Electronic Supplementary Material (ESI) for Green Chemistry.

Mechanistic insights into the effect of feed concentration on product formation during acid-catalyzed conversion of glucose in ethanol

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SUPPLEMENTARY INFORMATION

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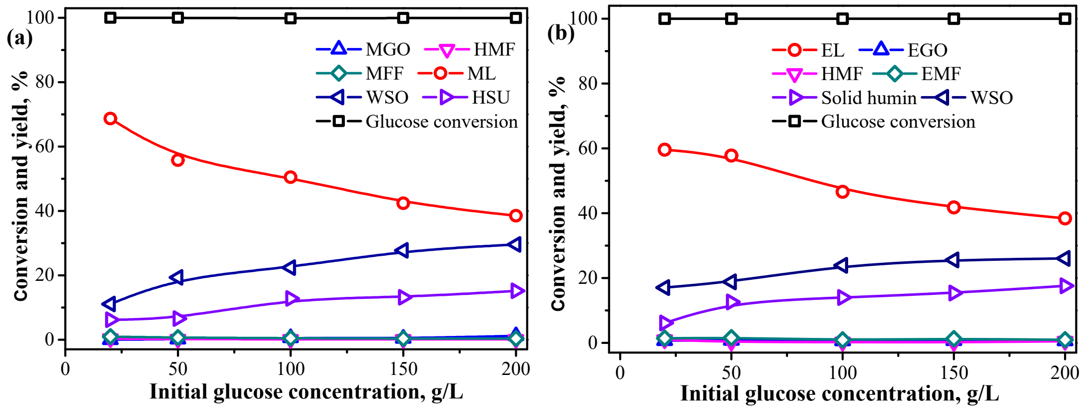

Figure S1. The conversion of glucose to alkyl levulinate over $Al_2(SO_4)_3$ in methanol (a) and ethanol (b). Reaction conditions: 0.01 mol $Al_2(SO_4)_3$, 50 mL alcohol, 180 °C, 180 min. (MGO and EGO represents methyl- and ethyl-D-glucopyraoside, respectively; MFF and EMF represents 5-methoxy- and 5-ethoxy-methylfurfural respectively)

NOTE: As shown in Figure S1, the substrate concentration has similar influence on the conversion of glucose in methanol and ethanol, the processing of glucose in ethanol at two distinct concentrations (20 and 200 g/L) was selected as model reaction to investigate the evolution of humins during the conversion of dilute and concentrated glucose.

