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Supplementary material for

New insights into the effect of pressure on catalytic hydropyrolysis of biomass

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Coke buildup on filter

Only a thin layer of dust (char) was located on the filter after the experiments when the hydrogen pressure was 15.9 bar or higher. However, decreasing the hydrogen pressure to below 15.9 bar increased the coke on the filter. Figure S.1 A shows an image of the filter after an experiment conducted at 8.2 bar, which shows a solid (coke) buildup on the filter, but not the char inlet pipe or the thermocouple. Conducting the experiment at 3.0 bar hydrogen produce a filter cake, which is approximately 5 mm thick and also a solids buildup on the char inlet pipe and thermocouple, see Figure S.1 B.

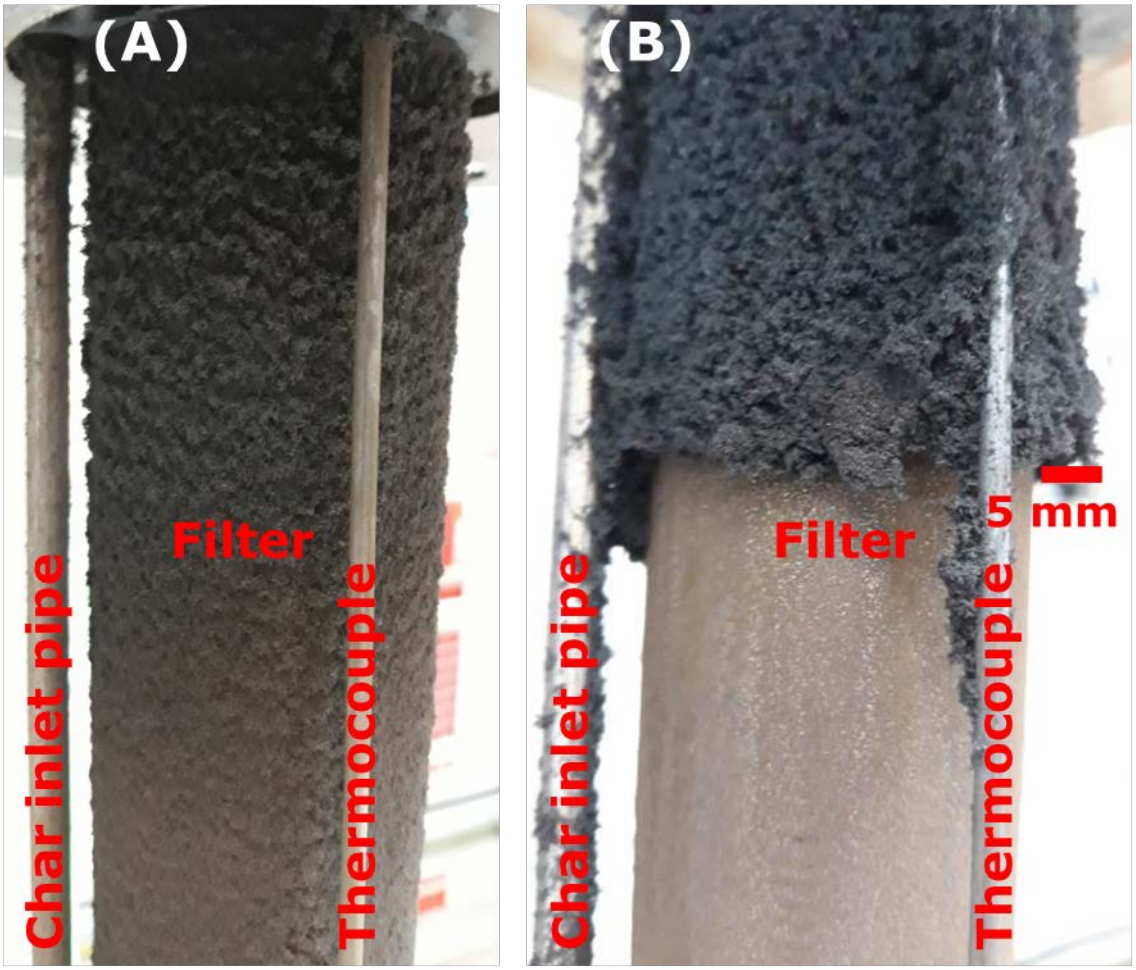

Figure S.1 Image of filter after an experiment conducted at 8.2 bar hydrogen (A) and 3.0 bar hydrogen (B). Conditions: fluid bed temperature 447-454 °C, HDO temperature: 364-386 °C, biomass feeding rate: 350-354 g/min, H_2S concentration: 464-475 ppm, H_2 flow: 11.4-30.9 NL/min, N_2 flow: 7.0-26.5 NL/min

