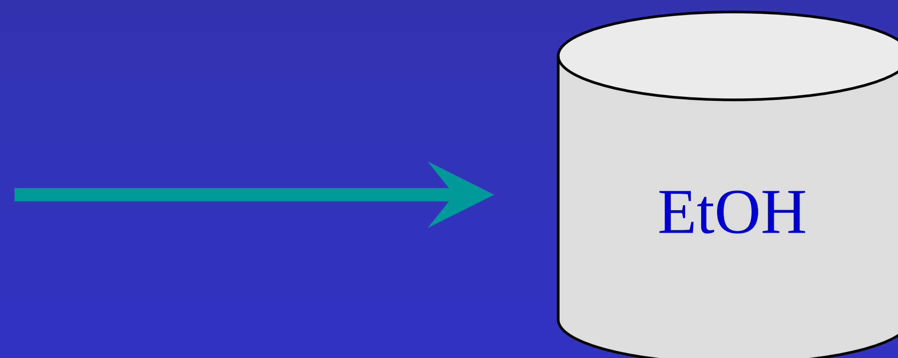
Pretreatment and Hydrolysis of Recovered Fibre for Ethanol Production



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Outline

- Project objectives and rationale
- Oxygen delignification pretreatment
- Enzymes and their function
- Pretreatment experimental design
- Empirical enzymatic hydrolysis model
- Summary and questions

Project Objectives

1. Evaluation of oxygen delignification as a pretreatment for recovered fibre
2. Utilize enzymatic hydrolysis for the conversion of the recovered fibre
3. Develop and empirical equation that could predict sugar concentration as a function of:
    - Kappa number;
    - Enzyme loading; and
    - Initial fibre concentration

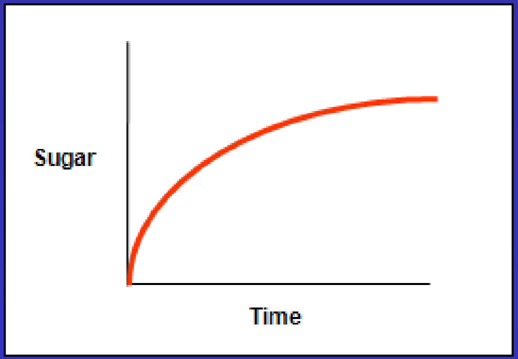
Rationale for the Project

- Pretreatment
  - Important chemical and physical properties that determine the hydrolyzability of cellulosic substrate
  - The major role of lignin – both inhibits and affects the accessibility of enzymes to cellulose

- Hydrolysis
  - Enzyme production a major cost in the hydrolysis process
  - Efficient enzymes, synergistic cocktails, improved hydrolysis regimes

Factors that Affect Enzymatic Hydrolysis

- Substrate limitations
  - Degree of polymerization
  - Crystallinity
  - Lignin content and distribution
  - Enzyme accessible surface area

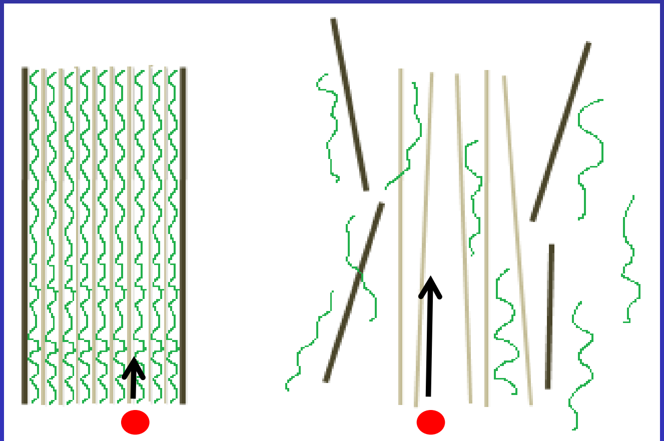


- Enzyme limitations
  - End-product inhibition
  - Thermal inactivation
  - Irreversible enzyme adsorption

Pretreatment Options

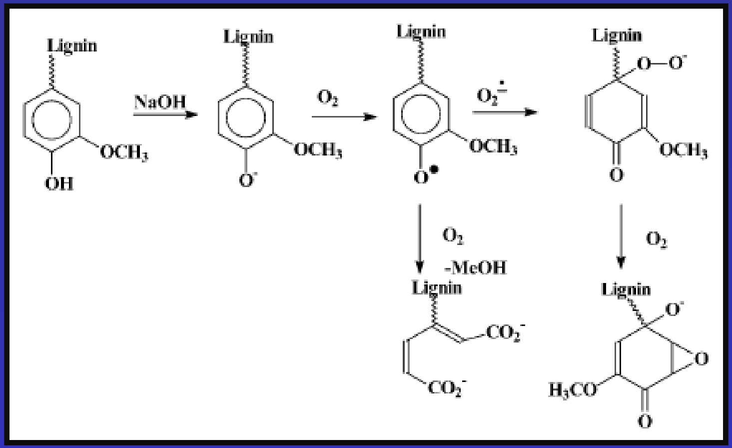
- Acid (steam explosion)
- AFEX
- Organosolv
- Oxygen delignification

