
White poplar


Norway spruce


Wheat straw


Corn stover


DDGS

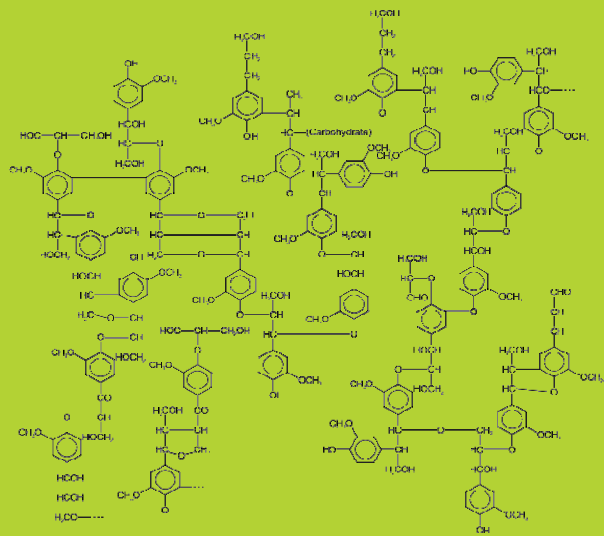
WP 2: Innovative thermochemical conversion

Paul de Wild, ECN

WORKSHOP
Development of multi-product lignocellulose biorefinery technology with focus on residues (pentoses, lignin) from cellulose thanol production

Results of the Integrated Project BIOSYNERGY

17 November 2010;
Grand Hotel de L'Univers, Reims (France)


Idealised lignin structure

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Content

- Introduction
  objective, WP2 in BIOSYNERGY, partners and tasks
- Aquathermolysis - pyrolysis
  furfural, levoglucosan and phenols from straw and straw-derived lignin