GC×GC-FID/MS on the condensed organic phase

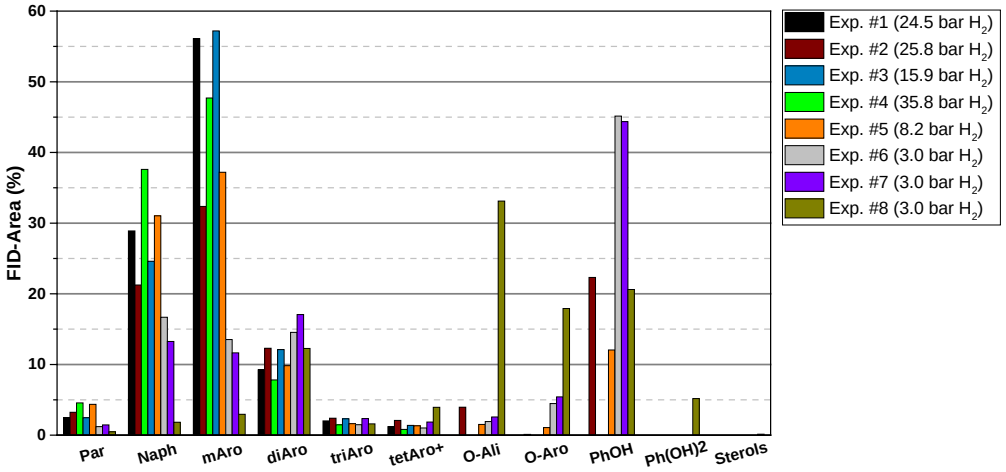

Figure S.2 Composition of the condensed organic phases. The components in the condensed organics are divided into paraffins (Par), naphthenes (Naph), monoaromatics (mAro), diaromatics (diAro), triaromatics (triAro), tetraaromatics and larger aromatics (tetAro+), oxygenated aliphatics (O-ali), phenols (PhOH), dihydroxybenzenes (Ph(OH)2), and larger oxygenated aromatics (O-aro).

Overview of sulfur containing molecules detected with sulfur specific GC-AED

Table S.1 List of detected molecules with sulfur specific GC-AED in the organic phase from experiment 1 (24.5 bar H_2)

Compound	Retention time (min)	Amount (wt-ppm S)
Unidentified	1.55	22.44
Hydrogensulfide	1.60	28.64
Methanethiol	1.98	3.32
Methylethylsulfide	6.36	10.65
Dimethyl disulfide	9.36	9.48
c-Trimethylthiophene	17.04	35.57
Benzothiophene	23.62	2.87
Unidentified	36.02	4.96
4-Methyl-DBT	36.12	48.08

Table S.2 List of detected molecules with sulfur specific GC-AED in the organic phase from experiment 5 (8.2 bar H_2)

