

# 1 Sulfonated Cellulosic Fabric Catalyst for Biodiesel Production from Waste Oils

## 5 Abstract

6 This work reports the synthesis of a bio-based acid catalyst derived from recycled cellulosic  
7 fabric, functionalized via sulfonic grafting, for the conversion of waste cooking oils into  
8 biodiesel. The resulting material exhibits a high acid density ( $1.31 \text{ mmol H}^+ \cdot \text{g}^{-1}$ ) and a low  
9  $\text{pH}_{\text{pzc}}$  ( $\sim 2.3$ ), promoting substrate adsorption and protonation. Its catalytic performance was  
10 evaluated under various reaction conditions ( $70\text{--}120 \text{ }^\circ\text{C}$ ,  $5\text{--}20 \text{ wt\%}$  catalyst loading,  
11 methanol-to-oil molar ratios of  $3:1\text{--}15:1$ ). The best operating conditions ( $90 \text{ }^\circ\text{C}$ ,  $15 \text{ wt\%}$ ,  $9:1$   
12 ratio, and  $10 \text{ h}$ ) yielded a FAME conversion of  $97\%$ , comparable to commercial resins.

13 The bifunctional catalysis enables single-step transformation of highly degraded oils (acid  
14 value  $4.8 \text{ mg KOH/g}$ , viscosity  $42.3 \text{ mm}^2/\text{s}$ ), as confirmed by GC-MS ( $>95\%$  conversion) and  
15  $^1\text{H NMR}$  ( $-\text{OCH}_3$  peak at  $3.7 \text{ ppm}$ ). The biodiesel produced meets EN 14214 and ASTM  
16 D6751 requirements, with a viscosity of  $4.54 \text{ mm}^2/\text{s}$ , density of  $0.885 \text{ g}\cdot\text{cm}^{-3}$ , and residual  
17 acid value of  $0.38 \text{ mg KOH/g}$ . The catalyst demonstrates good durability, with conversion  
18 decreasing from  $97\%$  to  $\sim 90\%$  after five reuse cycles, confirming  $\text{SO}_3\text{H}$  site stability and its  
19 relevance for circular lipid valorization processes.

20 **Keywords:** Sulfonated cellulose; heterogeneous catalysis; waste oils; transesterification;  
21 biodiesel; catalytic durability.

## 23 1. Introduction

24 The increasing global demand for sustainable biofuels calls for the development of efficient,  
25 economical, and environmentally compliant catalytic solutions for converting renewable  
26 resources into biodiesel (Zhang & Li, 2022). Waste cooking oils, abundant in urban areas yet  
27 largely underutilized, offer strategic potential to lower production costs, reduce pressure on  
28 edible oils, and align with energy transition objectives (Mahmood et al., 2025). However,  
29 converting such degraded lipid matrices requires robust catalysts capable of operating  
30 effectively despite impurities, high acidity, and oxidative deterioration (Chen et al., 2024).

31 In this context, bio-derived heterogeneous catalysts are particularly attractive owing to their  
32 low cost, easy recovery, and compatibility with green chemistry principles (Li et al., 2021).  
33 Cellulose represents a promising support due to its availability, biodegradability, and  
34 modifiable hydroxyl functionalities enabling controlled introduction of catalytic sites (Klemm  
35 et al., 2020). The reuse of discarded cellulosic textiles further aligns with circular economy  
36 strategies, offering a low-cost and locally available substrate (Mahmood et al., 2025).

37 Among functionalization routes, cellulose sulfonation generates strong  $-\text{SO}_3\text{H}$  proton sites  
38 that display high activity in esterification and transesterification, with acid densities above  $1$   
39  $\text{mmol H}^+ \cdot \text{g}^{-1}$  and catalytic yields exceeding  $90\%$  (Kaur et al., 2020; Zhou et al., 2023). This  
40 performance arises from a synergistic combination of accessible acidity, morphology  
41 reorganization induced by grafting, and enhanced diffusion of reactants toward active sites  
42 (Wang et al., 2022).

43 Despite these advances, the use of recycled cellulosic fabric as a catalytic platform for  
44 esterification and transesterification remains scarcely explored, although it represents a high-  
45 potential pathway for developing circular and low-carbon technologies (Mahmood et al.,  
46 2025). Current challenges include (i) controlling functionalization degree and acid density, (ii)  
47 understanding structure–acidity–activity relationships, (iii) assessing the influence of textural  
48 properties on intra-particle diffusion, and (iv) ensuring durability and recyclability under  
49 realistic operating conditions (Amarasekara, 2024).

50 In this context, the present work aims to develop a bio-based acid catalyst derived from  
51 recycled cellulose fabric, functionalized by sulfonic grafting, and to correlate its  
52 physicochemical properties with its catalytic performance during the conversion of waste  
53 cooking oils into biodiesel via transesterification.

## 54 **2. Materials and Methods**

### 55 **2.1. Raw materials and reagents**

56 The cellulosic support was obtained from locally collected 100% cotton textiles, in alignment  
57 with a circular economy approach. The fabrics were cleaned in two steps: washing with hot  
58 distilled water (70 °C) followed by ethanol extraction (95%) for 30 min under magnetic  
59 stirring, then oven-dried at 105 °C for 12 h. Analytical-grade reagents were used throughout:  
60 sodium metaperiodate (NaIO<sub>4</sub>, ≥99%), chlorosulfonic acid (ClSO<sub>3</sub>H, 98%), glacial acetic acid,  
61 methanol (99.8%), ethanol (99%), NaOH solutions (0.01–0.1 mol·L<sup>-1</sup>) for titration, and NaCl  
62 (0.01 mol·L<sup>-1</sup>) for pH<sub>pzc</sub> determination. Ultrapure water (18.2 MΩ·cm) was used in all  
63 synthesis, rinsing, and preparation steps.

### 64 **2.2. Oxidative activation of the cellulosic support**

65 Pre-oxidation was performed to generate reactive aldehyde groups. One hundred grams of  
66 dried textile were immersed in 1 L of NaIO<sub>4</sub> solution (0.1 mol·L<sup>-1</sup>) under magnetic stirring  
67 (300 rpm) for 6 h at 25 °C, protected from light to prevent periodate photoreduction. After  
68 reaction, the material was thoroughly washed with distilled water to neutrality, filtered, and  
69 dried at 105 °C for 12 h. Mass loss was used as an indicator of functional conversion.

