

# **In-depth analysis of raw bio-oil and its hydrodeoxygenated products for a comprehensive catalyst performance evaluation**

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Number of Tables: 1

Number of Figures: 8

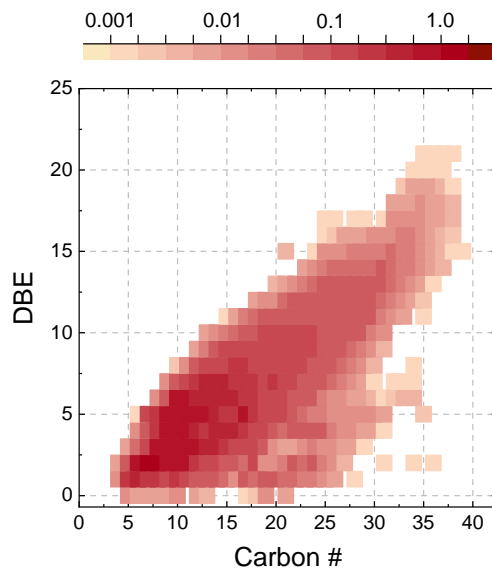
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## S1. Detailed chromatographic methods

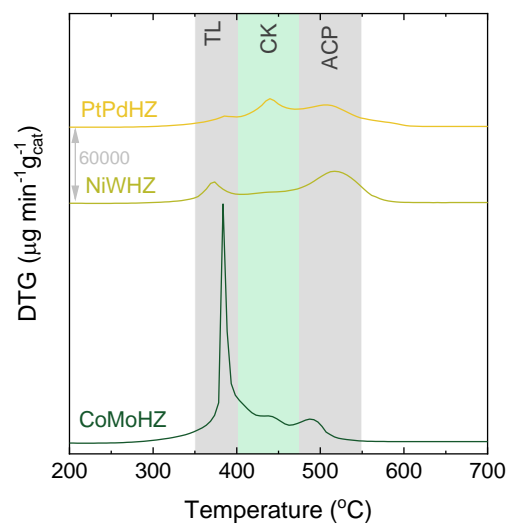
The chemical composition of the raw bi-oil and aqueous liquid products was analysed by means of gas chromatography in a Shimadzu GC-MS QP2010 unit. The injection was conducted in split mode (split ratio 300:1) with the inlet at 180 °C, and the injected sample volume was of 5  $\mu\text{L}$ . He was used as carrier gas. The temperature program consisted of a temperature ramp from 45 °C up to 280 °C at a 15 °C  $\text{min}^{-1}$  rate, with a final 5 min isotherm. The pressure in the column was of 153.4 kPa with a total flow of 303.7  $\text{mL min}^{-1}$  and a column flow of 1  $\text{mL min}^{-1}$ .

The organic product phase was analysed by two-dimensional gas chromatography in an Agilent 7890A unit (provided with an FID detector) coupled online with an Agilent 5975C series mass spectrometer (GC $\times$ GC-MS). This unit consists of two columns of different polarities connected through a flow modulator, being the first column a non-polar DB-5MS (length, 30 m; internal diameter, 0.25 mm) and the second one a polar TRB-50 HT (length, 5 m; internal diameter, 0.25 mm).  $\text{H}_2$  was used as carrier gas. The flowrate was of 0.75  $\text{mL min}^{-1}$  in the first column, and 35  $\text{mL min}^{-1}$  in the second one. The sample was injected in split mode (split ratio 50:1), with the inlet at 300 °C and 10  $\mu\text{L}$  of sample were injected. The temperature program consisted of a 1 min isotherm at 50 °C followed by a ramp up to 260 °C at a 2 °C  $\text{min}^{-1}$  rate, with a final 40 min isotherm. The FID was heated at 350 °C, with a  $\text{H}_2$  flow of 20  $\text{mL min}^{-1}$  and an air flow of 450  $\text{mL min}^{-1}$ .

