Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Electronic Supplementary Information

2-Methyl furan production by catalytic hydrogenation of furfural obtained in pinewood molten-salt pyrolysis

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Catalyst preparation and characterization

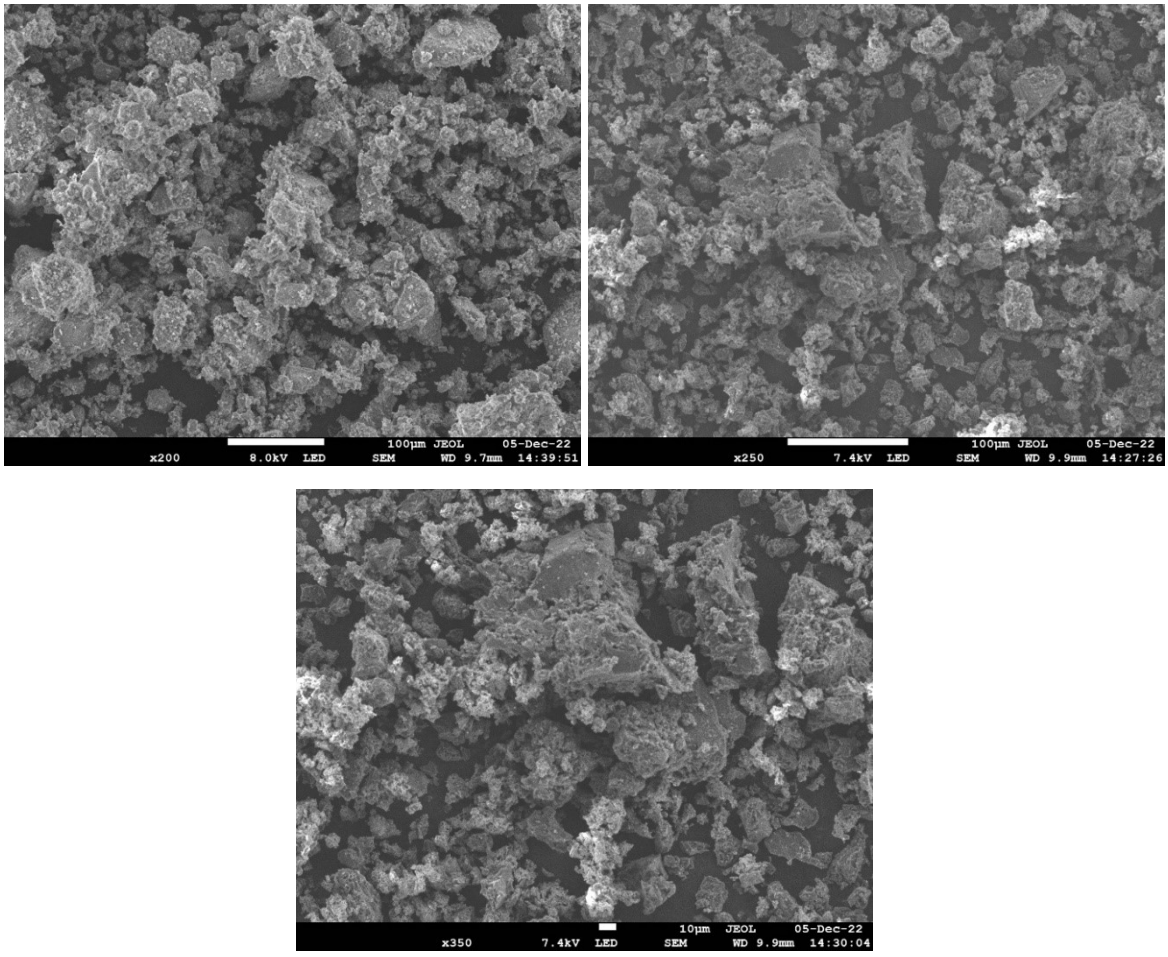

Figure S. 1: Emission Scanning Electron Microscopy images (SEM) of Cu/SiO_2 catalyst with 200-500x magnification.