- (Catalytic) fast pyrolysis
  production of bio-oil from BIOSYNERGY feedstocks
- Product separation & upgrading
  fractionation of bio-oil for wood-adhesives application
- Conclusions, highlights
- Outlook, follow-up
- Acknowledgements

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WP2 Objective

Valorisation of (residual) biomass into value-added chemicals, fuels and / or materials for a wheat straw based 2nd generation bio-ethanol plant by innovative thermochemical processing

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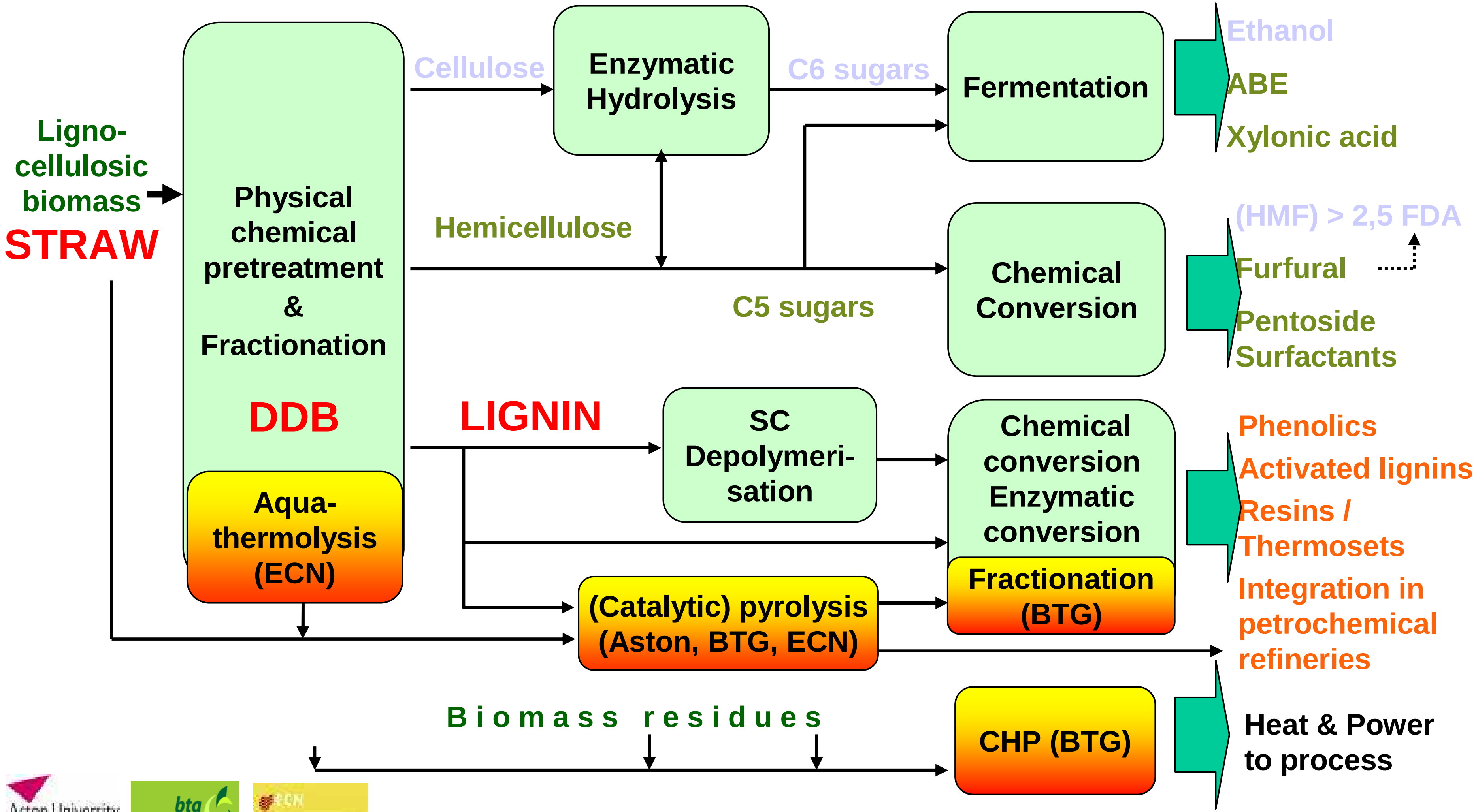
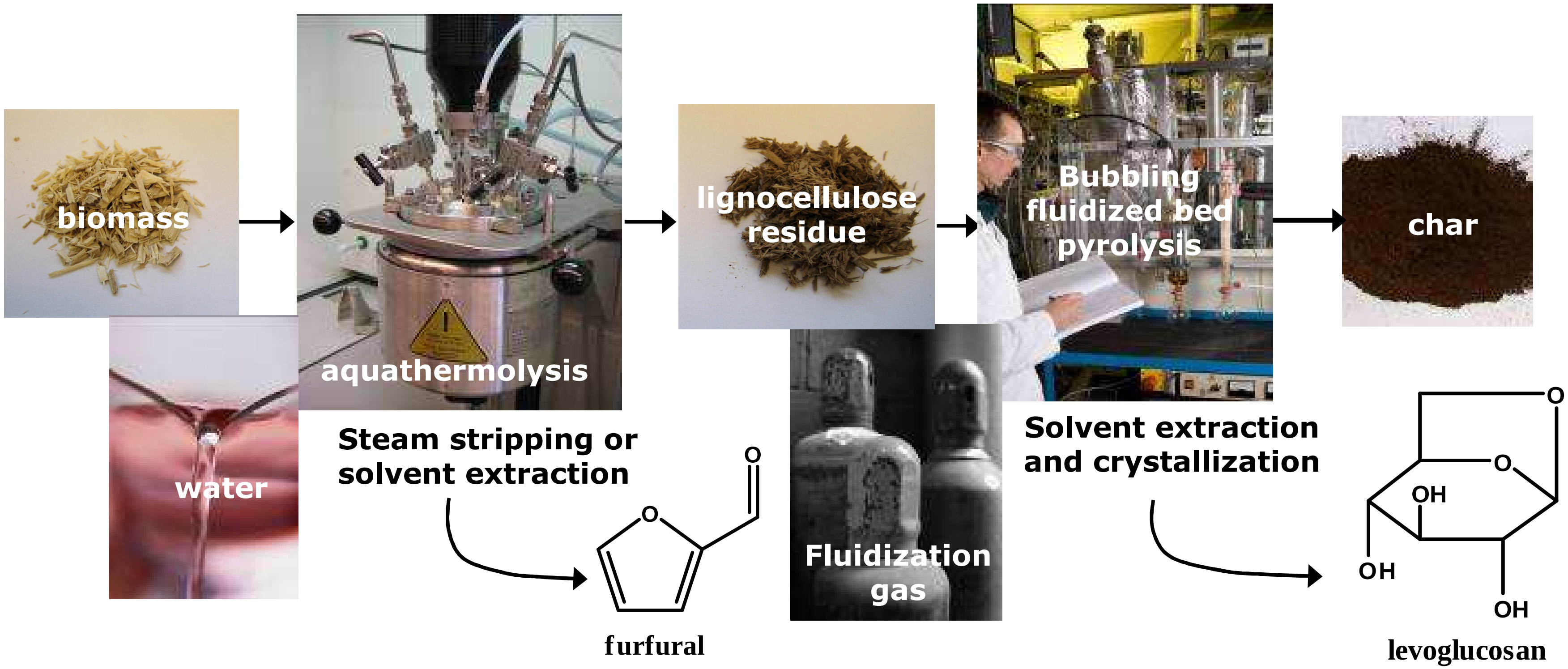
Integration of WP2 in the multi-product biorefinery