Compound	Retention time (min)	Amount (wt-ppm S)	Compound	Retention time (min)	Amount (wt-ppm S)
Hydrogensulfide	1.45	63.70	2-Methylthiophene	10.15	6.06
Carbonylsulfide	1.50	11.30	Unidentified	11.76	2.79
2-Propanethiol	3.19	1.15	Unidentified	13.03	2.23
Unidentified	3.50	1.11	Benzothiophene	22.80	2.99
Unidentified	3.66	23.06	Dimethylbenzothiophene (a)	27.37	13.13
Unidentified	4.06	6.71	Unidentified	32.92	6.70
Thiophene	6.24	32.08			

Table S.3 List of detected molecules with sulfur specific GC-AED in the organic phase from experiment 6 (3.0 bar H_2)

Compound	Retention time (min)	Amount (wt-ppm S)	Compound	Retention time (min)	Amount (wt-ppm S)
Hydrogensulfide	1.45	16.80	Unidentified	13.77	9.00
Carbonylsulfide	1.51	3.53	a-Dimethylthiophene	13.81	8.25
Unidentified	3.67	4.13	b-Dimethylthiophene	14.15	4.92
Thiophene	6.23	250.40	a-Trimethylthiophene	16.29	2.61
Unidentified	9.46	7.44	b-Trimethylthiophene	16.45	4.58
Unidentified	9.64	2.47	d-Trimethylthiophene	16.63	1.27
2-Methylthiophene	10.10	121.83	c-Trimethylthiophene	16.80	3.01
3-Methylthiophene	10.35	26.95	e-Trimethylthiophene	17.10	2.11
Unidentified	11.76	1.61	Unidentified	19.03	2.04
Unidentified	13.01	2.45	Unidentified	19.46	2.34
2-Methyl-THT	13.40	17.41	Unidentified	32.81	2.43
3-Methyl-THT	13.57	19.75			

Table S.4 List of detected molecules with sulfur specific GC-AED in the organic phase from experiment 7 (3.0 bar H_2)

Compound	Retention time (min)	Amount (wt-ppm S)	Compound	Retention time (min)	Amount (wt-ppm S)
Hydrogensulfide	1.45	26.43	3-Methyl-THT	13.57	11.96
Carbonylsulfide	1.49	4.85	Unidentified	13.76	6.43
Unidentified	2.35	1.39	a-Dimethylthiophene	13.80	5.67
Unidentified	3.67	4.36	b-Dimethylthiophene	14.15	3.37
Methylethylsulfide	6.10	14.59	a-Trimethylthiophene	16.29	2.20
Thiophene	6.23	166.19	b-Trimethylthiophene	16.45	3.00
Unidentified	9.46	2.31	d-Trimethylthiophene	16.63	1.38
2-Methylthiophene	10.10	70.74	c-Trimethylthiophene	16.80	2.73
3-Methylthiophene	10.35	17.31	e-Trimethylthiophene	17.10	1.54
2-Methyl-THT	13.40	11.84			

Table S.5 List of detected molecules with sulfur specific GC-AED in the organic phase from experiment 8 (3.0 bar H_2, HDO reactor bypassed)

Compound	Retention time (min)	Amount (wt-ppm S)	Compound	Retention time (min)	Amount (wt-ppm S)
Hydrogensulfide	1.45	231.82	a-Dimethylthiophene	13.79	4.20
Unidentified	1.85	20.23	b-Dimethylthiophene	14.13	3.58
Unidentified	2.35	9.19	c-Dimethylthiophene	14.45	12.20
Thiophene	6.22	73.60	Dimethyl-THT	15.32	6.54
Unidentified	9.54	4.28	b-Trimethylthiophene	16.43	7.78
2-Methylthiophene	10.07	42.22	a-Trimethylthiophene	16.58	17.87
Unidentified	10.29	1.51	c-Trimethylthiophene	16.72	15.90
3-Methylthiophene	10.36	13.59	d-Trimethylthiophene	16.94	3.75
Unidentified	11.15	6.59	Unidentified	18.05	9.69
Unidentified	11.86	23.20	Unidentified	19.18	4.61
Unidentified	13.22	18.86	Unidentified	19.53	9.49
2-Methyl-THT	13.37	9.49	Unidentified	19.77	11.82
3-Methyl-THT	13.55	8.57	Methylbenzothiophene (a)	25.27	5.01
Unidentified	13.74	5.67			

