Fast Pyrolysis of Lignocellulosic Biomass - a Versatile Tool for Making Chemicals

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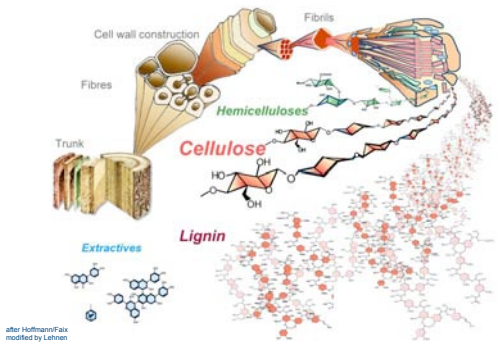
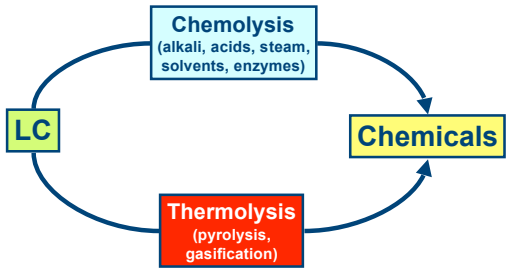
Content

- Fundamentals
- Production processes / biorefinery concepts
- Separation options
- Upgrading options
- „zero waste“ concept

Lignocellulose Constituents (Wood)

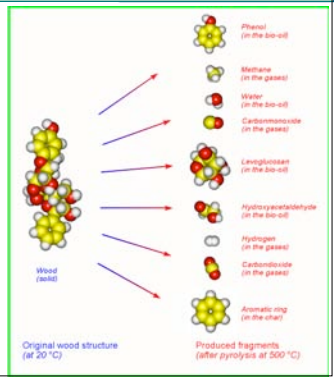


From Lignocelluloses to Chemicals



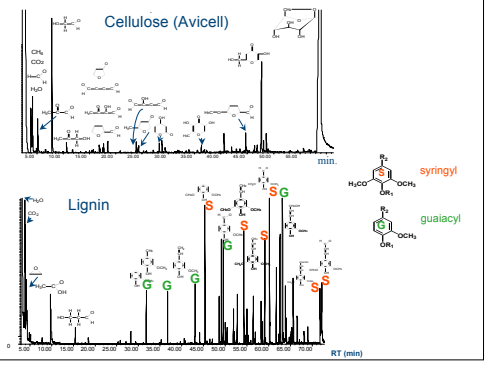
Fast Pyrolysis Principle

- Fast chemical degradation due to rapid heating in the absence of oxygen
- Process characteristics:
  - Temperature 500 °C
  - Pressure 1 bar
  - Particle size < 5 mm
  - t vapours < 2 s
- The main product is a liquid: Bio-Oil or Bio Crude Oil (BCO; approx. 70 wt.%)



Prins, W., 2007

Products of Fast Pyrolysis from Py-GC/MS



Biorefinery Concepts

- General
  - Use of lignocelluloses (LC): wood, residues (e.g. straw, bagasse)
  - no competion with food
  - restricted accessibility of biopolymers => pretreatment =>conversion

- Classic approach
  - **limited feedstock** selectivity (conditioning)
  - (pretreatment necessary with **pressure processes**, e.g. organosolv, steam)
  - separation & cleaning
  - Use **only after conversion** or modification (degradation to monomers, functionalisation, polymerisation)

- Thermochemical approach
  - **broad selection of raw LC** materials (e.g. straw, bark, DDGs, shells, etc.)
  - simple thermal treatment by fast-pyrolysis at **atmospheric pressure**
  - **decentral conversion - central refining** (separation & cleaning)
  - **Direct or indirect** use after modificationen

... and the Concept

LC Materials

↓

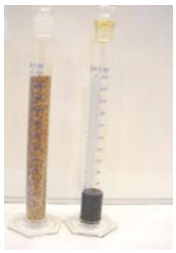
„Homogenization“ thermo-chemical conversion by fast-pyrolysis into Bio-Oil + Coke