## S2. Supplementary Results



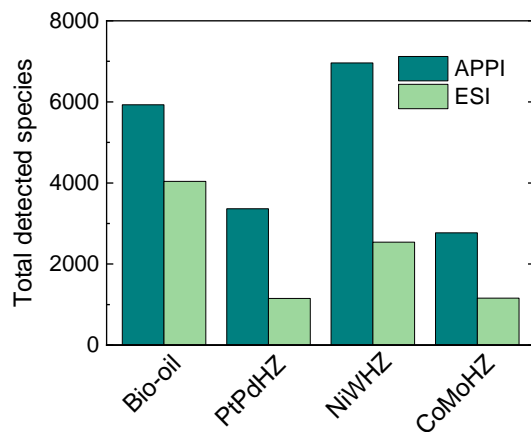
**Figure S1.** Color-coded isoabundance plots of DBE versus carbon number for the  $\text{O}_x$  species in the raw bio-oil as measured through (-)ESI FT-ICR/MS.



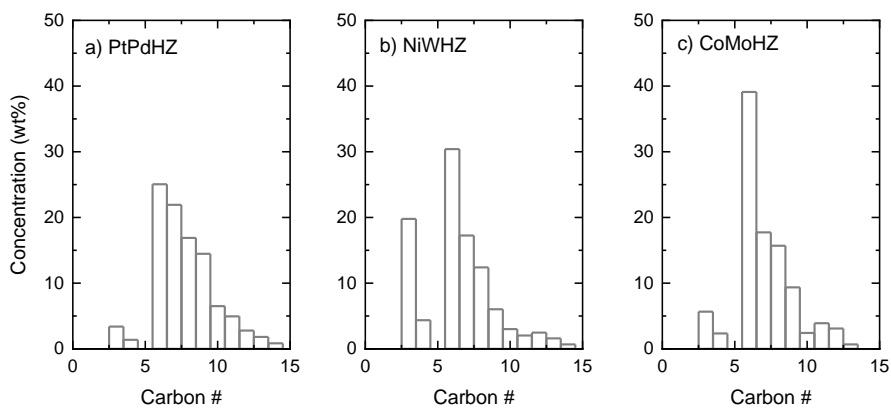
**Figure S2.** DTG-TPO curves for the used catalyst samples

**Table S1.** Detailed chemical composition of the organic product fractions from the HDO of raw bio-oil using the different catalysts

