PYRENA: PYRolysis Equipment for New Approaches to produce better bio-oil

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PYRENA
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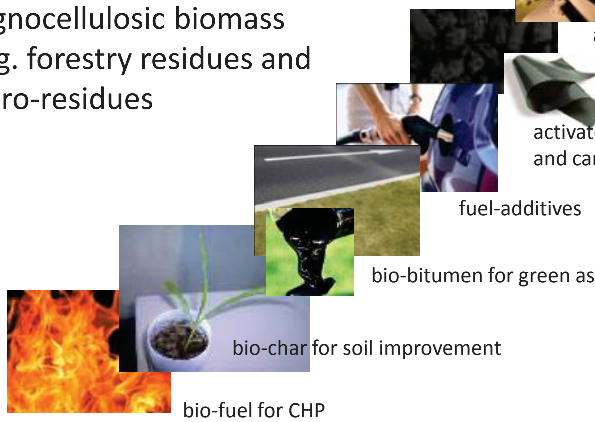
Catalytic fast pyrolysis

- 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

low volume - high value market 10000 €/t

Lignocellulosic biomass e.g. forestry residues and agro-residues



specialty chemicals for food, fragrance and pharmaceuticals

bio-plastics

bio-resins for wood-adhesives

additives for flooring material

activated carbon, carbon-fibres and carbon-black

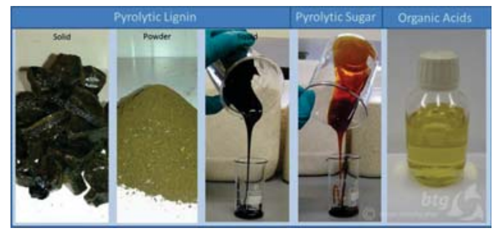
fuel-additives

bio-bitumen for green asphalt

bio-char for soil improvement

bio-fuel for CHP

high volume - low value market 100 €/t



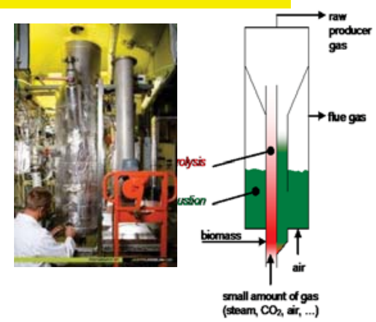
Primary pyrolysis products

Pyrolysis facilities at ECN

- Bubbling fluidised bed (BFB)
  - Multifunctional unit for pyrolysis, gasification, combustion, 1 kg/hr, T up to 1100°C, continuous operation
    → intermediate – fast pyrolysis
- Entrained flow (EF) – BFB (CFB)
  - Multifunctional unit, 5 kg/hr, T up to 900°C, continuous
    → fast pyrolysis?

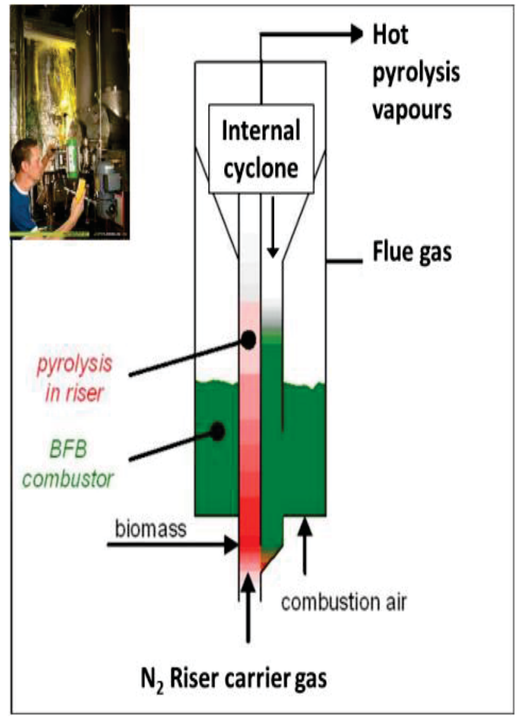
NEW!

