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Catalytic pyrolysis of forest thinnings in a circulating fluidized bed reactor

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Business from technology

Catalytic pyrolysis of forest thinnings in a 20 kg/h circulating fluidized bed reactor

ECI Bioenergy IV, June 10th 2013, Otranto, Italy
Ville Paasikallio, Christian Lindfors, Anja Oasmaa, Jani Lehto, Eeva Kuoppala, Yrjö Solantausta
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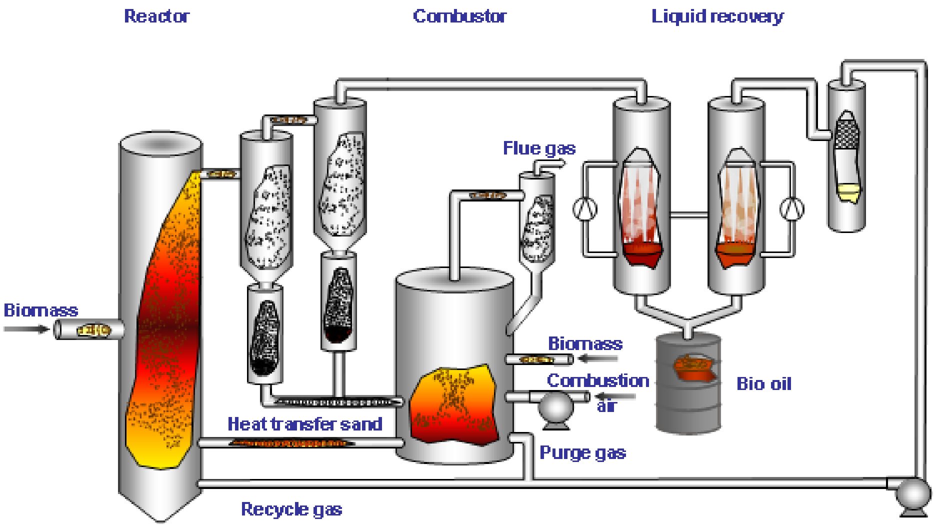
From conventional to catalytic fast pyrolysis

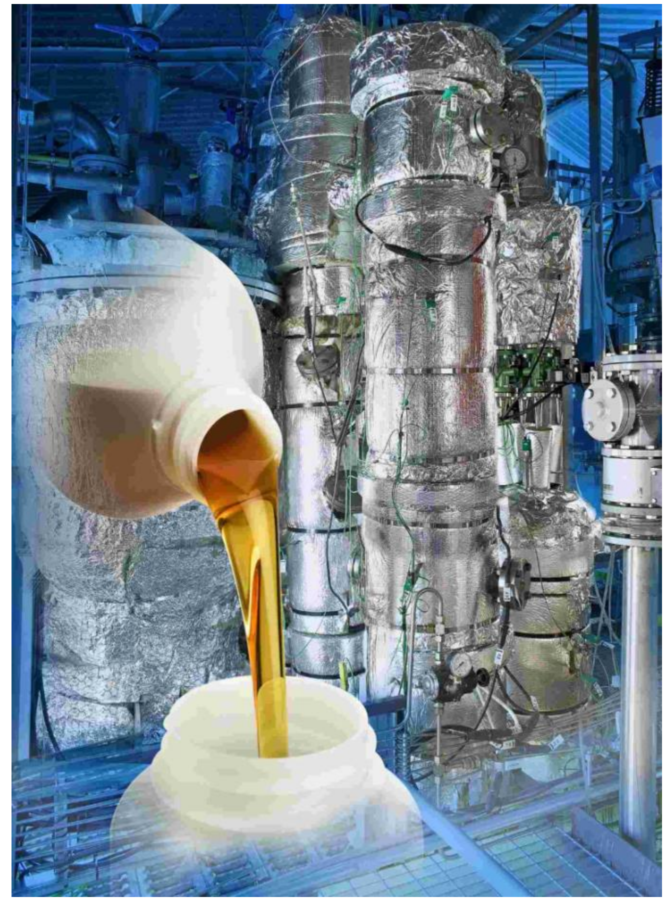
- More than 40 tonnes of pyrolysis oil produced in VTT's Process Development Unit since 1996
- 50 000 t/a industrial scale-up in process in Finland
- Replacing the sand with a solid catalyst
- How challenging can it be?

Quite challenging.



Background

- Catalytic pyrolysis – a way to produce pyrolysis oil with improved fuel properties
- Most of public experimental work limited to laboratory and bench scale with limited time spans
- Catalyst deactivation and regeneration a major issue for continuous operation
- A circulating fluidized bed (CFB) reactor offers both possibilities and challenges



Operation in a CFB reactor – what to expect?

