WASTE2ROAD

Fast pyrolysis of waste materials

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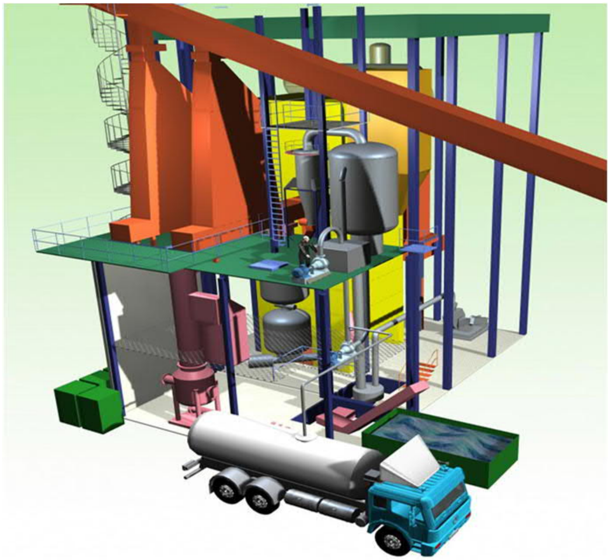
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

Outline

- Fast pyrolysis
  - How, why
  - Fast pyrolysis technologies
- Fast pyrolysis of waste materials
- Metal reduction in bio-oil
  - Metal removal before fast pyrolysis by feedstock washing
  - Metal removal in the pyrolysis process by hot vapour filtration



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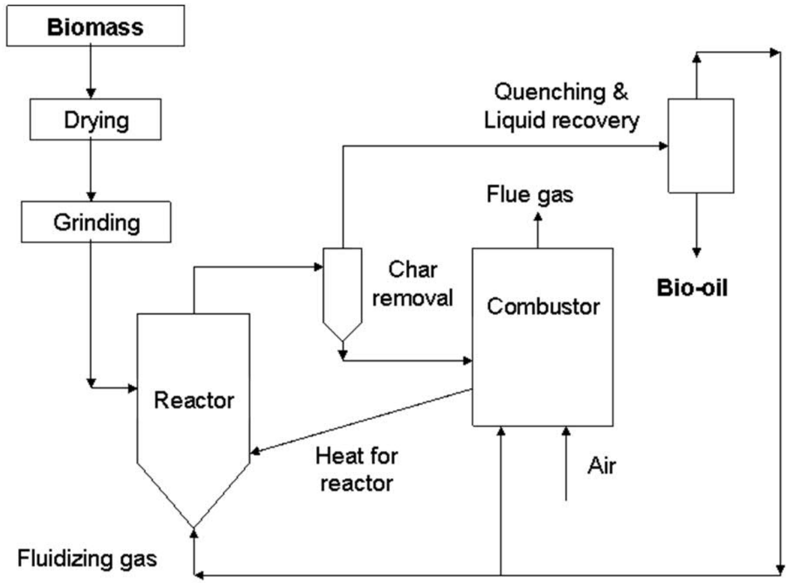
Fast Pyrolysis

Fast pyrolysis technology:

- Thermal decomposition process at around 500 °C
- High heating rate in inert atmosphere
- Residence time about 1-2 s

Typical product distribution for bark-free wood:

- 64 wt % organics
- 12 wt % pyrolysis water
- 12 wt % char
- 12 wt % product gas



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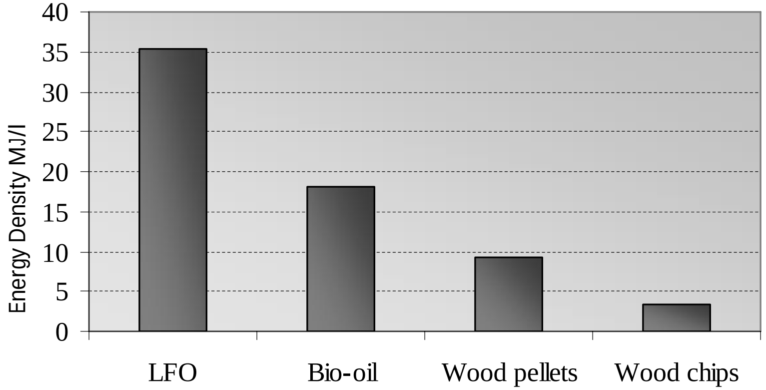
Why Fast Pyrolysis

- Production
  - Feasible at relatively small scale
- Transport, storage
  - Fluid product for easy logistics
  - Energy density
- Utilisation
  - Replace heavy fuel oil in burners
  - Potential for upgrading to higher value products



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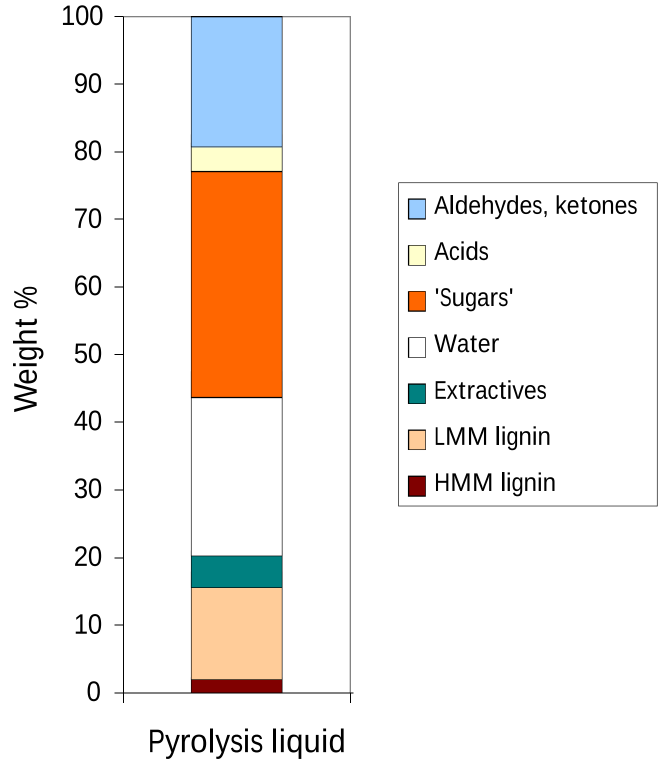
Bio-oil Properties

