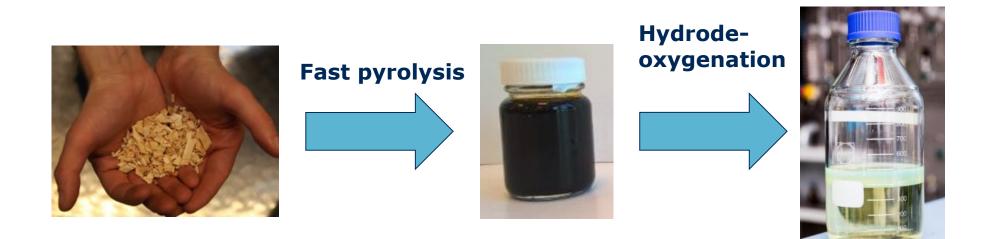
Deactivation of a CoMo catalyst during catalytic hydropyrolysis of biomass

<u>M. Z. Stummann^{1,2}</u>, J. Gabrielsen², M. Høj¹, P. Beato², A. B. Hansen², B. Davidsen², P. Wiwel², L. P. Hansen², P. A. Jensen¹, A. D. Jensen^{1*} 1 Technical University of Denmark, Kgs. Lyngby 2800 (Denmark), 2 Haldor Topsøe A/S, Kgs. Lyngby 2800 (Denmark) *A J@ kt.dtu.dk

Biomass to green fuels



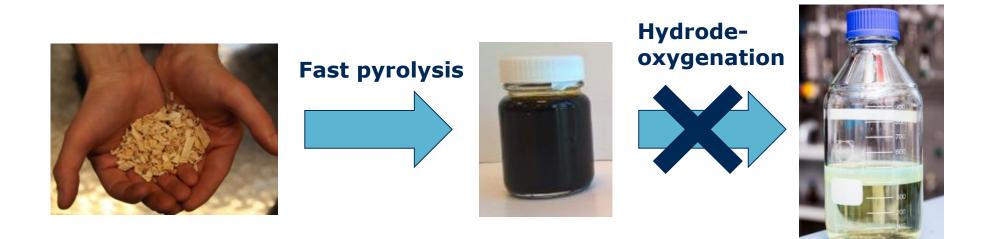


Biomass

Pyrolysis oil HHV ~ 16-19 MJ/kg 28-40 wt. % oxygen **Fuel + water** ~ 45 MJ/kg <0.1 wt. % oxygen