↓

Generation of Chemicals

BCO Properties

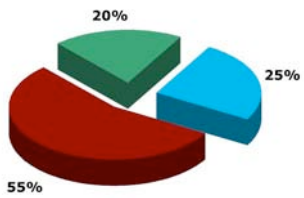
Analysis	Pyrolysis liquids	Light fuel oil (Tempera 15)
Water, wt %	20-30	0.025
Solids, wt %	0.01-1	0
Ash, wt %	0.01-0.2	0.01
Nitrogen, wt %	0-0.4	0
Sulfur, wt %	0-0.05	0.2
Stability	Unstable	Stable
Viscosity (40 °C), cSt	15-35	3.0-7.5
Density (15 °C), kg/dm ^{3}	1.10-1.30	0.89
Flash point, °C	40-110	60
Pour point, °C	-9- -36	-15
LHV, MJ/kg	13-18	40.3
pH	2-3	Neutral
Distillability	Not distillable	160-400 °C



1 MJ Feedstock 1 MJ Product

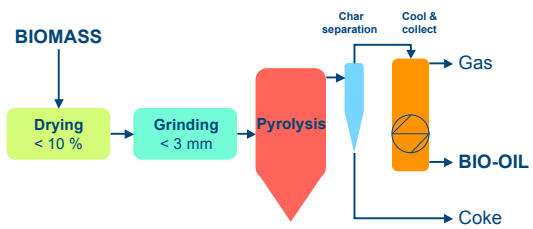
Prins, W., 2007

BCO Overall Composition

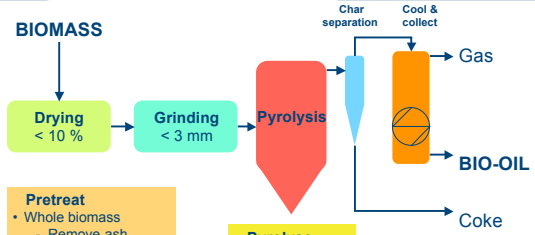


■ Monomers ■ Oligomers (pyrolytic lignin) ■ Water

Conceptual Pyrolysis Process



Process Modifications

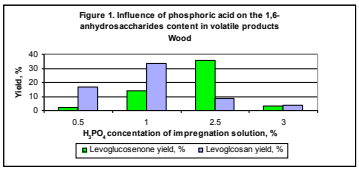


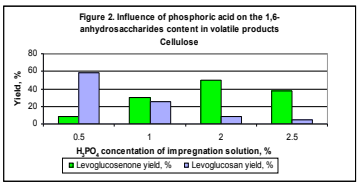
Pretreat
- Whole biomass
  - Remove ash
  - Add catalyst
- Separate bio-polymers into cellulose and lignin
  - Pulping
  - Biorefineries

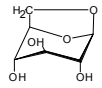
Pyrolyse
- Vary parameters
  - Temperature
  - Time
  - Pressure
  - Atmosphere
- Add catalysts

Upgrade
- Physically
  - Staged condens.
- Chemically
  - React, derivatize
  - De-oxygenate
  - Gasify to syngas

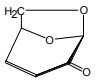
Pretreat: Acid Addition => Carbohydrate Synthons







