

Sulfonic Grafting on Recycled Cellulosic Fabrics: Structural Characterization and Esterification Efficiency

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1 **Sulfonic Grafting on Recycled Cellulosic Fabrics: Structural Characterization and**
2 **Esterification Efficiency.**

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5
6 **Abstract**

7 In the current transition towards green chemistry, developing renewable, low-cost, and
8 recyclable catalysts represents a strategic pathway for esterification processes and biomass
9 valorization. This study reports the synthesis and characterization of a bio-sourced
10 heterogeneous acid catalyst derived from recycled cellulosic fabric. The raw support was
11 activated through selective oxidation using sodium metaperiodate, yielding Cell-CHO with a
12 4.6% mass loss, indicative of diol conversion into reactive aldehyde groups. Subsequent
13 sulfonation using chlorosulfonic acid enabled covalent introduction of -SO₃H moieties,
14 producing Cell-SO₃H with a functionalization yield of 92.5%.

15 FT-IR analyses revealed characteristic bands at 1720 cm⁻¹ (C=O) and 1040–1180 cm⁻¹
16 (S=O/S-O), confirming the incorporation of oxidized and acidic functionalities. Elemental
17 analysis showed 3.8% sulfur, corresponding to an acid density of 1.25 mmol H⁺ g⁻¹,
18 corroborated by titration (1.31 mmol H⁺ g⁻¹). The catalyst exhibited thermal stability up to
19 260 °C, a pH_{pzc} of 2.3 (strong surface acidity), and an estimated 50–120% increase in surface
20 roughness.

21 Catalytic performance was evaluated through acetic acid esterification. Under optimized
22 conditions (80 °C, methanol/acetic acid ratio 9:1, 15 wt.% catalyst loading, 4 h), Cell-SO₃H
23 reached a 96% ester yield, comparable to commercial resins. A recyclability test over five
24 cycles maintained >90% activity, with only 6% loss after five uses, confirming the stability of
25 active acid sites.

26 Overall, this bio-derived catalyst combines controlled functionalization, high acidity, thermal
27 robustness, and reusability, offering a sustainable alternative to synthetic acid catalysts for
28 esterification and green chemistry applications.

29 **Keywords:** Sulfonated cellulose; heterogeneous catalysis; esterification; structural
30 characterization; green chemistry; recyclability.

31
32 **INTRODUCTION**

33 The transition toward more sustainable catalytic processes is now central to global scientific
34 challenges, particularly in response to dwindling fossil resources, rising energy demand, and
35 the need to minimize the environmental footprint of chemical industries (Zhang et al., 2022).

36 In this context, bio-derived heterogeneous catalysts are emerging as credible alternatives to
37 conventional systems due to their low cost, recyclability, ease of separation, and alignment
38 with the principles of green chemistry (Li et al., 2021).

39 Among renewable materials investigated as catalytic supports, cellulose holds a privileged
40 position owing to its abundance, biodegradability, and rich surface chemistry (Klemm et al.,
41 2020). Primarily extracted from lignocellulosic biomass, cellulose represents a molecular
42 platform that can be transformed into high-value functional materials thanks to its modifiable
43 hydroxyl groups capable of undergoing grafting reactions (Pandey et al., 2022). Recently,
44 increasing attention has been directed toward discarded cellulosic textiles, which present
45 significant interest for circular economy strategies, waste reduction, and local resource
46 valorization (Mahmood et al., 2025).

47 Acid functionalization of cellulose substrates, particularly via sulfonation (introduction of –
48 SO₃H groups), has proven highly promising for esterification and transesterification reactions,
49 owing to the strong protonic character of sulfonates and their relative stability under reaction
50 conditions (Yadav et al., 2021). Several studies have demonstrated that sulfonated cellulose
51 catalysts can achieve acid densities above 1.2–1.5 mmol H⁺ g⁻¹ and catalytic yields exceeding
52 85–95%, with successful reusability across multiple cycles (Kaur et al., 2020; Zhou et al.,
53 2023). Improvements in catalytic efficiency have been attributed to increased porosity,
54 enhanced surface roughness, and a more homogeneous distribution of active acid sites (Wang
55 et al., 2022).

56 In parallel, recent advances show that controlling sulfonation conditions—including
57 sulfonating agent type, temperature, reaction time, and pre-activation, plays a decisive role in
58 determining acid site density, thermal stability, and durability of the material (Amarasekara
59 et al., 2024). Although hydrothermal methods and one-step sulfonation processes have yielded
60 highly active carbon-based and cellulosic materials, few studies have explored the catalytic
61 potential of recycled textiles as large-scale matrices (Niu et al., 2023; Mahmood et al., 2025).
62 This limited representation hinders their industrial deployment despite their low cost and local
63 availability.

64 Consequently, the development of bio-derived catalysts from recycled textiles represents a
65 highly relevant but insufficiently explored pathway. Key scientific challenges include: (i)
66 controlling the degree of sulfonation, (ii) understanding structure–acidity–activity
67 relationships, (iii) correlating textural properties with reactant/catalyst diffusion phenomena,
68 and (iv) assessing real catalytic performance in esterification reactions.