- Contains 45-50 wt- % oxygen
- Contains 20-30 wt- % water
- Low heating value (14,5-17 MJ/kg)
- Low pH (2-3)
- Unstable during storage and especially when heated
- Contains solids, typically < 0.5 wt-%



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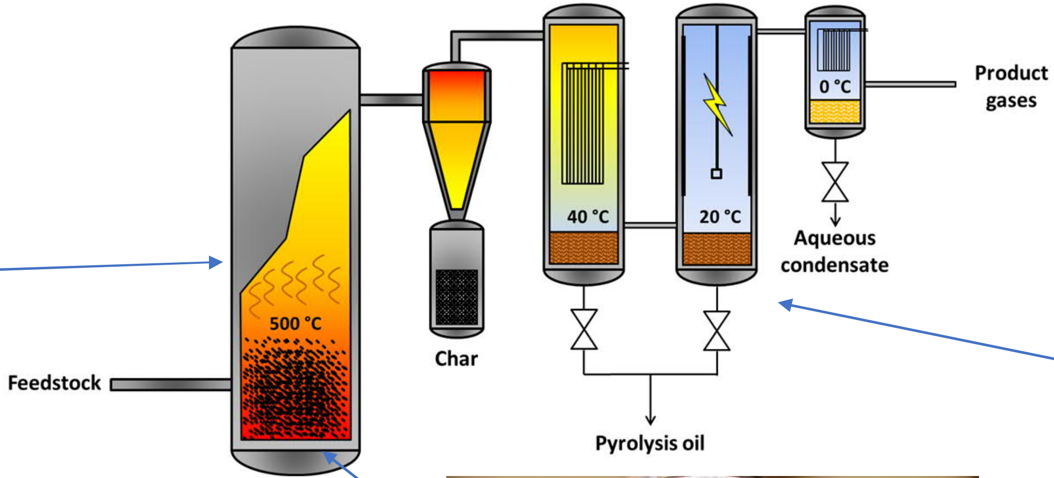
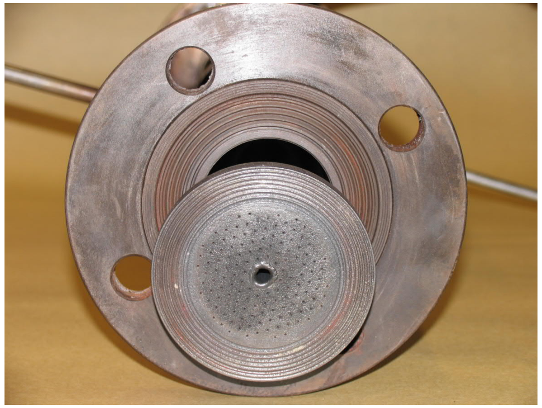
Bubbling fluidized bed (BFB)





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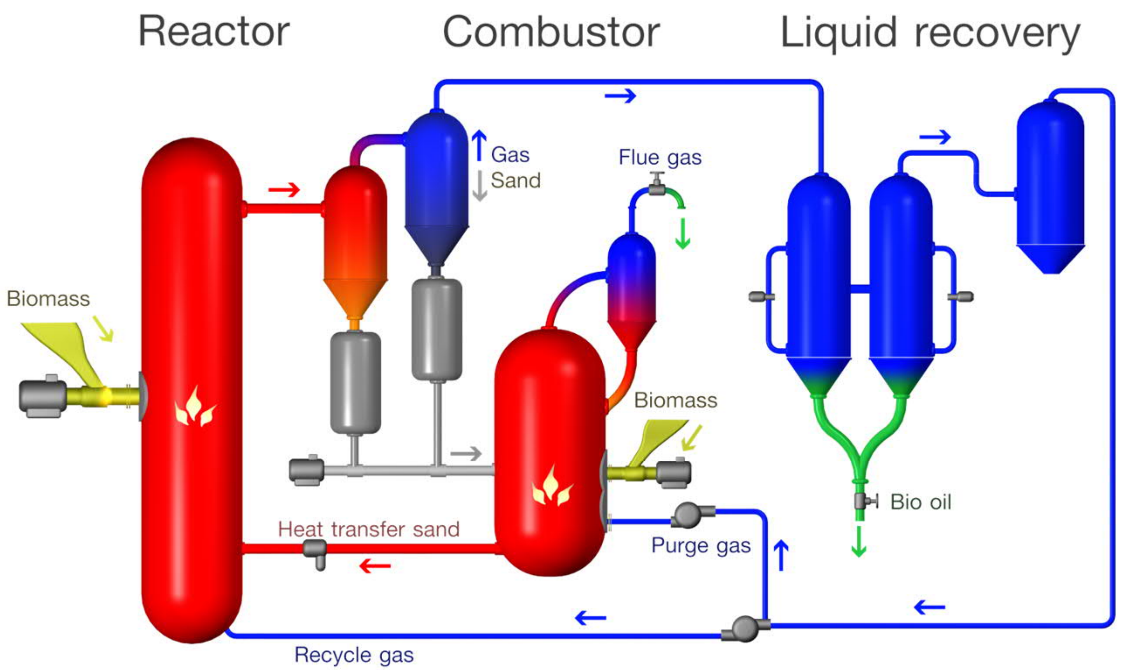
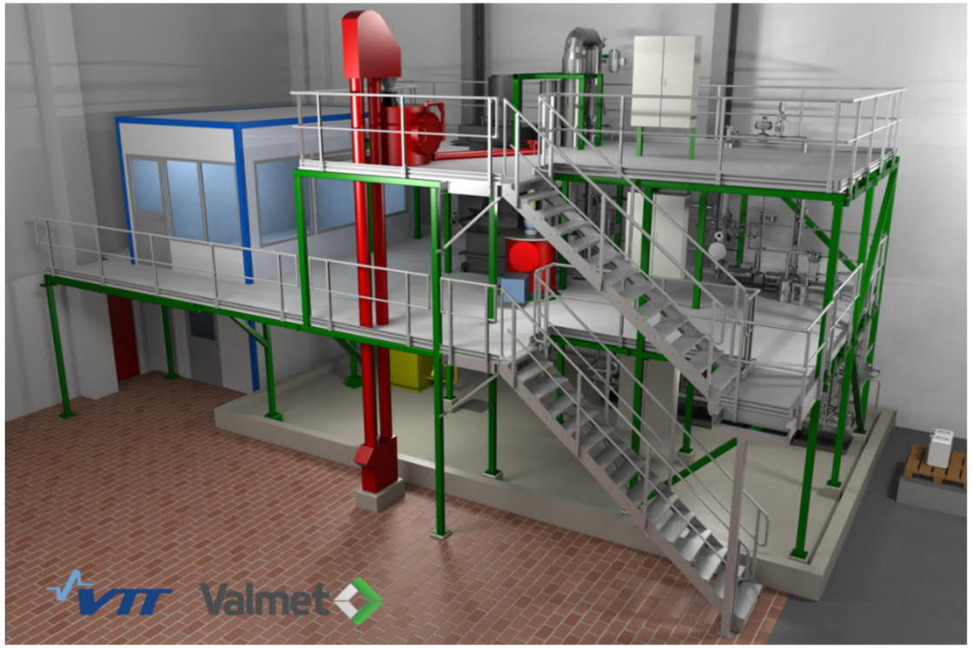
Circulating fluidized bed (CFB)





