PYRENA: Pyrolysis equipment for new approaches in circulating fluidised bed catalytic pyrolysis for better bio-oil as precursor for fuels and chemicals

P.J. de Wild
R.R. van der Laan
R. Sumbharaju
H. Bodenstaff
E.J. Brouwer
C.M. van der Meijden

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PYRENA

PYROLYSIS EQUIPMENT FOR NEW APPROACHES in circulating fluidised bed catalytic pyrolysis for better bio-oil as precursor for fuels and chemicals

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Pyro 2016

Paul de Wild, Ron van der Laan, Raghu Sumbharaju,
Herman Bodenstaff, Edwin Brouwer, Christiaan van der Meijden

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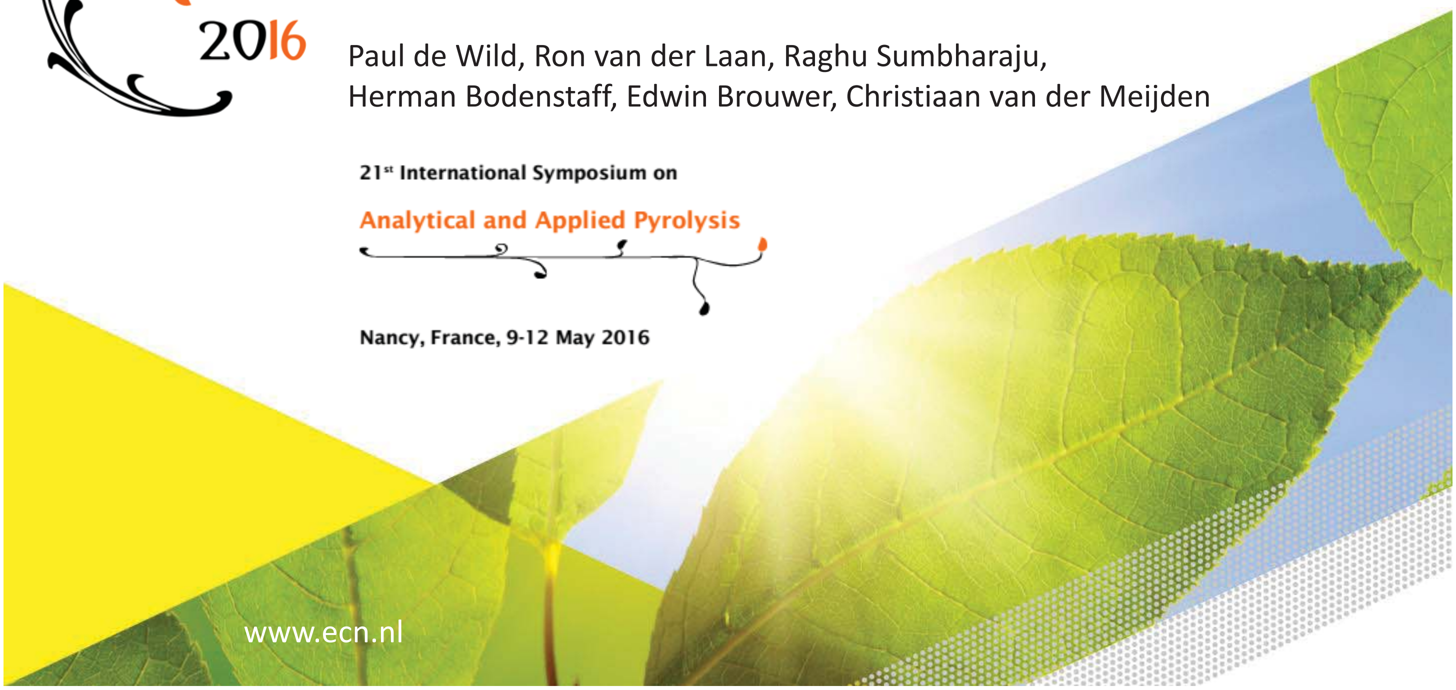
Analytical and Applied Pyrolysis

Nancy, France, 9-12 May 2016



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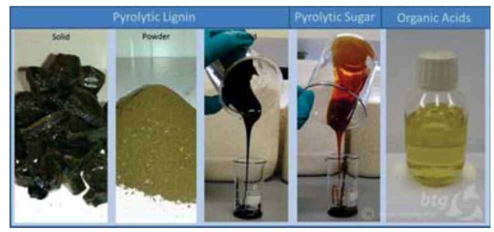
Catalytic fast pyrolysis