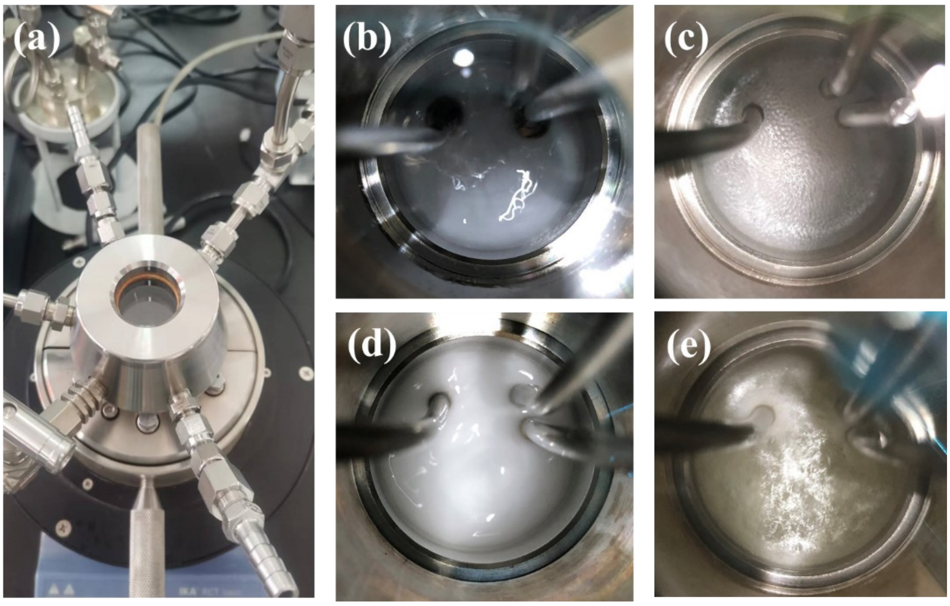

Figure S2. The photo of photocatalytic reactor with a transparent quartz seal (a), 20 g/L glucose solution at 30 °C (b) and after the temperature of the reactor increased to 160 °C (c), 200 g/L glucose solution at 30 °C (d) and after the temperature of the reactor increased to 160 °C (e).

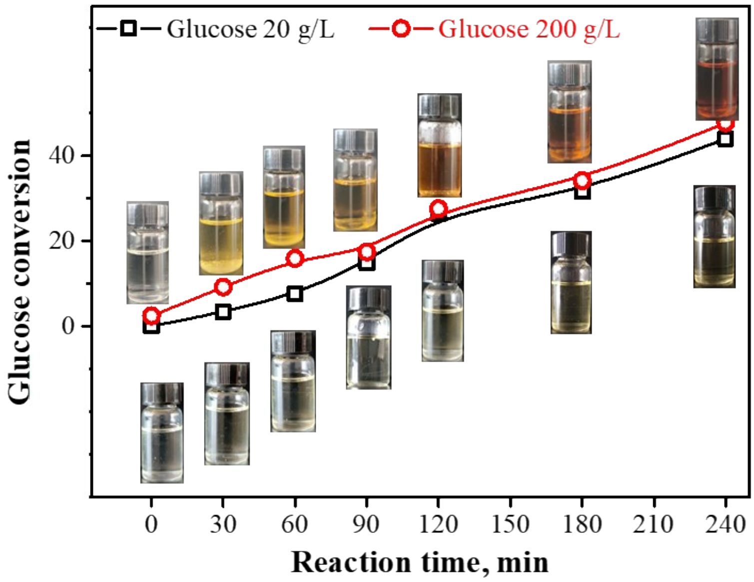

Figure S3. The conversion of glucose under catalyst-free conditions at two different concentrations. Reaction conditions: 20 g/L or 200 g/L glucose, no catalyst, 50 mL ethanol, 180 °C.

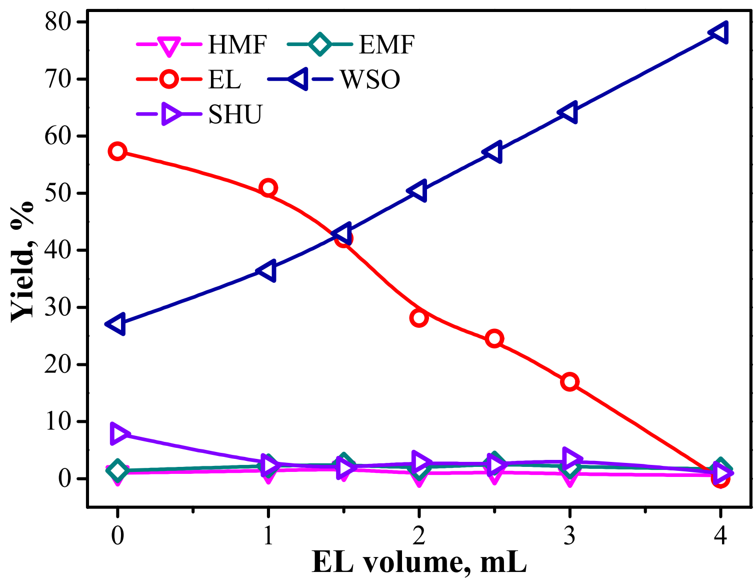

Figure S4. Effect of added EL on the formation of products in the reaction process. Reaction conditions: 20 g/L glucose, 0.001 mol $Al_2(SO_4)_3$, 50 mL ethanol-containing different volume additional EL, 180 °C for 3 h.

