catalysts

MDPI

Supplementary information

Sulfonated hydrothermal carbons from cellulose and glucose as catalysts for glycerol ketalization

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1.-Hydrothermal Index definition for HTC.

The use of different parameters (temperature, time, acid in different concentrations) in carbon hydrothermal synthesis with cellulose as starting material made difficult to find which combination of parameters could be considered as harsher conditions for a deeper hydrothermal synthesis.

A set of 12 hydrothermal carbons were prepared and a rather unexpected effect was observed on the textural properties (surface area and pore volume, with both properties correlated) measured by CO_2 adsorption isotherms. The obviously mildest conditions (195 ℃, 20h, without HCl) led to rather low surface area (201 m^2/g), but the harshest conditions (215 ℃, 40h, 5M HCl) led to even lower surface area (104 m^2/g). Thus going from mildest to harsher conditions produced an increase in surface area up to a maximum of 386 m^2/g at intermediate conditions (195 ℃, 40h, 2M HCl), and then a decrease of the surface area.

Thus, we used surface area as an indication of the harshness of the hydrothermal conditions, and we proposed an arbitrary scale of a parameter that we called “hydrothermal index”. We set the zero point for the mildest conditions, but using glucose as the starting material, as the surface area of the prepared hydrothermal carbon

(143 m^2/g) was even lower than the one prepared from cellulose. The middle point was set for the conditions leading to the highest surface area and an arbitrary value of 10 was given to it. Finally, a value of 20 was given to the final point, for the harshest conditions.

A volcano shape graph was then constructed with the two straight lines, one with positive slope from 0 to 10, and one with negative slope from 10 to 20. Finally, the values of hydrothermal index for the rest of the hydrothermal conditions were assigned by using the surface area obtained and the corresponding straight line. Some ambiguities were solved using the simple rules of 215 ℃ > 195 ℃, 40h > 20h, and 5M HCl > 2M HCl > no acid.

2.-SEM images of non-sulfonated and sulfonated hydrothermal carbons from cellulose.