- Goal(s)
  - Improve pyrolysis oil quality regarding its application as a (precursor for) transportation fuels (lower O, less acidic, less unstable, less water, etc.)
  - Change pyrolysis oil composition to facilitate the production of value-added chemicals and/or groups of chemicals from the crude liquid product(s)
- Challenges
  - Low organic yield (low carbon efficiency)
  - Unfavourable economics due to high operating costs (feedstock, expensive catalysts) and relatively low value of the liquid product → low price fossil oil!
- Our approach
  - Combine the production of better bio-(fuel)oil with recovery of specific chemicals (e.g. acids, phenolics, anhydrosugars, etc.)
  - Research is supported by techno-economic assessments

Applications for bio-oil and its fractions

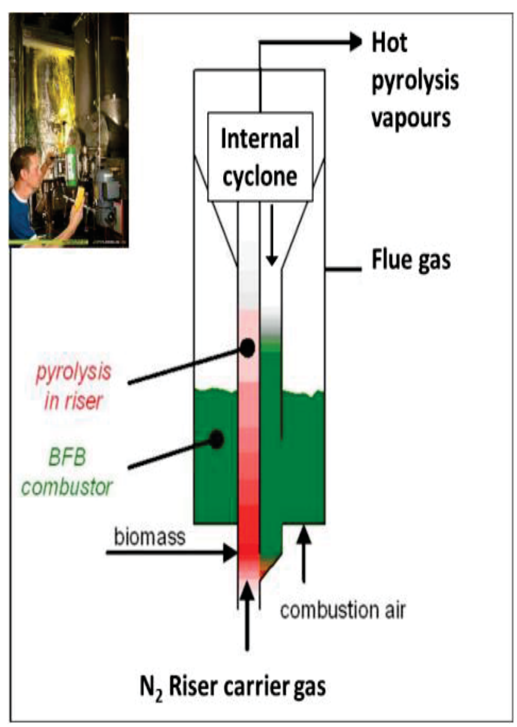
Cheap lignocellulosic biomass e.g. forestry residues and agro-residues

Primary pyrolysis products

PYRENA fast pyrolysis

- Integrated reactor system:
  - EF pyrolysis (riser) – BFB combustor (annulus)
  - 1-5 kg/hr, T up to 900°C, continuous operation
  - Thermal pyrolysis (no catalysts)
  - Ex-situ pyrolysis (downstream catalyst)
  - In-situ pyrolysis (catalyst in combustor bed), suitable for continuous catalyst regeneration
  - In-situ and ex-situ combined….
- Pyrolysis oil recovery
  - Condensation train with 4°C gas cooler, ambient temperature ESP, -30°C cooler



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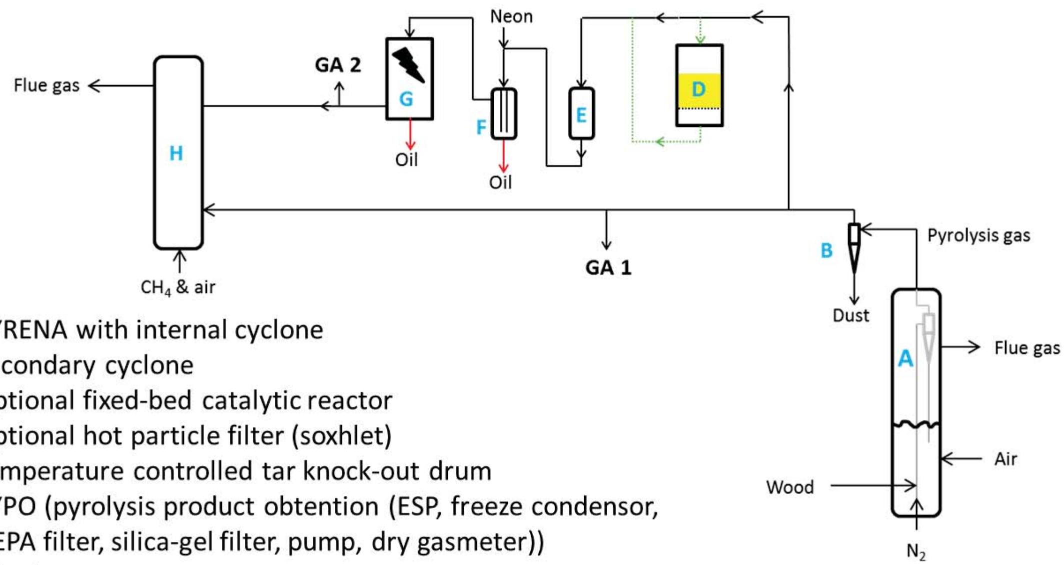
PYRENA process flow diagram



