Secondary vapor phase reactions of lignin derived oligomers obtained by fast pyrolysis of pine wood

Shai Zhou  
*Washington State University*

Brannan Pecha  
*Washington State University*

Armando McDonald  
*University of Idaho*

Sascha Kersten  
*University of Twente*

Roel Westerhof  
*University of Twente*

*See next page for additional authors*

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Authors
Shai Zhou, Brannan Pecha, Armando McDonald, Sascha Kersten, Roel Westerhof, and Manuel Garcia-Perez
SECONDARY VAPOR PHASE REACTIONS OF LIGNIN DERIVED OLIGOMERS OBTAINED BY FAST PYROLYSIS OF PINE WOOD

SHUAI ZHOU¹, BRENNAN PECHA¹, ARMANDO MCDONALD², SASCHA R.A. KERSTEN³, ROEL J.M. WESTERHOF³, MANUEL GARCIA-PEREZ³

¹ WASHINGTON STATE UNIVERSITY, ² UNIVERSITY OF IDAHO, ³ UNIVERSITY OF TWENTE
OUTLINE

- Introduction
- Objective
- Materials and Methods
- Analysis of Results
- Conclusions
Lignin structure (Softwood lignin)

- Ether linkages: β-O-4, α-O-4, and 4-O-5
- C-C linkages: β-5, 5-5, β-1, and β-β.
**INTRODUCTION**

**Lignin**
- The only renewable phenolic resource and second abundant polymer in nature.

**Pyrolysis**
- High temperature process (300-600°C) in which biomass is rapidly heated in the absence of oxygen.

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Lignin → Pyrolysis → Monomeric lignols (10-20%)
               Lignin oligomers (Pyrolytic lignin) (20-40%)
                             Char + Gases (difference)
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Lignin Pyrolysis: History and Current status

- Feedstock: Organosolv lignin; Kraft Lignin; Model compounds.
- Pyrolysis reactors: Py-GC/MS; Thermogravimetric Analyzer; Fluidized bed reactor; Auger reactor, Tubular reactor.
- Products studied: Mainly mono-phenols (very limited studies on lignin oligomers).
- Kinetic studies: (Phillip Britt (ORNL 1995-2007); Michael T Klein (MIT-U Delaware 1983-2009); Kawamoto – Saka (Kyoto U 2007-2011) (Models only describe the formation of monomers)
- Lignin oligomer characterization: (Dietrich Meier (U Hamburg 1987-2010)).
- Identification of lignin oligomers as one of the most reactive fractions during the pyrolysis of lignocellulosic materials (M. Garcia – C-Z Li – S. Kersten- R. Westerhof) (2005-2012)
INTRODUCTION

THERMO-CHEMICAL REACTIONS

- PRIMARY THERMOCHEMICAL REACTIONS

  REACTIONS IN SOLID PHASE
  - HOMOGENEOUS REACTIONS
  - HETEROGENEOUS REACTIONS

- SECONDARY THERMOCHEMICAL REACTIONS

  INTRA-PARTICLE (WITHIN A PARTICLE) REACTIONS
  HOMOGENEOUS REACTIONS
  HETEROGENEOUS REACTIONS

  INTER PARTICLE REACTION (BETWEEN PARTICLES)
  HETEROGENEOUS REACTIONS

HOMOGENEOUS REACTIONS IN VAPOR PHASE
Our current View of Lignin Pyrolysis

Lignin Structure

Clusters with one aromatic ring

Clusters 2-5 aromatic rings

Cluster 6+ aromatic rings

Low Temperature Reactions (180-300 °C)

High Temperature Reactions (300-600 °C)

Lignin monomers

Lignin liquid intermediate

Lignin Solid Residue

Cross-linked lignin

Char + CH₃OH + formaldehyde

Lignin monomers

Lignin Oligomers
Study of Secondary Reactions in Vapor Phase

Objectives:

- To study the effect of secondary reactions in vapor phase on the yield and composition of lignin oligomer.