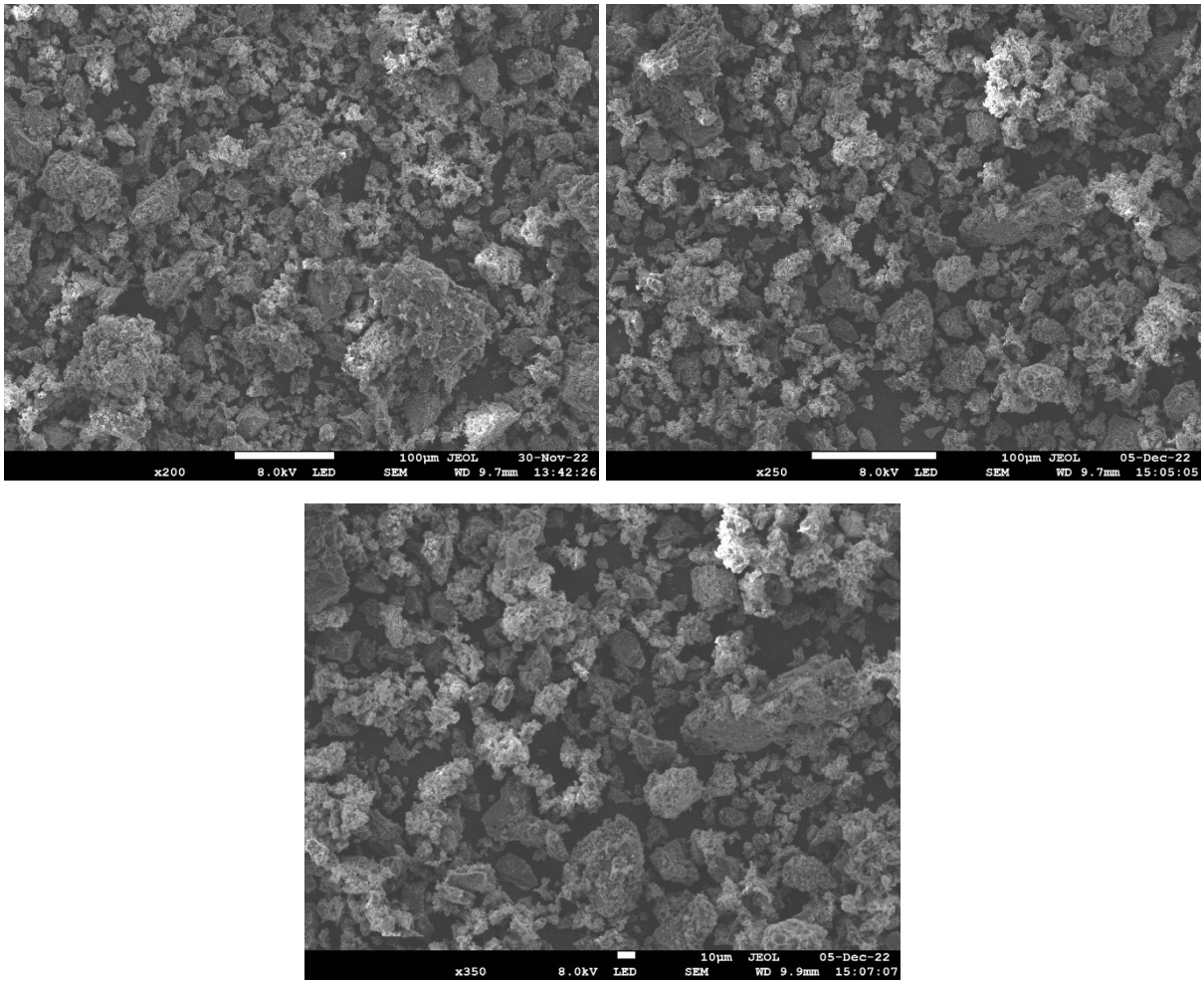

Figure S. 2: Emission Scanning Electron Microscopy images (SEM) of Cu/AC catalyst with 200-500x magnification.

