UNIVERSITEIT GENT

FACULTY OF **ENGINEERING AND ARCHITECTURE**

ON THE REACTIVITY OF MONO-LIGNOL DERIVATIVES

SriBala Gorugantu [a], Julie Van Overloop [a], Diana C. Vargas [a,b], Hans-Heinrich Carstensen [a], Kevin M. Van Geem [a]*, Guy B. Marin [a]

[a] Ghent University, Laboratory for Chemical Technology, Technologiepark 914, 9052 Gent, Belgium
http://www.lct.UGent.be

[b] Laboratorio de Desarrollo de Energías Alternativas Departamento de Ingeniería Química, Universidad San Francisco de Quito, Casilla Postal: 17-12-841, Quito, Ecuador

*E-mail: Kevin.VanGeem@UGent.be

European Research Institute of Catalysis

Introduction

- Depleting petroleum sources
- Rising energy demands
- Environmental concerns

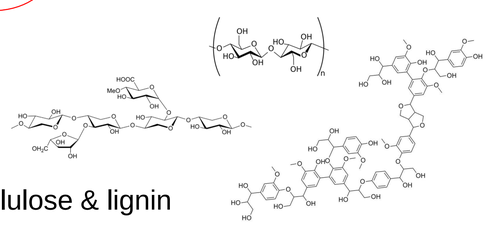
BIOMASS

- ✓ Sustainable
- ✓ Renewable

Products: Bio char | Bio oil | Non condensable gases

Lignocellulosic Biomass

- Most abundant
- No competition with food supply
- Wood, plants, crops, algae
- Mainly C, H, O as cellulose, hemicellulose & lignin



Fast Pyrolysis

- Thermal decomposition in the absence of oxygen
- Temperatures of 500 – 900°C in a few seconds
- Most promising method for bio oil production

Bio mass

- ✓ Fuel
- ✓ Fine chemicals

Motivation

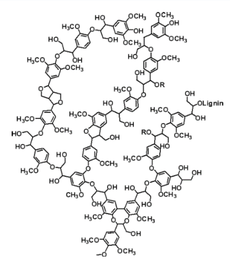
Until recently:

- Chemistry of biomass pyrolysis and more specifically lignin is not fully understood
- Influence of feedstock composition and process conditions on product distributions not clear in detail

→ Provide experimental data for the development of a mechanistic model for lignin pyrolysis using model compounds

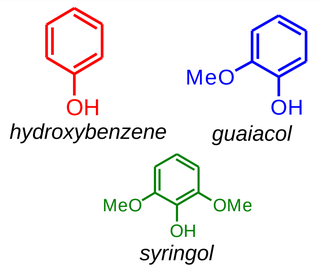
→ Contribute to a future with better control over product yields

Model compounds



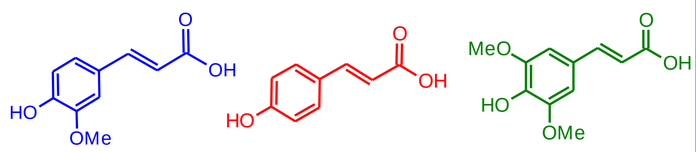
Lignin

Structure too complex for modelling

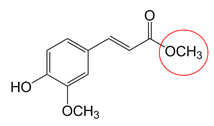


Model compounds

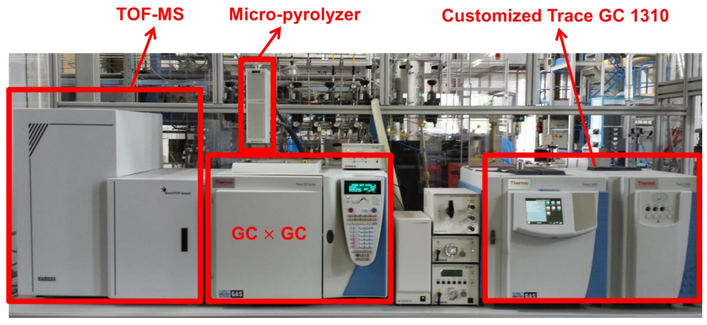
Lignin contains mainly **H**, **G**, **S** units