Aston University btg ECN

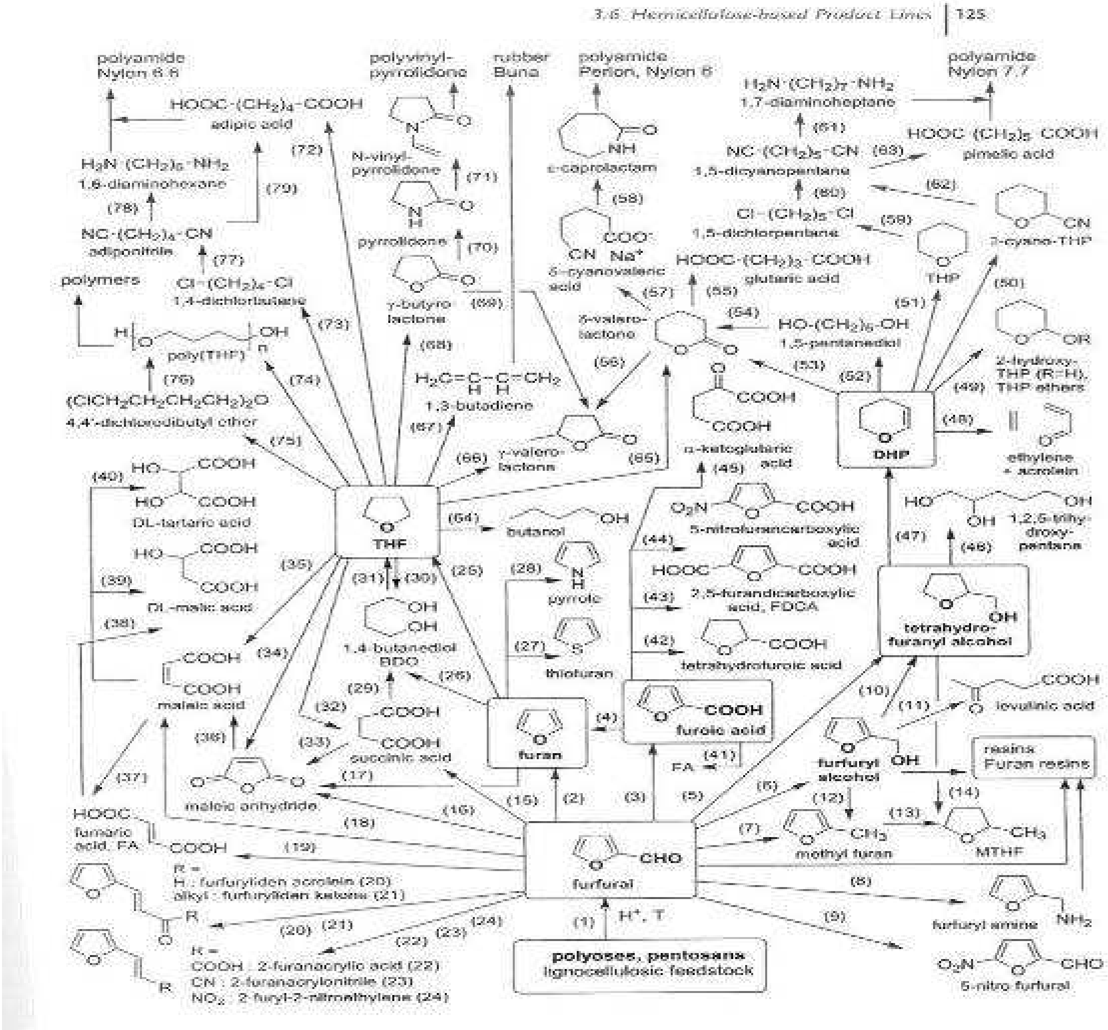
Aquathermolysis – pyrolysis concept



- Aquathermolysis (hot pressurised water treatment), selectively hydrolyses hemicellulose, dehydrates C5 sugars to furfural and leaches out soluble ash minerals. Autocatalysis by innate organic acids such as acetic acid.
- The dried hemicellulose- and ash-free lignocellulose residu is a good feedstock for the pyrolytic production of levoglucosan from the cellulose.

Furfural from hemicellulose

- Solvents
- Products of organic synthesis
  (e.g. furfuryl alcohol)
- Paints and varnishes
- Agriculture
- Medicine
- Plastics, resins
- Synthetic fibres, etc.



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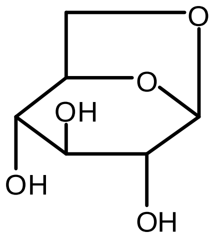
Levoglucosan from cellulose

Medicines

Food applications



Levoglucosan
(1,6-anhydro-
β-D-glucopyranose)

Ring-opening polymeization →

Stereoregular polysaccharides
- dextrans
- carbohydrate liquid crystals
- glycolipids (synthetic biomembranes)
- detergents for membrane protein solubilisation
- non-fattening fillers in low-calorie food
- water thickening agents

Acid catalysis polymerization →

Branched oligo- and polysaccharides
- dextrins
- non-fattening fillers in low-calorie food
- water thickening agents

Fermentation →

Direct fermentation products
- itaconic acid
- citric acid

Acid hydrolysis →

Glucose
- ethanol

Basic catalysis copolymerization →

Copolymers
- polyethers
- polyesters
- polymethacrylates
- polyols
- polyurethanes
- epoxy-resins

Acid catalysis + higher alcohols →

Alkyl-glucosides
- gelling agents
- wetting agents
- lubricants
- dyeing assistant
- textile softener
- food emulsifier

Chiral synthesis →

Complex asymmetric molecules
- pharmaceuticals (antibiotics)
- herbicides / plant growth regulators
- insecticides
- pesticides

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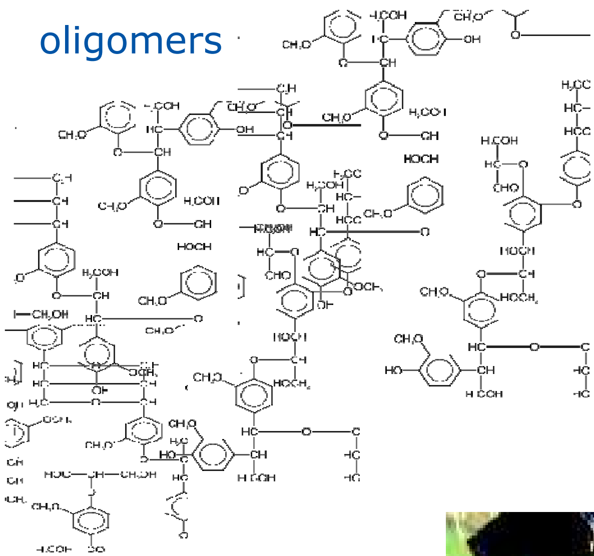
Phenols and char from lignin

