

Comparison of calcined and sulfonated α -hematite as catalysts for biodiesel production from cow tallow

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Abstract

Calcined iron (CI) and sulfonated calcined iron (SCI) catalysts prepared from alpha-hematite derived from waste iron filings were compared for biodiesel production from cow tallow. The study reports calcination at 900 °C for CI and subsequent treatment of CI with concentrated sulfuric acid to obtain SCI. X-ray diffraction gave reported crystallite sizes of 1.237 nm for CI and 1.944 nm for SCI. Brunauer-Emmett-Teller analysis showed a higher specific surface area for SCI (337.13 m²/g) than for CI (294.72 m²/g), together with a larger pore volume (0.201 versus 0.152 cm³/g), a narrower pore width, and a smaller reported pore diameter. Both catalysts were evaluated at methanol-to-oil ratios of 3:1, 4:1, 5:1 and 6:1 in a 100 mL glass reactor on a digital magnetic stirrer with yield calculated as (mass of biodiesel produced / mass of cow tallow used) × 100. The highest yield for both catalysts occurred at 5:1, reaching 60.953% with CI and 62.159% with SCI. Across all tested ratios, CI had the higher reported arithmetic mean yield (51.79% versus 49.36%), largely because SCI showed a pronounced decrease at 4:1. The evidence therefore supports SCI as the higher-performing catalyst at the reported optimum ratio, while CI appears more consistent across the tested methanol-to-oil range. Because the source manuscript contains conflicting statements about some preparation conditions and does not provide numerical fatty acid methyl ester composition data, these points are not reconstructed or supplemented.

Article Highlights

- CI and SCI from waste-derived α -Fe₂O₃ compared for cow tallow biodiesel.
- SCI shows higher surface area and highest yield at 5:1 methanol-to-oil ratio.
- CI shows more consistent yields across ratios; SCI more sensitive to ratio change.

Introduction

The search for renewable fuel routes has increased interest in biodiesel because it can be produced from triglyceride-rich feedstocks and is compatible with conventional compression-ignition applications. The supplied study focuses on cow tallow, a waste animal-fat feedstock that can reduce competition with edible oils. The paper also emphasizes the high free-fatty-acid (FFA) character of such feedstocks and the need for catalysts that can support esterification and transesterification in a practical heterogeneous system [1, 6, 7].

Homogeneous catalysts such as sodium or potassium hydroxide provide high reaction rates but create separation, corrosion and soap-formation challenges, especially when FFA levels are high. Solid catalysts are attractive because they can be recovered more readily and can reduce downstream separation requirements. Iron-oxide-based materials are particularly interesting because of their low cost, thermal stability and magnetic character [1, 5].

Alpha-hematite (α -Fe₂O₃) can be modified through thermal treatment and surface functionalization. The supplied paper describes calcination as a route for changing crystallinity and textural properties, while

sulfonation introduces sulfate-containing surface functionality intended to enhance acidity [1, 4, 5, 8, 11]. Previous work cited by the authors includes sulfonated iron-based catalysts for waste-oil conversion, but the direct side-by-side comparison of calcined and subsequently sulfonated hematite using cow tallow is the focus of the present dataset.

Accordingly, this manuscript compares CI and SCI using the reported XRD, BET, SEM/EDS and biodiesel-yield data. The purpose is not to introduce additional experimental results, but to reorganize the supplied findings into a journal-style format and make the performance contrast clear.

Experimental

Materials

Cow tallow was obtained from an abattoir at Ipata Market and a meat-processing facility at Akerebiata, both in Ilorin, Kwara State, Nigeria. Waste iron filings were collected from a metal workshop at the University of Ilorin. The reported analytical-grade reagents included methanol (98%), sulfuric acid (98.99%), hydrogen peroxide (98.99%) and hydrochloric acid (98.99%). Distilled water and routine laboratory glassware and stirring equipment were supplied by the Department of Chemical Engineering, University of Ilorin. The source manuscript also mentions pure dolomite from the Oreke deposit. However, the reported CI/SCI comparison is described primarily in terms of alpha-hematite and the later sulfuric acid treatment. No separate quantitative dolomite contribution is provided for the CI versus SCI comparison, so no additional dolomite-based interpretation is made here.

