Deactivation of a CoMo catalyst during catalytic hydropyrolysis of biomass

M. Z. Stummann[1,2], J. Gabrielsen[2], M. Høj[1], P. Beato[2], A. B. Hansen[2], B. Davidsen[2], P. Wiwel[2], L. P. Hansen[2], P. A. Jensen[1], A. D. Jensen[1]*
1 Technical University of Denmark, Kgs. Lyngby 2800 (Denmark),
2 Haldor Topsøe A/S, Kgs. Lyngby 2800 (Denmark)
*AJ@kt.dtu.dk

Biomass to green fuels

Fast pyrolysis

Hydrode-
oxygenation

Biomass

Pyrolysis oil
HHV ~ 16-19 MJ/kg
28-40 wt. % oxygen

Fuel + water
~ 45 MJ/kg
<0.1 wt. % oxygen

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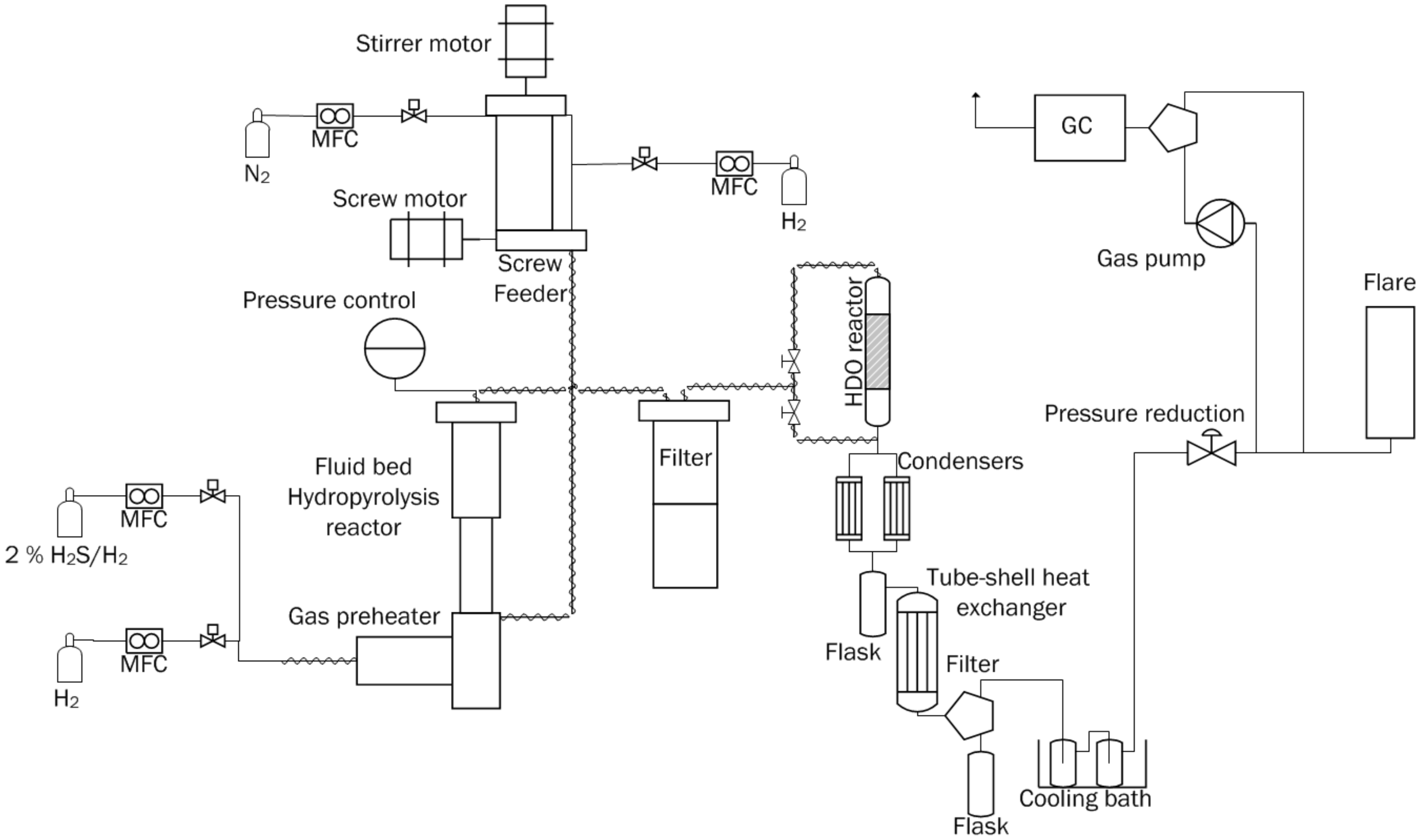
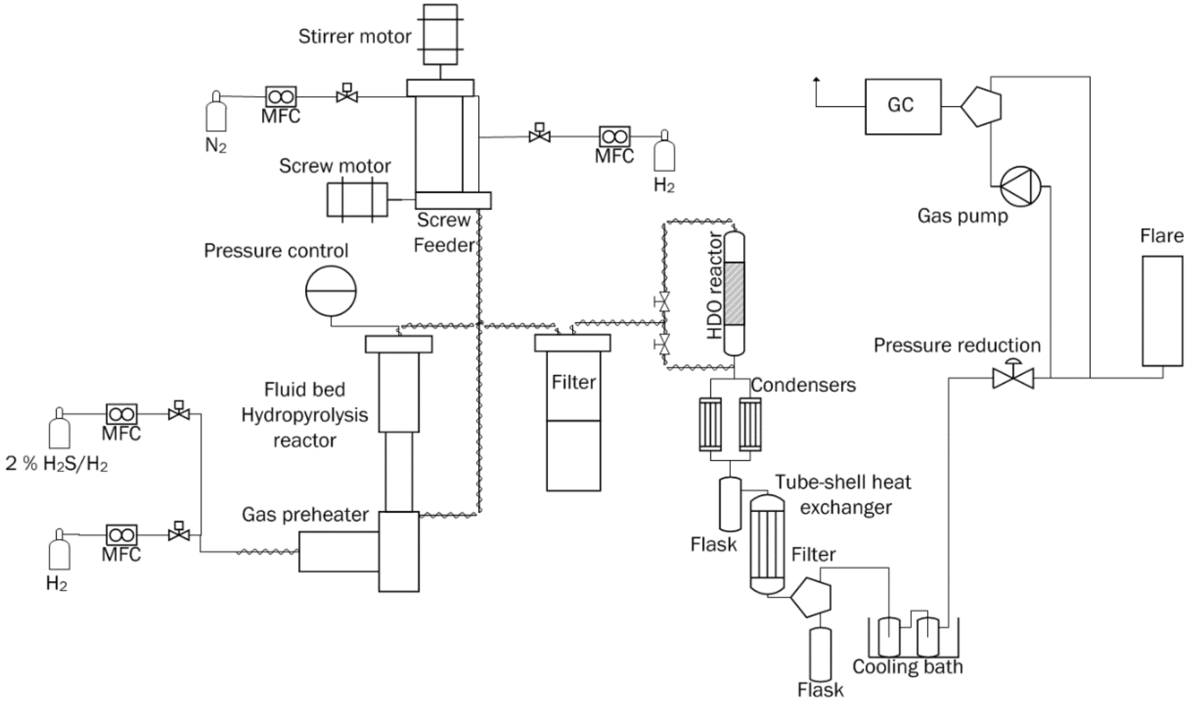
Catalyst stability