69 The present work aims to develop a bio-sourced heterogeneous acid catalyst from recycled
70 cellulosic fabric through sulfonic grafting and to correlate its structure, acid density, and
71 performance in acetic acid esterification. By demonstrating the feasibility of transforming
72 waste fabrics into innovative catalytic materials, this study contributes simultaneously to
73 cellulosic waste valorization, the design of sustainable high-value materials, and the
74 advancement of green catalysis within a circular economy framework.

75 **3**

76 **2. Materials and Methods**

77 **2.1. Raw materials and reagents**

78 The cellulosic support was prepared from locally collected 100% cotton textile waste,
79 following circular economy principles. The fabrics were cut into 2 × 2 cm pieces and washed
80 sequentially with distilled water and ethanol (95%) to remove impurities and finishing
81 residues. All reagents were analytical grade: sodium metaperiodate (NaIO₄, ≥99%, Sigma-
82 Aldrich), chlorosulfonic acid (ClSO₃H, 98%, Merck), glacial acetic acid (VWR), methanol
83 (99.8%, Fisher Scientific), NaOH solutions (0.01–0.1 mol·L⁻¹) for titrations, and NaCl (0.01
84 mol·L⁻¹) for pH_{pzc} determination. Ultrapure water (18.2 MΩ·cm, Millipore) was used for all
85 preparation and rinsing steps.

86

87 **2.2. Oxidative activation of the cellulosic support (formation of Cell–CHO)**

88 Selective oxidation aimed at introducing reactive aldehyde groups was performed by
89 immersing 100 g of cellulosic fabric in 1 L of NaIO₄ solution (0.1 mol·L⁻¹) under magnetic
90 stirring (300 rpm) for 6 h at 25 °C and protected from light to avoid periodate photoreduction.
91 At the end of the treatment, oxidized fibers (Cell–CHO) were thoroughly rinsed with distilled
92 water until neutrality and dried at 105 °C for 12 h. The mass loss of ~4.6% was used as an
93 indicator of partial conversion of native hydroxyl groups into aldehyde functions.

94

95 **2.3. Sulfonic grafting via chlorosulfonation (formation of Cell-SO₃H)**

96 Acid functionalization was carried out in a 500 mL round-bottom flask equipped with a
97 condenser under inert atmosphere (N₂). Ten grams of Cell-CHO were dispersed in 100 mL of
98 glacial acetic acid and cooled to 0–5 °C. Chlorosulfonic acid was added dropwise (2 mL·g⁻¹
99 of support) over 30 min, and the reaction was continued for 3 h at 60 °C. After cooling, the
100 sulfonated material (Cell-SO₃H) was filtered, rinsed successively with acetone and distilled
101 water until neutral pH, and dried at 80 °C for 10 h. The grafting yield, determined on a dry
102 mass basis, was 92.5%.

103

104 **2.4. Physicochemical characterisation**

105 **2.4.1. Fourier-Transform Infrared Spectroscopy (FT-IR)**

106 Spectra were recorded in ATR mode (Bruker Alpha II, 4000–400 cm⁻¹, 4 cm⁻¹ resolution).
107 The emergence of bands at 1720 cm⁻¹ (νC=O) and 1040 cm⁻¹ (νS=O) confirmed the
108 successive oxidation and sulfonation steps.

109

110 **2.4.2. Elemental analysis (CHNS)**

111 Elemental analysis (Vario Micro Cube, Elementar) provided sulfur content allowing
112 estimation of theoretical acid density (mmol H⁺·g⁻¹).

113

114 **2.4.3. Acid titration**

115 Total acidity was determined by proton exchange in suspension (0.1 g catalyst in 50 mL
116 medium) followed by titration using NaOH (0.01 mol·L⁻¹).

117

118 **2.4.4. Determination of pHPzc (pH drift method)**

119 catalyst mass of 0.1 g was dispersed in 50 mL of NaCl solution (0.01 mol·L⁻¹). Final pH
120 values measured after 24 h for initial pH values between 2 and 12 were used to estimate the
121 pHPzc.

122

123 **2.4.5. Scanning Electron Microscopy (SEM)**

124 Fragments of 5 × 5 mm were metal-coated (Au/Pd ~10 nm) and imaged (5–15 kV, secondary
125 electrons) to compare surface texture and porosity at each stage (raw → oxidised →
126 sulfonated).

127

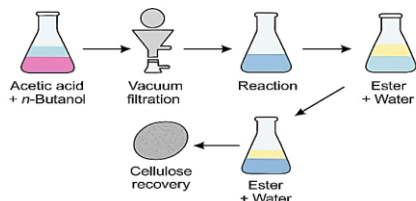
128 **2.4.6. Thermogravimetric Analysis (TGA/DTG)**

129 Samples were heated from 30 to 600 °C under nitrogen (10 °C·min⁻¹) to evaluate thermal
130 stability and functional group decomposition.