- Coke deposition no longer a problem
- More interdependency between process variables
  → Less freedom in process control
- Short contact time between catalyst and pyrolysis vapors
- Continuous regeneration of the catalyst – effect of temperature and biomass alkalis?
- Mechanical integrity of the catalyst

Materials and operating conditions

- Finnish forest thinnings feedstock – a mixture of softwood and hardwood
- Spray-dried ZSM-5 catalyst from Zeolyst International $SiO_2/Al_2O_3 = 280$
- Pyrolysis temperature 480-500°C
- Regeneration temperature 650-680°C
- Biomass feedrate 20 kg/h, catalyst 120-140 kg/h
- Fluidization velocity 6 m/s
- Scrubber temperature 40-50°C

Product distribution

Stage	Reactor (°C)	Organics	Water	Gases	Char/coke
1	480	36	16	14	34
2	480	37	15	14	34
3	500	42	13	13	33

- Yield of organics typically 50-55 wt-% in non-catalytic fast pyrolysis
- Use of catalyst slightly increased water/gas yields
- High yield of char/coke
- Product distribution suggests possible catalyst deactivation

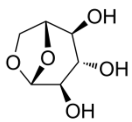
Pyrolysis oil physical properties

	Reference	Stage 1	Stage 2	Stage 3
	As received	As received	As received	As received
Water, wt%	24.4	33.3	27.2	24.4
pH	2.7	2.5	2.7	2.6
TAN, mgKOH/g	102	106.6	103.8	104
Solids, wt%	0.01	0.41	0.46	0.39
MCR, wt%	18.1	16.4	19.0	20.0
Ash, wt%	0.02	0.17	0.22	0.23
Viscosity, cSt, 40°C	14	-	15	18
Density, kg/l, 15°C	1.200	1.155	1.181	1.192
	Dry basis	Dry basis	Dry basis	Dry basis
HHV, MJ/kg	22.4	24.0	23.7	23.6
LHV, MJ/kg	20.1	21.4	21.4	21.5
C, wt%	**54.6**	**57.0**	**56.7**	**56.3**
H, wt%	**6.8**	**6.1**	**6.3**	**6.0**
N, wt%	**0.3**	**0.1**	**0.3**	**0.3**
O, wt%	**38.3**	**36.8**	**36.7**	**37.3**

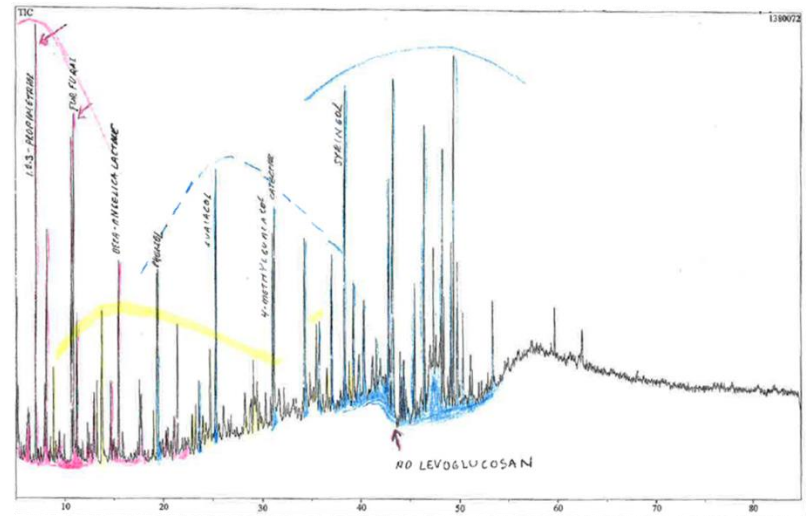
→ Very little change compared to non-catalytically produced pyrolysis oil

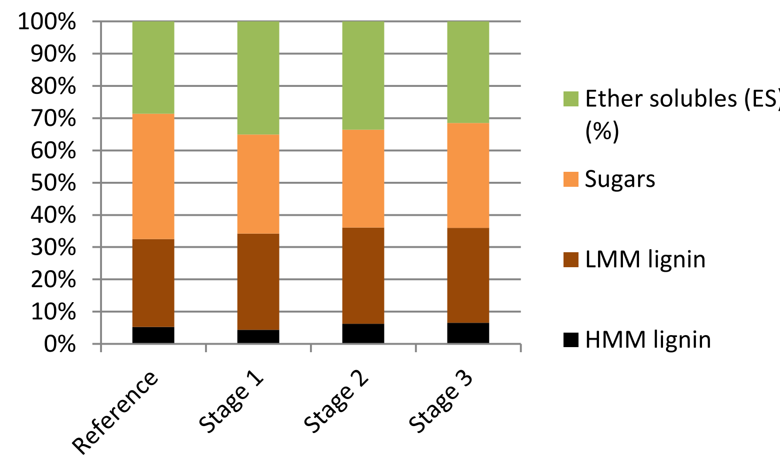
→ Are there any changes in the chemical composition?