Setup at DTU Chemical Engineering



Catalysts (sulfide)	
Fluid bed reactor	50 g ($CoMo/MgAl_2O_4$)
HDO reactor	173 g ($NiMo/Al_2O_3$)
Temperatures	
Fluid bed	450 °C
Filter	335 °C
Heat tracing	350 °C
Pressure	26 bar
H_2S concentration:	460 ppm
Biomass (beech) feeding rate	275 g/h
Run time	3.5 h

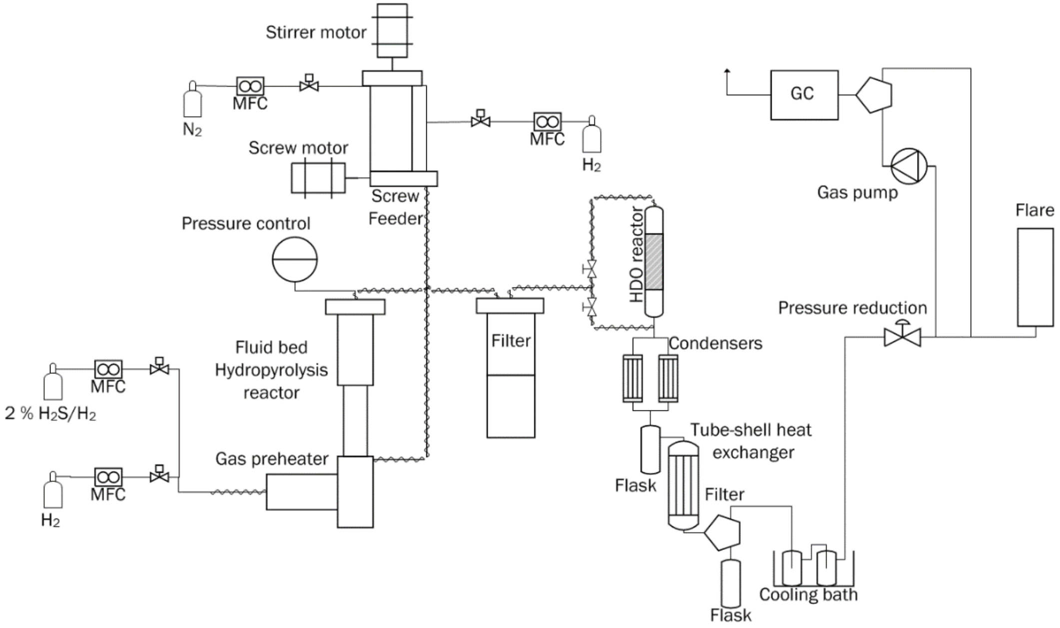
Setup at DTU Chemical Engineering



Experimental procedure

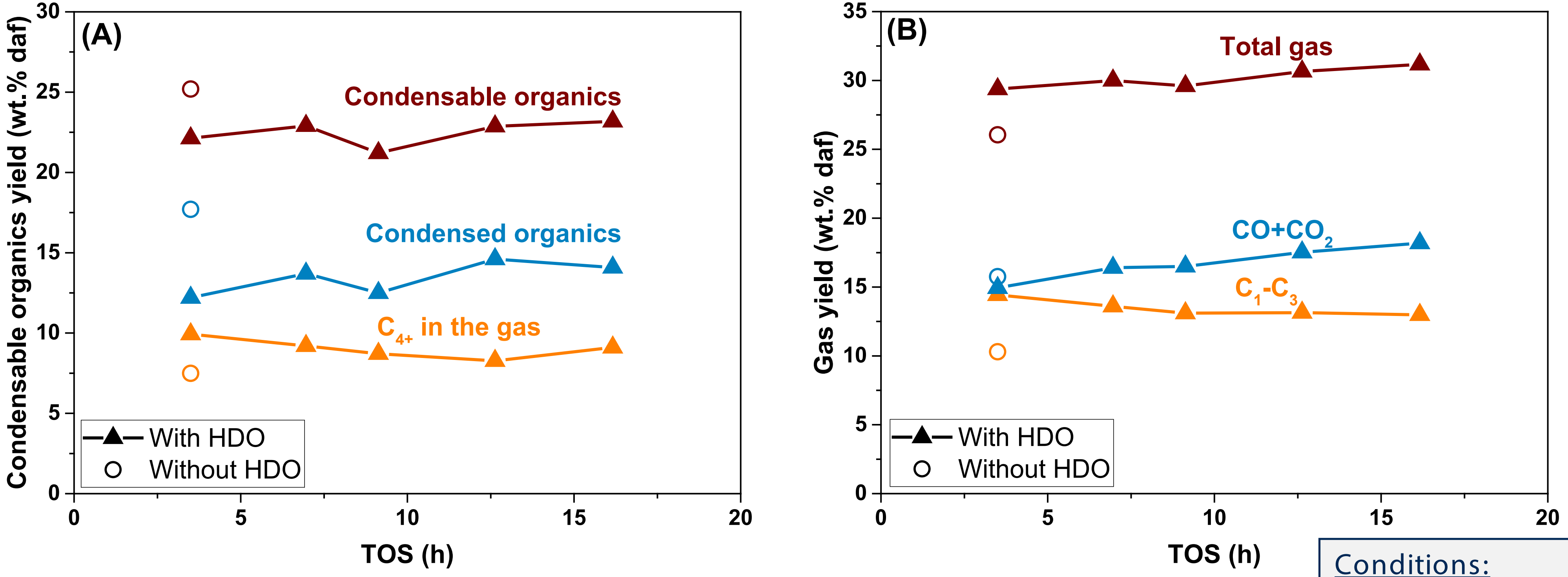
- Total time on stream: 16 h (over 5 days)
- Biomass used: 4.4 kg
- Oil and solids in the filter collected each day
- 40 wt% of the catalyst in fluid bed was lost
- The lost catalyst was not replaced