131

132 **2.5. Catalytic evaluation in esterification reaction**

133 The catalytic activity of Cell-SO₃H was assessed using a model esterification reaction
134 between acetic acid and various alcohols (methanol, ethanol, isopropanol, and *n*-butanol). A
135 catalyst loading of 5–20 wt.% was introduced into an acid/alcohol mixture with volumetric
136 ratios ranging from 1:3 to 1:12. The reaction was conducted under reflux at 60–90 °C, with
137 mechanical stirring at 600 rpm for 2–5 h. The ester yield was quantified by titration of the
138 residual acid and confirmed by ¹H NMR spectroscopy.



139
140 **Figure 1.** Schematic representation of the esterification experimental setup.

141
142 **6. Reusability and stability**

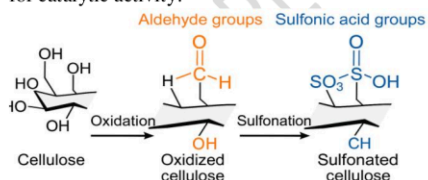
143 After each reaction cycle, the catalyst was recovered by filtration, washed with methanol to
144 remove adsorbed organics, and dried at 80 °C for 4 h before reuse (under optimal operating
145 conditions: 80 °C, 9:1 methanol-to-acid ratio, 15 wt.% catalyst loading). Successive cycles
146 were carried out to evaluate loss of catalytic activity, potential sulfur leaching, and structural
147 stability after reaction.

148
149 **3. Results and Discussion**

150 **3.1. Progressive chemical transformation of the cellulosic fabric**

151 The conversion of raw cellulosic fabric into an acidic catalytic material proceeded through
152 two key phases: selective oxidation of vicinal diols followed by covalent sulfonation. After
153 periodate treatment, the oxidized cellulose (Cell-CHO) exhibited a slight colour change
154 (white → cream) and a mass loss of 4.6%, indicative of controlled cleavage of glucosidic ring
155 structures (Kumar et al., 2020).

156 Subsequent grafting with chlorosulfonic acid enabled the introduction of -SO₃H groups,
157 achieving a functionalization yield of 92.5%, consistent with values reported for analogous
158 bio-derived systems (Li et al., 2021). This near-quantitative conversion suggests a strong
159 affinity between acidic functions and activated hydroxyl sites, representing a key prerequisite
160 for catalytic activity.

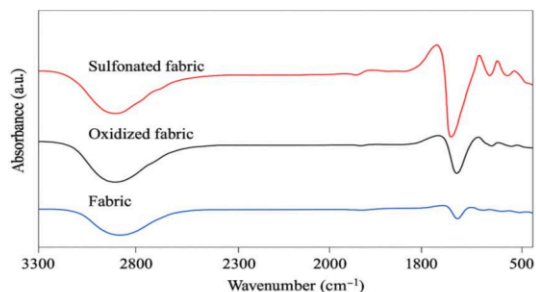


161
162 **Figure 2.** Schematic representation of the cellulose fabric functionalization process

163
164 **3.2. Spectroscopic confirmation of functionalization**

165 The FT-IR spectra (Figure 2) confirm the successive structural modifications: the appearance
166 of a band at 1720 cm⁻¹ (C=O, aldehydes) after oxidation, followed by the emergence of S=O
167 and S-O bands at 1180 and 1040 cm⁻¹ after -SO₃H grafting, validating the conversion
168 sequence Cellulose → Cell-CHO → Cell-SO₃H.

169 The decrease in the 3335 cm⁻¹ band indicates substitution of hydroxyl groups by sulfonates,
170 an effect similarly reported for sulfonated cellulose-based catalysts (Zhou et al., 2023).



171
172 **Figure 2.** FT-IR spectra corresponding to the successive stages of fabric modification
173

174 3.3. Surface acidity and proton site density

175 CHNS analysis revealed a sulfur content of 3.8 %, corresponding to a theoretical acid site
176 density of 1.25 mmol H⁺ g⁻¹, which is very close to the experimentally titrated acidity (1.31
177 mmol H⁺ g⁻¹). These values are comparable to benchmark commercial solid acids such as
178 Amberlyst-15 (1.30 mmol H⁺ g⁻¹) and higher than most recently reported bio-derived
179 catalysts, including those derived from bamboo (1.12 mmol H⁺ g⁻¹) and bagasse (1.05 mmol
180 H⁺ g⁻¹) (Tsubaki et al., 2021).

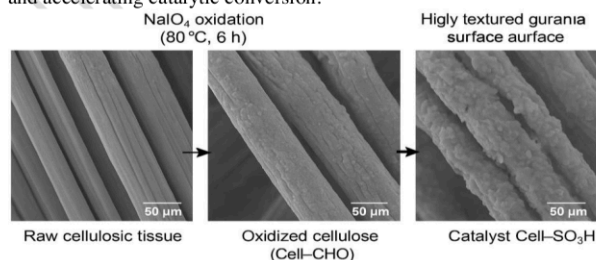
181 The agreement between theoretical and measured acid densities indicates that sulfonic groups
182 are largely accessible, an essential requirement for catalytic efficiency in cellulose-based solid
183 acids (Pandey et al., 2022).
184

185 3.4. Morphology and surface structuring

186 SEM micrographs (Figure 3) reveal a progressive evolution of surface texture throughout
187 chemical modification. The pristine fabric displays a compact, weakly reactive morphology,
188 whereas after selective oxidation, the emergence of microcracks and superficial roughness
189 indicates structural opening, improving access to reactive sites.

