Contaminants in fast pyrolysis

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Workshop – webinar

Valorization of organic waste

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

Fast Pyrolysis – development timeline BTG







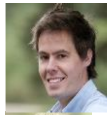

Roll-out / *development* / *research*

2019	Empyro sold to Twence; roll out thrugh GreenFuelNordic and Pyrocell
2015	Start-up Empyro plant & Boiler at FrieslandCampina
2014	Start construction 120 t/d Empyro plant
2013	Long-term FPBO supply contract signed
2009	Establishment of Empyro BV to demonstrate technology
2007	Establishment of BTG Bioliquids BV to commercialize BTG Fast Pyrolysis technology
2005	Delivery of 50 t/d FP-plant to Malaysia
2004	Large-scale co-firing test at Harculo Power Plant
1998	Start-up of 200 kg/hr FP pilot plant in BTG Laboratory
1994	Delivery semi-continous test unit (50 kg/hr) to Shenyang (China)
1993	Knowledge transferred from UT to BTG
1989, 1987	Rotating cone reactor 'invented' at University of Twente (UT)

BTL

UT









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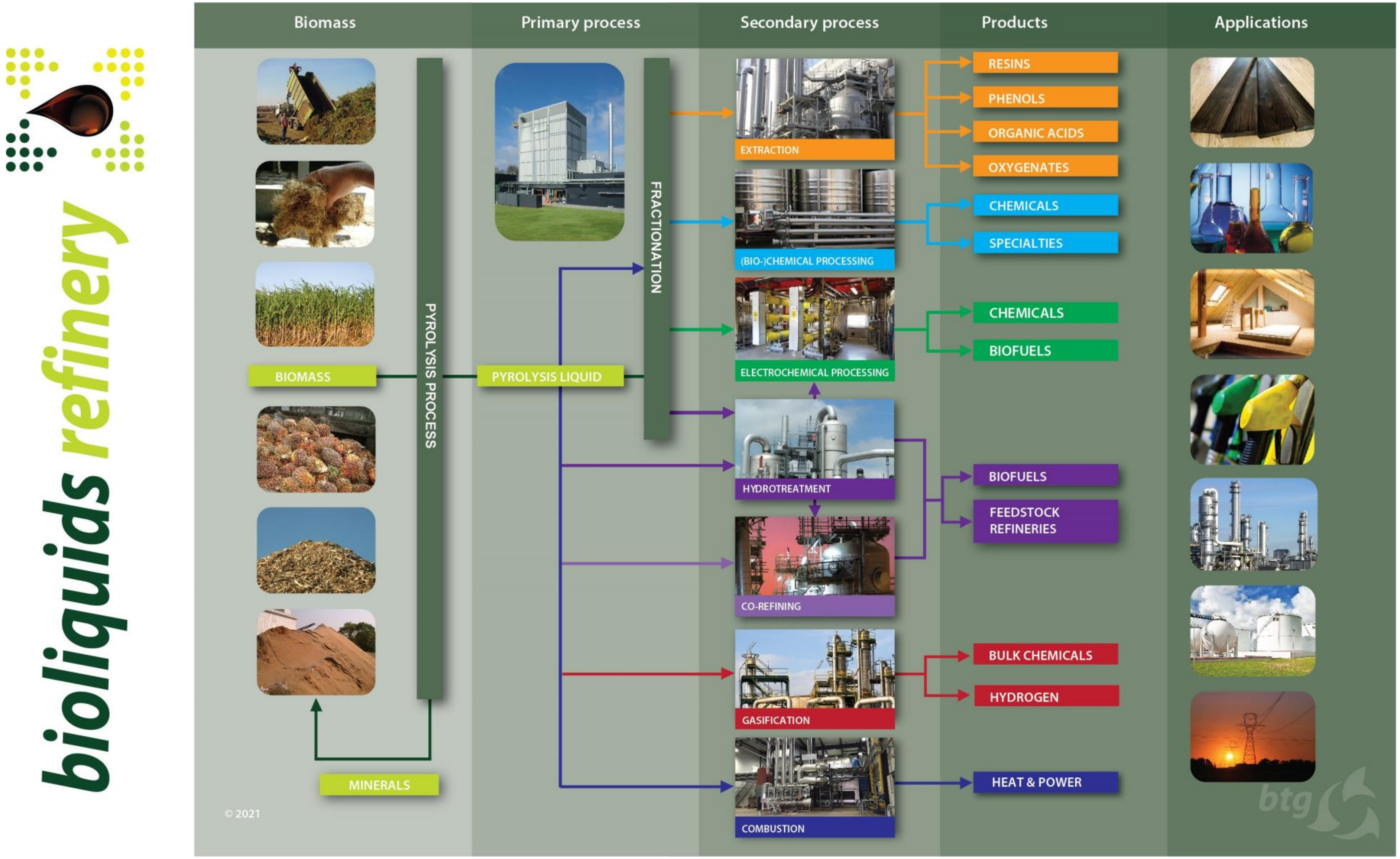
The Bioliquid Refinery