Biomass to green fuels



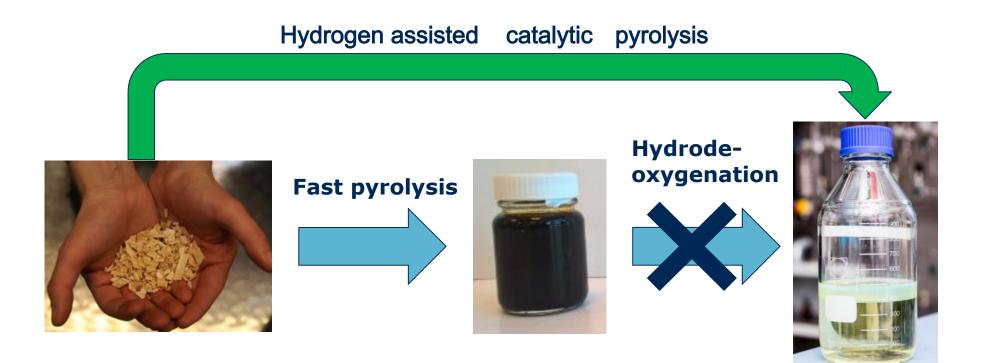


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Biomass to green fuels



Biomass

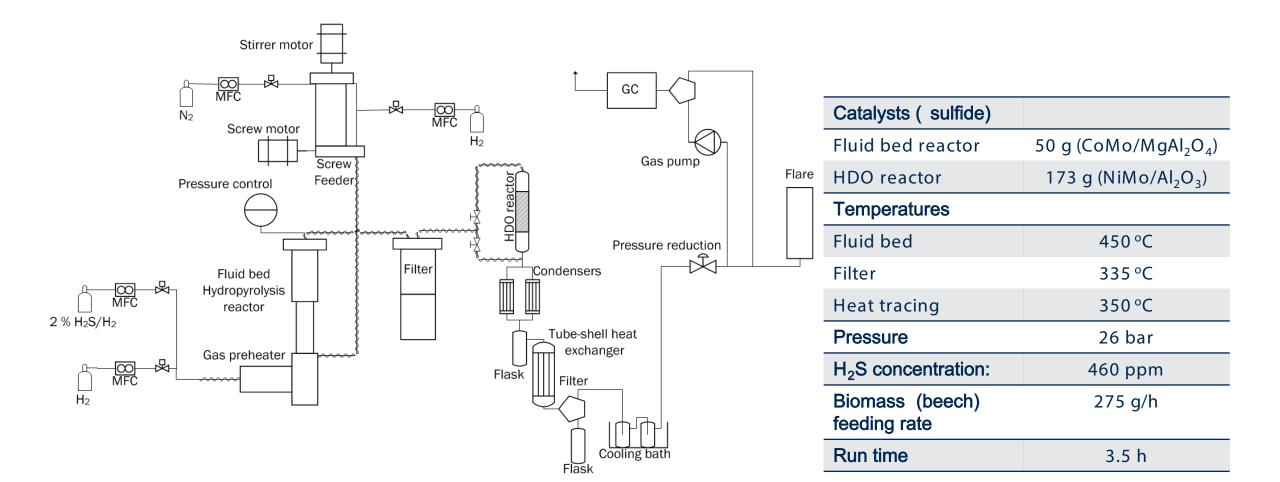
Pyrolysis oil HHV ~ 16-19 MJ/kg 28-40 wt. % oxygen **Fuel + water** ~ 45 MJ/kg <0.1 wt. % oxygen



