# Predicting Sawdust Pyrolysis Yields Using the CPD Code with a Tar Cracking Model

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BYU

# Outline

- Importance of pyrolysis modeling
- CPD model background
- Changes made to use CPD model for sawdust
- BYU flat-flame burner sawdust experiments
- Comparison of model with literature

# Why Modeling Pyrolysis Is Important

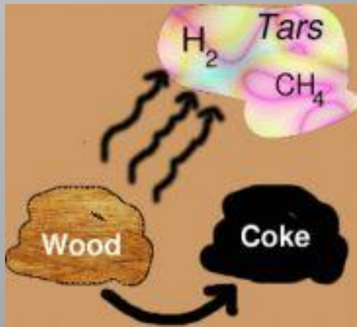
- Pyrolysis – thermal decomposition of solid fuel into permanent gases, condensable vapors, & solid residue

- Heating of particles is the first step in thermal conversion of solid particles, and influences subsequent steps like combustion and gasification.

- Provides predictive models for processes for converting renewable resources to clean fuels and chemical feedstocks

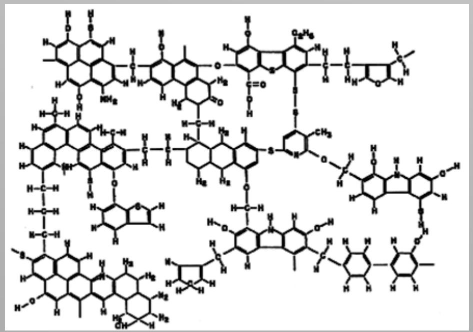
  Ex) maximum organic liquid yields for use as low grade fuel

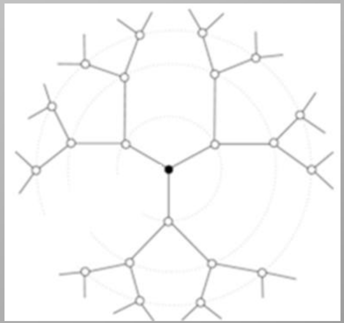
  Ex) gasify biomass and combust gas in turbine



# CPD Model

- Originally developed to predict coal devolatilization and is based on coal structure
- Coal is described as a series of aromatic clusters connected by labile bridges.
- Uses percolation statistics for Bethe lattices to predict bridges broken and detached clusters





# CPD Model

- Predicts amount of tar formation and cross-linking
- Uses structural and kinetic parameters as inputs to the code
- Calculates pyrolysis yields as a function of time, temperature, heating rate, and pressure

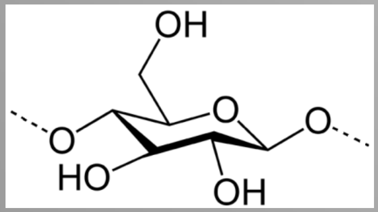
# Composition of Biomass

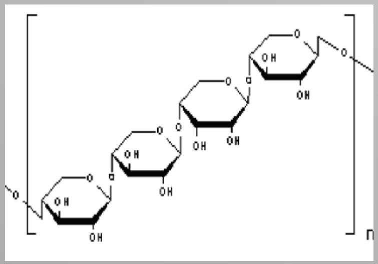
- Biomass is mainly comprised of cellulose, hemicellulose, and lignin

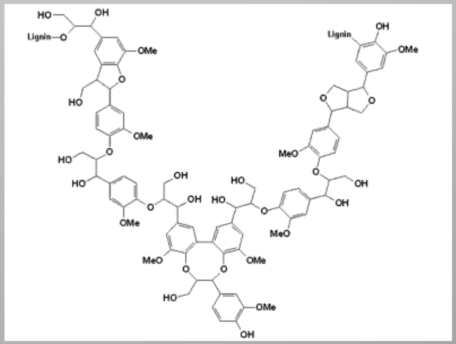
__Cellulose__ provides support to the primary cell wall with its strong, crystalline structure

__Hemicellulose__ is a group of carbohydrates that surround the cellulose fibers in plant cells

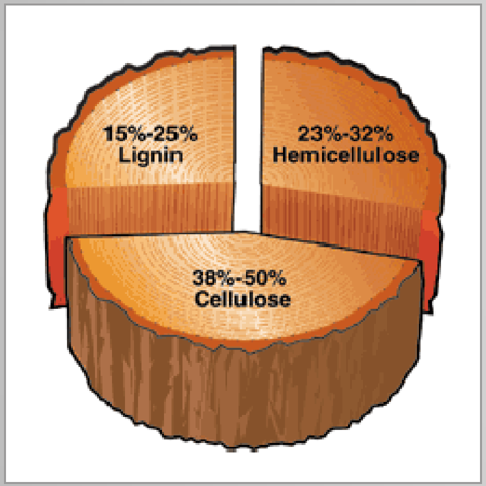
__Lignin__ is found mostly between the cell walls of plants and has a very stable aromatic structure like low rank coals





# Basic Idea of Using CPD Code for Sawdust




- Sawdust pyrolysis is modeled as a weighted average of the individual components of cellulose, hemicellulose, and lignin assuming biomass components in a mixture behave in the same way as they do separately

- We simply need the composition of the biomass and CPD parameters for biomass components

# How to Obtain Biomass Composition

1) Get sample analyzed by a lab

2) Find the data in literature

3) Use empirical equations:

$$\text{Cellulose} = -1019 + 293.8\,(O/C) - 187.6\,(O/C)^2 + 65.1\,(H/C) - 19.3\,(H/C)^2 + 21.7\,(VM) - 0.13\,(VM)^2$$

$$\text{Lignin} = 612.1 + 195.4\,(O/C) - 156.5\,(O/C)^2 + 511.4\,(H/C) - 177\,(H/C)^2 - 24.3\,(VM) + 0.15\,(VM)^2$$

C.D. Sheng and J.L.T. Azevedo, Modeling Biomass Devolatilization Using the Chemical Percolation Devolatilization Model for the Main Components, *Proceedings of the Combustion Institute* (2002), p. 29.