Setup at DTU Chemical Engineering



Catalyst stability

Product distribution



<u>Conditions:</u>

Fluid bed temperature: 450°C

Total pressure: 26 bar

Biomass feeding rate: 275 g/h

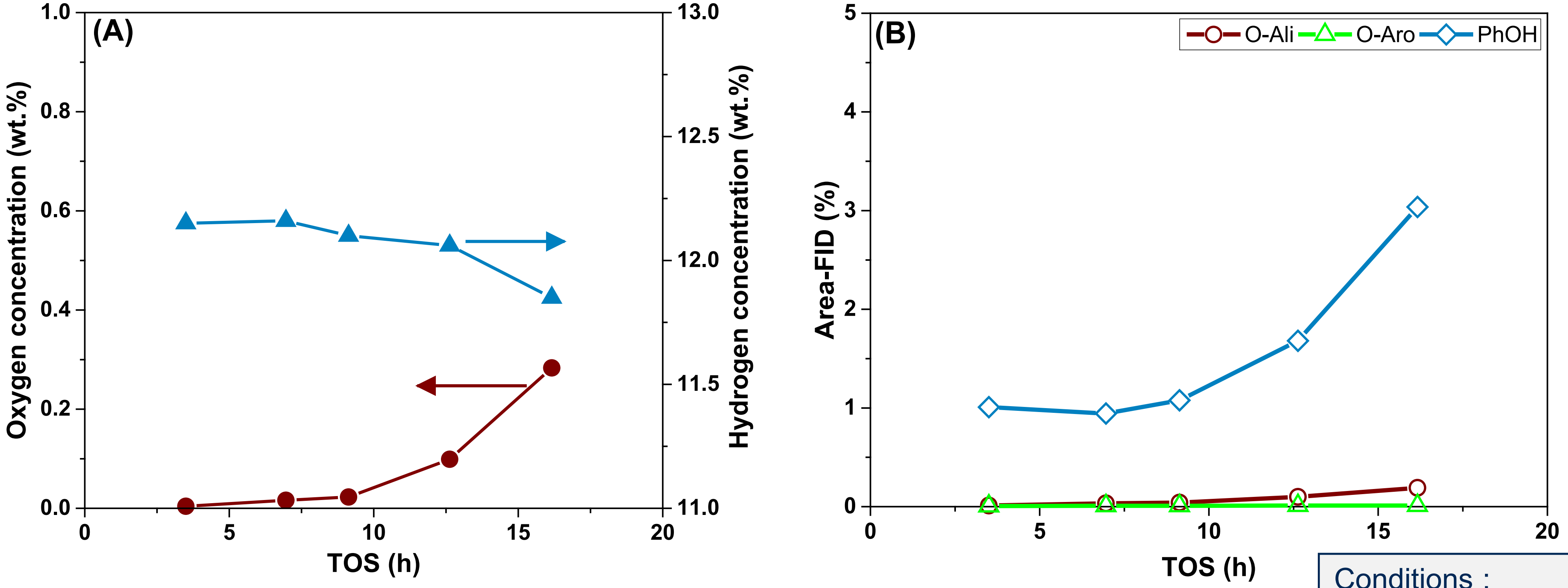
H_2 flow: 82 NL/min

N_2 flow: 5 NL/min

H_2S conc: 460 ppm.

Catalyst stability

Chemical composition of the condensed liquids



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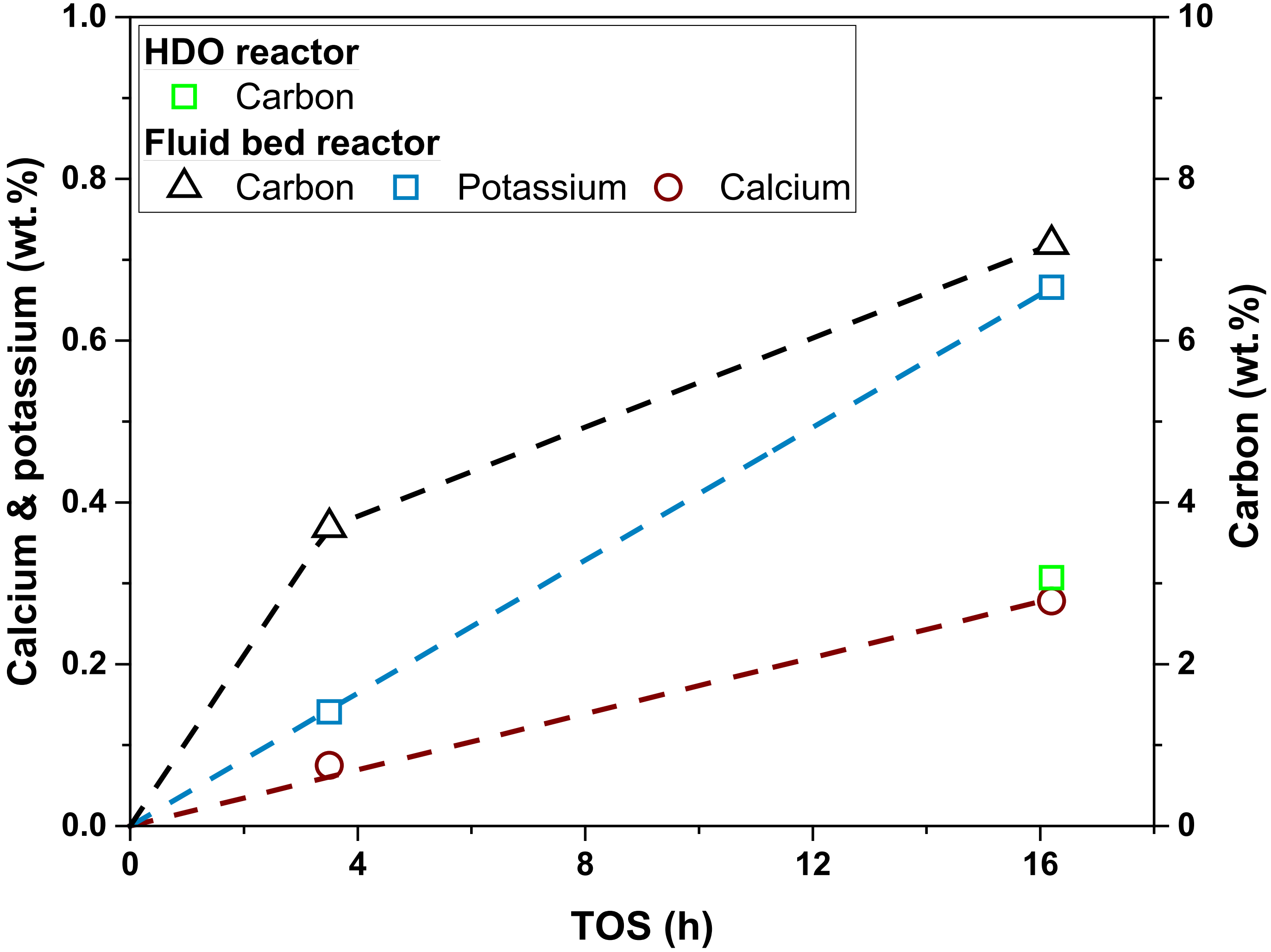
Catalyst stability