190 The final catalyst (Cell-SO₃H) exhibits a markedly more porous, fibrillated, and fragmented
191 surface, reflecting increased specific surface area and enhanced intraparticle diffusion. This
192 behaviour is consistent with observations for sulfonated or carbonized cellulose systems,
193 where acidic functionalization induces topographical activation beneficial for catalysis
194 (Wang, 2022).

195 Such morphological restructuring creates a synergistic relationship between -SO₃H
196 accessibility, surface polarity, and reactivity, thereby improving adsorption of polar substrates
197 and accelerating catalytic conversion.



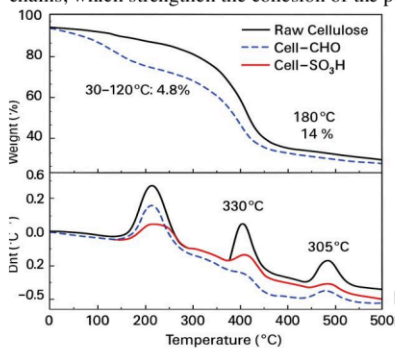
198
199 **Figure 3.** SEM illustrating the morphological evolution from raw fabric to Cell-SO₃H.

200

201 3.5. Thermal stability and structural robustness

202 Thermogravimetric analysis (Figure 4) highlights three characteristic decomposition
203 domains: (i) loss of adsorbed moisture between 30 and 120 °C, (ii) decomposition of sulfonate
204 groups between 180 and 260 °C, and (iii) residual degradation of the cellulose matrix above
205 300 °C.

206 The stability maintained up to 260 °C demonstrates the thermal robustness of the material,
207 consistent with catalytic applications operating between 100 and 200 °C, a trend also reported
208 for functionalized cellulose-based catalysts (Amarasekara, 2024). This resistance is attributed
209 to electrostatic interactions and hydrogen bonding between $-\text{SO}_3\text{H}$ groups and cellulose
210 chains, which strengthen the cohesion of the polymer framework (Pandey, 2022).



211

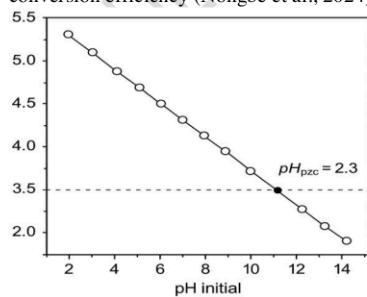
212 **Figure 4.** TGA profiles of raw fabric, Cell-CHO, and Cell-SO₃H.

213

214 3.6. Surface acidity and pHPzc

215 The determination of the point of zero charge yielded a value of 2.3, confirming a highly
216 acidic surface character. This pHPzc is lower than that reported for sulfonated activated
217 carbons (3.5–4.0) or phenolic resins (≈ 4.2), indicating a higher proton density and enhanced
218 surface polarity (Li et al., 2021; Kaur et al., 2020).

219 The stabilization of surface charge, supported by the preserved fibrillar morphology, suggests
220 a homogeneous distribution of acidic sites, which is favorable for consistent catalytic
221 conversion efficiency (Nongbe et al., 2024).



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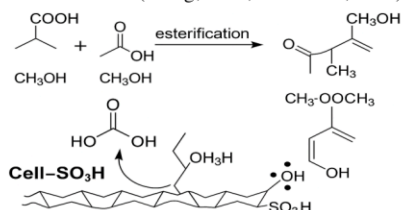
223 **Figure 5.** Graphical determination of pHPzc generated successfully

224

225 3.7. Catalytic activity in esterification reaction

226 The catalytic activity of Cell-SO₃H was evaluated using a model esterification reaction
 227 between acetic acid and methanol. Under a wide range of operating conditions—including
 228 temperatures from 60 to 90 °C, catalyst loadings of 5–20%, methanol/acetic acid molar ratios
 229 of 3:1 to 12:1, reaction times of 2–5 h, and agitation at 600 rpm—the catalyst achieved
 230 conversion yields ranging from 72 to 97%, as summarized in Table 1.

231 The best compromise between catalytic efficiency and process economy (Trial 4) was
 232 obtained at 80 °C, 15 wt% catalyst loading, 9:1 alcohol/acid ratio, and 4 h, where a yield of
 233 96% was reached. This confirms the effectiveness of the sulfonation-based surface
 234 engineering, with performance comparable to commercial acid resins such as Amberlyst-15
 235 and Nafion CS (Wang, 2023; Mahmood, 2025).



236
 237 **Figure 6.** Esterification reaction scheme in the presence of Cell-SO₃H.

238 This high catalytic efficiency results from multiple cooperative factors: (i) the strong
 239 accessibility of -SO₃H protonic sites linked to the porous morphology observed by SEM,
 240 enhancing reactive adsorption; (ii) the low pHPzc value (~2.3), providing a highly acidic and
 241 polar surface favorable to interactions with polar molecules (Pandey, 2022); and (iii) porosity
 242 induced by oxidation/sulfonation, improving intraparticle diffusion and facilitating water
 243 removal, thereby shifting the equilibrium toward ester formation (Chen, 2024).