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Contaminants in fast pyrolysis

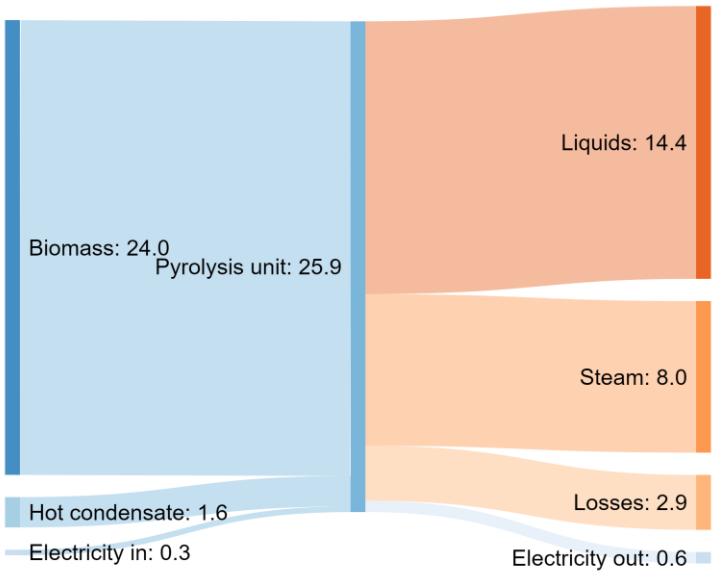
- Developments in fast pyrolysis are largely trial-and-error:
  - Clean wood is relatively well understood

    65 -70 wt.% yield, 15-20 wt.% gas ; 15-20 wt.% char

    High overall energy efficiency, >85% of biomass ends up in useable products (liquids; heat)

    https://www.cocosimulator.org/

    Pyrolysis does not yield an oil ≠ crude oil



- Focus on industrial feedstocks
  - High alkali ash content;
  - higher contaminants (S; N) contents;
  - other oxygenates (type of lignin; type of defragmented carbohydrates; effects of nitogen containing compounds)

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Effects Contaminants in fast pyrolysis

- Primary pyrolysis process

  Challenges to overcome in diversifying feedstocks

  - Gain know how in effects of contaminants in fast pyrolysis processes
  - Role and fate of alkali (char; combustion; piping, ….)

- Liquid conversion processes
  - Challenges /opportunities of these compounds in routes to chemicals and fuels
    - Role of such alien materials in further catalytic processing: cracking / repolymerization, hydrotreatment

- Analysis
    - standardization
    - specifications

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Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Measuring inorganics in biomass fast pyrolysis oils

Charles-Philippe Lienemann, Alain Quignard *, Nathalie Texier, Nadège Charon

IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP3, 69360, Solaize, France

Table 5
Contents of major inorganics in a bio-oil (sample A) determined according to several analytical methods (mean values are reported except for significantly different results).