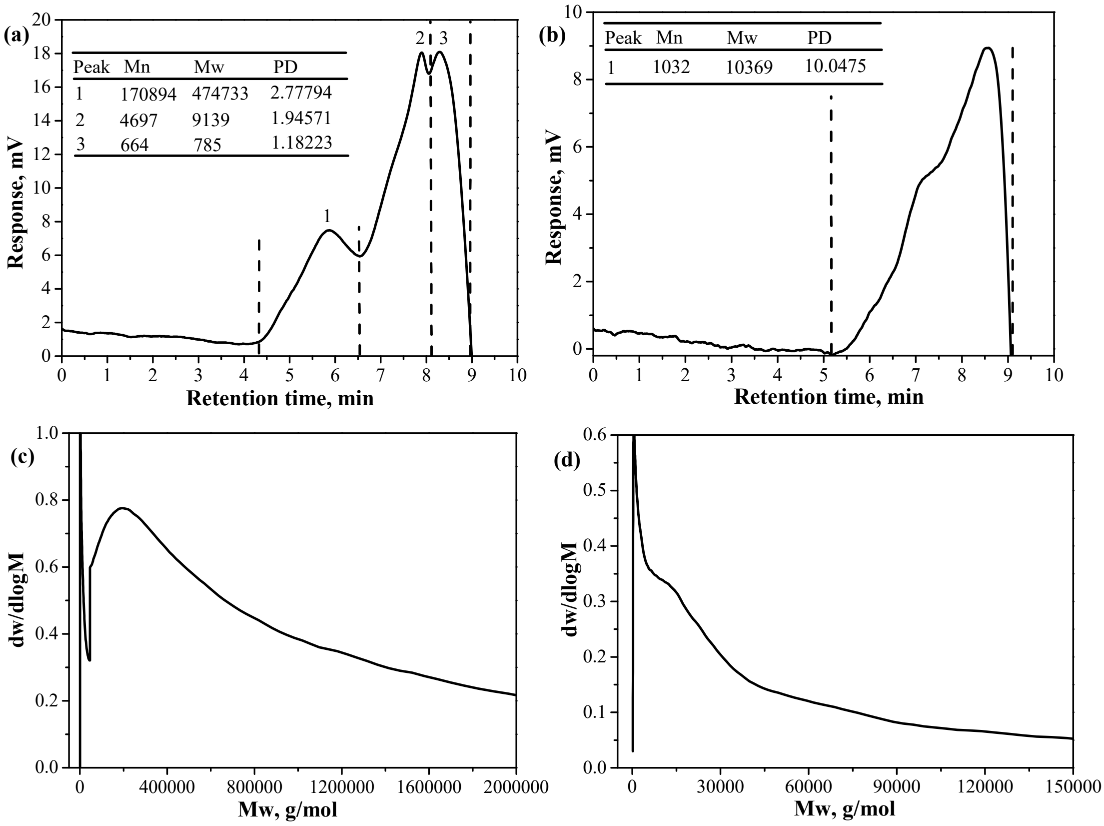

Figure S5. GPC spectra and average molecular weight of WSO_{20} (a) and WSO_{200} (b); molecular weight distribution of WSO_{20} (c) and WSO_{200} (d).

