achieved more than 97% conversion and 58.9% triacetin selectivity after 3 h. Higher carbonization temperatures can enhance aromatization, porosity, and C–S bond stability [7,9,20,22]. However, the

abundance of oxygen-containing groups that promote sulfonation may also decrease [7,9,22]. In the present sub-400°C range, glycerol conversion increased from 250 to 300°C and then decreased at 350°C. This trend is consistent with the proposed reduction in reactive anchoring sites at 350°C, although direct measurements of acid-site density are needed to confirm this interpretation [7,9,20]. Accordingly, the present results identify 300°C as the best-tested carbonization temperature within the investigated range.

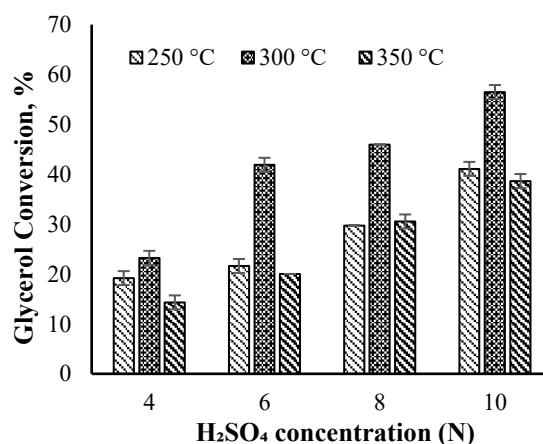


Figure 1. Effect of carbonization temperature (250, 300, and 350°C) and H_2SO_4 concentration (4, 6, 8, and 10 N) on mean glycerol conversion (%) in the glycerol acetylation reaction with acetic acid.

3.3. Statistical Analysis of Glycerol Conversion

Table 2 confirms that carbonization temperature, H_2SO_4 concentration, and their interaction significantly affected glycerol conversion (all $p < 0.0001$). The interaction term is particularly important because it demonstrates that the concentration effect cannot be interpreted independently of carbonization temperature. The two-way factorial ANOVA is appropriate for comparing the replicated treatment combinations and testing their interaction. The grand mean glycerol conversion across the 12 treatment combinations was 31.90%, corresponding to μ in Equation (1).

Table 2. ANOVA for the effects of carbonization temperature and H₂SO₄ concentration on glycerol conversion.

Source of Variation	df	F-value	p-value
Carbonization temperature	2	693.93	< 0.0001
H ₂ SO ₄ concentration	3	866.41	< 0.0001
Temp × Conc.	6	31.71	< 0.0001
Error	24	—	—

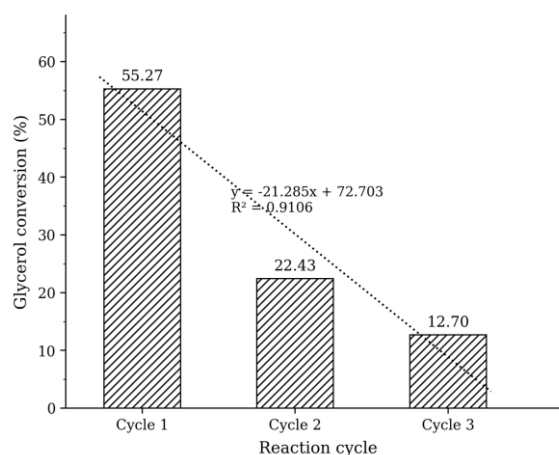
Post hoc multiple-comparison analysis (Table 3) revealed a clear performance hierarchy among the 12 catalyst preparation conditions. The catalyst prepared at 300°C with 10 N H₂SO₄ was the highest significance group (group "a"), while the condition of 350°C with 4 N H₂SO₄ yielded the lowest conversion ($14.33 \pm 1.40\%$, group "h"). Catalysts prepared at 300°C consistently outperformed those prepared at the same H₂SO₄ concentrations, particularly at high sulfonation intensity. This confirms that a moderate carbonization temperature, combined with high sulfonation, provides the most favorable balance of carbon structure development and acid functionality.