A. PYRENA with internal cyclone
B. Secondary cyclone
D. Optional fixed-bed catalytic reactor
E. Optional hot particle filter (soxhlet)
F. Temperature controlled tar knock-out drum
G. PYPO (pyrolysis product obtention (ESP, freeze condensor, HEPA filter, silica-gel filter, pump, dry gasmeter))
H. Afterburner

GA1, GA2: gas analysis points, including a presample system

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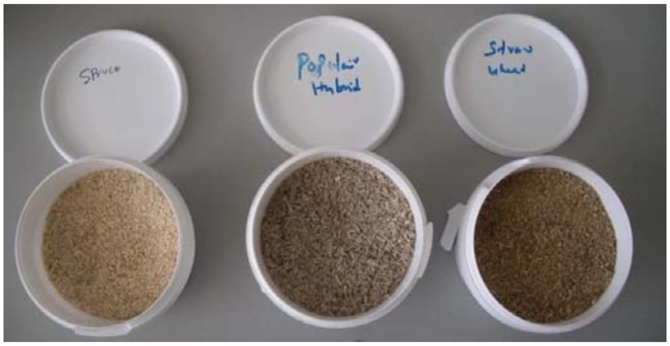
- Advantages
  - Compact integrated design
  - Autothermal operation via char combustion
  - Lower fluidisation gas flow rate (riser) when compared to CFB
  - Continuous catalyst regeneration, combination in-situ – ex-situ catalysis
  - Pyrolysis – combustion and pyrolysis – gasification possible
  - Production of larger bio-oil samples for further evaluation / application trials
  - Scale-up possibilities
- Challenges
  - Compact integrated design
  - Start-up; adjusting proper hydrodynamics

Fast pyrolysis experiments

- Materials
  - Softwood: Rettenmaier Lignocel grade 9: 0.9 – 1.1 mm sawdust from selected conifers
  - Hybrid poplar fines < 0.5 mm (from Idaho National Lab. US; for Round Robin test)
  - Wheat straw fines < 0.5 mm (from Idaho National Lab. US; for Round Robin test)



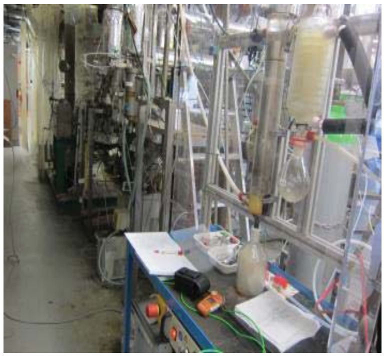
Ash content at 550°C:

Softwood : 0.5 wt%
Poplar : 3.3 wt%
Straw : 16 wt%

  - Bed material: silica sand 60 – 200 µm
  - In-situ catalysis: alkali metal-based, powder 80 -140 µm

Fast pyrolysis experiments

- Pyrolysis and sampling conditions
  - Feedstock intake 1 - 3 kg/hr, 500 - 520°C, 1 atm, N_2 fluidization gas
  - Catalyst : biomass ratio ~6, contact time ~seconds, hold-up in combustor ~1 hr
  - Overall hot vapour residence time 2-3 sec
  - Fractionated pyrolysis oil collection via 4°C gas cooler, ESP and -30°C freeze condenser
  - Non catalytic experiments: after collection samples are back-mixed (ultrathurrax)



IEA-T34 Fast pyrolysis Round Robin: non-catalytic results poplar and wheat straw

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- Poplar
  - **64% oil** (22% water, 42% organics); 1-phase oil
  - **98%** mass balance (64% oil, 12% gas, 22% char)

- Wheat straw
  - **44% oil** (24% water, 20% organics); 2-phase oil
  - **82%** mass balance (44% oil, 9% gas, 29% char)

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Round Robin analysis results