Overview of hydrocarbons detected in the aqueous phase with GC-MS/FID

Table S.6 List of detected molecules with GC-MS/FID in the aqueous phase from experiment 2 (24.5 bar H_2, HDO reactor bypassed)

Compound	Retention time (min)	Area-FID (%)	Compound	Retention time (min)	Area-FID (%)
Methanol	2.47	9.70	1-butanol	3.28	1.69
Ethanol	2.55	32.82	Ethylene glycol	3.55	0.61
Acetone	2.62	13.94	Cyclopentanone	4.60	1.02
1-Propanol	2.78	5.20	Phenol	8.66	26.60
2-Butanone	2.94	3.51	3-methyl phenol	10.33	1.15
2-Me-1-PrOH	3.06	0.43	Unidentified	10.74	1.41

Table S.7 List of detected molecules with GC-MS/FID in the aqueous phase from experiment 5 (8.2 bar H_2)

Compound	Retention time (min)	Area-FID (%)	Compound	Retention time (min)	Area-FID (%)
Acetone	2.62	0.46	Unidentified	15.95	2.88
Unidentified	4.15	0.25	Unidentified	16.04	1.77
Phenol	8.62	11.99	Unidentified	16.23	6.83
Unidentified	9.38	1.17	Unidentified	16.53	2.88
Unidentified	9.64	1.83	Unidentified	16.70	2.99
Cresol	10.23	2.05	Unidentified	16.86	2.21
Cresol	10.61	2.55	Unidentified	17.04	1.91
2 ethyl phenol	10.88	0.08	Unidentified	17.24	0.67
Unidentified	11.38	0.38	Unidentified	17.31	0.70
Unidentified	11.51	0.76	Unidentified	17.42	0.58
Unidentified	11.74	0.32	Unidentified	17.49	0.41
Unidentified	12.05	1.58	Unidentified	17.72	3.82
Unidentified	12.23	2.47	Unidentified	17.94	1.68
Unidentified	12.34	0.58	Unidentified	18.13	4.20
Unidentified	12.43	0.30	Unidentified	18.27	4.44
Unidentified	12.54	0.37	Unidentified	18.56	2.18
Unidentified	12.66	0.37	Unidentified	18.72	1.62
Unidentified	12.90	0.64	Unidentified	18.91	3.55
Unidentified	13.05	0.54	Unidentified	19.13	1.34
Unidentified	13.15	0.35	Unidentified	19.24	0.94
Unidentified	13.32	0.09	Unidentified	19.44	1.18
Unidentified	13.38	0.09	Unidentified	19.59	2.64
Unidentified	13.58	0.28	Unidentified	19.95	1.23
Unidentified	13.66	0.18	Unidentified	20.09	1.31
Unidentified	13.80	0.18	Unidentified	20.25	1.51
Unidentified	13.91	0.12	Unidentified	20.48	0.58
Unidentified	14.40	0.12	Unidentified	20.58	0.61
Unidentified	14.58	0.48	Unidentified	20.70	0.25
Unidentified	14.78	0.82	Unidentified	20.82	1.06
Unidentified	15.33	0.13	Unidentified	20.93	1.68
Unidentified	15.53	0.43	Unidentified	21.08	2.92
Unidentified	15.63	0.81	Unidentified	21.34	2.62
Unidentified	15.69	0.62	Unidentified	21.55	0.61
Unidentified	15.83	0.51	Unidentified	21.80	0.28

Table S.8 List of detected molecules with GC-MS/FID in the aqueous phase from experiment 6 (3.0 bar H_2)