Pretreatment: Oxygen Delignification



CELLULASE ENZYME
DIFFICULT ACCESS

CELLULASE ENZYME
EASY ACCESS

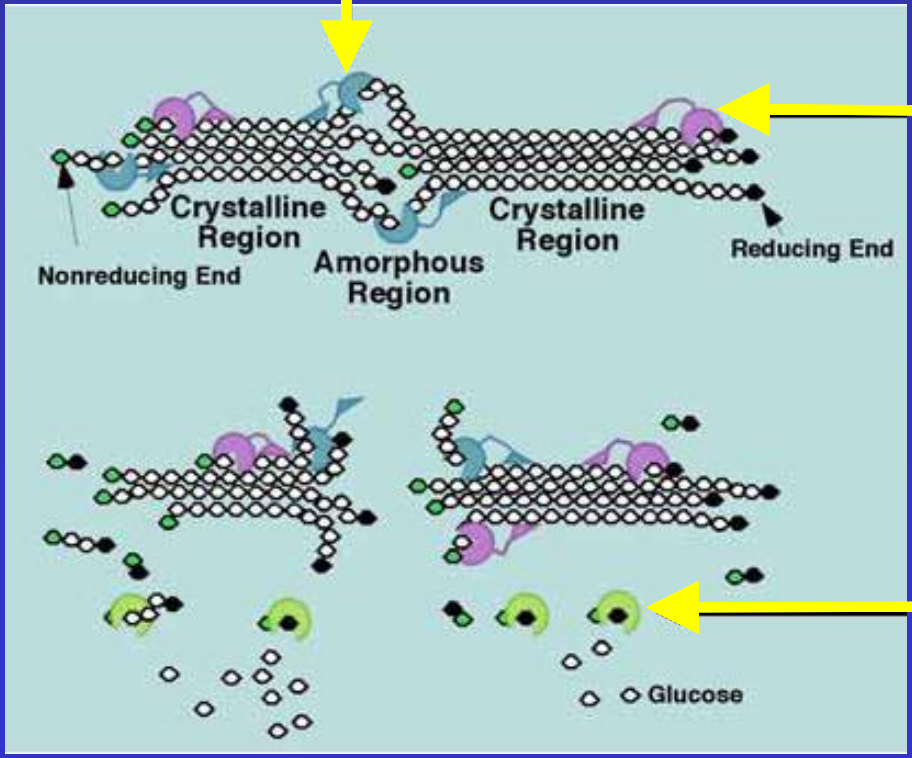


Pure Appl. Chem., Vol. 73, No. 12, pp. 2059–2065, 2001.

- In the O2 delignification process, lignin is activated by alkali and degraded by oxygen derived radicals

