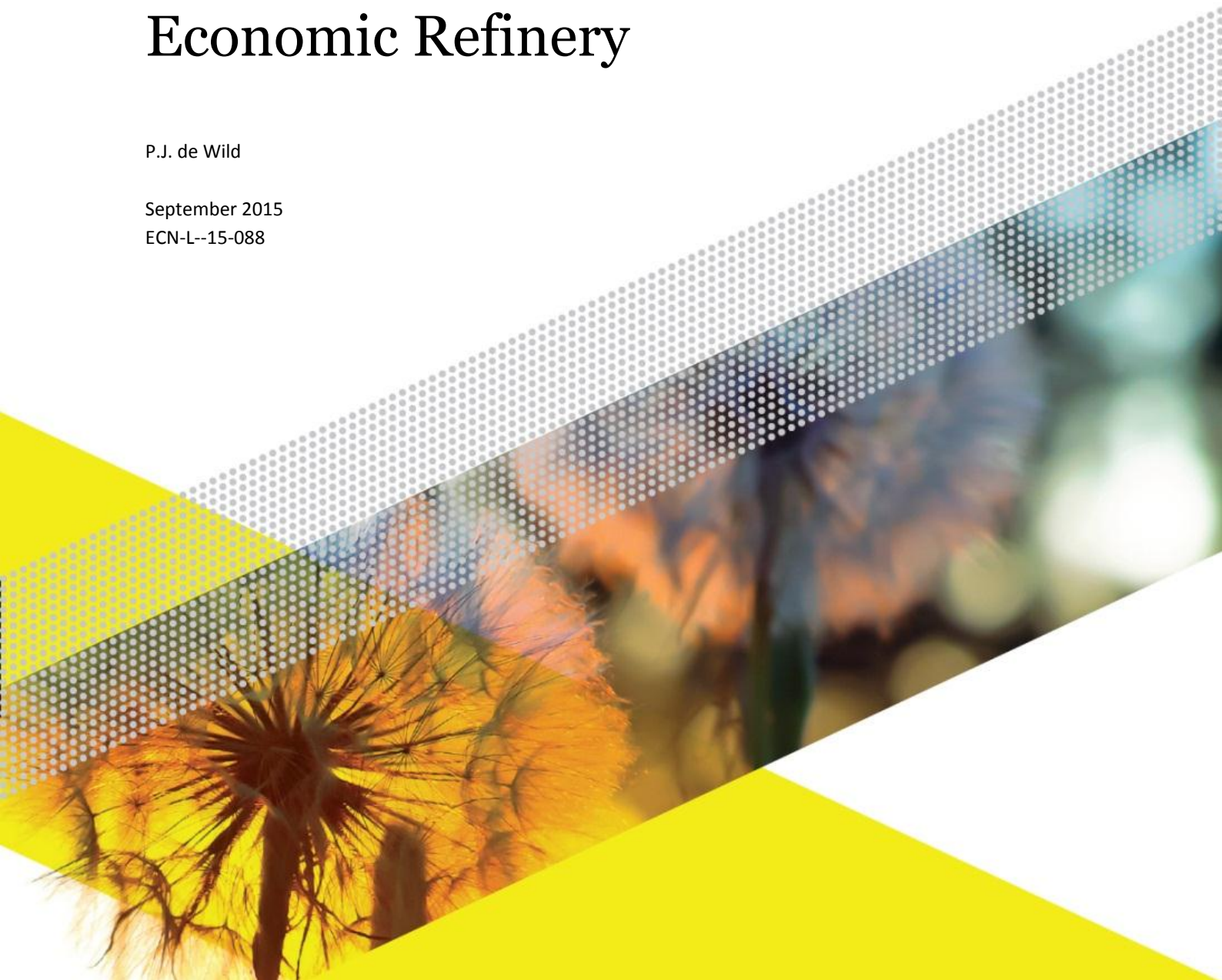
BIORECOVER BIOmass REsidues COnversion & Valorisation for an Economic Refinery