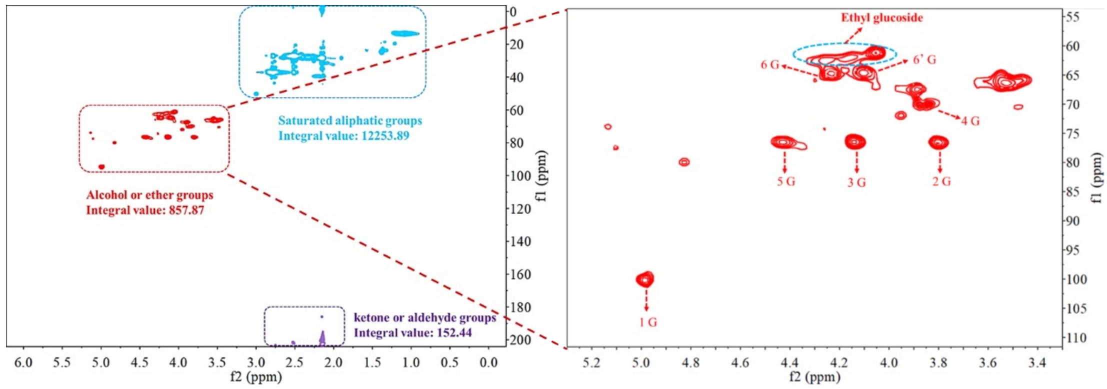

Figure S6. Assignment of the ^{1}H-^{13}C HSQC-NMR spectrum corresponding to WSO_{200}. Abbreviations: as an example, "1(G)" means signal from the H-1 and C-1 of the glucose residue (G).

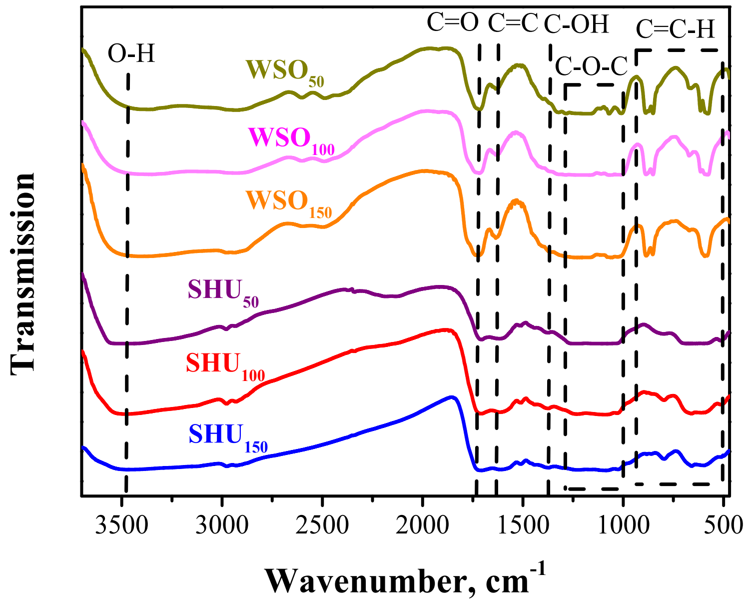

Figure S7. FTIR spectra of WSO and SHU from 50 g/L and 150 g/L of glucose conversion.

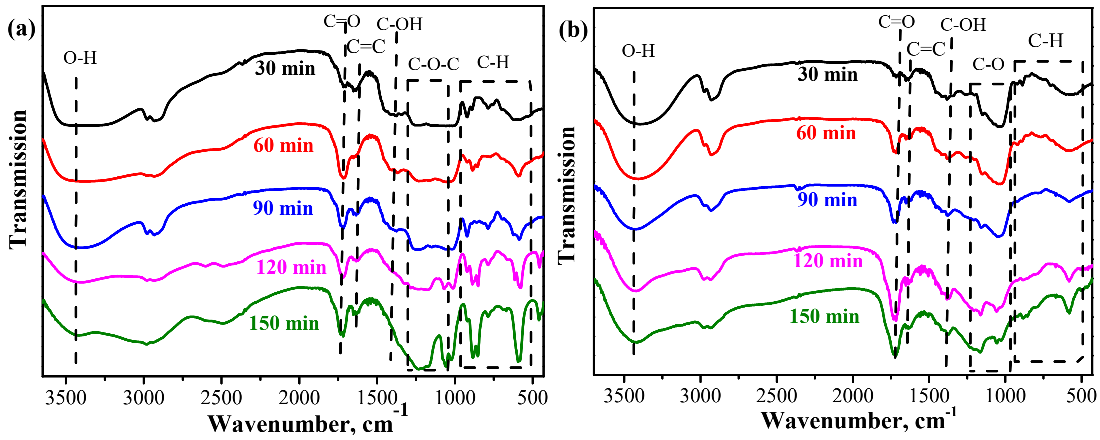

Figure S8. FT-IR spectra of WSO from 20 g/L (a) and 200 g/L (b) of glucose conversion with the increasing of the reaction time.

