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SIMULATION OF CELLULOSE NITRATION PROCESS UNDER ACID-EXCESS CONDITIONS

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Outline

- Introduction
- Experimental Studies
- Model Formulation
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- Conclusion
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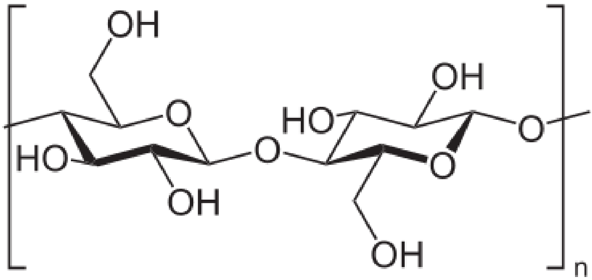
Introduction

- **Cellulose**
  - Organic compound $(C_6H_{10}O_5)_n$ consisting of polymeric carbohydrate structures (linked glucose units)



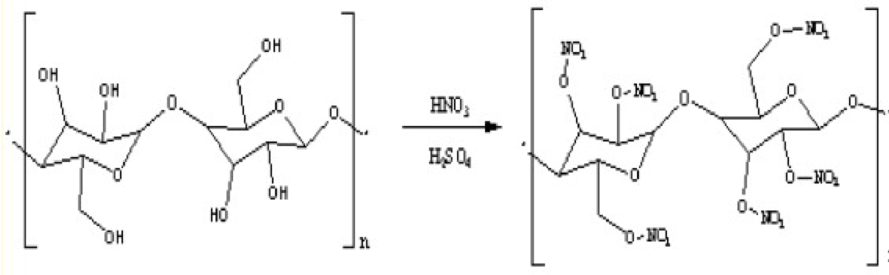
  - Different cellulose sources are different in:
    - **Cellulose Percentage**: Softwood Pulp, Hardwood Pulp<Sisal Fiber<Cotton Fiber (cotton: 93~95% cellulose; wood such as Fir/Pine/Aspen: 40~55% Cellulose)
    - **Molecular weight** (n=100~14000)
    - **Impurity; Specific Surface Area; Macro-scale Porosity: (affecting acid diffusion/absorption and, consequently, reaction rate and uniformity; product stability)**

Introduction

- **Cellulose nitration**
  - Reacting cellulose in the presence of mixed sulfuric and nitric acid.
  - Esterification process:
    - $3HNO_3 + [C_6H_{10}O_5]_n \rightarrow [C_6H_7(NO_2)_3O_5]_n + 3nH_2O$

	Mononitrocellulose	Dinitrocellulose	Trinitrocellulose
% Nitrogen	6.75	11.11	14.14