Element	Contents measured from the bio-oil analysis [mg/kg]		Contents calculated from the ashes analysis [mg/kg]	
	ISO 16967 protocol	Wondimu protocol	ICP-OES	WXRF
Fe	952.0 ± 95.2	812.0 ± 81.2	734.0	682.0
Si	271.0 ± 27.1	45.3 ± 4.5	292.0	291.0
K	159.0 ± 15.9	176.0 ± 17.6	136.0	134.0
Ca	59.0 ; 235.0	238.0 ; 94.3	97.3	109.0
P	10.3 ; 132.2	160.0 ± 16.0	2.9 ; 2.3	5.0
S	not measured	117.0 ± 11.7	46.3 ; 40.2	35.0
Al	22.3 ; 19.8	37.6 ; 78.6	15.2	12.0
Na	13.5 ; 17.6	13.8 ± 1.4	10.2	7.0
Mg	16.0 ± 0.2	<25.0	14.0	12.0
Pt	not measured	<12.5	1.6	15.0

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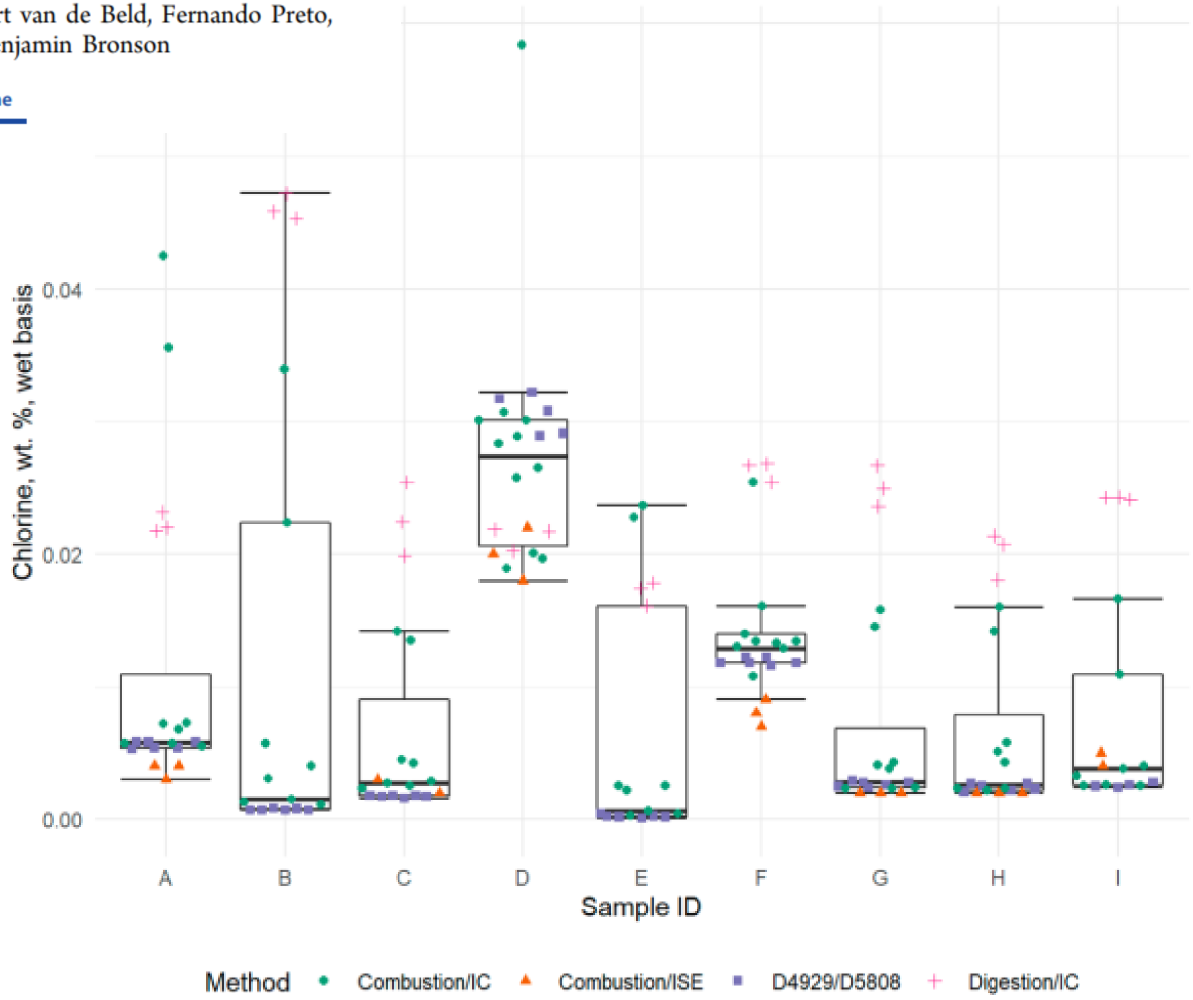
energy&fuels
pubs.acs.org/EF
Article

