Lignin-first biorefinery approach for valorization of cotton stalks to phenolic monomers

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Catalyst characterization

On a Bruker D8 advance X-ray diffractometer equipped with a Lynx eye high-speed strip detector, Cu K (= 1.5418) radiation was used to record X-ray diffraction (XRD). XRD patterns were recorded in the 2 - 80˚ range with 0.02 step time and 2 seconds step time. Inductively coupled plasma atomic absorption spectroscopy (ICP-AES) was used to determine the ruthenium content in catalyst.

N_2 physisorption of catalyst was performed on 3Flex Physisorption, Micromeritic and Belsorbmax, BEL at liquid nitrogen temperature (-196 °C). Before the analysis, the sample was pre-treated at 250 °C for 6 h under vacuum (1×10^{-5} Torr) for degassing the samples. Brunauer–Emmett–Teller (BET) was used to calculate the surface area of all the samples using the adsorption data obtained in the relative pressure (P/P_0) range of 0.05-0.25. Barrett–Joyner–Halenda (BJH) algorithm was used to determine pore size distributions, and the maxima of pore size distributions were considered as the average pore size. The sample's pore volume was considered the volume of liquid nitrogen adsorbed at $P/P^0 \approx 1$. Temperature programmed reduction (TPR) and temperature programmed desorption (TPD) of the catalyst was carried out on Micromeritics, Autochem II-HP 2950, equipped with a thermal conductivity detector (TCD). For TPR, the sample was pre-treated at 300 ˚C for 1 h in Ar, and then the sample was treated with 10% H_2-Ar in the temperature range of 50-700 ˚C at the heating rate of 10 ˚C.min^{-1}. The signals were recorded on TCD. For TPD, the sample was pre-treated at 300 ˚C for 1 h in He, and then it was exposed to 30 ml.min^{-1} flow of 10% NH_3-He for 30 min. After the adsorption, it was exposed to He for 30 min to remove extra NH_3-He present over the surface; then, the temperature was raised to 700 ˚C for TPD measurements.

FT-IR was performed in the range of 400 – 4000 cm^{-1} using the Perkin Elmer- Spectrum II instrument. The pellets for analysis were prepared using KBr. Thermogravimetric analysis (TGA) was performed using Shimadzu DTG-60. The samples were heated in alumina cells up to 600 ˚C at 5 ˚C.min^{-1} under 100 ml min^{-1} N_2 flow to identify the weight loss.

X-ray photoelectron spectroscopy (XPS) was performed using a non-monochromatic Mg Kα X-ray source under high vacuum conditions at K-alpha, Thermo scientific corporation to identify the chemical state of Ru. High-resolution spectra (HR-XPS) were collected by passing energy of 69.0 eV with a step size of 0.125 eV. Using the Gaussian function, HR-XPS profiles of elements were fitted and corresponding to C1s (284.8 eV), positions of the peaks were normalized. Transmission electron microscopy (TEM) was performed using JEM 2100 (JEOL, Japan) microscope at an operating voltage of 200 kV. The sample for analysis was prepared by loading an ethanol-dispersed sample on a lacey carbon formvar Cu grid. Energy-dispersive X-ray spectroscopy, in connection with TEM, was used for the elemental composition of samples. The same spectrophotometer was used for the elemental mapping as well.

Lignin product analysis

Organic fraction extracted using ethyl acetate was qualitatively analysed through Agilent GC-MS equipped with mid-polar capillary column (DB-35MS, 35% phenyl/65% dimethylpolysiloxane, 30 m × 0.32 mm × 0.25 μm) in the split mode with 1:50 split ratio. Before the analysis, the sample was filtered using 0.2 μm filter. The GC-MS interface temperature was 300 °C. The temperature of the GC (7890B) oven was raised at a rate of 5 °C.min^{-1} from 50 °C (holding time: 2 min) to 280 °C (holding time: 5 min) for chromatographic separation of products with a flow rate of less than 1 mL. min^{-1} of He. Eluted compounds were matched using the NIST library after mass spectra were collected on 5977A MSD in electron ionisation mode at 70 eV in the range of 40-700 m/z.

NMR analysis was performed on Bruker ADVANCE III 500 MHz. The sample was dissolved in DMSO-d_6 solvent for the analysis. Gel permeation chromatography (GPC) analysis was carried out at room temperature on Shimadzu SPD-20A equipped with a photodiode array detector (280 nm), containing PL Multisolvent 30, 4.6 × 150 mm column using THF as a solvent and UV detection at 280 nm. The system was calibrated using polystyrene standards. For GPC analysis, the lignin oil sample was filtered through 0.2-micron filter and then solubilized in THF (2-5 mg/mL).