Characterization of the spent catalyst



Potassium and calcium are transferred from the biomass to the catalyst

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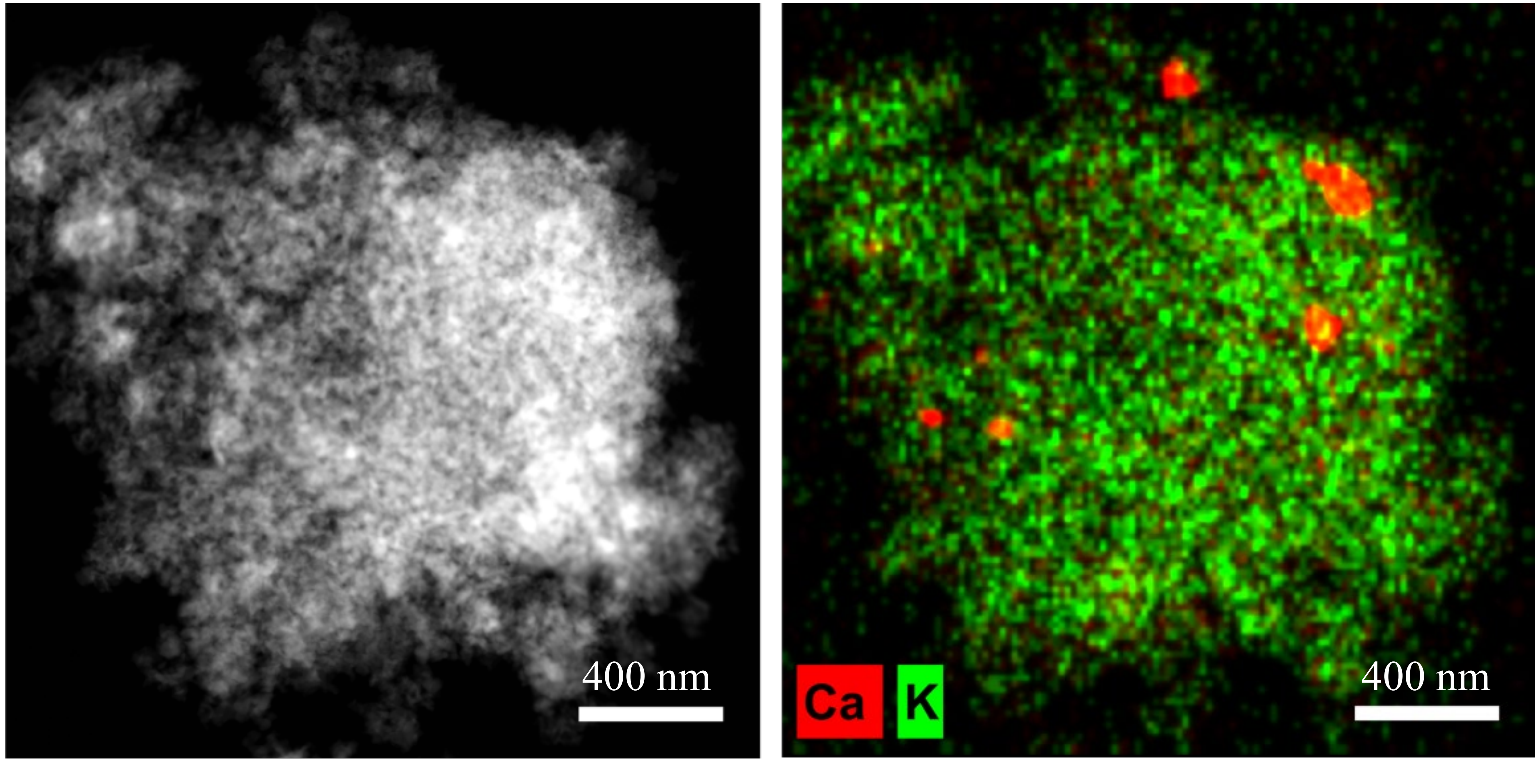
Characterization of the spent catalyst

STEM-HAADF of the spent catalysts

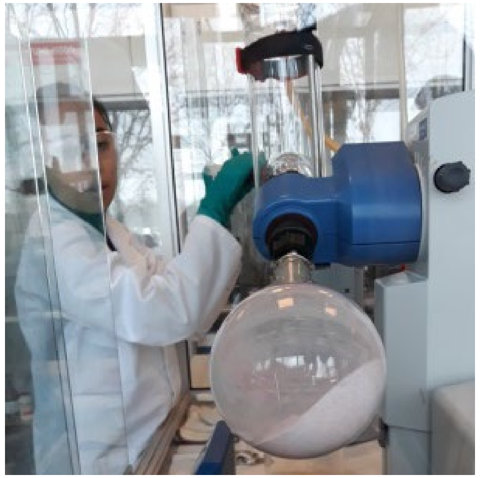


Calcium was observed as larger particles (40-200 nm), while potassium was well-distributed on the particles.