low volume high value market

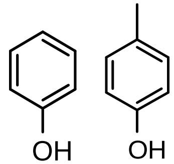
oligomers



specialty chemicals

bio-plastics

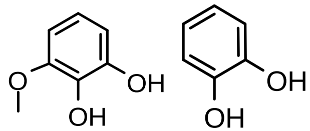
bio-resins for wood-adhesives



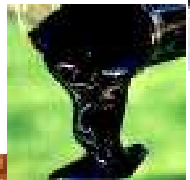
alkylphenols

activated carbon, carbon-fibres and carbon-black

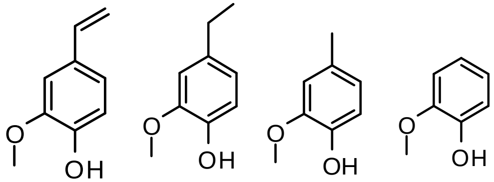
catechols



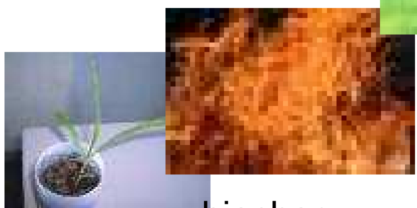
fuel-additives



guaiacols



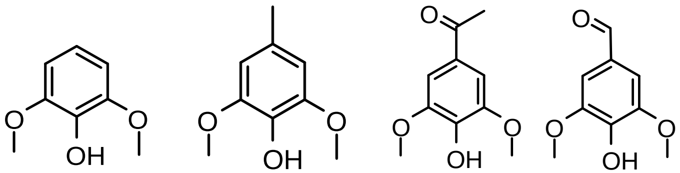
bio-bitumen for green asphalt



biofuel

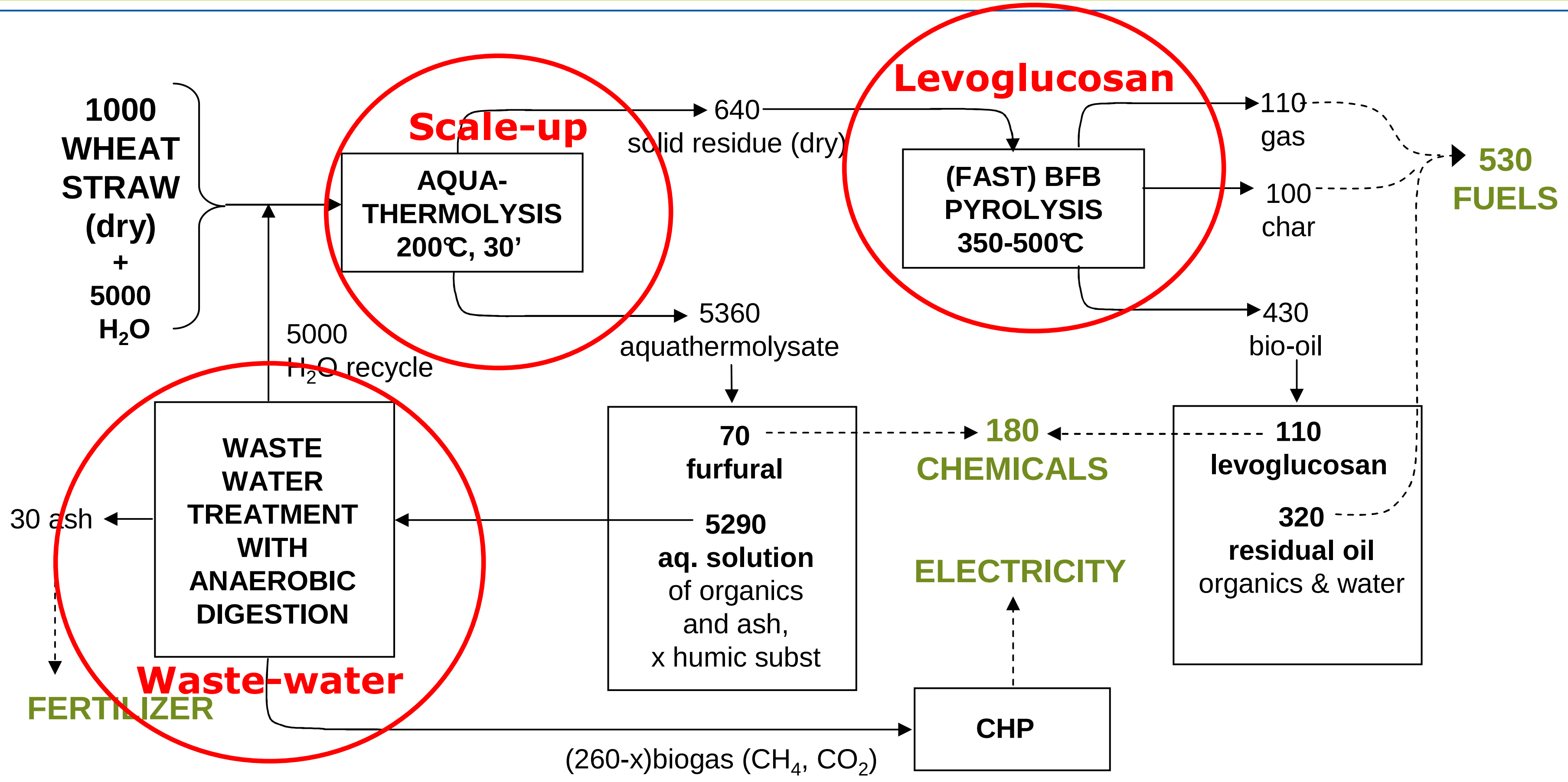
biochar

syringols



high volume low value market

Results aquathermolysis – pyrolysis for straw



Positive results from limited scale up of the aquathermolysis (0.5L → 2L → 20L)
Techno-economic assessment results indicate a positive economic viability.

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Scale-up aquathermolysis 0.5 → 20 L; furfural

EXPERIMENTAL CONDITIONS AQUATHERMOLYSIS	
Parameter	**Value**
Temperature [°C]	200
Reaction time [min]	30
Wheat straw (a.r.) [g]	1300
Moisture [wt%]	8.64
Added water [g]	11768
L / S (d.b.) ratio [w/w]	10
PRODUCT YIELDS AQUATHERMOLYSIS	
Material	**Yield (wt% d.b.)**
Residu (d.b.)	63
Solubilised straw (d.b.)	37
Furfural + HMF	5
Acetic + formic acid	5

Slightly lower yields when compared to small scale tests; probably due to longer heating & cooling times

Solvent extraction of the aquathermolysate for anaerobic digestion tests at the university of Southampton