- Auger moving bed (Pyromaat)
  - Multifunctional unit, 3 kg/hr, T up to 600°C, continuous
    → slow – intermediate pyrolysis
- Analytical pyrolysis - GCMS
  - High throughput screening, 350 – 1000°C, mg scale, batch operation



PYRENA fast pyrolysis

- Based on MILENA™ indirect gasifier technology
- Integrated reactor system:
  – EF pyrolysis (riser) – BFB combustor (annulus)
  – 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 freeze condenser



PYRENA pros and cons

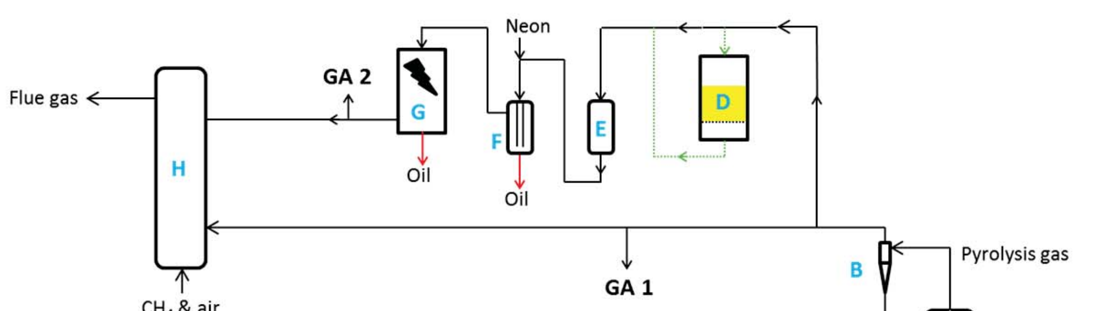
- Advantages
  – Compact integrated design
  – Autothermal operation
  – Lower fluidisation gas flow rate (riser) when compared to CFB
  – Continuous catalyst regeneration, combination in-situ – ex-situ catalysis
  – Pyrolysis – combustion and pyrolysis – gasification possible
  – Production of larger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

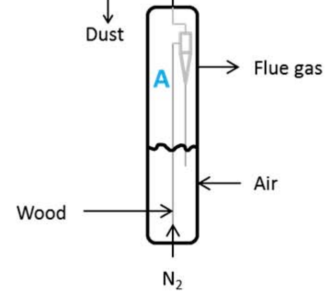
![ECN]

Current fast pyrolysis activities at ECN

- **Optimization of PYRENA**
  - Participation in international Round Robin on fast pyrolysis (poster 39; Doug Elliott)
  - Improving reactor hydrodynamics and decreasing hot vapour residence time
  - Techno-economic evaluations
- **Application of catalysts, in-situ and/or ex-situ**
  - Using commercial and alternative (natural mineral – based) catalysts to improve / alter the composition of the resulting pyrolysis oil
- **DSP of fast pyrolysis products**
  - Staged condensation, e.g. to separate water / organics
  - Off-line removal of water / low-boilers by Rotavapping

PYRENA lay-out scheme





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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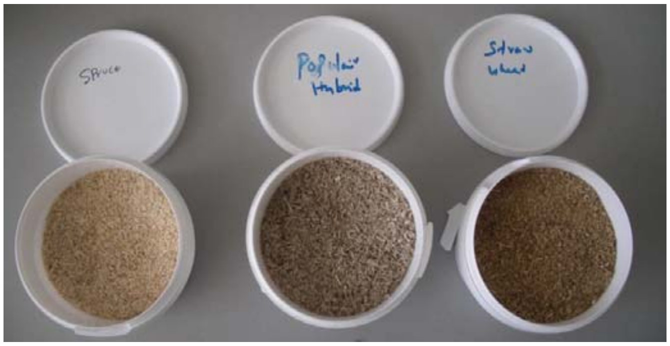
Fast pyrolysis experiments

- 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 0.06 – 2 mm;
  - In-situ catalysis: Austrian olivine, sieved < 0.15 mm for in-situ catalysis
  - Ex-situ catalysis: commercial zeolites

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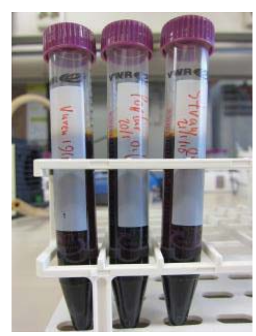
Fast pyrolysis experiments

- Pyrolysis and sampling conditions
  - Feedstock intake 3 kg/hr
  - 530°C, 1 atm, N_2 fluidization gas
  - Overall hot vapour residence time 2-3 sec
  - Pyrolysis oil collection via
    4°C condenser, ESP and -30°C freeze condenser
  - After collection samples are back-mixed (ultrathurrax)



First results softwood

- Non-catalytic pyrolysis
  - **78% oil** (34% water, 44% organics); 2-phase oil
  - 105% mass balance (78% oil, 14% gas, 14% char)
- Catalytic pyrolysis with downstream fixed bed 1:10 zeolite:alumina at 440°C
  - **70% oil** (33% water, 37% organics); also 2-phase oil
  - 99% mass balance (70% oil, 15% gas, 14% char)
  - Severely coked catalyst
- Catalytic pyrolysis with sand-diluted olivine as in-bed catalyst
  - **81% oil** 2-phase oil
  - 114% mass balance (81% oil, 14% gas, 19% char)

Results poplar and wheat straw

- IEA-T34 Round Robin on fast pyrolysis of biomass
- 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!