Effect of catalyst pre-deactivation with potassium

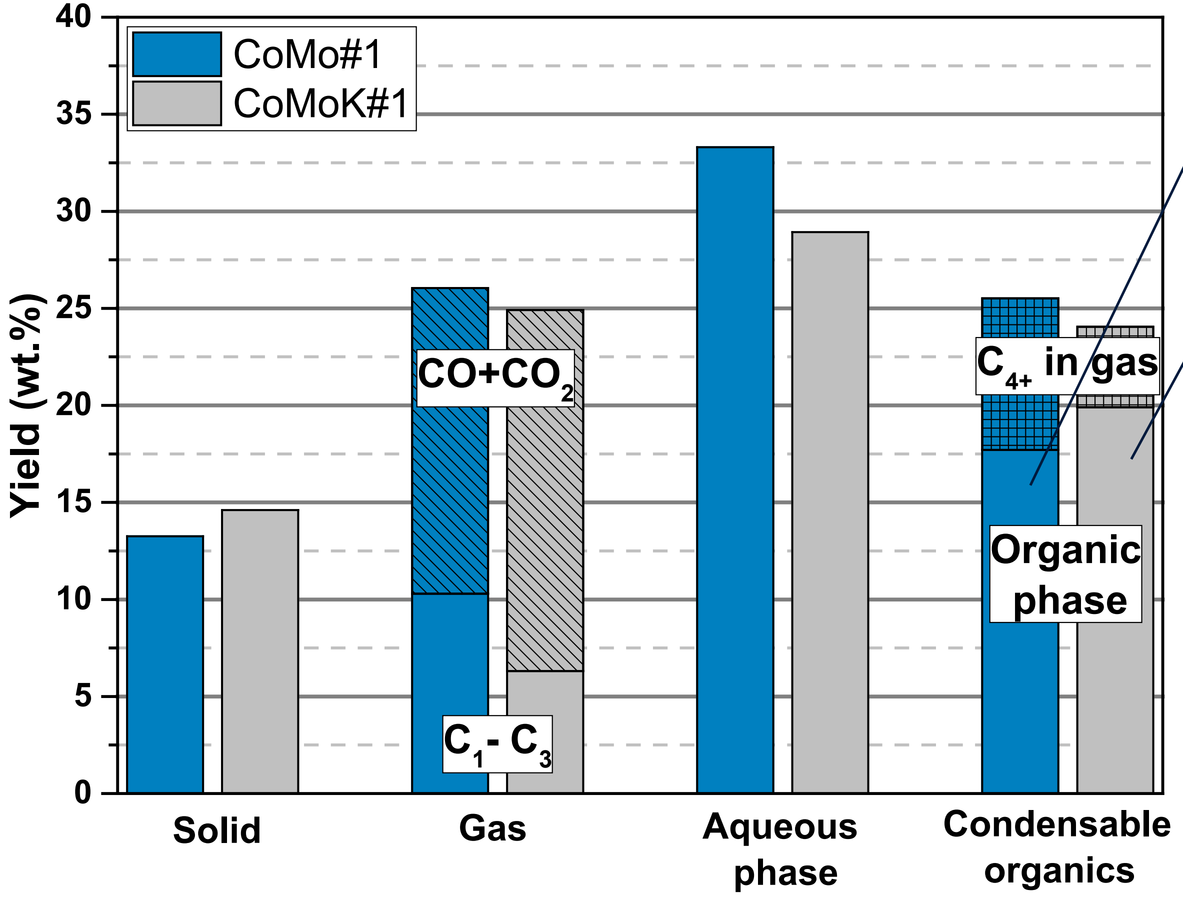
Effect of catalyst pre-deactivation with potassium
Catalyst composition

Catalyst	Mo (wt.%)	Co (wt.%)	K (wt.%)	Co/Mo (mol / mol)	Mo load (Atoms/nm^2)	BET SSA (m^2/g)
CoMo#1	3.41	0.637	-	0.30	3.6	60
CoMoK#1	3.43	0.603	1.935	0.29	3.9	55



The catalysts were prepared by sequential incipient wetness impregnation

Effect of catalyst pre -deactivation with potassium
Product distribution



O content: 9.0 wt.% db
TAN: 4.0 mg_{KOH}/g

O content: 13.8 wt.% db
TAN: 14.7 mg_{KOH}/g

Potassium decreases the HDO activity

CoMoK#1 was doped with 1.9 wt.% K prior to the experiment
The HDO reactor was bypassed

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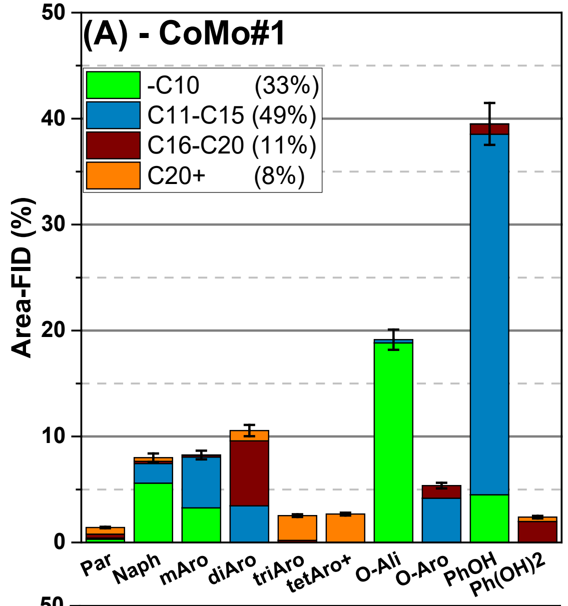
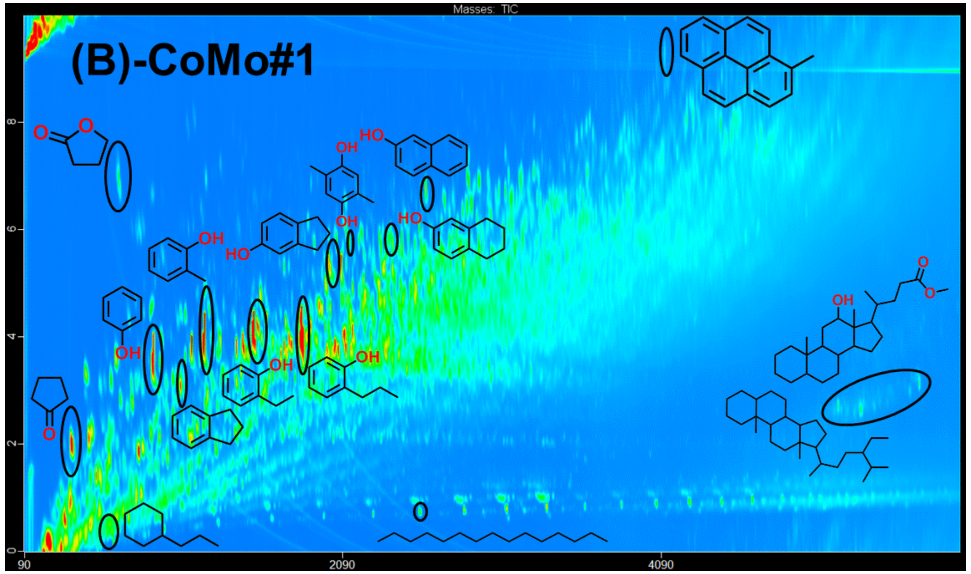
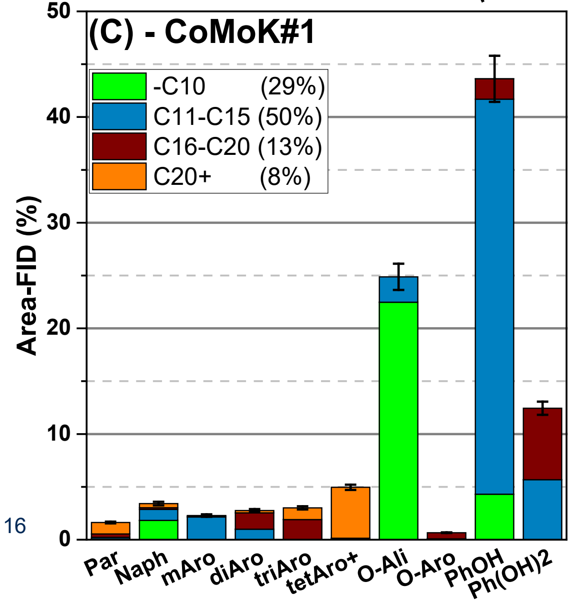
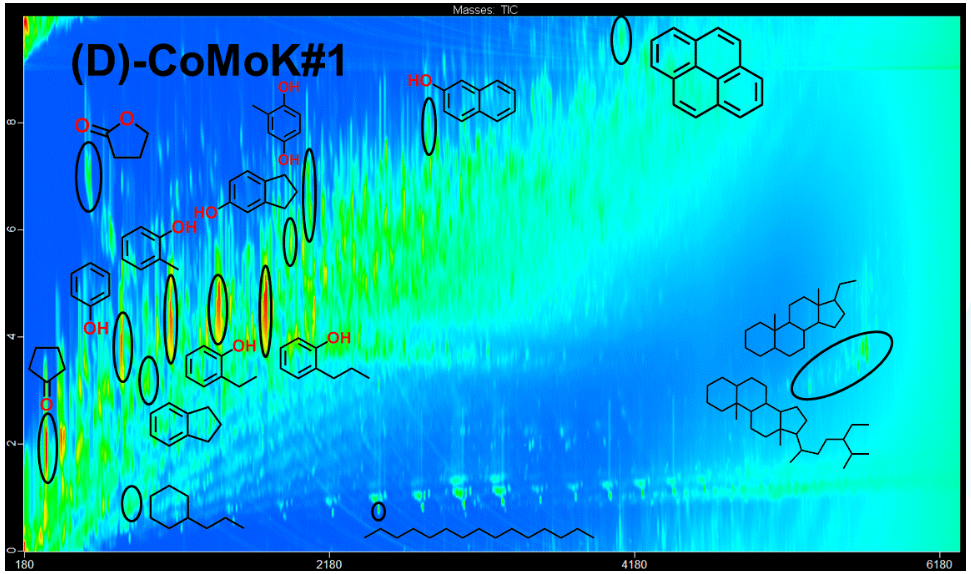
Effect of catalyst pre -deactivation with potassium
GC×GC-FID/MS