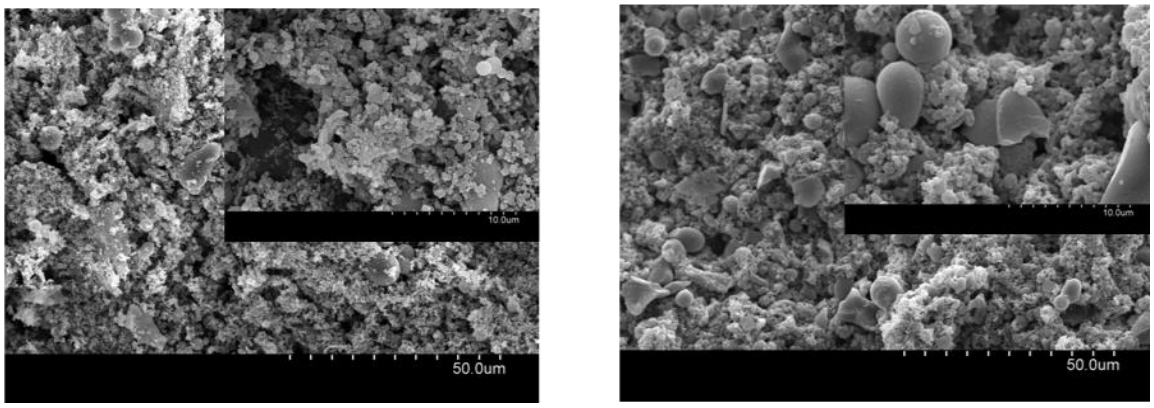

Figure S1. SEM images of Cel-195-2M-20h and Cel-195-2M-20h-S

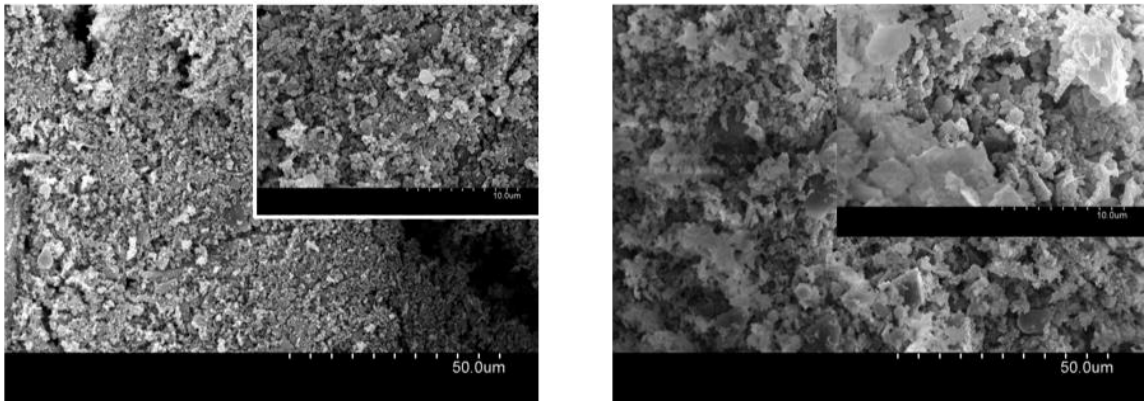

Figure S2. SEM images of Cel-195-2M-40h and Cel-195-2M-40h-S

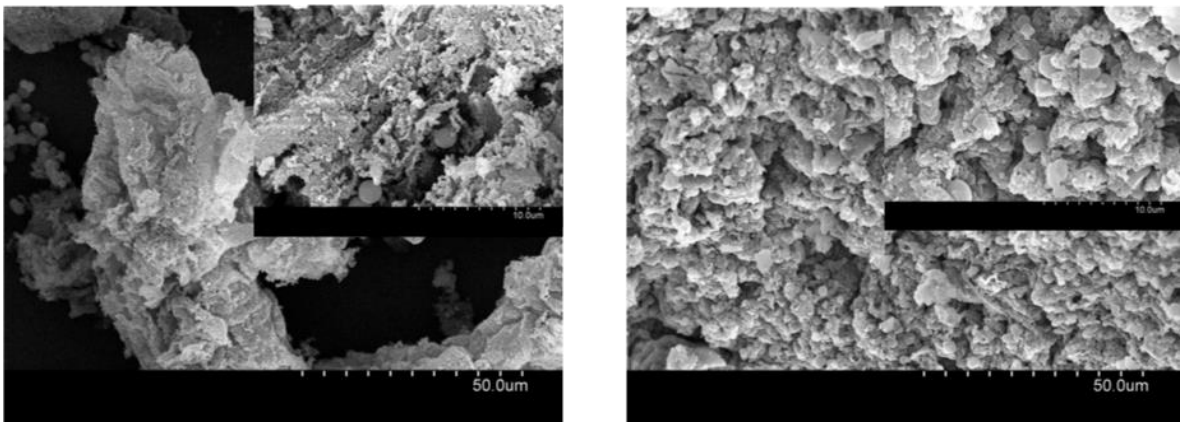

Figure S3. SEM images of Cel-195-5M-20h and Cel-195-5M-20h-S

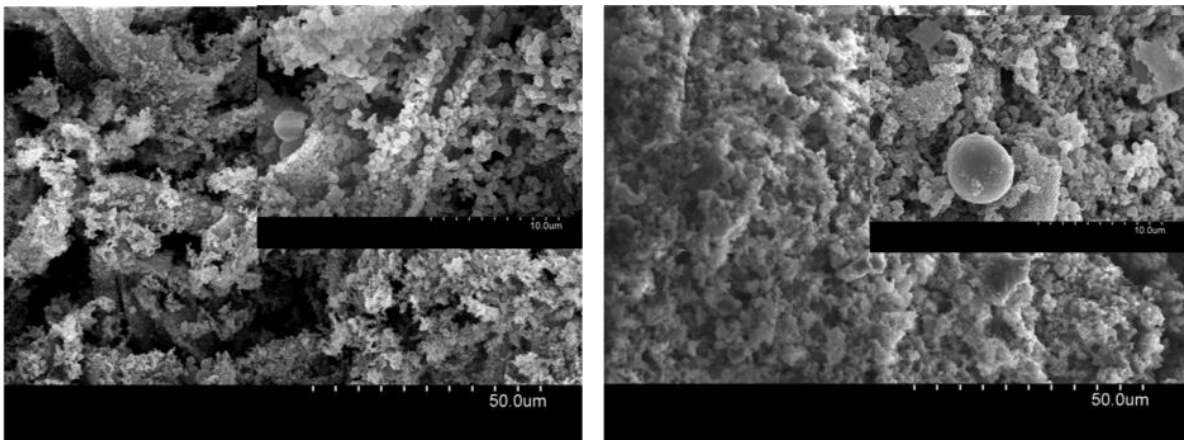

Figure S4. SEM images of Cel-215-20h and Cel-215-20h-S