Hydrolysis: Cellulase Enzyme Complex

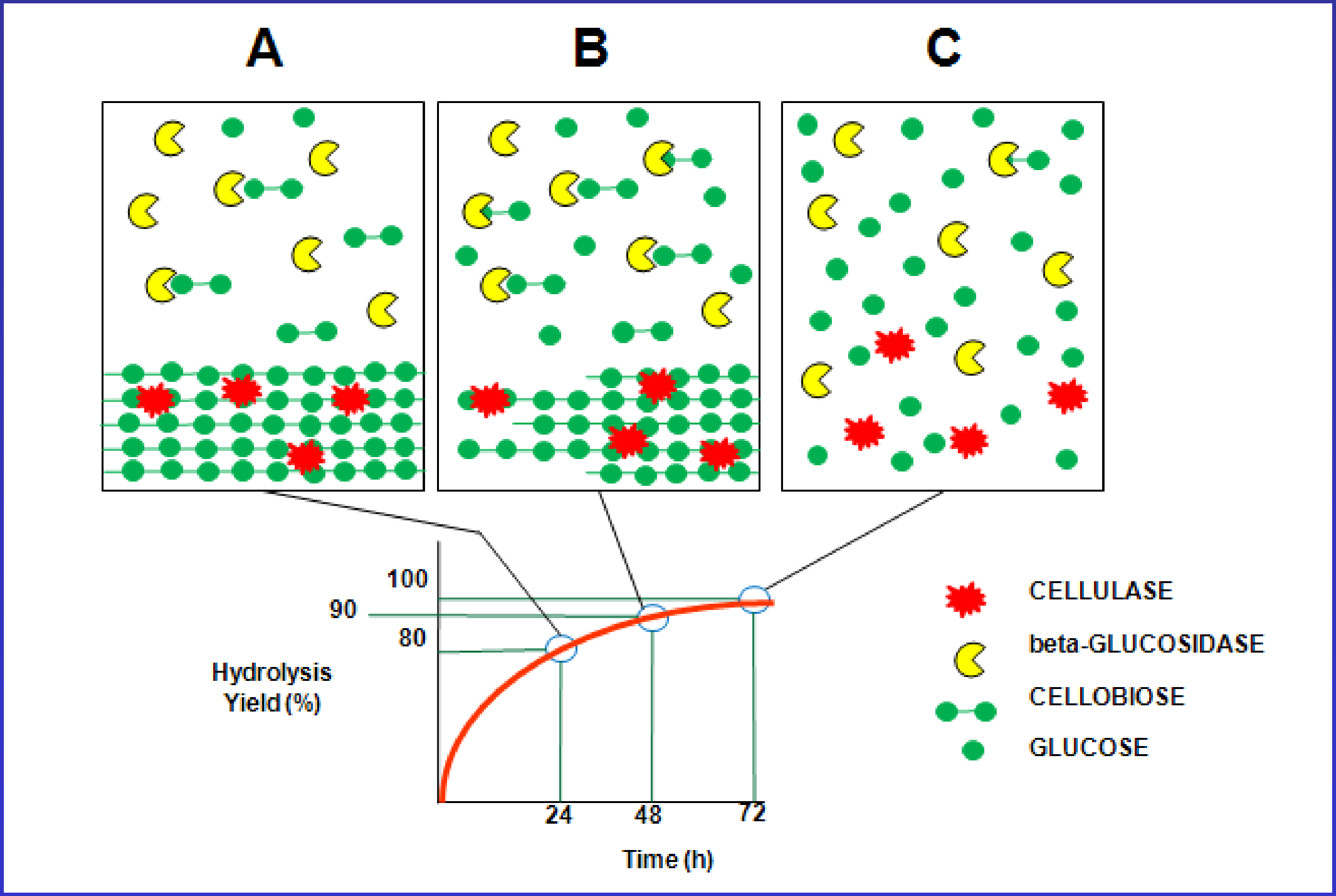
Endo-cellulase: attacks non-crystalline, amorphous regions of the cellulose chain producing cellodextrins
(3-10 component sugar polymers)



Exo-cellulase: attacks chain ends, producing a glucose dimer (cellobiose)

β-glucosidase: produces glucose by attacking oligosaccharides and cellobiose

Enzymatic Action During Hydrolysis



Recovered Fibre

- Chemical composition:

	Arabinose (%)	Galactose (%)	Glucose (%)	Xylose (%)	Mannose (%)	Lignin (%)
Recovered Fibre	0.66	0.63	72.16	8.91	5.40	12.98