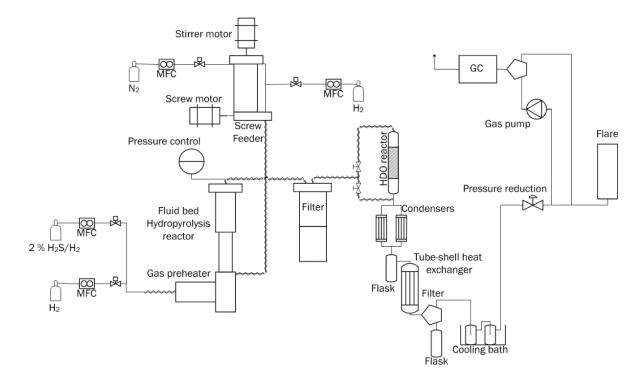
Catalyst stability

Setup at DTU Chemical Engineering





Setup at DTU Chemical Engineering



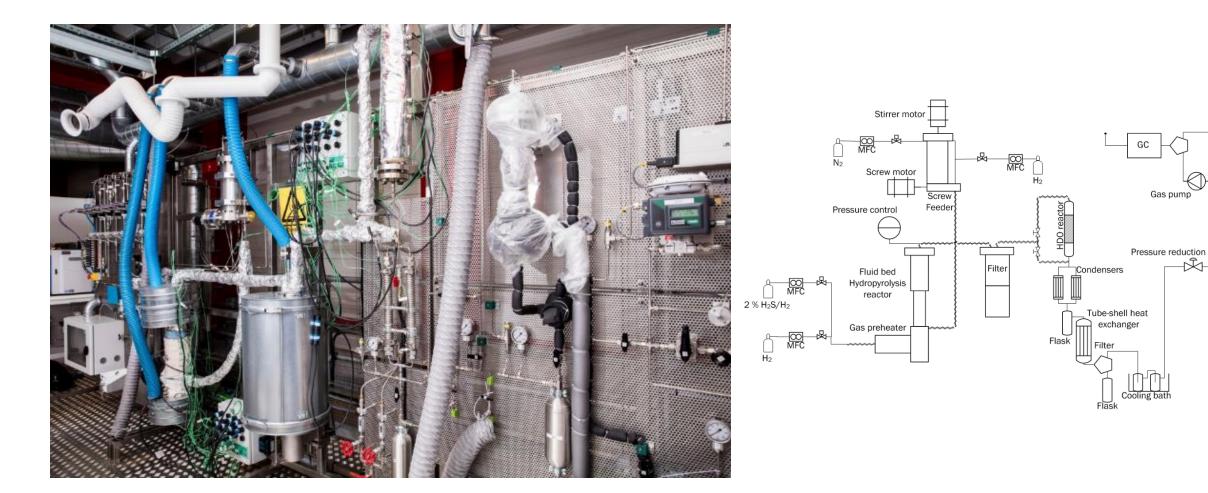
Experimental procedure

- 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



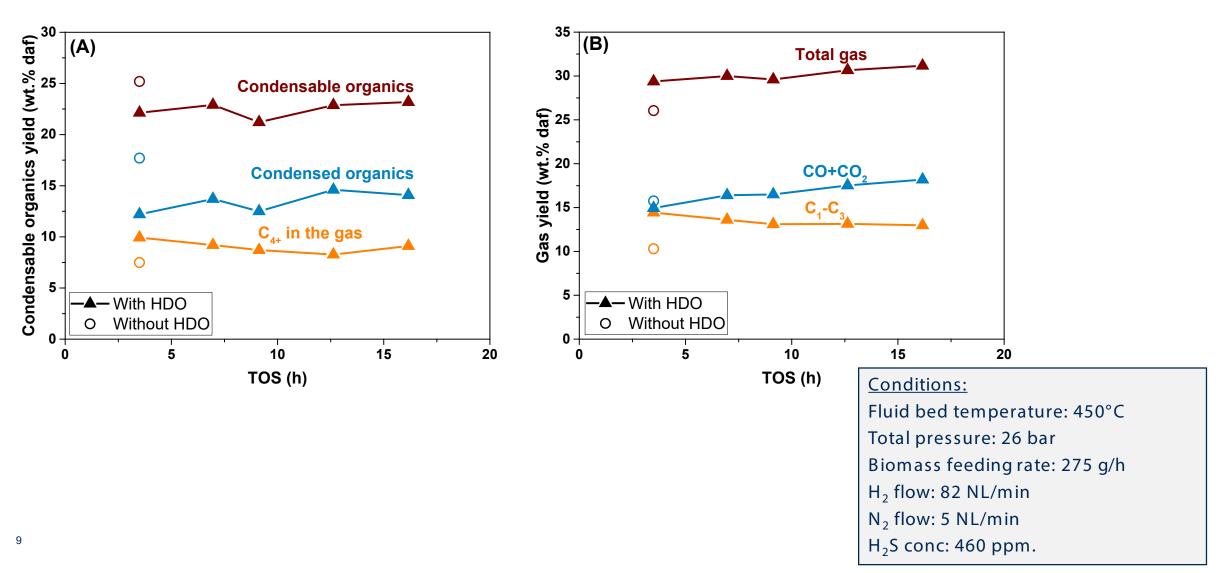
Flare



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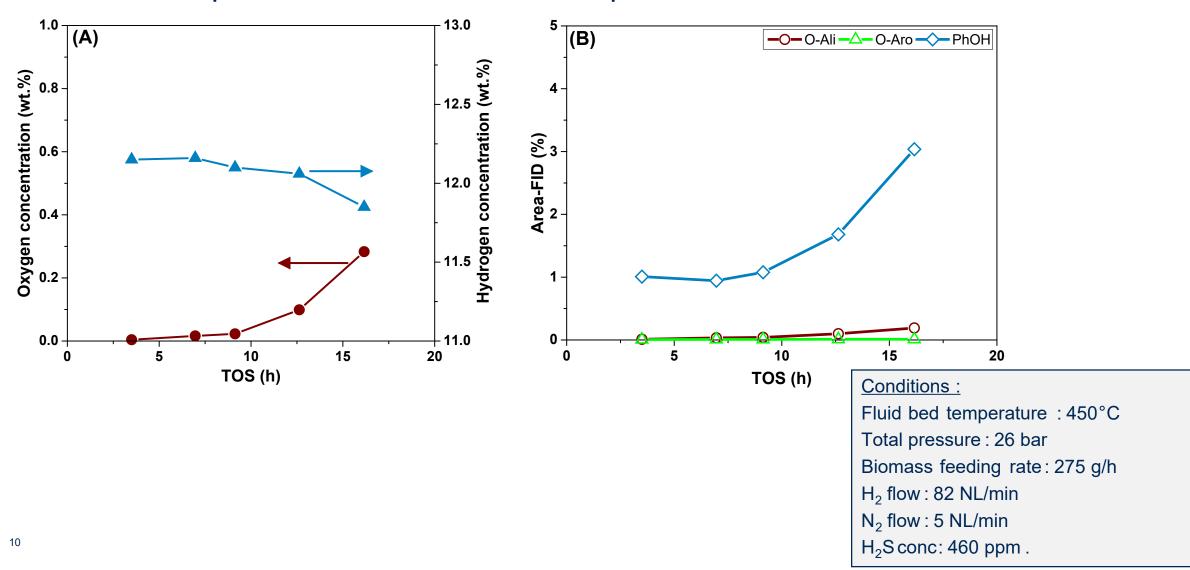


Catalyst stability Product distribution

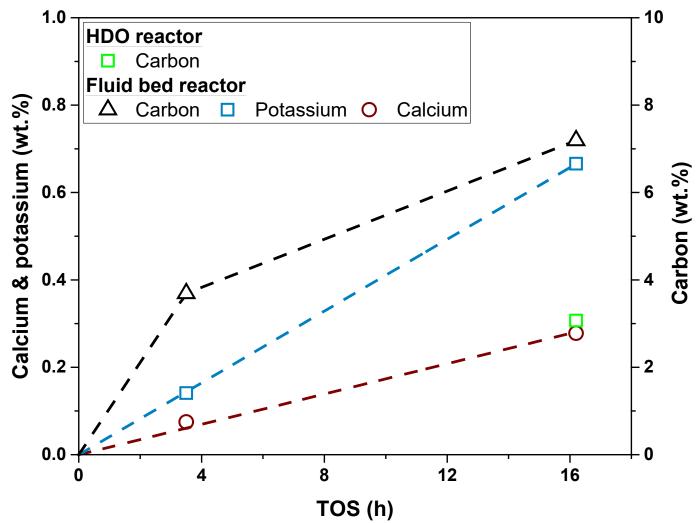




Catalyst stability Chemical composition of the condensed liquids