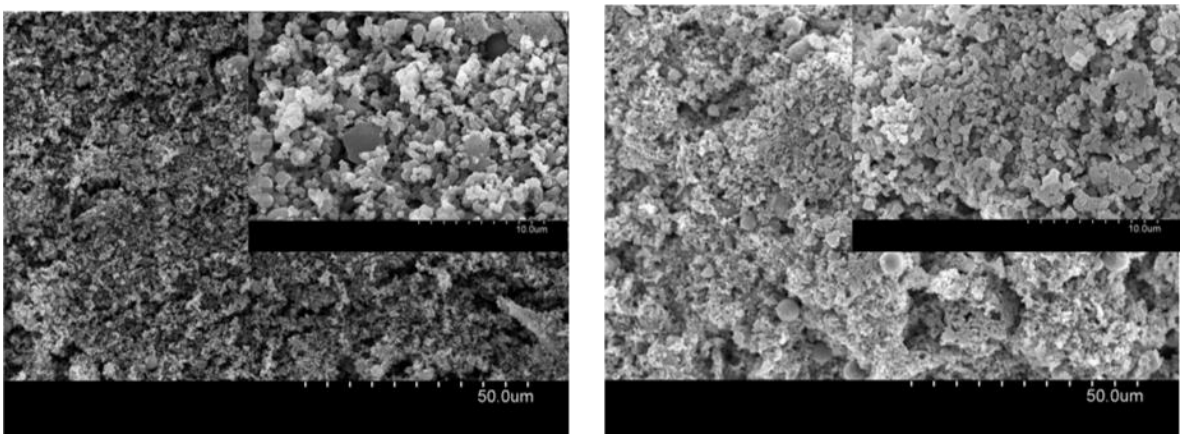

Figure S5. SEM images of Cel-215-2M-40h and Cel-215-2M-40h-S

3.-Plots of CO_2 adsorption isotherms and pore distribution for non-sulfonated and sulfonated hydrothermal carbons from cellulose.

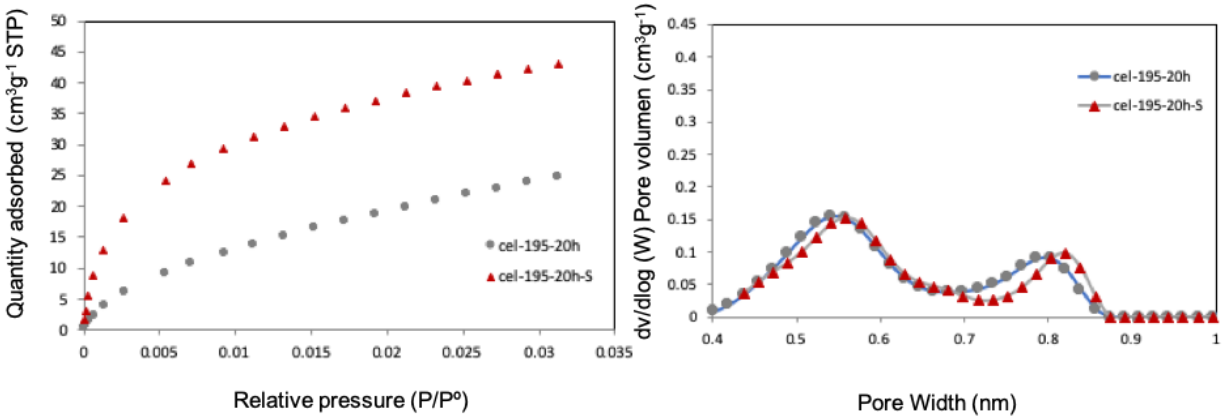

Figure S6. Plots of CO_2 adsorption isotherms and pore distribution for Cel-195-20h and Cel-195-20h-S