HARDWOOD

18-25% Lignin

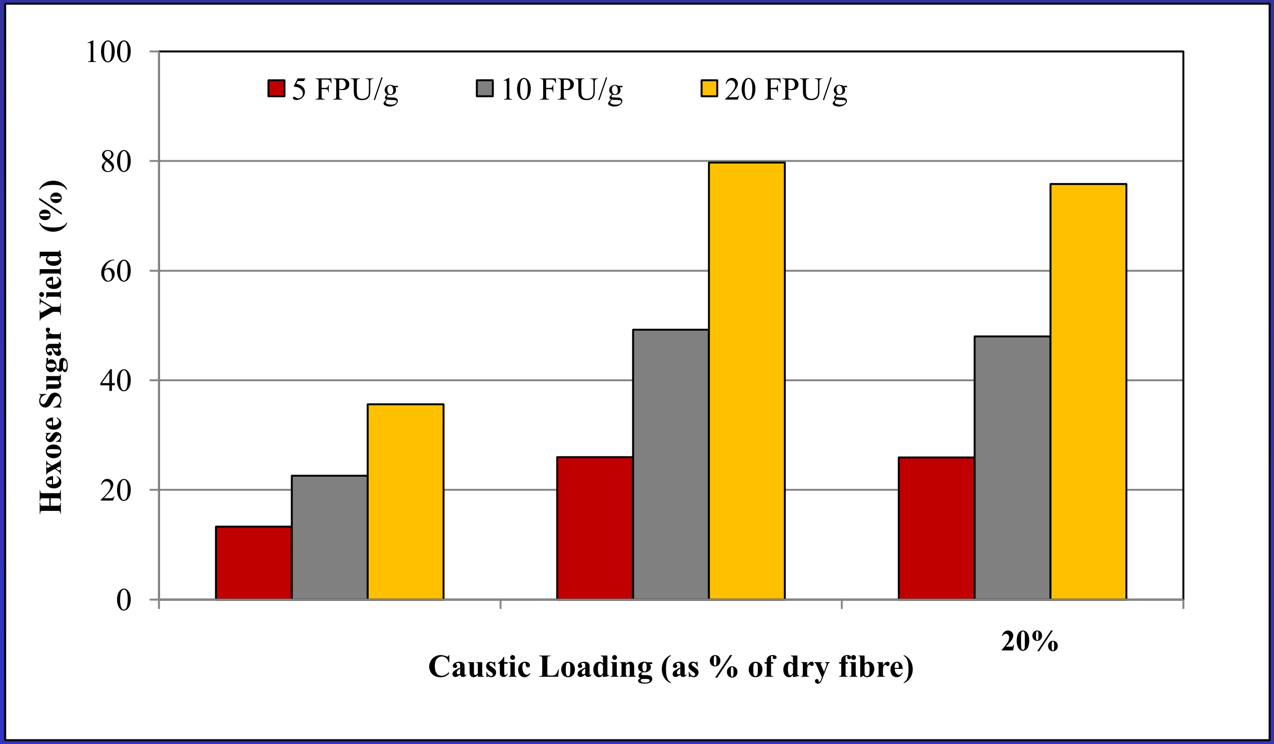
SOFTWOOD

25-35% Lignin

CORN STOVER

15% Lignin

O_2 Delignification: Recovered Fibre



Pretreatment Conditions:

- **T = 150 C**
- **t = 60 min**
- **p(O2) = 100 psi**

$$\text{Hexose sugar yield}(\%) = \frac{(\text{g sugar})}{(\text{g substrate})} \times \frac{\text{g substrate}}{1.11\,\text{g sugar}} \times 100$$