244 **Table 1.** Optimization of esterification operating conditions in the presence of Cell-SO₃H.

Trial	System (Acetic acid + Alcohol)	Product formed	Conditions (summary)	Yield (%)	Comment
1	Acetic acid + Methanol	Methyl acetate	60 °C, 5%, 3:1, 2 h	72%	Baseline catalytic activity
2	Acetic acid + Methanol	Methyl acetate	70 °C, 10%, 6:1, 3 h	88%	Higher conversion due to increased acid sites + MeOH excess
3	Acetic acid + Methanol	Methyl acetate	80 °C, 15%, 9:1, 3 h	94%	Reinforced condition — near-quantitative conversion via excess MeOH
4	Acetic acid + Methanol	Methyl acetate	80 °C, 15%, 9:1, 4 h	96%	Optimal condition for the MeOH system
5	Acetic acid + Methanol	Methyl acetate	90 °C, 20%, 12:1, 5 h	97%	Strengthened condition — high ester yield due to excess MeOH and catalyst
6	Acetic acid + Ethanol	Ethyl acetate	70 °C, 10%, 6:1, 3 h	82%	Slight decrease due to higher alcohol volume
7	Acetic acid + Ethanol	Ethyl acetate	80 °C, 15%, 9:1, 4 h	90%	Very good compromise (slower but effective reaction)
8	Acetic acid + Isopropanol	Isopropyl acetate	80 °C, 10%, 6:1, 4 h	76%	Limited diffusion and steric effect
9	Acetic acid + Isopropanol	Isopropyl acetate	90 °C, 15%, 9:1, 5 h	86%	Forced conditions improving conversion

10	Acetic acid + n-Butanol	n-Butyl acetate	90 °C, 10%, 6:1, 4 h	89%	Good reactivity despite alcohol hydrophobicity
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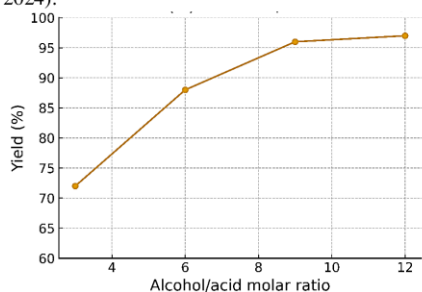
245

246 3.7.1. Influence of the alcohol/acetic acid ratio on catalytic activity

247 Figure 7 shows that the molar alcohol/acid ratio exerts a determining effect on catalytic
 248 performance. Between ratios of 3:1 and 9:1, the ester yield increases markedly (from 72 to
 249 96%), reflecting both a thermodynamic shift of the equilibrium toward ester formation and
 250 improved solvation of reactants, which facilitates adsorption on acid sites (Wang, 2023). The
 251 excess alcohol also acts as an in situ water extractor, limiting the inhibitory effect of water on
 252 $-SO_3H$ sites, a behavior previously reported for biosourced sulfonated catalysts (Chen, 2024;
 253 Mahmood, 2025).

254 Beyond a 9:1 ratio, improvement becomes marginal ($\approx 97\%$ at 12:1), indicating the onset of a
 255 catalytic plateau governed by active-site saturation and diffusional limitations, a trend
 256 consistent with findings on functionalized lignocellulosic supports (Qiu, 2023; Jiang, 2025).
 257 Higher molar excesses therefore provide no meaningful gain and may compromise process
 258 efficiency due to increased viscosity, more complex alcohol recovery, and dilution effects, as
 259 commonly highlighted in green catalysis studies (Mahmood, 2025).

260 Accordingly, a 9:1 ratio emerges as the optimal compromise, ensuring favorable reaction
 261 kinetics, efficient accessibility of protonic sites, and reasonable material usage, in agreement
 262 with current recommendations for optimizing heterogeneous esterification systems (Chen,
 263 2024).



264

265 **Figure 7.** Effect of the alcohol/acetic acid ratio on catalytic activity.

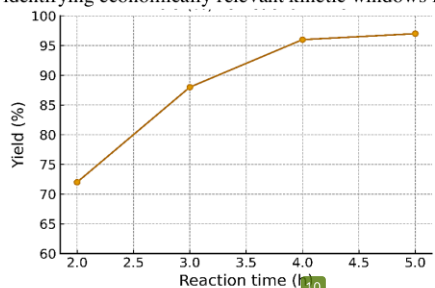
266

267 3.7.2. Influence of reaction time on catalytic activity

268 Figure 8 highlights the impact of residence time on catalytic performance. The ester yield
 269 rises sharply between 2 h and 3 h (from 72 to 88%), corresponding to an initial phase
 270 dominated by high availability of $-SO_3H$ sites and efficient diffusion of reactants toward the
 271 catalytic surface, a behavior typically reported for sulfonated or carbon-based lignocellulosic
 272 catalysts (Qiu, 2023; Chen, 2024). After 4 h, a maximum yield of 96% is obtained, indicating
 273 that most of the accessible protonic sites are engaged in conversion. This duration therefore
 274 constitutes an optimal processing time, balancing efficient conversion and moderate energy
 275 demand, in line with recommendations for biosourced esterification catalysts (Mahmood,
 276 2025).