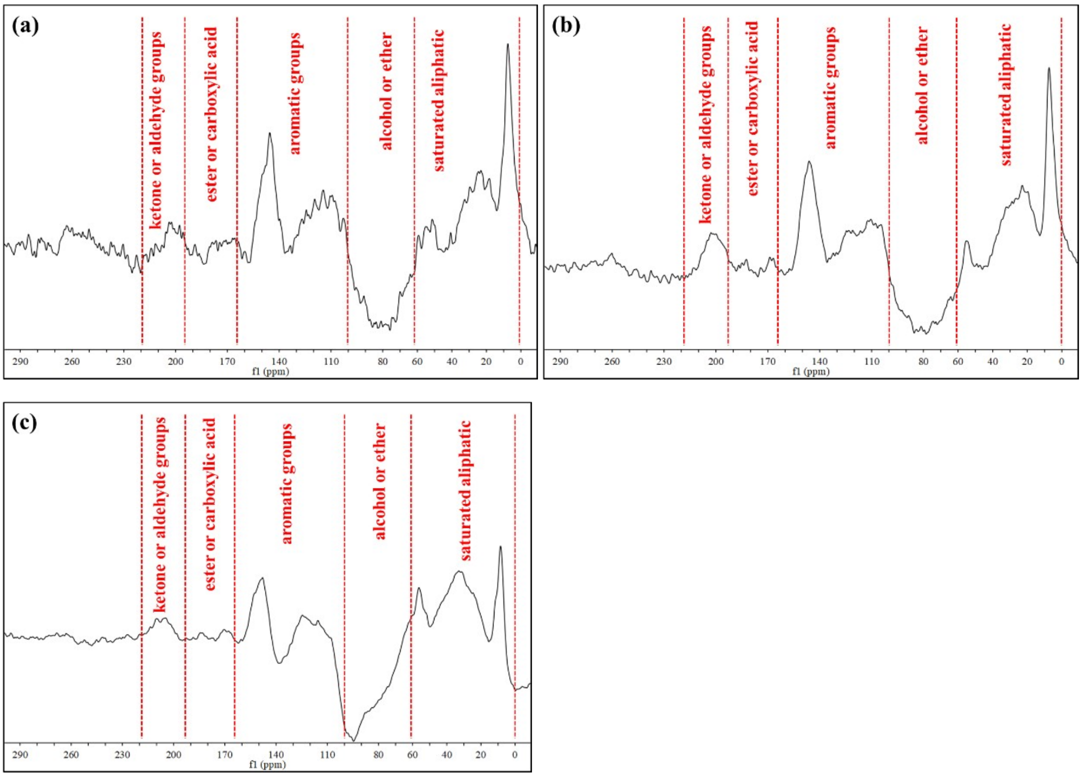

Figure S9. ^{13}C CP MAS NMR spectra of SHU from 50 g/L (a), 100 g/L (b) and 150 g/L (c) of glucose conversion.