CS and CS-RCF characterizations

Compositional analysis of CS before and after RCF was performed using Fibertec 8000 to determine the cellulose, hemicellulose and lignin content. Briefly, sample (500 mg) and celite 545 AW (200 mg) were taken in the crucible and placed into a hot extraction unit (HEU) for the NDF (Neutral Detergent Fiber) and ADF (Acid Detergent Fiber) analysis. Then, the crucible was placed into cold extraction unit (CEU) for defatting using acetone as a defatting agent and acid detergent lignin (ADL) method was applied. Then the crucible was dried in a vacuum oven at 105 ˚C for 5 h, cooled, and weighed. The dried crucible was placed in a muffle furnace at 500 ˚C for 3 h for ashing. The following formula was used to calculate cellulose, hemicellulose and lignin content.

NDF - ADF = Hemicellulose; ADF - ADL = Cellulose; ADL = Lignin

X-ray diffraction measurements were recorded on a Bruker D8 advance X-ray diffractometer equipped with a Lynx eye high-speed strip detector. The crystallinity index was calculated according to Segal's method using the following formula.

Crystallinity Index (CrI), % = $\dfrac{I_{002} - I_{AM}}{I_{002}} \times 100$

Where I_{002} represents the maximum intensity corresponding to 002 reflection at 2θ = 22.5˚ and I_{AM} represents the minimal intensity between 002 and 101 reflections around 2θ = 18˚.

Proximate analysis of the feedstock was done in doublets using ELTRA Thermostep advanced thermogravimetric analyzer. Similarly, ultimate analyses were carried out in triplets using Elementar Vario, CHNS analyzer with TCD detector. Oxygen amount was calculated using the weight difference method. SEM images were taken with FEI Quanta 200 F, having tungsten filament as an X-ray source doped in lanthanum hexaboride (LaB_6), fitted with an ET (Everhart–Thornley) detector, using secondary electrons and an acceleration tension of 10 or 30 kV in high vacuum.

TGA was performed on Shimadzu DTG-60. FT-IR spectra was recorded using the Perkin Elmer- Spectrum II instrument.

CS and CS-RCF carbon characterization

Raman spectra of the samples was recorded from 500 to 3000 cm^{-1} using Horbia Jobin Yvon Lab Ram HR Evolution Spectrometer equipped with CCD (charged coupled device) detector with excitation laser wavelength of 523 nm. Surface morphology was examined using Quanta 200 F scanning electron microscope (SEM).

Thioacidolysis

Thioacidolysis of the woody biomass samples was performed according to a published standard procedure[1–3] using 5 mg of extract-free cotton stalks and 5 mL of thioacidolysis reagent (10% EtSH, 2.5% BF3·2Et2O, in freshly distilled dry 1,4-dioxane (v/v)). The reaction was performed in a pressure tube with Teflon-lined screw cap. The reaction mixture was heated at 100 °C for 4 h. The reaction was stopped by placing vial in ice-cold water for 5 min. Internal standard–tetracosane–was added to each vial (5 mg mL-1 in DCM, 0.2 mL). Reactions were basified to pH 3–4 by 0.4 M NaHCO$_3$ solution. To extract reaction products, 2 mL of water and 1 mL of DCM were added to the vial, the vial was vortex treated and organic phase was separated and filtrated. Obtained organic liquors were evaporated under vacuum. Residue was dissolved in 1 mL DCM and then derivatized using N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) and pyridine as a co-solvent (0.2 mL, 20μL). Samples were incubated at 50 °C for 1.5 h and then analyzed by GC-MS. For the quantification of phenolic monomers, response factors were considered as 0.42, 0.47 and 0.53 for H, G and S units respectively as reported in the literature.[4] The β-O-4 linkages were calculated using the following relation:

$$\beta - O - 4_{moiety\ frequency} = \sqrt{\frac{Yield\ monomers\ (\%)}{100\%}} \times 100\%$$

Tables

Table S1: Surface properties of catalyst

Catalyst	BET surface area, m²·g⁻¹	Pore size, Å	Pore volume, cm³·g⁻¹	Ru content, wt% (ICP-AES)	Metal dispersion, %	NH₃ desorbed, cm³·g⁻¹ (TPD)	Metal particle size, nm (HR-TEM)
HY	290	104.2	0.52	-	-	45.6	-
HRO@HY	264	35	0.41	4.7	12.5	55.3	3.3