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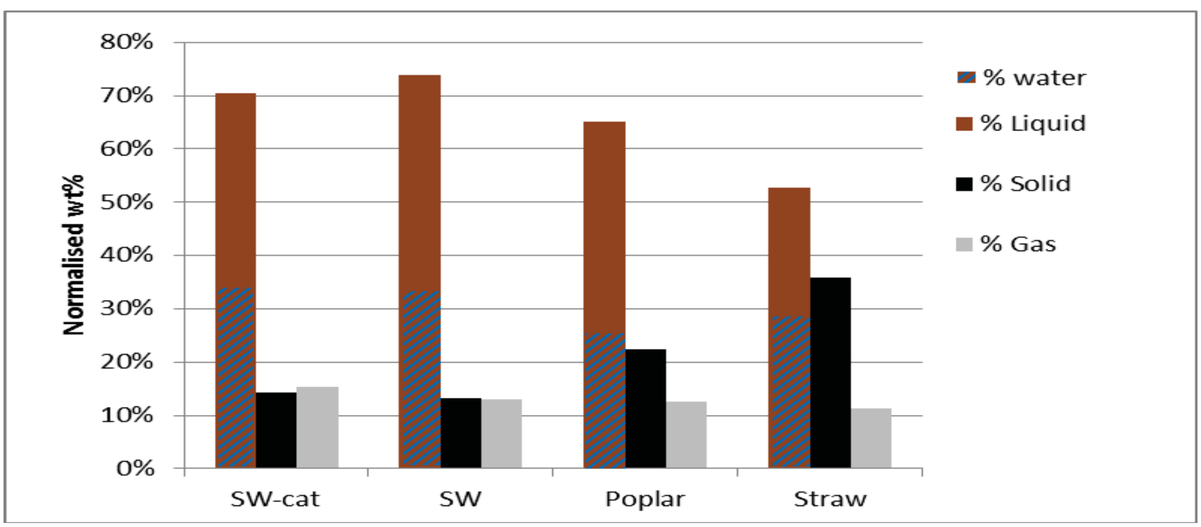
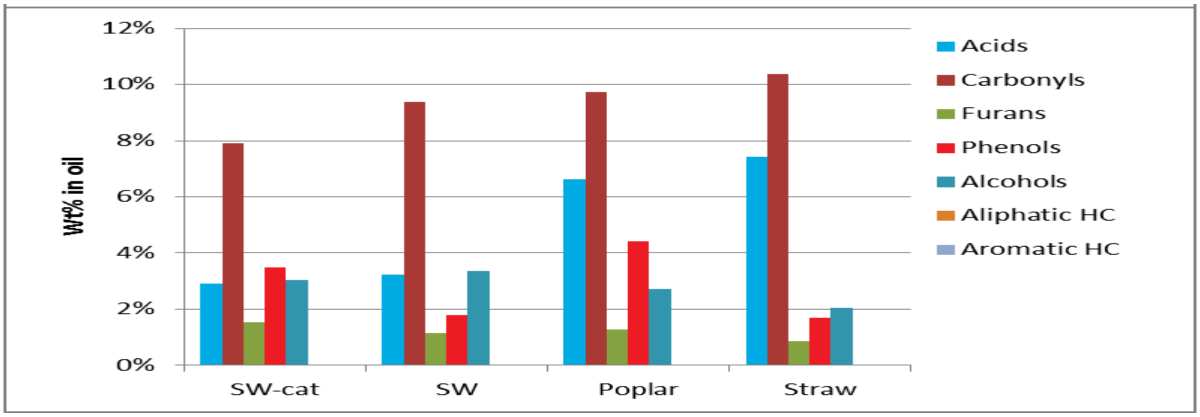
Major products for softwood, poplar, straw



– 35 – 45% of water in oils;
(too long hot vapour residence time and/or too short solids residence time)
– Less than 15 wt% gas
– Most solids (char+ash) for straw, due to its high ash content