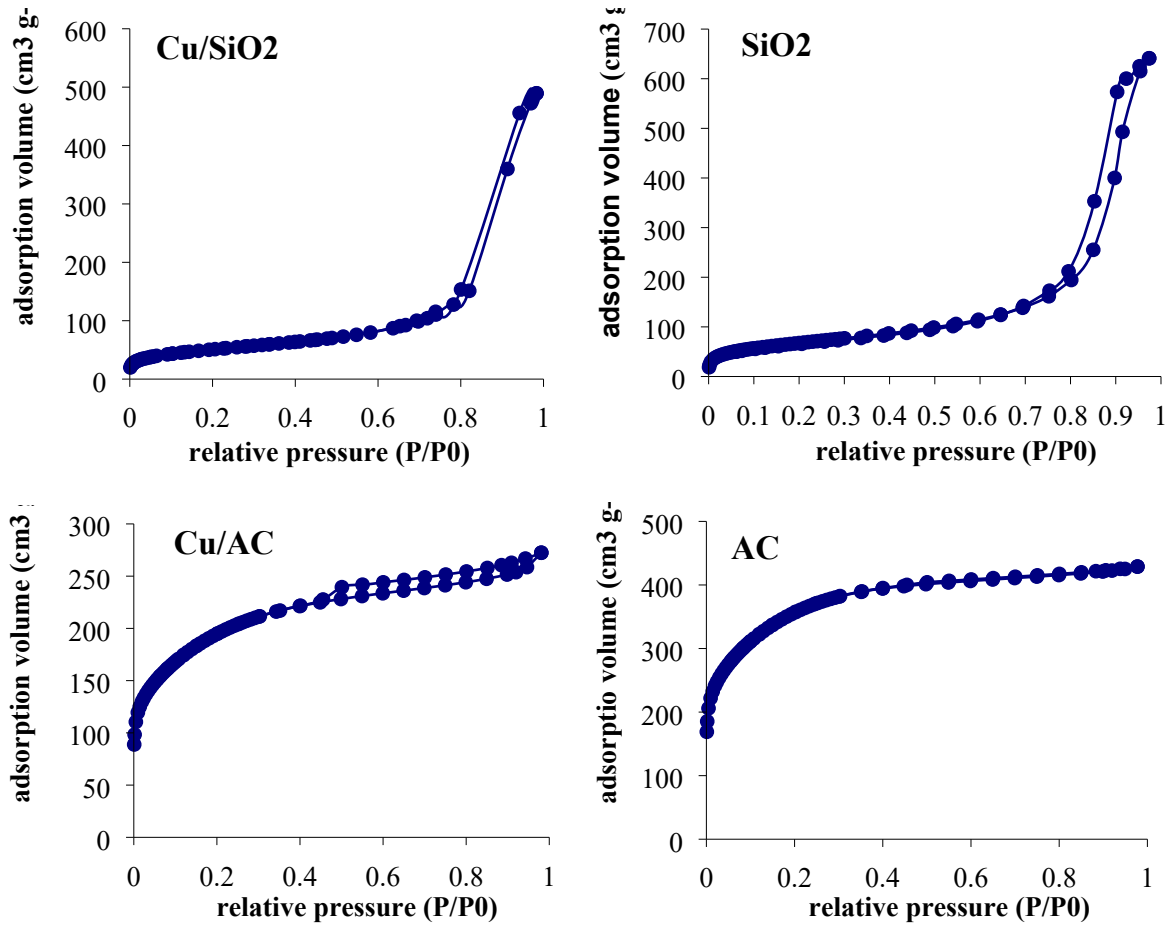

Figure S. 3: BET nitrogen adsorption/desorption isotherm plots for Cu-based catalysts and their corresponding supports; Cu/SiO_2 is copper supported on silica and Cu/AC is copper supported on activated carbon.