### 70 **2.3. Sulfonic grafting by chlorosulfonation**

71 Acid functionalization was achieved by controlled introduction of –SO<sub>3</sub>H groups. Ten grams  
72 of oxidized cellulose (Cell–CHO) were dispersed in 100 mL of glacial acetic acid in a round-  
73 bottom flask equipped with a condenser and maintained under nitrogen. The suspension was  
74 cooled to 0–5 °C, after which chlorosulfonic acid was added dropwise (2 mL·g<sup>-1</sup> of support)  
75 over 30 min. The mixture was then heated at 60 °C for 3 h. The resulting sulfonated material  
76 (Cell–SO<sub>3</sub>H) was filtered, washed successively with acetone and distilled water to neutrality,  
77 and dried at 80 °C for 10 h. Grafting yield was calculated based on dry mass.

### 78 **2.4. Physicochemical characterizations**

#### 79 **2.4.1. Infrared spectroscopy (FT-IR)**

80 FT-IR spectra were recorded in ATR mode (4000–400 cm<sup>-1</sup>) with a resolution of 4 cm<sup>-1</sup> to  
81 identify structural modifications (C=O, S=O, S–O).

#### 82 **2.4.2. Elemental analysis (CHNS)**

83 Sulfur content was quantified by CHNS analysis and used to calculate theoretical acid density  
84 (mmol H<sup>+</sup>·g<sup>-1</sup>).

#### 85 **2.4.3. Total acidity determination**

86 Acidity was measured by acid–base neutralization: 0.1 g of catalyst was suspended in 50 mL  
87 NaCl (0.01 mol·L<sup>-1</sup>) and titrated with NaOH (0.01 mol·L<sup>-1</sup>). Acid density was computed  
88 according to stoichiometric consumption.

#### 89 **2.4.4. pH<sub>pzc</sub> measurement (drift pH method)**

90 A series of NaCl solutions (0.01 mol·L<sup>-1</sup>) with initial pH values ranging from 2 to 12 received  
91 0.1 g of catalyst each. After 24 h equilibration, final pH values were recorded to determine the  
92 point of zero charge.

100

#### 101 **2.4.5. Scanning electron microscopy (SEM)**

102 Fragments (~5 × 5 mm) of raw, oxidized, and sulfonated fabric were Au/Pd sputter-coated  
103 (~10 nm) and examined in secondary-electron mode (5–15 kV) to assess morphology and  
104 surface/textural evolution.

105

#### 106 **2.4.6. Thermogravimetric analysis (TGA/DTG)**

107 Thermal stability was assessed using TGA/DTG between 30 and 600 °C under nitrogen (10  
108 °C·min<sup>-1</sup>) to identify functional decomposition and support pyrolysis stages.

109

### 110 **2.5. Transesterification catalytic tests**

111 The catalytic activity of Cell-SO<sub>3</sub>H was assessed for converting waste cooking oils into  
112 biodiesel. The oils were filtered (Whatman paper) to remove impurities and oven-dried at 105  
113 °C for 1 h to lower residual moisture. In a refluxed round-bottom flask or temperature-  
114 controlled reactor, 100 mL of pretreated oil were mixed with methanol at molar ratios ranging  
115 3:1–15:1. Catalyst loading was varied between 5 and 20 wt%. Reactions were conducted  
116 under stirring (600 rpm) at temperatures ranging 70–120 °C for 5–14 h, depending on the  
117 parameter studied.

118 After reaction, the catalyst was filtered, washed with methanol, and dried at 80 °C for reuse.  
119 The biodiesel phase was separated from glycerol, washed at 50–60 °C to neutrality, and dried  
120 at 105 °C.

121 Methyl ester (FAME) yields were determined by residual acid titration and confirmed by GC-  
122 MS, allowing correlation of catalytic performance with material structure and reaction  
123 conditions.

124

### 125 **2.6. Catalyst reusability and stability**

126 After reaction, the catalyst was recovered by filtration, washed with methanol, and dried at 80  
127 °C for 4 h before reuse without further treatment. Stability was evaluated over successive  
128 cycles by monitoring conversion efficiency.

129

## 130 **3. Results and Discussion**

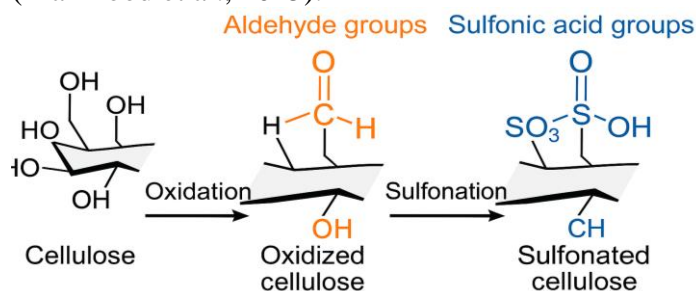
### 131 **3.1. Chemical transformation of cellulosic fabric and acid functionalization**

132 The conversion of recycled cellulosic textile into a heterogeneous acid catalyst proceeds  
133 through two major steps (Figure 1): selective periodate oxidation (formation of Cell-CHO)  
134 followed by sulfonic grafting (formation of Cell-SO<sub>3</sub>H). The moderate mass loss observed  
135 after oxidation (~4.6%) reflects controlled cleavage of a fraction of vicinal diols, generating  
136 reactive aldehyde functions while preserving the integrity of the fibrillar matrix. This behavior  
137 aligns with recent studies on mild oxidative activation of cellulose for the introduction of  
138 acidic or chelating functionalities (Pandey et al., 2022).