Table S2: Effect of reaction conditions on molecular weight distribution of bio-oil

Reaction conditions				Molecular weight, M_w
Temperature, ˚C	Pressure, bar	Time, h	Solvent Ethanol: water	
210	30	2	20:0	1453[a]
210	30	2	20:0	751[b]
210	30	2	20:0	137
190	30	2	20:0	3367
200	30	2	20:0	336
220	30	2	20:0	201
230	30	2	20:0	1957
210	1	2	20:0	475
210	10	2	20:0	399
210	20	2	20:0	186
210	40	2	20:0	126
210	30	1	20:0	137
210	30	3	20:0	313
210	30	4	20:0	562
210	30	2	15:5	305
210	30	2	10:10	456
210	30	2	5:15	956
210	30	2	0:20	257

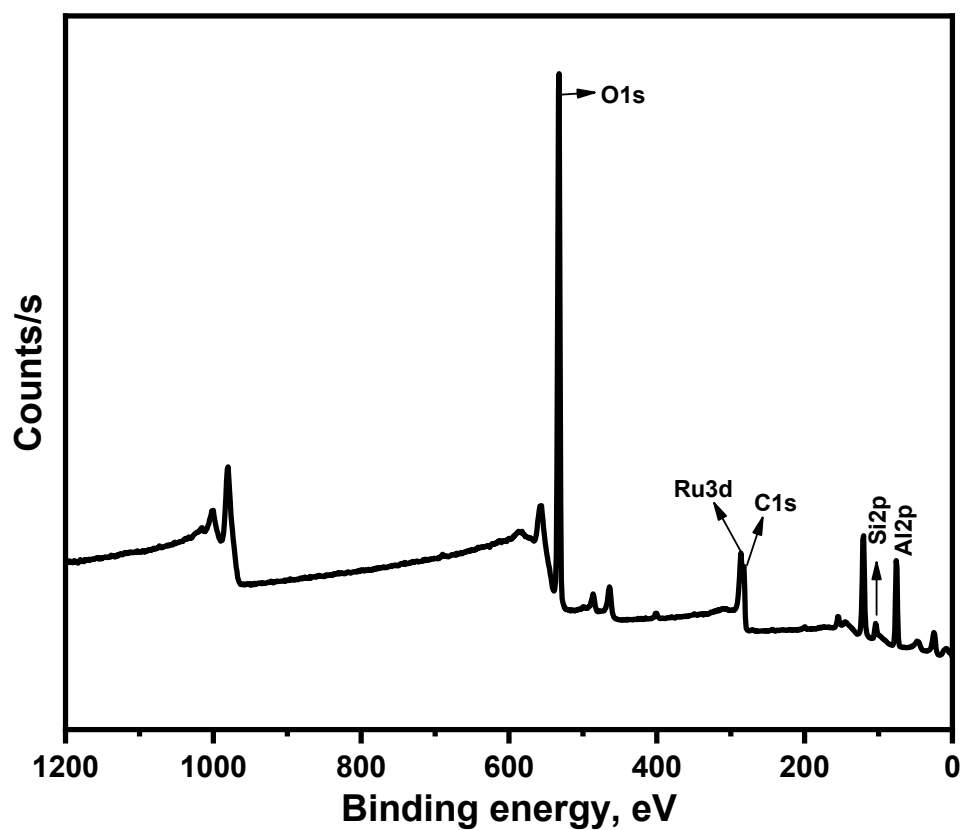[a] without catalyst, [b] HY

Figures

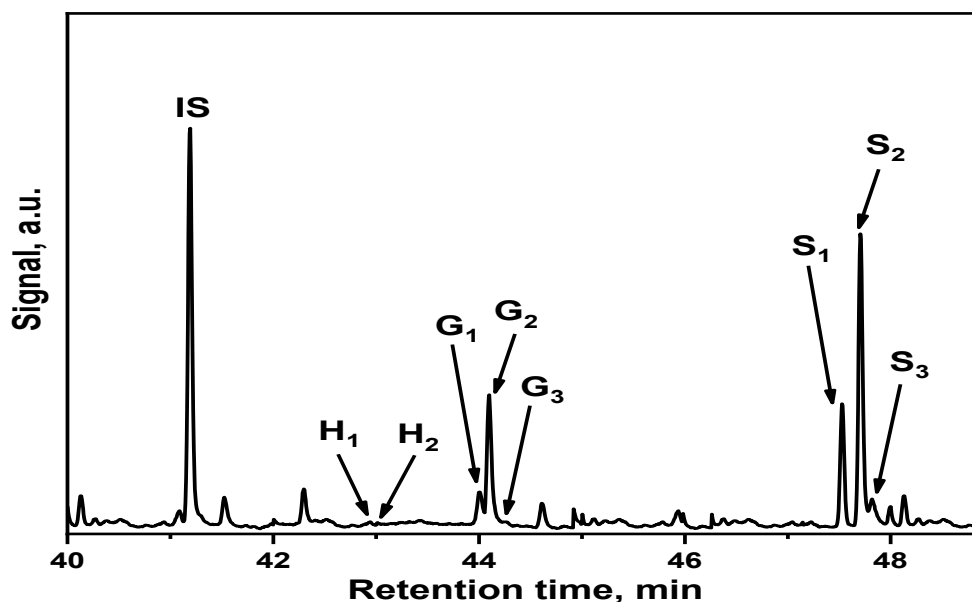**Figure S1:** XPS analysis: Survey scan of HROY.

