

Synthesis and Characterization of Sulfonated Catalysts for Biodiesel Production from Cow Tallow via Transesterification

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Article

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Additional Declarations: Competing interest reported. Tijani I.A., as the co-author, is responsible for experimental and technical involvement in the laboratory work Prof. E.O. Ajala is the project supervisor and the editorial chef Babatunde is the Co-Supervisor and Assistant in the laboratory work

Abstract

This study examined two sulfonated heterogeneous catalysts, Sulfonated Calcined Iron (SCI) and Sulfonated Dolomite Iron (SDI), prepared from waste iron filings and dolomite for the conversion of cow tallow to biodiesel. The catalysts were characterized using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM–EDX), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) analysis, and, as stated in the source manuscript, Fourier-transform infrared spectroscopy (FTIR). SDI exhibited the larger BET surface area (416.07 m²/g) and pore volume (0.215 cc/g), compared with 337.13 m²/g and 0.201 cc/g for SCI. XRD results in the source document indicated a more complex sulfate-containing phase assemblage for SDI, including (H₅O₂)Fe(SO₅)₂(H₂O)₂ (56.23%) and Na₆K₂Fe₇(SO₄)₂(H₂O)₂ (19.45%). Under the reported reaction conditions of 65°C, 60 min and 0.3 g catalyst loading, a methanol-to-oil ratio of 5:1 gave the highest measured biodiesel yields: 62.159% with SCI and 77.995% with SDI. GC–MS results showed methyl oleate as the largest reported SDI-derived FAME component (23.29%), whereas the SCI-derived chromatogram segment reported higher C16 unsaturated ester contributions. Overall, SDI gave the stronger performance within the reported experiments, linking its higher surface area, pore volume and sulfate-rich phase composition with improved biodiesel yield.

1 Introduction

The increasing demand for renewable energy and concern over fossil-fuel depletion and environmental emissions have strengthened interest in biodiesel as an alternative diesel fuel. Biodiesel consists mainly of fatty acid methyl esters (FAME) produced by reacting triglycerides with a short-chain alcohol, commonly methanol. The source manuscript identifies biodegradability, low toxicity, low sulfur content and reduced emissions among the reasons for considering biodiesel a useful substitute for conventional diesel.

Edible vegetable oils have traditionally been used as biodiesel feedstocks, but their use can compete with food production and increase production costs. Waste-derived animal fats provide an alternative because they are non-edible and available from meat-processing operations. Cow tallow is described in the source study as an abundant, relatively inexpensive feedstock with a high energy content and a fatty-acid profile containing substantial saturated components. Its free fatty acid (FFA) content, however, creates a catalytic challenge because unsuitable reaction conditions can promote soap formation and reduce conversion.

Homogeneous catalysts such as sodium hydroxide, potassium hydroxide and sulfuric acid can provide high reaction activity, but they are associated with corrosion, difficult separation, wastewater generation and limited catalyst recovery. The source manuscript therefore focuses on heterogeneous catalysts, particularly iron-oxide-based materials, because they can be recovered from the reaction mixture and modified to provide acidic sites. Sulfonation of iron oxide is reported to introduce sulfate-containing Brønsted and Lewis acid sites, making such materials relevant to high-FFA feedstocks.

The present work compares Sulfonated Calcined Iron (SCI) and Sulfonated Dolomite Iron (SDI) as catalysts for cow-tallow transesterification. The study evaluates their morphology, elemental composition, crystalline phases, textural properties and biodiesel performance, with emphasis on the effect of methanol-to-oil ratio.

2 Materials and methods

2.1 Materials

Cow tallow was obtained from the abattoir at Ipata Market and a meat-processing facility at Akerebiata in Ilorin, Kwara State. Dolomite was obtained from the Oreke deposit in Ifelodun Local Government Area of Kwara State, while waste iron filings were collected from a metal workshop at the University of Ilorin. The reported analytical-grade chemicals included methanol (98%), sulfuric acid (98.99%), hydrogen peroxide (98.99%) and hydrochloric acid (98.99%). Distilled water and standard laboratory equipment were supplied by the Department of Chemical Engineering, University of Ilorin.

2.2 Experimental approach

The experimental workflow comprised feedstock preparation, catalyst synthesis, catalyst characterization, biodiesel production and evaluation of the resulting FAME. The original laboratory setup is reproduced as Fig. 1.