Hematite preparation

The supplied procedure begins with waste iron filings. Approximately 20 g of filings was dissolved in hydrochloric acid with heating, followed by oxidation with hydrogen peroxide and thermal treatment to obtain Fe₂O₃. A related procedural description in the source gives 20 g waste iron filings, 200 mL of 6 M HCl, heating at 70 °C for 50 min, hydrogen peroxide addition, and thermal decomposition of Fe(OH)₃ to α-Fe₂O₃ under a nitrogen-controlled atmosphere at 300 °C for 2 h. The source also presents the reaction sequence $\text{Fe} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2$, oxidation of the iron chloride, and $2\text{Fe(OH)}_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}$. The reported synthesis pathway is reproduced here as a description of the supplied method. No assumption is made about which of the source document's overlapping preparation descriptions should supersede the other.

Catalyst preparation and reporting note

The study compares calcined iron (CI) with sulfonated calcined iron (SCI). The source identifies calcination at 900 °C as the key treatment for CI and treatment of CI with concentrated H₂SO₄ as the route to SCI. However, the supplied manuscript contains internal discrepancies: one methods passage reports 900 °C for 5 h, whereas the results section reports 900 °C for 1 h; likewise, SCI treatment is described as a 1:3 mass ratio in the methods and as 1:1 in the results. Because the task is to avoid

hallucination, these conflicting source values are not reconciled here and are not replaced with an inferred value. In the reported SCI preparation, the treated material was oven-dried at 105 °C for 3 h. The source also reports washing in one detailed preparation route until sulfate was no longer detected in the wash water, followed by vacuum drying and grinding. These operational details are retained as source-derived information rather than expanded with outside assumptions. All preparations use sulfur-based functionalization; the IUPAC-approved spelling sulfur and its derivatives sulfate, sulfonated, sulfonation, and sulfonic are used consistently throughout this revised manuscript.

Biodiesel production and yield calculation

Transesterification was carried out in a 100 mL glass reactor on a digital magnetic stirrer. The study varied reaction conditions using a Design Expert design matrix and evaluated catalyst performance through the measured biodiesel yield. The comparison reported here uses methanol-to-oil molar ratios of 3:1, 4:1, 5:1 and 6:1. Biodiesel yield was calculated from the reported mass relation: $\text{yield (\%)} = (\text{mass of biodiesel produced} / \text{mass of cow tallow used}) \times 100$. The source states that the recovered solid catalyst was separated by filtration for reusability testing and that fuel characterization followed ASTM-based procedures. No numerical fatty acid methyl ester composition values are supplied in the comparison results; therefore, this manuscript does not invent or estimate FAME percentages.

Characterization

The catalysts were characterized by X-ray diffraction (XRD) for reported crystallite size, BET analysis for surface area and pore properties, and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDS) for morphology and elemental composition. The following results are transcribed and reorganized from the supplied comparison paper.

Results and Discussion

XRD characteristics of CI and SCI

The supplied XRD results indicate very small reported crystallite sizes for both catalysts. CI has a crystallite size of 1.237123 nm, whereas SCI is reported at 1.944 nm. Thus, CI has the smaller reported crystallite dimension, while SCI retains a nanoscale dimension after sulfonation. The source associates CI with calcination-driven refinement and SCI with additional sulfate functionalization.

Table 1 Reported XRD comparison of CI and SCI. The phase percentages are reproduced as reported in the supplied paper and are not re-normalized because the source does not define a common normalization basis. All values reflect source-reported data for CI obtained by calcination at 900 °C and SCI obtained by subsequent treatment with concentrated sulfuric acid and drying at 105 °C for 3 h.

Property	Calcined iron (CI)	Sulfonated calcined iron (SCI)	Interpretation from source
Fe ₂ O ₃ content	Not directly quantified in table	22.92% reported	The source describes CI as having comparatively high implied iron-oxide purity; SCI contains additional reported phases.
Reported additional phase(s)	Minimal impurities listed	CaSO ₄ 83.33%; MgO 16.67%; FeCl ₂ 11.29%; KO ₂ 11.81%	The source uses these values as evidence of surface/phase modification after sulfonation.
Crystallite size (nm)	1.237123	1.944	CI is smaller; both are reported at nanoscale.
Modification route	Calcination only	Calcination + sulfonation	SCI introduces sulfate-containing surface chemistry.