Figure S2: Part of Gas chromatography-Mass spectrometry detector (MS) trace for cotton stalks thioacidolysis products. IS (internal standard) is tetracosane. H_1 and H_2 are erythron and threo forms of trimethyl(4-(1,2,3-tris(ethylthio)propyl)phenoxy)silane, G_1 and G_2 are erhythro and threo forms of (2-methoxy-4-(1,2,3-tris(ethylthio)propyl)phenoxy)trimethylsilane and G_3 is (2-methoxy-4-(2,3,3-tris(ethylthio)propyl)phenoxy)trimethylsilane, S_1 and S_2 are (2,6-dimethoxy-4-(1,2,3-tris(ethylthio)propyl)phenoxy)trimethylsilane, S_3 is (2,6-dimethoxy-4- (2,3,3-tris(ethylthio)propyl)phenoxy)trimethylsilane.
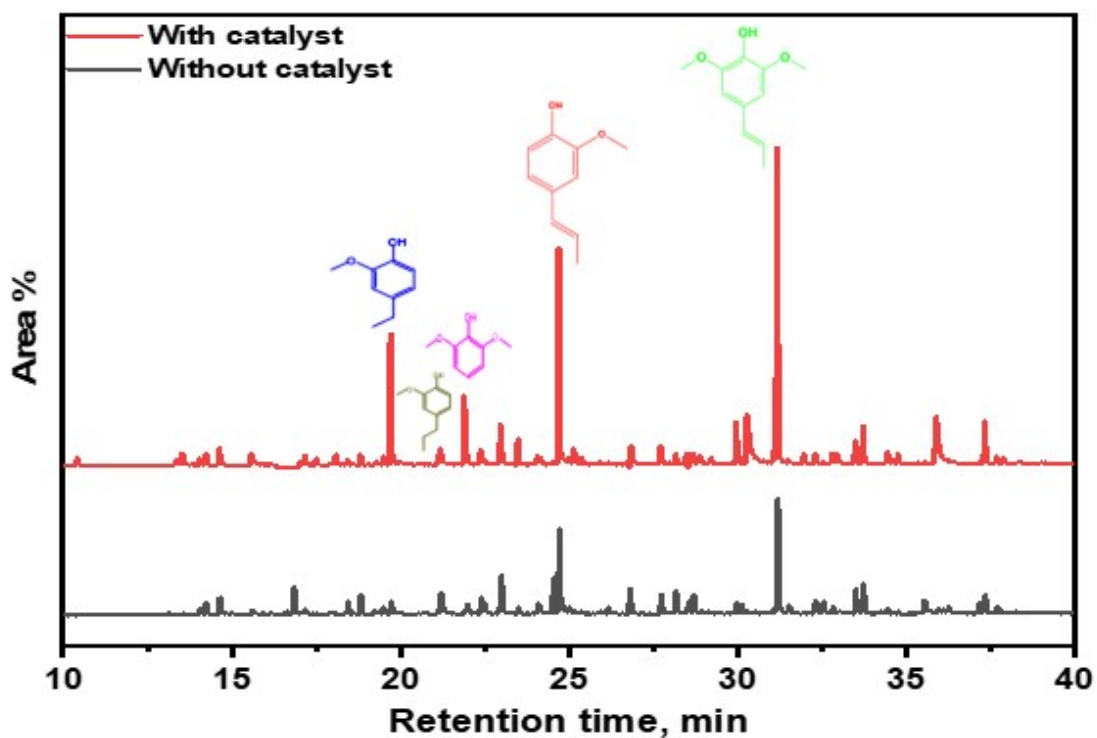
Figure S3: The GC/MS total ion chromatogram (TIC) of bio-oils obtained through catalytic and non-catalytic RCF of cotton stalks. Reaction conditions: CS = 1 g, catalyst = 100 mg, Ethanol = 20 mL, Temperature = 210 ˚C, Pressure = 30 bar, Time = 2h.
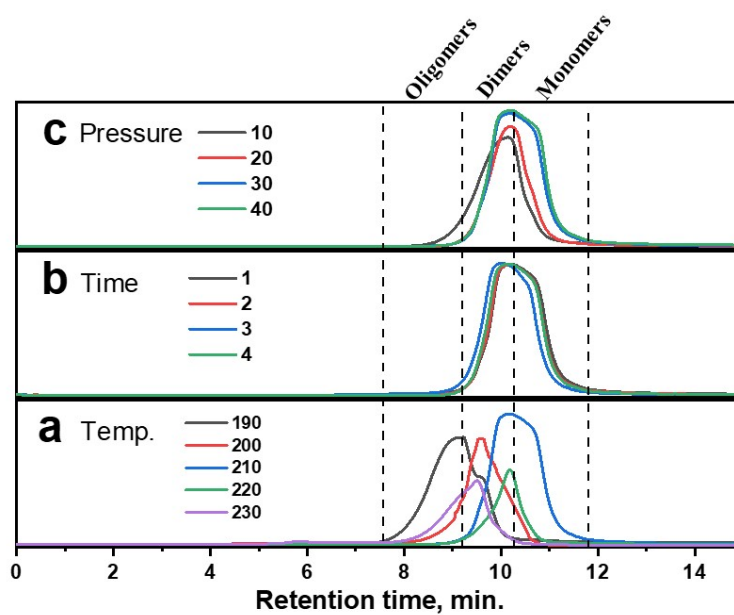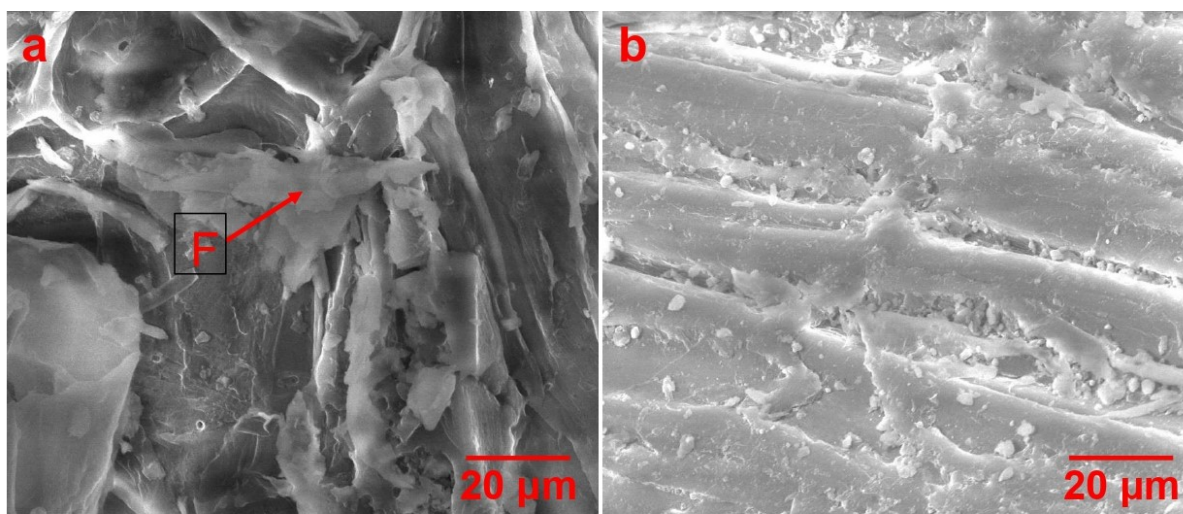

Figure S4: GPC trace of bio-oils.