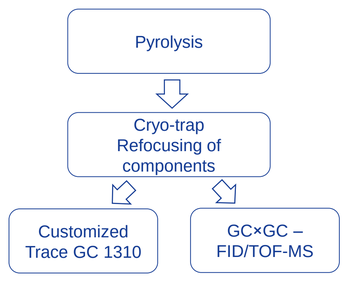


- Test influence of structural changes on pyrolysis chemistry
  - Acrylic acid group
  - Vinyl group (after CO_2 release)
  - Acrylic acid ester group



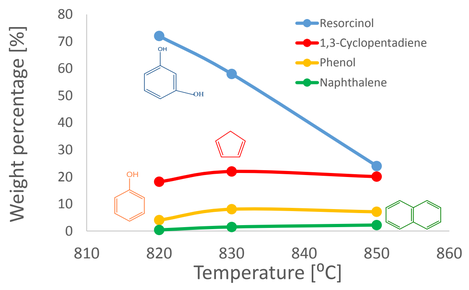
Tandem micro-pyrolyzer setup





Purpose

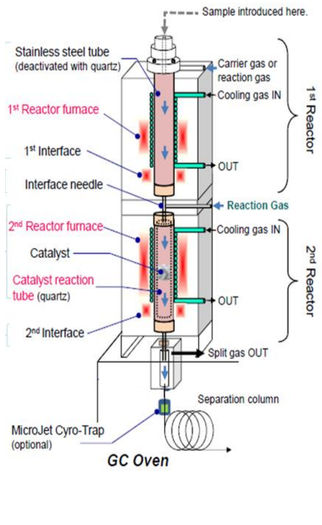
- Comprehensive and quantitative analysis of fast pyrolysis product distribution of polymers incl. biomass
- Determination of intrinsic rate coefficients for solid to gas transition
- Investigation of gas-phase reactions of solid model components at isothermal conditions



Example: Gas phase pyrolysis study of resorcinol

Micro-pyrolyzer

- Two stage reactor
- Solid, liquid or gas samples
  < 50 µg sample size
- Isothermal, linear and stepwise temperature profiles
- Large T-range:
  40 - 900 ^{0}C
- Cryo-trap for fast injection



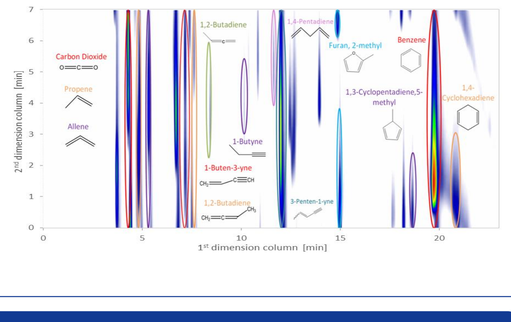
Analytics section

Customized Trace GC 1310 with 3 Detectors

- TCD-1
  Water, formaldehyde
- TCD-2 and PDD
  Permanent gases incl. H_2 and C2 - components