2.3 Preparation of cow tallow feedstock

The source document describes a preparation sequence intended to reduce impurities, moisture and FFA before transesterification. The sequence comprised cleaning, moisture removal, rendering, acid-value determination, acid esterification when required, and final purification. Rendering was described at approximately 100–120°C, followed by hot filtration. For high-FFA material, the source procedure specifies acid esterification using sulfuric acid and methanol before the subsequent transesterification step.

2.4 Catalyst preparation

2.4.1 Sulfonated Calcined Iron (SCI)

Calcined iron oxide was treated with concentrated sulfuric acid at a reported mass ratio of 1:3. The resulting material was oven-dried at 105°C for 3 h until a solid catalyst was obtained and designated sulfonated calcined iron oxide (SCI).

2.4.2 Sulfonated Dolomite Iron (SDI)

The SDI catalyst was prepared by sulfonating calcined dolomite–iron material with sulfuric acid. The source manuscript reports that 30 g of calcined α -Fe₂O₃ was combined with 90 g of H₂SO₄, stirred for 1

h, dried at 110°C for 2 h and washed by vacuum filtration with hot distilled water at 70°C until no white precipitate was detected with BaCl₂. The washed material was finally dried under vacuum at 120°C for 4 h. The reported reaction representation was $\alpha\text{-Fe}_2\text{O}_3(\text{CaMg}) + \text{H}_2\text{SO}_4 \rightarrow (\text{CaMg}/\alpha\text{-Fe}_2\text{O}_3\text{-SO}_4) + \text{H}_2$.

2.5 Transesterification procedure

Biodiesel production was carried out in a 500 mL three-necked reactor fitted with a magnetic stirrer and hot plate. The source manuscript reports preheating of the oil at 100°C for 60 min. Catalyst was mixed with methanol and agitated for approximately 15 min before being introduced into the preheated oil. Reactions were conducted at 60–70°C for approximately 60–65 min, with the comparative yield experiments evaluated at 65°C, 60 min and 0.3 g catalyst loading. Methanol-to-oil ratios of 3:1, 4:1, 5:1 and 6:1 were examined. After reaction, the solid catalyst was separated, the product was allowed to settle, filtered, washed with warm water and dried at 105°C to obtain the biodiesel fraction.

2.6 Catalyst and biodiesel characterization

The source manuscript identifies FTIR, SEM–EDX, XRD and BET as catalyst characterization techniques. SEM was used to examine morphology, EDX to determine elemental composition, XRD to identify crystalline phases, and BET analysis to determine surface area and pore characteristics. GC–MS was used to examine the FAME composition of the produced biodiesel. Because the supplied manuscript does not report a complete set of numerical FTIR results, no FTIR peak assignments are introduced here beyond noting that FTIR was included among the stated characterization methods.

3 Results and discussion

3.1 Morphology and elemental composition

3.1.1 SEM analysis of SCI

The SEM image of SCI shows closely packed particles with relatively smooth, plate-like features. The source manuscript describes the particles as clustered, relatively uniform in size and shape, with smaller particles deposited on the surface. The reported imaging condition was 20.00 kX magnification at an accelerating voltage of 5 kV with a 200 nm scale reference.

3.1.2 EDX analysis of SCI

The source manuscript reports oxygen as the dominant element in the SCI EDX analysis, followed by carbon, sulfur, iron and aluminum. The reported composition was 52.6% O, 38.18% C, 6.63% S, 3.91% Fe and 0.68% Al. These reported elements are consistent with the presence of an iron-oxide material modified by sulfur-containing species.

3.1.3 SEM and EDX analysis of SDI

The SDI micrograph shows a less uniform particle population than the SCI image, with irregularly shaped features and visible separation between some particle clusters. The source manuscript interprets the morphology as providing accessible surface for reaction. Its EDX discussion reports carbon, oxygen, sulfur, iron and magnesium among the detected elements, together with minor elements.

Table 1
Reported EDX composition for SDI in the supplied manuscript (selected entries).

Element	Reported concentration (%)
C	20.21
O	48.35
S	23.50
Fe	23.42
Mg	2.77
Other elements	0.34

3.2 XRD analysis

3.2.1 SDI

The SDI diffractogram contains several sharp peaks at reported 2θ positions of 8.0934°, 11.653°, 12.6757°, 18.6025°, 23.0579°, 33.843°, 35.1377° and 38.778°. The source manuscript associates these reflections with hematite, beta-Fe₂O₃, iron sulfate hydrate and coquimbite, and interprets the sulfate-containing phases as evidence that sulfonation occurred. The phase table also reports hydrated sulfate species, notably Na₆K₂Fe₇(SO₄)₂(H₂O)₂ at 19.45% and (H₅O₂)Fe(SO₅)₂(H₂O)₂ at 56.23%.