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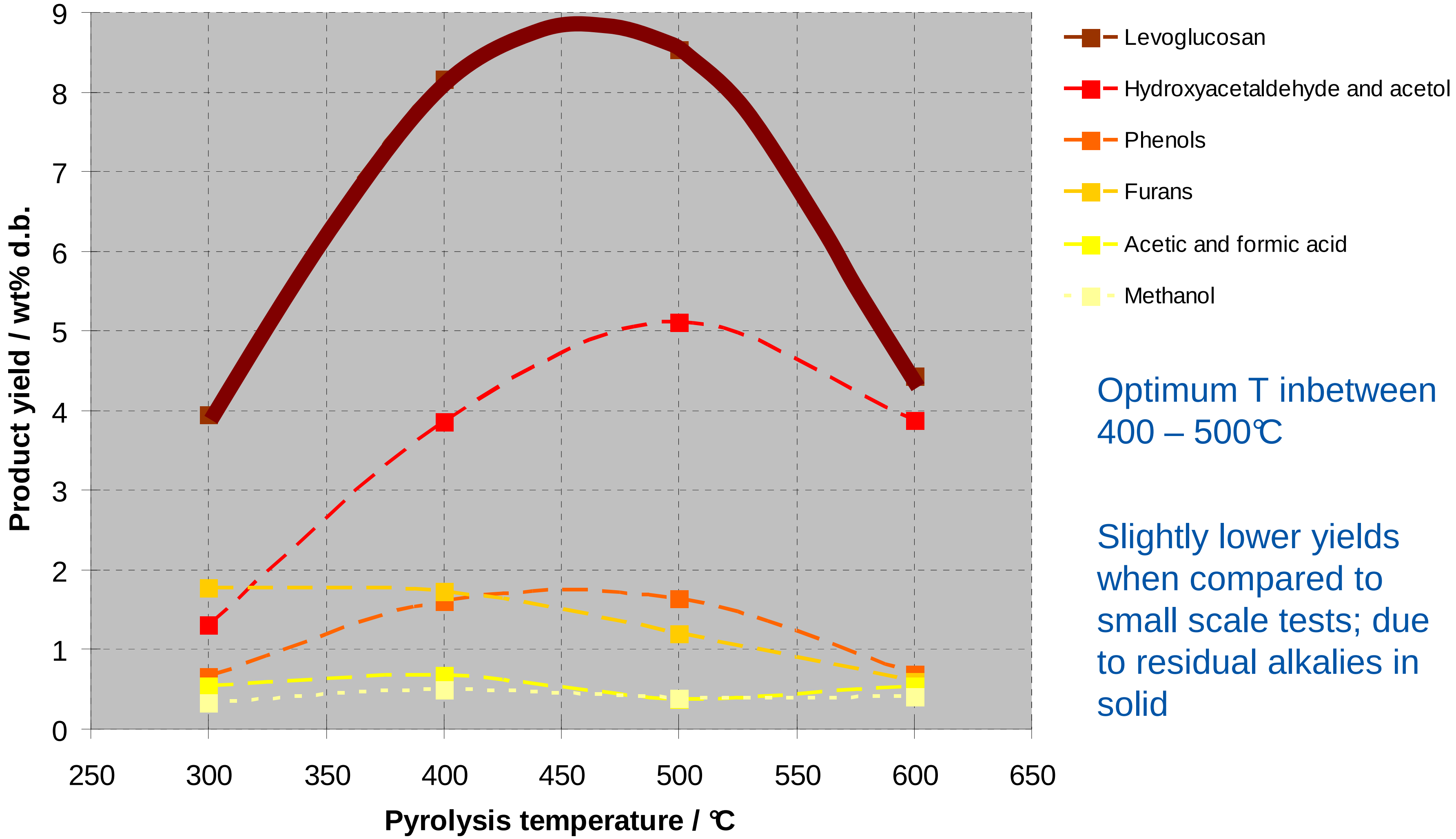
Levoglucosan production from aquastraw by pyrolysis



Optimum T inbetween 400 – 500℃

Slightly lower yields when compared to small scale tests; due to residual alkalies in solid

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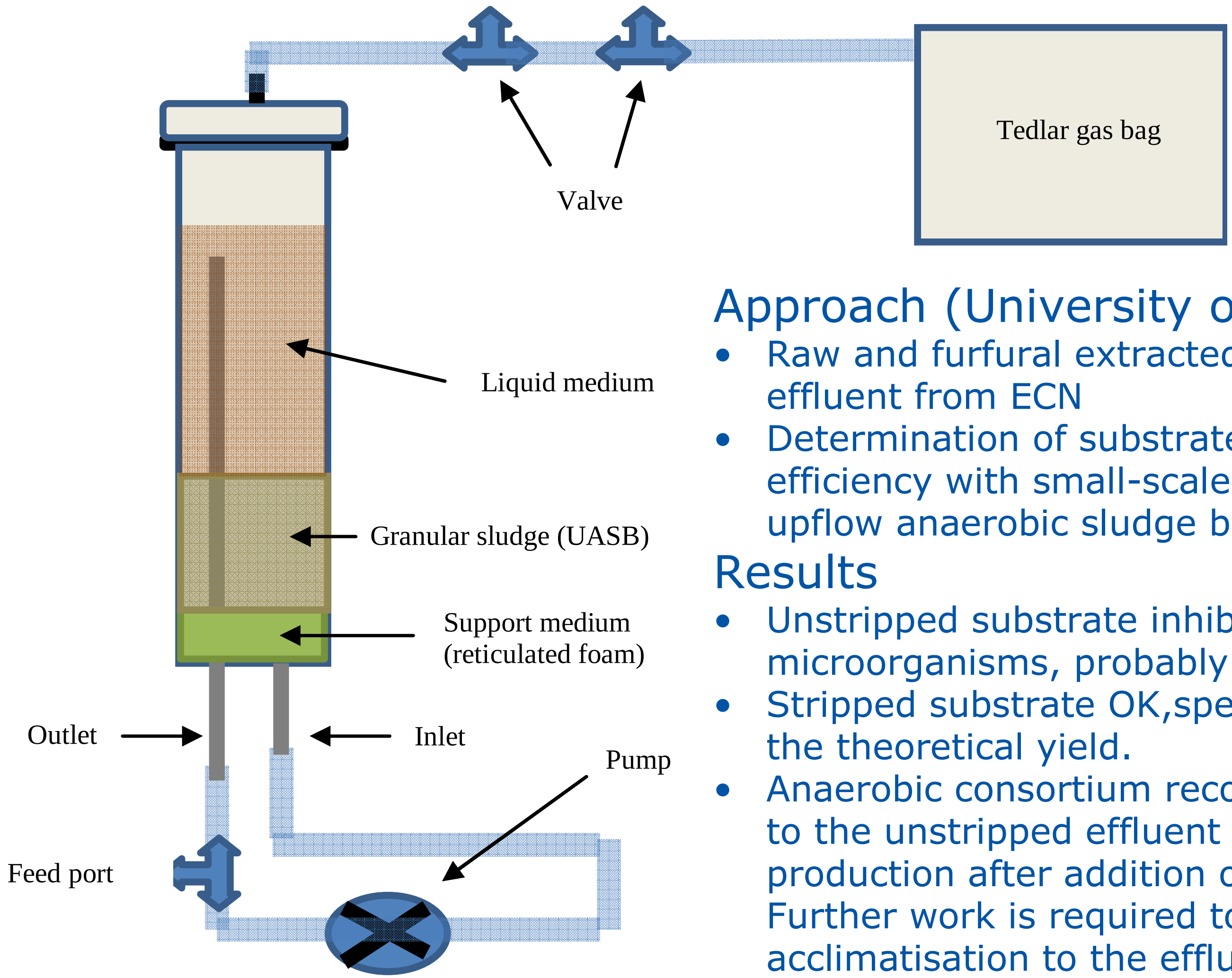
Anaerobic digestion aquathermolysate