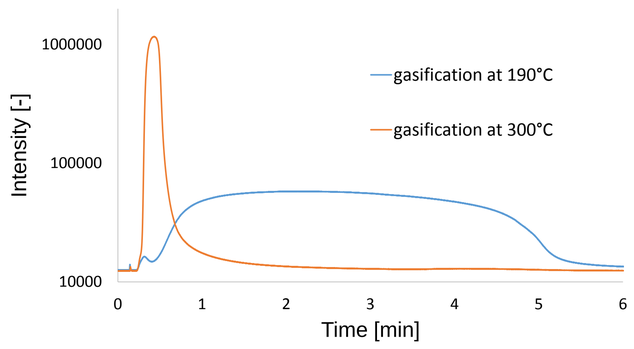
GC×GC - FID/TOF-MS

- Simultaneous identification and quantification



Preliminary results for ferulic acid

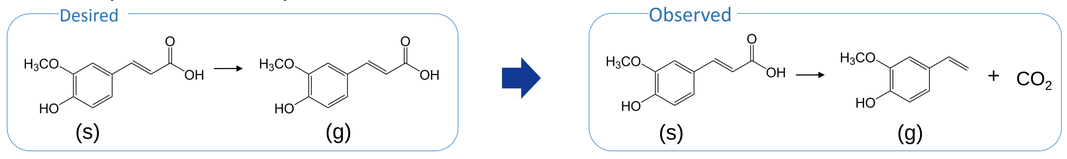
Gasification at low temperatures



Successful generation of short/long pulses of gas phase species

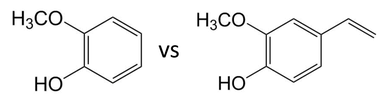
- Allows to control the ratio between uni- and bi-molecular chemistry in the 2nd reactor
- Ensures plug flow like conditions in the 2nd reactor

- Decomposition, not vaporization



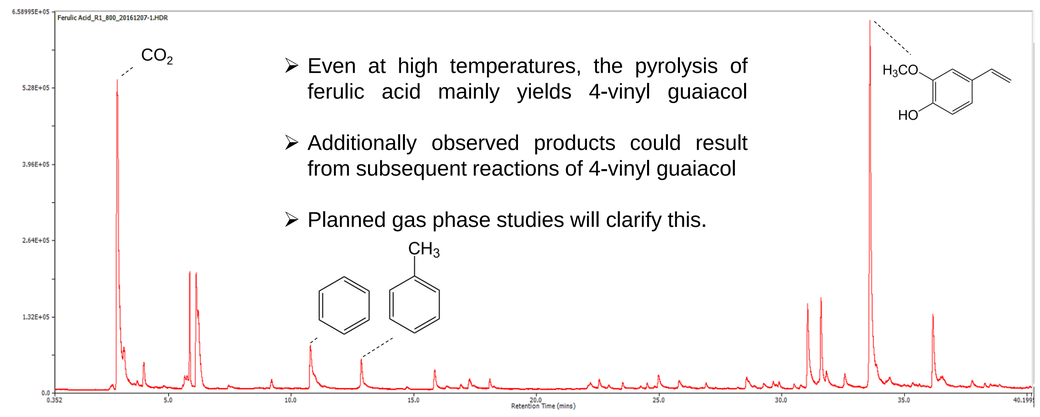
The decomposition is clean and quantitative – no ferulic acid signal detectable

- Use ferulic acid as precursor to study 4-vinyl guaiacol pyrolysis chemistry



***Hypothesis**: vinyl group will have a stabilizing effect on the radical, thus impacting its reactivity*

Pyrolysis at high temperatures



- Even at high temperatures, the pyrolysis of ferulic acid mainly yields 4-vinyl guaiacol
- Additionally observed products could result from subsequent reactions of 4-vinyl guaiacol
- Planned gas phase studies will clarify this.

TOF-MS chromatogram for the pyrolysis of ferulic acid at 800°C

Conclusions

- ✓ The micro-pyrolyzer setup offers a unique opportunity to study solid and gas phase chemistry of several lignin model compounds
- ✓ Qualitative and quantitative analysis can be performed with the GCxGC-FID and TOF-MS
- ✓ Ferulic acid can be gasified in preliminary experiments, although not without decomposition
- ✓ Ferulic acid is a suitable precursor to investigate the gas phase pyrolysis chemistry of 4-vinylguaiacol

Future work

- ✓ Further investigate vaporization/gasification of ferulic acid and the other model compounds
- ✓ Study the influence of a vinyl group on the reactivity as a function of temperature by comparing the lignin compounds phenol, guaiacol and syringol to their vinyl counterparts
- ✓ Investigate the influence of the presence of a methyl ester on reactivity
- ✓ Obtain complete experimental data sets to develop a kinetic model

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