Results of the International Energy Agency Bioenergy Round Robin on the Analysis of Heteroatoms in Biomass Liquefaction Oils

Philip Bulsink,* Ferran de Miguel Mercader, Linda Sandström, Bert van de Beld, Fernando Preto, Alan Zacher, Anja Oasmaa, Nicolaus Dahmen, Axel Funke, and Benjamin Bronson

Cite This: *Energy Fuels* 2020, 34, 11123−11133
Read Online



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WASTE2ROAD

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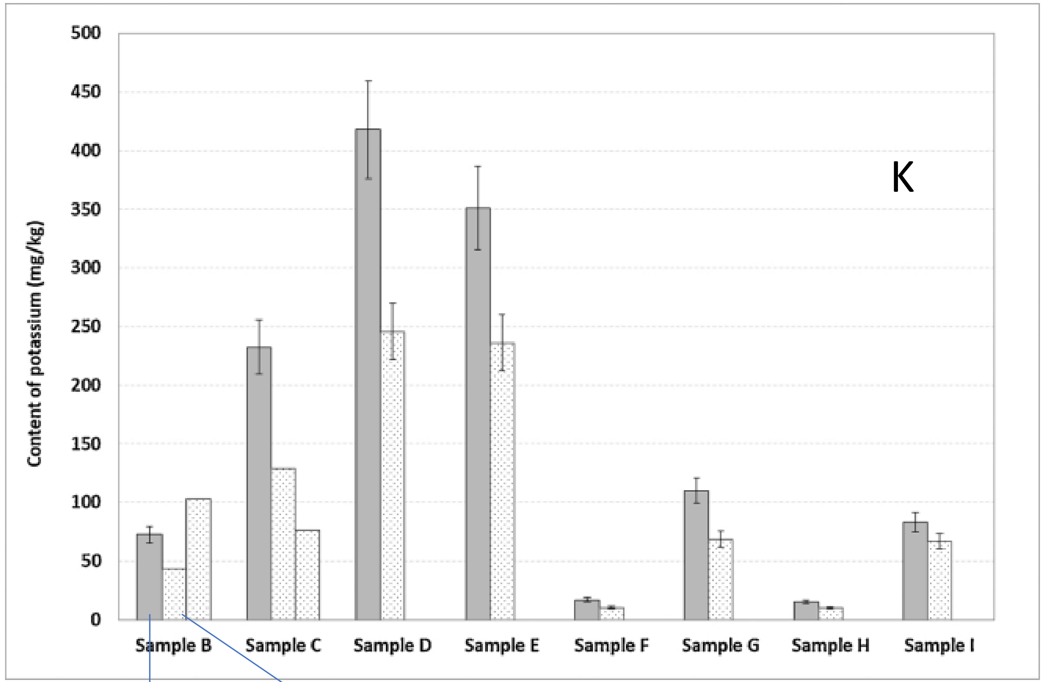
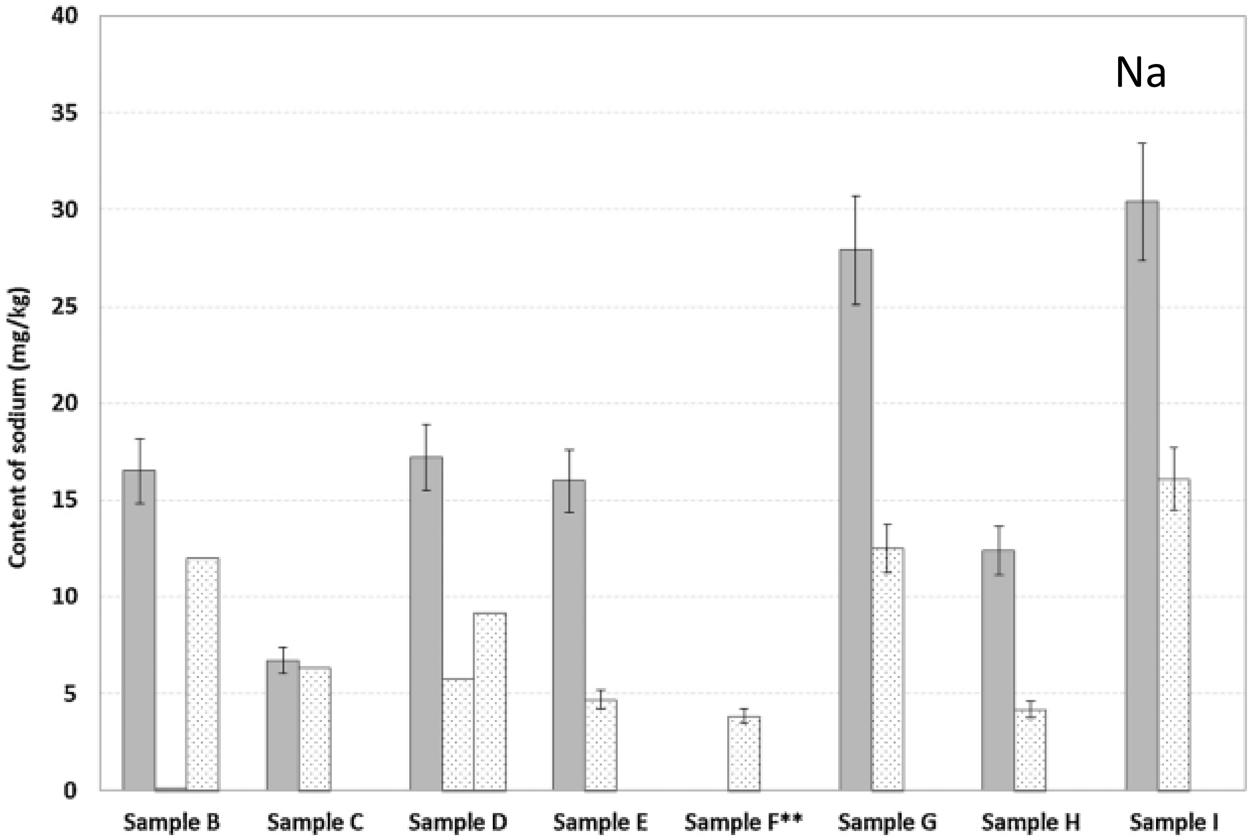