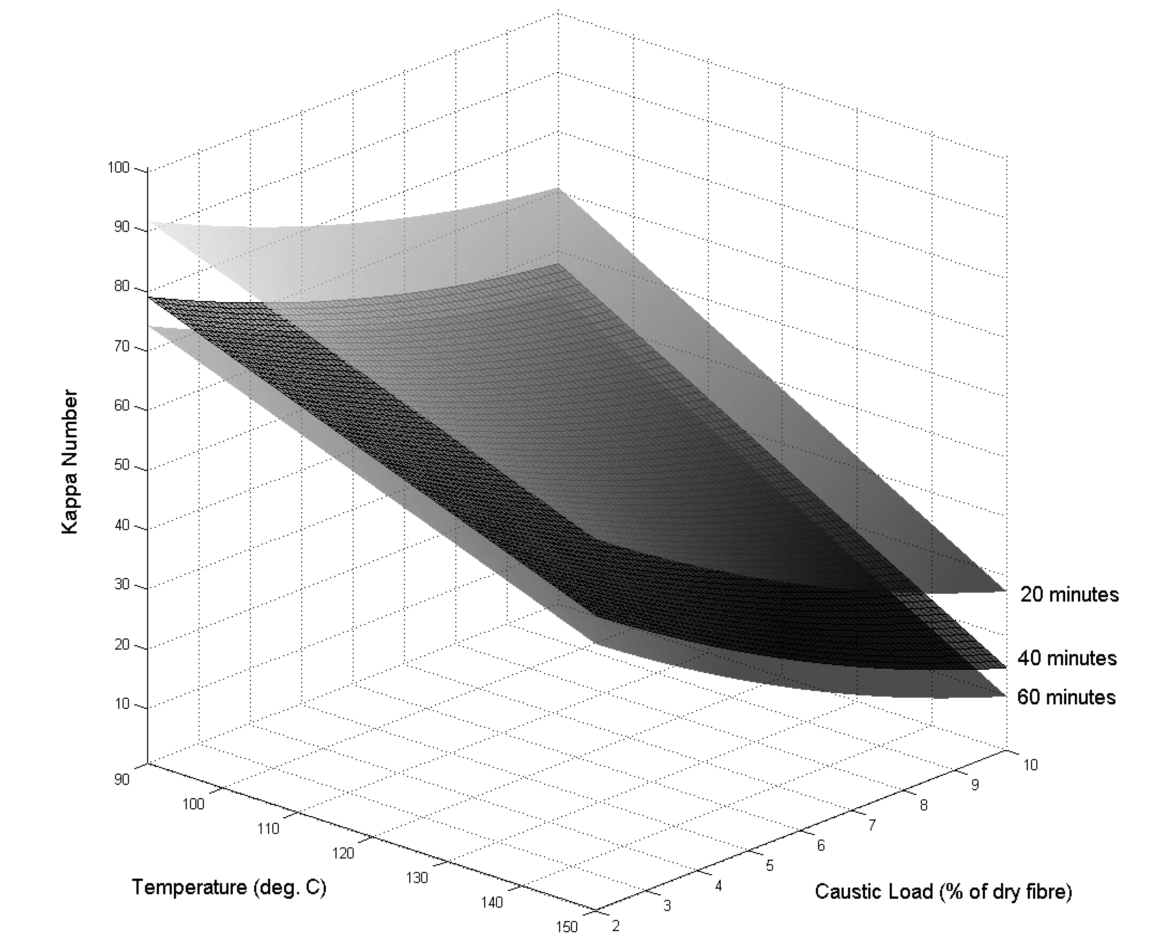
Pretreatment Experimental Design

- Experimental design looked at the following parameters:
  - Independent variables
    - Temperature (^oC): 90, 120, 150
    - Caustic (% of dry fibre): 2, 6, 10
    - Time (min): 20, 40, 60
  - Dependent variables
    - Kappa: measure of lignin fraction
    - Yield (%): initial pulp mass vs. delignified pulp mass
    - Hydrolyzability (%): hexose sugar yield

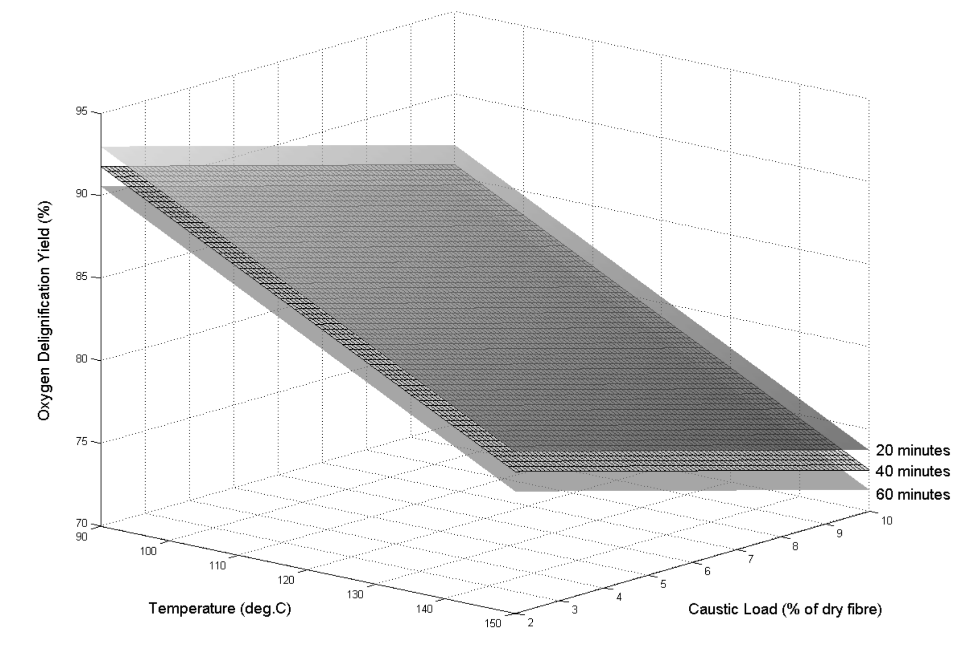
Dependent Variable: Kappa

Kappa = 128.56 – 0.35(T) – 2.64(C) – 0.74(t) – 0.011(C)(T) + 0.21(C)² + 0.0069(t)² – 0.024(t)(C)

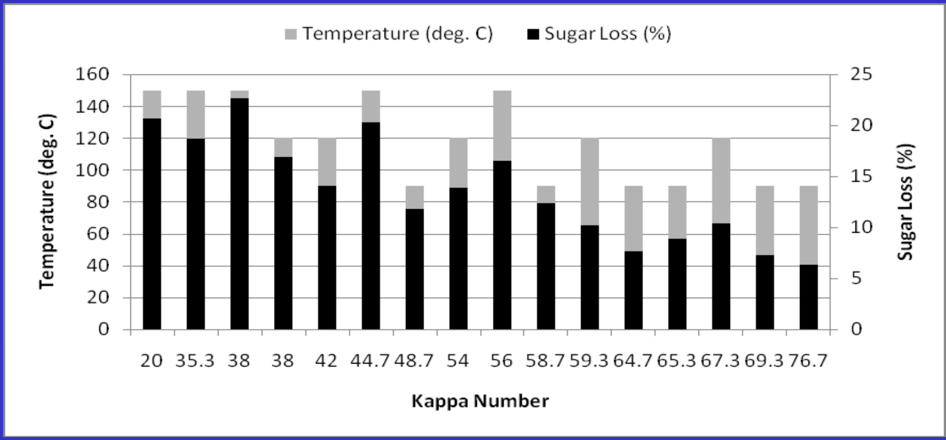
$$\text{Kappa} = 128.56 - 0.35(T) - 2.64(C) - 0.74(t) - 0.011(C)(T) + 0.21(C)^2 + 0.0069(t)^2 - 0.024(t)(C)$$