Pyrolysis oil chemical composition



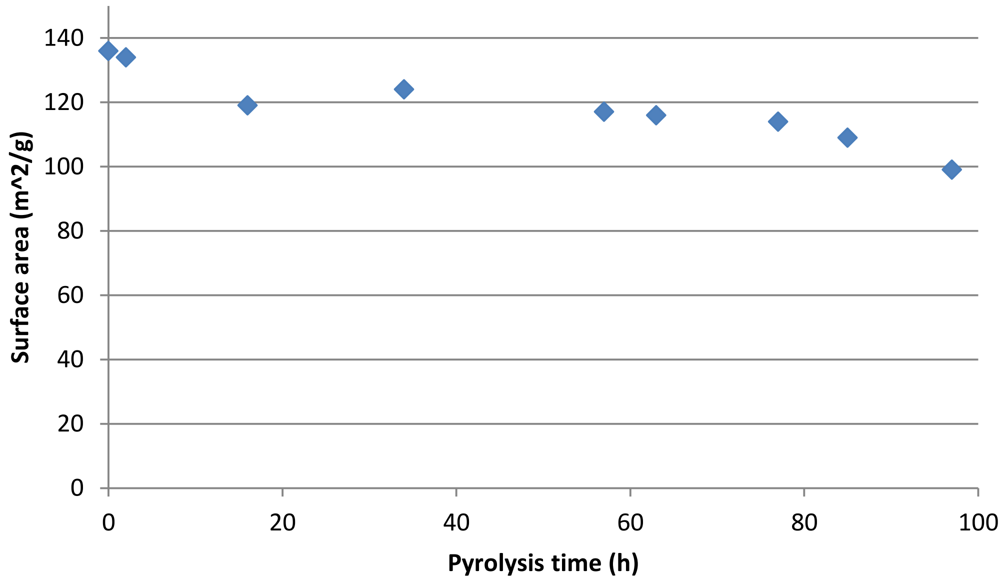
- Levoglucosan converted into other oxygenates
- Some aromatic hydrocarbons present
- Sugar type compounds decreased





Relatively small changes here as well – what about the catalyst?

Catalyst characterisation: Specific surface area

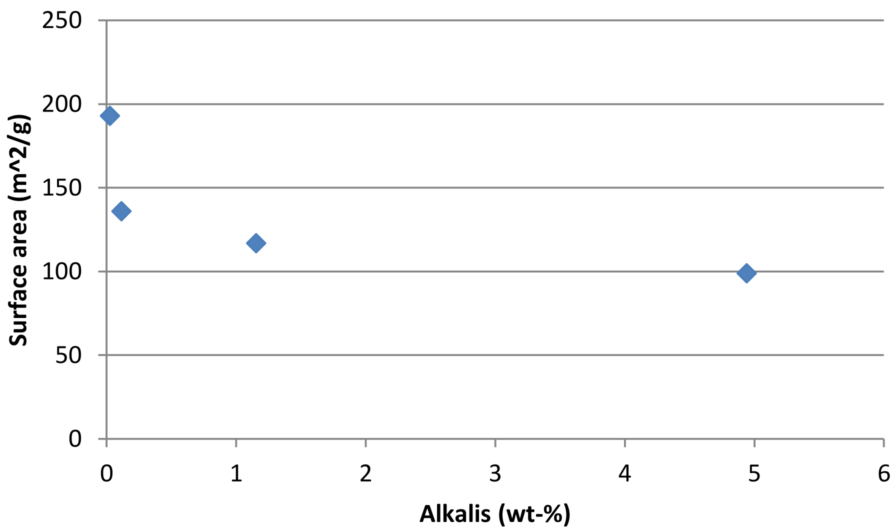


- Fresh catalyst 193 m^2/g, calcined catalyst 163 m^2/g
- Surface area loss during initial heat-up phase and pyrolysis phase
- No notable carbon build-up on catalyst