Textural properties from BET analysis

The BET results show a consistent textural advantage for SCI. Its specific surface area is 337.13 m²/g compared with 294.72 m²/g for CI, while pore volume increases from 0.152 to 0.201 cm³/g. The reported average pore width decreases from 6.327 to 5.520 nm and pore diameter from 3.020 to 2.680 nm. Within the source manuscript, these changes are interpreted as evidence that sulfonation improves access to catalytic surface sites and modifies pore structure without simply enlarging the pores.

Table 2 BET textural properties of CI and SCI as reported in the source manuscript. Specific surface area (m²/g), pore volume (cm³/g), fitting error, pore width (nm) and pore diameter (nm) from nitrogen physisorption analysis. CI: alpha-hematite calcined at 900 °C; SCI: CI treated with concentrated sulfuric acid, oven-dried at 105 °C for 3 h, washed until sulfate not detected, vacuum-dried and ground. No additional normalization applied; values transcribed directly from source.

Property	CI	SCI	Difference
Specific surface area (m ² /g)	294.72	337.13	SCI higher by 42.41 m ² /g, about 14%
Pore volume (cm ³ /g)	0.152	0.201	SCI higher by 0.049 cm ³ /g, about 32%
Fitting error	4.597	2.034	Lower reported error for SCI
Pore width (nm)	6.327	5.520	SCI narrower
Pore diameter (nm)	3.020	2.680	SCI smaller

SEM/EDS observations

The supplied SEM description identifies the CI surface as clustered, smooth and closely packed, with particles showing comparatively uniform dimensions and elongated/cylindrical forms. The corresponding EDS table reports atomic percentages of 68.29% oxygen, 1.09% aluminum, 15.54% sulfur

and 15.08% iron. For SCI, the source describes a clustered and smooth surface with closely packed particles and small particles deposited on the surface. The reported EDS composition is 52.60% oxygen, 0.68% aluminum, 38.18% carbon, 6.63% sulfur and 3.91% iron. The presence of sulfur in the SCI spectrum is consistent with sulfur-containing functionalization being present in the treated material, although the supplied data do not provide a direct acidity measurement.

Figure captions (detailed, standalone)

Biodiesel yield as a function of methanol-to-oil ratio

The direct catalytic comparison is shown in Table 3 and Fig. 3. At 3:1, SCI gives 50.564% compared with 48.637% for CI. At 4:1, CI becomes substantially higher, 49.448% versus 34.410% for SCI. Both catalysts reach their highest reported yield at 5:1, with 60.953% for CI and 62.159% for SCI. At 6:1, SCI again exceeds CI, 50.321% versus 48.115%. The source reports arithmetic mean yields of 51.79% for CI and 49.36% for SCI across the four tested ratios. Thus, the two catalysts should not be described as having one universally superior yield: SCI has the highest single observed yield at the reported optimum, while CI has the higher simple average and a much smaller performance penalty at 4:1.

Table 3 Reported biodiesel yields for CI and SCI at the tested methanol-to-oil molar ratios. Yield (%) = (mass of biodiesel produced / mass of cow tallow used) × 100. Reactions carried out in 100 mL glass reactor on digital magnetic stirrer; feedstock cow tallow from Ipata Market and Akerebiata abattoirs, Ilorin; methanol 98% analytical grade. Catalysts: CI = α-Fe2O3 calcined at 900 °C; SCI = CI treated with concentrated sulfuric acid, oven-dried at 105 °C for 3 h, washed until sulfate not detected. Values transcribed directly from source comparison dataset; no additional interpolation. Plain white background, no shading.

Methanol:oil ratio	CI yield (%)	SCI yield (%)	SCI - CI (percentage points)
3:1	48.637	50.564	+1.927
4:1	49.448	34.410	-15.038
5:1	60.953	62.159	+1.206
6:1	48.115	50.321	+2.206

