Prediction of Tar and Light Gas During Pyrolysis of Black Liquor and Biomass

Harland R. Pond

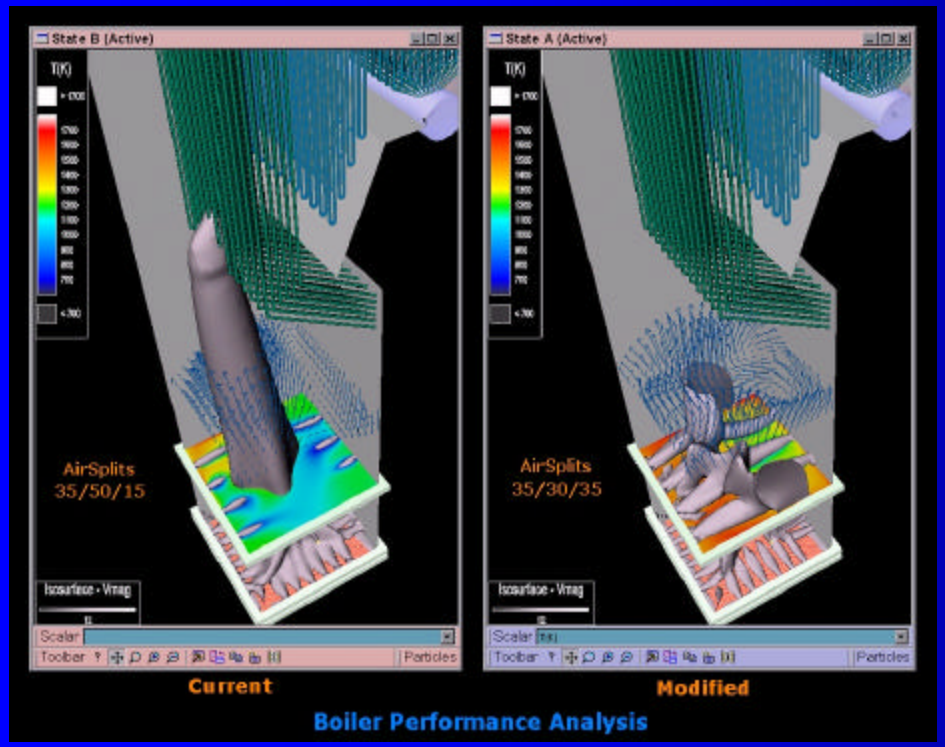
Thomas H. Fletcher

Larry L. Baxter

Chemical Engineering Department

Brigham Young University

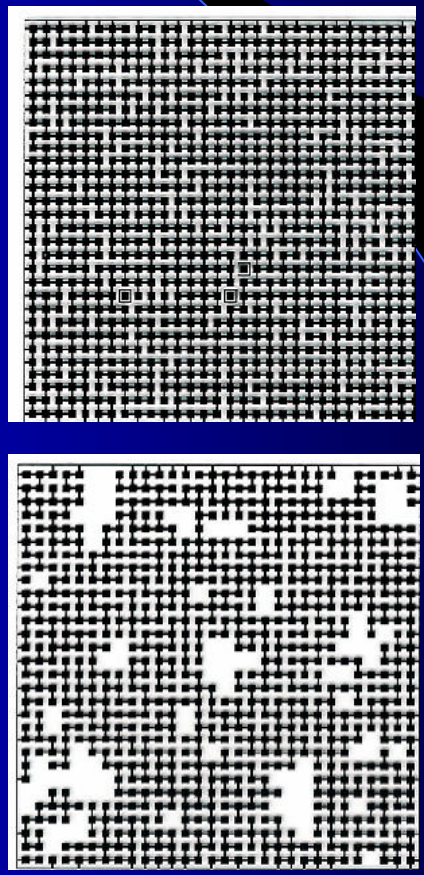
Model Background



- Creation of model characterizing pyrolysis of biomass fuels
- Model combines individual components
- Inclusion of model in FLUENT and PCGC – 3 combustion packages