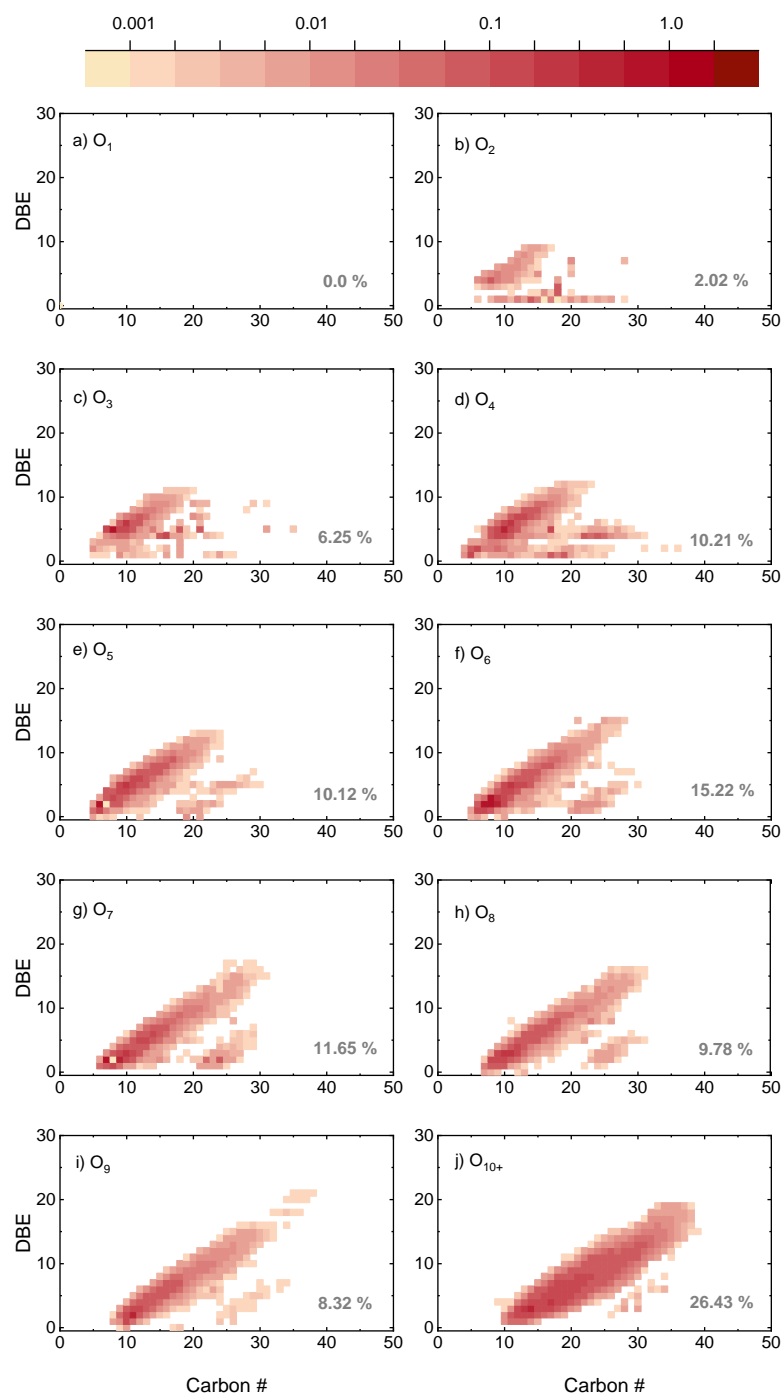
	PtPdHZ	NiWHZ	CoMoHZ
<i>Total paraffins (%)</i>	23.29	6.89	3.74
Cyclopentane, -methyl	2.66	0.46	0.09
Cyclohexane	2.77	1.06	0.57
Cyclohexane, -methyl	2.43	0.26	0.11
Cyclopentane, -ethyl	1.54	0.39	0.15
Cyclopentane, -dimethyl	1.27	0.53	0.07
Cyclopentane, 1-ethyl-3-methyl	1.16	0.31	0.17
Cyclopentane, -propyl	0.74	0.00	0.01
Cyclopentane, 1-methyl-2-propyl	0.61	0.17	0.00
Cyclohexane, -propyl	1.20	0.16	0.00
<i>Total ketones (%)</i>	6.29	23.66	9.67
Acetone	1.86	8.91	2.37
2-Butanone	0.75	1.97	0.98
Cyclopentanone, 2-methyl	0.48	2.20	0.58
<i>Total phenolics (%)</i>	8.57	27.60	40.80
Phenol	3.38	9.66	14.88
Phenol, 2-methyl	0.67	1.35	0.55
Phenol, 3-methyl	1.22	4.61	5.93
Phenol, 2,3-dimethyl	0.87	1.21	2.42
Phenol, 3,4-dimethyl	0.45	2.15	2.87
Phenol, -propyl	0.41	1.31	2.87
<i>Total 1-ring aromatics (A<sub>1</sub>, %)</i>	48.26	23.33	27.28
Benzene	4.43	0.32	0.23
Toluene	4.88	0.63	0.61
Benzene, -ethyl	2.88	0.27	0.31
Benzene, 1,3-dimethyl	2.60	0.72	0.43
Xylene	1.41	0.93	0.35
Benzene, -propyl	2.55	0.12	0.41
Benzene, -cyclopropyl	1.07	0.40	0.24
Benzene, 1-methyl-3-propyl	1.03	0.14	0.41
Benzene, 1-2-diethyl	1.28	0.18	0.22
Benzene, 1-ethyl-2-methyl	2.09	0.55	0.39
<i>Total 2-ring aromatics (A<sub>2</sub>, %)</i>	12.82	17.18	16.08
Naphthalene	1.25	1.03	0.38
Naphthalene, 1-methyl	1.87	0.56	0.68
Naphthalene, 2-methyl	0.84	0.36	0.95
Naphthalene, 1-ethyl	0.30	0.18	0.33
Naphthalene, 2,5-dimethyl	0.52	0.28	0.37
Naphthalene, 2,3-dimethyl	0.71	0.65	0.60
Naphthalene, 1-(2-propenyl)	1.00	0.72	0.28
<i>Total 3-ring aromatics (A<sub>3</sub>, %)</i>	0.76	1.33	2.44
Phenanthrene	0.46	0.30	0.87