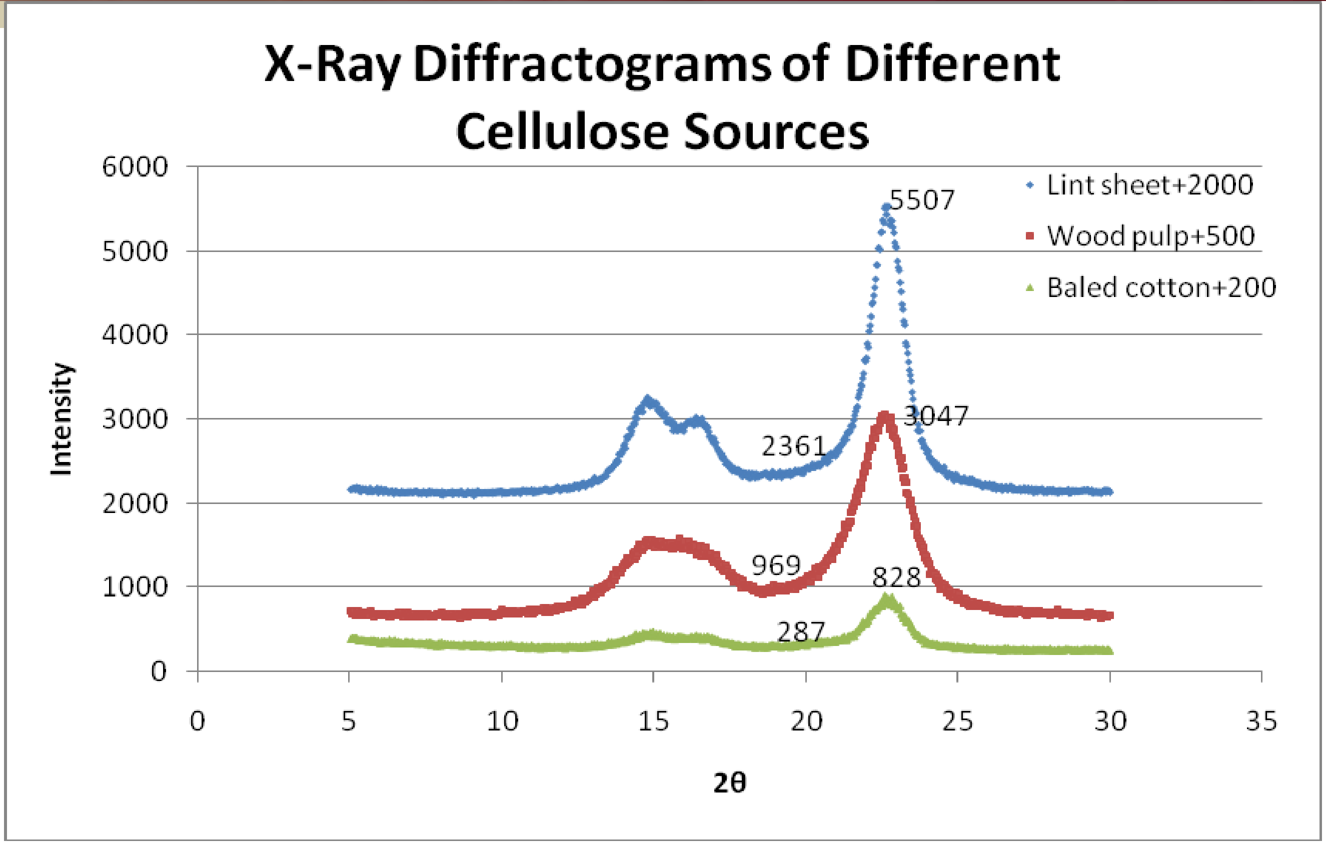
  - Propellants and gunpowder applications: nitrogen content ranges from 12%-13.8%



Factors Affecting Acid Absorption and Diffusion

- Surface area of the fibers
- Porosity of the fibers
- Cellulose crystallinity
  - Rigid anhydroglucose rings
  - Hydrogen bonding capacity-laterally ordered
- Moisture uptake
- Fiber Impurity