Table 3. Post hoc multiple-comparison results for glycerol conversion under different catalyst preparation conditions (mean $\pm$ SD, n = 3).

Temp. (°C)	H ₂ SO ₄ (N)	Conversion (mean $\pm$ SD, %)	Group
250	4	19.19 ± 1.40	gh
250	6	21.63 ± 1.40	fg
250	8	29.73 ± 0.00	de
250	10	41.09 ± 1.40	bc
300	4	23.25 ± 1.40	f
300	6	41.90 ± 0.00	bc
300	8	45.95 ± 1.40	b
300	10	56.49 ± 0.00	a
350	4	14.33 ± 1.40	h
350	6	20.01 ± 0.00	gh
350	8	30.55 ± 1.40	d
350	10	38.65 ± 1.40	c

3.4. Catalyst Reusability

The best-performing catalyst within the investigated range (300°C, 10 N H₂SO₄) was tested over three successive glycerol acetylation cycles. The glycerol conversion rate declined sharply from 56.49% (cycle 1) to 22.43% (cycle 2) and further to 12.71% (cycle 3) as shown in Figure 2. This rapid deactivation is common for sulfonated carbon catalysts when used under acidic liquid-phase conditions at elevated temperatures.

**Figure 2.** Reusability of the sulfonated activated carbon catalyst (best-tested condition: 300°C carbonization, 10 N H₂SO₄) over three successive glycerol acetylation cycles.

The dotted line in Figure 2 represents the linear regression fit ($y = -21.285x + 72.703$, $R^2 = 0.9106$), indicating a consistent decrease in glycerol conversion due to $-\text{SO}_3\text{H}$ leaching and pore blockage by adsorbed by-products.

Two concurrent deactivation mechanisms are proposed. The first proposed mechanism is the hydrolytic cleavage of weakly bound aryl-sulfonic acid groups, resulting in the release of sulfuric acid: $-\text{Ar}-\text{SO}_3\text{H} + \text{H}_2\text{O} \rightarrow -\text{Ar}-\text{H} + \text{H}_2\text{SO}_4$. This hydrolysis process accelerates in the acidic aqueous environment generated by acetic acid and the water by-product of acetylation at 115°C. This process is further exacerbated when the carbon matrix is insufficiently graphitized to support strong covalent C-S bonds, which

occur during carbonization below 400°C [7,9,22–24]. The second mechanism involves progressive blockage of active pore channels due to deposition of high-boiling acetylated glycerol by-products and oligomeric species, reducing reactant accessibility to the remaining $-\text{SO}_3\text{H}$ sites [7,8]. Proposed strategies to improve recyclability include mild resulfonation after each cycle, solvent washing to remove adsorbed products, sulfonating more graphitized precursors (carbonized at 500°C or higher), and introducing silica or metal oxide supports to stabilize the sulfonic acid framework [9,22,25–28].

3.5. Comparison with Published Catalysts

Table 4 compares glycerol conversion obtained with the coffee husk-derived catalyst and selected heterogeneous catalysts reported in the literature. The coffee husk catalyst achieved 56.49% conversion, whereas the published systems yielded 85–>97%.

Table 4. Comparison of glycerol conversion over coffee husk-derived and published catalyst systems.

Catalyst	Temp. (°C)	AcOH:Gly	Time (h)	Conversion (%)	Ref.
Mixed biomass-derived sulfonated carbon	120	6:1	3	>97	[7]
Sulfonated carbon	120	6:1	3	90–95	[14]
Graphene oxide	110	6:1	3	85–90	[12]
MgO–KOH	120	6:1	3	88–92	[14]
Sulfonated activated carbon from coffee husk	115	8:1	2	56.49	This work

These values should not be interpreted as a direct ranking of intrinsic catalytic performance because the studies differed in catalyst composition and preparation, reaction temperature, acetic acid-to-glycerol

molar ratio, and reaction time. However, the comparison indicates that the current renewable catalyst needs further enhancement of accessible, stable acid sites and optimization of reaction conditions to achieve conversion levels similar to those reported for established catalyst systems.