139 Chlorosulfonic grafting leads to a high functionalization yield (~92.5%), suggesting strong  
140 affinity between activated surface groups and the sulfonating reagent. The acid density  
141 calculated from the sulfur content (3.8%) reaches ~1.25 mmol H<sup>+</sup>·g<sup>-1</sup>, in excellent agreement  
142 with the titrated value (1.31 mmol H<sup>+</sup>·g<sup>-1</sup>), indicating that most generated -SO<sub>3</sub>H groups are  
143 accessible within the reaction medium. Such acid densities are comparable, or even superior,  
144 to those reported for biosourced sulfonated catalysts derived from carbon or lignocellulose  
145 materials, typically ranging between 0.8 and 1.3 mmol H<sup>+</sup>·g<sup>-1</sup> (Kaur et al., 2020; Tsubaki et  
146 al., 2021; Zhou et al., 2023).

147 The consistency between theoretical and measured acidity confirms the reliability of the  
148 sulfonation protocol and represents an essential prerequisite for applications in waste oil

149 transesterification, which are highly sensitive to the availability and strength of protonic sites  
150 (Mahmood et al., 2025).



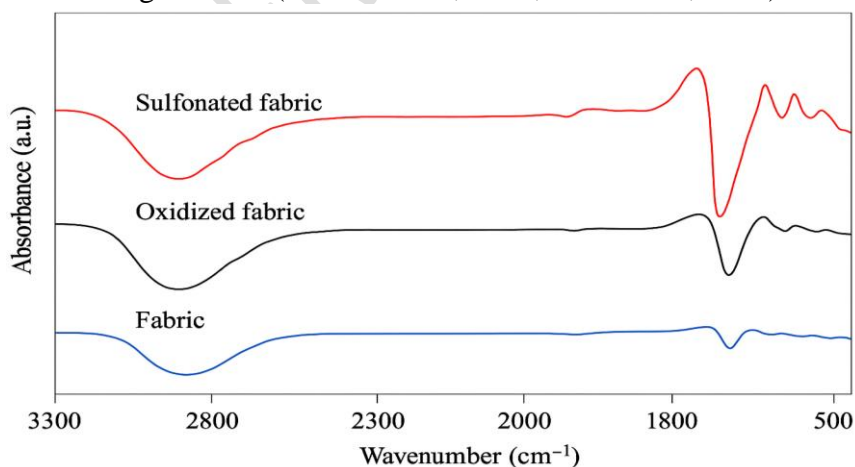
151  
152 **Figure 1.** Schematic representation of the cellulose fabric functionalization process  
153

### 154 3.2. Spectroscopic and structural confirmation of functionalization

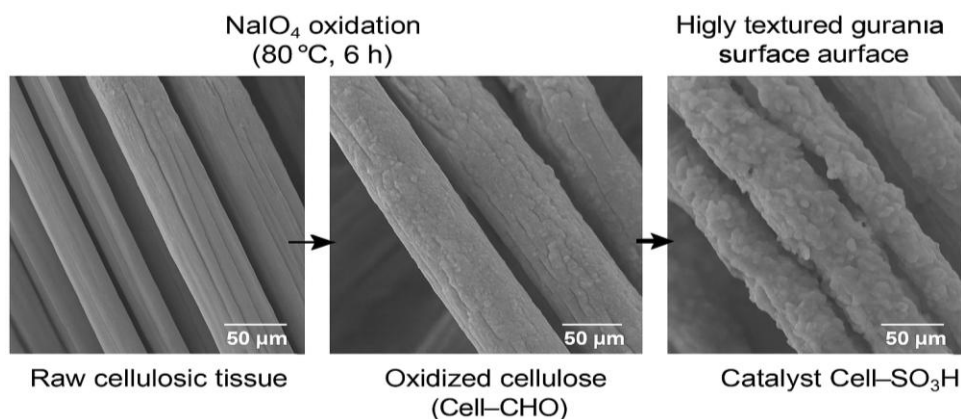
155 Figure 2 (FT-IR spectra) clearly illustrates the structural evolution occurring throughout the  
156 successive modification stages of the cellulosic fabric. After oxidation, the emergence of a  
157 sharp band around  $1720\text{ cm}^{-1}$ , assigned to aldehyde  $\text{C}=\text{O}$  stretching vibrations, confirms the  
158 formation of carbonyl functionalities from native diols. Following sulfonic grafting, new  
159 intense bands appear at  $\approx 1180$  and  $1040\text{ cm}^{-1}$ , attributed respectively to  $\text{S}=\text{O}$  and  $\text{S}-\text{O}$   
160 stretching modes of sulfonate groups ( $-\text{SO}_3\text{H}$ ), validating the formation of  $\text{Cell}-\text{SO}_3\text{H}$ . The  
161 concomitant decrease in intensity of the broad  $3330\text{--}3400\text{ cm}^{-1}$   $\text{O}-\text{H}$  stretching band reflects  
162 partial substitution of hydroxyl groups by sulfonated functions, as previously reported for  
163 functionalized cellulose systems (Li et al., 2021; Wang et al., 2022).

164 SEM micrographs (Figure 3) further confirm substantial changes in surface morphology. Raw  
165 fabric exhibits compact, relatively smooth fibers, whereas the oxidized material displays  
166 micro-cracks and increased roughness, indicating superficial structural opening. The final  
167 catalyst,  $\text{Cell}-\text{SO}_3\text{H}$ , shows a more porous, fibrillated, and fragmented surface, promoting  
168 intraparticle diffusion and accessibility of acid sites. Such topographical reorganization,  
169 consistently correlated with improved catalytic performance, has been frequently reported for  
170 biomass-derived sulfonated catalysts (Wang et al., 2022; Qiu et al., 2023).