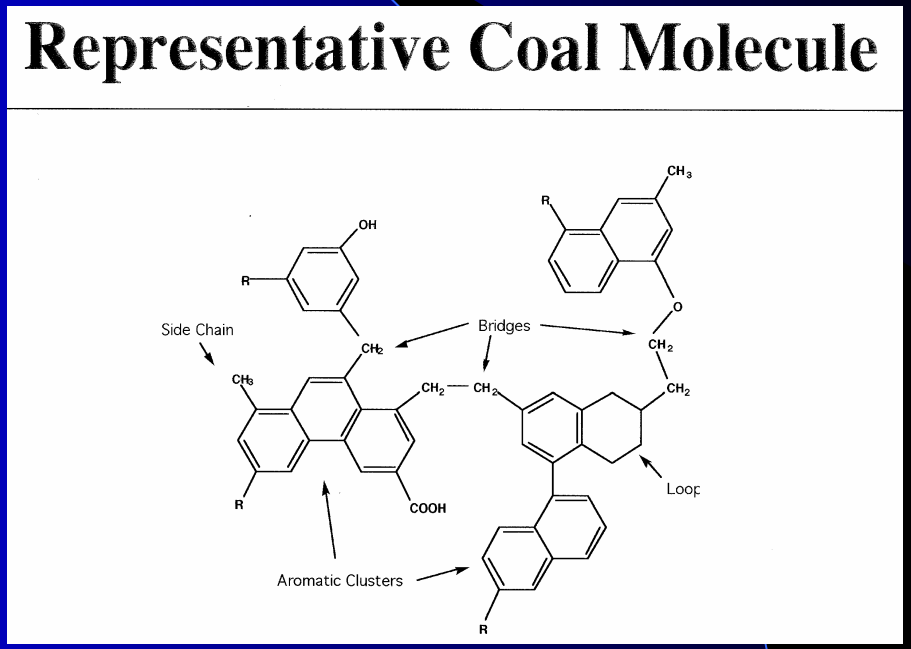
Chemical Percolation Devolatilization (CPD) Model Approach

- CPD looks at a lattice of coal rings
- Focuses on bridges between rings and their length, energy and statistical breaking
- Includes ring structure, bond energy and vapor pressure
- Function of coal type, heating rate, temperature and pressure



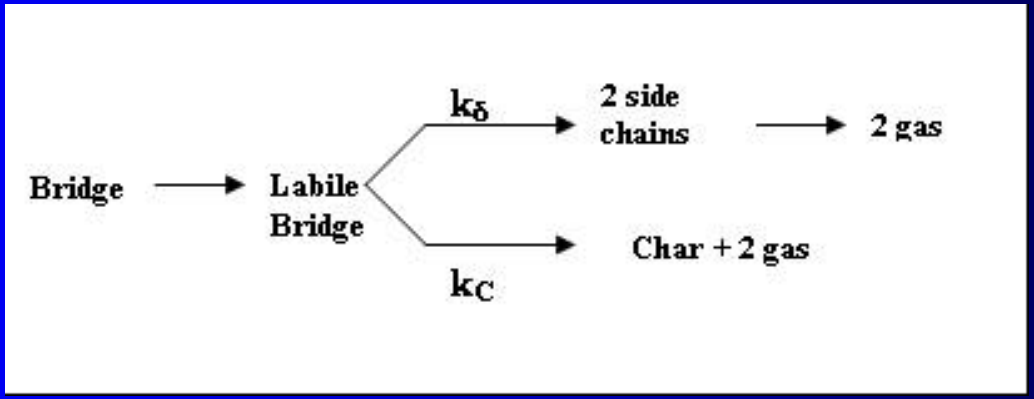
CPD Lattice

- Structural Parameters required
  - Number of attachments per cluster ($s + 1$)
  - Fraction that are stable bridges (p_o)
  - Molecular weight per cluster (M_{CL})
  - MW per side chain (M_d)



CPD Parameters

- Structural parameters
  - M_d, p_o, M_{CL}, $s + 1$,elemental analysis
  - Fraction of char links (c_o)
- Kinetic Parameters
  - Kinetics for two competing reactions



Model Goals

- Each biomass fuel consists of cellulose, lignin and hemi-cellulose (hard- and softwood)
- Black liquor consists of Kraft lignin and residual carboxylic acids
- Develop kinetic and structural parameters for each component
- Use mass weighted distribution of CPD predictions for individual components

CPD Application to Biomass

- Linear structure of cellulose is modeled with c_o and p_o
- Bridge weights for cellulose type components changed to model ether linkages