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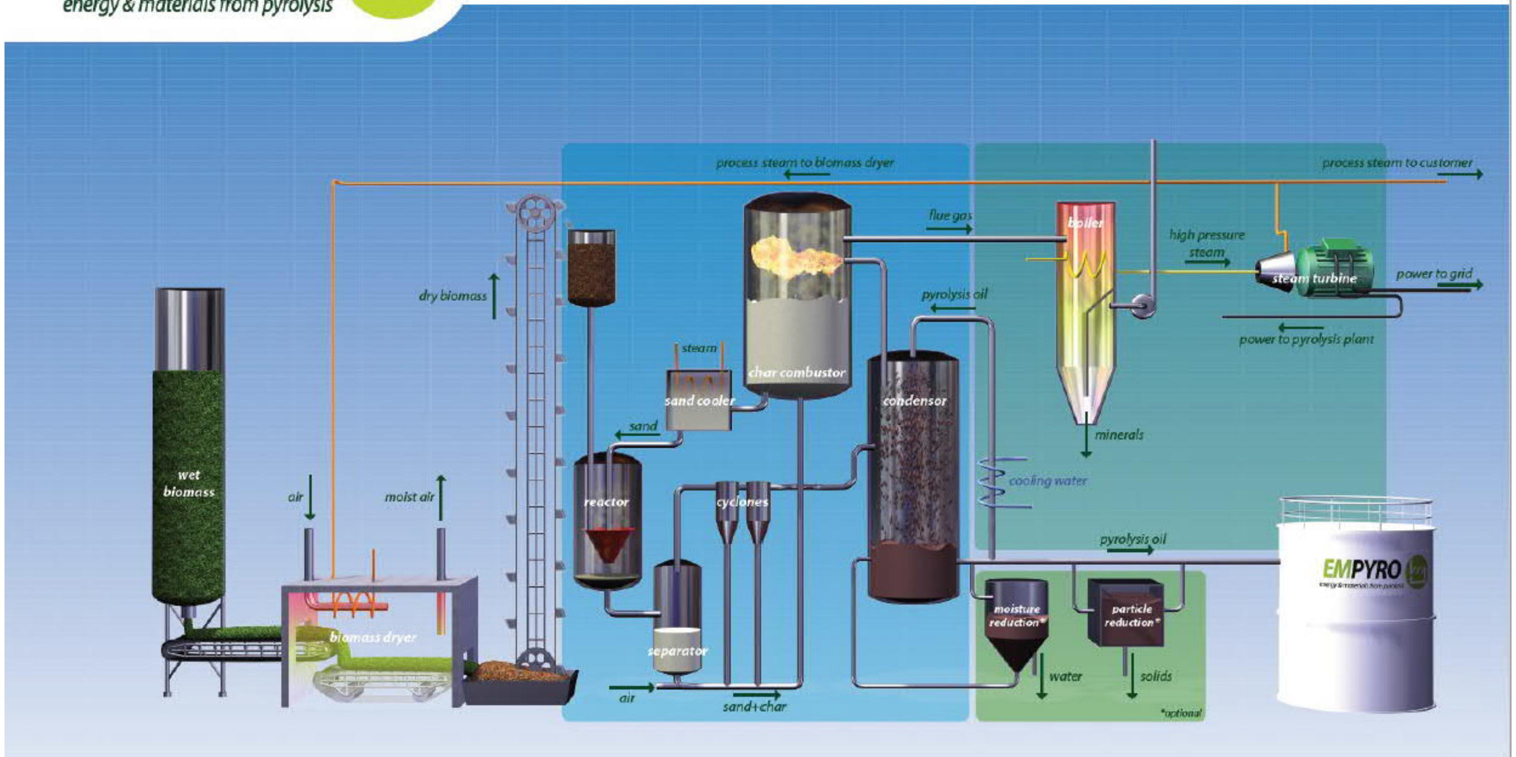
The fast pyrolysis process