Catalyst characterisation: Metal content

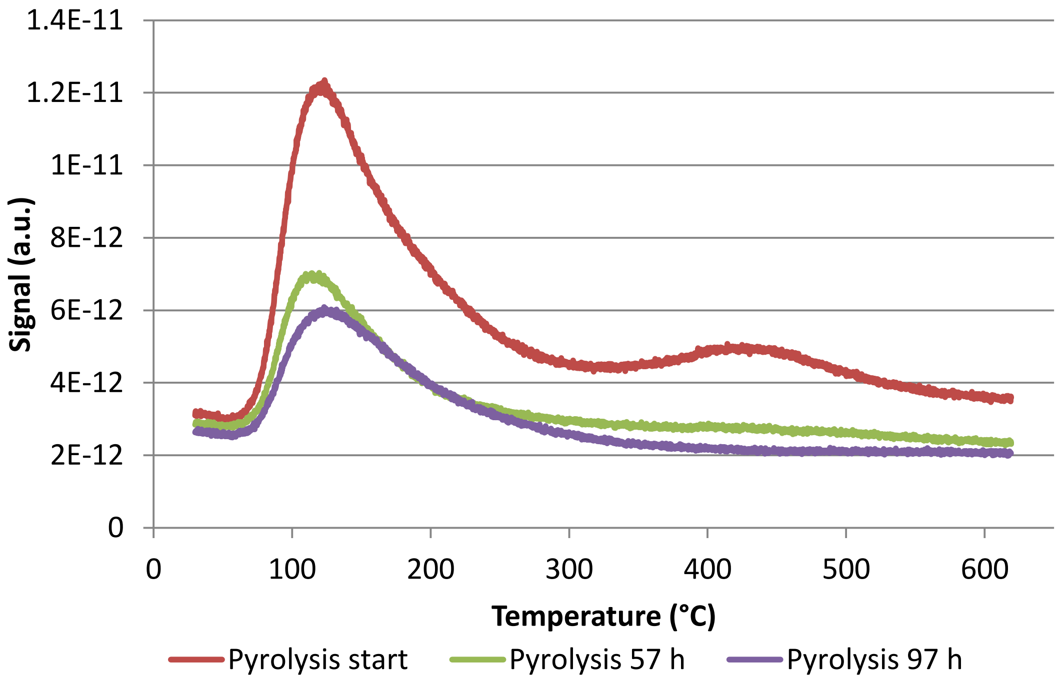
Sample	K (wt-%)	Na (wt-%)	P (wt-%)	Ca (wt-%)	Mg (wt-%)	Sum of alkalis (wt-%)
Fresh	0.01	0.01	< 0.05	< 0.05	< 0.05	0.02
Pyrolysis start	0.04	0.01	< 0.05	0.07	< 0.05	0.11
57 h	0.51	0.04	< 0.05	0.50	0.10	1.15
97 h	1.59	0.05	0.75	2.05	0.50	4.94

Does alkali deposition appear to cause pore blockage?



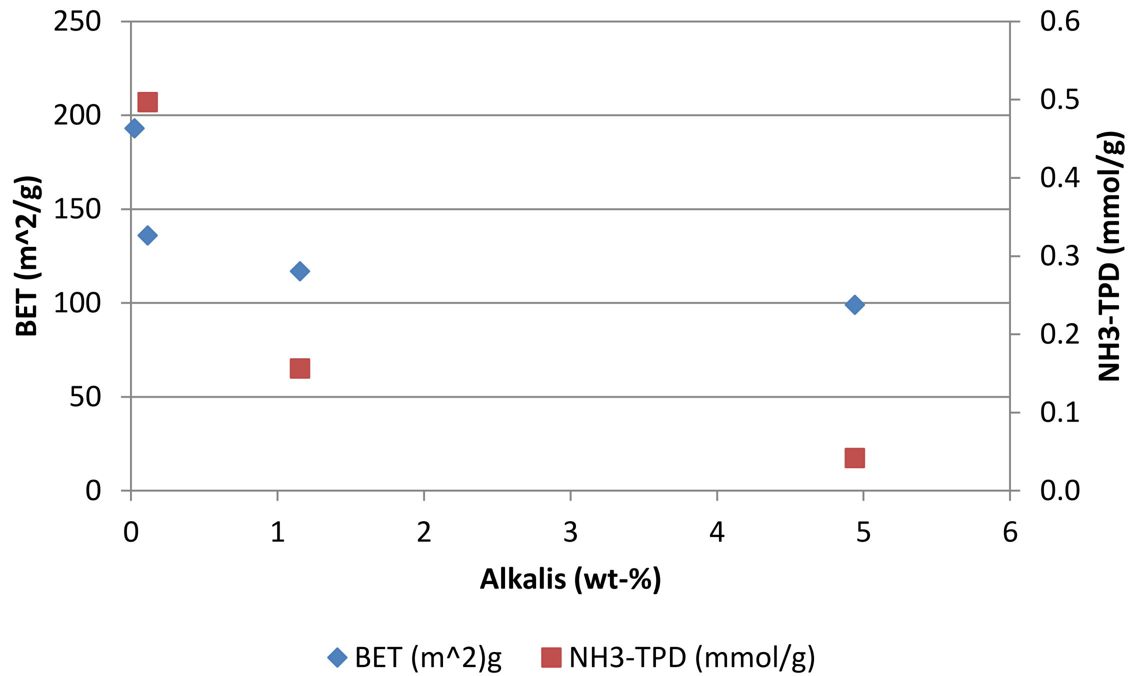
No observable linear correlation.