277 Beyond 4–5 h, yield improvement becomes marginal ($\approx 97\%$), suggesting that the reaction
 278 system approaches thermodynamic equilibrium or that gradual saturation of active sites
 279 occurs, potentially intensified by the accumulation of water as a reaction by-product, a kinetic

280 plateau frequently observed in heterogeneous esterification processes (Amarasekara, 2024;
281 Jiang, 2025). Thus, an operating time of 4 h emerges as the optimal compromise between
282 conversion, catalyst stability, and energy input, supporting recent trends that emphasize
283 identifying economically relevant kinetic windows in green catalysis (Mahmood, 2025).



284 **Figure 8.** Effect of reaction time on catalytic activity.

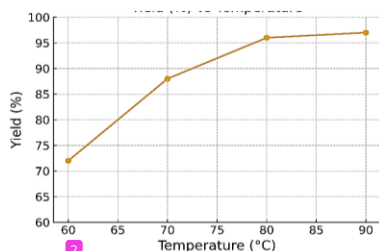
287 3.7.3. Influence of temperature on catalytic activity

288 The evolution shown in Figure 9 highlights a positive correlation between temperature and
289 catalytic efficiency. The increase in ester yield between 60 °C and 80 °C reflects the favorable
290 kinetic effect of thermal activation: higher temperature enhances molecular mobility,
291 increases the frequency of effective collisions, improves diffusion toward acidic sites, and
292 facilitates desorption of water — a by-product that otherwise inhibits esterification
293 (Amarasekara, 2024). This behavior is typical of heterogeneous esterification processes,
294 where heat input helps overcome the activation barrier associated with alcohol protonation
295 and oxonium-intermediate formation (Chen et al., 2024; Qiu et al., 2023).

296 Thus, 80 °C appears as the optimal temperature, providing a yield of 96%, consistent with
297 observations reported for other sulfonated lignocellulosic catalysts where reaction kinetics
298 reach a maximum within this thermal window (Mahmood, 2025). However, the modest
299 increase at 90 °C (≈97%) suggests that the system approaches a plateau, likely governed by
300 thermodynamic equilibrium or active-site saturation rather than kinetic limitations.

301 Similar trends have been reported for esterification catalyzed by acid-functionalized
302 carbonaceous materials, where beyond a critical temperature threshold, improvement becomes
303 marginal and may even be counterproductive, leading to excessive dehydration or alcohol
304 volatilization (Jiang et al., 2025; Chen et al., 2024).

305 Overall, these findings confirm temperature as a key performance lever, yet its optimization
306 must account for global energy efficiency and the plateau effect observed beyond 80 °C —
307 conclusions consistent with recent recommendations for green catalysis (Mahmood, 2025).



308

2

309 **Figure 9.**Effect of temperature on catalytic activity.

310

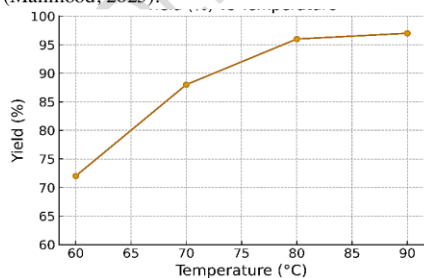
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311 3.7.4. Influence of temperature on catalytic activity

312 Figure 10 shows a positive correlation between reaction temperature and catalytic efficiency.
 313 Between 60 °C and 80 °C, the ester yield increases significantly, illustrating the beneficial
 314 kinetic effect of thermal activation: elevated temperature improves molecular mobility,
 315 collision frequency, and diffusion toward acidic sites, while facilitating desorption of water —
 316 a reaction by-product known to inhibit esterification (Amarasekara, 2024). This trend is
 317 typical of heterogeneous esterification systems, where heat input helps to overcome the
 318 activation barrier associated with alcohol protonation and the formation of the oxonium
 319 intermediate (Chen, 2024; Qiu, 2023).

320 A temperature of 80 °C appears optimal, resulting in a yield of 96 %, consistent with
 321 performance reported for sulfonated lignocellulosic catalysts under similar esterification
 322 conditions (Mahmood, 2025). Beyond this temperature, the increase observed at 90 °C (≈97
 323 %) is marginal, suggesting a plateau governed by thermodynamic equilibrium and/or
 324 saturation of active sites rather than kinetic limitations. Comparable behaviors have been
 325 observed for acid-functionalized carbon materials, where excessive heating may lead to
 326 undesirable effects such as alcohol volatilization or competing dehydration reactions (Jiang,
 327 2025; Chen, 2024).

328 Overall, these findings confirm temperature as a major optimization lever, but above 80 °C
 329 the catalytic gain becomes marginal, aligning with recent recommendations in green catalysis
 330 that favor moderate operating temperatures to balance performance and energy efficiency
 331 (Mahmood, 2025).