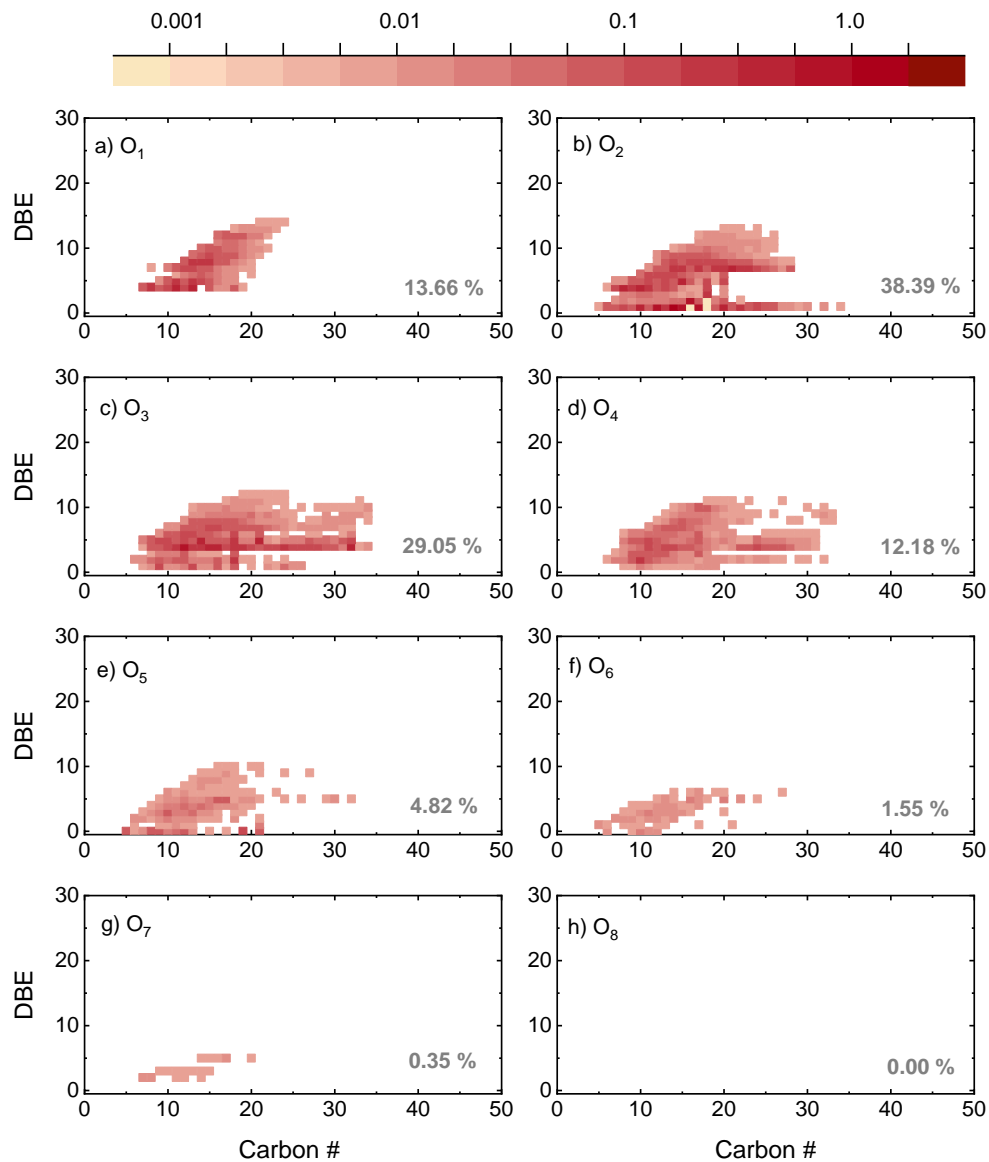
**Figure S3.** Total detected species through the two different FT-ICR/MS ionization methods for the raw bio-oil and the organic HDO product oils using the different catalysts