Figure S5: Scanning electron microscopy (SEM) images of (a) CS and (b) CS-RCF.
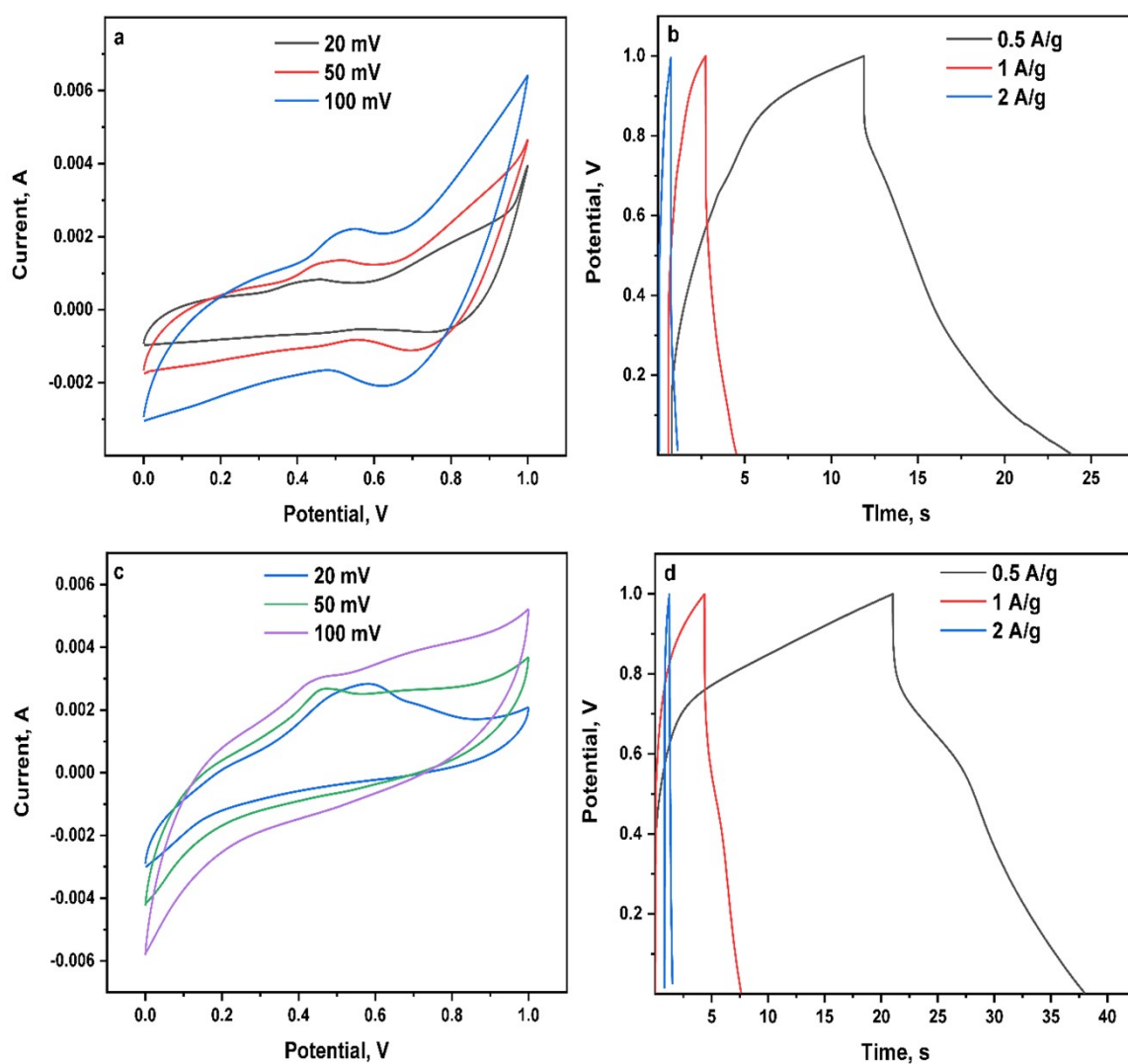
Figure S6: (a, b) CV and CD profile of CS carbon; (c,d) CV and CD profiles of CS-RCF carbon at different scan rates and different current densities respectively.
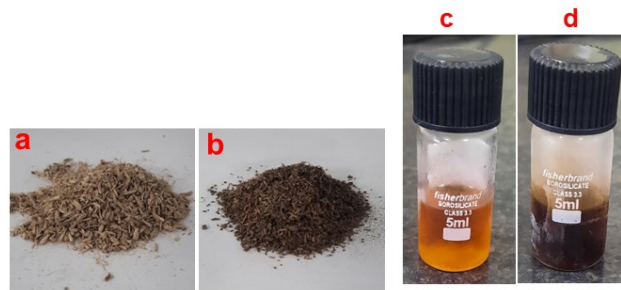

Figure S7: Cotton stalk: (a) before and (b) after the RCF process, RCF bio-oil: (c) without and (d) with catalyst.