EMPYRO
energy & materials from pyrolysis



TechnipFMC
btg-btl

Pyrolysis oil, the sustainable alternative

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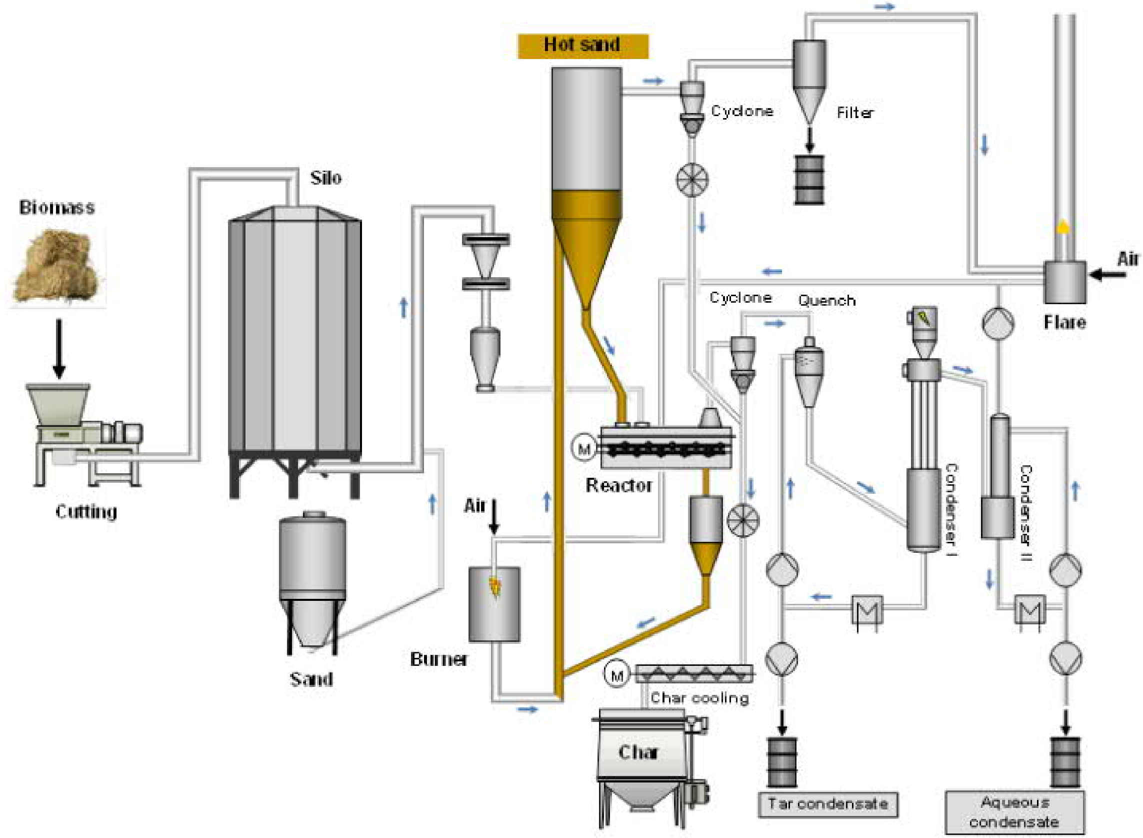
Karlsruhe institute of technology Bioliq process

- Synthetic fuel by pyrolysis and gasification
- In the concept bio-oil and char is produced in decentralized plants, which is transported to a centralized gasification plant
- Feed capacity of the unit 500 kg/h



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Status of pyrolysis plants

Company	Technology	Location	Feedstock	Processing capacity, kg/h	Production capacity	Start-up	Status
Red Arrow (5 plants), nowadays Kerry group	RTP (Ensyn)	Wisconsin (USA)	Wood residues	1750		1995, 2002, 2014	Operational
BTG - BTL and Genting Sanyen Bhd	RCR (BTG)	Malaysia	Palm oil industry residue	2000	1200 kg/h	2005	Shut down
Dynamotive Energy System	BFB	West Lorne (Ontario Canada)	Wood residues	4150		2005	Shut down
Kerry group (Ensyn)	RTP (Ensyn)	Renfrew (Ontario Canada)	Wood residues	3500	12 ML/year	2006	Operational
Dynamotive Energy System	BFB	Guelph (Ontario Canada)	Wood residues	8300		2008	Shut down
KIT (Bioliq)	Twin-screw mixing reactor	Karlsruhe (Germany)	Agriculture residues	500	2 ML/year	2010	Operational
Savon Voima	CFB	Joensuu (Finland)	Wood residues	10000	50 ML/year	2013	Operational?
Twence (Empyro)	RCR (BTG)	Hengelo (Netherlands)	Wood residues	5000	20 ML/year	2015	Operational
Ensyn, Arbec Forest Products and Groupe Remabec (Cote Nord)	RTP (Ensyn)	Port-Cartier (Quebec Canada)	Wood residues	9000	40 ML/year	2018	Operational
Green Fuel Nordic	RCR (BTG)	Lieksa (Finland)	Wood residues	5000	20 ML/year	2020	Operational
Pyrocell, (Preem and Setra)	RCR (BTG)	Kastet sawmill in Gävle (Sweden)	Wood residues		21 ML/year	2021	Under planning
Ensyn and Fibria Celulose S.A.	RTP (Ensyn)	Aracruz (Espirito Santo Brazil)	Wood residues		83 ML/year		Under planning
Ensyn and Renova Capital Partners	RTP (Ensyn)	Dooley country (Georgia USA)	Wood residues		76 ML/year		Under planning

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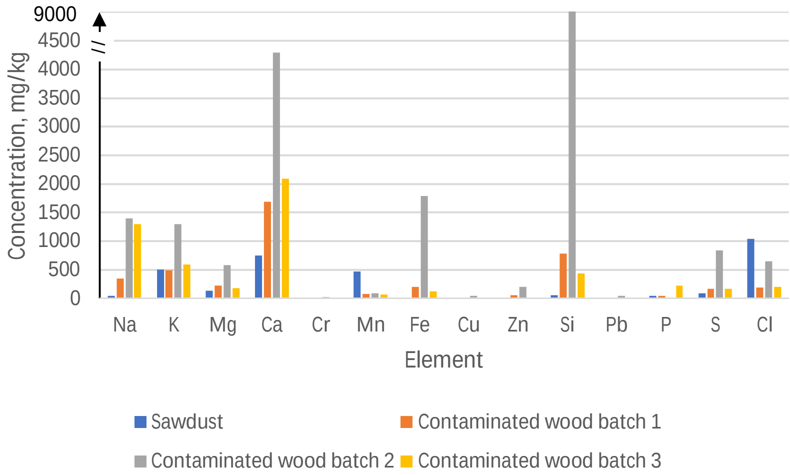
Waste material feedstock for pyrolysis