Doping the catalyst with potassium increased the concentration of oxygenated aliphatics, phenols, and dihydroxybenzenes

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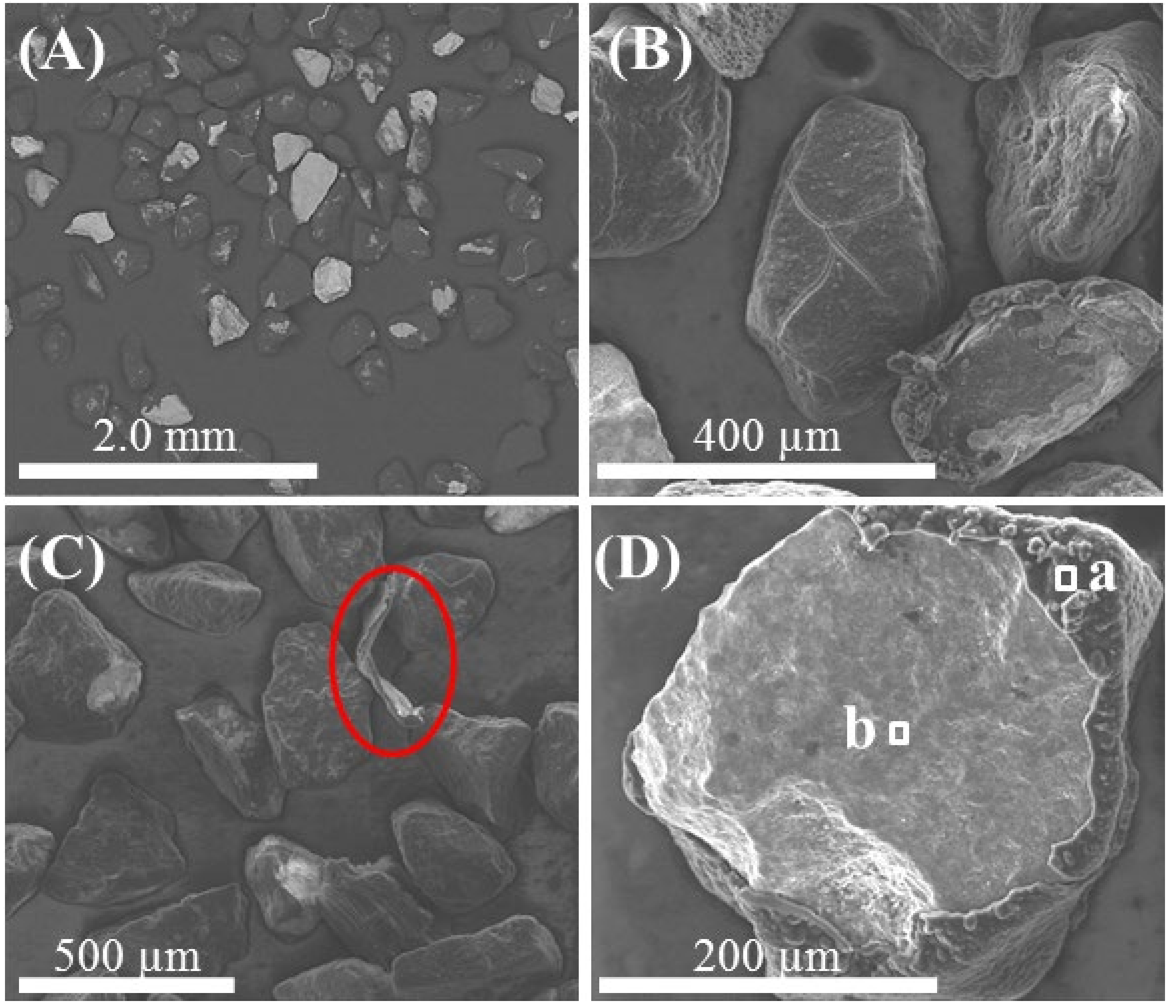
Effect of catalyst pre -deactivation with potassium