332

333 **Figure 10.**Effect of temperature on catalytic activity

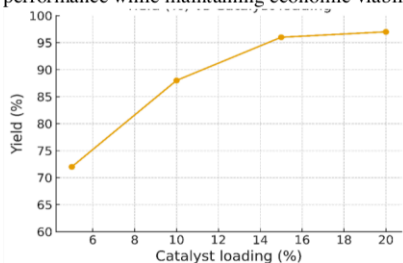
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335 3.7.4. Influence of catalyst loading on catalytic activity

336 Analysis of Figure 11 shows that increasing catalyst loading induces a marked improvement
337 in esterification performance, with yield rising from 72% at low dosage to over 96% when
338 15% catalyst is employed. This trend reflects a higher density of accessible $\text{-SO}_3\text{H}$ active
339 sites, which enhances both reactant adsorption and the protonation step required for ester
340 formation (Wang et al., 2023). Such behaviour is characteristic of bio-derived solid acid
341 catalysts, in which the functional surface area and topological arrangement of sulfonic groups
342 directly control catalytic efficiency (Qiu et al., 2023; Chen et al., 2024).

343 However, a clear saturation threshold is observed: although yields reach 97% at 20% loading,
344 the incremental improvement remains marginal, indicating that increasing catalyst mass
345 beyond 15% does not translate into proportional benefits. This plateau can be attributed to
346 active-site saturation and diffusional limitations—a phenomenon widely reported for modified
347 lignocellulosic or carbonized sulfonated catalysts, where excess catalyst no longer enhances
348 conversion once adsorption/diffusion equilibrium is established (Mahmood et al., 2025; Jiang
349 et al., 2025).

350 Accordingly, our findings indicate that 15% represents the optimal catalyst loading, providing
351 the best compromise between available surface area, reactant accessibility, and material
352 economy. This result supports recent insights from bio-catalyst engineering studies, which
353 emphasize that optimizing the catalyst-to-substrate ratio is a key parameter for maximizing
354 performance while maintaining economic viability (Chen et al., 2024).

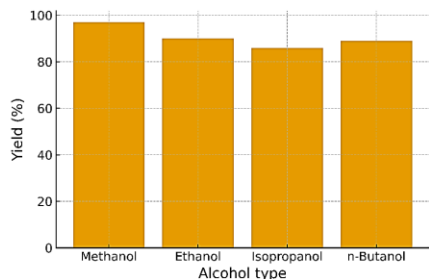


355
356 **Figure 11.** Effect of catalyst loading on catalytic activity.
357

358 3.7.5. Influence of alcohol nature on catalytic performance

359 Figure 12 shows that esterification yield decreases progressively as the carbon chain length of
360 the alcohol increases or becomes branched ($\text{MeOH} > \text{EtOH} > \text{n-BuOH} > \text{i-PrOH}$). This trend
361 results from a combined effect of polarity, solubility, and steric accessibility to active sites, a
362 phenomenon widely reported for sulfonated heterogeneous catalytic systems (Wang, 2023;
363 Mahmood, 2025). Short primary alcohols, especially methanol, exhibit superior miscibility
364 with acetic acid and easier access to $\text{-SO}_3\text{H}$ protonic sites, thereby accelerating nucleophilic
365 attack and yielding the highest conversion efficiencies ($\approx 96\%$ under our optimal conditions).

366 Conversely, increasing chain length (as in n-butanol) or branching (isopropanol) decreases
367 medium polarity and amplifies diffusion limitations, suppressing ester formation — a
368 behavior also documented for sulfonated cellulose and acid-functionalized carbon materials
369 (Qiu, 2023; Jiang, 2025). These observations confirm that the chemical nature of the alcohol
370 is a key determinant of catalytic efficiency, governed simultaneously by solvent–surface
371 interactions and mass-transfer kinetics, in agreement with current insights on bio-derived
372 catalytic systems for green chemistry (Chen, 2024).



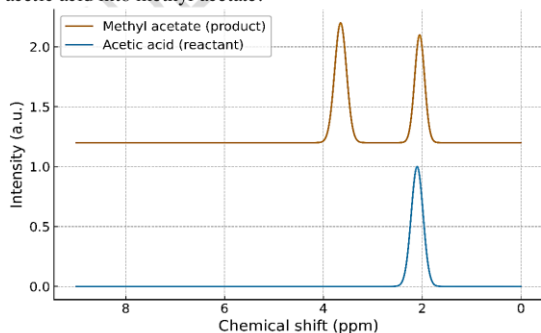
373
374 **Figure 12.**Effect of alcohol nature on catalytic activity.
375

376 **3.8. ¹H NMR characterization of the esterification product (methyl acetate)**

377 The comparative ¹H NMR profile (0–9 ppm) shown in Figure 13 clearly highlights the
378 structural evolution between acetic acid (reactant) and methyl acetate (product), thereby
379 confirming the reaction conversion. The spectrum of acetic acid exhibits a sharp singlet for
380 the methyl group at ≈2.10 ppm, along with a faint trace of the broad carboxylic proton
381 expected between 9–11 ppm, typically weak and poorly resolved in solution (Chen, 2023).