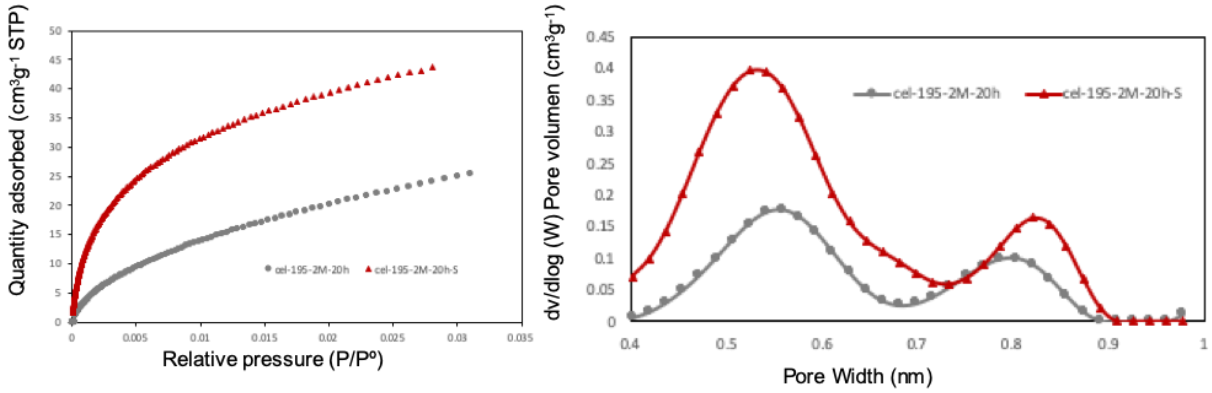

Figure S7. Plots of CO_2 adsorption isotherms and pore distribution for Cel-195-2M-20h and Cel-195-2M-20h-S

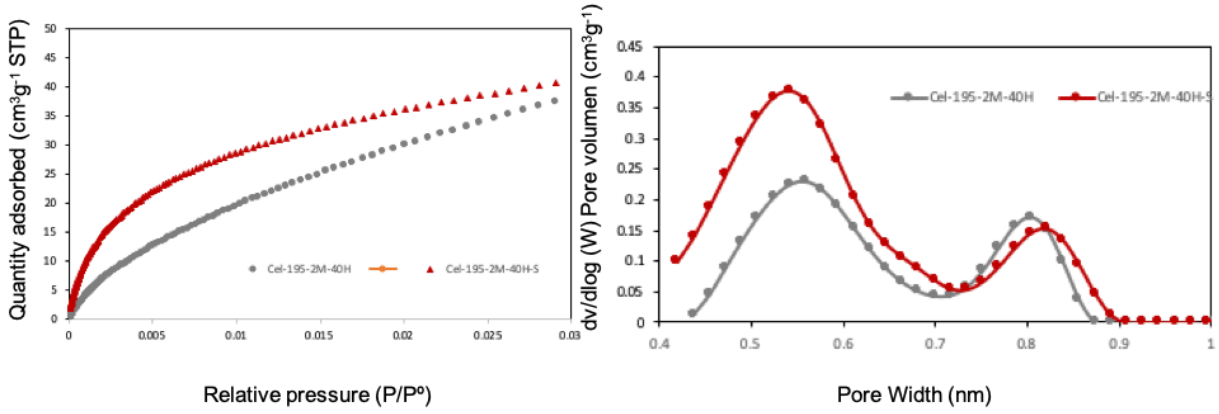

Figure S8. Plots of CO_2 adsorption isotherms and pore distribution for Cel-195-2M-40h Cel-195-2M-40h-S

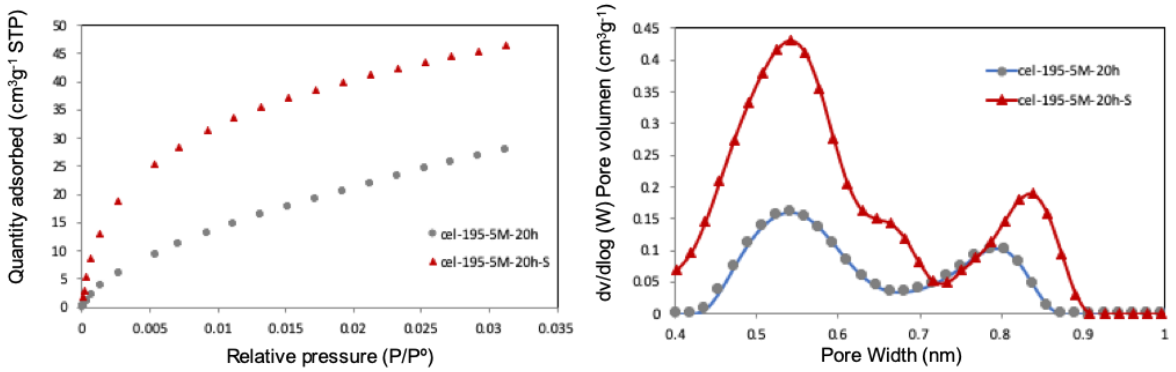

Figure S9. Plots of CO_2 adsorption isotherms and pore distribution for Cel-195-5M-20h Cel-195-5M-20h-S