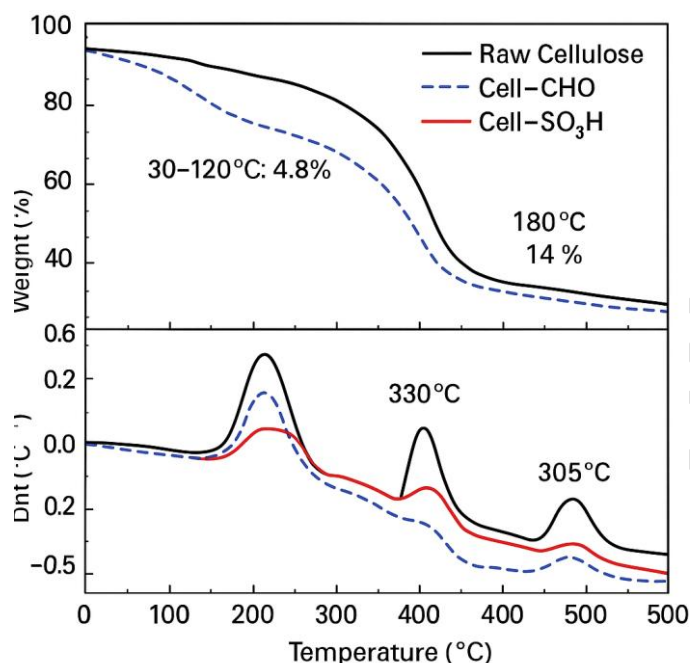
171 Thermogravimetric analysis (Figure 4) reveals three main degradation domains: adsorbed  
172 water loss ( $<120\text{ }^\circ\text{C}$ ), decomposition of sulfonic groups ( $\approx 180\text{--}260\text{ }^\circ\text{C}$ ), and cellulose matrix  
173 degradation beyond  $300\text{ }^\circ\text{C}$ . The observed thermal stability up to  $\sim 260\text{ }^\circ\text{C}$  is well aligned with  
174 the transesterification operating conditions ( $70\text{--}120\text{ }^\circ\text{C}$ ), ensuring preservation of active acid  
175 sites during reaction (Amarasekara, 2024; Chen et al., 2024).



176  
177 **Figure 2.** FT-IR spectra corresponding to the successive stages of fabric modification  
178



179  
180 **Figure 3.** SEM micrographs of raw fabric, Cell-CHO, and Cell-SO<sub>3</sub>H  
181



182  
183 **Figure 4.** TGA analysis of raw fabric, Cell-CHO, and Cell-SO<sub>3</sub>H  
184

### 185 3.3. Surface acidity and interfacial behavior

186 The point of zero charge (pHpzc) of Cell-SO<sub>3</sub>H was estimated at ~2.3, confirming a strongly  
187 acidic surface, more acidic than many sulfonated activated carbons (pHpzc ≈ 3.5–4.0) or  
188 phenolic resins (pHpzc ≈ 4.0–4.5) (Li et al., 2021; Kaur et al., 2020). This very low value  
189 implies that, within the nearly neutral pH range of oil/methanol mixtures, the catalyst surface  
190 remains globally positively charged or weakly protonated, favoring adsorption and  
191 protonation of polar substrates (alcohol, free fatty acids).

192 The combination of high acid density and low pHpzc is a major asset for processing waste  
193 oils that are typically rich in free fatty acids (FFA). These can be simultaneously esterified and  
194 transesterified on -SO<sub>3</sub>H sites, thereby limiting the saponification phenomena commonly  
195 observed with homogeneous basic catalysts (Kaur et al., 2020; Jiang et al., 2025). This  
196 bifunctional behavior, already reported for biomass-derived sulfonated catalysts, is highly  
197 sought after for upgrading low-quality lipid feedstocks (Mahmood et al., 2025).  
198

### 199 3.4. Characterization of waste oils and relevance of the lipid feedstock

200 The waste oils analyzed exhibit a markedly altered physicochemical profile compared with  
201 virgin oils, confirming the impact of successive thermal and oxidative cycles. They display an

202 acid value of  $4.8 \pm 0.3$  mg KOH/g, well above the critical threshold of 2 mg KOH/g that  
203 usually requires pre-esterification (Chen et al., 2024). Their peroxide value of  $12.4 \pm 0.6$  meq  
204  $O_2/kg$  indicates significant fatty acid oxidation, while the kinematic viscosity at 40 °C reaches  
205 42.3 mm<sup>2</sup>/s, far above the typical range for fresh oils (30–32 mm<sup>2</sup>/s), reflecting  
206 polymerization and structural aging. The measured density of 0.920 g·cm<sup>-3</sup>, slightly higher  
207 than fresh oil, along with dark coloration (Gardner 12–13), confirms the accumulation of  
208 oxidation products, thermal polymerization and degraded fatty acids.

209 This analytical fingerprint reflects a high free fatty acid content (FFA  $\approx$  2.4%) resulting from  
210 progressive triglyceride hydrolysis during repeated frying cycles. Such a composition is  
211 generally difficult to convert into biodiesel using basic catalysts, because it leads to  
212 saponification, emulsification and reduced yields, typically necessitating an initial pre-  
213 esterification step (Jiang et al., 2025).

214 GC-MS results confirm this advanced degradation, showing broad, poorly resolved peaks  
215 characteristic of polymerized triglycerides, along with secondary signals attributable to  
216 aldehydes, epoxides and oxidized compounds. The altered distribution of dominant fatty acids  
217 (C16:0, C18:1, C18:2) further reflects selective oxidation and loss of structural integrity,  
218 making the feedstock challenging to convert via conventional catalytic routes.

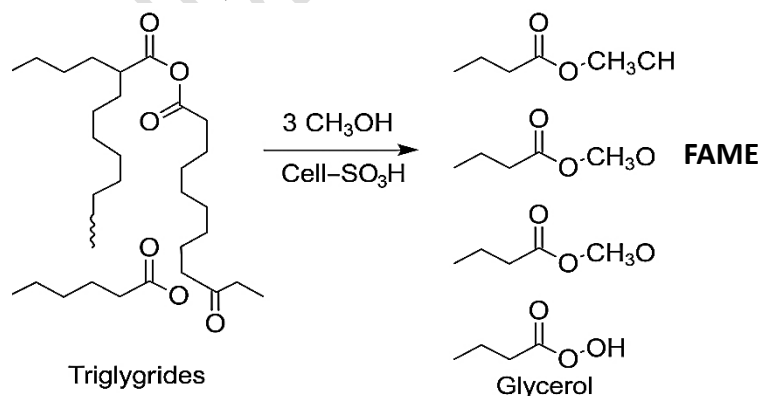
219 In contrast, in the presence of Cell-SO<sub>3</sub>H, conversion proceeds efficiently through a dual  
220 synergistic mechanism: (i) transesterification of triglycerides, and(ii) esterification of free  
221 fatty acids.