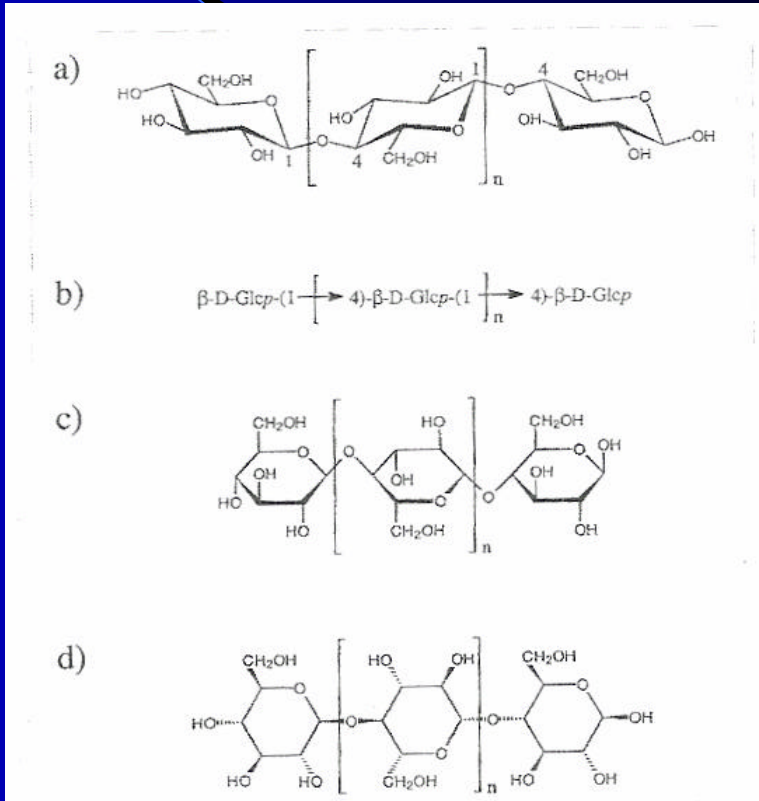
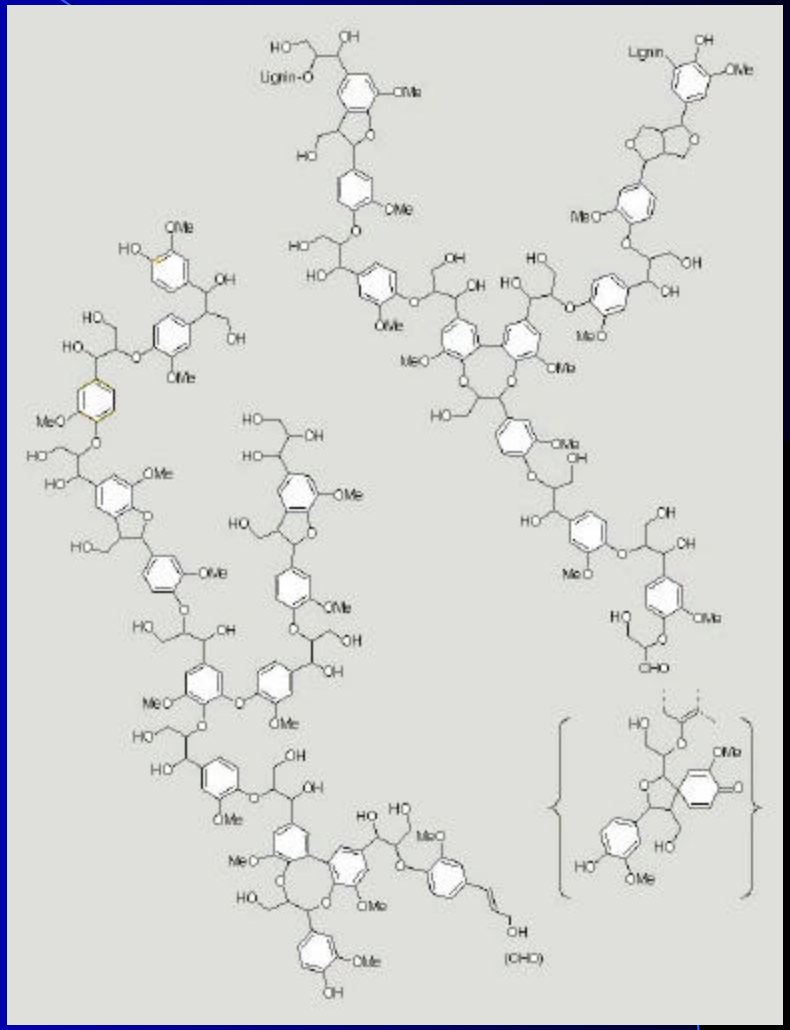


Figure 13. Structure of cellulose. Stereochemical (a), abbreviated (b), Haworth perspective (c), and Mills' (d) formulas.