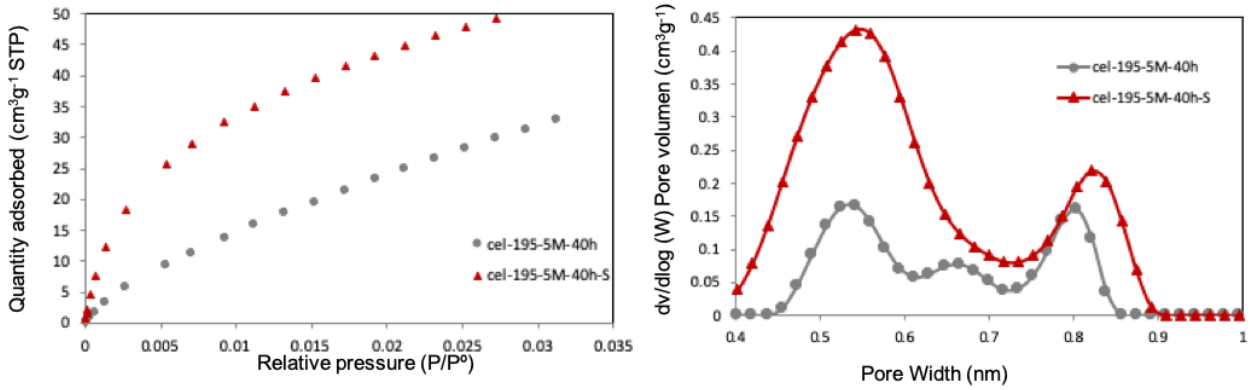

Figure S10. Plots of CO_2 adsorption isotherms and pore distribution for Cel-195-5M-40h Cel-195-5M-40h-S

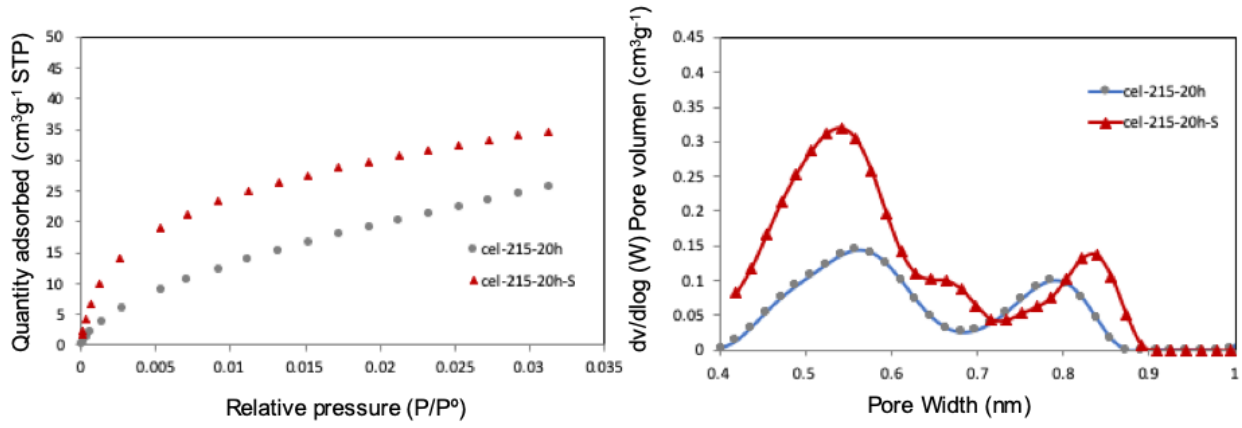

Figure S11. Plots of CO_2 adsorption isotherms and pore distribution for Cel-215-20h Cel-215-20h-S