ISO 16967 ICP-OES analysis



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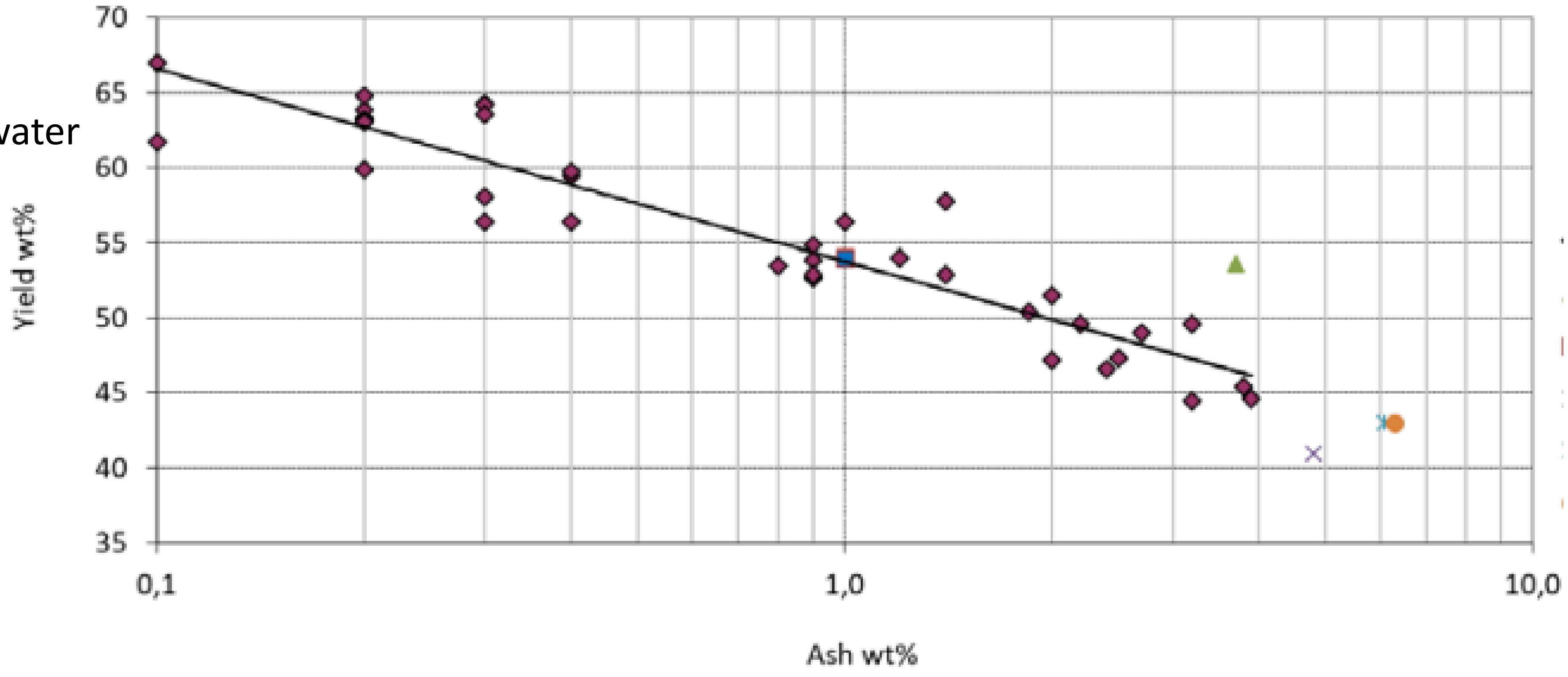
Primary pyrolysis process