Lignin Chemical Model

- Lignin is similar to low rank coal with lattice structure
- Coniferyl, sinapyl and p-coumaryl acids base cluster in the CPD model

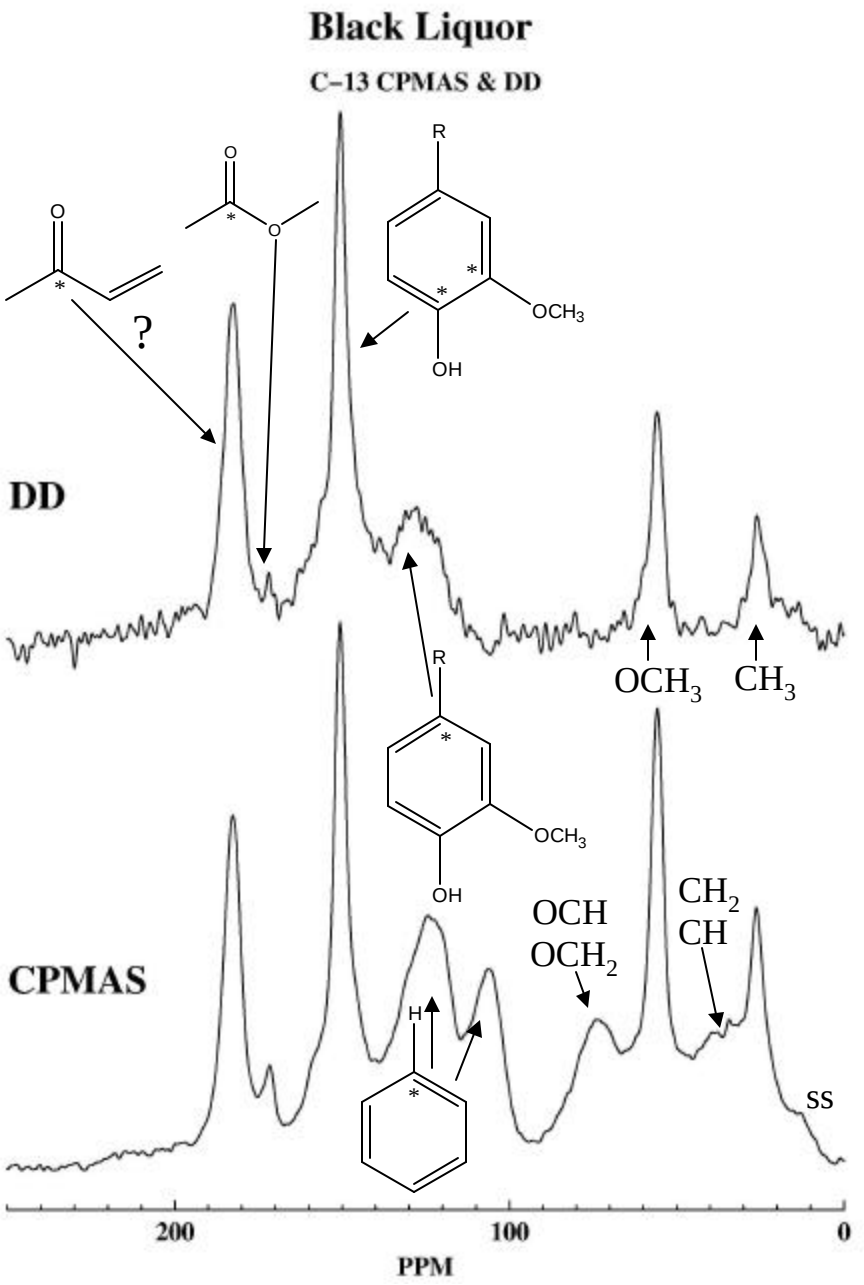


Setting Parameters

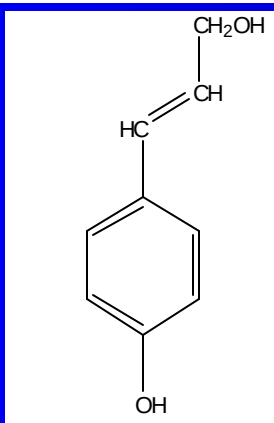
- Structural parameters (p_o, M_{CL}, M_d *and* $s+1$) set with ^{13}CNMR and theory research
- Kinetic parameters taken from previous research (Sricharoenchaikul , Fletcher, Serio, Azevedo)
- 3 parameters need to be fitted to volatile yield data (c_o, E_c, r)

^{13}CNMR Analysis on Black Liquor

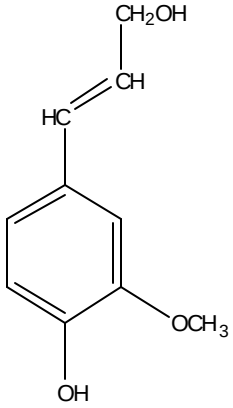
- Structural parameters for black liquor composite obtained from ^{13}CNMR analysis
- Parent samples sent to Pugmire and Solum at the University of Utah for analysis
- Reacted samples from flat flame burner experiments were sent for analysis (Webster, BYU 2002)