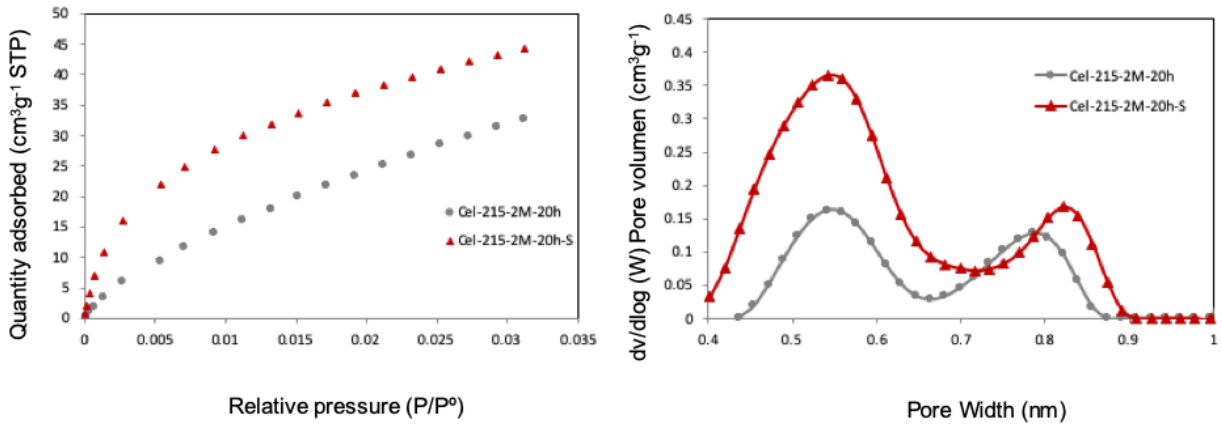

Figure S12. Plots of CO_2 adsorption isotherms and pore distribution for Cel-215-2M-20h Cel-215-2M-20h-S

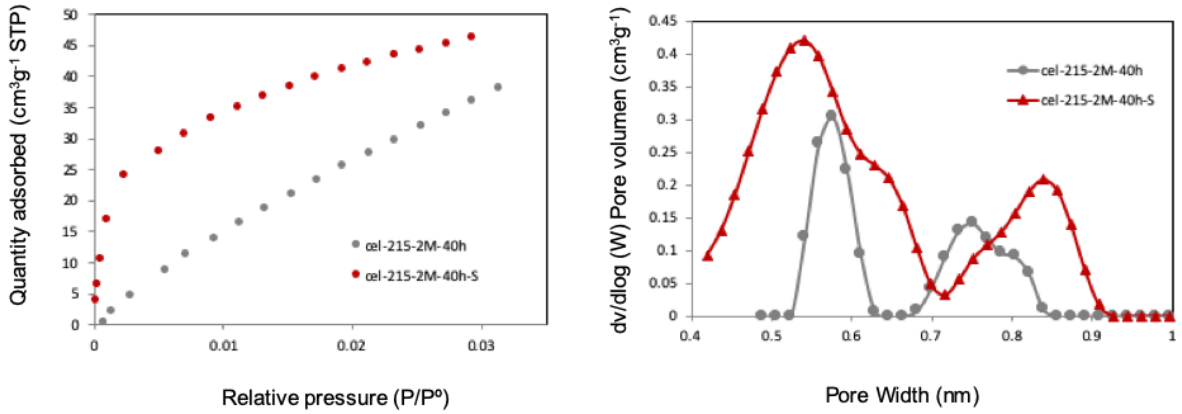

Figure S13. Plots of CO_2 adsorption isotherms and pore distribution for Cel-215-2M-40h Cel-215-2M-40h-S

4.-Data of Microporevolume values vs H.I. (Hydrothermal Index)

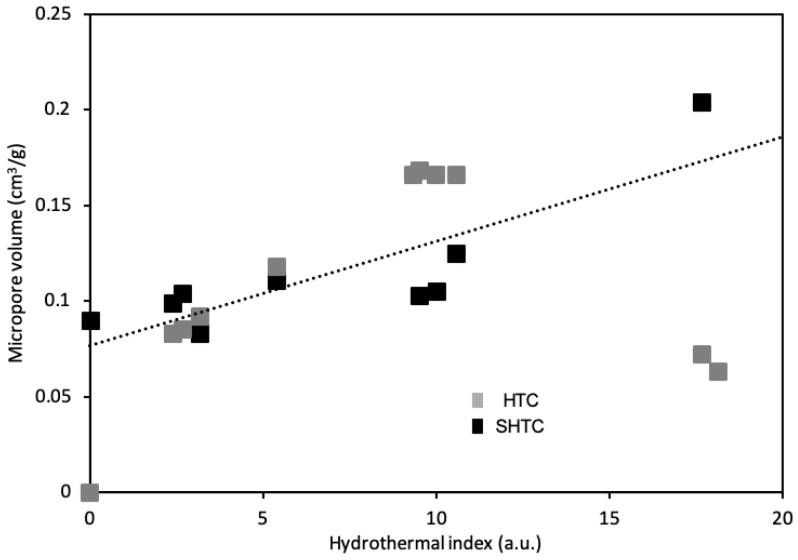

Figure S14. Relationship between hydrothermal index (H.I.) and micropore volume

5.-Data of Productivity vs time for Solketal synthesis catalyzed by sulfonated hydrothermal carbons.