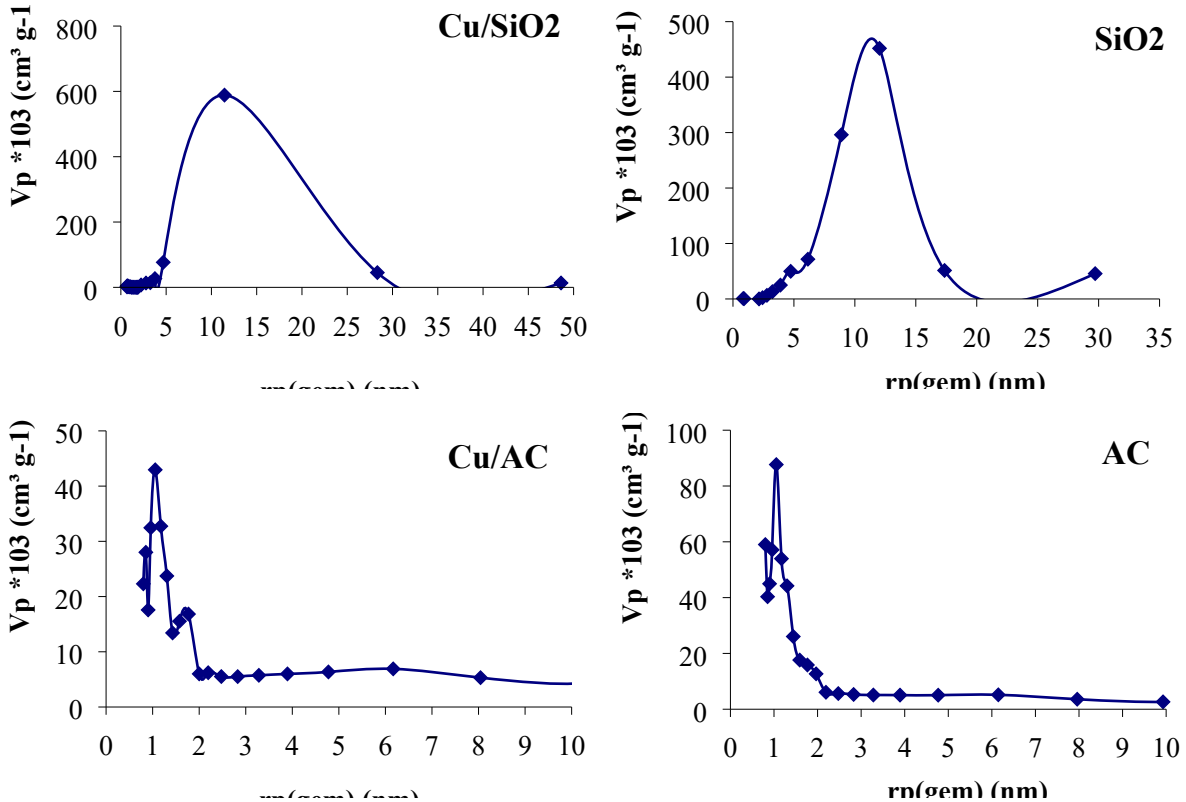

Figure S. 4: Pore size distributions of Cu-based catalysts and their corresponding supports; Cu/SiO_2 is copper supported on silica and Cu/AC is copper supported on activated carbon.

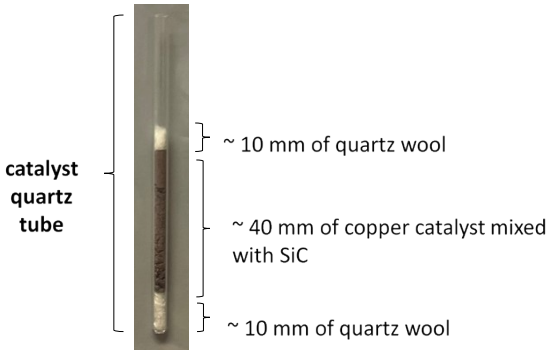

Figure S. 5: Assembly of the copper catalyst in the reactor tubes used for hydrodeoxygenation of furfural derived from molten salts hydropyrolysis. HDO temperatures studied range from 200 °C up to 600 °C.

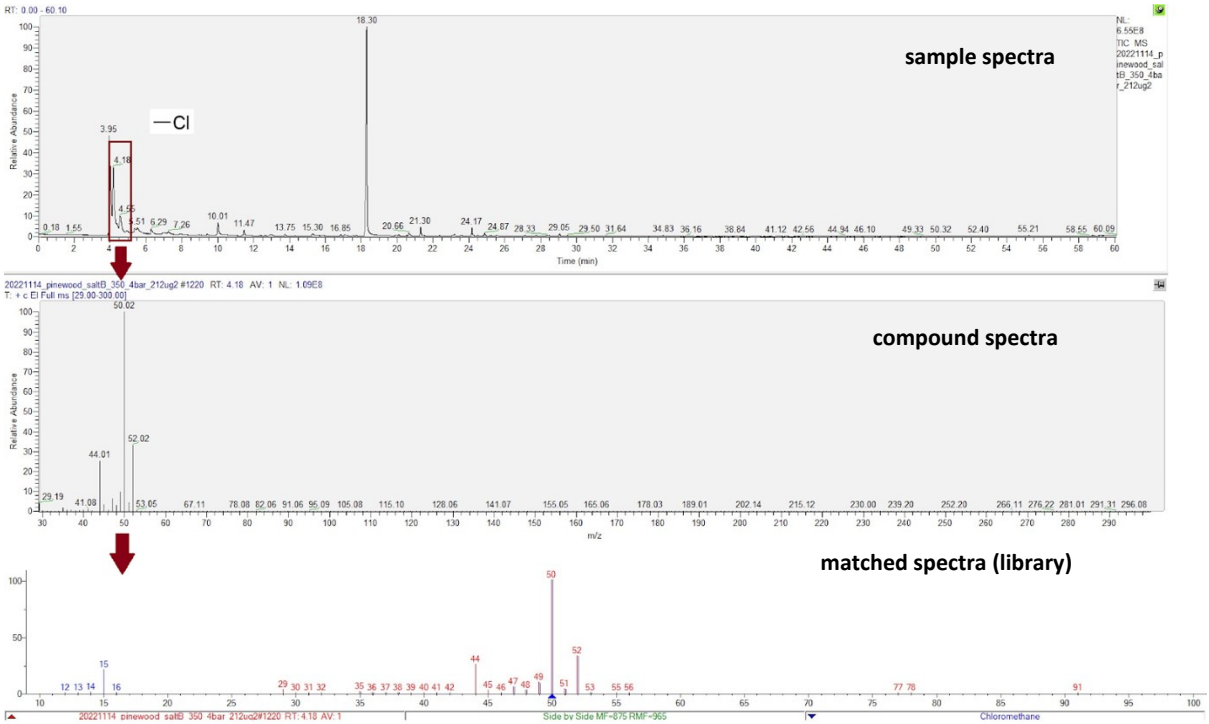

Figure S. 6: GC-MS total ion chromatogram (TIC) and mass spectrum for chloromethane identification using the NIST Tandem Mass Spectral Library (version 2.3)