# Parameters for Biomass Components

| Kinetic Parameter | Cellulose | Hemi-Cellulose | Lignin |
|---|---|---|---|
| $E_b$, kcal/mol | 51.5 | 51.5 | 54.0 |
| $A_b$, $s^{-1}$ | 1.0E+18 | 1.0E+18 | 2.60E+15 |
| $\sigma_b$, kcal/mol | 3.0 | 3.0 | 3.972 |
| $E_g$, kcal/mol | 42.0 | 42.0 | 66.0 |
| $A_g$, $s^{-1}$ | 8.23E+12 | 8.23E+12 | 3.0E+15 |
| $\sigma_g$, kcal/mol | 3.0 | 3.0 | 4.776 |
| $\rho$ | 5.0 | 5.0 | 3.9 |
| $E_c$, kcal/mol | 0.0 | 0.0 | 0.0 |
| $E_{cross}$, kcal/mol | 65.0 | 65.0 | 55.68 |
| $A_{cross}$, $s^{-1}$ | 3.0E+15 | 3.0E+15 | 3.0E+15 |

| Structural Parameter | $MW_1$ | $M_d$ | $p_o$ | $\sigma + 1$ | $c_o$ |
|---|---|---|---|---|---|
| Cellulose | 81 | 22.67 | 1.0 | 3.0 | 0.0 |
| Hardwood hemi-cellulose | 77.5 | 21.5 | 1.0 | 3.0 | 0.0 |
| Softwood hemi-cellulose | 81 | 22.67 | 1.0 | 3.0 | 0.0 |
| Hardwood lignin | 208 | 39 | 0.71 | 3.5 | 0.10 |
| Softwood lignin | 186 | 34 | 0.71 | 3.5 | 0.10 |

The CPD model can now be used!

H.R. Pond, T.H. Fletcher and L.L. Baxter, Prediction of tar and light gas during pyrolysis of black liquor and biomass, *Proceedings of the Third Annual Joint Meeting of the U.S. Sections of the Combustion Institute* Chicago (2003).

# Secondary Tar Cracking
## Tar → Gas

- Secondary tar-cracking kinetics are applied to the predicted CPD tar yields of the individual components of cellulose, hemicellulose, and lignin

- The cracked tar is added to the gas, and yields are determined by a weighted average of the individual biomass components.

- First-order tar-cracking kinetics came from Rath's work

Rath J, Stauddinger G. Cracking Reactions of Tar from Pyrolysis of Spruce Wood. Fuel 2001;80:1379-89.