Black Liquor
C-13 CPMAS & DD
R
O
O
O
*
*
*
OCH3
OH
?
DD
OCH3
CH3
R
*
OCH3
OH
CPMAS
OCH
OCH2
CH2
CH
H
*
SS
200
100
0
PPM

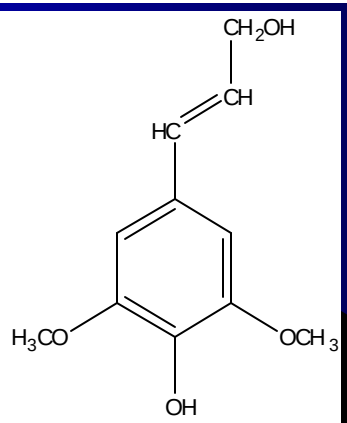
Lignin Precursors and Oxidation Products



p-coumaryl alcohol



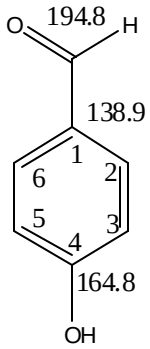
coniferyl alcohol



sinapyl alcohol

{6,2} 129.7,127.1

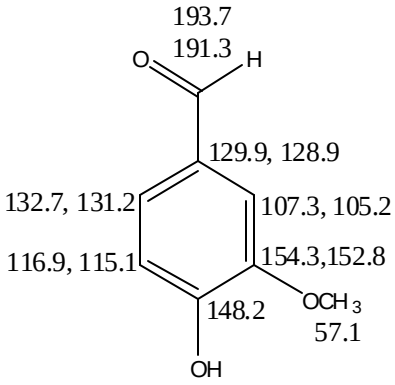
{3,5} 117.8,115.4



p-hydroxybenzaldehyde

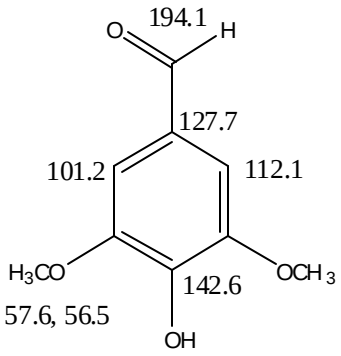
193.7

191.3



vanillin

{3,5} 148.2, 148.9



syringaldehyde

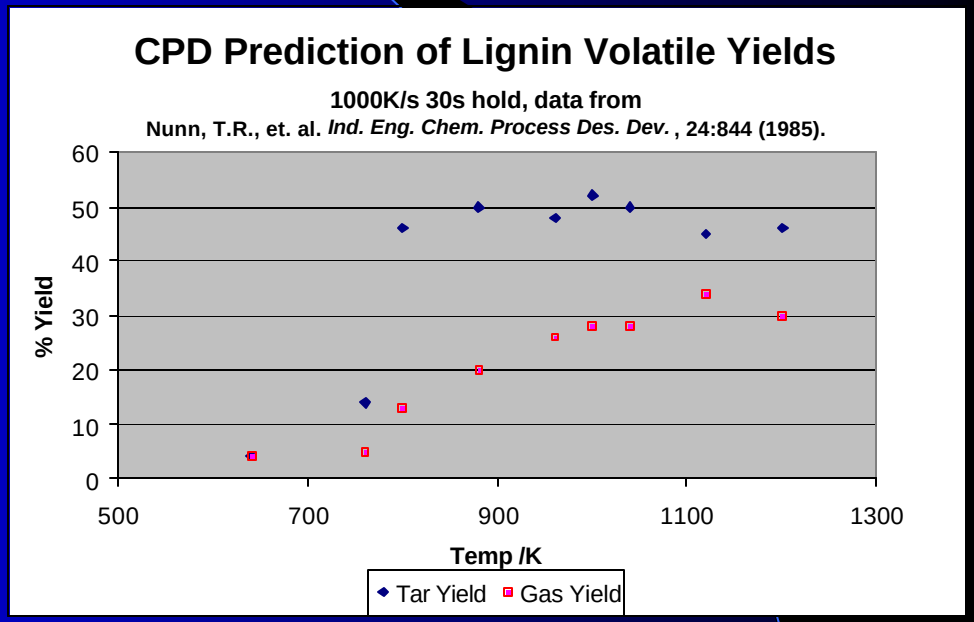
Structural Parameters

- Parameters obtained from theory for hardwood and softwood lignin and Kraft lignin
- CNMR parameters used for composite Black Liquor parameters

Parameter Structural Parameters	*Lignin Hardwood*	*Lignin Softwood*	*Kraft Lignin*	*Black Liquor Composite*
MW_1	207.5	186	195	296.5
M_d	39	34	21.5	206.43
p_o	0.710	0.710	0.710	0.330
$\sigma+1$	3.50	3.50	3.50	3.60

Pyrolysis Data

- Volatile yield data required for fitting the model
- Need data with heating rates and yields at different temperatures
- Data obtained
  - Lignin: Nunn, et. al. heated grid data
  - Black Liquor: BYU Furnace data