Composition pyrolysis oils via GC-MS



- Largest differences for acids (acetic and formic) and phenols
- Highest concentration of phenols in poplar oil,
  due to its thermally less stable lignin when compared to softwood?
- Highest concentration of acid and lowest conc of phenols in straw oil,
  due to cracking activity of innate inorganic matter
- Phenols concentrationin catalytic SW oil higher than in non-catalytic SW oil.
  Hypothesis: some cracking of lignin (oligomers) by the partial deactivated zeolite catalyst

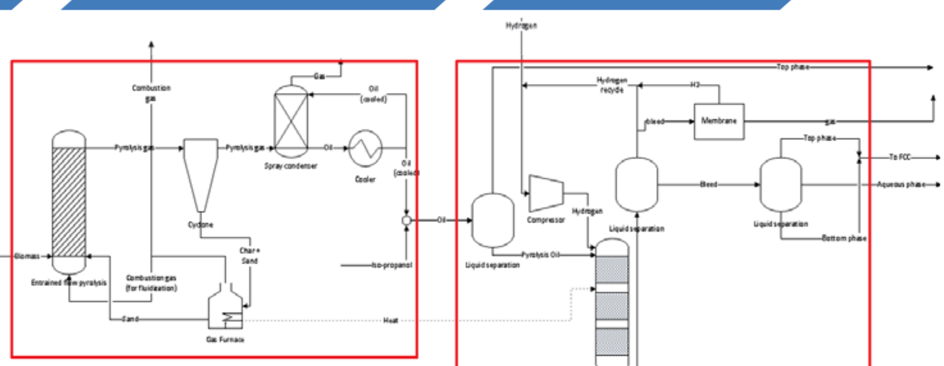
Preliminary techno-economic assessment

Biomass pretreatment
- washing
- drying

Biomass pyrolysis
- pyrolysis
- pyrolysis oil recovery

Pyrolysis oil DSP
- HDO
- co-FCC

Feedstock streams	kton/yr
Scandinavian Pine (10% moisture)	333.3
i-Propanol	4.3
Hydrogen for HDO	5.2
Total	342.8
Product streams	
Char	50.0
Pyrolysis gas	66.7
Forest residue pyrolysis oil (top phase)	23.4
Aqueous phase HDO	85.0
Gas HDO	8.7
Top oil + bottom oil	109.0
Total	342.8



Pyrolysis section

HDO section

Preliminary CAPEX estd: ~70 M€ TBD

CAPEX acc to Bridgwater correlation: 68 M€ (2008); Bridgwater, 2009 :

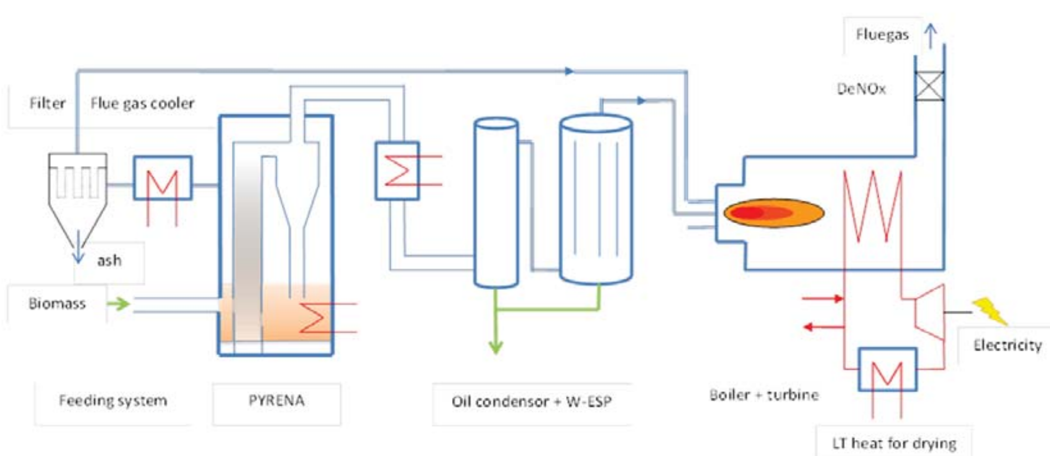
Capital cost fast pyrolysis plant, euros million 2008=6.03 * (biomass feed rate dry t/h)$^{0.67}$

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; bio-oil is currently analysed
- 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
  - Identify best combination feedstock - catalyst – products

Thank you for your attention!

Questions and more information: dewild@ecn.nl



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Questions?

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