# Temperature Affects Tar Yields

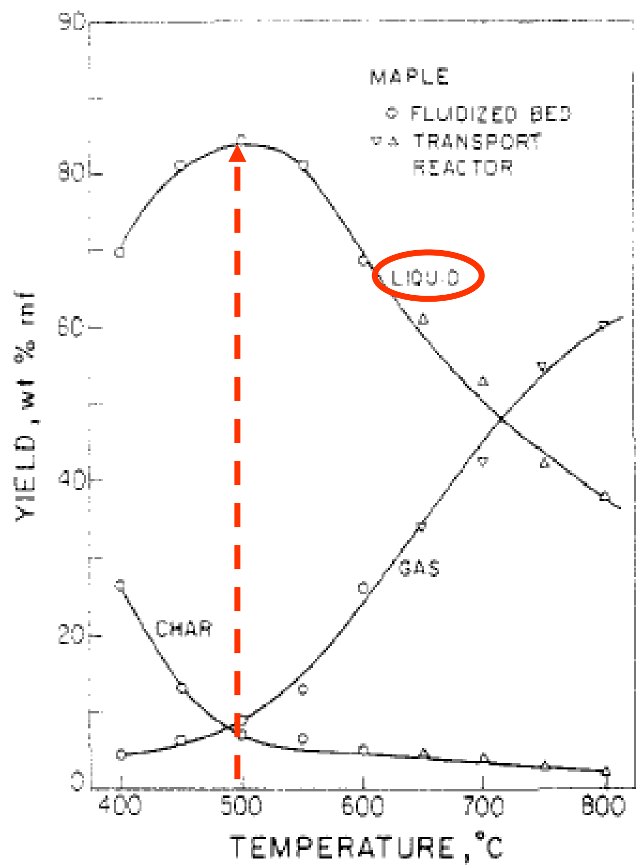
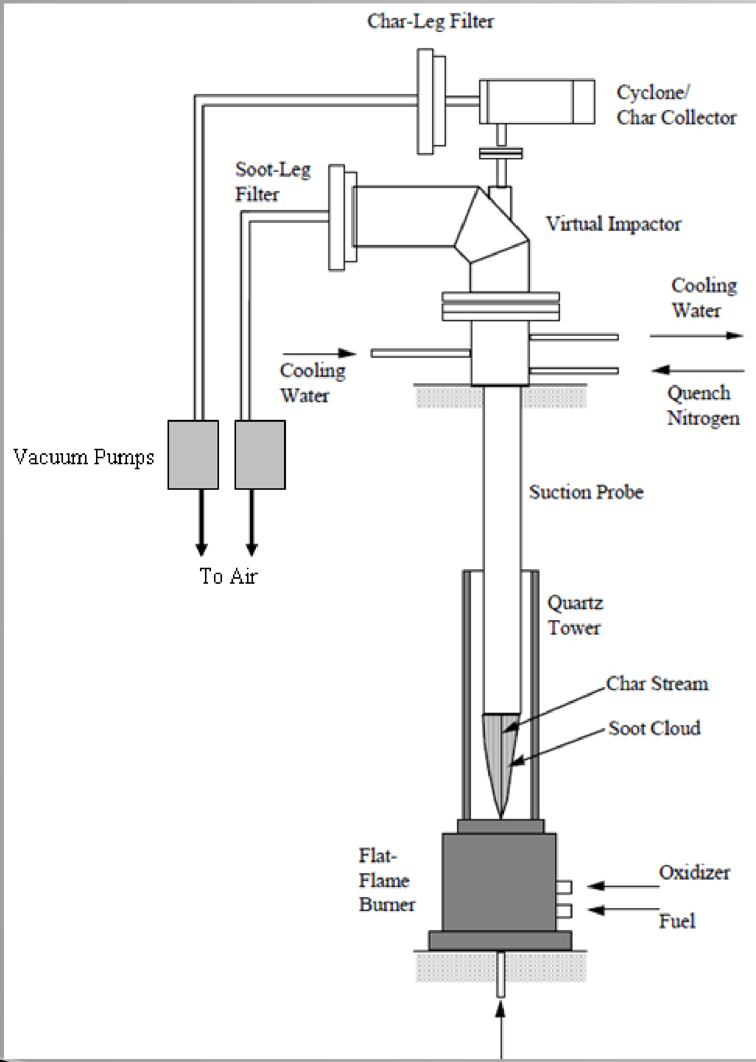


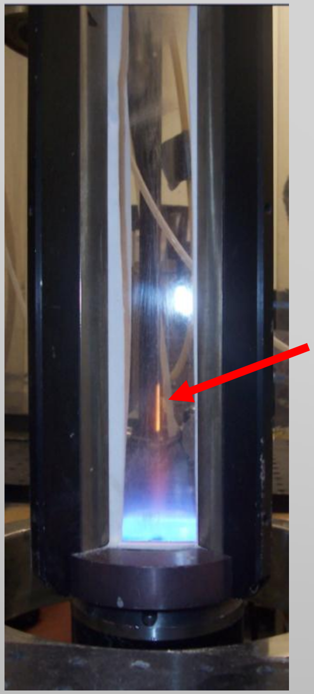

**Figure 9.** Product yields from Eastern red maple from two reactors: 0.5-s vapor residence time.

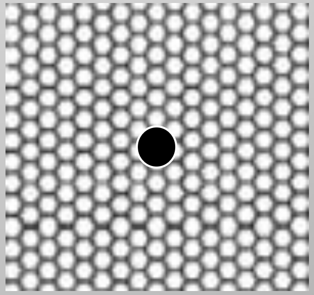
- Tar cracks at high temperature, and turns to gas.
- Tar cracking becomes important above 500  C

Scott, S. S.; Piskorz, J.; Radlein, D. The Role of Temperature in the Fast Pyrolysis of Cellulose and Wood. *Ind. Eng. Chem. Res.* 1988, *27*, 8.