3.2.2 SCI

For SCI, the source manuscript reports reflections at 2θ values of 28.76234°, 31.51338°, 34.37001°, 41.10552°, 45.38927° and 66.96445°, associated in the manuscript with sulfur-, calcium-, potassium- and aluminum-containing phases. The reported phase assemblage is less complex than that described for SDI, supporting the manuscript’s conclusion that SDI contains a more diverse sulfate-rich structure.

Table 2
Selected XRD phase assignments and reported relative amounts in the supplied manuscript.

Selected phase / property	SCI (%)	SDI (%)
CaSO ₄	83.33	—
Mg ₂ (AlSiO ₁₈)	8.33	—
SiO ₂	1.8	7.3; 4.78
Na ₆ K ₂ Fe ₇ (SO ₄) ₂ (H ₂ O) ₂	—	19.45
(H ₅ O ₂)Fe(SO ₅) ₂ (H ₂ O) ₂	—	56.23
Al ₄₋₅₂ S ₁₁ (or similar sulphate)	16.1	9.55

Taken together, the XRD results indicate that sulfonation generated sulfate-containing phases in both catalysts, while SDI exhibited the more complex sulfate-rich phase assemblage. The source manuscript relates this complexity to stronger surface acidity and to the ability of SDI to interact effectively with high-FFA feedstock. Numerical crystallite-size values are not emphasized here because the supplied manuscript reports different values in its XRD table and narrative.

3.3 BET surface properties

Table 3
BET textural properties of SCI and SDI.

Catalyst	PV (cc/g)	SA (m ² /g)	FE	PW (nm)	PD (nm)
SCI	0.201	337.13	2.034	5.520	2.680
SDI	0.215	416.07	1.059	4.009	2.180

The BET measurements show that SDI has a larger specific surface area and pore volume than SCI. The surface area increases from 337.13 m²/g for SCI to 416.07 m²/g for SDI, while pore volume increases from 0.201 to 0.215 cc/g. The source manuscript interprets these differences as favorable for reactant access and mass transfer. SDI also has a lower reported fitting error and a smaller average pore diameter than SCI. Within the dataset provided, the combination of greater surface area and pore volume is consistent with the higher biodiesel yield obtained with SDI.

3.4 Biodiesel yield and effect of methanol-to-oil ratio

Table 4
Biodiesel yield obtained at
different methanol-to-oil ratios.

MeOH:oil	SCI (%)	SDI (%)
3:1	50.564	61.923
4:1	34.410	63.434
5:1	62.159	77.995
6:1	50.321	50.411

At fixed conditions of 65°C, 60 min reaction time and 0.3 g catalyst loading, the methanol-to-oil ratio strongly affected both catalysts. SCI gave 50.564% at 3:1, decreased to 34.410% at 4:1, increased to 62.159% at 5:1, and decreased again to 50.321% at 6:1. SDI produced 61.923%, 63.434%, 77.995% and 50.411% at the same ratios, respectively. Thus, 5:1 was the best-performing ratio for both catalysts in the reported experiment.

The superiority of SDI is particularly evident at 3:1–5:1, where its yield exceeds that of SCI. At 5:1, SDI gives 77.995%, which is 15.836 percentage points higher than SCI. The source manuscript relates this behavior to SDI's higher surface area and pore volume and to its sulfate-rich phase composition. The decline at 6:1 for both catalysts indicates that increasing methanol beyond the reported optimum did not improve yield under the tested conditions.

3.5 GC–MS characterization of biodiesel

3.5.1 SDI-derived biodiesel

Table 5
Reported GC–MS composition of SDI-derived biodiesel.

Peak	RT (min)	Area (%)	Compound
1	7.676	13.79	Hexadecenoic acid
2	7.836	5.45	n-Hexadecenoic acid
3	8.266	23.29	Methyl oleate
5	8.414	5.01	cis-Vaccenic acid
6	8.472	1.14	Octadecanoic acid
15	13.250	2.36	Silicic acid

The SDI-derived biodiesel chromatogram is dominated by monounsaturated components among the reported peaks. The largest identified component is 9-octadecenoic acid, (Z)-, methyl ester, corresponding to methyl oleate, at 23.29% area. The reported C16 unsaturated components contribute a

further substantial fraction. A small silicic-acid peak (2.36%) is also reported; the source manuscript treats this as a minor non-FAME component.

