Expanding the scope of biogenic substrates for the selective production of formic acid from water-insoluble and wet waste biomasses

Supplementary Information

Elemental analysis of different substrates

The elementary analysis of all complex, water-insoluble biomasses of 2nd and 3rd generation (Tables 1 & 5) as well as all chemically contaminated biomass substrates (Table 2) applied in this study were carried out using a Euro Vector EA 3000.

Table ESI-1: Elementary analysis of all applied biogenic substrates and contaminated materials

Substrate	Amount of C [wt%]	Amount of H [wt%]	Amount of N [wt%]	Amount of S [wt%]	Amount of O [wt%]
Pomace	13.95	7.74	1.24	0.00	77.07
Cane trash	37.87	7.02	0.49	0.00	54.62
Fruit pulp	39.59	6.38	1.23	0.00	52.80
Spruce chips	46.52	5.92	0.00	0.00	47.56
Poplar splint	46.82	5.88	0.11	0.00	47.19
Grass clippings	42.56	6.22	2.93	0.00	48.29
Chondrus crispus	30.22	4.64	2.44	6.05	56.65
Chlorella	47.43	6.90	7.87	0.33	37.47
Oak bark	44.56	5.78	0.62	0.00	49.04
Willow bark	46.38	6.26	1.17	0.00	46.19
Cyanobacter	30.93	4.76	6.38	0.93	57.00
Spirulina	46.14	6.79	10.58	0.42	36.07
Birch bark	47.38	6.58	0.48	0.00	45.56
Ascophyllum nodosum	35.11	5.08	1.05	1.93	56.83
Straw	42.62	5.50	1.06	0.05	50.77
Nettle leafs	40.08	6.01	5.34	0.28	48.29
Ulva lactuca	31.29	5.33	3.88	4.01	55.49
Effluent sludge	36.33	5.48	6.71	0.68	50.80
Railway sleeper	39.18	6.13	1.11	0.00	53.58
Beech condensate	44.87	5.79	0.06	0.00	49.28
Deinking sludge	21.43	2.26	0.25	0.04	76.02
Beech wood	45.20	5.72	0.04	0.00	49.04
Pine wood	46.62	6.05	0.00	0.00	47.33

NMR Spectroscopy

The ^{13}C-NMR spectra were recorded on a JEOL ECX-400 MHz spectrometer. The following spectrum shows the ^{13}C-NMR of the defined poisoning experiment for the POM catalyst with Ni (II) species.

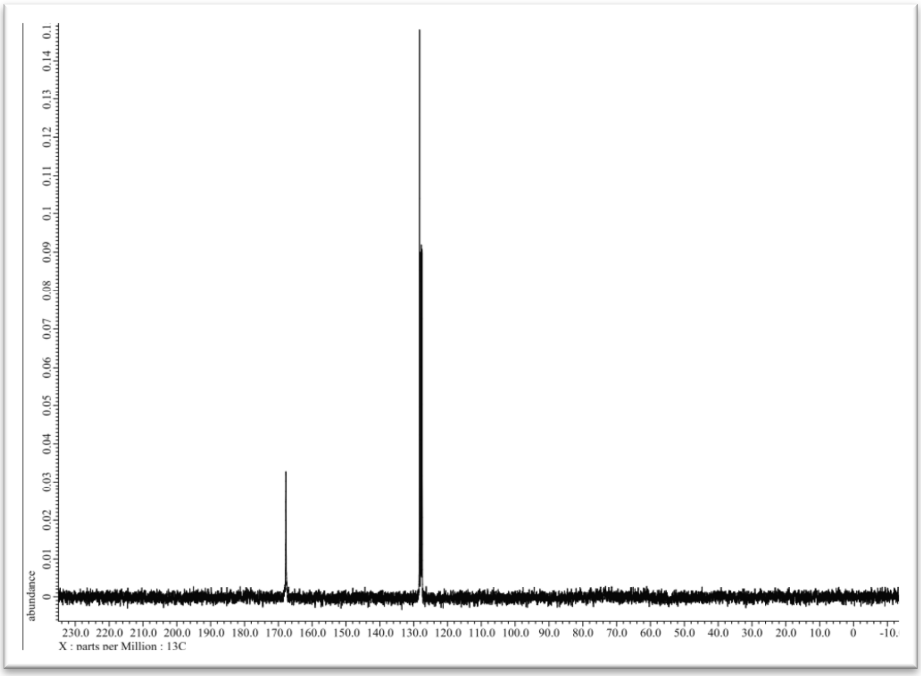

Figure 1: ^{13}C NMR spectrum of the reaction solution of 5 g (25 mmol) glucose as a substrate; 1.74 g (0.9 mmol) HPA-2 as a catalyst dissolved in 100.0 mL H_2O together with 1.01 g (8 mmol) of $NiCl_2$ impurity after 6.5 h under 30 bar O_2, 90 °C, 1000 rpm (peak at 128.5 ppm: external standard benzene; peak at 167 ppm: reaction product formic acid).