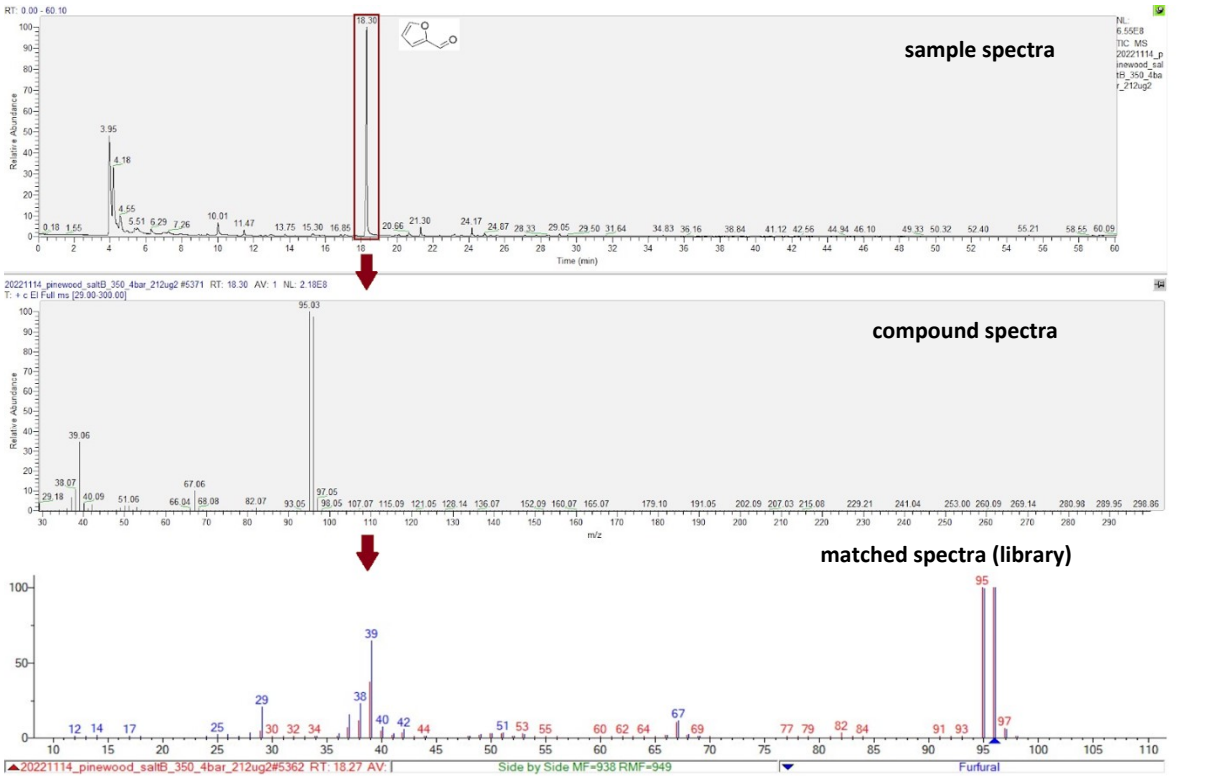

Figure S. 7: GC-MS total ion chromatogram (TIC) and mass spectrum for furfural identification using the NIST Tandem Mass Spectral Library (version 2.3)