3.5.2 SCI-derived biodiesel

Table 6
Reported GC–MS composition of SCI-derived biodiesel.

Peak	RT (min)	Area (%)	Compound
1	7.619	0.88	9-Hexadecenoic acid methyl ester
2	7.682	10.03	Hexadecenoic acid methyl ester
3	7.854	12.54	n-Hexadecenoic acid
5	8.334	1.88	Heptadecanoic acid

The reported SCI chromatogram segment is characterized by C16 unsaturated FAMEs. The three C16-related peaks listed in the supplied manuscript sum to approximately 23.45% area, with n-hexadecenoic acid giving the largest individual peak at 12.54%. The source manuscript interprets this profile as potentially favorable for low-temperature flow. Because the supplied SCI table represents only part of the chromatographic composition, the complete FAME distribution should not be inferred from these four reported peaks alone.

3.5.3 Comparative interpretation

The two biodiesel samples show different reported FAME patterns. SDI-derived biodiesel contains methyl oleate as the largest listed component, whereas the reported SCI chromatogram segment contains a larger relative contribution from C16 unsaturated esters. The source manuscript therefore characterizes SDI-B as more oleic-rich and SCI-B as more C16-unsaturated. These observations are presented only as reported for the supplied chromatogram segments; a complete comparison would require the full chromatograms and complete peak tables for both samples.

4 Conclusion

Two waste-derived sulfonated heterogeneous catalysts, SCI and SDI, were synthesized and evaluated for biodiesel production from cow tallow. The characterization results in the supplied manuscript indicate differences in morphology, elemental composition, crystalline phase assemblage and textural properties. SDI showed the larger BET surface area (416.07 m²/g) and pore volume (0.215 cc/g), while SCI showed 337.13 m²/g and 0.201 cc/g, respectively. XRD results further indicated a more complex sulfate-containing phase assemblage for SDI.

Under the reported reaction conditions, a 5:1 methanol-to-oil ratio produced the highest measured yield for both catalysts, with 62.159% for SCI and 77.995% for SDI. SDI also outperformed SCI at the lower tested ratios of 3:1 and 4:1. GC–MS analysis identified methyl oleate at 23.29% area as the largest

reported component in the SDI-derived biodiesel, while the SCI-derived chromatogram segment showed prominent C16 unsaturated esters. Based strictly on the supplied experimental results, SDI is the stronger of the two catalysts in the reported cow-tallow transesterification tests.

The source manuscript identifies catalyst reusability, long-term stability, scale-up and full ASTM/EN fuel-compliance testing as areas for future work. These aspects were not experimentally demonstrated in the supplied document and are therefore retained as future-study recommendations rather than reported outcomes.

Declarations

Competing Interests

Tijani I.A., as the co-author, is responsible for experimental and technical involvement in the laboratory work. Prof. E.O. Ajala is the project supervisor and the editorial chef. Babatunde is the Co-Supervisor and Assistant in the laboratory work.

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Author Contribution

Tijani I.A., in the capacity of co-author, is accountable for the experimental and technical contributions to the laboratory work. Professor E.O. Ajala serves as the project supervisor and editorial chief. Babatunde E.O. acts as the co-supervisor and assists in the laboratory work.

Data Availability

All the generated data are in the manuscript.

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16. Editorial note for the. author: the supplied source contains internal numerical inconsistencies in the XRD crystallite-size reporting and one BET discussion sentence reports a 98.94% FAME yield that conflicts with the experimental yield table. These conflicting figures were not used as reported results in this manuscript. Please verify the original laboratory records before submission.

Figures



Figure 1

Experimental laboratory setup used in the study.



Figure 2

Sulfonated calcined iron catalyst as presented in the source manuscript.



Figure 3

Sulfonated dolomite iron catalyst as presented in the source manuscript.