P.J. de Wild

September 2015
ECN-L--15-088



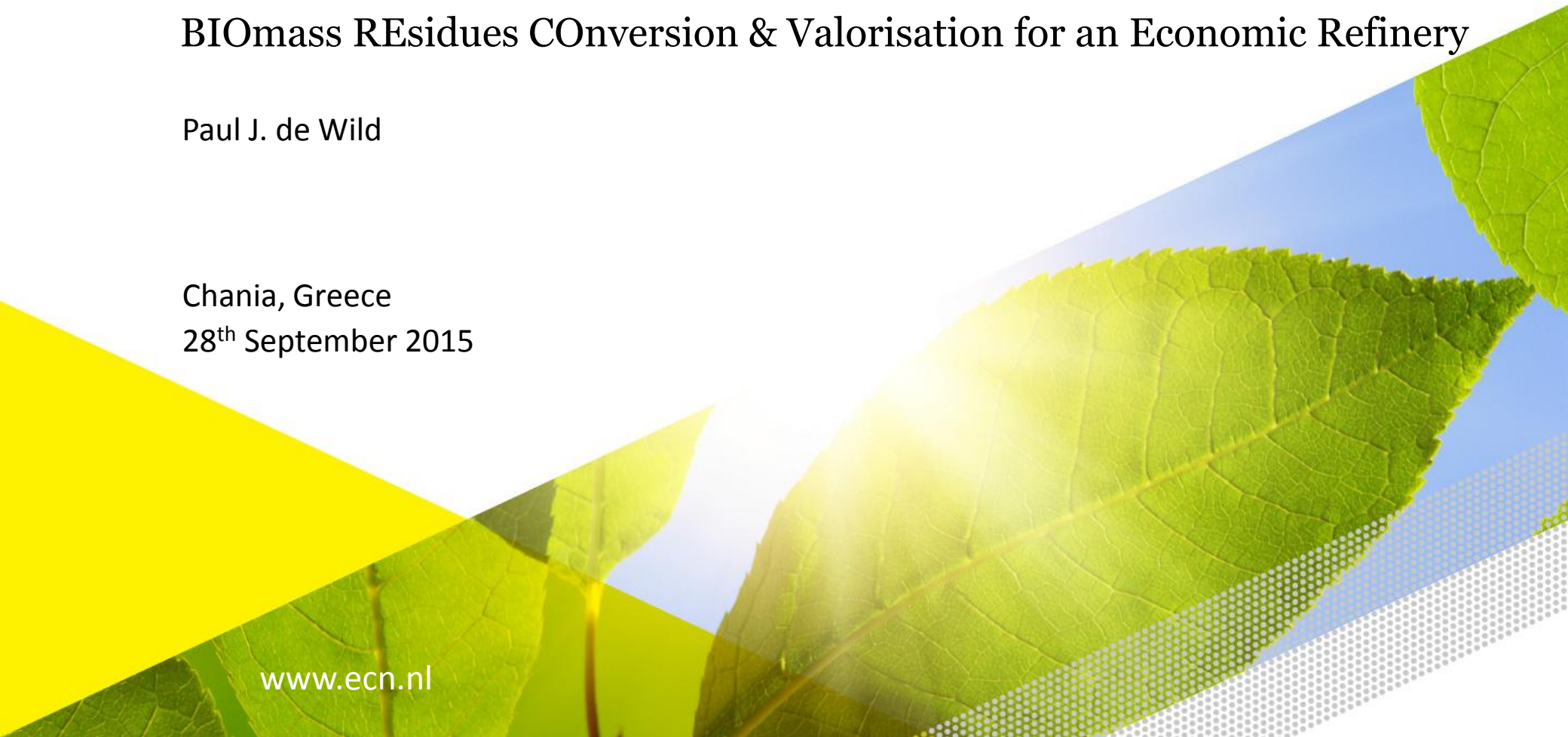
ECN
Your energy. Our passion.