Compound	Retention time (min)	Area-FID (%)	Compound	Retention time (min)	Area-FID (%)
Ethanol	2.54	1.41	Unidentified	15.24	2.64
Acetone	2.61	9.71	Unidentified	15.64	1.98
Aceic acid	2.82	1.13	Unidentified	15.94	3.27
2-Butanone	2.92	1.79	Unidentified	16.27	4.06
Cyclopentaone	4.72	0.15	Unidentified	16.45	0.58
Phenol	8.61	12.01	Unidentified	16.54	1.74
Cresol	10.22	1.85	Unidentified	16.81	3.45
Cresol	10.61	3.61	Unidentified	17.13	3.00
2-ethyl phenol	11.75	0.88	Unidentified	17.42	4.26
Unidentified	11.95	0.58	Unidentified	17.62	1.03
3-ethyl phenol	12.25	0.45	Unidentified	17.71	2.63
3.4-dimethyl phenol	12.66	0.25	Unidentified	18.06	2.59
Unidentified	13.25	2.13	Unidentified	18.41	2.45
Unidentified	13.67	1.88	Unidentified	18.79	2.03
Unidentified	13.90	0.56	Unidentified	19.19	1.73
Unidentified	14.01	0.53	Unidentified	19.66	1.67
Unidentified	14.17	1.24	Unidentified	20.16	1.91
Unidentified	14.35	1.45	Unidentified	20.57	2.45
Unidentified	14.55	4.04	Unidentified	21.12	3.09
Unidentified	14.76	0.78	Unidentified	21.34	0.35
Unidentified	14.89	1.52	Unidentified	21.61	1.83
Unidentified	14.97	1.72	Unidentified	21.77	0.95
Unidentified	15.11	0.67			

Table S.9 List of detected molecules with GC-MS/FID in the aqueous phase from experiment 7 (3.0 bar H_2)

Compound	Retention time (min)	Area-FID (%)	Compound	Retention time (min)	Area-FID (%)
Ethanol	2.54	7.40	Unidentified	13.33	0.29
Acetone	2.61	9.43	Unidentified	15.20	0.37
1-propanol	2.77	0.44	Unidentified	15.36	0.42
acetic acid	2.83	11.53	Unidentified	15.47	0.49
Unidentified	2.92	3.10	Unidentified	15.58	0.44
Propanoic acid	3.34	0.75	Unidentified	15.77	0.69
Unidentified	4.16	0.32	Unidentified	16.49	0.73
Butanoic acid	4.27	0.34	Unidentified	16.66	2.58
Cyclopentanon	4.72	0.69	Unidentified	17.06	1.49
2-methyl cyclopentanon	5.61	0.11	Unidentified	17.43	1.63
phenol	8.62	27.25	Unidentified	17.84	0.70
Cresol	10.22	4.99	Unidentified	18.23	1.21
Cresol	10.61	8.32	Unidentified	19.17	2.94
2-ethyl phenol	11.75	0.88	Unidentified	19.59	3.29
2.5-dimethyl phenol	11.95	1.28	Unidentified	20.08	1.00
3-ethyl phenol	12.24	1.63	Unidentified	20.90	0.32
2.3-dimethyl phenol	12.44	0.51	Unidentified	21.11	0.36
3.4-dimethylphenol	12.66	0.36	Unidentified	21.72	1.74

Table S.10 List of detected molecules with GC-MS/FID in the aqueous phase from experiment 8 (3.0 bar H_2, HDO reactor bypassed)