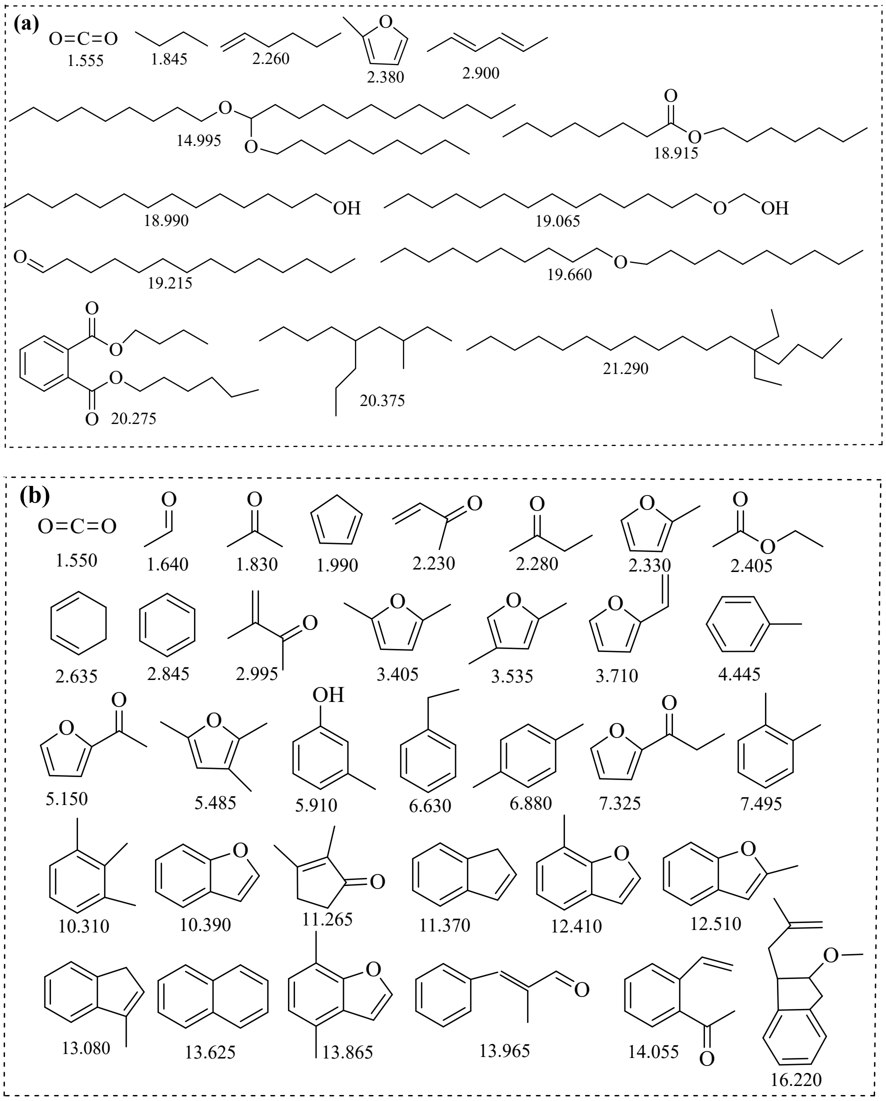

Figure S10. Pyrolysis/GC–MS chromatogram of SHU_{20} (a) and SHU_{200} (b).

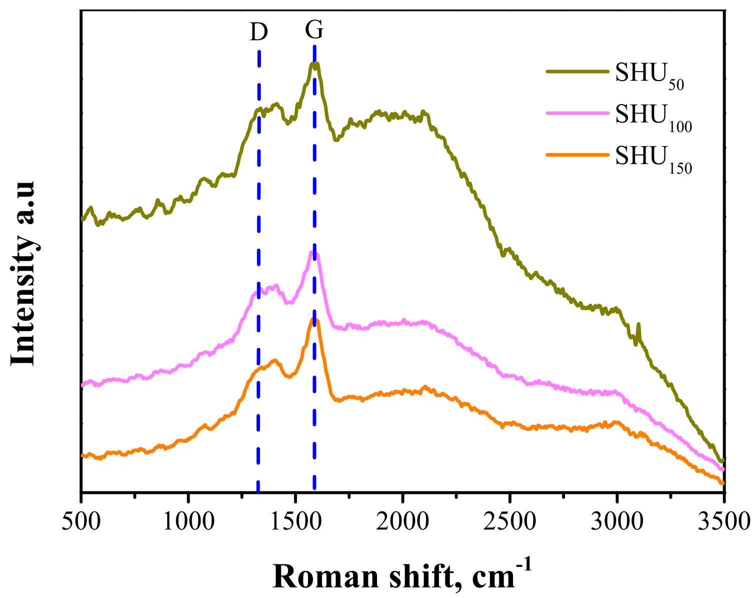

Figure S11. Raman spectra of SHU from 50 g/L (a), 100 g/L (b) and 150 g/L (c) of glucose conversion.