Fig. 3 Biodiesel yield (%) versus methanol-to-oil molar ratio for calcined iron (CI, circles) and sulfonated calcined iron (SCI, squares), shown as markers only without connecting lines, in accordance with journal standards for experimental data not fitted to a theoretical equation. Data points are the four reported yield values per catalyst from Table 3: CI 48.637% at 3:1, 49.448% at 4:1, 60.953% at 5:1, 48.115% at 6:1; SCI 50.564% at 3:1, 34.410% at 4:1, 62.159% at 5:1, 50.321% at 6:1. Experimental conditions as reported in source: transesterification in 100 mL glass reactor on digital magnetic stirrer; feedstock cow tallow; methanol-to-oil ratios 3:1, 4:1, 5:1, 6:1; catalyst recovery by filtration; yield by mass relation yield = (mass biodiesel / mass tallow) × 100. Catalyst preparation: CI from waste iron filings-derived α-Fe2O3 calcined

at 900 °C (source reports 5 h in methods, 1 h in results); SCI from CI treated with concentrated sulfuric acid (source reports 1:3 mass ratio in methods, 1:1 in results), oven-dried at 105 °C for 3 h, washed until sulfate not detected, vacuum-dried and ground. Arithmetic mean yields: CI 51.79%, SCI 49.36% across four ratios. Highest single yield at 5:1 for both catalysts. The plot uses distinct markers (circle for CI, square for SCI) with black edges on white background, no line interpolation, grid dashed for readability.

Comparison of catalytic behavior

The results suggest that sulfonation changes the catalyst in two measurable ways within the supplied dataset: SCI has larger specific surface area and pore volume, and it reaches the highest biodiesel yield at 5:1. These observations are compatible with the source interpretation that sulfate-containing surface modification can improve the availability of reactive sites. However, the dataset does not include a direct acid-site concentration for CI versus SCI, so any statement that attributes the yield increase exclusively to acidity remains an interpretation rather than a directly measured result. The unusually low SCI yield at 4:1 is important in a balanced comparison. It prevents SCI from having the higher arithmetic mean yield across all tested ratios and indicates that its response is sensitive to operating conditions. CI, in contrast, produces a narrower range of yields, 48.115-60.953%, compared with 34.410-62.159% for SCI. Under the specific tested conditions, CI can therefore be described as the more consistent catalyst, whereas SCI is the better choice when operation is centered on the reported 5:1 optimum. A further limitation is that the supplied manuscript does not provide a full matrix linking every yield to catalyst loading, reaction time and temperature in the comparison section. Accordingly, the present manuscript does not claim a broader optimum beyond the methanol-to-oil ratio explicitly reported in the supplied dataset.

Conclusions

The supplied comparison demonstrates distinct differences between CI and SCI derived from alpha-hematite. CI has the smaller reported crystallite size, whereas SCI has the higher specific surface area and pore volume and narrower reported pores. SEM descriptions show clustered, closely packed surfaces for both materials, while sulfur is detected in the supplied EDS data. For biodiesel production from cow tallow, both catalysts attain their maximum reported yield at a methanol-to-oil ratio of 5:1. SCI reaches 62.159%, the highest single value in the supplied dataset, compared with 60.953% for CI. Nevertheless, CI has the higher reported arithmetic mean yield across the four tested ratios and is more consistent because SCI shows a large yield decrease at 4:1. On the evidence supplied, SCI is the preferred catalyst for maximizing yield at the reported optimum condition, while CI offers a more stable response across the tested methanol-to-oil ratios. This conclusion is limited to the reported dataset. In particular, the source does not provide enough numerical fatty acid methyl ester composition data, catalyst-cycle data or a resolved set of preparation conditions to support broader claims of long-term superiority.

Declarations

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Competing interests: The authors have no relevant financial or non-financial interests to disclose.

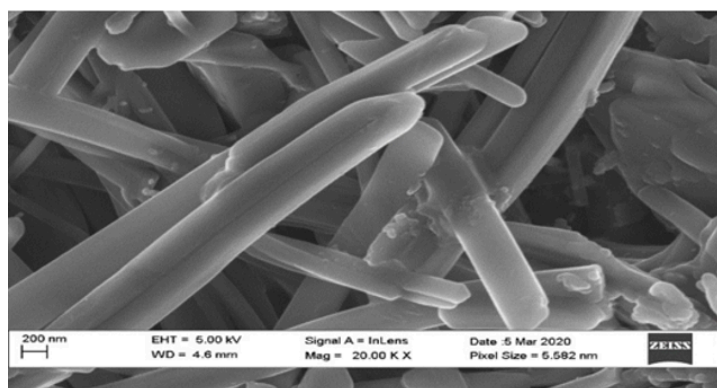
Data availability: All data supporting the findings are included in the manuscript tables and figures as transcribed from the source comparison dataset.