University of Southampton



Approach (University of Southampton)

- Raw and furfural extracted aquathermolysis straw effluent from ECN
- Determination of substrate to CH_4 conversion efficiency with small-scale (1.5L) semi-continuous upflow anaerobic sludge blanket (UASB) digesters.

Results

- Unstripped substrate inhibits anaerobic microorganisms, probably due to furfural.
- Stripped substrate OK,specific CH_4 yields >90% of the theoretical yield.
- Anaerobic consortium recovers from short exposure to the unstripped effluent and resumes methane production after addition of buffer to raise the pH. Further work is required to determine whether acclimatisation to the effluent would be possible.

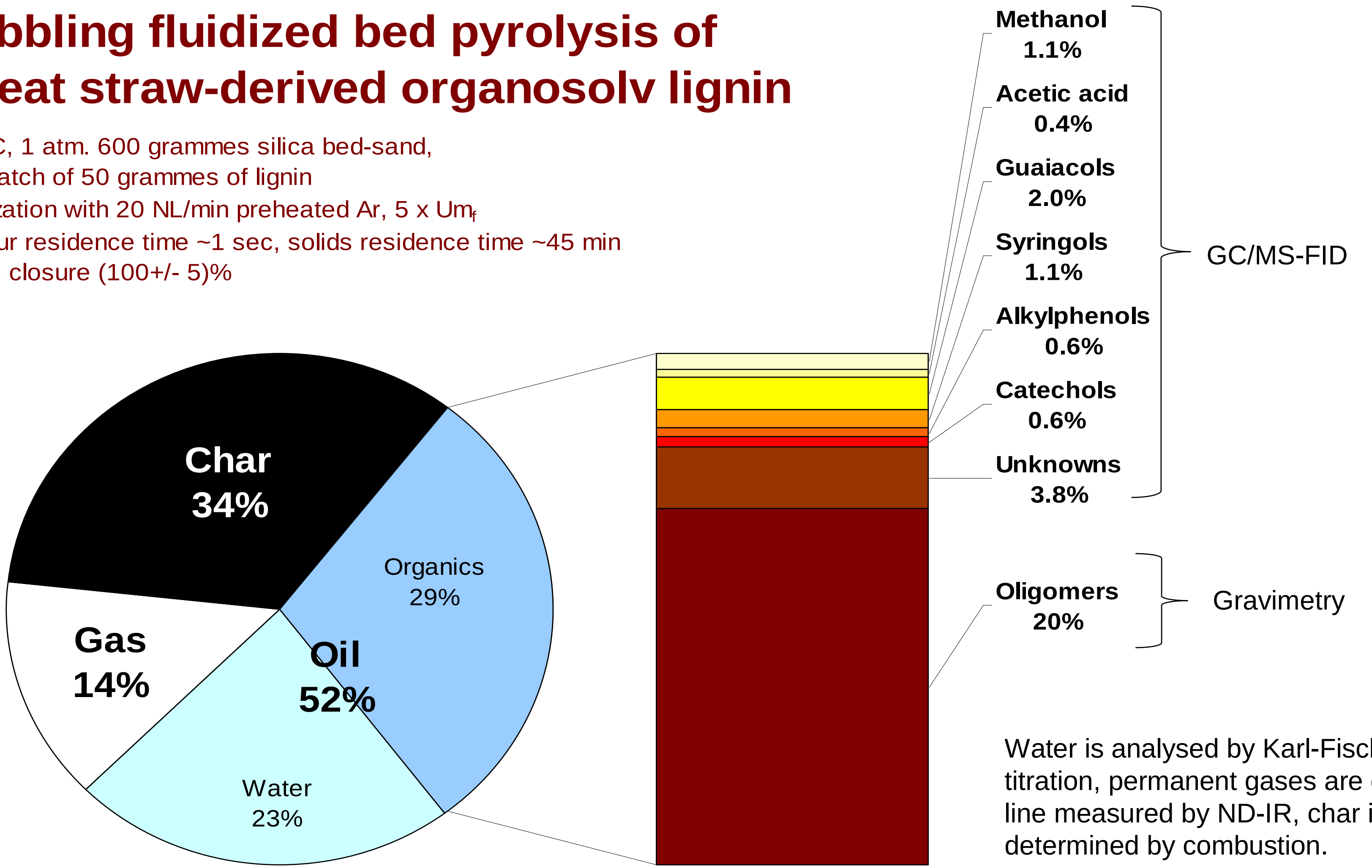
Valorization of straw residu: production of DDB