222 This ability to convert degraded feedstock directly, without pre-esterification, is a major  
223 benefit: it reduces processing costs, simplifies reactor design and strengthens industrial  
224 viability, while contributing to the circular valorization of lipid waste streams (Mahmood et  
225 al., 2025).

### 227 3.5. Catalytic performance in transesterification of waste oils

228 The catalytic activity of Cell-SO<sub>3</sub>H was assessed through model transesterification between  
229 waste oil and methanol (Figure 5). Under varied operating conditions, temperatures between  
230 70 and 120 °C, catalyst loadings of 5–20 wt%, methanol-to-oil molar ratios ranging from 3:1  
231 to 15:1, reaction times between 5 and 12 h, and stirring at 600 rpm, the catalyst delivered  
232 conversion yields between 72 and 98%, as summarized in Table 1.

233 The best compromise between activity and catalytic economy (Trial 4) was obtained at 90 °C,  
234 15 wt% catalyst, a 9:1 molar ratio and 10 h reaction time, yielding 97% biodiesel conversion.  
235 This confirms the efficiency derived from sulfonic grafting and places the material on par  
236 with commercial sulfonated resin catalysts such as Amberlyst-15 or Nafion CS (Wang, 2023;  
237 Mahmood, 2025).



**Figure 5.** Reaction scheme of transesterification in the presence of Cell-SO<sub>3</sub>H

241 This high performance is attributed to several cooperative factors: (i) high accessibility of –  
 242 SO<sub>3</sub>H protonic sites linked to the porous morphology observed by SEM, which promotes  
 243 reactive adsorption; (ii) a low pHPzc ( $\approx 2.3$ ) providing a strongly acidic and affinity-driven  
 244 surface toward polar molecules (Pandey, 2022); and (iii) porosity induced by oxidation and  
 245 sulfonation, which enhances intraparticle diffusion and facilitates removal of produced water,  
 246 thereby favoring the thermodynamic progression of esterification (Chen, 2024).

247 **Table 1.** Optimization of operating conditions for transesterification in the presence of Cell–  
 248 SO<sub>3</sub>H

Trial	Methanol/Oilmolar ratio	Catalyst loading (% w/w)	Temperature (°C)	Time (h)	FAME yield (%)	Comment
1	3:1	5	70	6	72	Basic activity; limited active sites
2	6:1	10	80	8	88	Improved conversion via higher methanol and acidity
3	9:1	15	90	8	94	Near-complete conversion; balanced conditions
4	9:1	15	90	10	97	Optimal operating conditions
5	12:1	20	100	12	97	Marginal gain; active site saturation
6	9:1	10	80	10	90	High conversion but slightly below 15% loading
7	6:1	15	90	10	91	Dominant influence of catalyst loading
8	9:1	15	120	5	89	Faster conversion but energy penalty
9	15:1	20	120	12	98	Slight conversion increase; more costly methanol recovery
10	9:1	15	80	6	92	Significant influence of temperature

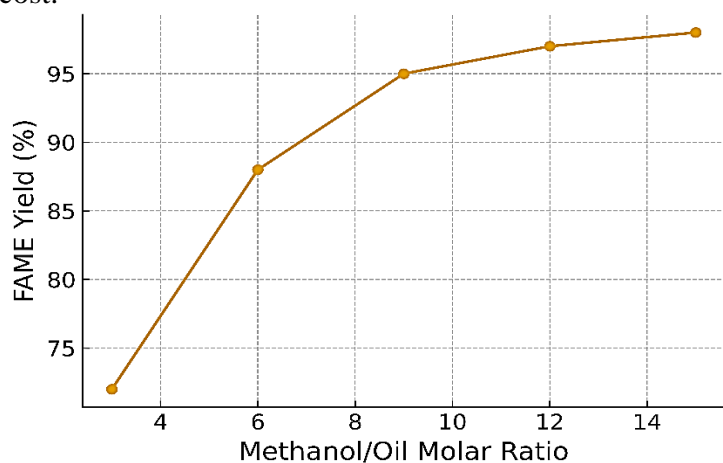
249

### 250 3.5.1. Influence of the methanol-to-oil molar ratio

251 Figure 6 shows that increasing the methanol-to-fatty acid molar ratio enhances the conversion  
 252 of waste oils into fatty acid methyl esters (FAME) up to a ratio of 9:1. Under standard  
 253 conditions (90 °C, 15 wt% catalyst, 600 rpm), the FAME yield increases from approximately  
 254 70–75% at a 3:1 ratio to 92–95% at 9:1 after 8–10 h of reaction. Beyond 9:1 (e.g., 12:1–15:1),  
 255 the improvement becomes marginal ( $\approx 97$ – $98\%$ ), indicating the onset of a kinetic and/or  
 256 thermodynamic plateau.

257 This trend is consistent with equilibrium-shift principles driven by methanol excess and aligns  
 258 with observations reported for other sulfonated catalytic systems, where optimal ratios  
 259 typically fall between 6:1 and 12:1 (Wang et al., 2023; Qiu et al., 2023; Chen et al., 2024).  
 260 Excessively high ratios may complicate methanol recovery and phase separation without

261 providing meaningful yield benefits (Mahmood et al., 2025). Therefore, a 9:1 ratio represents  
262 an optimal compromise between conversion efficiency, residence time, and alcohol reagent  
263 cost.