Catalyst stability Characterization of the spent catalyst

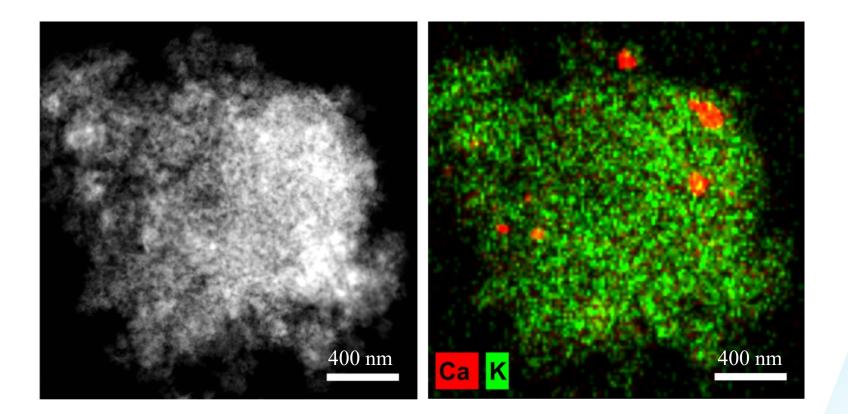


Potassium and calcium are transferred from the biomass to the catalyst

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Characterization of the spent catalyst STEMHAADF of the spent catalysts



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

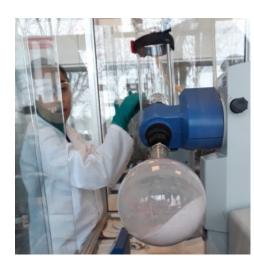


Effect of catalyst pre-deactivation with potassium

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 (m²/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