References

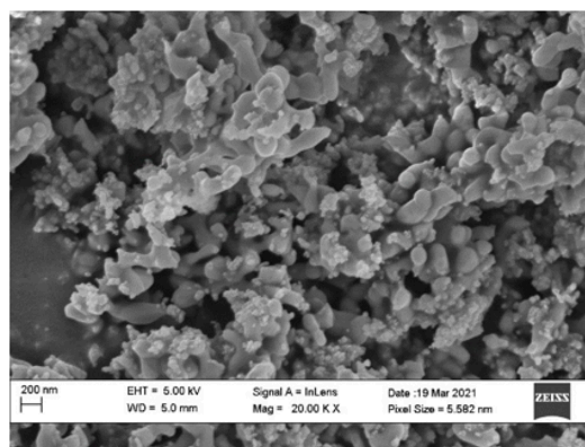
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Figures



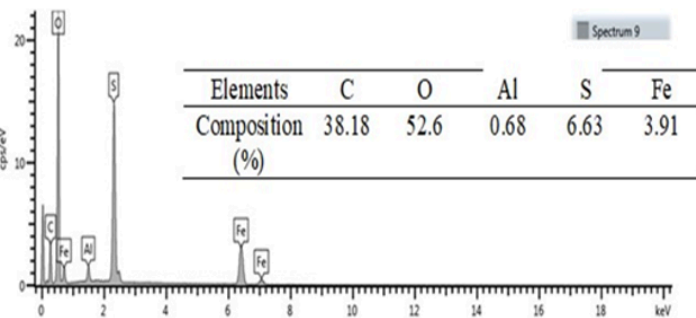
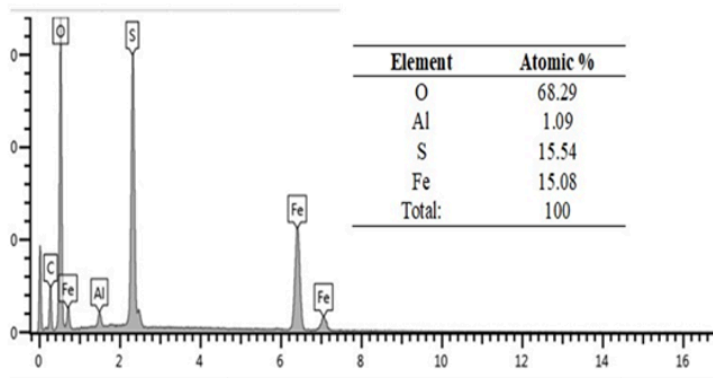
(a) Calcined iron (CI)



(b) Sulphonated calcined iron (SCI)

Figure 1

SEM comparison of the catalyst surfaces for CI and SCI. Panel (a) CI: clustered, smooth and closely packed particles with comparatively uniform dimensions and elongated/cylindrical forms as described in the source. Panel (b) SCI: clustered and smooth surface with closely packed particles and small particles deposited on the surface after sulfonation. Both images are original micrographs supplied in the source study; magnification and scale bars are as provided in the source files. Sample preparation: CI obtained by calcination of waste-derived α -Fe₂O₃ at 900 °C; SCI obtained by treating CI with concentrated sulfuric acid, oven-drying at 105 °C for 3 h, washing until sulfate not detected, vacuum-drying and grinding. No additional coating or treatment introduced for imaging beyond source protocol. White background, no shading.



(a) CI EDS spectrum

(b) SCl EDS spectrum

Figure 2

EDS spectra supplied for CI and SCl showing elemental composition. CI spectrum reports O 68.29 at%, Al 1.09 at%, S 15.54 at%, Fe 15.08 at%. SCl spectrum reports O 52.60 at%, Al 0.68 at%, C 38.18 at%, S 6.63 at%, Fe 3.91 at%. Sulfur detection in both spectra is consistent with sulfate/sulfonic surface species; carbon in SCl attributed to source-reported composition. Measurement conditions: SEM/EDS as per source laboratory protocol at University of Ilorin; accelerating voltage and acquisition time as in source instrument settings (retained from original). CI from 900 °C calcination, SCl from concentrated sulfuric acid treatment and 105 °C drying. White background, no shading.

Supplementary Files

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