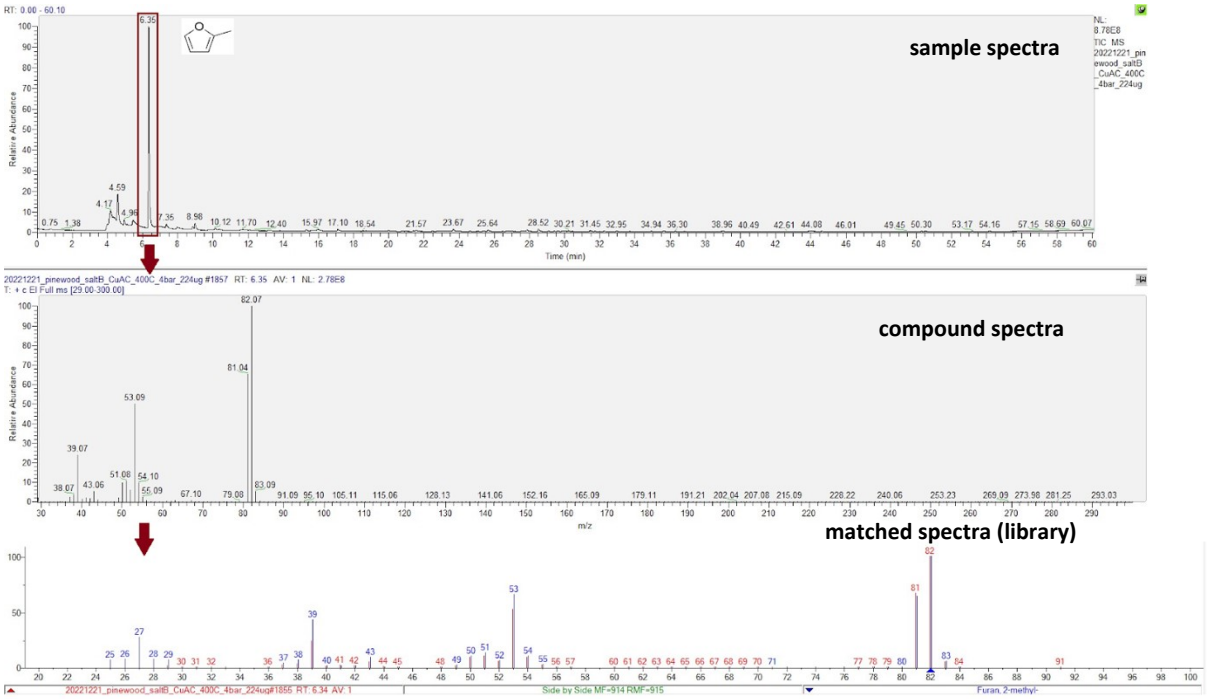

Figure S. 8: GC-MS total ion chromatogram (TIC) and mass spectrum for 2-methylfuran identification using the NIST Tandem Mass Spectral Library (version 2.3)

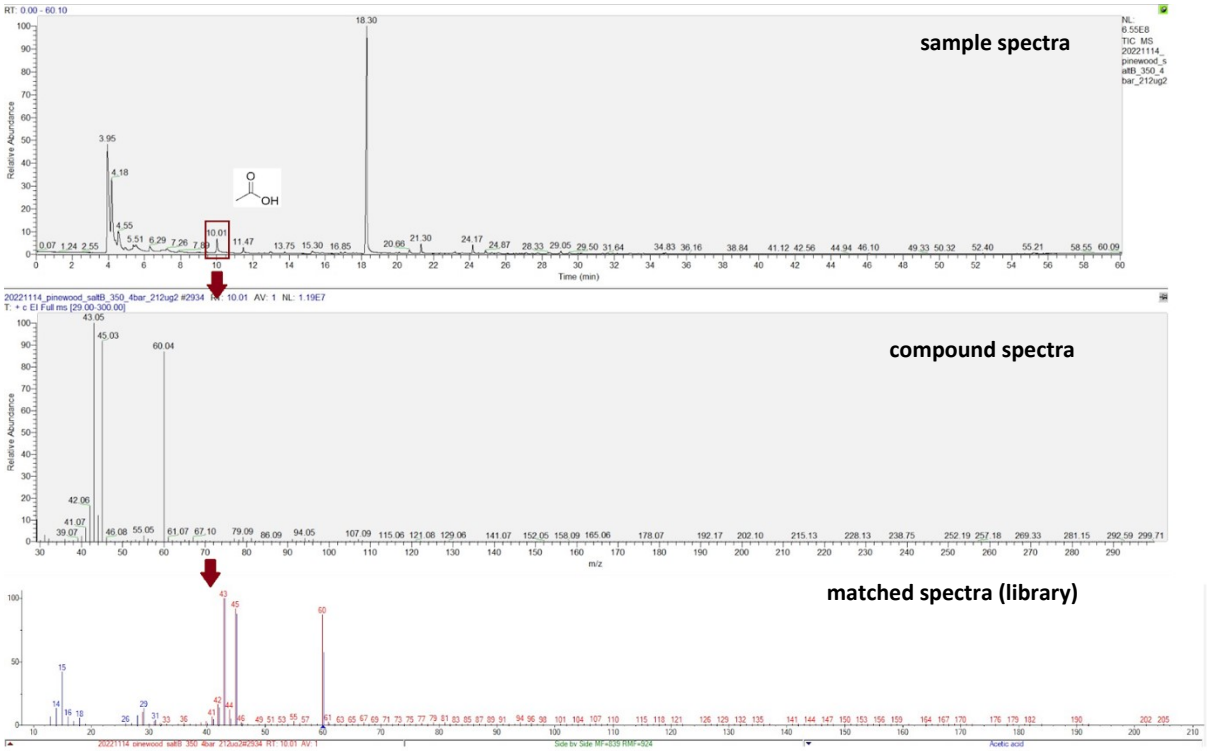

Figure S. 9: GC-MS total ion chromatogram (TIC) and mass spectrum for acetic acid identification using the NIST Tandem Mass Spectral Library (version 2.3)