3.6. FTIR Analysis

Figure 3 presents the FTIR spectra of the activated carbon before sulfonation (KA 300 °C, Figure 3a) and after H_2SO_4 sulfonation (S 300 C, Figure 3b), while Table 5 summarizes the corresponding peak assignments. The spectra were recorded on a Shimadzu IRSpirit-T in ATR mode (4 cm^{-1} resolution, 10 scans). In both spectra, a broad absorption band centered near 3400 cm^{-1} is attributed to O–H stretching vibrations from surface hydroxyl groups and adsorbed moisture [7,9]. The aromatic C=C skeletal stretching band at 1575.96 cm^{-1} (panel a) and 1584.52 cm^{-1} (panel b) confirms formation of a conjugated carbonaceous framework during carbonization. Critically, the retention and near-identical position of this aromatic C=C band in both spectra confirm that sulfonation preserved the carbon framework, a structural prerequisite for stable covalent C– SO_3H bond formation via electrophilic aromatic substitution [7,9]. An additional band at 1149.53 cm^{-1} present in panel (a) but absent in panel (b) is attributed to C–O–C stretching and/or P–O vibrations from residual phosphate ester linkages introduced during H_3PO_4 activation, consistent with the XRD evidence of a low-angle phosphate-related spacing in KA 300°C that disappears upon H_2SO_4 treatment [3,4,9,21].

Following H_2SO_4 sulfonation (Figure 3b), several absorption bands appeared that were absent from the KA 300°C spectrum, indicating changes in surface functionality consistent with sulfonation. First, the band at 1166.64 cm^{-1} is consistent with asymmetric S=O stretching associated with $-\text{SO}_3\text{H}$ groups and falls within the reported range of 1160–1200 cm^{-1} for sulfonated carbon catalysts [7,9,20]. Second, the weaker band at 1042.56 cm^{-1} is consistent with symmetric

S=O stretching associated with $-\text{SO}_3\text{H}$ groups and, together with the band at 1166.64 cm^{-1} , supports the proposed sulfonic acid functionalization [7,9]. Third, the band at 1423.36 cm^{-1} may be associated with O–H in-plane bending of sulfonic acid and carboxyl groups, whereas the band at 1698.62 cm^{-1} is consistent with C=O stretching of $-\text{COOH}$ groups that may have formed through oxidation of the carbon surface during H_2SO_4 treatment [7,9]. The disappearance of the 1149.53 cm^{-1} band and the appearance of the S=O-related bands are consistent with the removal or transformation of H_3PO_4 -derived surface species and the introduction of sulfonic acid functionalities [9,20,21]. The increase in glycerol conversion with H_2SO_4 concentration suggests that acid functionalities are more accessible. However, to confirm this relationship, direct quantification of $-\text{SO}_3\text{H}$ -site density is necessary [9,20].

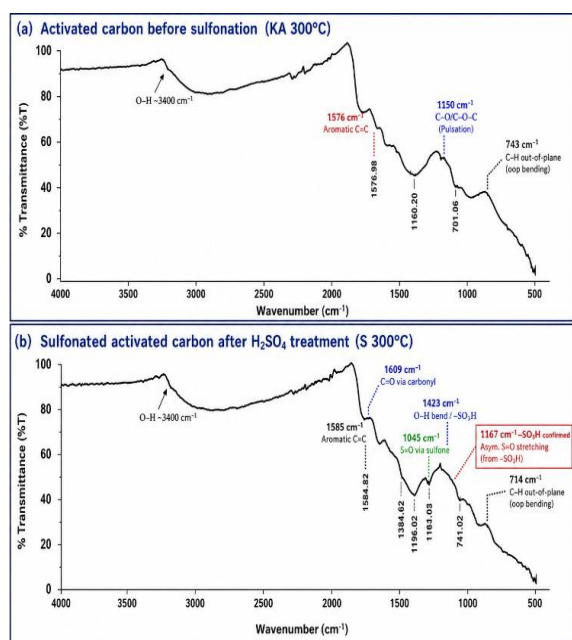


Figure 3. FTIR spectra of coffee husk-derived carbon prepared at 300°C : (a) activated carbon before sulfonation (KA 300°C) and (b) sulfonated activated carbon after H_2SO_4 treatment (S 300°C).