BIORECOVER

BIOmass REsidues COnversion & Valorisation for an Economic Refinery

Paul J. de Wild

Chania, Greece
28th September 2015



www.ecn.nl

Aim Study

Introduction

- Typical ethanol-producing lignocellulose-based biorefineries generate 30-50 wt% of various residues (based on the dry weight of the biomass intake).
- Valorisation of these residues enables better economics and a further step to a closed cycle processing of biomass without the emission of waste streams.
- However, to date most residues are considered waste and/or as fuel for generating process heat (low value valorisation).
- Lignin is by far the dominant residue.

- Challenge:
  - Variability in type, amount and origin of biorefinery residues calls for flexible and cost-effective conversion technologies in a cascading approach. In other words: step by step.

Aim of this work:

- To show the potential of low- ,medium- and high-temperature conversion technologies of typical biorefinery residues as a step towards valorisation.

Status lignocellulose biorefineries

Company and plant location	Feedstock	Fractionation	Scale***	Main product	Lignin use
Beta Renewables (Crescentino, Italy)	**Agricultural residues 270 kt/yr**	**Steam explosion**	**Commercial**	**Ethanol 60 kt/yr**	**Fuel**
ABNT* (Hugoton, Kansas, USA)	**Corn stover, wheat straw 315 kt/yr**	**Steam explosion**	**Commercial**	**Ethanol 80 kt/yr**	**Fuel for steam and power**
POET – DSM (Emmetsburg, USA)	**Agricultural residues 280 kt/yr**	**Enzymatic hydrolysis**	**Commercial**	**Ethanol, biogas 76 kt/yr**	**Fuel**
ABNT* (Babilafuente, Spain)	**Wheat straw / MSW 24 kt/yr**	**Steam explosion**	**Demo**	**Ethanol 4 kt/yr**	**Fuel, feed additive**
Chempolis (Oulu, Finland)	**Agricultural residues 25 kt/yr**	**Organosolv**	**Demo**	**Ethanol 5 kt/yr**	**Fuel**
CIMV** (Pomacle, France)	**Agricultural residues, hardwoods ~ 100 kg/hr**	**Organic acid organosolv**	**Pilot**	**Cellulose, C5 sugars, lignin**	**Performance materials**

*ABNT: Abengoa Bioenergy New Technologies, **CIMV: Compagnie Industrielle de la Matière Végétale, *** commercial: >1000 kg/hr feedstock intake, demo: ~1000 kg/hr intake, pilot: ~100 kg/hr.

- Most biorefineries produce ethanol (for transportation fuel).
- Lignin is mostly utilized as fuel for the generation of process heat.

Cascading bioresidue conversion approach





Raw lignocellulosic biomass
Sizing
Lignocellulosic biomass
Fines, dust
Combustion, gasification, fast pyrolysis
• Washing
Purified residue
Minerals and extractives
Separation purification
• Organosolv
Dissolved Lignin
Solid cellulose
Hydrolysis chemical conversion
• Separation
Pure solid lignin
Aqueous hemicellulose
Hydrolysis chemical conversion
• Pyrolysis
Lignin pyrolysis oil
Solid char/ash
Recovery gasification combustion
• Fractionation
Mono- & oligophenols
Aqueous fraction
Purification
Separation hydrodeoxygenation

€

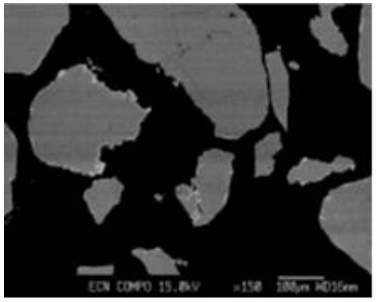
CHP, fertiliser, construction
Cellulase Saver
C6 sugar derivatives
C5 sugar derivatives
CHP biochar
Bio-pesticides
(Phenolic) aromatics