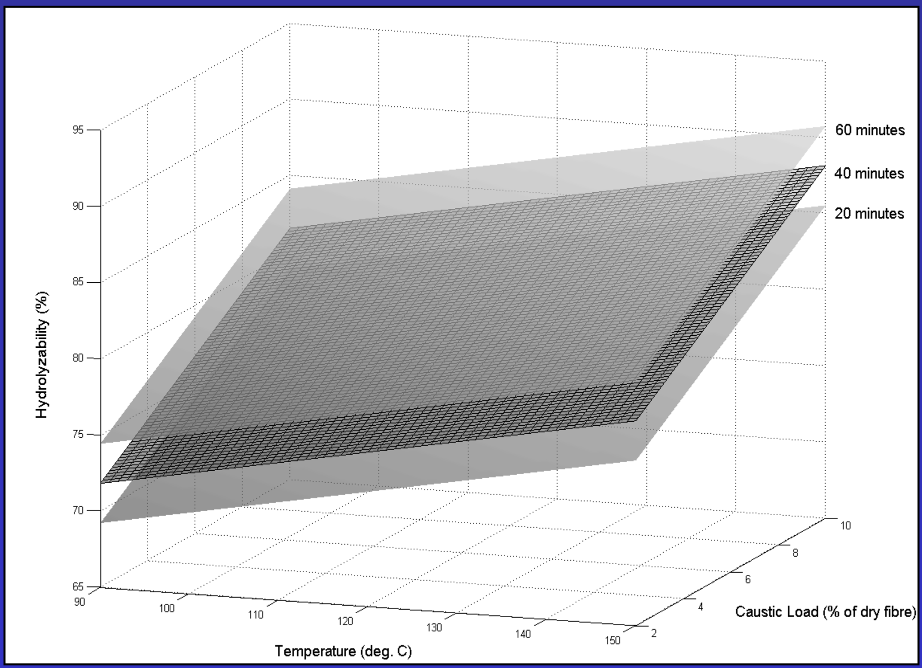
Dependent Variable: Yield



Yield (%) = 116.47 - 0.22(T) – 0.70(C) – 0.088(t)