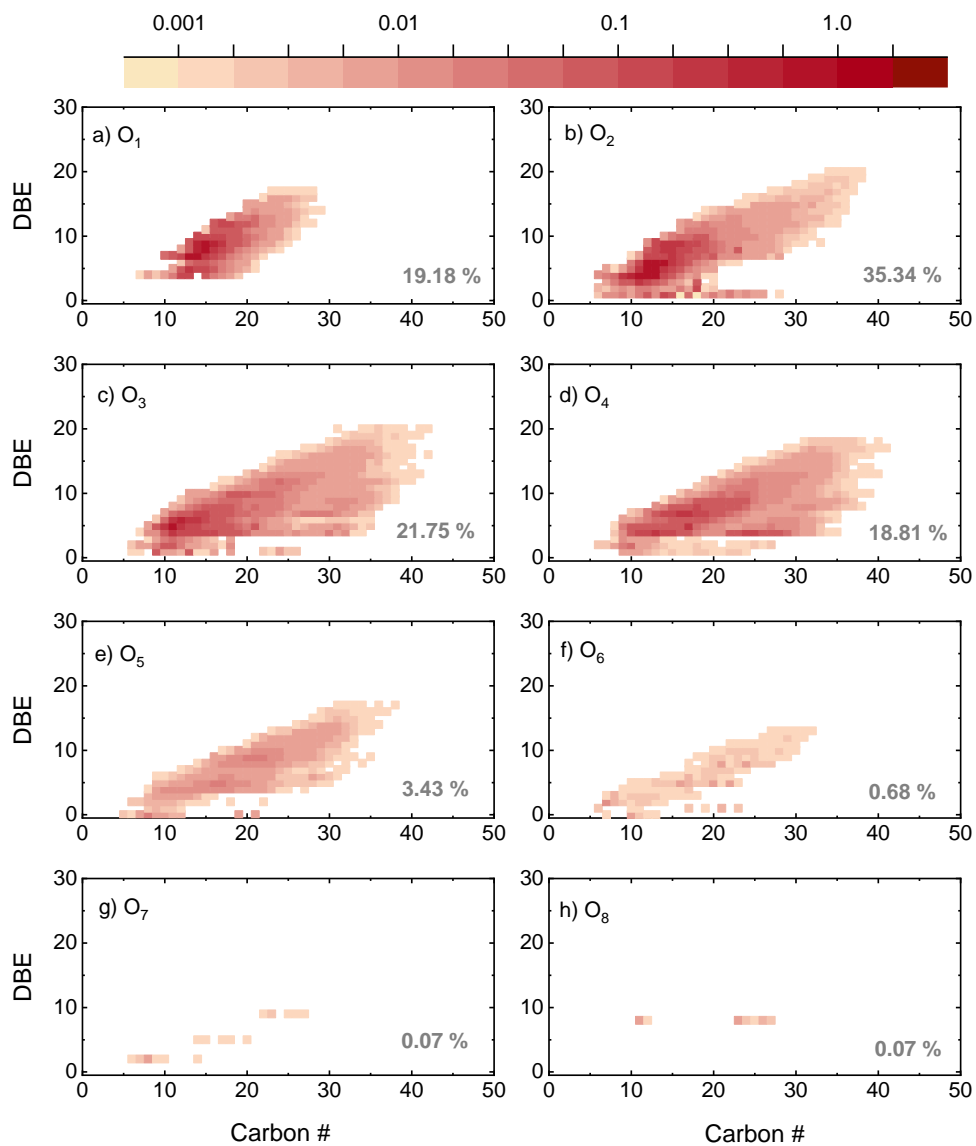
**Figure S4.** Carbon number distribution of the main compounds detected through GCxGC/MS in the organic HDO product oils using the different catalysts



**Figure S5.** Color-coded isoabundance plots of DBE versus carbon number for the oxygenated (O<sub>x</sub>) species of the raw bio-oil as measured through (-)ESI FT-ICR/MS.

