



# Biodiesel production catalyzed by highly acidic carbonaceous catalysts synthesized *via* carbonizing lignin in sub- and super-critical ethanol



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## ABSTRACT

Carbonaceous acids were synthesized from dealkaline lignin *via* solvothermal carbonization, pyrolysis and sulfonation. Carbonization of lignin in sub- and super-critical ethanol provided good surface properties with abundant functional groups (2.81 and 1.35 mmol [H<sup>+</sup>]/g) for the subsequent sulfonation to result in high active and stable catalysts for biodiesel production. Both catalysts (E-P400-2-SO<sub>3</sub>H and E-260-20-SO<sub>3</sub>H carbonized in sub- and super-critical ethanol) had high acid content of 5.35 and 5.05 (mmol [H<sup>+</sup>]/g), respectively. Highest biodiesel yields of 95.4% and 95.5% were obtained from the esterification of oleic acid at 80 °C with E-260-20-SO<sub>3</sub>H and E-P400-2-SO<sub>3</sub>H, respectively, with 5 cycles for E-260-20-SO<sub>3</sub>H (≥81.9% yield) and 3 cycles for E-P400-2-SO<sub>3</sub>H (≥84.6% yield). Both catalysts also applied to produce biodiesel from actual plant oils at 220 °C. High biodiesel yields of 90.9% and 93.2% were obtained from *Jatropha* and blended soybean oils with high acid value of 17.2 and 22.1 mg KOH/g, respectively.

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## 1. Introduction

Compared with currently used fossil fuels, biodiesel derived from edible and non-edible oils is renewable, biodegradable, less polluted, non-toxic and environmental friendly, and gains significant attentions [1–3]. Non-edible oils such as *Jatropha curcas* L. oil are important raw materials for biodiesel production, because they do not compete with land for food production, and are cheap and sustainable [4–6]. Solid catalysts including solid acids [7–10] and solid bases [3,11] are widely studied for biodiesel production because they are less corrosive than liquid acids or liquid bases, produce less liquid pollutants after catalytic reactions and can be easily recycled. For the transformation of *Jatropha* oil, the critical challenge is its high content of free fatty acids (FFAs) that greatly limits the activity and reuse of base catalysts, and brings serious saponification in base-catalyzed reactions [6]. But, solid acid catalysts can solve this problem, as they can catalyze both esterification and transesterification and produce biodiesel directly from high acid value (AV) oils in one step [7].

Lignin is the second-most abundant organic material in the nature after cellulose. It is largely obtained from industrial pulp-

ing process and can be used as feedstock for producing energy, chemicals and fuels [12–14]. Lignin has higher carbon content than carbohydrates that benefits the economics in biochar production. Recently, carbonaceous catalysts from lignin have been studied (Table 1) [4,15–17]. Compared with char from pyrolysis, hydrothermal biochar prepared under relatively mild condition of hot water provides rich oxygen-containing groups [18–20]. Generally, hydrothermal char from carbohydrates (but not from lignin) has regular morphology with well-distributed functional groups [21]. The main reason is that sugars dissolved in hot-compressed water undergo homogeneous carbonization, however lignin decomposes under both heterogeneous and homogeneous conditions with different routes towards polyaromatic hydrochar [15,22,23]. A proper solvent is required for lignin reaction system such as small molecule alcohols that can help to dissolve lignin to limit heterogeneous routes for the production of lignin biochar with better surface properties to load active sites [24,25].

This work aims to produce carbonaceous acids with high acid content from lignin for biodiesel production. Ethanol as solvent was first screened from different alcohols for lignin char production, and further optimized under sub- and super-critical conditions. The yielded char was sulfonated to carbonaceous acids for the production of biodiesel from oleic acid, *Jatropha* oil and blended soybean oils with high AV according to single-factor and orthogonal experimental designs. The carbonaceous acid prepared in this work with

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**Table 1**  
Comparison of activity of carbonaceous acids derived from lignin in this work with previous studies.

Catalyst	Carbonization materials	Synthesis conditions	Acid content		Esterification of oleic acid		Annotation	Ref.
			NaOH titration (mmol [H <sup>+</sup> ]/g)	Calculated by S content (mmol/g)	Reaction conditions	Biodiesel yield (%)		
Carbonaceous solid acid	Kraft lignin	Impregnation: 85% H <sub>3</sub> PO <sub>4</sub> , 1 h; Drying: 105 °C, 24 h; Carbonization: N <sub>2</sub> , 400 °C, 1 h; Sulfonation: 98% H <sub>2</sub> SO <sub>4</sub> , 200 °C, 2 h	1.30	2.10	80 °C, 5 h, 12/1 methanol/oil ratio	96.1	3 cycles with biodiesel yield ≥ 93.6%	[4]
Sulfonated catalyst	Dealkaline lignin	Carbonization: hydrothermal, 225 °C, 20 h; Sulfonation: 98% H <sub>2</sub> SO <sub>4</sub> , 150 °C, 12 h	–	0.87	–	–	–	[15]
Carbonaceous sulfonic acid	Kraft lignin	Impregnation: 85% H <sub>3</sub> PO <sub>4</sub> , 3 h; Drying: 105 °C, 12 h; Carbonization: N <sub>2</sub> , 550 °C, 3 h; Sulfonation: 98% H <sub>2</sub> SO <sub>4</sub> , 200 °C, 10 h	3.46	0.48	80 °C, 7.5 h, 10/1 methanol/oil ratio	88.7	Biodiesel yield < 77% at the second cycle	[16]
Lignin-based solid acid	Pine Klason lignin	Sulfonation: sulfuryl chloride, 50 °C, 5 h	2.22	0.37	–	–	–	[17]
E-260-20-SO <sub>3</sub> H <sup>a</sup>	Dealkaline lignin	Carbonization: supercritical ethanol, 260 °C, 8.4 MPa, 20 h; Sulfonation: 98% H <sub>2</sub> SO <sub>4</sub> , 150 °C, 10 h	5.05	1.41	80 °C, 7 h, 12/1 methanol/oil ratio	95.4	5 cycles with biodiesel yield ≥ 81.9%	This work
E-P400-2-SO <sub>3</sub> H <sup>b</sup>	Dealkaline lignin	Carbonization: subcritical ethanol, 180 °C, 7.8 MPa, 1 h; Pyrolysis: N <sub>2</sub> , 400 °C, 2 h; Sulfonation: 98% H <sub>2</sub> SO <sub>4</sub> , 150 °C, 10 h	5.35	1.06	80 °C, 5 h, 15/1 methanol/oil ratio	95.5	3 cycles with biodiesel yield ≥ 84.6%	This work

<sup>a</sup> E-260-20-SO<sub>3</sub>H obtained after lignin carbonized in ethanol at 260 °C for 20 h, and sulfonation.

<sup>b</sup> E-P400-2-SO<sub>3</sub>H obtained after lignin carbonized in ethanol at 180 °C for 1 h, pyrolysis at 400 °C for 2 h, and sulfonation.

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