Research questions to be answered:

- The nature of the transformations happening to the structure of lignin oligomers during secondary reactions in vapor phase.
MATERIAL AND METHODS

Study of Secondary Reactions in Vapor Phase

Pine Wood → Fluidized bed reactor (at 500°C) → Vapors

Tubular reactor
Residence time: 0-15 s
Temperature: 400, 500, 550°C

Pyrolysis oils → Pyrolytic Lignin

Analysis
(UV-Fluo, TGA, Py-GC/MS, FTIR, ESI-MS and 1H-NMR)

Fluidized Bed and Tubular Reactor (University of Twente)
MATERIAL AND METHODS

Pyrolytic lignin (lignin oligomer) extraction and analysis

Cold Water Precipitation

Bio-oil

Pyrolytic Lignin Extraction

Py-GC/MS

UV-Fluorescence

ESI-MS

FTIR

TG

NMR
One of the main causes for the effect of residence time on the yield of bio-oil is the dramatic effect of this variable on the yield of pyrolytic lignin. Based on this result we decided to study the effect of secondary homogeneous reactions in vapor phase on the composition of pyrolytic lignin.
ANALYSIS OF RESULTS

Study of Secondary Reactions in Vapor Phase

Analysis of lignin oligomer by Py-GC/MS: Guaiacols

Demethoxylation of Pyrolytic lignin
ANALYSIS OF RESULTS

Study of Secondary Reactions in Vapor Phase

Analysis of lignin oligomer by Py-GC/MS: CO₂ and Acetone

![Graph 1: Carbon dioxide (peak area/µg PL) vs. Vapor residence time (s) for 400°C, 500°C, 550°C.]

![Graph 2: Acetone (peak area/µg PL) vs. Vapor residence time (s) for 400°C, 500°C, 550°C.]

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ANALYSIS OF RESULTS

Study of Secondary Reactions in Vapor Phase

Analysis of lignin oligomer by $^1$H NMR analysis

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ANALYSIS OF RESULTS

Study of Secondary Reactions in Vapor Phase

Analysis of lignin oligomer by TGA

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ANALYSIS OF RESULTS

Study of Secondary Reactions in Vapor Phase

Analysis of lignin oligomer by TGA

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ANALYSIS OF RESULTS

Study of Secondary Reactions in Vapor Phase

Analysis of lignin oligomer by UV-Fluorescence

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ANALYSIS OF RESULTS

Study of Secondary Reactions in Vapor Phase

Analysis of lignin oligomer by UV-Fluorescence

Peak A

Peak B

Peak C
ANALYSIS OF RESULTS

Study of Secondary Reactions in Vapor Phase

Analysis of lignin oligomer by ESI-MS

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ANALYSIS OF RESULTS

Study of Secondary Reactions in Vapor Phase

Reaction mechanism of lignin oligomer secondary reactions

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INTRODUCTION

Our current View of Lignin Pyrolysis

Lignin Structure

Clusters with one aromatic ring

Clusters 2-5 aromatic rings

Cluster 6+ aromatic rings

Lignin monomers
Lignin Liquid Intermediate
Lignin Solid Residue

Lignin monomers
Lignin Oligomers

Cross-linked lignin

Char + CH₃OH + formaldehyde

Low Temperature Reactions (180-300 °C)

High Temperature Reactions (180-300 °C)

Perhaps over 500 °C
Conclusions:

- When pyrolytic lignin is exposed to temperatures over 500 °C in vapor phase, secondary reactions occur resulting in the reduction of the yield of this fraction.
- Vapor temperature and residence time are the main parameters affecting conversion of the pyrolytic lignin.
- In the range of temperatures studied (400-550 °C) cracking (responsible for the reduction of molecular weight) and polycondensation reactions (responsible for the increase in molecular weight) compete.
THANK YOU! & QUESTIONS?