CPD Model in Previous Research

- Kinetic parameters for biomass and black liquor identified from original and previous research (Serio)
- Some structural parameters in previous applications of the CPD model not set correctly – misunderstood
  - Sheng & Azevedo (2000)
  - Sricharoenchaikul (2002)
- Sricharoenchaikul fit model only to tar yields
  - Measured tar yields were too low (not all tar accounted and carbon balance not closed)

Optimization and Data Fitting

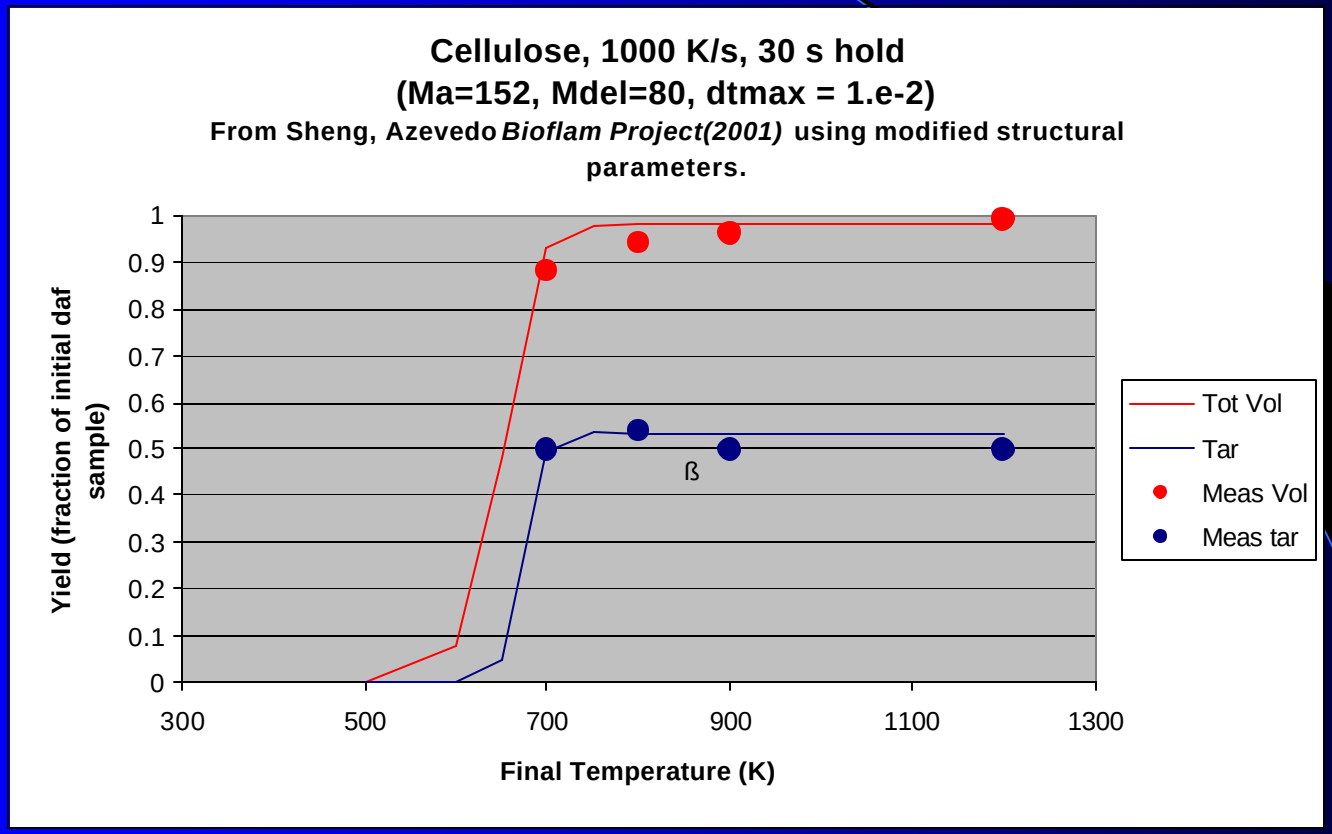
- Optimization required for three parameters (E_c, r, c_o)
- CPD model used with optimization program to find global optimized parameter values
  - Values of $E_c = 0$ gave best model results
  - Value of r set to 3.9
- Model fit to data through fine tuning kinetic parameters and c_o