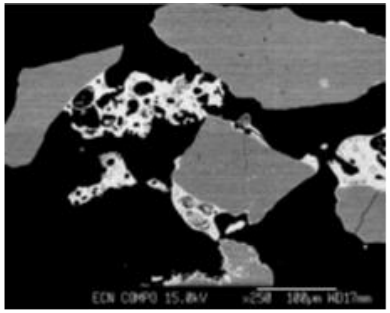
Case 1: Fines and (saw)dust residues

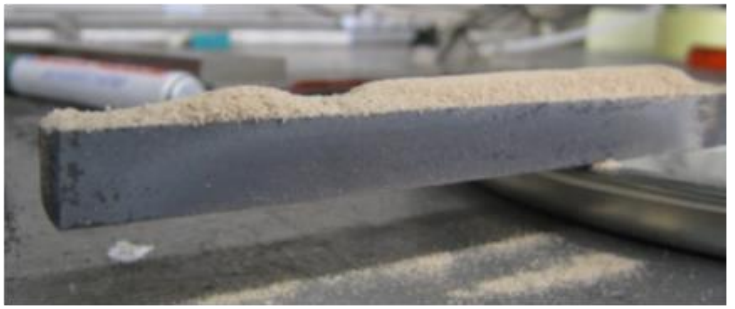
- Mechanical pretreatment such as comminution of lignocellulosic biomass causes substantial amounts of fines and dust that are not suitable for the regular process.
- Combustion or –gasification are high-T conversion technologies that can be deployed to valorise fines for heat, power and materials.
- Case study for wheat-straw fines.

Conversion of fines for CHP in a BFB reactor

- Testing of wheat and rice straw in Bubbling Fluid Bed (5 kWth) combustion:
  - Wheat straw fines show stable combustion, no bed agglomeration,
  - Combustion of rice straw fines causes bed agglomeration,
  - Ash deposits could be removed easily,
  - Overall combustion behaviour more difficult than wood.
- Flue gas cleaning to remove HCl, SO_x, NO_x is required
- Fly-ash is –to a certain extent- suitable as fertilizer, not for building materials