# BYU's Atmospheric Flat-Flame Burner

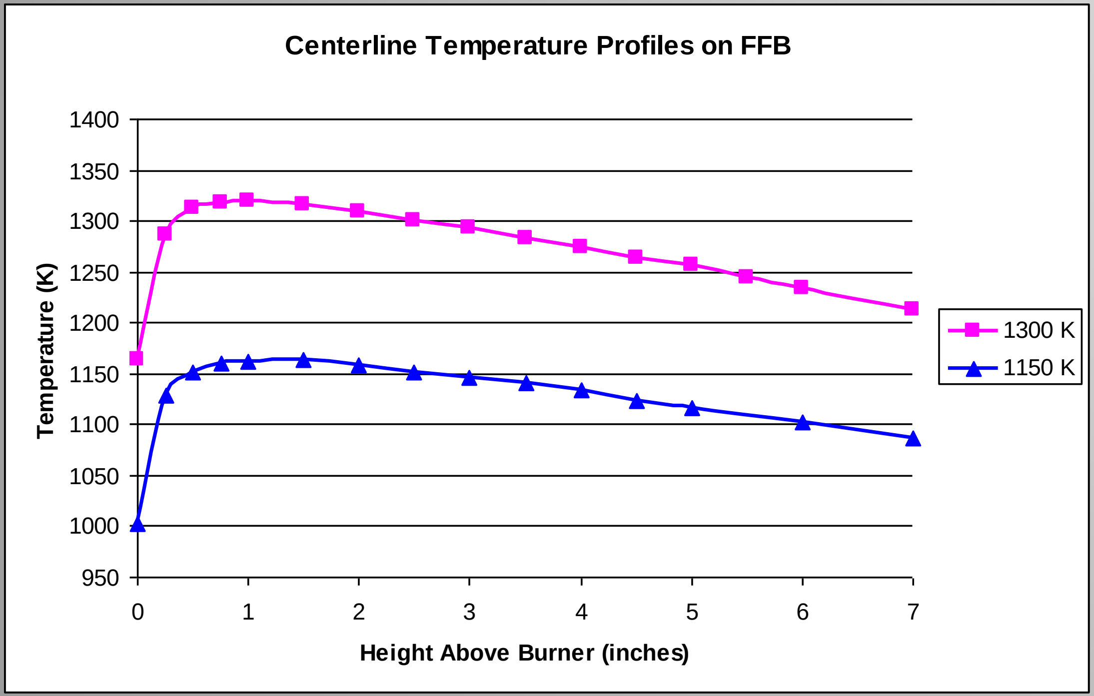




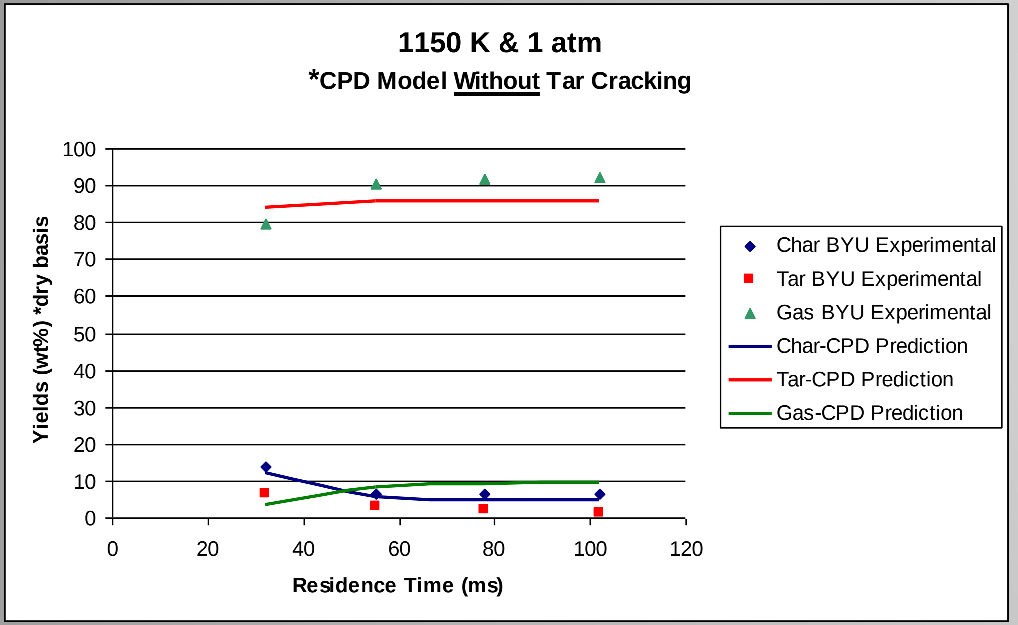
- Used to measure sawdust pyrolysis yields