Table 5. FTIR peak assignments of activated carbon before (KA 300°C) and after (S 300°C) H_2SO_4 sulfonation.

Wavenumber (cm^{-1})	Sample	%T	Peak assignment
3400 (broad band)	KA 300°C	~90	O–H stretching (surface –OH and adsorbed H_2O)
1575.96	KA 300°C	56.80	Aromatic C=C skeletal stretching
1149.53	KA 300°C	51.09	C–O–C / P–O stretching (H_3PO_4 -derived phosphate ester)
743.06	KA 300°C	47.58	C–H out-of-plane bending
3400 (broad band)	S 300°C	~90	O–H stretching (surface –OH and adsorbed H_2O)
1698.62	S 300°C	74.30	C=O stretching ($-\text{COOH}$, H_2SO_4 surface oxidation)
1584.52	S 300°C	61.10	Aromatic C=C skeletal stretching (framework preserved)
1423.36	S 300°C	67.50	O–H in-plane bending ($-\text{SO}_3\text{H}$ and $-\text{COOH}$ groups)
1166.64	S 300°C	48.59	Asymmetric S=O stretching ($-\text{SO}_3\text{H}$, new after sulfonation)
1042.56	S 300°C	52.72	Symmetric S=O stretching ($-\text{SO}_3\text{H}$)
744.48	S 300°C	47.22	C–H out-of-plane bending

3.7. BET Analysis

BET analysis (Table 6) showed that both samples were mesoporous, with average pore diameters of 20.47 nm before and 20.29 nm after sulfonation, within the IUPAC mesopore range of $2\text{--}50\text{ nm}$ [3,5]. Thus, the pore diameter did not increase. It decreased slightly by 0.18 nm (approximately 0.9%), a minor change relative to the pore size. The retained mesoporous character favors diffusion of glycerol and acetic acid to internal acid sites under liquid-phase conditions [3,5,16].

Following H₂SO₄ treatment, the BET surface area increased from 0.0677 to 0.1491 m²/g and pore volume from 0.00047 to 0.00102 cm³/g, consistent with partial acid cleaning or etching that opened previously inaccessible voids. In contrast, the nearly unchanged mean pore diameter indicates that 10 N H₂SO₄ mainly altered pore accessibility and surface chemistry rather than widening the existing mesopore network. Sulfonic groups grafted on pore walls can also partly offset acid-induced widening by occupying internal surface space.

The absolute BET surface area values (0.07–0.15 m²/g) are markedly lower than those of commercial activated carbons (500–1500 m²/g) and of coffee husk-derived carbons activated at higher temperatures (200–450 m²/g at 600–900°C) [19,29]. This difference arises from the deliberate choice of mild carbonization temperatures (250–350°C) to preserve reactive oxygen-containing surface functionalities over pore development, a rational trade-off in this system, since Brønsted acid site density (mol –SO₃H g^{–1}) rather than total BET surface area is the primary determinant of catalytic activity in liquid-phase acid-catalyzed acetylation [7,9,30]. The consistent increase in glycerol conversion with H₂SO₄ concentration, despite modest changes in textural properties, confirms this interpretation.

Table 6. BET textural characteristics of activated carbon before and after H₂SO₄ sulfonation.

Parameter	Before Sulfonation	After Sulfonation
Avg. pore diameter (nm)	20.47	20.29
Surface area (m ² /g)	0.0677	0.1491
Pore volume (cm ³ /g)	0.00047	0.00102

3.8. XRD Analysis

Figure 4 shows the XRD patterns of activated carbon before sulfonation (KA 300 °C) and after H₂SO₄ sulfonation (S 300 °C), and Table 7 reports the structural parameters

derived from Scherrer analysis. Both samples exhibit broad diffraction features without sharp graphitic peaks, indicating an amorphous turbostratic carbon structure typical of lignocellulosic biomass carbonized at mild temperatures [4,5]. After sulfonation, the main carbon (002) reflection shifted slightly from 2θ = 24.06° (d = 3.696 Å) to 24.30° (d = 3.660 Å), accompanied by an increase in full width at half maximum (FWHM) and a decrease in crystallite size from 13.1 to 11.8 Å. These changes suggest partial acid etching and increased structural disorder caused by H₂SO₄ treatment.