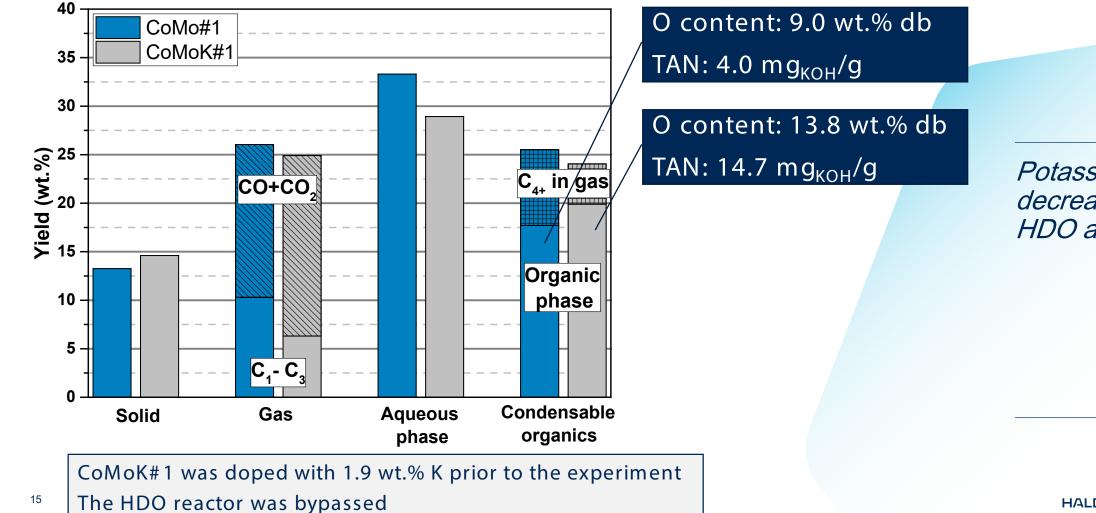
The catalysts were prepared by sequential incipient wetness impregnation



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Effect of catalyst pre -deactivation with potassium Product distribution



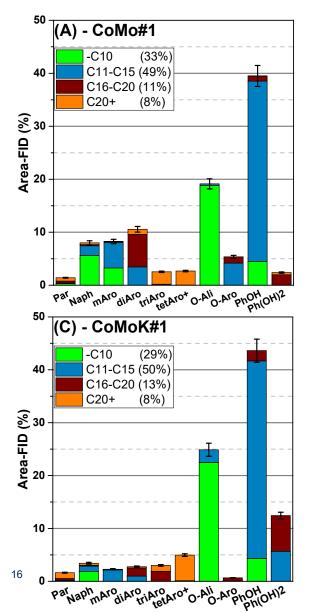
Potassium decreases the HDO activity

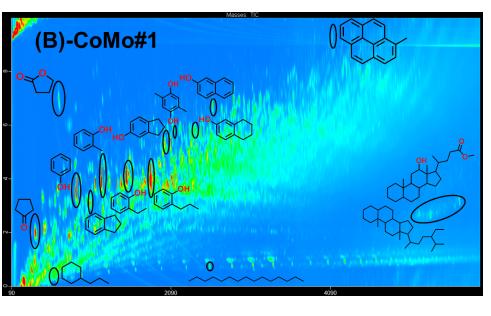
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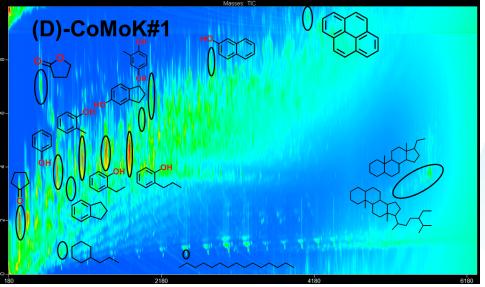
Effect of catalyst pre GC×GC-FID/MS