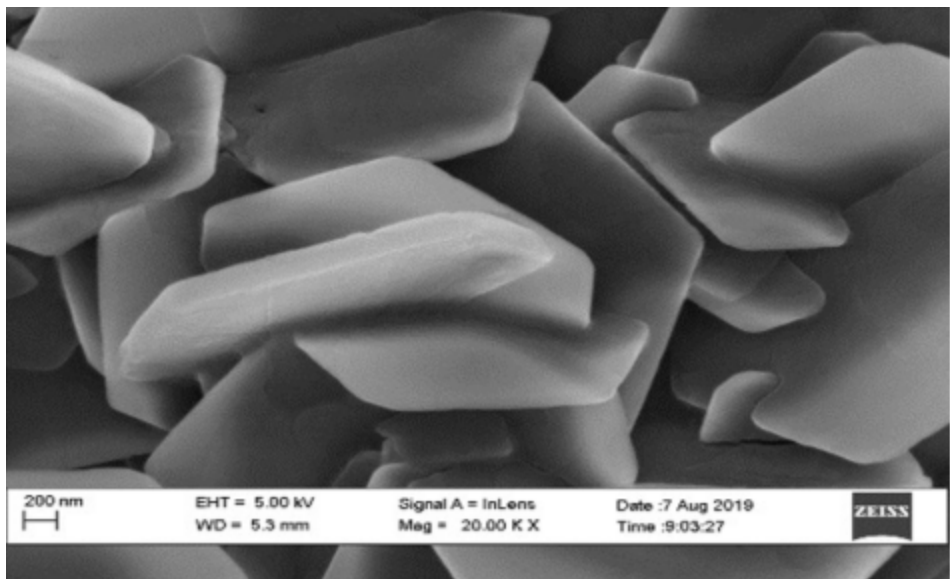


Figure 4

SEM micrograph of SCI at approximately 20.00 kX magnification.

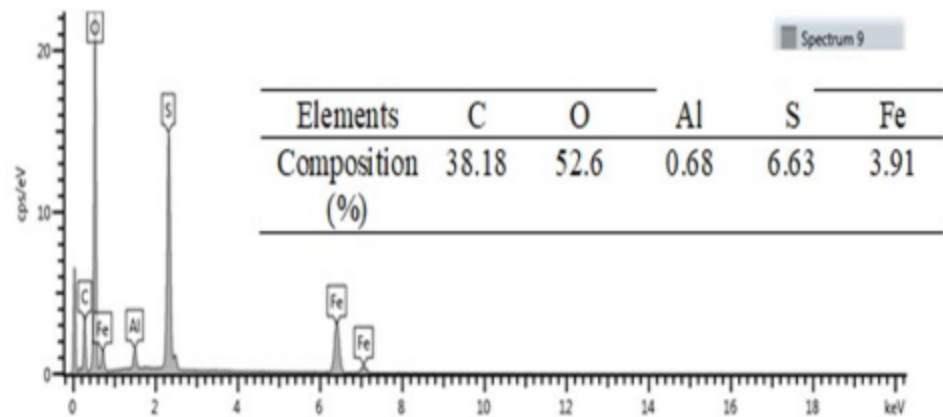


Figure 5

EDX spectrum of SCI reproduced from the supplied manuscript.