# BYU Flat-Flame Burner



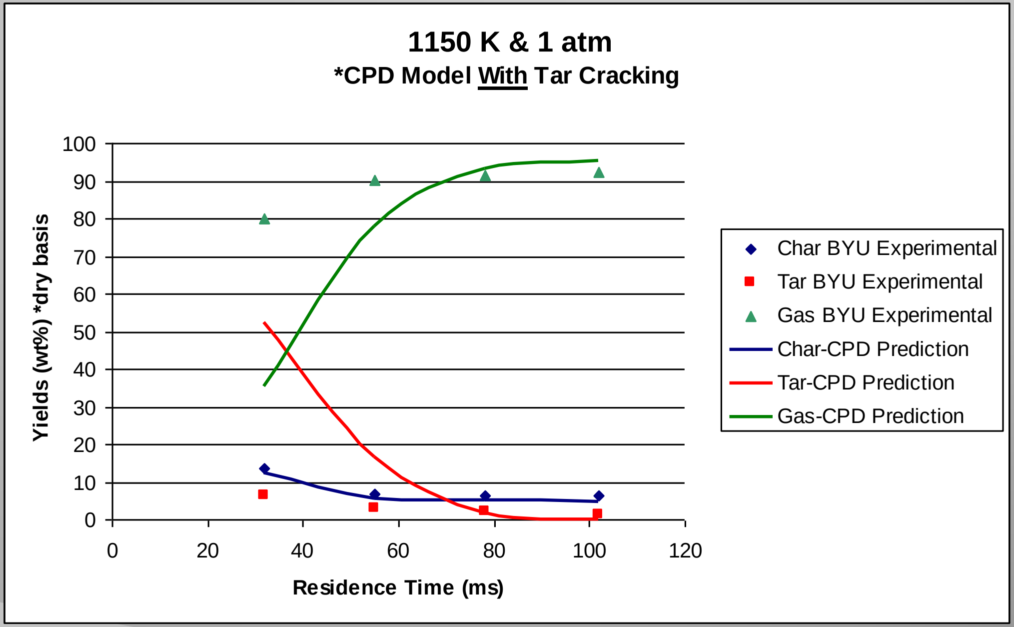

Particle residence times obtained using a high-speed camera

# Model Comparison with Experiments




- BYU
- Flat-flame burner
- 1150 & 1300 K
- 45-75 micron
- Sawdust

Points = experiment
Line = model



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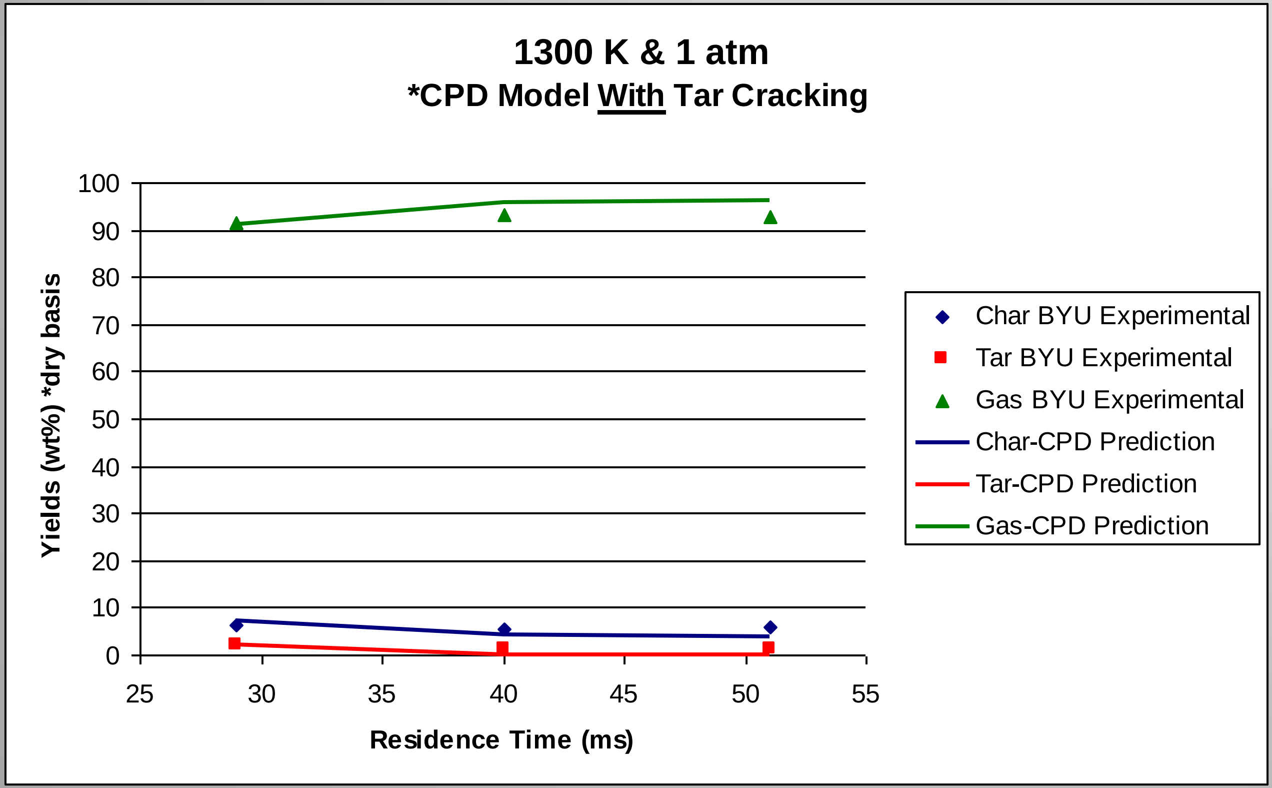
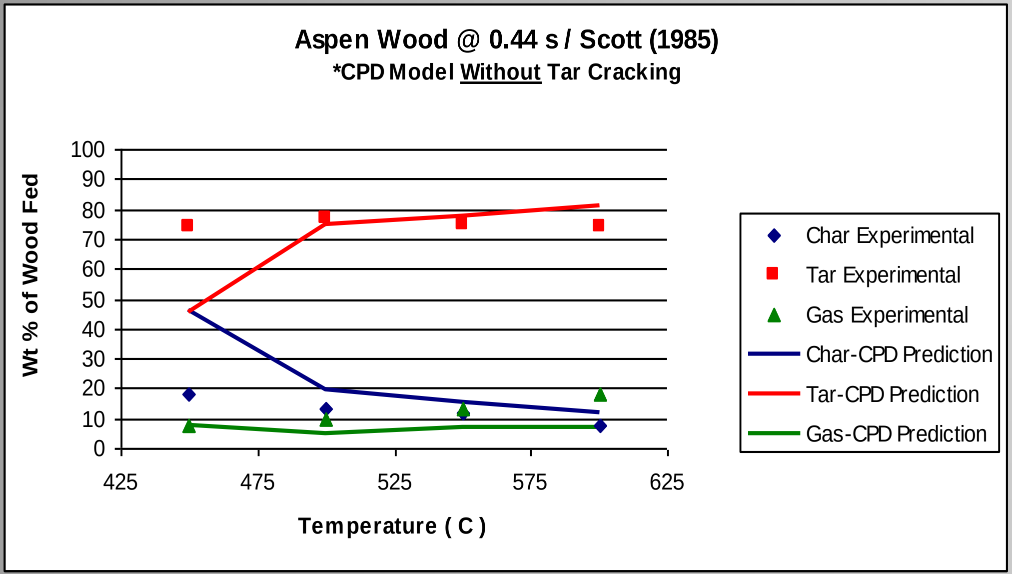
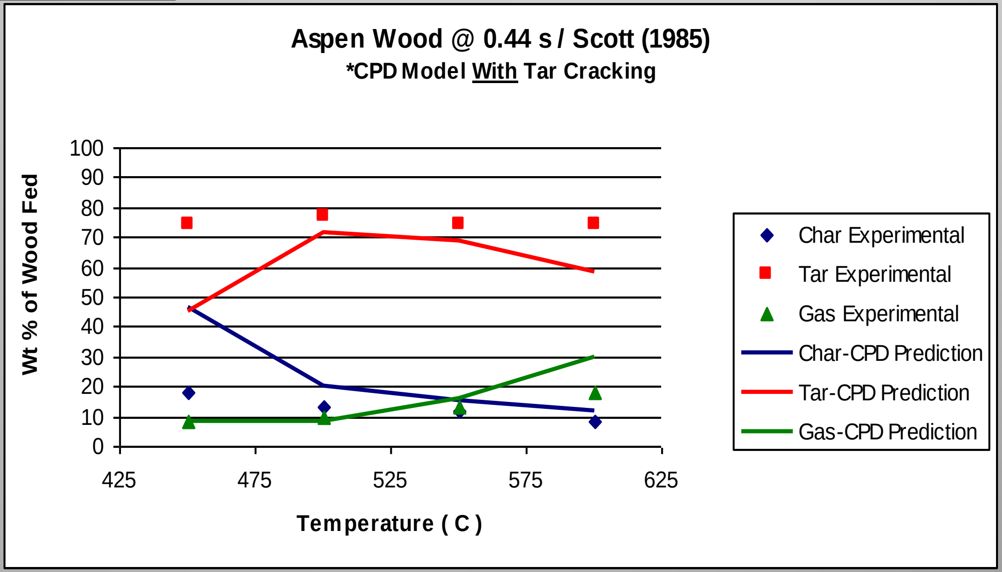