Table S. 1: Py-GC-MS/FID data from pinewood hydropyrolysis in molten chloride salts (salt B) at 350 °C and subsequent vapor phase upgrade with Cu/SiO_2 at different temperatures. Pressure: 0.4 MPa. The yields in wt.% represent the mass of volatiles per mass of biomass.

experiment number (1st series)			*	1	2	3	4
temperature [°C]			/	200	300	400	500
groups	**retention time [min.]**	**compound**			**wt.%**		
alcohols	4.51 - 4.57	methanol	0.87	0.67	1.16	1.20	0.30
aldehydes	4.35 - 4.41	acetaldehyde	1.75	1.57	1.93	1.73	1.58
	5.27 - 5.33	propanal		0.66	0.73		
alkenes	5.47 - 5.54	cyclopentene	0.27			0.44	
carboxylic acids	9.97	acetic acid	4.07				
cyclo alkenes	6.96	3-methylcyclopentene				0.25	
furans	6.25 - 5.32	2-methylfuran	0.34	1.98	3.23	5.96	6.95
	18.27 - 18.30	furfural	10.73		5.50	5.03	
	8.94 - 8.96	2,5-dimethyl furan		0.24	0.20	0.41	0.75
	24.9 - 24.93	2,4-dimethyl furan			0.09	0.22	0.00
	21.27 - 21.37	acetylfuran	0.54		0.48	0.49	0.48
	4.92 - 4.94	furan		0.52	0.88	0.85	0.90
	24.14	5-methylfurfural	0.59				
	20.11 - 20.19	furfuryl alcohol		1.42	1.93	1.28	
halogens	4.15 - 4.21	chloromethane	1.51	1.30	2.21	1.19	0.47
ketones	5.34 - 5.55	acetone	++	++	++		++
	12.96	acetoin	0.07				
	7.29 - 7.49	2-butanone		0.06	0.06	0.08	0.10
	15.24 - 15.59	cyclopentanone		0.63	0.69	0.97	1.48

experiment number (1st series)			*	1	2	3	4
temperature [°C]			/	200	300	400	500
groups	**retention time [min.]**	**compound**			**wt.%**		
	11.44	hydroxyacetone	6.24				
	17.04 - 17.14	α-methylcyclopentanone			0.11	0.27	0.29
	20.66 - 20.72	2-methyl-2-cyclopentenone			0.09	0.15	0.14
	18.21	cyclopentenone					1.79
	10.05	2-pentanone					0.10
	10.29	3-pentanone					0.08
methoxy phenols	29.02	guaiacol	0.39				
monoaromatics	46.19	4-methylbiphenyl			0.49		
	28.49	2-ethenyl-1,3-dimethylbenzene			0.50		
	7.88	benzene			0.51		
non-condensable gases	3.97 - 4.02	CO, CH_4, propane				++	++

***++** was detected with a peak area > 1%, but could not be quantified.*

** benchmark sample (without vapor-phase upgrading)*

experiment number (2nd series)			5	6	7	8	9
temperature [°C]			300	400	500	600	300
groups	**retention time [min.]**	**compound**			**wt.%**		
alcohols	4.54 - 4.58	methanol	1,08	0,90	0,35		0,83
aldehydes	4.39 - 4.41	acetaldehyde	1,62	2,03	1,63	2,24	
alkenes	4.17	(E)-2-butene			4,17		
	5.16 - 5.65	cyclopentene	0,28	0,22		0,29	0,21

experiment number (2nd series)			5	6	7	8	9
temperature [°C]			300	400	500	600	300
groups	**retention time [min.]**	**compound**			**wt.%**		
cyclo alkenes	17,75	3-methylcyclopentene	0,18				
furans	6.31 - 6.54	2-methylfuran	5,24	6,54	5,77	4,53	4,29
	8.92 - 8.96	2,5-dimethyl furan	0,36	0,46	0,63	0,33	0,35
	21.32 - 21.33	acetylfuran		0,44	0,48		
	4.90 - 4.95	furan	0,63	0,77	0,88	1,01	0,61
halogens	4.17 - 4.22	chloromethane	1,67	1,43	0,37	0,62	1,22
ketones	5.39 - 5.55	acetone	++	++	++	++	++
	7.28 - 7.29	2-butanone		0,08	0,10	0,11	
	15.22 - 15.28	cyclopentanone	0,52	0,88	1,45	0,73	0,50
	17.03 - 17.11	α-methylcyclopentanone	0,26	0,24	0,25		0,20
	20,65	2-methyl-2-cyclopentenone			0,13		
	18,20	cyclopentenone		18,20	18,20		
	10.03 - 10.05	2-pentanone	10,05	10,03	10,03		
non-condensable gases	3.94 - 3.96	CO, CH4, propane	++	++	++	++	++
phenols	10,16	phenol			0,21		