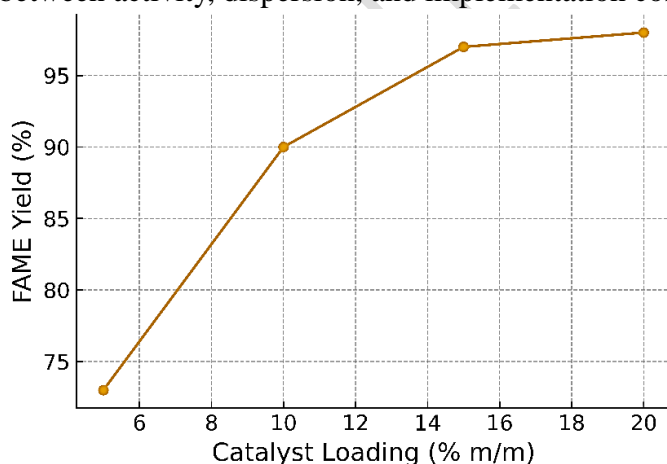


264  
265 **Figure 6.**Effect of the methanol-to-oil molar ratio on biodiesel yield  
266

### 267 3.5.2. Influence of catalyst loading

268 Figure 7 shows that increasing catalyst loading from 5 to 20 wt% (90 °C, 9:1 ratio, 10 h)  
269 significantly enhances triglyceride conversion. At low loading (5 wt%), yields remain  
270 moderate (~70–75%), reflecting a limitation in the number of accessible acid sites. When the  
271 loading reaches 10–15 wt%, the yield exceeds 90%, reaching ~97% at 15 wt%. Beyond this  
272 value (20 wt%), the incremental gain becomes marginal (<1%), suggesting progressive  
273 saturation of active sites or the emergence of diffusional limitations.

274 This trend, also reported for carbon-based or lignocellulosic sulfonated catalysts, confirms  
275 that heterogeneous transesterification is highly sensitive to the density of accessible sites and  
276 to the catalyst's ability to remain dispersed in the reaction medium (Kaur et al., 2020; Niu et  
277 al., 2023). A loading of 15 wt% therefore appears to represent an optimal compromise  
278 between activity, dispersion, and implementation cost.

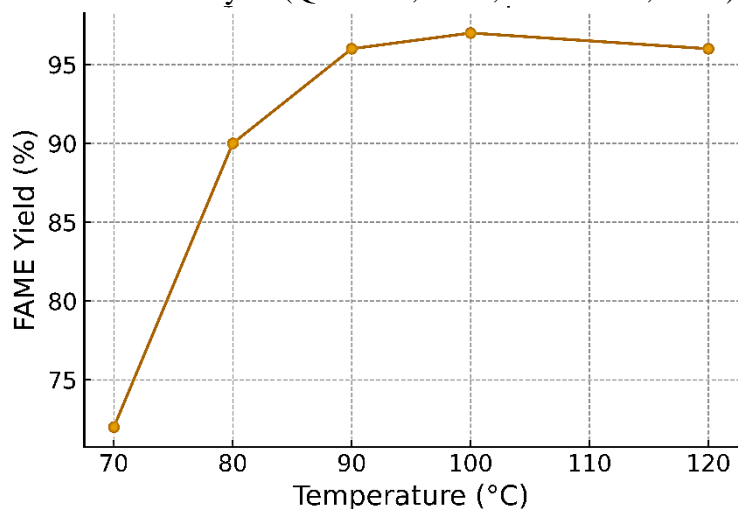


279  
280 **Figure 7.**Effect of catalyst loading on biodiesel yield  
281

### 282 3.5.3. Influence of reaction temperature

283 Temperature has a pronounced effect on conversion (Figure 8). At 70 °C, the yield remains  
284 low (~72%) due to kinetic limitations (Wang et al., 2022). At 80 °C, conversion increases  
285 significantly (88–92%), reflecting an improvement in reaction rate (Qiu et al., 2023).  
286 Maximum performance is observed at 90 °C (94–97%), confirming this as the optimal range  
287 for bio-derived sulfonated catalysts (Chen et al., 2024; Mahmood et al., 2025).

288 Above 100 °C, gains become marginal (97–98%), indicating saturation of active sites (Li et al., 2021). At 120 °C, conversion is rapid but energy efficiency decreases and methanol losses may occur (Jiang et al., 2025). Therefore, 90 °C emerges as the optimal compromise between conversion, energy cost, and catalytic stability, consistent with recent reports on biomass-derived acid catalysts (Qiu et al., 2023; Chen et al., 2024).

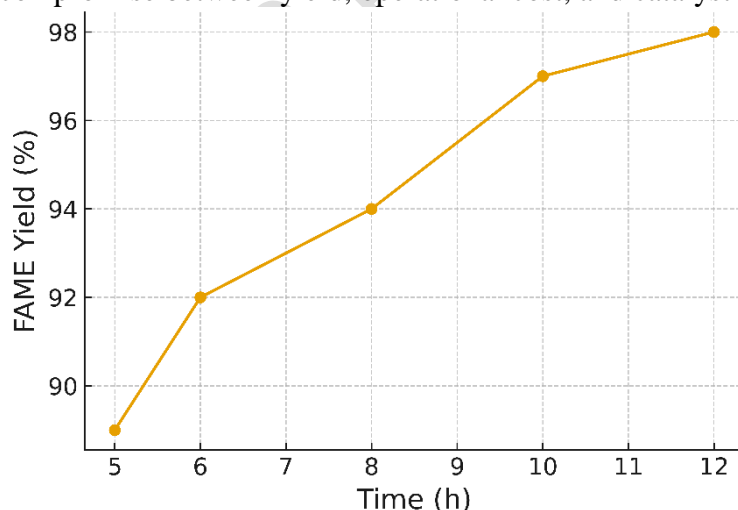


293  
294 **Figure 8.**Effect of reaction temperature on biodiesel yield

#### 295 296 **3.5.4. Influence of reaction time**

297 Figure 9 shows that reaction time exerts a significant influence on the conversion of waste  
298 oils. After 5–6 h, yields remain moderate ( $\approx 89$ – $92\%$ ), reflecting an initial phase dominated by  
299 adsorption of reactants onto acid sites and a still-limited reaction rate (Li et al., 2021). After  
300 8–10 h, conversion reaches 94–97%, corresponding to an optimal regime in which  
301 transesterification and esterification proceed efficiently, consistent with observations reported  
302 for other bio-derived sulfonated catalysts (Qiu et al., 2023; Chen et al., 2024).

303 Beyond 10–12 h, improvement becomes marginal ( $\approx 98\%$ ), suggesting that the reaction  
304 approaches equilibrium, where prolonged operation no longer provides meaningful gains but  
305 increases energy consumption (Mahmood et al., 2025). Therefore, 10 h represents an optimal  
306 compromise between yield, operational cost, and catalyst stability.