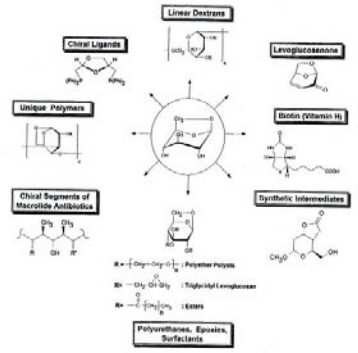
Levoglucosan



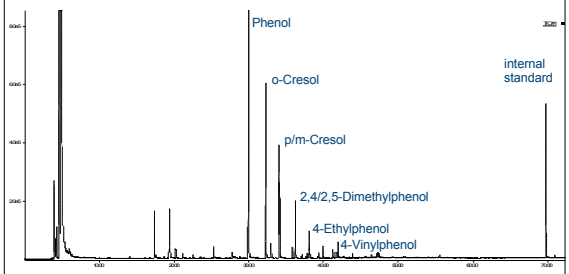
Levoglucosenone

Dobele, G., G. Rossinskaja, T. Dizhbite, G. Telysheva, D. Meier, and O. Faix, "Application of catalysts for obtaining 1,6-anhydrosaccharides from cellulose and wood by fast pyrolysis". Journal of Analytical and Applied Pyrolysis, 2003, 74, 1-2, 401-405.

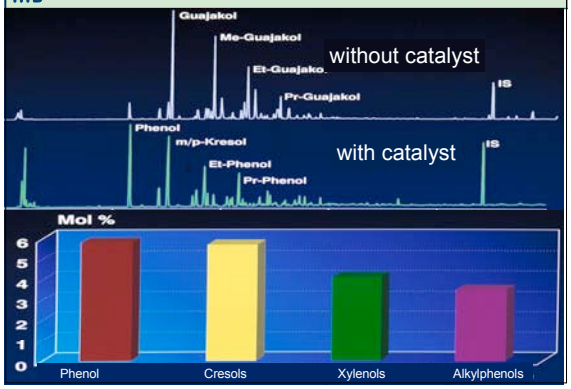
Possible Applications for Levoglucosan



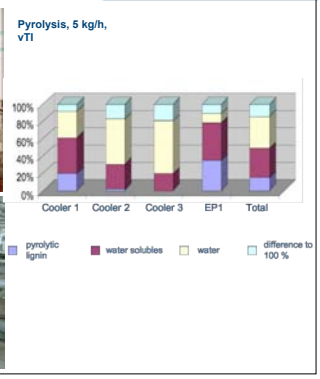
Pretreat: Separate => Phenols from Fast Pyrolysis of Kraft Lignin in a CFB



Pyrolysis: Pressurised H_2 and Catalyst



Upgrade Physically: Staged Condensation

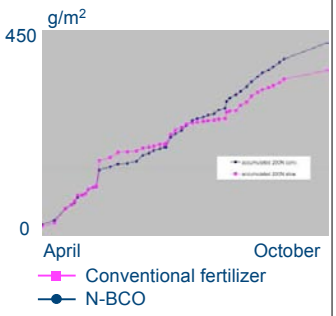


Upgrading Options for BCO

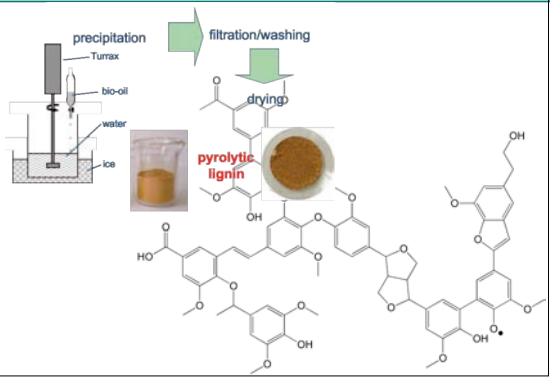
- **Reaction**
  - ***Add NH_3, urea*** =>Slow N-release fertilizer
  - ***Add lime*** => BioLime™ =>NOx/SO_2 reduction
- **Separation**
  - ***Add water*** => Flavour, Adhesives
  - ***Add high pressure steam*** (HPTT) => oxygenates, tar
- **Cracking**
  - ***Synthesis gas*** => FT-Diesel, MeOH, DME