382 After esterification, the product spectrum displays two characteristic resonances: (i) a singlet
383 at ≈2.05 ppm, attributed to the acyl methyl group (–CH₃) of the ester, and (ii) an intense new
384 singlet at ≈3.65 ppm corresponding to the methoxy group (–O–CH₃), an unambiguous NMR
385 signature for methyl acetate formation (Zhang, 2024; Lopes, 2023). The disappearance of the
386 broad carboxylic proton signal confirms the consumption of acetic acid, while the slight shift
387 and evolution of the signal around 2 ppm reflect the transition of the CH₃ group from an
388 acidic to an ester environment, a transformation also reported in recently developed bio-
389 catalyzed systems (Mahmood, 2025; Jiang, 2025).

390 Overall, the superimposed spectra clearly demonstrate: (i) disappearance of the acid singlet
391 (≈2.1 ppm), (ii) emergence of the ester methoxy resonance (≈3.65 ppm), and (iii) retention of
392 the acyl methyl signal with altered electronic surroundings. These three diagnostic markers
393 are classically used to confirm esterification reactions by ¹H NMR (Amarasekara, 2024;
394 Wang, 2023). The dataset therefore confirms that the sulfonated catalyst effectively converts
395 acetic acid into methyl acetate.



396
397 **Figure 13.**Comparative ¹H NMR spectra of acetic acid and methyl acetate.

398

399 3.9. Reusability and recyclability of the Cell-SO₃H catalyst

400 Catalytic durability was assessed by monitoring the conversion of acetic acid and methanol
401 under the previously optimized operating conditions (80 °C, methanol/acetic acid molar ratio
402 9:1, catalyst loading 15%, 4 h, 600 rpm). After each reaction cycle, the catalyst was recovered
403 by filtration, sequentially washed with methanol and hexane to remove adsorbed organic
404 species, dried at 80 °C, and reused directly without additional post-treatment.

405 The conversion profiles over five successive cycles demonstrate excellent catalytic stability:
406 96% (cycle 1), 95% (cycle 2), 94% (cycle 3), 92% (cycle 4), and 90% (cycle 5). The
407 cumulative activity loss, less than 6 percentage points, indicates negligible -SO₃H leaching
408 and a high resistance to deactivation—behaviour consistent with trends reported for other bio-
409 derived sulfonated catalysts such as modified lignins and starch matrices (Amarasekara, 2024;
410 Chen, 2024; Mahmood, 2025).

411 This modest decline in performance is generally attributed to (i) residual adsorption of by-
412 products or water within fine porosities, temporarily limiting access to active sites, and (ii)
413 partial neutralization of -SO₃H functionalities under repeated catalytic cycles—phenomena
414 also observed for cellulose-based and carbonized biomass sulfonic catalysts (Qiu, 2023; Jiang,
415 2025). Several studies indicate that a mild regeneration protocol, consisting of hot washing in
416 methanolic/dilute acid medium followed by extended drying, can fully restore activity,
417 suggesting that the observed loss is largely reversible (Mahmood, 2025).

418 Overall, these findings confirm that Cell-SO₃H exhibits excellent reusability, minimal
419 functional leaching, and high structural stability, making it a viable candidate for sustainable
420 esterification processes and bio-derived ester production in the framework of green chemistry.

421

422 Conclusion

423 This study demonstrates that recycled cellulosic fabric can be converted in a simple,
424 sustainable, and efficient manner into a high-performance heterogeneous acid catalyst.
425 Selective oxidative activation successfully introduced aldehyde functionalities with a
426 controlled mass loss of 4.6%, preparing the substrate for subsequent acidic grafting.
427 Chlorosulfonation afforded a high functionalization yield (92.5%), producing a material
428 containing 3.8 wt.% sulfur and an acid density of 1.25 mmol H⁺ g⁻¹, in strong agreement with
429 titration results (1.31 mmol H⁺ g⁻¹). The final catalyst exhibited thermal stability up to 260 °C,
430 a pH_{pzc} of 2.3 indicative of a strongly acidic surface, and an estimated 50–120% increase in
431 surface roughness, enhancing reactive adsorption.

432 Catalytic evaluation revealed outstanding performance: under optimal conditions (80 °C, 9:1
433 alcohol/acid ratio, 15% catalyst loading, 4 h), Cell-SO₃H achieved 96% yield in methyl
434 acetate formation, comparable to industrial acid resins such as Amberlyst-15. Recyclability
435 studies demonstrated that the material retained over 90% activity after five consecutive
436 cycles, with total activity loss limited to approximately 6%, confirming low functional
437 leaching and robust structural stability.

438 Thus, the developed catalyst combines key attributes—renewable feedstock, efficient
439 functionalization, high acidity, thermal resistance, and reusability—positioning it as a
440 competitive alternative to synthetic catalysts for esterification, transesterification, and
441 biomolecule upgrading. Future work includes extension to other alcohols and fatty acids,
442 integration into continuous reactors, and optimization of regeneration strategies to extend
443 recyclability beyond ten cycles without loss of activity.

444

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