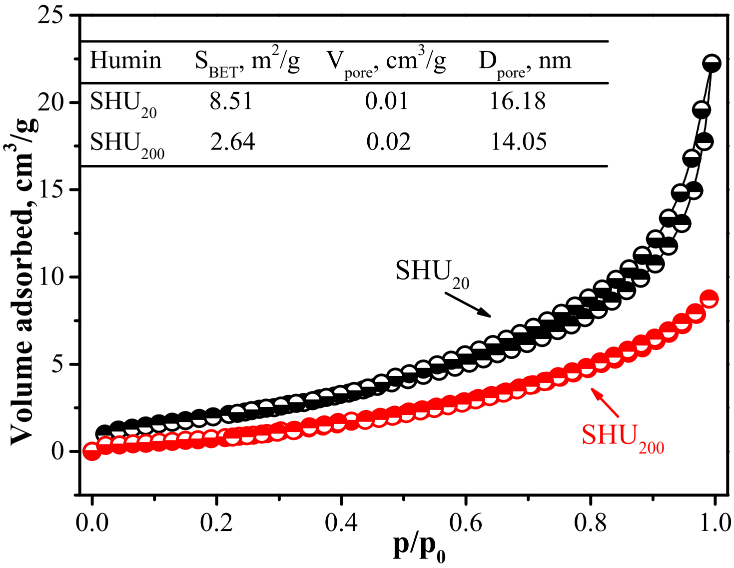

Figure S12. N_2 adsorption–desorption of SHU_{20} and SHU_{200}.

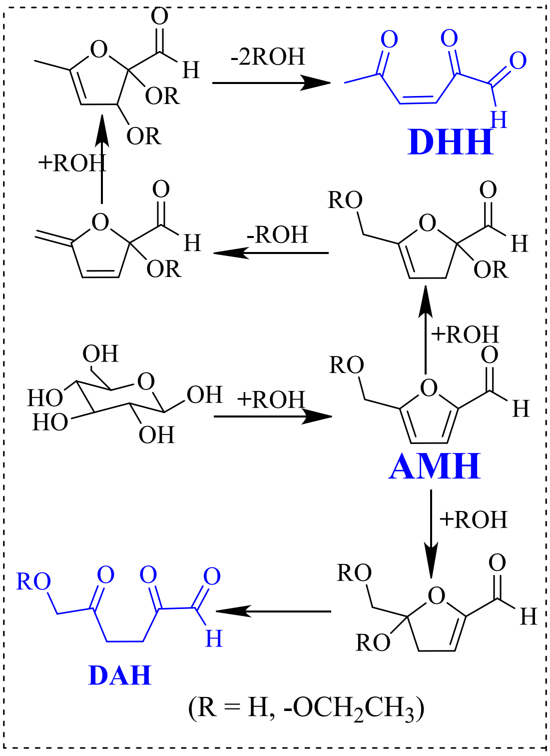

Figure S13. Transformation pathway of glucose to form DAH and DH.

Table S1. Assignment of the signals in the ^{13}C CP MAS NMR spectra of SHU[1].

δ, ppm	Functional group	Chemical formula
205	ketone, aldehyde	C=O, HC=O
175	Acid, ester	COOH, COOR
150	a carbon furan linked	C=C-O
142	a carbon furan terminal	C=C-O
128	furan conjugated	C-C=C-C
120	β carbon furan linked	C-C=C-O
112	β carbon furan	C-C=C-O
78	alcohol, ether	C-OH, C-O-C
48	aliphatic	C-H, C
39	aliphatic	C-H, C
28	aliphatic	$-CH_2-$
15	aliphatic	$-CH_3$

References:

1. van Zandvoort, I.; Wang, Y. H.; Rasrendra, C. B.; van Eck, E. R. H.; Bruijnincx, P. C. A.; Heeres, H. J.; Weckhuysen, B. M., Formation, Molecular Structure, and Morphology of Humins in Biomass Conversion: Influence of Feedstock and Processing Conditions. *ChemSusChem* **2013,** *6* (9), 1745-1758.