Feedstock		Sawdust	Contaminated wood, B class	Roadside grass	Organic fraction of municipal solid waste	Sunflower husk
Moisture	wt%	6.7	8.0	4.1	6.9	11.0
Volatiles, dry	wt%	85.1	84.7	-	-	-
Ash, dry	wt%	0.3	0.8	11.7	28.4	3.0
Carbon, dry	wt%	51.4	50.4	40.9	36.1	46.4
Hydrogen, dry	wt%	6.0	6.0	4.8	5.0	6.3
Nitrogen, dry	wt%	0.1	0.4	2.1	1.4	0.7
HHV, dry	MJ/kg	19.6	20.2	15.0	13.8	18.2
LHV, dry	MJ/kg	18.3	18.9	13.9	12.7	16.8
Cl, dry	wt%	-	0.02	-	0.609	0.061
S, dry	wt%	0.01	0.02	-	0.27	0.12



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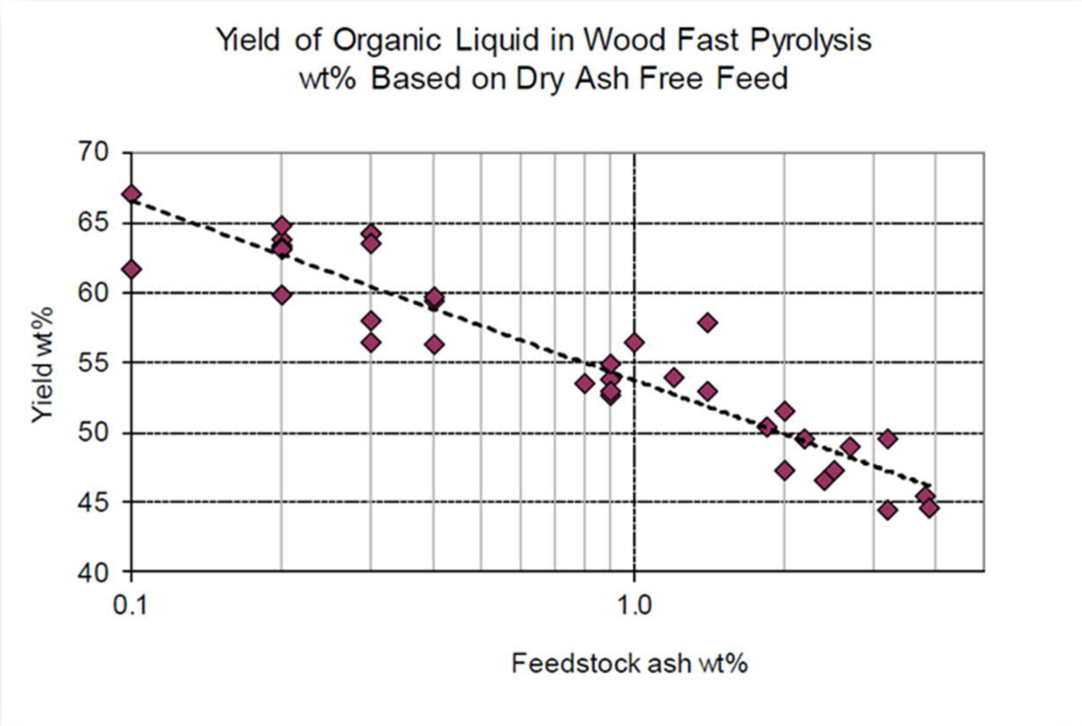
Fast pyrolysis of waste materials

- Pyrolysis liquid yield and quality is dependent on the feedstock.
- Highest liquid yield is obtained with bark free wood and lowest with agro-biomass.
- Ash content correlates to liquid yield
- Alkali metals, mainly potassium are known to catalyse pyrolysis reactions to yield more gas and water and decrease the organic liquid yield



Oasmaa, A.; Solantausta, Y.; Arpiainen, V.; Kuoppala, E.; Sipilä, K. Fast Pyrolysis from Wood and Agricultural Residues. Energy Fuels, 2010, 24, 1380-1388.

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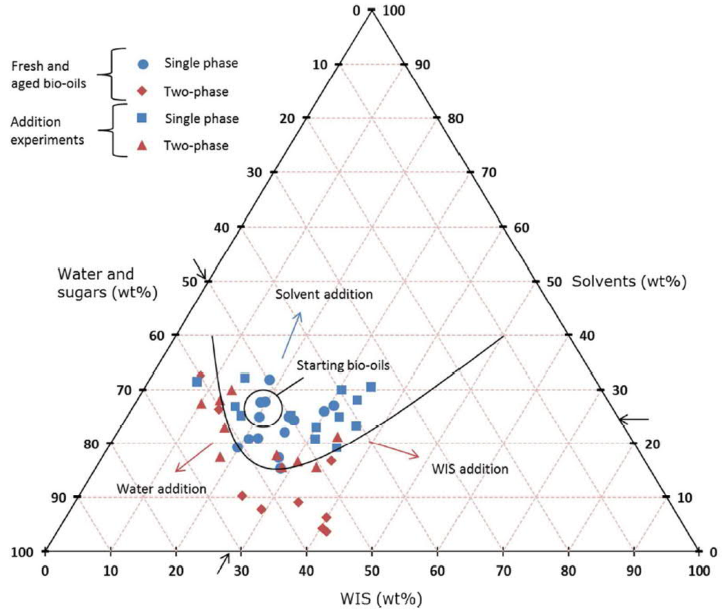
Phase stability of bio-oil

- There are two main types of phase separation related to the feedstock used to produce the FPBO
  - Phase separation of the extractive-rich top phase
  - Phase separation of the aqueous phase and lignin derived phase
- Phase separation of the aqueous phase and lignin derived phase is caused by
  - High water content of the feedstock
  - High ash content of the feedstock, which catalyzes dehydration reactions
  - Higher pyrolysis temperature, which reduce the oxygen content in the bio-oil and makes the organic phase more hydrophobic
  - Aging of the bio-oil, which increase the amount of water insoluble material and reduce the amount of light volatile compounds
- A chemical—composition-based phase stability diagram shows how close to phase separation any given FPBO is
- An increase in the relative amount of polar fraction above 60 wt% or a WIS fraction above 35 wt% or a decrease in the amount of co-solvent below 15 wt% may lead to phase separation



Oasmaa, a.; Sundqvist, T.; Kuoppala, E; Garcia-Perez, M.; Solantausta, Y.; Lindfors, C.; Paasikallio, V. Controlling the Phase Stability of Biomass Fast Pyrolysis Bio-oils. Energy Fuels, 2015, 29, 4373-4381.