CPD Component Parameters

Parameter Structural Parameters	Lignin Hardwood	Lignin Softwood	Kraft Lignin
MW_1	207.5	186	195
M_d	39	34	21.5
Kinetic Parameters			
E_b, kcal/mol	54.00	54.00	5.56E+04
A_b, s^{-1}	2.60E+15	2.60E+15	2.60E+15
s_b, kcal/mol	3.972	3.972	3.972
E_g, kcal/mol	66.00	66.00	6.60E+04
A_g, s-1	3.00E+15	3.00E+15	3.00E+15
s_g, kcal/mol	4.776	4.776	4.776
r	3.9	3.9	3.9
E_c, kcal/mol	0	0	0
E_{cross}, kcal/mol	55.68	55.68	55.68
A_{cross}, s^{-1}	3.00E+15	3.00E+15	3.00E+15
c_o	0.10	0.10	0.28
p_o	0.710	0.710	0.330
s+1	3.50	3.50	3.60
fst	0.60	0.60	0.60

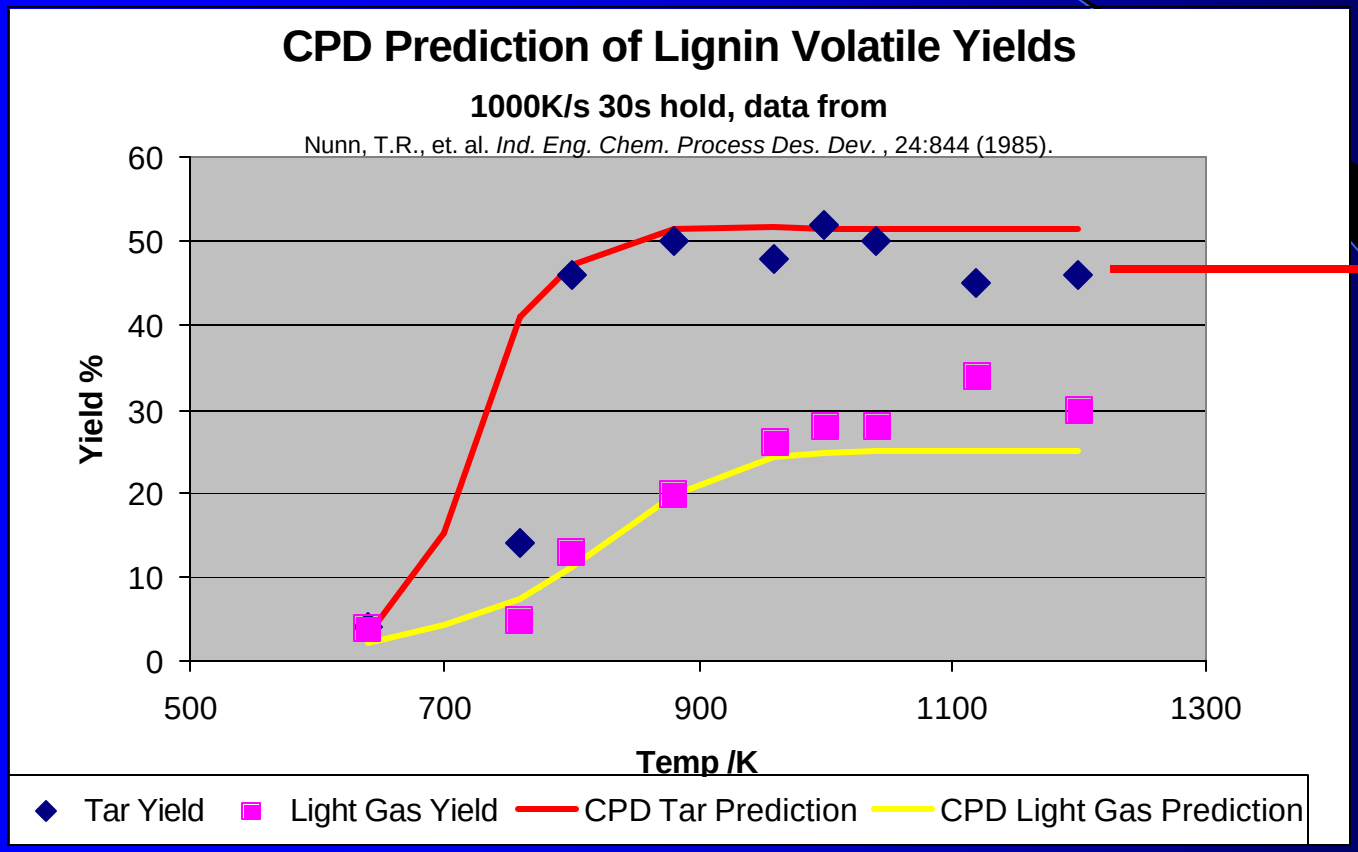
Results

Preliminary Cellulose



- Initial cellulose study using modified Sheng parameters with heated grid data

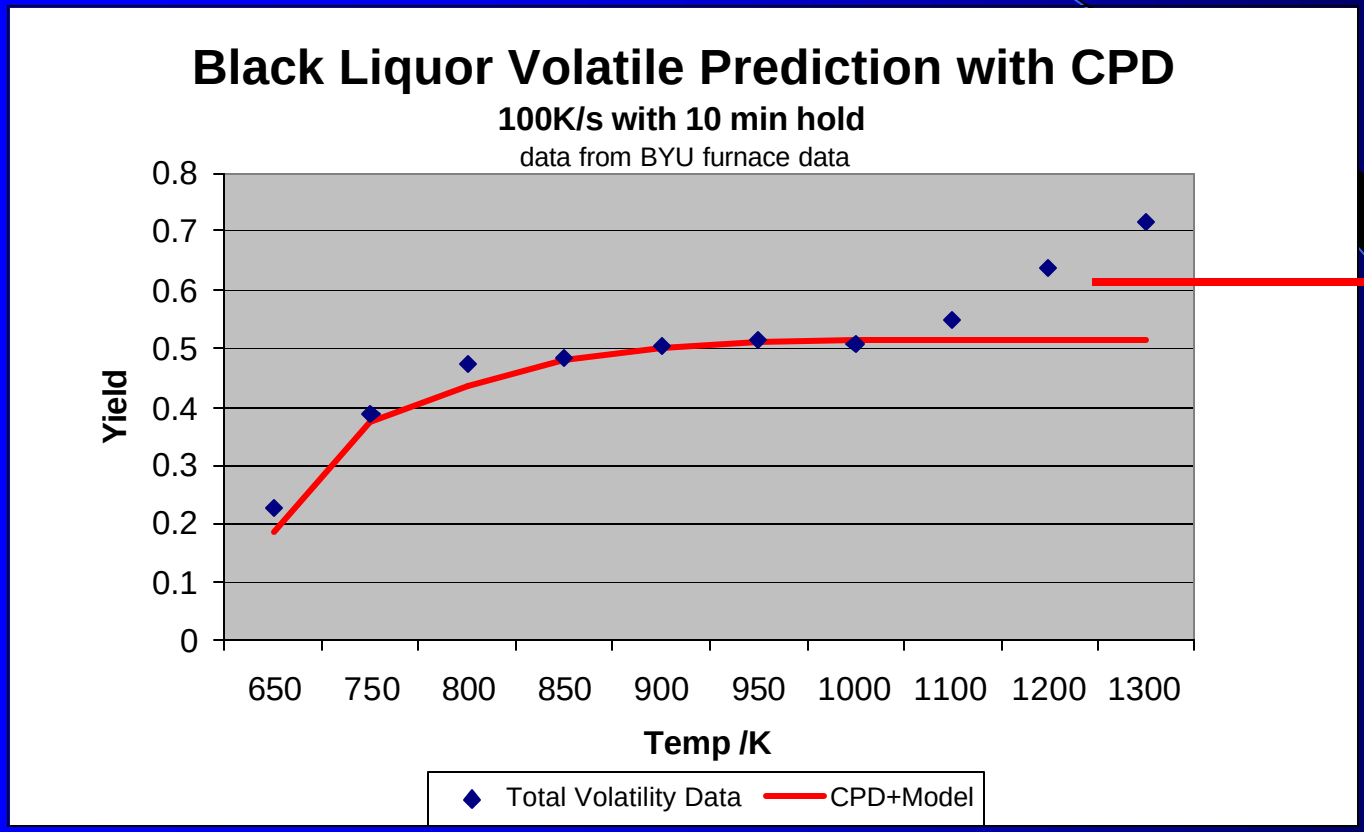
Lignin



Secondary tar reactions to form light gas

- Yields fit heated grid data well, secondary tar reactions not modeled

Black Liquor



$Na_2CO_3 + 2C \rightarrow 2Na + 3CO$

$Na_2CO_3 + C \rightarrow 2Na + CO + CO_2$

- Yields fit well with furnace data, sodium – carbon reactions not modeled

Future Work

- More volatile data needed for black liquor, cellulose and hemi-cellulose
- Integration of a program calculating component composition from elemental analysis
- Predict volatile yield from weighted average of biomass components

Summary & Conclusion

- CPD modified slightly to describe biomass
- Previous attempts to use CPD model were incomplete
- Developed chemical structural and kinetic parameters for Kraft lignin and lignin based on theory, literature review and curve-fitting

Summary & Conclusion cont'd

- Three cases described accurately
  - Preliminary Cellulose study (heated grid)
  - Lignin (heated grid)
  - Black liquor (furnace)
- More data needed to see if parameters have general applicability
- More study needed for cellulose, hemi-cellulose and carboxylic acid parameters
- Need better understanding and model of secondary reactions