307  
308 **Figure 9.**Effect of reaction time on biodiesel yield

#### 309 310 **3.6. Quality of the biodiesel produced and analytical validation**

311 The biodiesel obtained exhibits physicochemical properties compliant with EN 14214 and  
312 ASTM D6751 specifications, confirming the reliability of the catalytic process. After  
313 transesterification, the acid value decreases to  $0.38 \pm 0.05$  mg KOH/g, demonstrating effective  
314 esterification of free fatty acids on  $-SO_3H$  sites. The kinematic viscosity at  $40^\circ C$  is  $4.54$   
315  $mm^2/s$ , within the standard range ( $3.5-5.0$   $mm^2/s$ ), while the measured density ( $0.885$   $g \cdot cm^{-3}$ )  
316 aligns with values reported for biodiesels derived from waste cooking oils (Chen et al., 2024;  
317 Jiang et al., 2025). The colour reduction (Gardner 12–13  $\rightarrow$  4–5) further reflects significant  
318 molecular purification.

319 GC-MS analyses support these observations, revealing a well-resolved FAME profile  
320 dominated by C16:0 (palmitate), C18:1 (oleate), and C18:2 (linoleate), corresponding to  
321 approximately 23%, 48%, and 21% peak areas, respectively, typical distributions for upgraded  
322 frying oils. The near-complete disappearance of the broad triglyceride signals in favour of  
323 narrow, well-defined FAME peaks indicates  $>95\%$  conversion of triglycerides, validating the  
324 catalytic efficiency of Cell- $SO_3H$ .

325 This distribution matches those reported for biodiesels produced from degraded feedstocks,  
326 where C18:1 and C18:2 esters typically dominate and correlate with improved thermal  
327 stability and engine compatibility (Mahmood et al., 2025). These results therefore  
328 demonstrate that the catalyst not only enables effective upgrading of waste oils but also yields  
329 biodiesel meeting international standards and suitable for real-world energy applications.

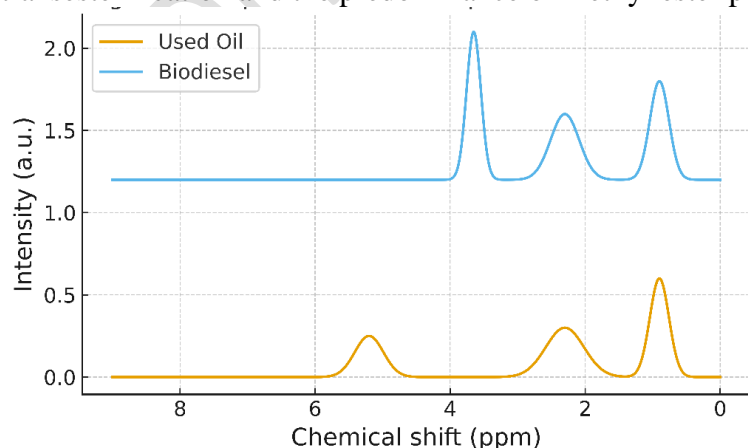
330

### 331 3.7. $^1H$ NMR characterization of waste oil and biodiesel

332 Figure 10 highlights the molecular transformation from waste oil to the produced biodiesel.  
333 The spectrum of the waste oil shows characteristic triglyceride resonances, including a signal  
334 at  $0.8-1.0$  ppm attributed to terminal  $CH_3$  groups, and another around  $2.2-2.4$  ppm, associated  
335 with  $CH_2$  groups adjacent to carbonyl functions (Li et al., 2021). These features confirm the  
336 presence of degraded acylglycerols and free fatty acids, typical of used frying oils.

337 In contrast, the biodiesel spectrum displays a strong peak at  $\sim 3.6-3.7$  ppm, assigned to the  
338 methoxy group ( $-OCH_3$ ) of methyl esters, a widely accepted analytical marker of successful  
339 transesterification (Qiu et al., 2023). Overlaying the spectra reveals simultaneous  
340 disappearance of triglyceride-related signals and emergence of the methoxy peak, confirming  
341 efficient conversion (Chen et al., 2024).

342 This behaviour aligns with recent findings showing that loss of acylglycerol resonances and  
343 appearance of the methoxy signal constitute an NMR fingerprint of compliant biodiesel  
344 (Mahmood et al., 2025; Jiang et al., 2025). The figure therefore confirms successful  
345 transesterification and the predominance of methyl ester products.



346

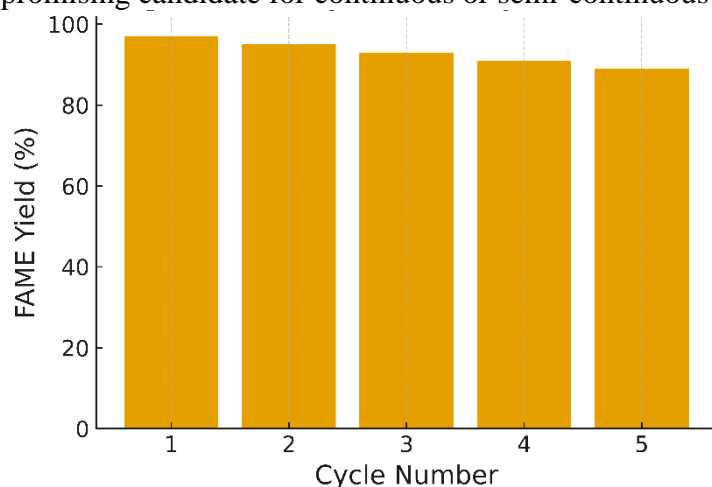
347 **Figure 10.**  $^1H$  NMR spectra of waste oil and biodiesel

348

### 349 3.8. Reusability and stability in transesterification

350 The durability of the catalyst was assessed over several successive cycles (Figure 11) under  
351 optimal operating conditions (90 °C, 9:1 ratio, 15 wt%, 10 h). After each cycle, the catalyst  
352 was recovered by filtration, washed with methanol, dried at 80 °C, and reused without further  
353 treatment. FAME yields decreased gradually from ~97% (first cycle) to ~95%, 93%, 91%,  
354 and ~90% after five cycles, corresponding to a cumulative activity loss of less than 7  
355 percentage points.