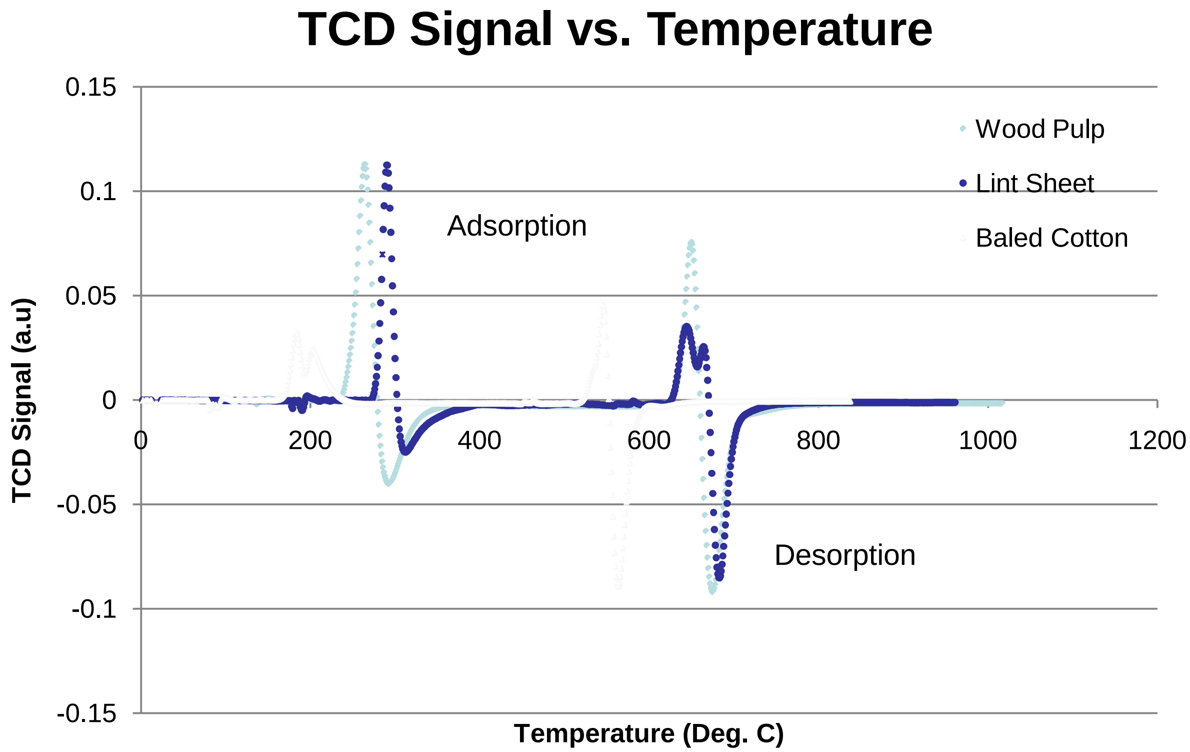
X-ray Diffraction



Cellulose Types	Crystal Size (nm)
Wood pulp	3.47
Lint sheet	5.66
Baled cotton	5.14

Surface Area of Fibers: BET Analysis

- Gas flow technique for surface area (SA) measurement
- Nitrogen as adsorbate
- Stronger binding for lint and wood pulp sheets