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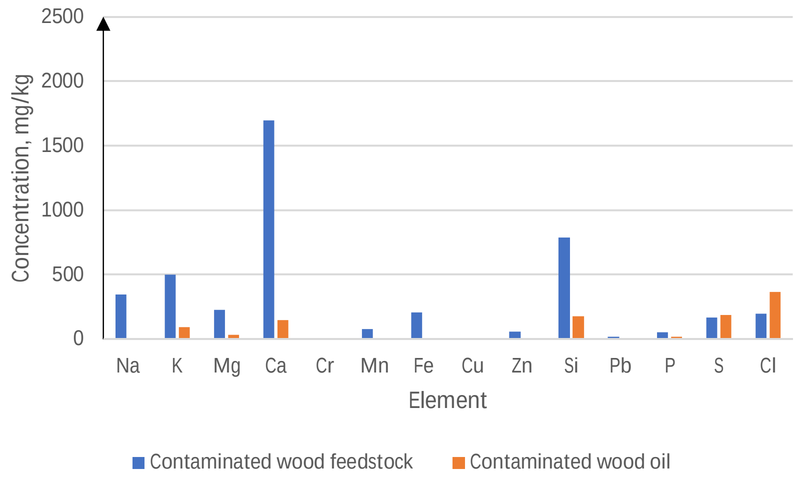
Bio-oil from waste material

- Metal, sulphur, nitrogen and chlorine content high in the oils from waste materials
- Pyrolysis reduced the metal content by 95 % compared to the feedstock

Oil	Sawdust	Contaminated wood	Roadside grass	Sunflower husk
Water, wt %	22.4	24.4	27.0	14.2
Solids, wt%	<0.01	0.17		
Ash dry, wt %	0.01	0.13		
MCR dry, wt%	23.1	27.5		
Carbon dry, wt%	56.7	54.1	59.0	67.4
Hydrogen dry, wt%	6.7	6.4	6.5	6.4
Nitrogen dry, wt %	0.3	0.5	1.2	1.7
Sulfur dry, wt%	0.02	0.03		
Chlorine dry, wt%	0.00	0.04		
Oxygen by difference dry, wt%	36	39	33	24
HHV dry, MJ/kg	23.6	22.6	24.7	28.3
LHV dry, MJ/kg	22.1	21.2	23.2	26.9



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High metal content in bio-oil will limits its further application

- In pyrolysis most of the metals are removed with the char in the cyclones
- Small particles (< 10 µm) will escape the cyclones and end in the product liquid
- Metals in the pyrolysis liquid
  - settle at the bottom of the vessel in form of sludge during bio-oil storage
  - cause erosion, corrosion and block injection nozzles in power generation systems
  - form deposits on the surface of the catalyst which changes its activity and shorten its lifetime, when pyrolysis liquid is further upgraded

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Alkali removal from FPBO is importand when residues are used as feedstocks

ALKALI REMOVAL BEFORE PYROLYSIS

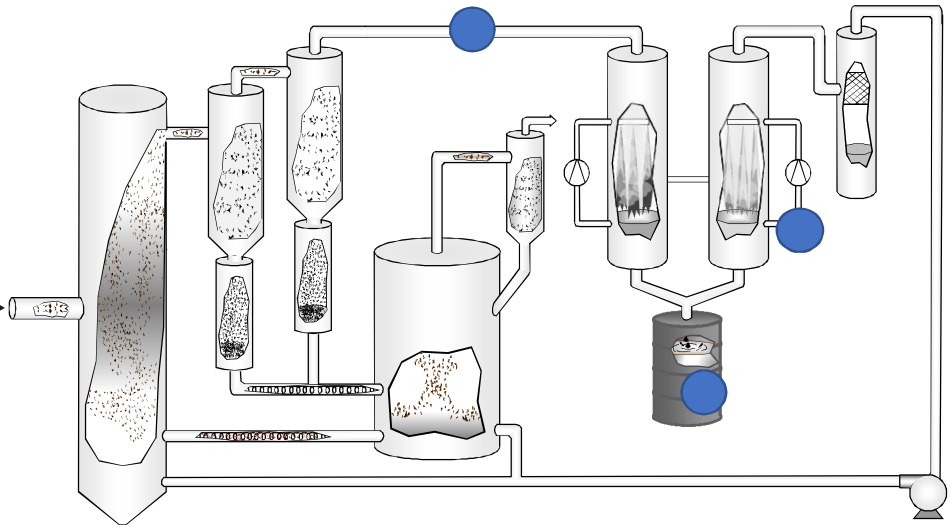
Washing of biomass

Steam explosion

Combination of alkali removal methods

SOLIDS/ALKALI REMOVAL BEFORE OIL CONDENSATION

Hot-filtration of vapours



US 2020/0061513 A1 Apparatus and method for cleaning stream.
Contact: Matti Nieminen, Christian Lindfors, VTT

SOLIDS/ALKALI REMOVAL AFTER OIL CONDENSATION

Bio-oil on-line filtration/ centrifugation Ion-exchange

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Alkali removal before pyrolysis from forest residue, eucalyptus and straw