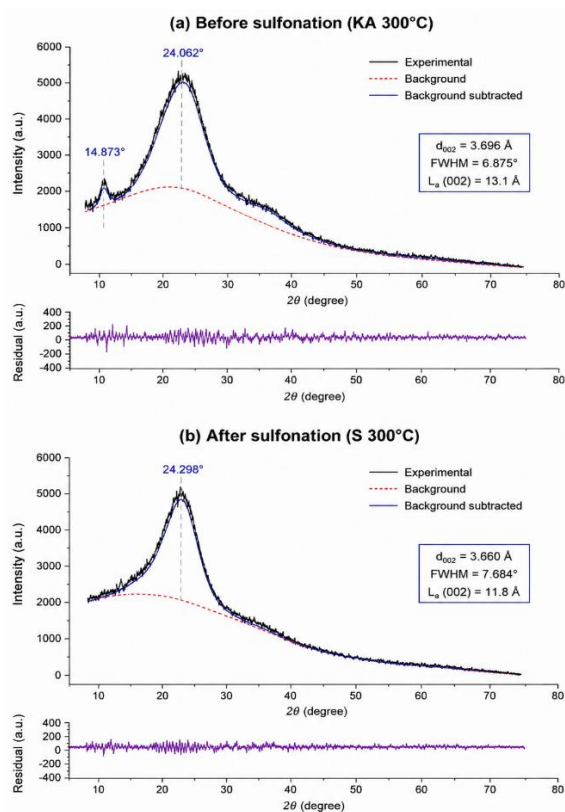


Figure 4. XRD patterns of the coffee husk-derived carbon at 300°C: (a) activated carbon before sulfonation (KA 300°C) and (b) sulfonated activated carbon after H₂SO₄ treatment (S 300°C).

The low-angle peak at 2θ = 14.87° observed in KA 300°C disappeared after sulfonation, indicating removal or conversion of H₃PO₄-derived phosphate species during H₂SO₄ treatment [7,9,21]. Overall, the XRD results confirm that sulfonation modified the surface

chemistry while preserving the amorphous carbon framework, supporting the FTIR evidence of $-\text{SO}_3\text{H}$ incorporation and the catalytic activity observed in glycerol acetylation.

Table 7. XRD structural parameters of activated carbon before (KA, 300°C) and after (S, 300°C) H_2SO_4 sulfonation derived from Scherrer analysis. Cu-K α radiation ($\lambda = 1.54060 \text{ \AA}$).

Parameter	KA 300°C (before)	S 300°C (after)	Change (Δ)
Peak position, 2θ ($^\circ$)	24.062	24.298	+0.236 $^\circ$ (increase)
d-spacing, d_{002} ($\text{\AA}$)	3.696	3.660	-0.036 $\text{\AA}$ (decrease)
FWHM ($^\circ$)	6.875	7.684	+0.809 $^\circ$ (increase)
Crystallite size, La ($\text{\AA}$)	13.1	11.8	-1.3 $\text{\AA}$ (-9.9%)
Low-angle 2θ ($^\circ$)	14.873	Absent	Phosphate phase removed
Carbon phase	Amorphous turbostratic	Amorphous turbostratic	Preserved

3.9. GC-MS Analysis

GC-MS analysis of the product mixture under the best-performing catalyst preparation condition (300°C, 10 N H_2SO_4) confirmed the sequential acetylation of glycerol, with monoacetin as the dominant product and triacetin as the secondary product (Table 8). Monoacetin accounted for approximately 82.77% of the total chromatographic peak area (peaks 1 and 2), while triacetin represented 14.38%.