# Model Comparison with Literature



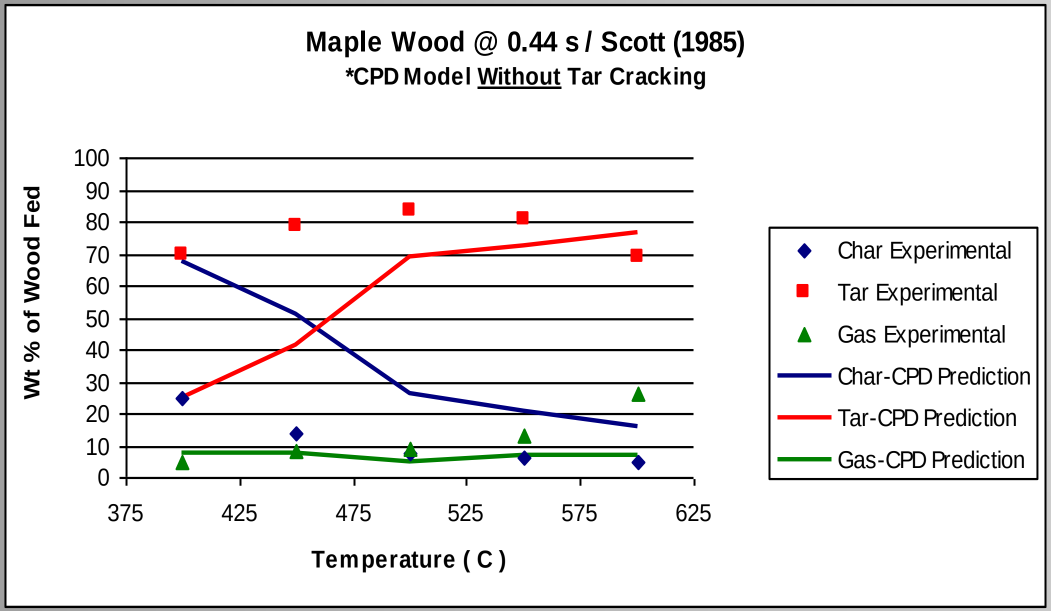

- University of Waterloo
- Fluidized bed at 1 atm
- Flash pyrolysis of maple, poplar-aspen, and aspen bark
- 0.44 sec residence time
- 105-250 μm