The ^{51}V-NMR spectra were recorded on a JEOL ECX-400 MHz spectrometer. The following spectra show the ^{51}V-NMR of different of the reaction solutions containing water-insoluble fillers and late transition-metal cations showing significant changes after addition of Cu-. Ni- and Pb-salts.

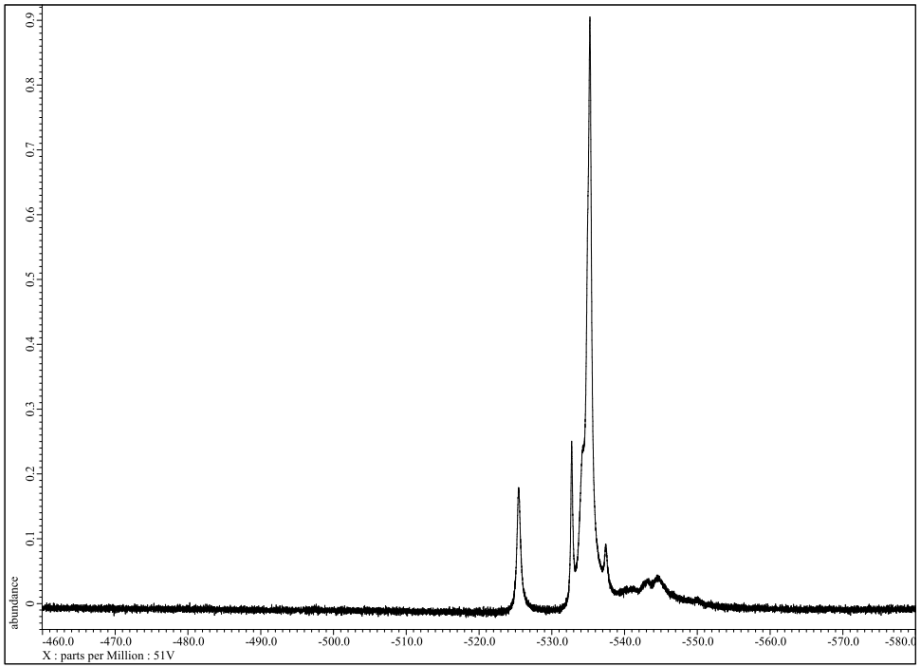

Figure 2: ^{51}V NMR spectrum of the reaction solution of 5 g (25 mmol) glucose as a substrate; 1.74 g (0.9 mmol) HPA-2 as a catalyst dissolved in 100.0 mL H_2O without impurity after 6.5 h under 30 bar O_2, 90 °C, 1000 rpm.

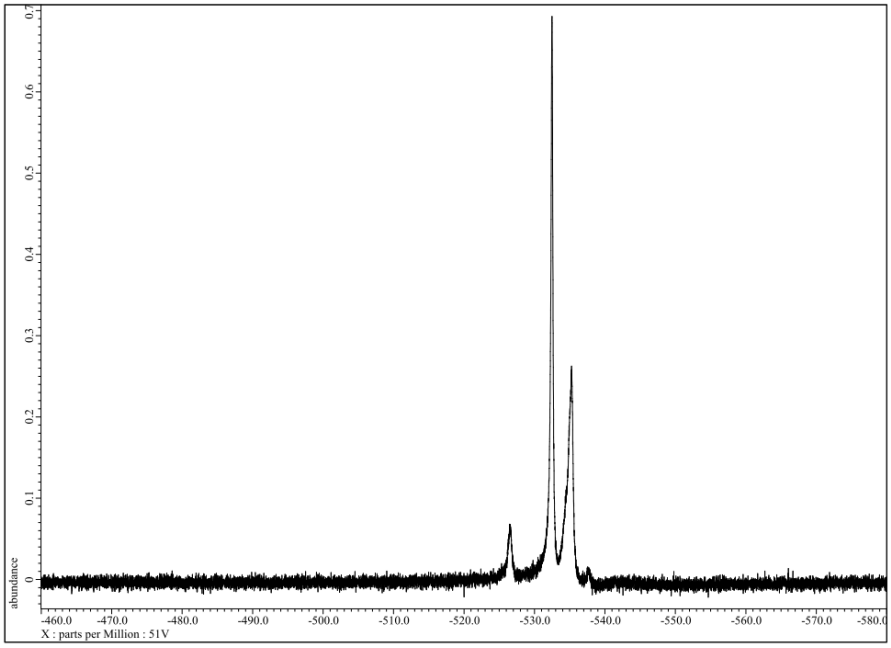

Figure 3: ^{51}V NMR spectrum of the reaction solution of 5 g (25 mmol) glucose as a substrate; 1.74 g (0.9 mmol) HPA-2 as a catalyst dissolved in 100.0 mL H_2O together with 1.25 g (8 mmol) of $CuSO_4$ impurity after 6.5 h under 30 bar O_2, 90 °C, 1000 rpm.