Compound	Retention time (min)	Area-FID (%)	Compound	Retention time (min)	Area-FID (%)
Methanol	2.45	6.00	Unidentified	12.10	0.12
Ehanol	2.53	1.46	3-ethyl phenol	12.23	0.22
Acetone	2.61	2.11	Unidentified	12.34	0.04
Methyl acetate	2.69	0.59	Unidentified	12.43	0.15
Acetic acid	2.91	27.03	1,2-Benznediol	12.68	1.55
2-Propanon	3.29	7.24	Unidentified	12.97	0.44
Propanoic acid	3.38	1.56	Unidentified	13.26	1.48
Ethylene glycol	3.48	0.97	1,3-Cyclopentanedione	13.38	0.41
2-Butanone	3.65	0.79	Unidentified	13.46	0.30
2-methyl propanoic acid	3.90	0.22	Unidentified	13.56	0.17
3-Penten-2-one	3.96	0.17	Unidentified	13.68	0.80
Propanal	4.15	0.19	Unidentified	13.75	1.37
Glycolic acid	4.26	0.45	Unidentified	13.98	0.77
1-Hydroxy2-butanone	4.31	2.27	Unidentified	14.14	0.17
Unidentified	4.46	1.07	Unidentified	14.20	0.28
Unidentified	4.56	0.24	Unidentified	14.38	0.26
Cyclopentanone	4.71	2.90	Unidentified	14.48	0.32
Unidentified	4.91	0.22	Unidentified	14.63	0.37
Unidentified	5.01	0.08	Phenol, 2,6-dimethoxy	14.81	1.01
4-hydroxy-2-petanone	5.15	0.26	Unidentified	15.00	0.43
2-cyclopentene-1-one	5.44	5.60	Unidentified	15.16	0.46
2-methyl cyclopentanone	5.60	0.36	Unidentified	15.28	0.20
3-methylcyclopentanone	5.72	0.13	Unidentified	15.37	0.10
3-methyl 2 heptanone	5.81	0.62	Unidentified	15.46	0.27
2-propanone, 1-(acetyloxy)	5.93	0.27	Unidentified	15.53	0.29
Pentanoic acid	6.04	0.28	Unidentified	15.67	0.23
2-cyclopenene-1-one, 3-methyl	6.19	0.21	Unidentified	15.88	0.56
Unidentified	6.35	0.11	Unidentified	16.01	0.27
2H-Pyran-3(4H)-one, dihydro	6.48	0.13	Unidentified	16.17	0.15
2-Furanol, tetrahydro-2-methyl	6.57	0.13	Beta-D-glucopyranose	16.40	2.78
Furan, tetrahydro-2.5-dimethyloxy	6.73	0.09	Unidentified	16.58	0.33
Cyclohexanone	6.83	0.06	Unidentified	16.70	0.26
Unidentified	6.92	0.75	Unidentified	16.77	0.11
2-cyclopeten-1-one, 2-methyl	7.06	0.84	Unidentified	16.83	0.20
Unidentified	7.17	1.58	Unidentified	16.92	0.52
1.2-cyclopentanedione	7.42	1.45	Unidentified	17.09	0.10
2(5H)-Furanone, 5-methyl	7.77	0.45	Unidentified	17.17	0.12
Unidentified	7.97	0.08	Unidentified	17.29	0.19
Unidentified	8.04	0.06	Unidentified	17.38	0.25
2(3H)-Furanone, dihydro-5-methyl	8.12	0.19	Unidentified	17.46	0.10
Unidentified	8.23	0.18	Unidentified	17.54	0.10