<u>Aspen Wood</u>

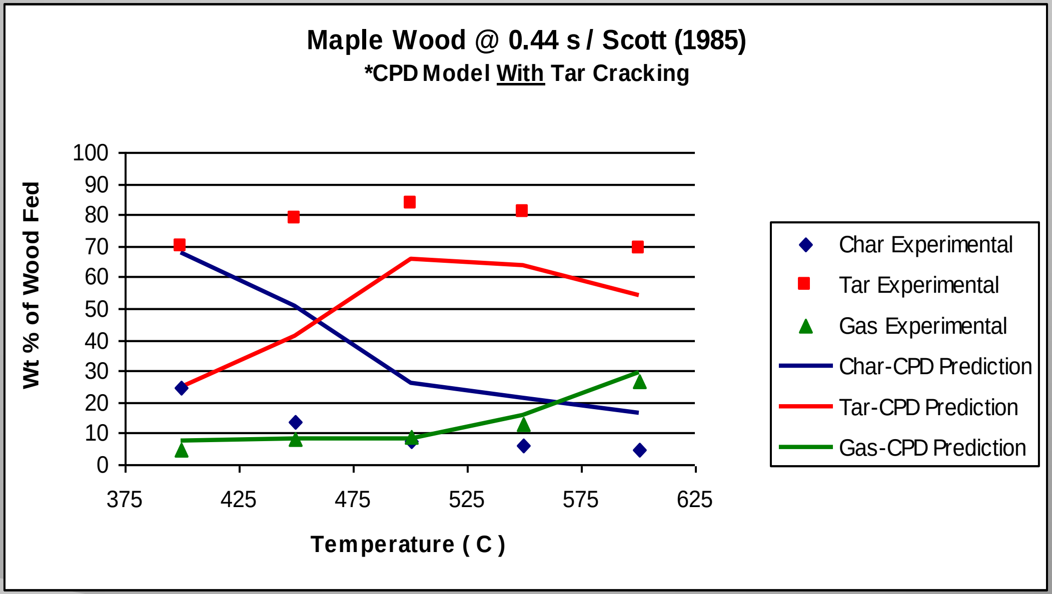



D.S. Scott, J. Piskorz and D. Radlein, Liquid Products from the Continuous Flash Pyrolysis of Biomass, *Ind Eng Chem Process Des Dev* 24 (1985), pp. 581–586.

# Model Comparison with Literature




Maple wood



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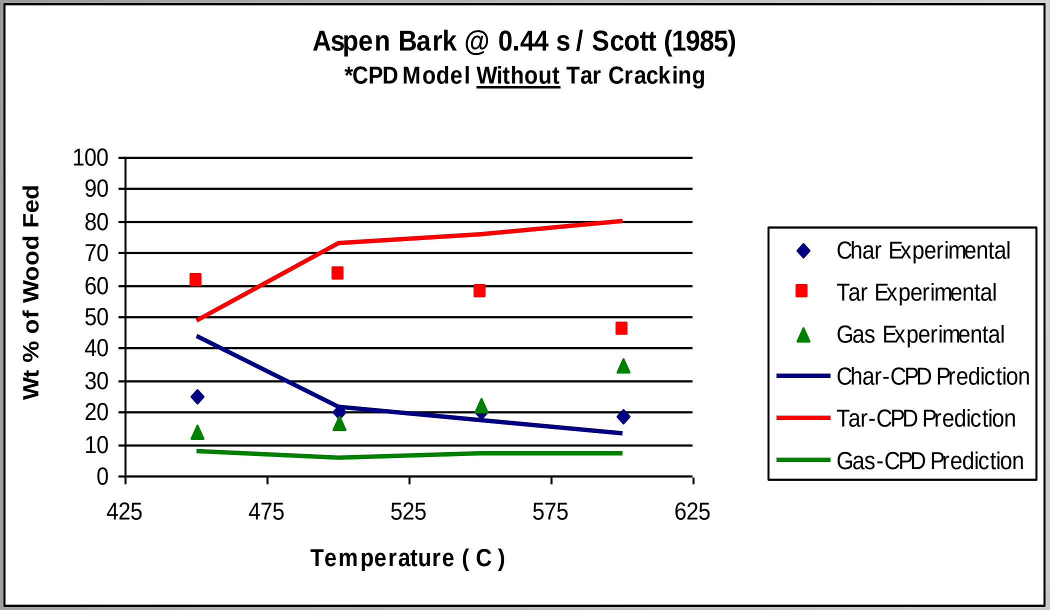
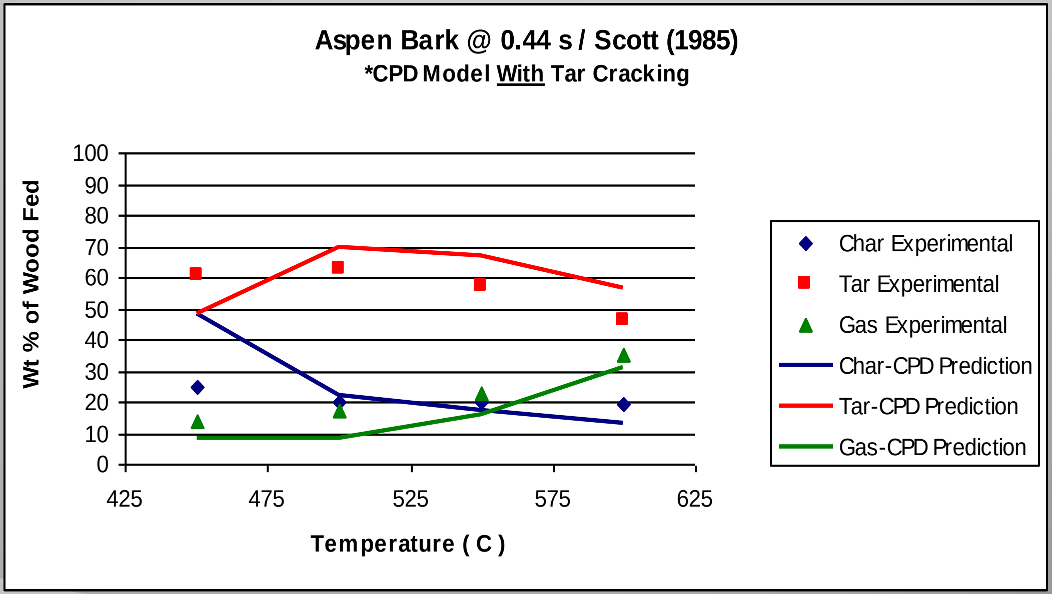