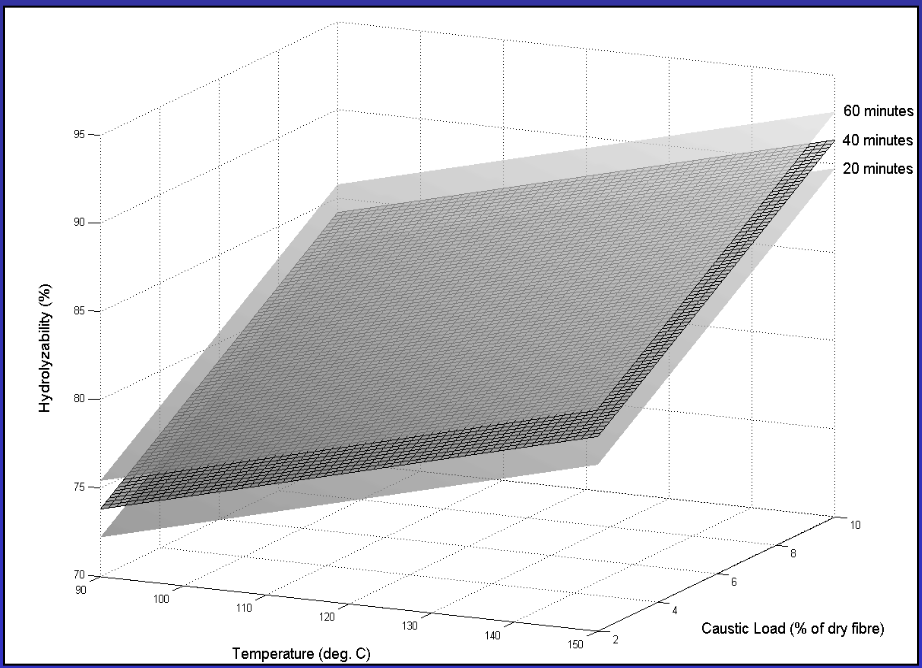


Dependent Variable: Hydrolyzability



20 g/L, 39 FPU/g

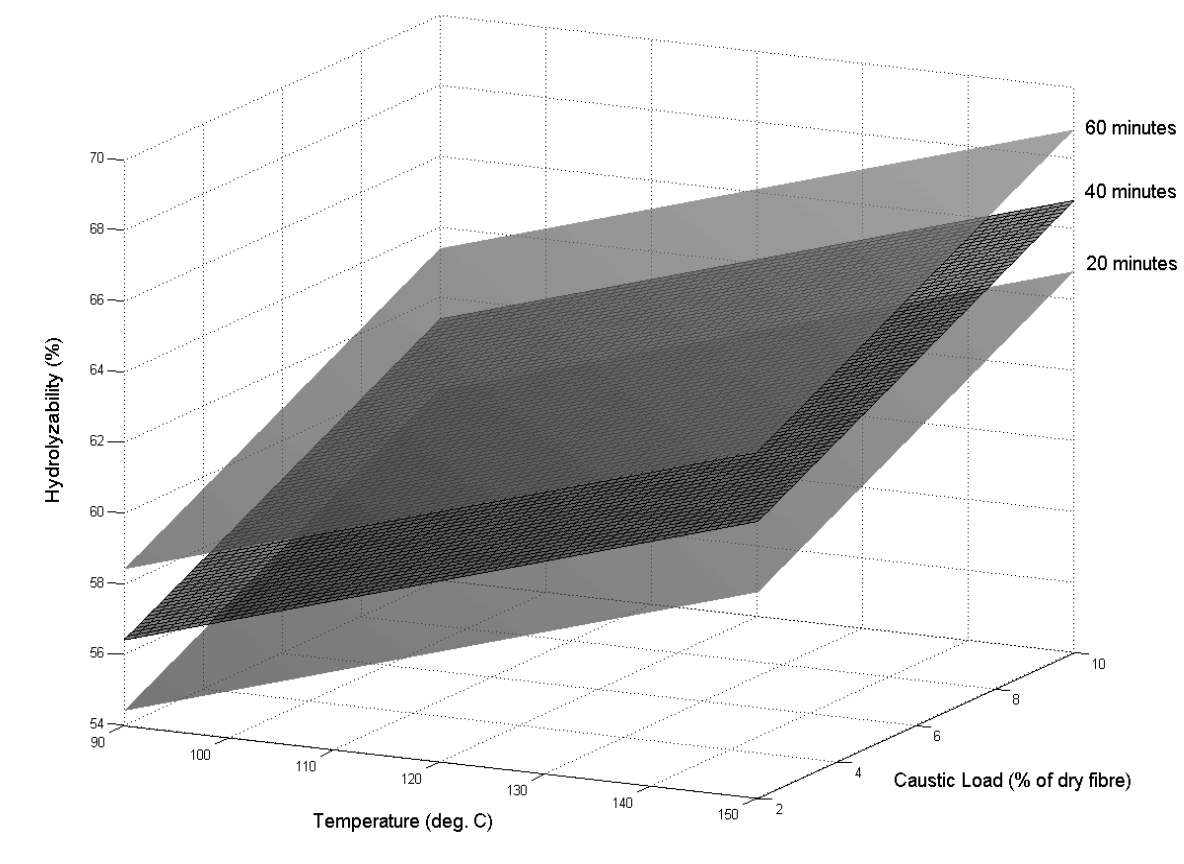
Hydrolyzability = 45.31 – 0.24(C^2) + 4.16(C) + 0.11(T) + 0.12(t)



20 g/L, 77 FPU/g

Hydrolyzability = 52.10 -0.16(C^2) + 3.22(C) + 0.11(T) + 0.092(t)

Dependent Variable: Hydrolyzability



100 g/L, 32 FPU/g

Hydrolyzability = 36.95 – 0.16(C^2) + 2.64(C) + 0.084(T) + 0.81(t)

Empirical Model for Enzymatic Hydrolysis

- Goal: construct an equation for sugar concentration as a function of Kappa number, enzyme loading, and starting fibre concentration

$$\frac{dC}{dt} = -k\left(\frac{C}{Co}\right)^{n}$$

Where:
C = cellulose concentration (g/L)
Co = starting cellulose concentration (g/L)
k, n = empirical constants

$$S = Co\left(1 - \left(\frac{1}{1 + kt(n-1)/Co}\right)^{1/(n-1)}\right)$$

Empirical Model for Enzymatic Hydrolysis

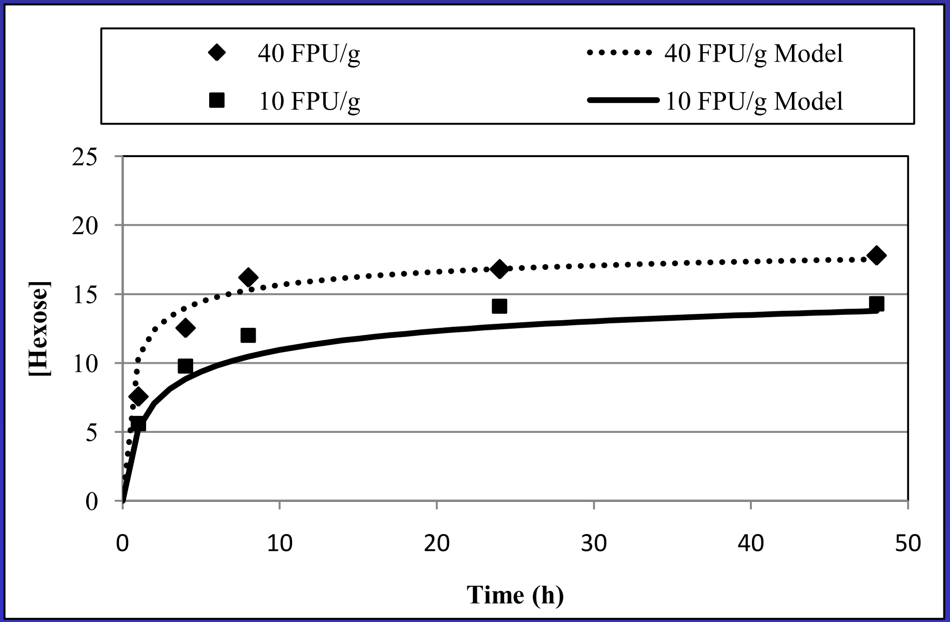
$$S = Co\left(1-\left(\frac{1}{1+kt(n-1)/Co}\right)^{1/n-1}\right)$$