N-modified BCO

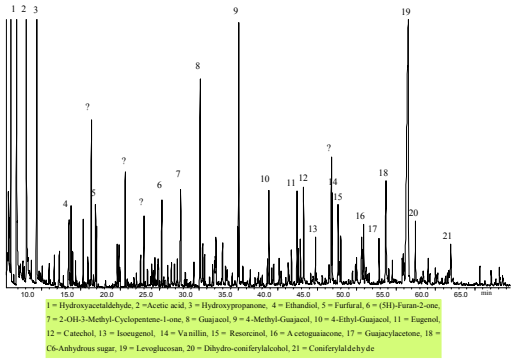
N-modified BCO



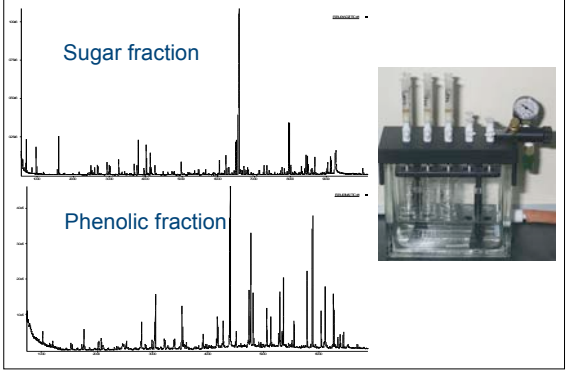
Add Water => Isolation of Pyrolytic Lignin => Resins



GC-Detectable Bio-Oil Components



SPE Sugars and Phenols

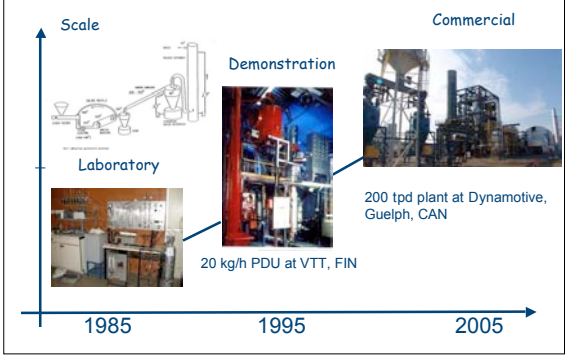


sc-CO_2 Extraction

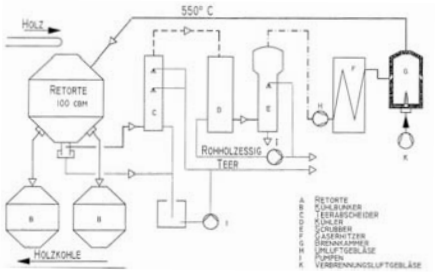
sc CO_2 mini-plant, vTI

sc-CO_2 Extracts

Evolution of Fast Pyrolysis Processes

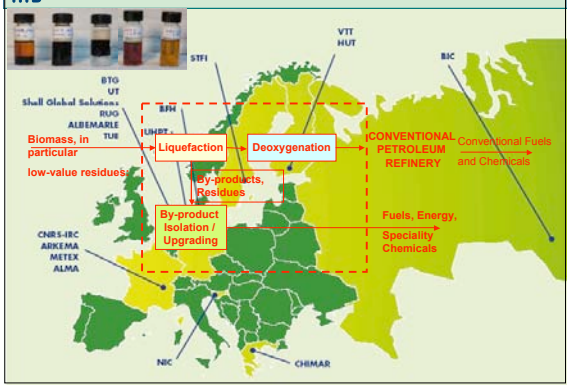


proFagus, Bodenfelde, Germany: Commercial Plant for Charcoal (35.000 tpy) & BCO (20.000 tpy)

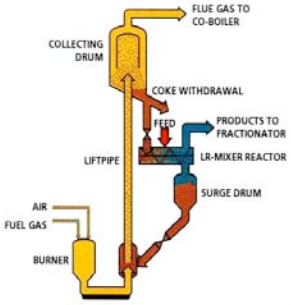


- Smoke aroma
- Maltol
- Cyclotene
- Acetic acid
- Tar oils
- Methanol

BCO Deoxygenation =>BIOCOUP (FP 6)



BCO Gasification => FZK-BIOLIQ => MeOH



„zero-waste“ Concept