The predominance of monoacetin is consistent with the stepwise Fischer esterification pathway. The sulfuric acid ($-\text{SO}_3\text{H}$) groups protonate acetic acid, allowing glycerol to undergo nucleophilic attack and form monoacetin. Converting monoacetin into diacetin and triacetin requires additional esterification steps. However, several factors impeded this process, including water accumulation, steric constraints, limited reaction time, and the

accessibility and density of acid sites [11,13,14]. The triacetin selectivity of 14.38% therefore reflects the combined influence of catalyst properties and the selected reaction conditions. Increasing acetic acid excess, extending reaction time, improving water management, and increasing stable acid-site density may shift the product distribution, but these effects must be tested directly for the coffee husk catalyst.

The minor fatty acid peaks (palmitic acid, 9-hexadecenoic acid, and oleic acid) come from residual lipid components naturally present in coffee husk and do not interfere with the acetylation reaction mechanism. The GC-MS data confirm the functional activity of the sulfonated activated carbon catalyst for glycerol acetylation and identify molar ratio, catalyst acidity, and reaction temperature optimization as the key levers for improving triacetin selectivity in future work [31–33].

Table 8. GC-MS identification of glycerol acetylation products under the best-performing catalyst preparation condition (300°C, 10 N H_2SO_4).

Peak	Retention time (min)	Area (%)	Component	Formula
1	13.554	15.38	Monoacetin	$\text{C}_5\text{H}_{10}\text{O}_4$
2	17.593	67.39	Monoacetin	$\text{C}_5\text{H}_{10}\text{O}_4$
3	20.098	14.38	Triacetin	$\text{C}_9\text{H}_{14}\text{O}_6$
4	35.172	0.51	Palmitic acid	$\text{C}_{16}\text{H}_{32}\text{O}_2$
5	38.771	2.12	9-Hexadecenoic acid	$\text{C}_{16}\text{H}_{30}\text{O}_2$
6	39.175	0.21	Oleic acid	$\text{C}_{18}\text{H}_{34}\text{O}_2$

4. CONCLUSION

This study establishes coffee husk waste as a promising, underexplored precursor for producing sulfonated activated carbon catalysts for glycerol acetylation. FTIR, BET, and XRD characterization of the best-performing catalyst supported successful $-\text{SO}_3\text{H}$ functionalization, mesoporous carbon properties, and preservation of an amorphous turbostratic framework, while GC-MS confirmed the formation of monoacetin and triacetin. Carbonization temperature, H_2SO_4

concentration, and their interaction significantly influenced glycerol conversion (all $p < 0.0001$). Within the investigated range, the best-performing condition was carbonization at 300°C with 10 N H₂SO₄, which achieved a mean glycerol conversion of $56.49 \pm 0.00\%$ and a triacetin selectivity of 14.38%. Reusability was limited, with conversion decreasing from 56.49% in cycle 1 to 22.43% in cycle 2 and 12.71% in cycle 3, indicating that future work should focus on stabilizing acid sites, improving regeneration, and optimizing reaction conditions.

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AUTHOR CONTRIBUTIONS

H.D.: Conceptualization, methodology, formal analysis, project administration, funding acquisition, writing – original draft, review & editing. **L.A.A.:** Methodology, investigation, formal analysis, data curation, visualization, writing – review & editing. **E.N.D.:** Investigation, formal analysis, data curation, writing – review & editing. **U.I.A.:** Formal analysis, data curation, writing – review & editing. **L.R.:** Writing – review & editing, supervision. **L.C.D.:** Formal analysis, data curation, writing – review & editing. **R.E.:** Investigation, experimental work, writing – review & editing.

CONFLICTS OF INTEREST

The authors declare no competing financial interests.

DECLARATION OF GENERATIVE AI AND AI-ASSISTED TECHNOLOGIES

During the preparation of this manuscript, the authors used Anthropic’s Claude and OpenAI’s ChatGPT solely to assist with

grammatical correction and language refinement. The authors reviewed and edited the manuscript as necessary and take full responsibility for the accuracy, integrity, and final content of the published article.

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