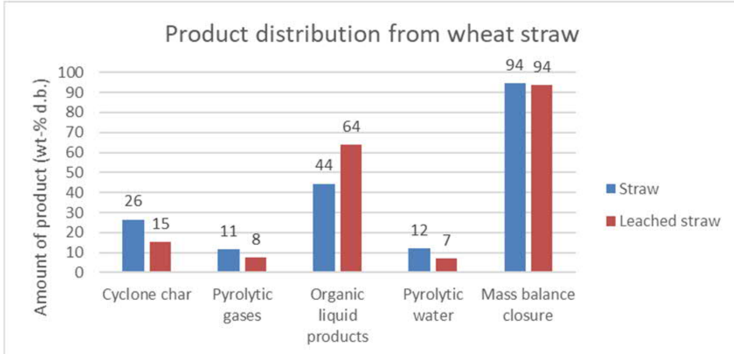
4refinery

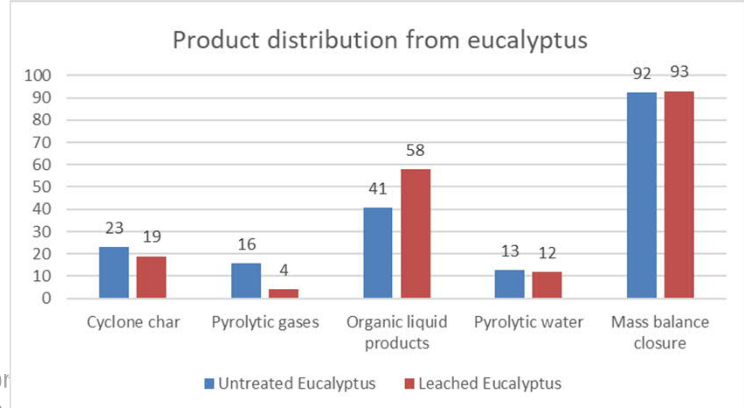
- Fast pyrolysis of forest residue, eucalyptus and straw have been carried out in bench scale before and after washing
- Noticeable increase in organic liquid yield was obtained with washed straw and eucalyptus
- Washed eucalyptus and forest residues behaved differently compared to untreated raw materials.
    - Washed feeds were found to agglomerate with heat carrier which disturbed feed and temperature control and eventually led to termination of the experiment.
    - With eucalyptus, problem was solved by decreasing the feed rate. Eucalyptus was successfully processed after adjustments
    - Even after the adjustments, forest residue particles were not pyrolyzed completely which led to clogging of the equipment. Absence of catalytic inorganic ash elements may change the optimal process conditions. Ash and AAEM content of the raw materials was also the lowest with forest residues.

	Feedstock					Washed feedstock				
	K (ppm)	Na (ppm)	Ca (ppm)	Mg (ppm)	Ash (wt%)	K (ppm)	Na (ppm)	Ca (ppm)	Mg (ppm)	Ash (wt%)
Forest residues	700	200	1300	200	0.74	< 50	< 50	< 50	< 50	0.29
Eucalyptus	2600	500	7500	900	4.75	400	100	800	100	2.81
Wheat straw	7600	< 50	1700	700	6.91	300	< 50	100	< 50	5.70

Table 1. Washing conditions in bench scale washing.

Sample	Temperature (°C)	Time (min)	Acid (w-%)	Washing liquid (B:WL)	Rinsing water (B:W)
Forest residues	50	30	1 %	1:10	1:10
Eucalyptus	50	30	1 %	1:10	1:10
Wheat straw	20	30	0,5 %	1:10	1:10





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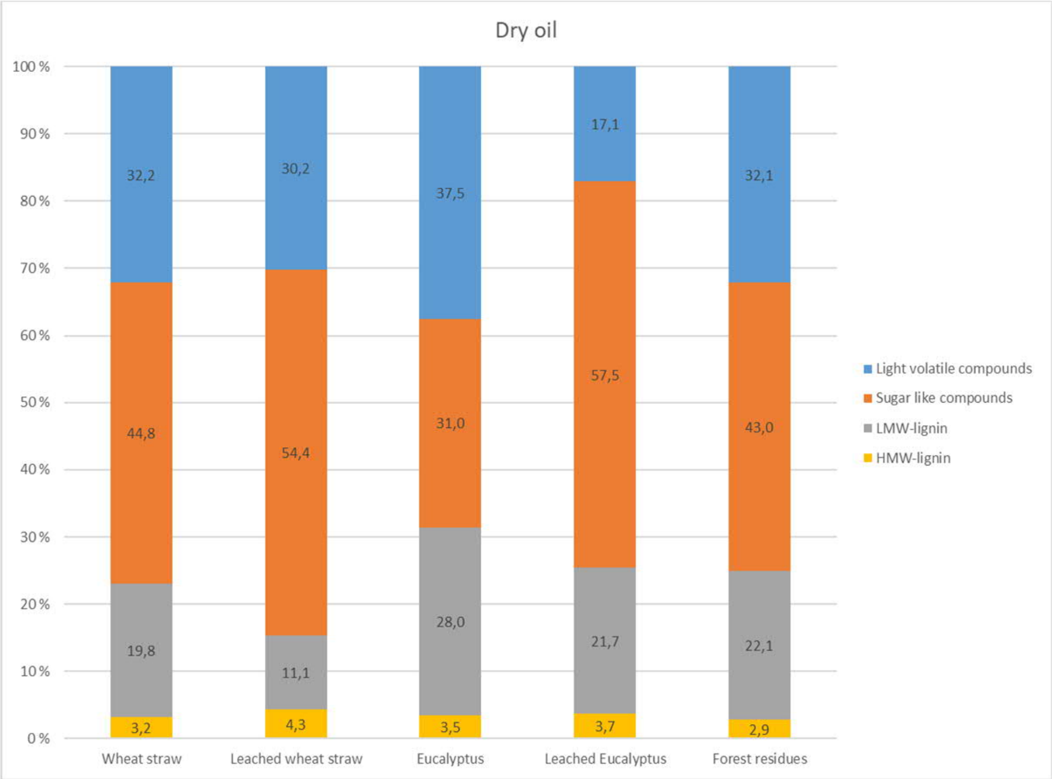
European Union's Horizon 2020 research and innovation program, GA No. 727531

Alkali removal before pyrolysis from forest residue, eucalyptus and straw

- Oil from the washed raw material had different chemical composition.
  - Fraction of "sugars" increased.
  - Oxygen content increased.
  - pH and CAN were reduced.