	Poplar	Wheat straw
Density [g/cm³]	1.149	1.026
Viscosity @ 20°C [cSt]	25.4	n/a
Viscosity @ 50°C [cSt]	5.9	n/a
Aging: Viscosity @ 20°C [cSt]		n/a
Aging: Viscosity @ 50°C [cSt]		n/a
Water content [%]	31.4	n/a
TAN [mg KOH/g]	83.3	n/a
Ash content in oil @ 775°C [%]		
Carbon C [%]	39.2	n/a
Hydrogen H [%]	8.3	n/a
Nitrogen N [%]	0.1	n/a
Py-Lignin [%]	11.75	10.61
Solids [%]		
Sodium Na [ppm]	2.2	10.6
Potassium K [ppm]	16.6	725.3
Magnesium Mg [ppm]	7.3	82.6
Calcium Ca [ppm]	28.5	445.3
Sulphur [ppm]	87.1	922.1
GPC [g/mol]	1555	2296
Dispersity	3.39	3.950

Measured by:
Thünen Institute of Wood Research, Germany (Dr. Dietrich Meier)
Incomplete analysis of wheat straw oil due to phase separation

Conclusion:
Results representative for proper fast pyrolysis!
PYRENA suitable for FP!

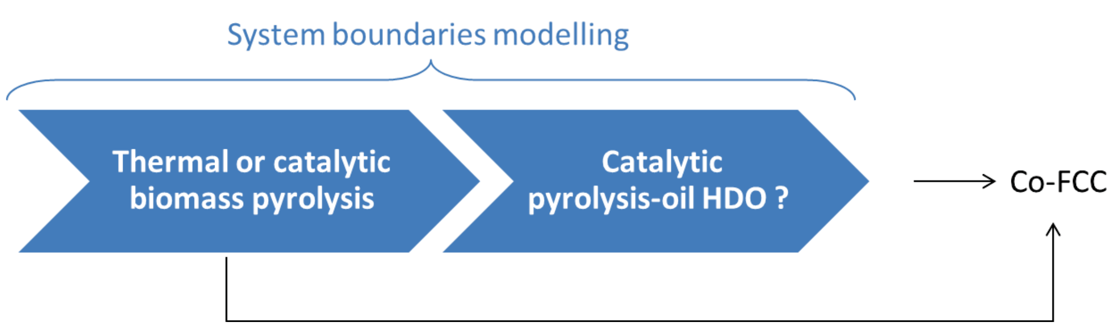
Preliminary catalytic results with softwood

- General observations
  - Succesful experiment with stable pyrolysis behaviour regarding temperatures, pressures and flows → stable hydrodynamics
  - Experiment duration 3 hrs at ~1.2 kg/hr feedstock intake
  - Acceptable mixing of sand with catalyst; acceptable loss of catalyst (<< 5% of the original per hour); mainly dust and fines
  - Very active catalyst converts most biomass to gases, water and coke
  - No decline in catalyst activity (continuous regeneration seems to work!)

- Product yields (feedstock a.r.)
  - 30 – 40% total liquid yield, ~7 – 8% organics
    - Fraction 1 (gas cooler) : 31%, 5% org (25%O)
    - Fraction 2 (ESP) : 2.3%, 2% org (13%O)
    - Fraction 3 (freeze cooler) : 1%, 0.3% org (30%O)
  - 20 – 30% non-condensable gases
  - 30 – 40% char/coke

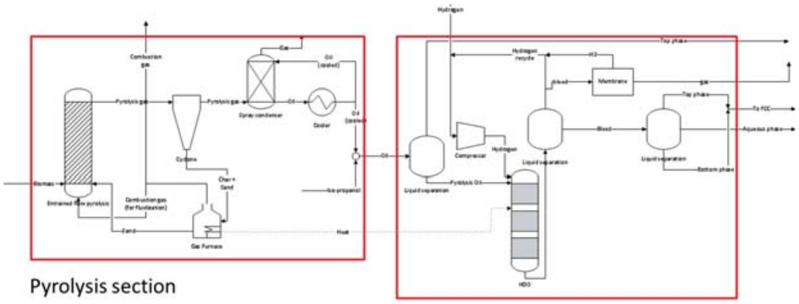
Techno-economic evaluation

- TEE to provide input for socio-economic assessment
  - Goal of the catalytic pyrolysis is to produce a bio-oil suitable as FCC co-feed
  - Modelling with input data from literature and from PYRENA experiments
  - Comparison of benchmark route (thermal pyrolysis – HDO) with catalytic route (catalytic pyrolysis – (HDO)) to check the effect of a dedicated fast pyrolysis catalyst on the subsequent (need for a) HDO treatment.