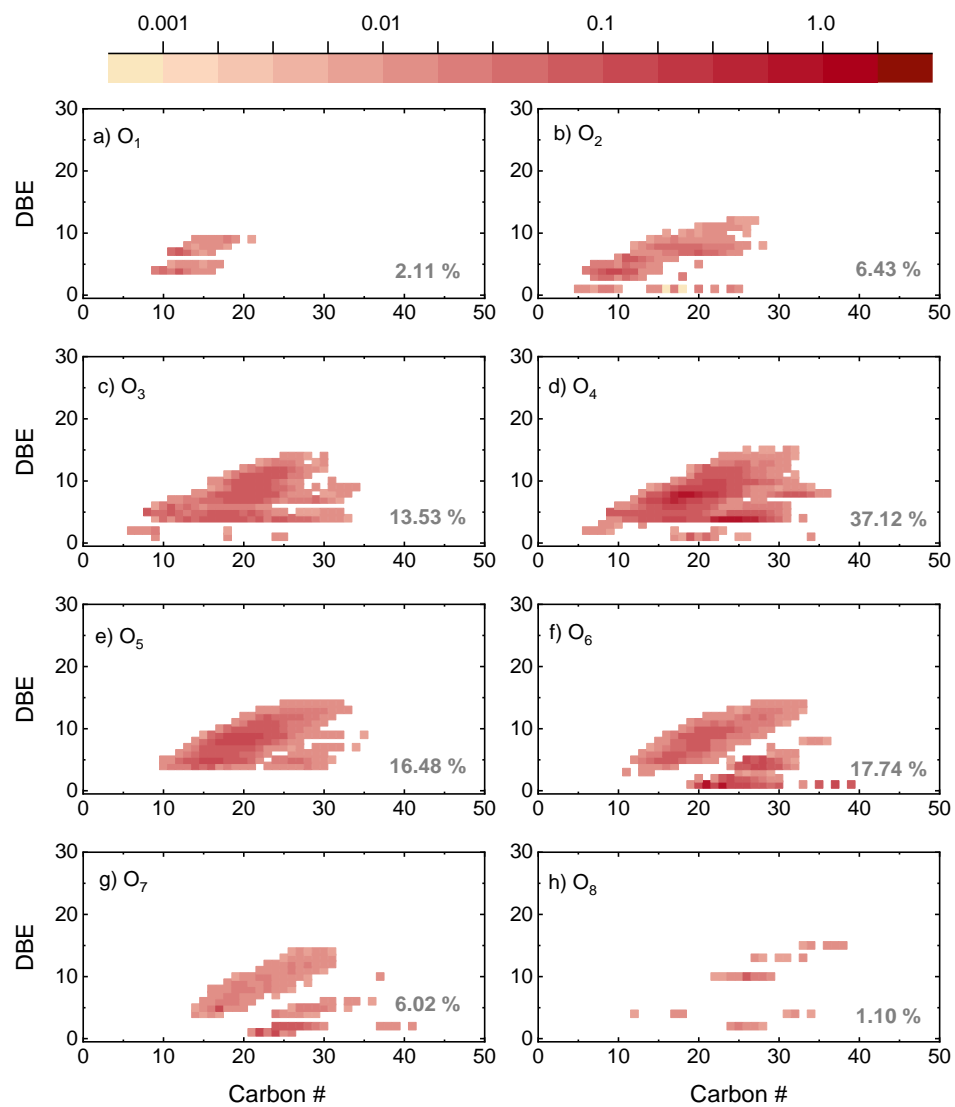


**Figure S6.** Color-coded isoabundance plots of DBE versus carbon number for the oxygenated (O<sub>x</sub>) species of the PtPdHZ organic product oils as measured through (-)ESI FT-ICR/MS.



**Figure S7.** Color-coded isoabundance plots of DBE versus carbon number for the oxygenated (O<sub>x</sub>) species of the NiWHZ organic product oils as measured through (-)ESI FT-ICR/MS.





**Figure S8.** Color-coded isoabundance plots of DBE versus carbon number for the oxygenated (O<sub>x</sub>) species of the CoMoHZ organic product oils as measured through (-)ESI FT-ICR/MS.