++ *was detected with a peak area > 1%, but could not be quantified.*

Table S. 2: Py-GC-MS/FID data from pinewood hydropyrolysis in molten chloride salts (salt B) at 350 °C and subsequent vapor phase upgrade with Cu/AC at different temperatures. Pressure: 0.4 MPa. The yields in wt.% represent the mass of volatiles per mass of biomass.

	experiment number		1	2	3	4	5	6
	temperature [°C]		300	400	400	500	500	300
groups	**retention time [min.]**	**compound**			**wt.%**			
alcohols	4.54	methanol	0.66	0.63	1.14	0.78	0.89	1.19
aldehydes	4.39 - 4.41	acetaldehyde	1.57					1.82
alkenes	4.13 - 4.14	(E)-2-butene			4.14	4.13		
	5.15 - 5.17	cyclopentene			5.17	5.15		
furans	6.30 - 6.44	2-methylfuran	1.38	6.21	10.17	7.88	10.34	9.24
	8.92 - 9.17	2,5-dimethyl furan		0.51	0.20	0.15	0.21	0.25
	4.90 - 4.96	furan	0.77	0.69	0.74	1.35	1.14	0.62
	8.81	2-ethylfuran		0.12	0.10			
halogens	4.17 - 4.19	chloromethane	0.40					1.47
ketones	5.42 - 5.47	acetone		++	++	++	++	++
	7.27 - 7.33	2-butanone		0.09	0.07	0.09	0.09	
	15.22 - 15.23	cyclopentanone				0.46	0.43	
	17.03 - 17.04	α-methylcyclopentanone			17.04	17.03		
	10.03 - 10.04	2-pentanone			10.04	10.03		
monoaromatics	46.16 - 46.17	4-methylbiphenyl				0.58	0.50	
	7.89 - 7.88	benzene			7.88	7.89		
non-condensable gases	3.92 - 3.95	CO, CH_4, propane	++	++	++	++	++	++
PAHs	35.55 - 35.55	1-methylnaphthalene				0.19	0.15	
phenols	28.36	phenol				0.23		

++ was detected with a peak area > 1%, but could not be quantified.

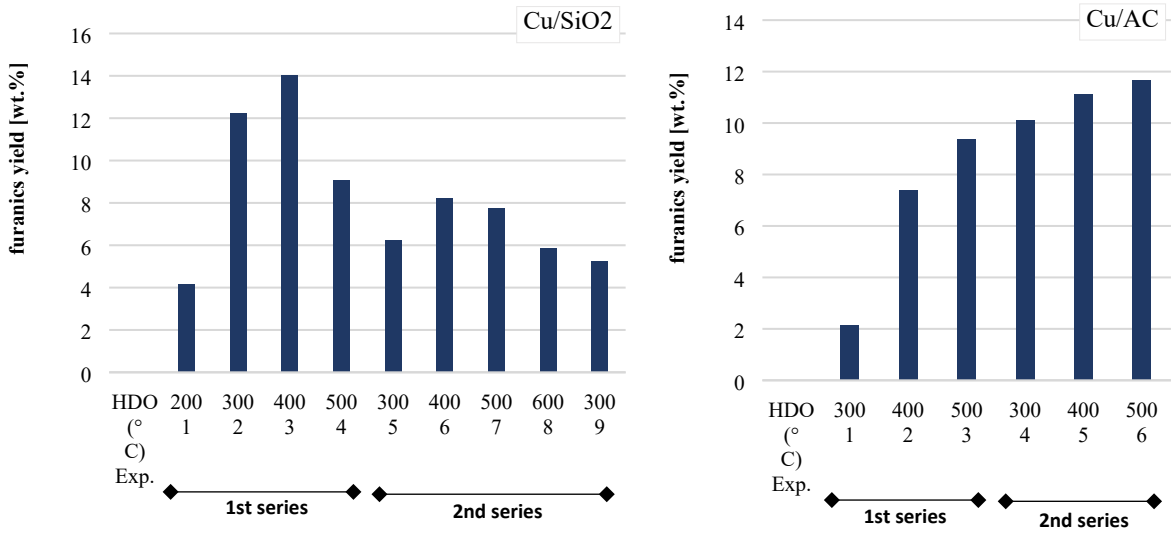

Figure S. 10: Total furanics yield from the combined molten salts hydropyrolysis of pinewood and subsequent HDO with Cu/SiO_2 (left) and Cu/AC (right).