WASTE2ROAD

Organics + water



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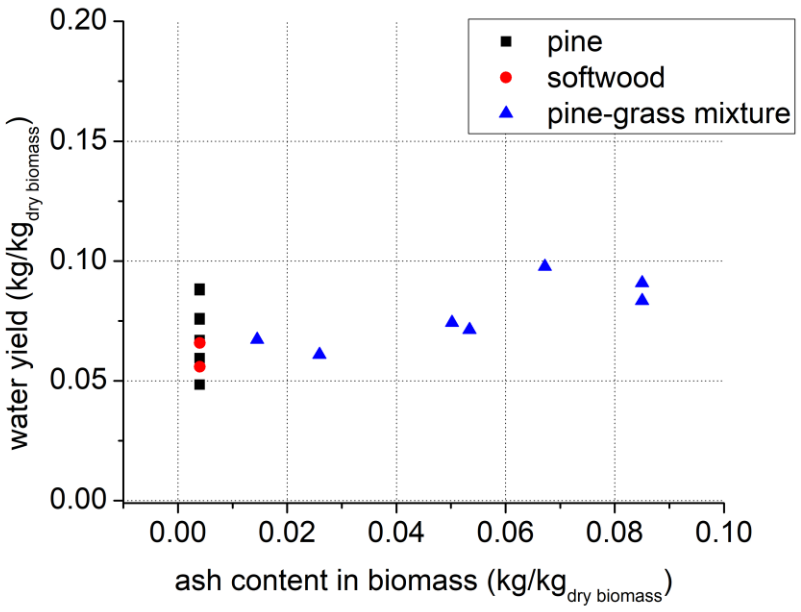
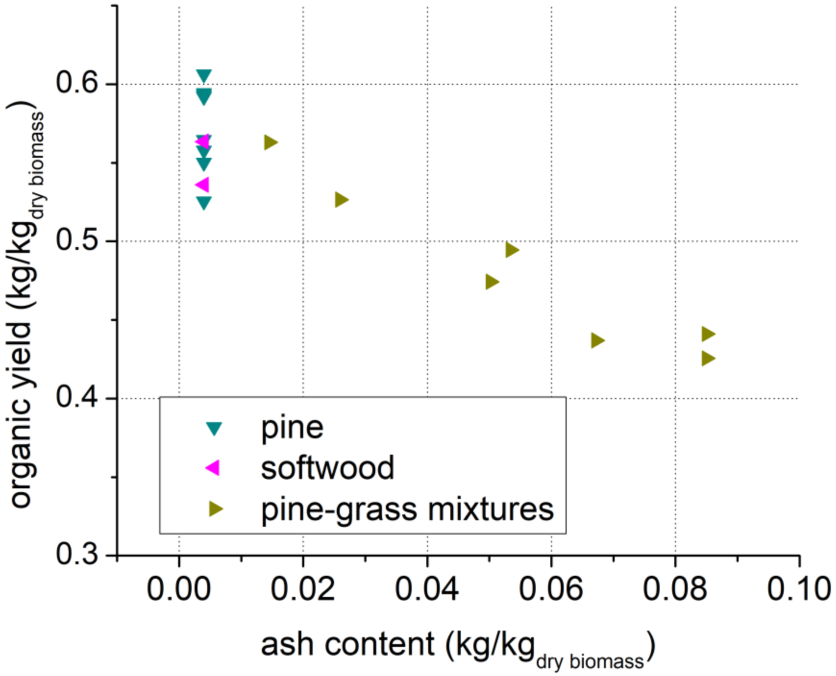
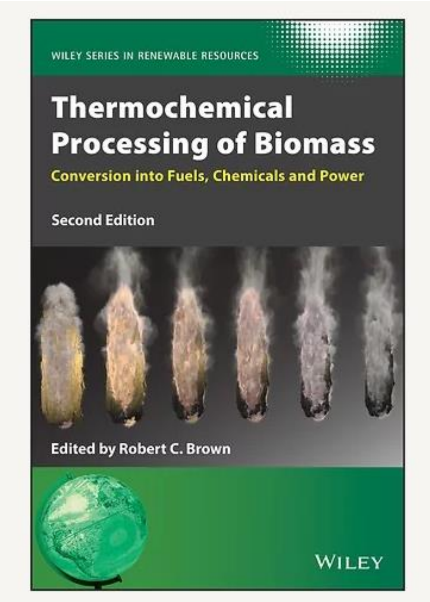
Primary pyrolysis process







Water (left) and organic yield (right), both in $kg/kg_{drybiomass}$, versus the ash content in the biomass.

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Less ash:

Carbohydrate:

Less dehydration- and cracking reactions: higher monomeric carbohydrates

Overall ‘oil’ yield higher and some ‘quality’ aspects better (less water)

Lignin:

Less lignin cracking likely

- As a general observation washing alkalis from biomass leads to operational problem due to fouling of bed material, clogging of the sand due to ‘lignitic melts’

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1. Washing prior to pyrolysis
2. Hot vapor filtration

VTT

3. Ex-situ decontamination
   - Filtration
   - Desulphurisation
   - Ion-exchange

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Ex-situ decontamination (W2R)

- Desulfurization
  - Absorbentia (various types used)

Feeds: bio-liquids from fast pyrolysis, clean / dirty
Long runs, several hundred hr
Elevated temperatures and pressures with H_2

- De-metallization
  - Amberlyst or any other anion and cation exchange.

Feeds: bio-liquids from fast pyrolysis, clean / dirty
Long runs, several tenths hr
Ambient pressures and slightly elevated temperatures (to reduce viscosity)

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Key messages

- Contaminants crucial importance in commercializing fast pyrolysis
- Identify key elements:
  - Organic (sulphur; nitrogen, phosphor)
  - Inorganic (alkali; iron, heavy metals …)
  - OXYGENATES (type of lignins, types of defragmented carbohydrates, acids, …?)
- Understanding role of contaminants better, in pyrolysis and in subsequent processing
  - Pyrolysis process: we need them
  - Subsequent (catalytic) processing processes: we may allow some, but too some extent
    Gasification; hydrogenation; catalytic cracking; …
- Analysis – we need standardized analysis techniques
- Specifications (alkali, Cl, S each < 10 ppm)

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Thanks for your attention

Any questions?

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