2-Cyclopenten-1-one, 3-methyl	8.44	0.92	Unidentified	17.64	0.13
Phenol	8.62	0.62	Unidentified	17.74	0.13
Unidentified	8.71	0.34	Unidentified	17.85	0.23
Unidentified	8.92	0.14	Unidentified	18.02	0.21
2-Cyclopentn-1-one, 3,4-dimethyl	9.06	0.08	Unidentified	18.12	0.21
Unidentified	9.18	0.41	Unidentified	18.23	0.08
Unidentified	9.48	0.06	Unidentified	18.30	0.11
Unidentified	9.54	0.09	Unidentified	18.47	0.24
1,2-Cyclopentanedione, 3-methyl	9.75	1.71	Unidentified	18.61	0.10
Unidentified	10.04	0.53	Unidentified	18.73	0.11
Unidentified	10.11	0.21	Unidentified	18.86	0.20
cresol	10.22	0.29	Unidentified	18.96	0.07
Unidentified	10.32	0.22	Unidentified	19.04	0.12
Furan, tetrahydro-2-methyl	10.40	0.17	Unidentified	19.21	0.19
Unidentified	10.51	0.11	Unidentified	19.34	0.09
cresol	10.61	0.58	Unidentified	19.44	0.12
Unidentified	10.81	0.45	Unidentified	19.63	0.09
Unidentified	10.92	0.11	Unidentified	19.76	0.07
Phenol, 4 methoxy	11.02	0.26	Unidentified	19.83	0.08
Unidentified	11.08	0.33	Unidentified	20.06	0.22
Unidentified	11.19	0.18	Unidentified	20.45	0.06
Unidentified	11.29	0.19	Unidentified	20.62	0.14
Unidentified	11.42	0.19	Unidentified	20.80	0.04
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy	11.51	0.35	Unidentified	20.86	0.04
Unidentified	11.69	0.30	Unidentified	21.09	0.04
Unidentified	11.91	0.33	Unidentified	21.43	0.11

Scanning Electron Microscopy

Table S.11 Carbon content measured with EDS at different acceleration voltages on fresh catalyst and spent catalysts

	3 kV	5 kV	10 kV	15 kV
Fresh Catalyst	3.3	3.9	4.6	5.0
Spent catalysts				
Exp. #1 (24.5 bar H_2)	10.5	9.7	11.2	10.5
Exp. #2 (25.8 bar H_2)	11.2	10.4	10.1	11.2
Exp. #3 (15.9 bar H_2)	7.8	8.1	9.0	9.8
Exp. #4 (35.8 bar H_2)	7.6	8.1	9.4	11.0
Exp. #5 (8.2 bar H_2)	14.4	15.2	14.5	13.8
Exp. #6 (3.0 bar H_2)	17.1	17.9	17.4	17.2
Exp. #7 (3.0 bar H_2)	24.1	22.6	21.6	21.0
Exp. #8 (3.0 bar H_2)	28.9	26.4	25.8	25.7

In order to account for the carbon measured from the background the carbon content on the spent catalyst are calculated from equation S.1 and the carbon content is shown as function of the acceleration voltage in

$$\text{Carbon content} = C_{\text{on spent catalyst}} - C_{\text{on fresh catalyst}} \quad \text{(S.1)}$$

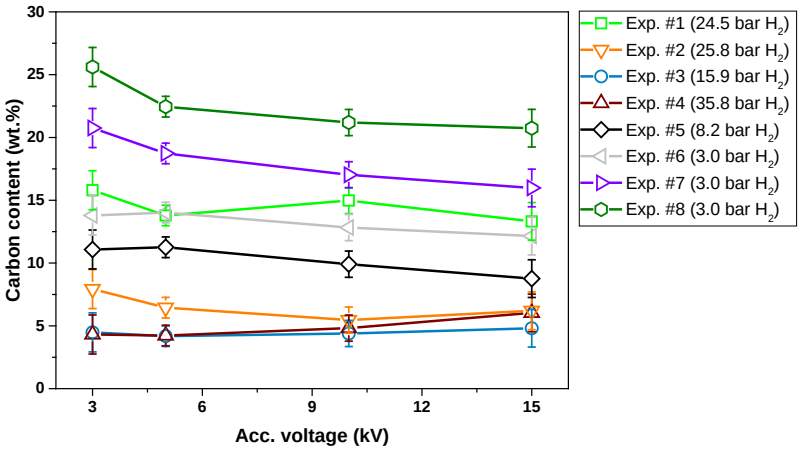

Figure S.3 Carbon content on the spent catalysts measured as a function of the acceleration voltage.