- Sugar concentration vs. time data was used to determine n and k values for an optimized fit
- n and k values were related to Kappa number (K), enzyme loading (E), and initial solids loading (Co)

$$n = 0.25\cdot K^{1.26}\cdot E^{-0.02}\cdot Co^{-0.4}$$

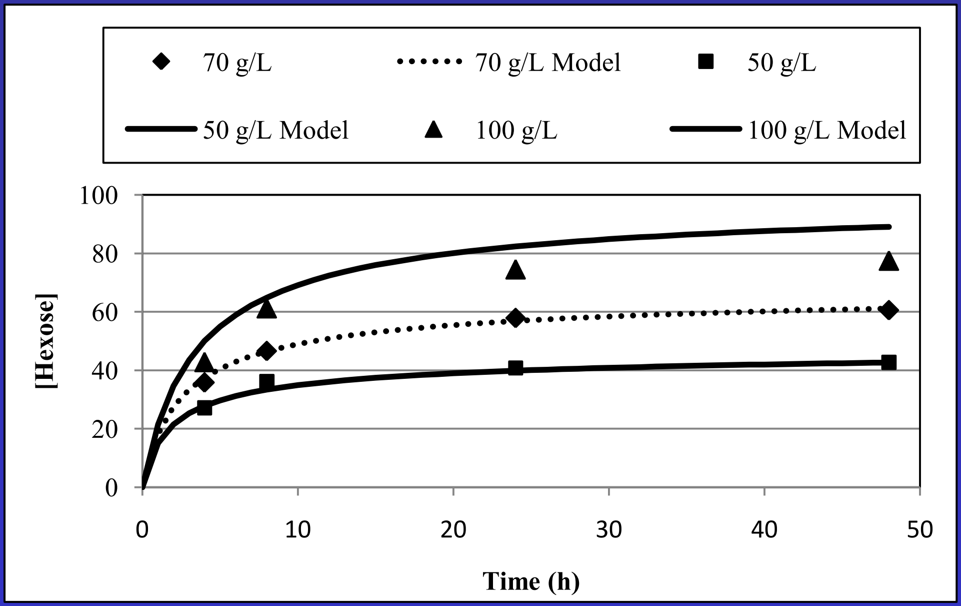
$$k = 0.9\cdot E\cdot Co^{0.1}$$

Model Fit



- Good model fit at Kappa 40, 20 g/L
- Initial rate/Final sugar concentration

Model Fit



- Poor model fit at very high substrate loading
- Mixing/Mass transfer

Conclusions

- Oxygen delignification pretreatment of recovered fibre (87 Kappa) produced dependent variables that related to temperature, reaction time, and caustic loading:

Yield (%) = 116.47 - 0.22(T) – 0.70(C) – 0.088(t)

Kappa = 128.56 – 0.35(T) – 2.64(C) – 0.74(t) – 0.011(C)(T) + 0.21$(C)^2$ + 0.0069$(t)^2$ – .024(t)(C)

Hydrolyzability (2% Solids, 20 FPU/g) = 45.31 – 0.24(C^2) + 4.16(C) + 0.11(T) + 0.12(t)

Where:

T: temperature (^{o}C)

C: caustic load (% of dry fibre)

t: time (minutes)

Conclusions

- An empirical model was constructed to predict sugar concentrations based on Kappa number, enzyme loading, and starting fibre concentration:

$$S = Co\left(1-\left(\frac{1}{1+kt(n-1)/Co}\right)^{\frac{1}{n-1}}\right)$$

S: sugar concentration (g/L)
Co: starting cellulose concentration (g/L)
k, n: empirical constants

- The empirical model produced r^2 between 0.80 - 0.99 at low substrate loadings, and decreased as the substrate loading increased
- Model is specific to O_2 delignified recovered fibre

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