Surface Area of Fibers: BET Analysis

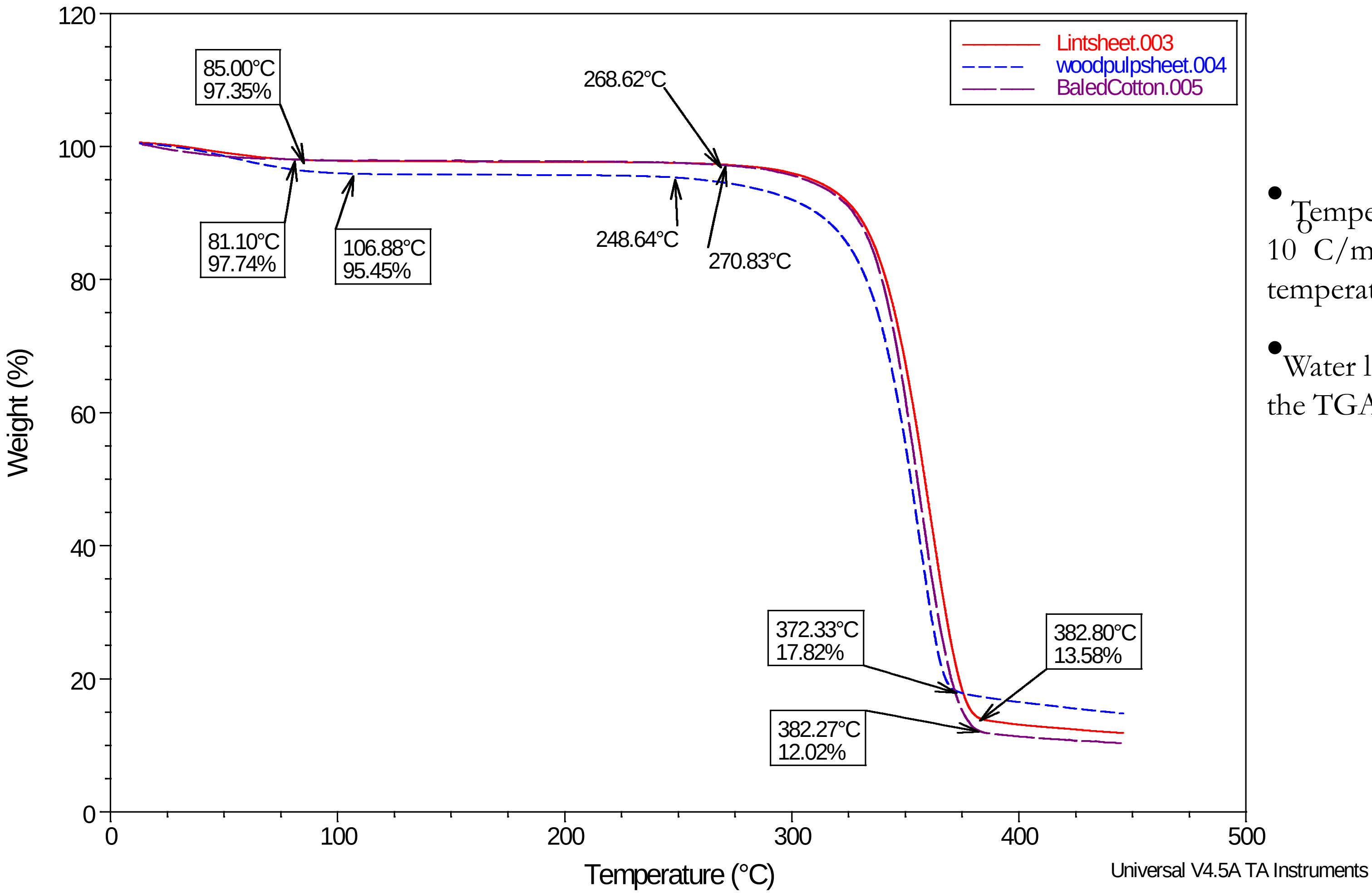
- Higher surface area (SA) causes moisture increase as comparing wood pulp and lint sheet
- Consistent with XRD results

$$B_i = \frac{\left(\frac{P}{P_o}\right)_i}{\left(1-\left(\frac{P}{P_o}\right)_i\right)V_{ads}} \qquad SA = \frac{A_{N2} * (6.02 * 10^{23})}{22414cm^3 * \left(\frac{10^{18}nm^2}{m^2}\right) * (m + Y_{int})}$$

Cellulose Types	BET Surface Area (m^2/g)
Lint Sheet	5.0845
Wood Pulp	5.9328
Baled Cotton	6.4392

Moisture Content Analysis: TGA Results

Lint-(97.35%)
Baled Cotton-(97.74%)
Woodpulp-(95.45%)



- Temperature ramping at 10 °C/min from room temperature to 450 °C
- Water loss was observed from the TGA thermographs

Moisture Content Measurement: Results and Discussion

- Wood pulp
  - Contains the most water
  - Least stable out of all the cellulose types in the experiment
- Baled cotton and lint sheet have shown to have similar water content
  - Similar onset of degradation
  - More extreme degradation than wood pulp
- Consistent with BET results