-deactivation with potassium





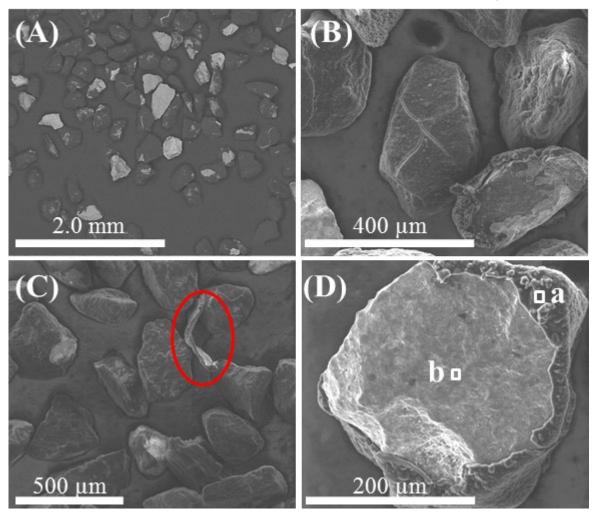




Doping the catalyst with potassium increased the concentration of oxygenated aliphatics, phenols, and dihydroxybenzenes

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Effect of catalyst pre -deactivation with potassium Characterization of the spent catalyst



Spot	а	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	
С	49.9	46.9	wt.% dry
Н	6.0	6.0	wt.% dry
Ν	0.13	0.56	wt.% dry
0*	43.0	41.6	wt.% dry
К	0.12	1.4	wt.% dry
Ca	0.13	0.23	wt.% dry
Si	140	3900	wt-ppm dry
Ρ	75	910	wt-ppm dry
Cl	2.0	6500	wt-ppm dry

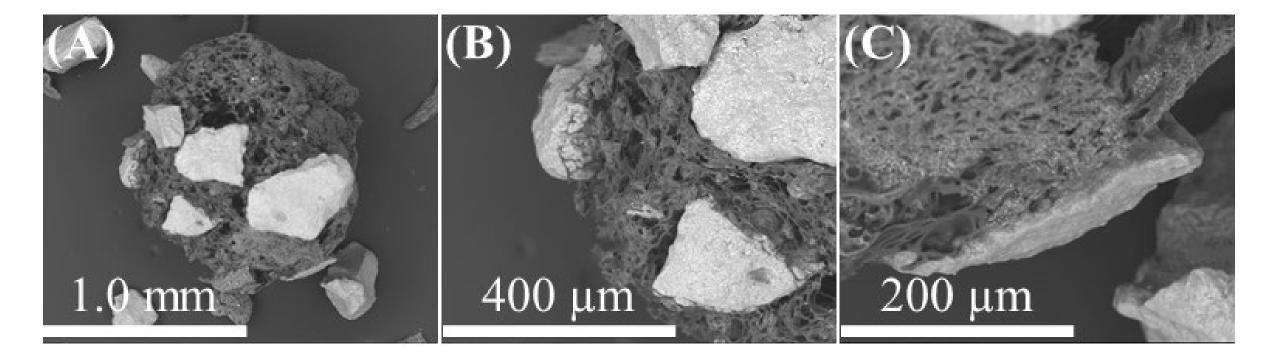
Straw contains approximately 10 times more potassium than beech wood

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Effect of using straw as feedstock Characterization of the spent catalyst and char

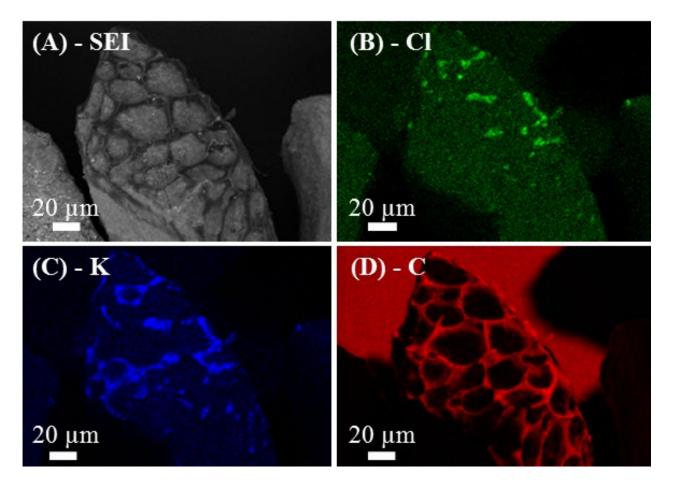




Investigations of the spent catalyst showed that agglomeration had taken place. The largest agglomerates had a diameter of 5 mm.