Approach TEE

- 300 kton/a (dry) biomass (softwood), 8000 hrs operation, CFB pyrolysis
- Comparison thermal pyrolysis → catalytic HDO vs catalytic pyrolysis (ZSM5)
- TP→HDO based on exp data, CP on literature data
- Construction of model (Excel) to calculate mass- and energy balances from both exp and literature data (Mercader, 2010, Paasikallio et al., 2014)
- Economics: estimation of CAPEX, OPEX and economic margin



Pyrolysis section

HDO section

PYROLYSIS OIL UPGRADING FOR
CO-PROCESSING IN STANDARD
REFINERY UNITS
PROEFSCHRIFT
ter verkrijging van
de graad van doctor aan de Universiteit Twente,
op gezag van de rector magnificus,
prof.dr.H. Brinksma,
volgens besluit van het College voor Promoties
in het openbaar te verdedigen
op vrijdag 12 november 2010 om 16.45 uur
door
Ferran de Miguel Mercader
geboren op 12 december 1981
te Balsareny, Spanje

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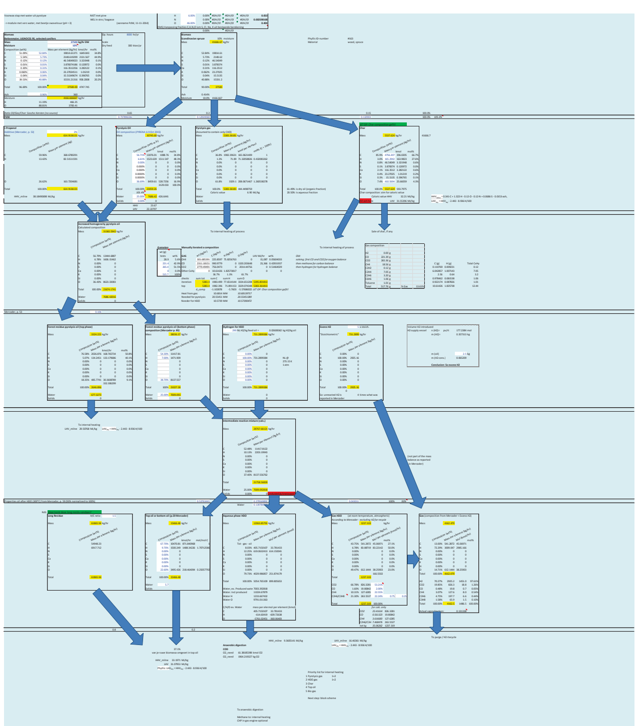
Product quality and catalyst deactivation in a four day catalytic fast pyrolysis production run†

Ville Paasikallio,*[a] Christian Lindfors,[a] Eeva Kuoppala,[a] Yrjö Solantausta,[a] Anja Oasmaa,[a] Jani Lehto[a] and Juha Lehtonen[b]

Modelling approach



- Feedstock input data
- Thermal pyrolysis
- Pyrolysis oil stabilising
- Pyrolysis oil fractionation and hydrodeoxygenation
- Intermediate HDO-oil
- HDO-oil fractionation
- Co – FCC feed

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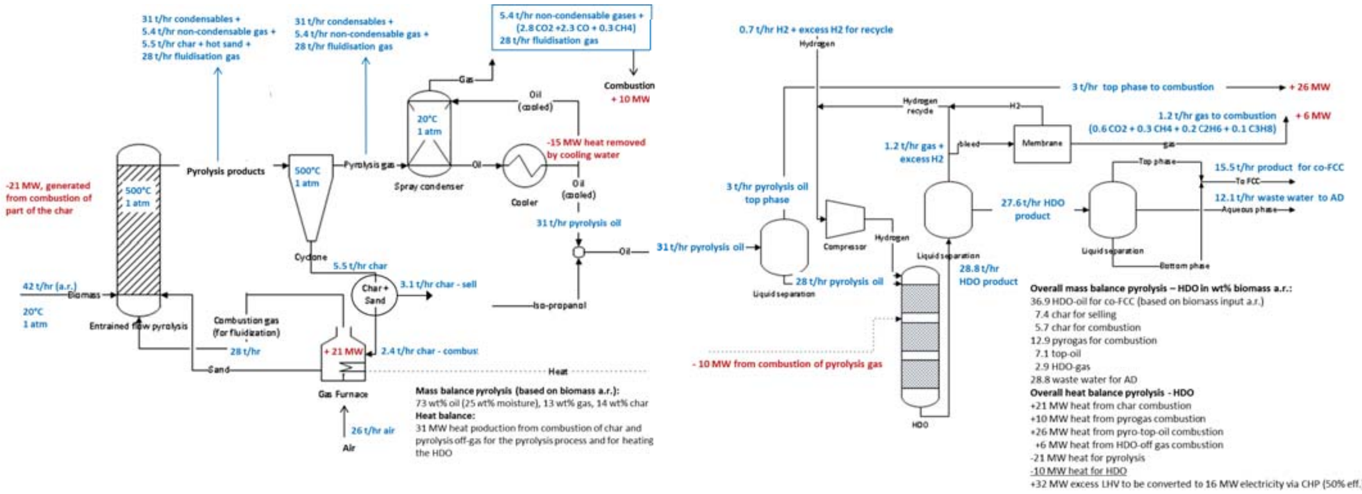
Mass- and energy balance