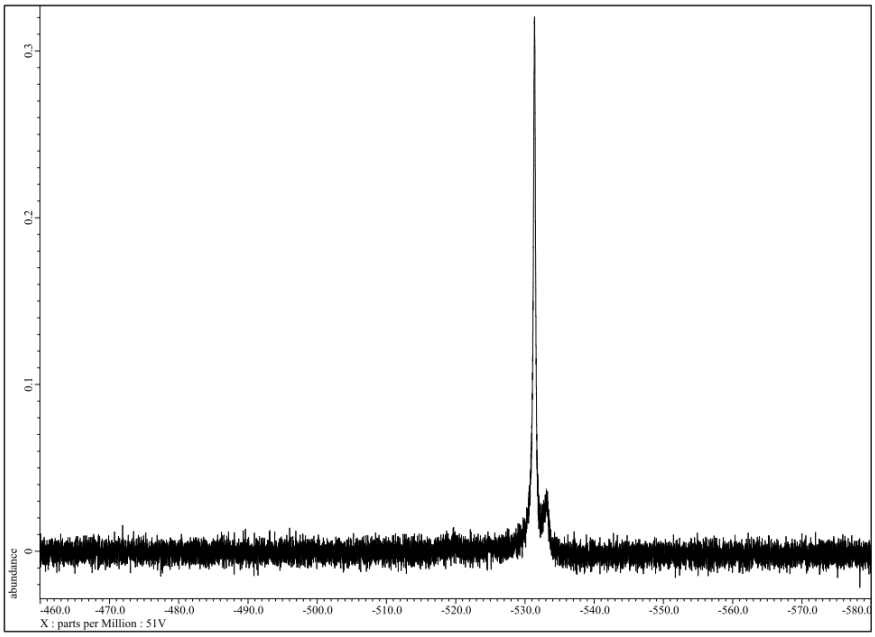

Figure 4: ^{51}V NMR spectrum of the reaction solution of 5 g (25 mmol) glucose as a substrate; 1.74 g (0.9 mmol) HPA-2 as a catalyst dissolved in 100.0 mL H_2O together with 1.01 g (8 mmol) of $NiCl_2$ impurity after 6.5 h under 30 bar O_2, 90 °C, 1000 rpm.

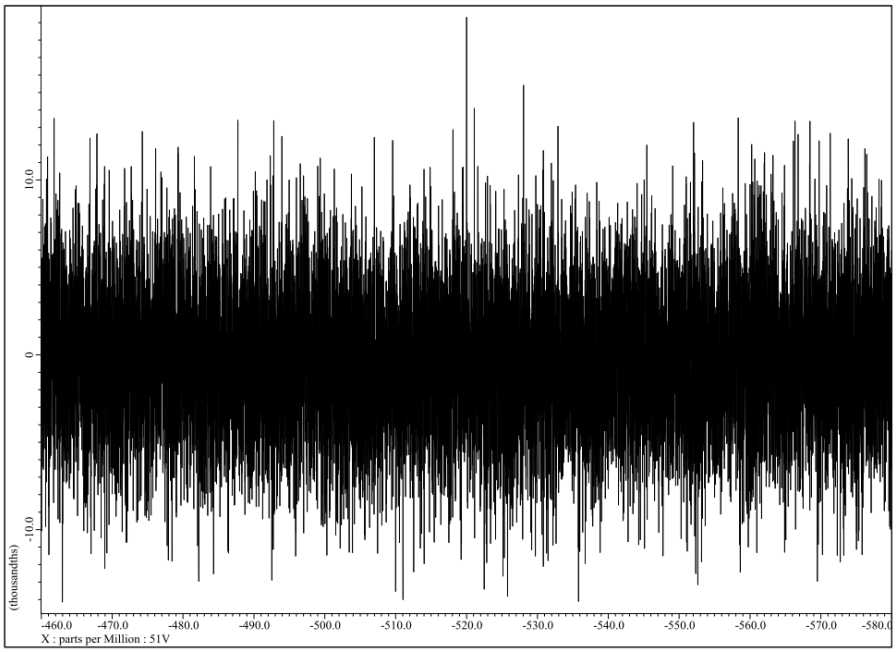

Figure 5: ^{51}V NMR spectrum of the reaction solution of 5 g (25 mmol) glucose as a substrate; 1.74 g (0.9 mmol) HPA-2 as a catalyst dissolved in 100.0 mL H_2O together with 2.18 g (8 mmol) of $PbCl_2$ impurity after 6.5 h under 30 bar O_2, 90 °C, 1000 rpm.