Aspen Bark



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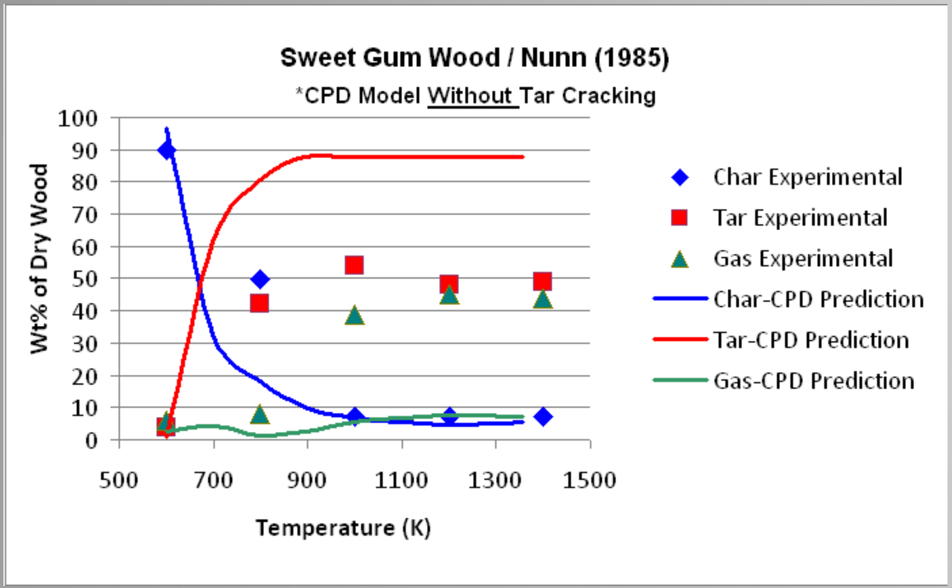
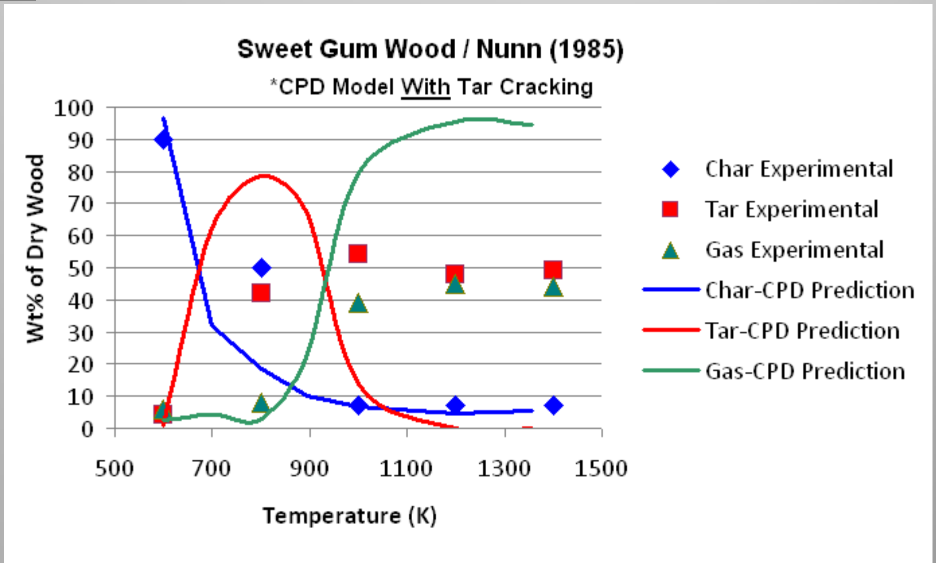



- MIT
- Electrical screen heater at 5 psig
- 1000 K/s heating
- 200 K/s cooling
- 45-88 μm

## Sweet Gum Wood




Nunn, T. R.; Howard, J. B.; Longwell, J. P.; Peters, W. A. Product Compositions and Kinetics in the Rapid Pyrolysis of Sweet Gum Hardwood. *Ind. Eng. Chem. Process Des. Dev.* 1985, *24*, 836.

# Summary

- Using CPD code to model biomass pyrolysis has potential
- Tar & gas yields could perhaps be improved by including secondary tar-cracking kinetics of sawdust, and not of the individual components of biomass
- CPD model predicts the correct trends in sawdust pyrolysis yields
- The model is not perfect, but can still be used as a tool