Catalyst characterisation: Acidity



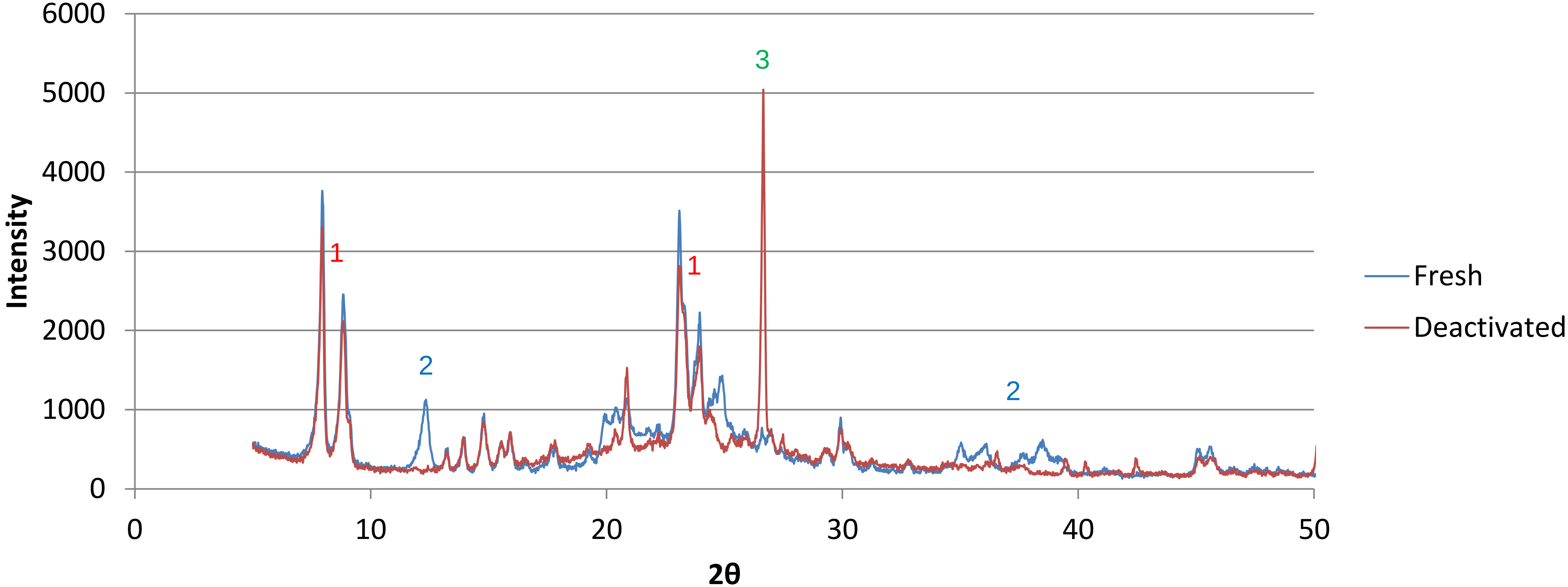
Clear change in NH_3-TPD spectra, how does this compare to alkali content?

Catalyst characterisation: Acidity



- Overall catalyst acidity decreases during experiment
- Alkalis might deposit on Brønsted acid sites without blocking the catalyst pores

Catalyst characterisation: X-ray diffraction



1. Decrease in ZSM-5 peak intensities
2. Disappearance of kaolinite peaks
3. Disappearance of silicalite peak and appearance of quartz peak

Summary

- VTT's 20 kg/h PDU operated smoothly with a spray-dried ZSM-5 catalyst
- Catalytic pyrolysis in a CFB reactor is not as simple as just replacing the sand with a catalyst
- Process conditions have to be chosen carefully to increase the effectiveness of the catalyst
- Catalyst properties change in a five day experiment
- Catalyst activity and lifetime are major issues

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VTT creates business from technology