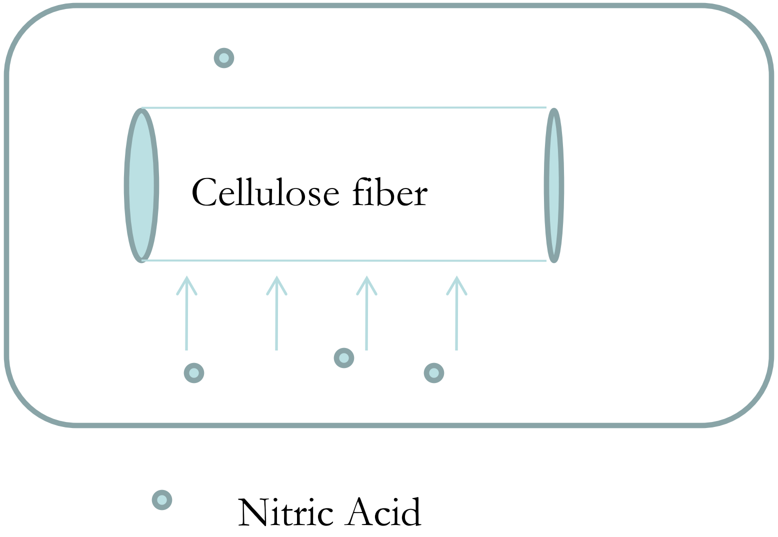
Cellulose Types	**Water Content (%)**	**Onset of Degradation (° C)**
Wood pulp	4.55	248.64
Lint sheet	2.65	268.62
Baled cotton	2.26	270.83