Dewatering and drying of wheat-straw stillage to produce DDB (dried distilled biomass) from ABNT – pilot bio-EtOH biorefinery near Salamanca

Catalytic pyrolysis of wheat straw organosolv lignin

Bubbling fluidized bed pyrolysis of wheat straw-derived organosolv lignin

500℃, 1 atm. 600 grammes silica bed-sand,
fed-batch of 50 grammes of lignin
fluidization with 20 NL/min preheated Ar, 5 x Um_f
vapour residence time ~1 sec, solids residence time ~45 min
Mass closure (100+/- 5)%



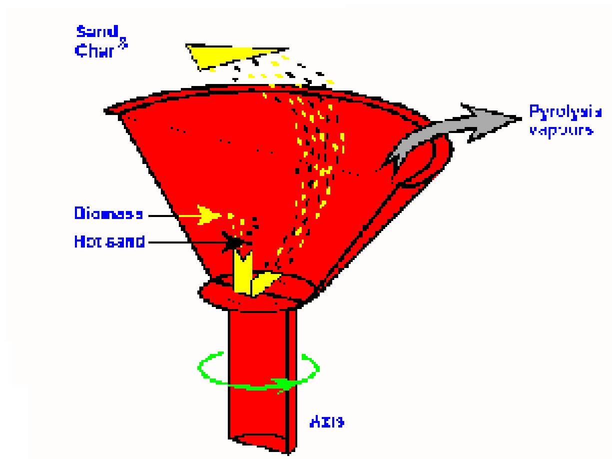
Water is analysed by Karl-Fischer titration, permanent gases are on-line measured by ND-IR, char is determined by combustion.

Fast pyrolysis of BIOSYNERGY feedstocks

All project feedstocks (spruce, poplar, straw, DDGS) can be pyrolysed successfully

Pyrolysis of spruce wood

Overall mass balance	98 wt.%
Oil yield	67 wt.%
Gas yield	11 wt.%
Char yield	19 wt.%
Ash yield	1%



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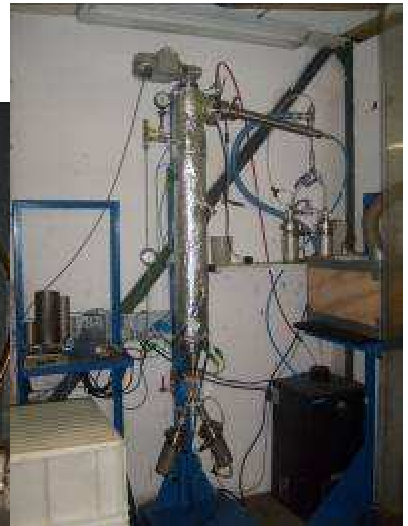
Pyrolysis oil quality improvement

- Removal of solids from pyrolysis oil
- Design, construction and testing of a bench-scale filtration unit
- Testing of continuous filtration in industrial size self-cleaning filter unit

Solid content remaining in oil		
Unfiltered oil	0.582	wt.%
Filtered 100 µm	0.136	wt.%
Filtered 40 µm	0.122	wt.%
Filtered 10 µm	0.102	wt.%
Filtered 5 µm	0.080	wt.%

- Preventing phase separation of pyrolysis-oil.
- Homogenization by water removal, lab scale research
- Design, construction and testing of bench scale unit



Phase separated oils (from Wheat Straw & DDGS) can be homogenized with ease, while retaining most of the energy-dense components in the homogeneous oil.