Characterization of the spent catalyst



Spot	a	b
C (wt.%)	95.7	15.9
O (wt.%)	3.0	23.2
S (wt.%)	1.4	10.1
K (wt.%)	0	1.4

Effect of using straw as feedstock

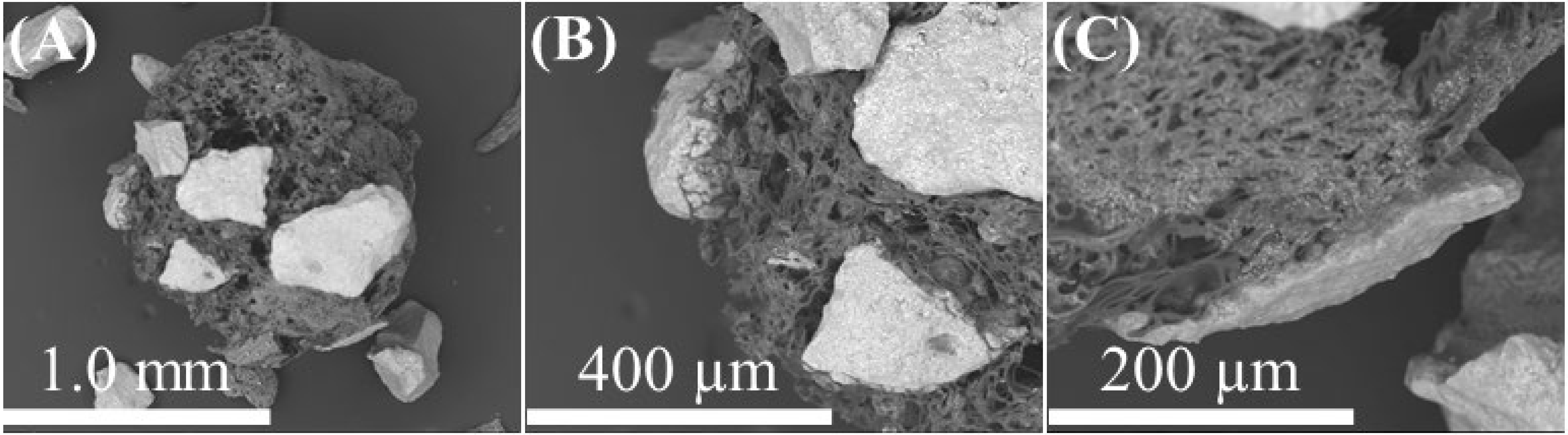
Effect of using straw as feedstock
Feedstock composition

	Beech	Straw	
C	49.9	46.9	wt.% dry
H	6.0	6.0	wt.% dry
N	0.13	0.56	wt.% dry
O*	43.0	41.6	wt.% dry
K	0.12	1.4	wt.% dry
Ca	0.13	0.23	wt.% dry
Si	140	3900	wt-ppm dry
P	75	910	wt-ppm dry
Cl	2.0	6500	wt-ppm dry

Straw contains approximately 10 times more potassium than beech wood

Effect of using straw as feedstock

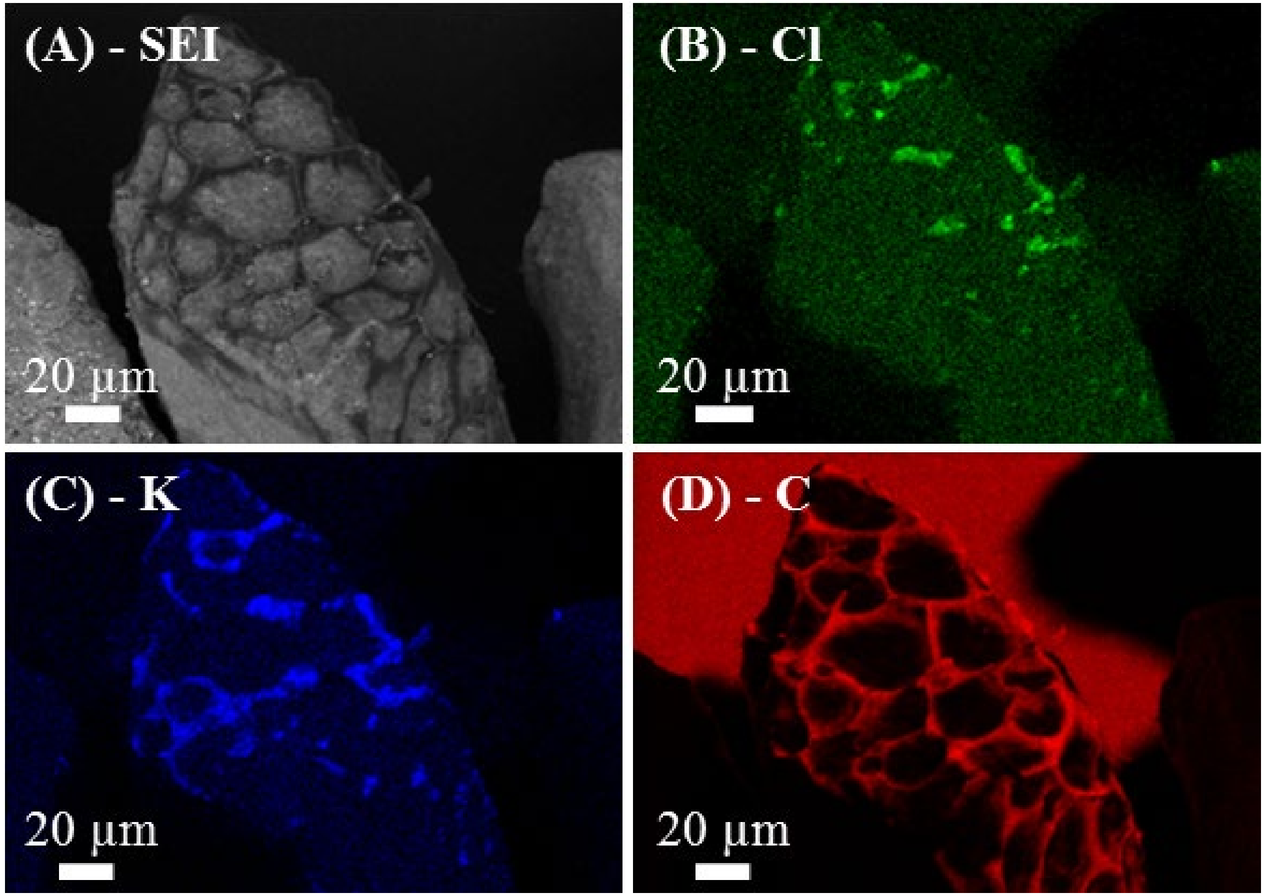
Characterization of the spent catalyst and char



Investigations of the spent catalyst showed that agglomeration had taken place. The largest agglomerates had a diameter of 5 mm.