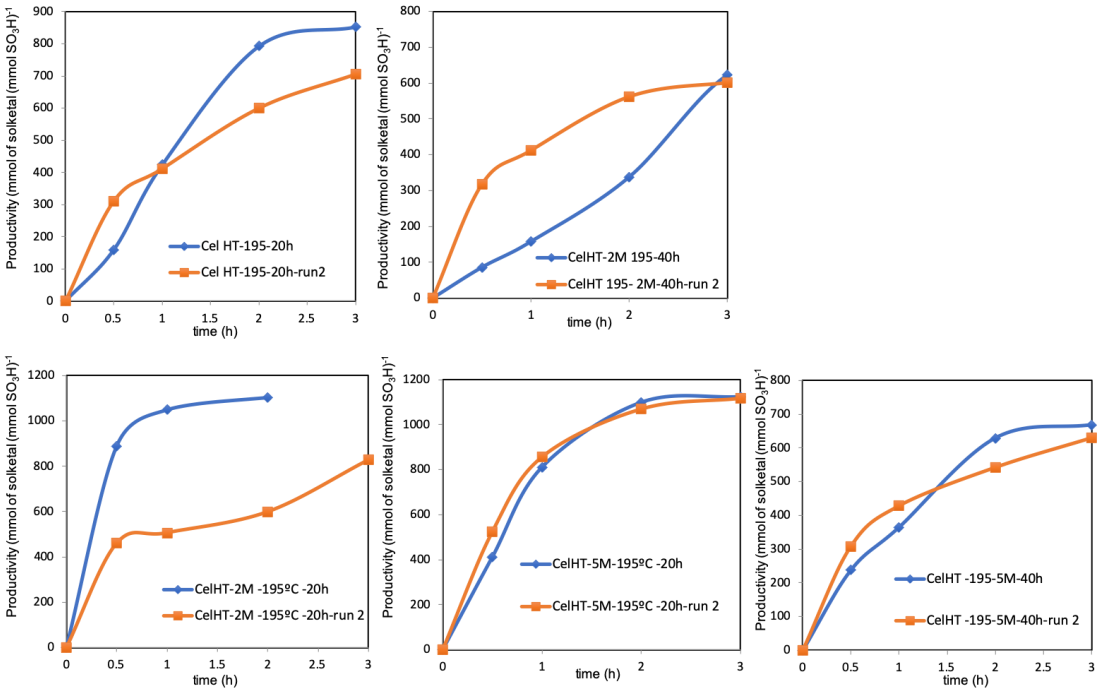

Figure S15. Productivity vs time plots for the synthesis of Solketal catalyzed by sulfonated hydrothermal carbons from cellulose prepared at 195ºC.

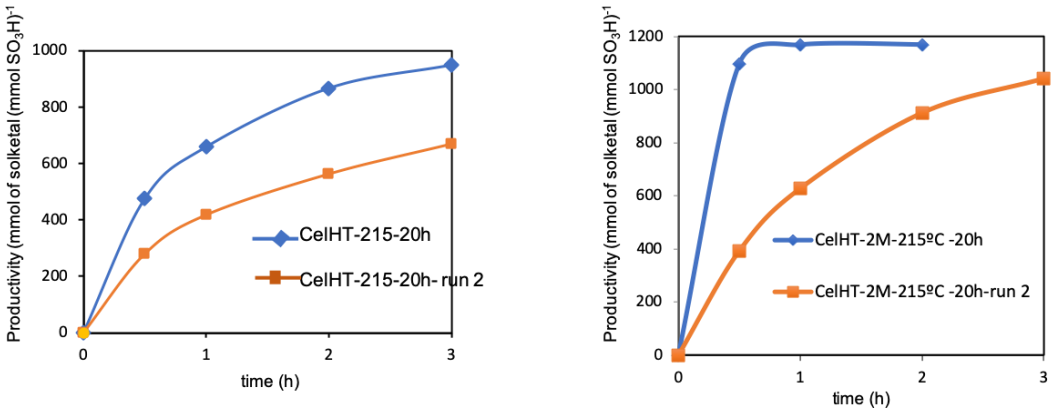

Figure S16. Productivity vs time plots for the synthesis of Solketal catalyzed by sulfonated hydrothermal carbons from cellulose prepared at 215ºC.