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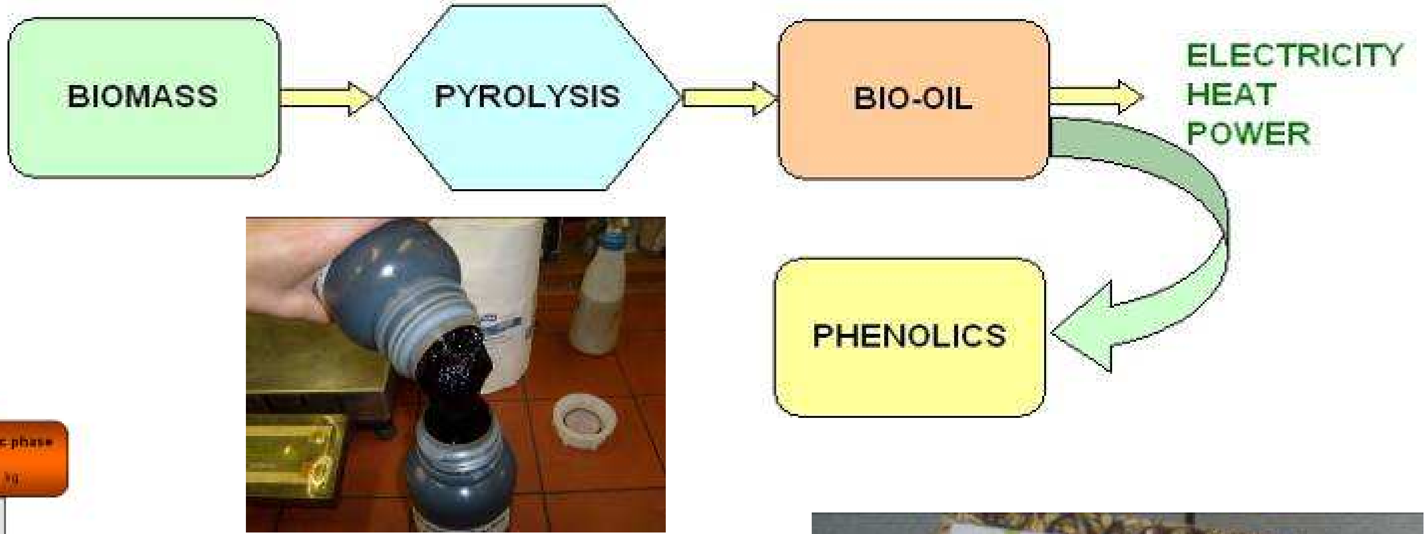
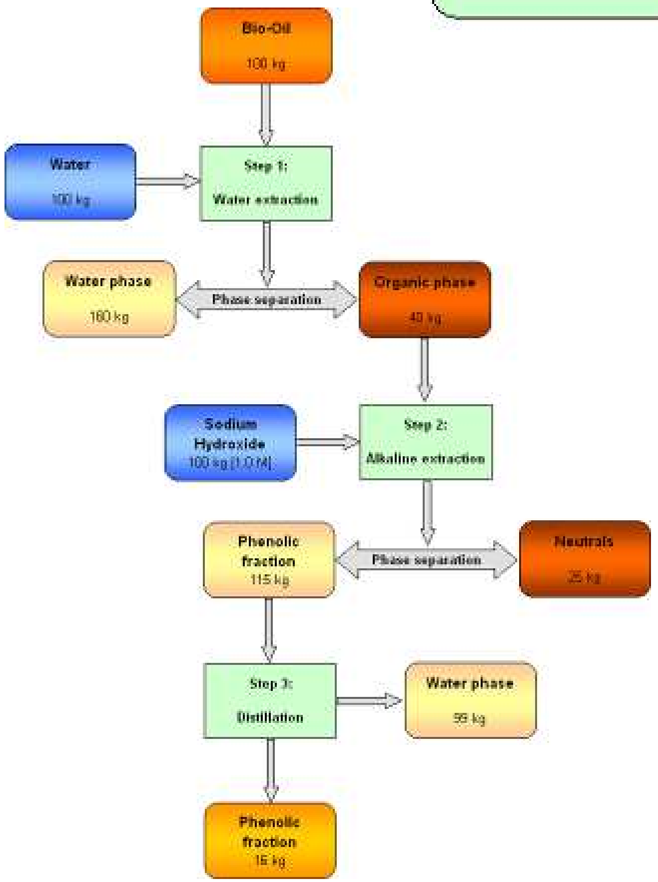
Oil fraction for application in phenol–formaldehyde resins



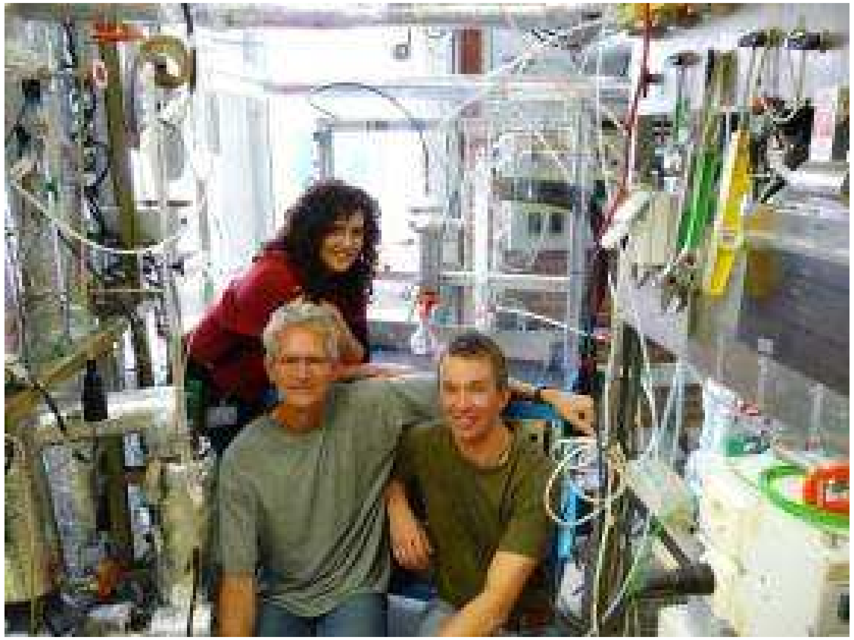


- Production of pyrolysis oil for production tests of phenolic fractions from different oils (DDGS,Wheat straw)l
- Production of spruce pyrolysis oil for testing at CEPSA (4 kg) & DOW (1 kg)

Researcher exchange Aston - ECN

- Fast pyrolysis of pre-treated poplar
- 1 kg/hr BFB reactor at ECN
- 0.1 kg/hr BFB reactor at Aston

Wet basis wt. %	ASTON	ECN
Gases	7	22
Char	25	17
Oil (total liquid)	59	52
Balance	**91**	**91**



0.1 kg/hr BFB reactor

Conclusions, highlights

- ## Aquathermolysis–pyrolysis
  Proof of principle for integration in a multi-product, multi-technology biorefinery or as a stand-alone thermochemical biorefinery for furfural, levoglucosan, phenols, fuels and heat & power.

- ## (Catalytic) fast pyrolysis
  Effective production of bio-oil from all BIOSYNERGY feedstocks for applications as fuel and as feedstock for further upgrading.

- ## Bio-oil upgrading & fractionation
  Development of a process that enables the production of a valuable fraction from biorefinery side streams suitable for application in phenol/formaldehyde resins.

- ## Dissemination
  5 peer-reviewed publications (2 accepted, 2 submitted and under review, 1 to be submitted), exposure on several congresses, workshops etc.

Outlook, plans

- Finalise TEE aquathermolysis-pyrolysis
- Write article on the system evaluation of the aquathermolysis – pyrolysis concept
- Promote pyrolysis within IEA-T34 (pyrolysis) and IEA-T42 (biorefinery) as an important part of the economic biorefinery, ensuring flexibility and side-stream valorization

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Thank you all for your attention, Merci!

Questions?