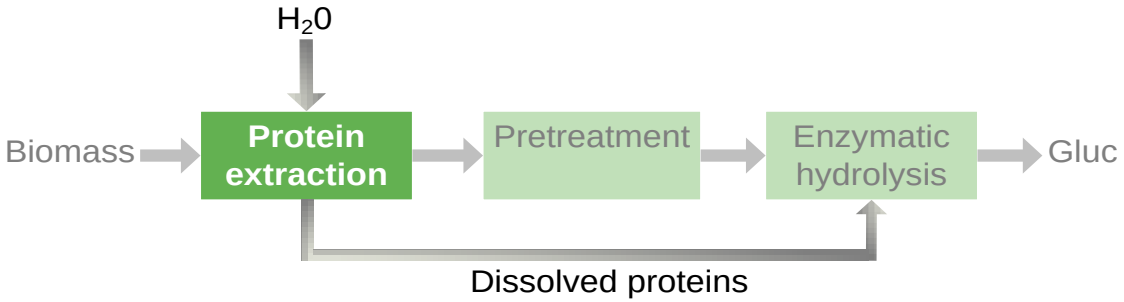


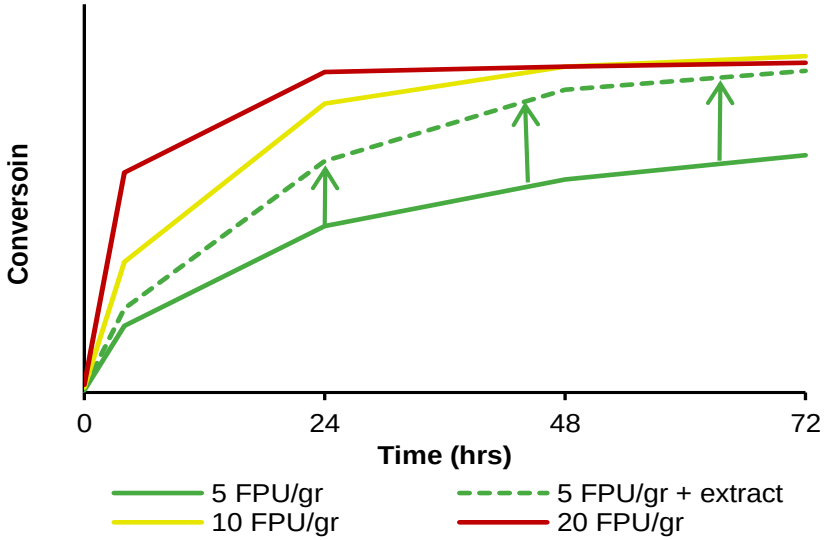
Case 2: Water soluble extractives

- Innate extractable species can seriously hamper biomass fractionation processes and cause impure primary fractions (cellulose, lignin).
- A simple extraction with water at T < 100°C removes water soluble extractives such as proteins.
- Specific organics in the aqueous product are suitable to shield lignin derived fragements from interfering with cellulose hydrolysis enzymes.
- Cellulase Saver: patent application!
- Example for wheat straw.

Cellulose to Glucose; Cellulase Saver

- High enzymatic digestibility of organosolv cellulose pulps.
- Spin-off organosolv development: Cellulase Saver
  - Method to reduce enzyme costs in production of sugars.
  - Works best for herbaceous biomass.
  - Pretreatment technology independent.





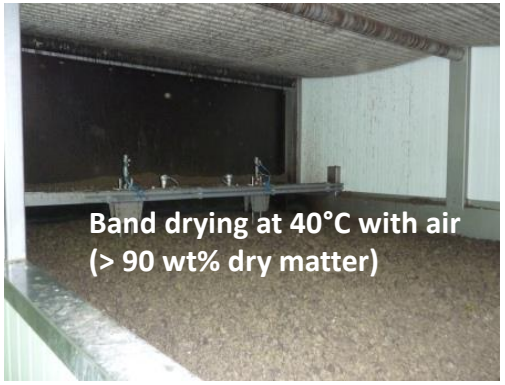
More information:
- www.ecn.nl/technology-transfer.
- Patent application WO 2014/098589.

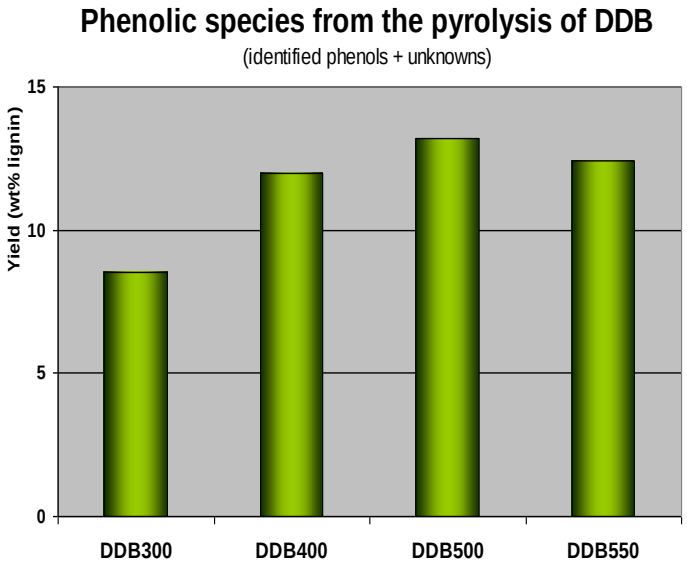
Case 3: Lignin and lignin-rich residues

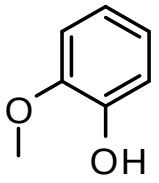
- Lignin containing residues are the major side-stream from ethanol producing biorefineries.
- To date, these residues are mostly burned for generating process heat.
- Pyrolysis of these residues yields a phenolic liquid product that can be used as such or further upgraded towards aromatic chemicals.
- Eamples: stillage from the processing of wheat straw and corn stover towards ethanol and relatively pure acid-hydrolysis lignin from corn stover.

Pyrolysis of dried distilled biomass from wheat straw stillage

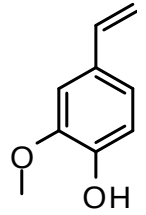
- Dewatering and drying of wheat-straw stillage to produce DDB (dried distilled biomass) from an EtOH biorefinery.
- Stillage contains ~50 wt% of lignin.
- Bubbling fluidised bed pyrolysis of the DDB to produce phenolic liquids.