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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.

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- 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.

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Transportation fuels from biomass fast pyrolysis, catalytic hvdrodeoxygenation, and catalytic fast hvdropyrolysis	New insights into the effect of pressure on catalytic hydropyrolysis of biomass	Magnus Zingler Stummann, [™] Asger Baltzer Hansen, [†] Lars Pløgzard Hansen, [†] Bente Davidsen, [†] Søren Birk Rasmussen, [†] Peter Wövel [†] , Jostein Gabrielsen, [‡] Peter Arendt Jensen, [™] ® Anker Deen Jensen, [®] and Martin Heit [™] ®	Effect of the catalyst in fluid bed catalytic hydropyrolysis M.Z. Stummani, 'M. Heij', B. Davidsen', A.B. Hansen', L.P. Hansen', P. Wiwel', C.B. Schandel', J. Gabrielon', P.A. Jenner', A.D. Jenner', 'M. Jenner', '	Research paper Hydrogen assisted catalytic biomass pyrolysis. Effect of temperature and
Trine M.H. Dabros ¹ , Magnus Zingler Stummann ¹ , Martin Høj ¹ , Peter Arendt Jensen ¹ , Jan-Dierk Grunwaldt ² , Jostein Gabrielsen ¹ , Peter M. Mortensen ¹ , Anker Degn Jensen ¹⁴	Magnus Zingler Stummann ¹ , Martin Høj ¹ , Asger Baltzer Hansen ¹ , Bente Davidsen ¹ , Peter Wiwel ¹ , Jostein Gabrielsen ¹ , Peter Arendt Jensen ¹ , Anker Degn Jensen ^{1,1}	¹ Department of Chemical and Bischenical Engineering, Technical University of Dennark (DTU), 2800 Kgs. Lyngby, Dennark ¹ Haldee Topuse A/S, 2800 Kgs. Lyngby, Dennark	J. SouthTERSET, J. YA. JOHENT, J. A.D. JOHENT, " "Approve of Orbital millionizatial Diplombing: Todasial University of Neurant (1975), 2000, Kgs. Lyngle, Denserk "Nature Toport, A.S., 2000, Kgs. Lyngle, Denserk	pressure M.Z. Stummann', M. Hoj', C.B. Schandel', A.B. Hansen', P. Wiwel', J. Gabrielsen', P.A. Jensen', A.D. Isensen' ²
*Department of Chemical and Bioteminial Regimening: Technical University of Demand (2003). EduCh Peloh 250 Kgs. (epubg 36: 5000). Chemical Technicage and Polyner Chemicage. Science and and of Technology (2013). Education 2013). EduCh Peloh 250 Kgs. (epubg 36: 5000). Technicage and Polyner Chemicage. Science and Antonio and Polynel Antonio a	* Separate of Chansal and Electronical Reporting. Technical University of Ionmark (2011), 2000 Ega, Lyngly, Connark * Nalder Espaie A:S. 2000 Ega, Lyngly, Formark	Supporting Information ABNTRACT: Catabatic Industryabula of burch wood was conducted in a fluid bod matter at 460 °C and a total pressure of 36	ARTICLE INFO ABSTRACT	A.L.J. 20150911 "Poparenet of Colonsial and Backwalad Jophanetig. Excluded University of Remark (2010), 2000 Kga. Lyngly, Domark "Bilder Tapux A.S. 2000 Kga. Lyngly, Domark
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M. Høj



A.D. Jensen



P.A. Jensen

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B. Davidsen



L.P. Hansen



A.B. Hansen



P. Wiwel



P. Beato



J. Gabrielsen





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DTU Chemical Engineering

Department of Chemical and Biochemical Engineering



Thank You