Feedstock	Acid leached wheat straw	Untreated wheat straw	Acid leached eucalyptus	Untreated eucalyptus	Forest residues
Water, wt %	16.4	21	7.8	27.5	22.3
Ash dry, wt %	0.04	0.05	0.03	0.04	0.13
MCR dry, wt%	27.4	23.7	31.2	24.4	25.1
Carbon dry, wt%	51.0	54.9	53.5	57.5	57.8
Hydrogen dry, wt%	6.1	6.8	6.2	6.8	6.3
Nitrogen dry, wt %	0.1	0.3	0.3	0.4	0.1
Sulfur dry, mg/kg	na	0.03	0.02	na	0.01
Chloride dry, mg/kg	na	0.05	0.03	na	0.00
Oxygen by difference dry, wt%	43	38	40	35	36
HHV dry, MJ/kg	20.4	22.7	21.7	24.1	24.3
LHV dry, MJ/kg	19.1	21.2	20.3	22.7	23.0
pH	2.3	2.52	2.5	3.1	2.6
CAN dry, mg KOH/g	90.1	115.3	53.6	109.1	85.6
Carbonyl dry, mmol/g	7.3	6.6	3.9	4.4	3.6



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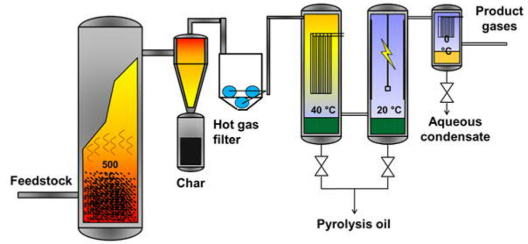
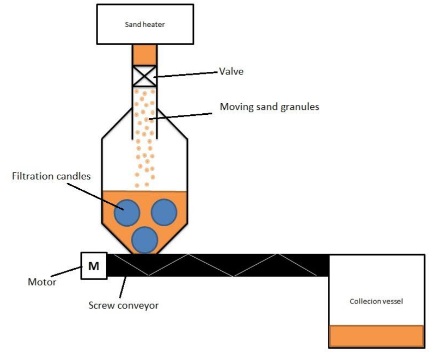
VTT’s new design of hot vapour filtration

- VTT’s new filter design is a combination of a so called moving bed filter and candle filter.
- Coarse particles of moving bed filter will enable avoiding of formation of sticky dust cake by removing captured particles from the filter surface.
- Filter conditions have been optimized in bench scale using:
  - Contaminated wood as feedstock
  - Varying the filter temperature: 450, 400, 360 °C
  - Varying the face velocity by using 3, 2, or 1 filter candle





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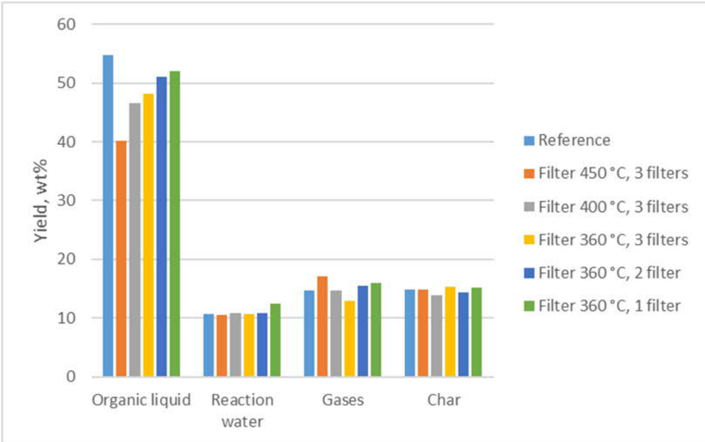
Solids removal by hot vapour filtration

- Fast pyrolysis vapours did not block the pores in the filters
- Hot vapour filtration reduced the organic liquid yield and increased the gas, water and char yield
- Higher filtration temperature reduced more the organic liquid yield
- Reducing the amount of filters increased also the organic liquid yield



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Solids removal by hot vapour filtration

- Hot vapour filtration did not significantly change the properties of bio-oil
- Metal content was reduced by hot vapour filtration

		Feedstock	Pyrolysis liquid			
Metals	Unit	Contaminated wood	Without filter	Filter 450 °C	Filter 400 °C	Filter 360 °C
Na	mg/kg	350	84	76	80	70
K	mg/kg	500	10	10	10	10
Mg	mg/kg	230	10	10	10	10
Ca	mg/kg	1700	28	10	10	10
Ash	wt%	0.8	<0.05	<0.05	<0.05	<0.05

		Pyrolysis liquid			
		Without filter	Filter 450 °C	Filter 400 °C	Filter 360 °C
Water	wt. %	16.3	22.4	21.2	22.6
Solids	wt. %	0.2	0.1	0.1	< 0.1
Ash	wt. %	< 0.05	< 0.05	< 0.05	< 0.05
MCR (dry)	wt. %	28.1	27.8	27.7	24.5
TAN (dry)	mg KOH/g	63.7	83.2	76.3	75.5
Carbonyl (dry)	mmol/g	5.34	5.15	4.95	5.04
WIS (dry)	wt. %	33.2	38.9	31.6	38.5
HHV	MJ/kg	19.3	18.7	18.7	18.1
LHV	MJ/kg	17.7	17	17.1	16.5
Carbon (dry)	wt. %	55.7	57.5	56.7	55.9
Hydrogen (dry)	wt. %	6.5	7.0	6.4	6.2
Nitrogen (dry)	wt. %	0.7	0.6	0.5	0.6
Oxygen by difference (dry)	wt. %	37	35	36	37

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Conclusions

- Pyrolysis liquid yield and quality depends on the feedstock
- Alkali metals mainly potassium are known to catalyse pyrolysis reactions to yield more gas and water
- Metal removal is needed before pyrolysis liquid can be used as a feedstock in oil refinery
- Metal removal from the feedstock before pyrolysis will increase the oil yield, but at the same time the pyrolysis reaction of the feedstock will change
- Metal removal by hot vapour filtration will reduce the metal content in the oil, but at the same time organic liquid yield will decrease

Acknowledgement

The authors gratefully acknowledge the support from 4REFINERY (grant agreement no. 727531) and WASTE2ROAD (grant agreement no. 818120) projects funded by the European Union's Horizon 2020 research and innovation programs