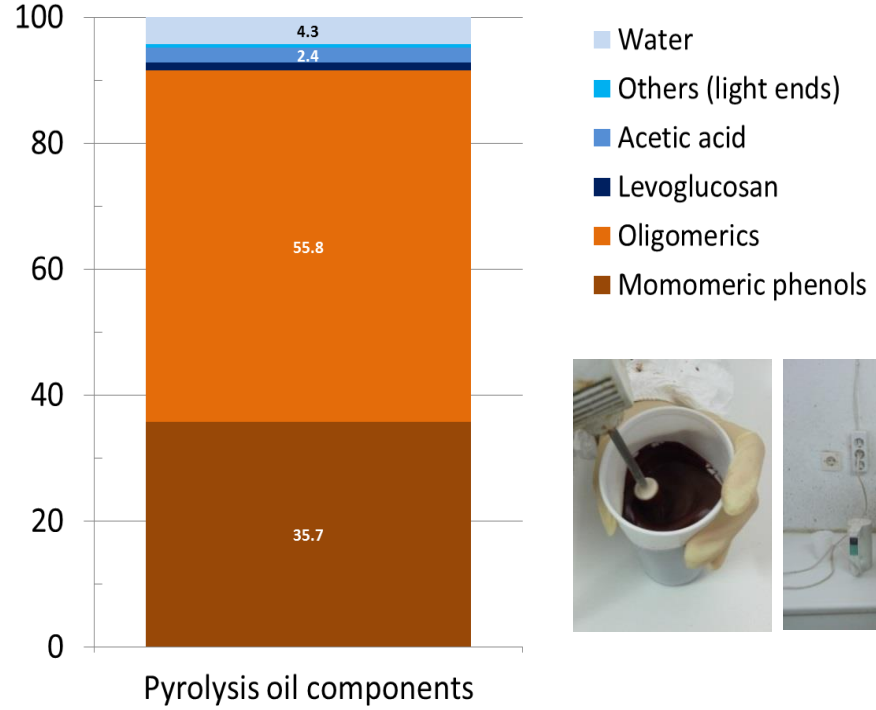
Successful pyrolysis of DDB to phenols



Pyrolysis of dried distilled biomass from corn stover stillage

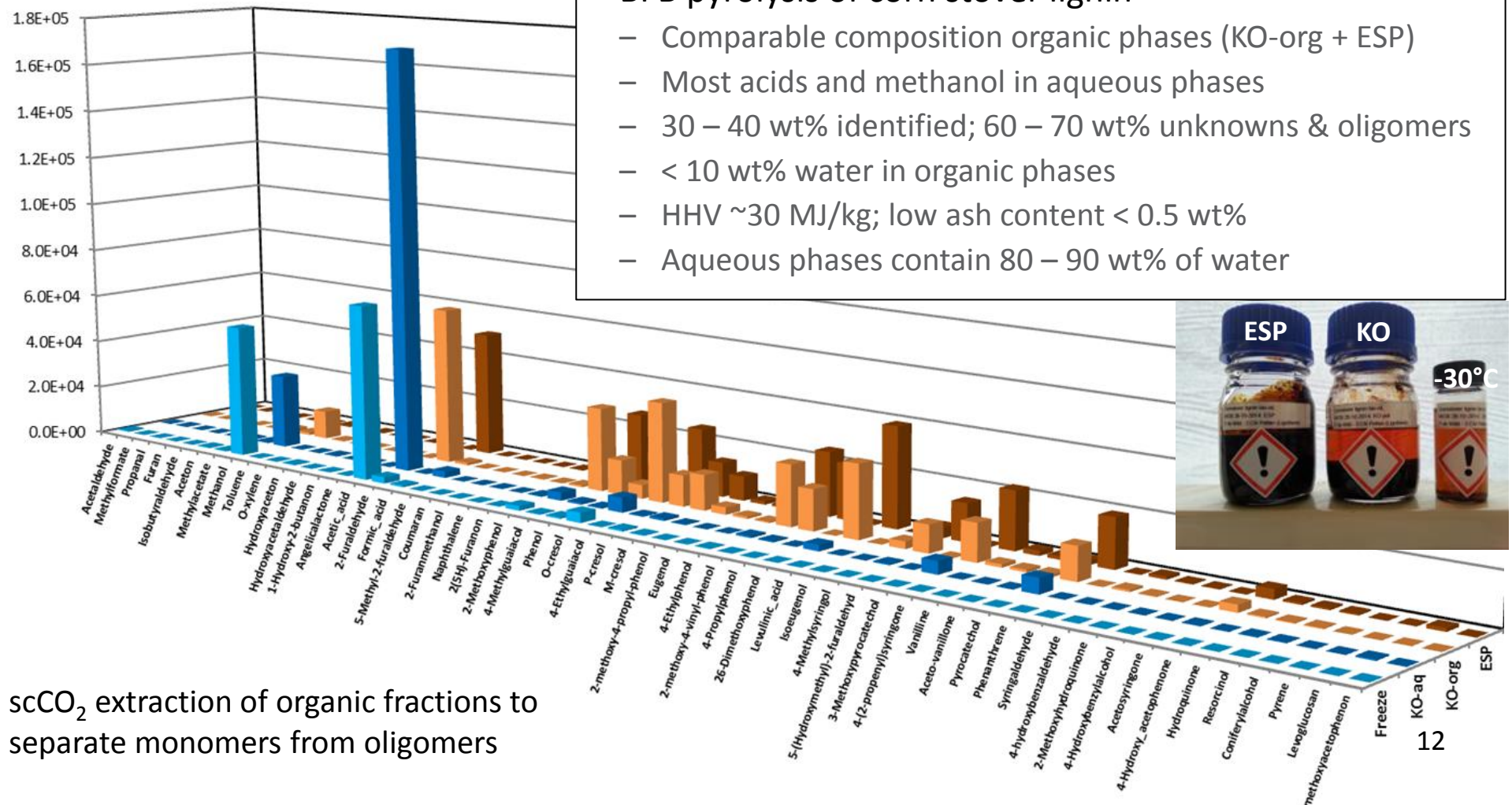
Bubbling fluidised bed pyrolysis of the corn stover DDB (~50 wt% lignin) to produce phenolic liquids for PF-resin aplications. Phenol substitution level 10 wt%.

Composition organic fraction of cornstover stillage-derived pyrolysis oil
Pyrolysis at 400°C in a bubbling fluidised bed



Pyrolysis of corn stover lignin

- BFB pyrolysis of corn stover lignin
  - Comparable composition organic phases (KO-org + ESP)
  - Most acids and methanol in aqueous phases
  - 30 – 40 wt% identified; 60 – 70 wt% unknowns & oligomers
  - < 10 wt% water in organic phases
  - HHV ~30 MJ/kg; low ash content < 0.5 wt%
  - Aqueous phases contain 80 – 90 wt% of water



- $scCO_2$ extraction of organic fractions to separate monomers from oligomers

Conclusions

- Major biorefinery residues can be efficiently converted in valorisable products via a flexible and cascading approach that involves state-of-the-art low-, medium and high temperature conversion technologies.

- LT aqueous extraction of (herbaceous) biomass yields a cellulase saver agent for cellulose → glucose hydrolysis.

- MT pyrolysis converts lignin-rich residues into a phenolic liquid that can be further processed for value-added chemicals and performance materials.

- HT combustion (and gasification) are suitable for biomass fines and dust.
  Next to heat and power, the residual ash minerals can be valorised as fertiliser.

Thank you for your attention

More information?
dewild@ecn.nl

ECN
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

Acknowledgments:
This work has been conducted as part of the EU-FP6 and FP7 projects BIOSYNERGY and BIOCORE and as part of the ongoing Dutch national project TKI-BBE LigniFAME. The financial support of the European Commission and the Dutch Ministry of Economic Affairs is gratefully acknowledged.


Questions?

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