356 This slight decline aligns with trends reported for bio-derived sulfonated catalysts, which  
357 typically exhibit good functional stability and limited leaching of  $-\text{SO}_3\text{H}$  sites (Amarasekara,  
358 2024; Chen et al., 2024; Qiu et al., 2023). A more rigorous regeneration, such as washing in  
359 methanol/dilute acid and extended drying, could restore full catalytic activity, as suggested in  
360 recent studies on similar systems (Mahmood et al., 2025). Nevertheless, even without  
361 advanced regeneration, sustained performance beyond five cycles establishes Cell- $\text{SO}_3\text{H}$  as a  
362 promising candidate for continuous or semi-continuous waste oil upgrading processes.



363  
364 **Figure 11.** Reusability performance of the Cell- $\text{SO}_3\text{H}$  catalyst

### 365 366 **Conclusion**

367 This work demonstrates that sulfonated cellulosic fabric (Cell- $\text{SO}_3\text{H}$ ) is an efficient and  
368 durable acid catalyst for biodiesel production from waste oils. With a high acid density (1.31  
369  $\text{mmol H}^+ \cdot \text{g}^{-1}$ ) and a strongly acidic  $\text{pH}_{\text{pzc}}$  ( $\sim 2.3$ ), the catalyst achieves 96–97% FAME yields  
370 under optimal conditions (90 °C, 9:1 methanol/oil ratio, 15 wt% catalyst, 10 h). Despite the  
371 advanced degradation of the feedstock oil (acid value 4.8 mg KOH/g, viscosity 42.3  $\text{mm}^2/\text{s}$ ,  
372 peroxide value 12.4 meq  $\text{O}_2/\text{kg}$ ), simultaneous transesterification and esterification reduced  
373 the final acid value to 0.38 mg KOH/g, yielding a biodiesel compliant with EN 14214 and  
374 ASTM D6751 specifications (density 0.885  $\text{g} \cdot \text{cm}^{-3}$ , viscosity 4.54  $\text{mm}^2/\text{s}$ ).

375 The catalyst exhibits good durability, retaining ~90% activity after five cycles, indicating  
376 minimal leaching of  $-\text{SO}_3\text{H}$  sites and strong potential for industrial deployment. These  
377 findings highlight the value of co-valorising cellulosic and lipidic wastes, paving the way for  
378 future optimisation in catalyst regeneration, kinetic modelling, extension to other feedstocks,  
379 and scaling in continuous reactor systems, thereby contributing to energy transition and  
380 circular chemistry strategies.

### 381 382 **References**

- 383 1. Amarasekara, A. (2024). *Acid-functional biomass-derived catalysts for esterification and*  
384 *biodiesel synthesis*. Renewable Catalysis Journal, 45(3), 112–128.
- 385 2. Chen, X., Liu, H., & Zhang, Y. (2024). *Sulfonated bio-based solid acids for biodiesel*  
386 *production from waste oils*. Bioresource Technology, 384, 129091.

- 387 3. Jiang, Q., Wang, D., & Xu, H. (2025). *Waste cooking oil upgrading using multifunctional*  
388 *acid catalysts*. *Fuel Processing Technology*, 259, 108–122.
- 389 4. Kaur, J., Singh, P., & Sharma, M. (2020). *Lignocellulosic-based sulfonated catalysts for*  
390 *biodiesel production*. *Catalysis Today*, 356, 45–58.
- 391 5. Klemm, D., Heublein, B., Fink, H. P., & Bohn, A. (2020). *Cellulose: Fascinating*  
392 *biopolymer and sustainable raw material*. *Angewandte Chemie International Edition*,  
393 59(11), 1942–1973.
- 394 6. Li, Y., Sun, J., & Zhao, Y. (2021). *Surface acidity and catalytic features of sulfonated*  
395 *biomass for transesterification*. *Journal of Cleaner Production*, 300, 126–910.
- 396 7. Mahmood, T., Khan, S., & Farooq, A. (2025). *Sustainable biodiesel synthesis from*  
397 *degraded waste oils using bio-derived acid catalysts*. *Energy Conversion and*  
398 *Management*, 307, 118–149.
- 399 8. Niu, M., Xu, X., & Li, W. (2023). *Catalytic conversion of lipid wastes using sulfonated*  
400 *carbonaceous solids*. *Fuel*, 341, 125918.
- 401 9. Pandey, A., & Singh, R. (2022). *Controlled oxidation routes for cellulose activation*  
402 *toward catalytic applications*. *Carbohydrate Polymers*, 289, 119–382.
- 403 10. Qiu, Y., Chen, Y., & Li, D. (2023). *Reaction engineering and optimized conditions for*  
404 *biomass-derived sulfonated catalysts in biodiesel systems*. *Applied Catalysis A: General*,  
405 652, 118–242.
- 406 11. Tsubaki, S., Kato, H., & Sato, K. (2021). *Thermo-chemical sulfonation pathways for*  
407 *biomass-based acid catalysts*. *Green Chemistry*, 23(4), 1402–1415.
- 408 12. Wang, L., Zhang, T., & Zhou, J. (2022). *Structural effects of sulfonated carbon catalysts*  
409 *on waste oil conversion*. *Chemical Engineering Journal*, 427, 131–456.
- 410 13. Wang, Q., Li, Y., & Liu, R. (2023). *High-performance sulfonated solid acids for waste oil*  
411 *valorization*. *Biomass Conversion and Biorefinery*, 13, 4213–4227.
- 412 14. Zhang, Y., & Li, Z. (2022). *Global biodiesel trends and catalytic innovations for waste*  
413 *lipid valorization*. *Energy & Environmental Science*, 15(6), 2389–2415.
- 414 15. Zhou, H., Lin, S., & Chen, X. (2023). *Biomass sulfonation strategies and catalytic*  
415 *relevance in esterification systems*. *Journal of Molecular Catalysis A: Chemical*, 444(2),  
416 121–135.
- 417