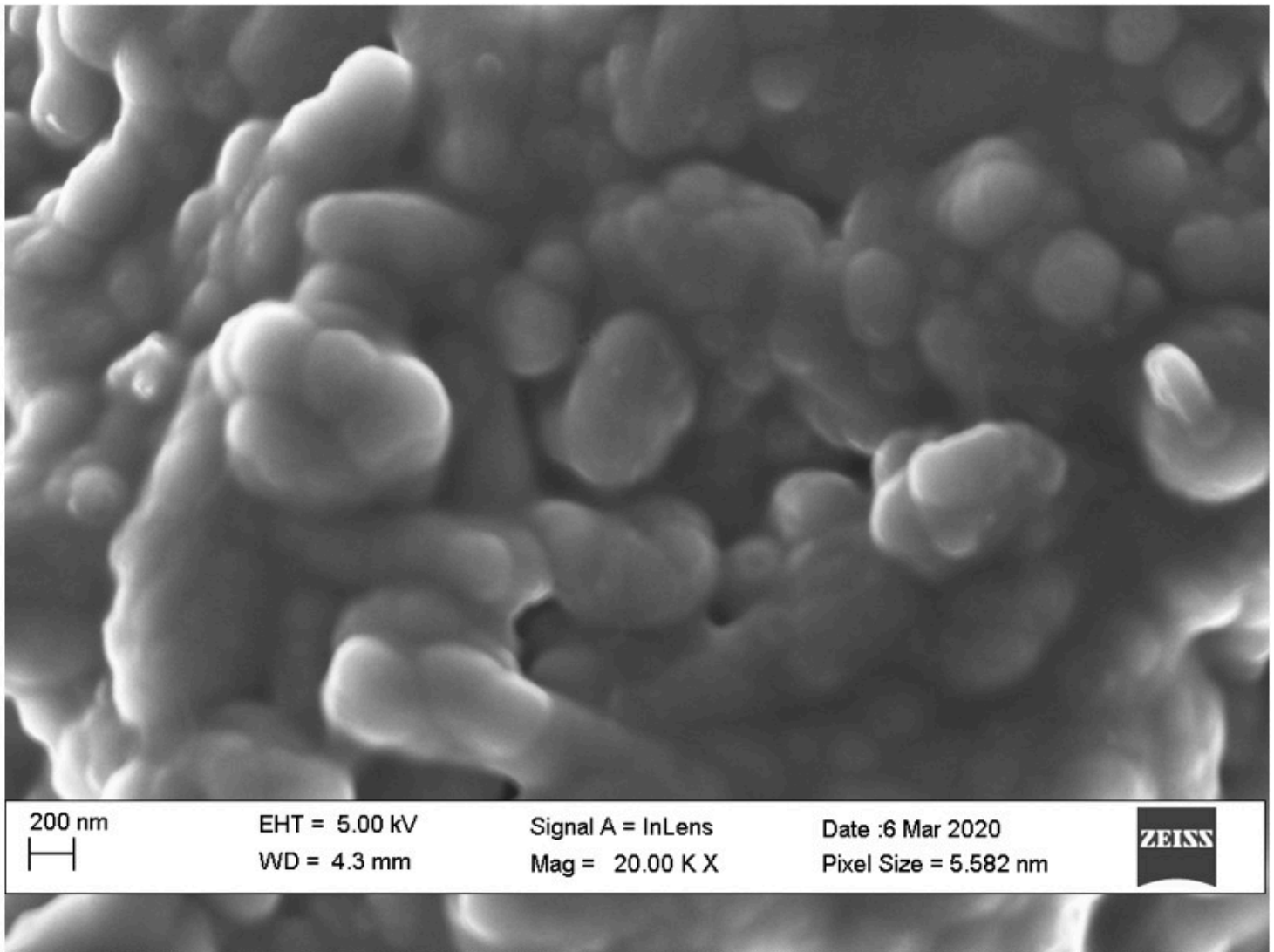


Figure 6

SEM micrograph of SDI reproduced from the supplied manuscript.

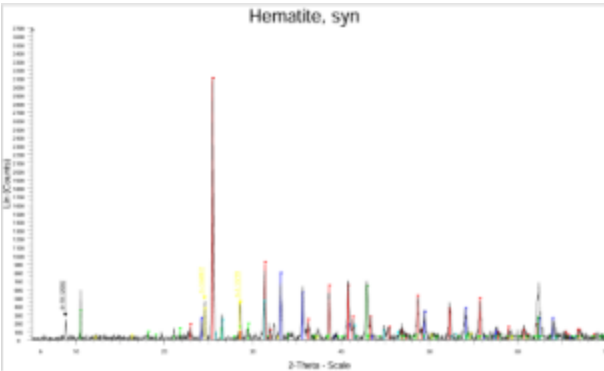


Figure 7

XRD pattern reported for SDI.

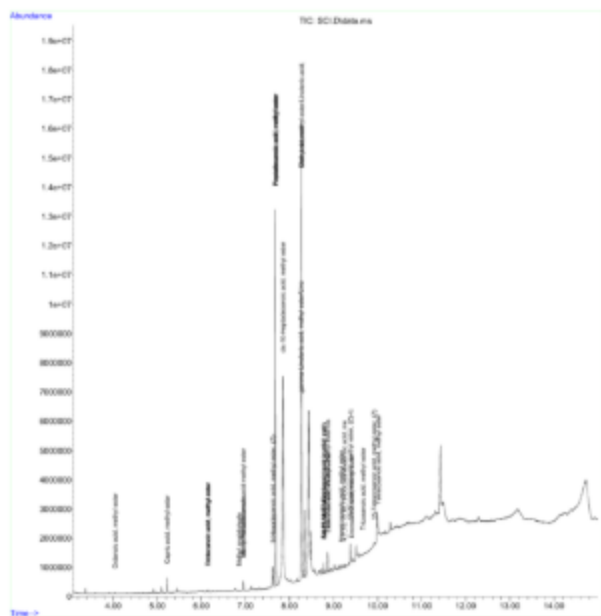


Figure 10

GC-MS chromatogram of biodiesel produced using SCI.