6.-Data of Productivity vs time for Solketal synthesis catalyzed by sulfonated commercial resins

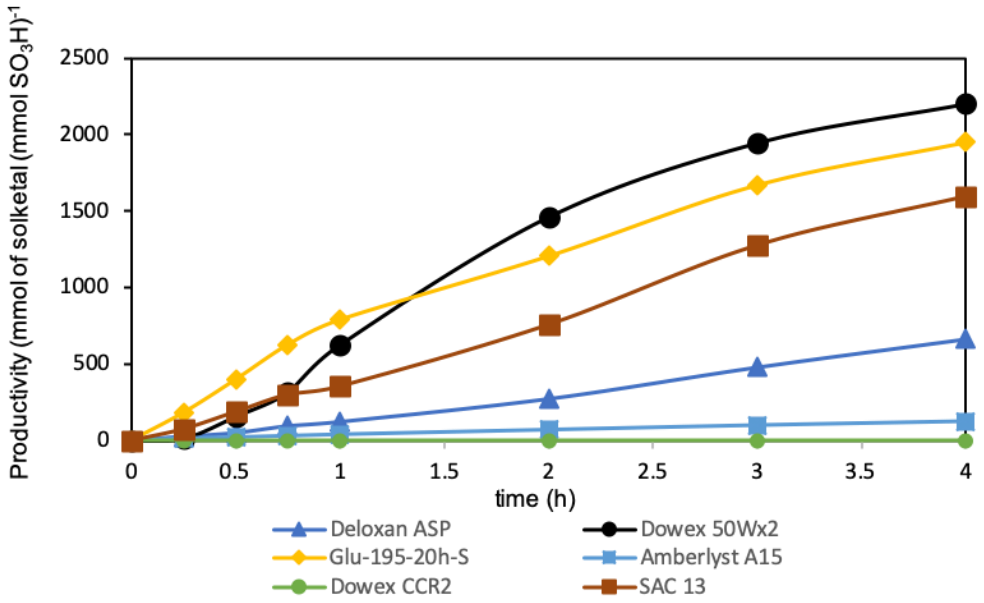

Figure S17. Productivity vs time plots for the synthesis of Solketal catalyzed by commercial resins and Glu-195-20h-S

7.-Data of Initial TOF vs acidity for Solketal synthesis catalyzed by reused sulfonated hydrothermal carbons.

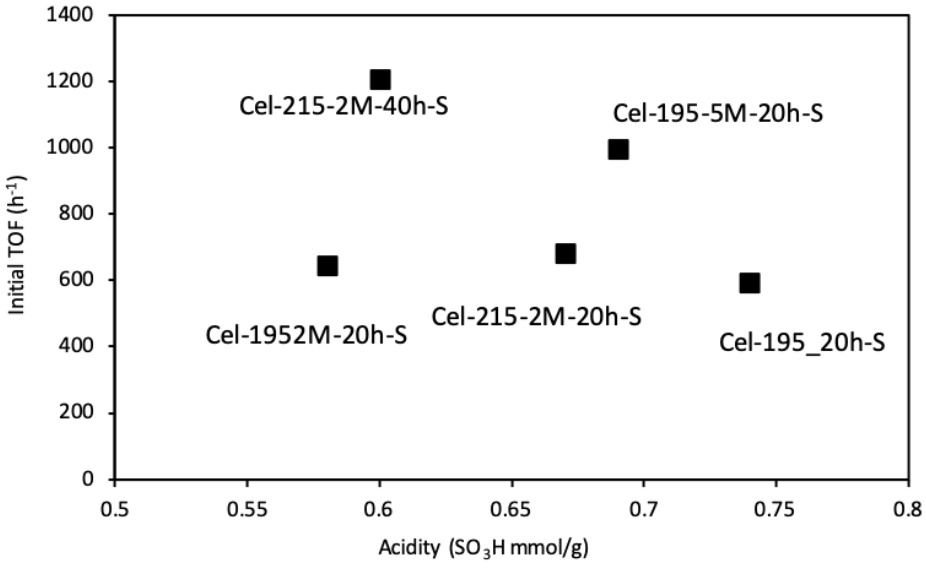

Figure S18: Initial TOF in solketal synthesis vs sulfonic acidity of reused catalyst plot with second-used SHTC as catalyst (reaction conditions: acetone: glycerol molar ratio 7:1, catalyst 1 % w/w with respect to glycerol, 25°C).