Effect of using straw as feedstock

Characterization of the spent catalyst and char



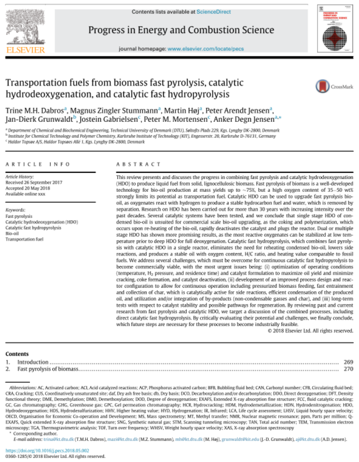
It can be assumed that this grid is not formed due to normal coke formation on the surface of the particle due to reacting vapors/gases, but must come from solidification of tar or metaplast.

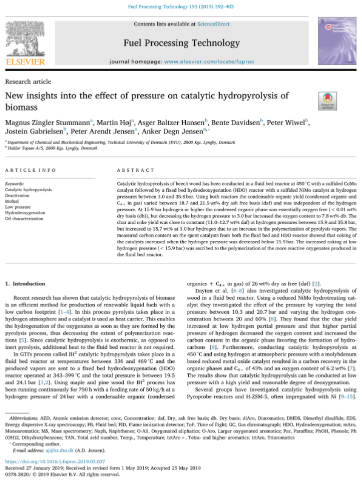
Conclusion

- The stability experiment gave a stable oil yield of 22.2±1 wt.% daf, but a small increase in the oxygen content was observed.
- Potassium and calcium is transferred from the biomass to the catalyst
- Doping the catalyst with potassium decreased the catalyst's hydrodeoxygenation and cracking activity
- Potassium catalyzes polymerization reactions, which can lead to catalyst encapsulation and agglomeration

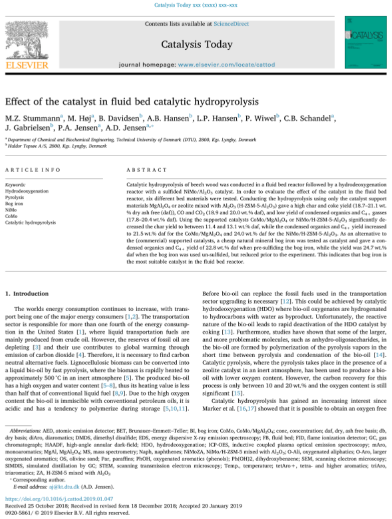
Published articles

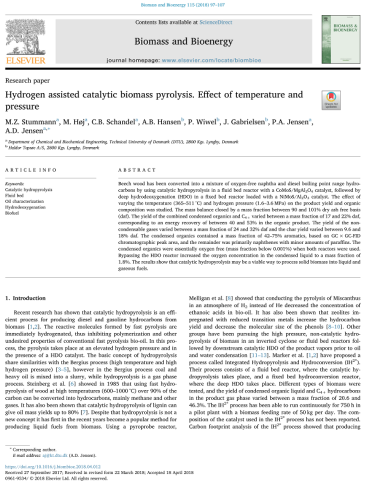
- M.Z. Stummann, M. Høj, C.B. Schandel, A.B. Hansen, P. Wiwel, J. Gabrielsen, P.A. Jensen, A.D. Jensen, Hydrogen assisted catalytic biomass pyrolysis. Effect of temperature and pressure, Biomass and Bioenergy. 115 (2018) 97–107. doi:10.1016/j.biombioe.2018.04.012.
- M.Z. Stummann, M. Høj, A.B. Hansen, B. Davidsen, P. Wiwel, J. Gabrielsen, P.A. Jensen, A.D. Jensen, New insights into the effect of pressure on catalytic hydropyrolysis of biomass, Fuel Process. Technol. 193 (2019) 392–403. doi:10.1016/j.fuproc.2019.05.037.
- M.Z. Stummann, A.B. Hansen, L.P. Hansen, B. Davidsen, S.B. Rasmussen, P. Wiwel, J. Gabrielsen, P.A. Jensen, A.D. Jensen, M. Høj, Catalytic Hydropyrolysis of Biomass Using Molybdenum Sulfide Based Catalyst. Effect of Promoters, Energy & Fuels. 33 (2019) 1302–1313. doi:10.1021/acs.energyfuels.8b04191.
- M.Z. Stummann, M. Høj, B. Davidsen, A.B. Hansen, L.P. Hansen, P. Wiwel, C.B. Schandel, J. Gabrielsen, P.A. Jensen, A.D. Jensen, Effect of the catalyst in fluid bed catalytic hydropyrolysis, Catal. Today. (2019). doi:10.1016/j.cattod.2019.01.047.
- T.M.H. Dabros, M.Z. Stummann, M. Høj, P.A. Jensen, J.-D. Grunwaldt, J. Gabrielsen, P.M. Mortensen, A.D. Jensen, Transportation fuels from biomass fast pyrolysis, catalytic hydrodeoxygenation, and catalytic fast hydropyrolysis, Prog. Energy Combust. Sci. 68 (2018) 268–309. doi:10.1016/j.pecs.2018.05.002.


Progress in Energy and Combustion Science
Transportation fuels from biomass fast pyrolysis, catalytic hydrodeoxygenation, and catalytic fast hydropyrolysis


Fuel Processing Technology
New insights into the effect of pressure on catalytic hydropyrolysis of biomass


energy&fuels
Catalytic Hydropyrolysis of Biomass Using Molybdenum Sulfide Based Catalyst. Effect of Promoters


Catalysis Today
Effect of the catalyst in fluid bed catalytic hydropyrolysis


Biomass and Bioenergy
Hydrogen assisted catalytic biomass pyrolysis. Effect of temperature and pressure

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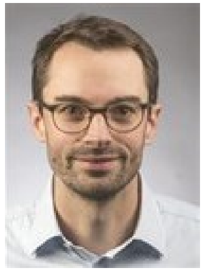
A.D. Jensen


M. Høj


P.A. Jensen

People at Haldor Topsøe


B. Davidsen


L.P. Hansen


A.B. Hansen


P. Wiwel


P. Beato


J. Gabrielsen

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Thank You