M & E balance for thermal pyrolysis → hydrodeoxygenation

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Preliminary TEE results

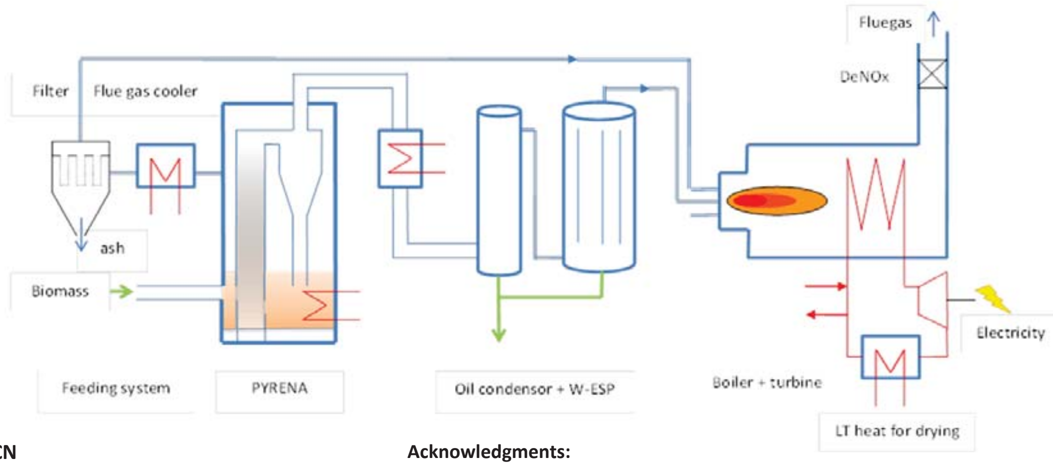
Parameter	Thermal pyrolysis → hydrodeoxygenation	Catalytic pyrolysis (ZSM5 catalyst)
Mass & energy balance		
Organic oil product yield (a.r.) for co-FCC	36.0 wt%	16.5 wt%
O content in the oil	22.6 wt%	21.5 wt%
Lower heating value	31 MJ/kg	29 MJ/kg
Gas yield (a.r.)	15.4 wt%	18.7 wt%
Char yield (a.r.)	12.8 wt%	24.0 wt%
Excess energy yield (e.g. for electricity and/or steam)	32 MW	51 MW
Economics		
Economic margin @ 100 $/t for wood and 44 $/b for crude oil	- 6 M€/a	- 3 M€/a
Approximate CAPEX	100 M€	70 M€
Wastes		
Waste water yield (a.r.)	28 wt%	41 wt%

Conclusions / outlook

- PYRENA suitable for (catalytic) fast pyrolysis
  - First promising results in IEA Round Robin collaboration
  - Recently: successful functional thermal pyrolysis and in-situ catalytic pyrolysis tests with softwood after several adaptations
- Approach to produce "better" bio-oil
  - Combine in-situ with ex-situ catalysis
  - Recover bio-oil in fractions → ensure direct phase separation to remove water
  - Use lower (< 500°C) pyrolysis temperature in combination with somewhat longer solid and vapour residence times to improve final product stability
  - Use reactive riser gas (e.g. steam, H_2, CO, CO_2,..)
- Techno-economics
  - Presently, both TP→HDO and CP do not seem to be economically feasible at the current market prices for wood and crude oil, → chemicals as money maker?

Thank you for your attention!

Questions and more information: dewild@ecn.nl



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Westerduinweg 3
1755 LE Petten
The Netherlands

P.O. Box 1
1755 ZG Petten
The Netherlands

T +31 224 56 49 49
F +31 224 56 44 80

info@ecn.nl
www.ecn.nl

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ECN

Westerduinweg 3
1755 LE Petten
The Netherlands

P.O. Box 1
1755 LG Petten
The Netherlands

T +31 88 515 4949
F +31 88 515 8338
info@ ecn.nl
www.ecn.nl