Model Formulation

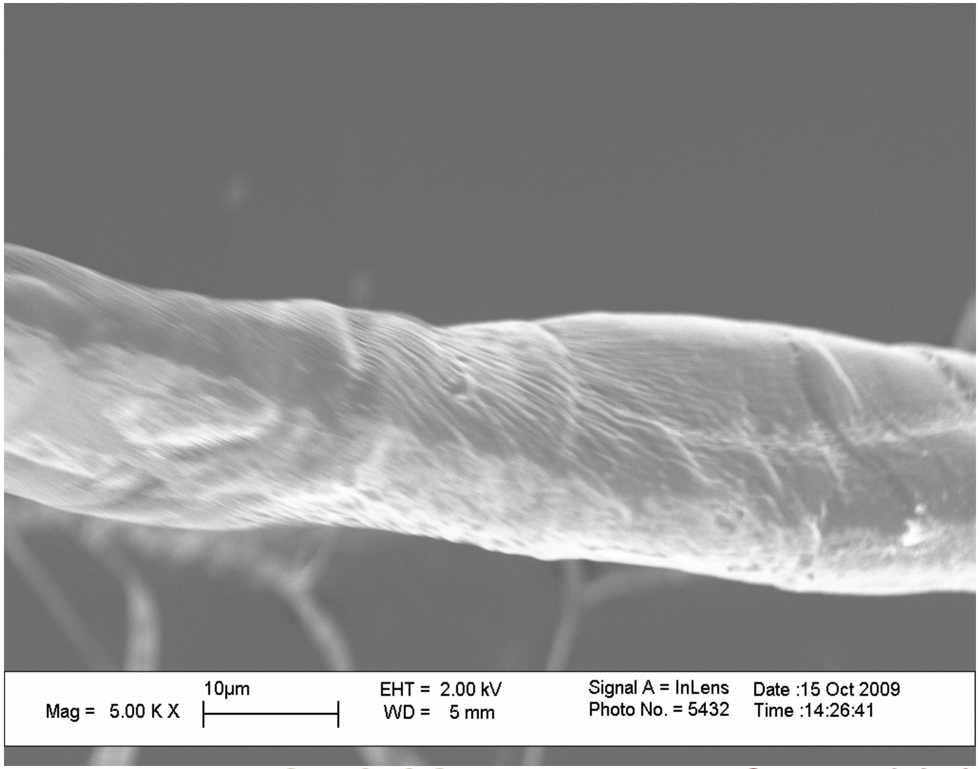
1) Simulation of reaction

$3nHNO_3 + [C_6H_{10}O_5]_n \rightarrow [C_6H_7(NO_2)_3O_5]_n + 3nH_2O$

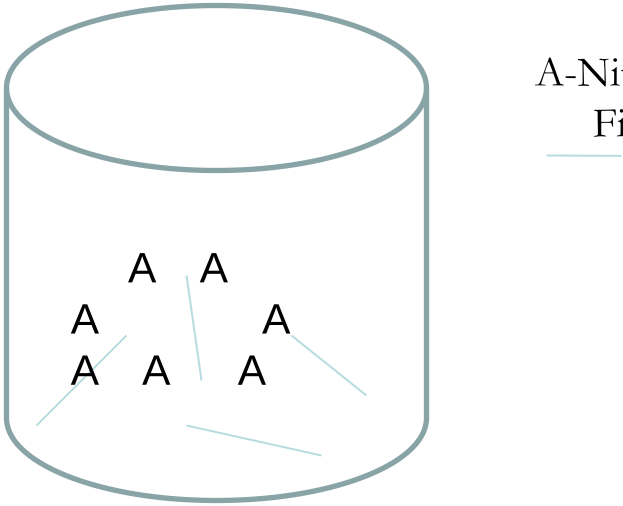
Layer by layer diffusion and reaction



Diameter of the fiber is roughly 10μm from the SEM image



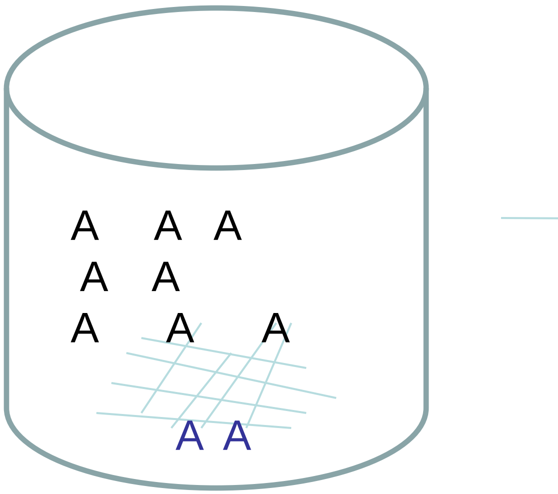
Model I: Dilute Fibers



A-Nitric Acid
Fibers

- Nitric acid is in excess of what the reaction needs
- Constant acid concentration at the fiber surface

Model II: Fiber Entanglements



A-Nitric Acid

Fibers

- Fibers are bundled into sheets
  - Presence of acid concentration gradient
  - Non constant acid concentration at the surface

Model Formulation

For convenience of subscripts and symbols, the nitration reaction is rewritten in a general form as shown below: $3A+B \Rightarrow C+3D$, where A-nitric acid, B-cellulose, C-nitrocellulose, D-water.

Assumptions:

1) Fibers are perfect of "infinite" length;
2) Liquid phase is perfectly mixed;
3) Nitric acid diffuses into the fiber and reacts with the cellulose.
4) Fibers are suspended uniformly in a nitric acid rich medium

$$\frac{\partial C_A}{\partial t} = \frac{D_{AB}}{r}\frac{\partial\left(r\frac{\partial C_A}{\partial r}\right)}{\partial r} - kC_AC_B$$

$$\frac{\partial C_B}{\partial t} = -\frac{1}{3}KC_AC_B$$

$$\frac{\partial C_C}{\partial t} = \frac{1}{3}KC_AC_C$$

where CA,CB and CC are the concentration of the nitric acid, cellulose and nitrocellulose, respectively; DAB is the diffusion coefficient of the nitric acid inside the fiber; k is the reaction rate constant of nitration; r is the radial direction of the fiber.

Model Formulation

$$C_C(r,t) = C_{Bo} - C_B(r,t)$$

Instead of expressing the nitrocellulose concentration in a differential form, it can be rewritten in the following form according to stoichiometry from the chemical equation:

- B.C 1: Constant surface

$$\frac{\partial C_A(r=0,t)}{\partial r} = 0 \quad C_A(r = 10\mu m, t) = 0.00222\,\frac{mol}{cm^3}$$

- Initial conditions:

$$C_A(r, t=0) = 0 \qquad C_B(r, t=0) = 0.00863$$

Equations in Dimensionless Form

$$\frac{\partial C_A^*}{\partial \tau} = \frac{1}{x}\frac{\partial}{\partial x}\left(x\frac{\partial C_A^*}{\partial x}\right) - \phi C_A^* C_B^*$$

$$\frac{\partial C_B^*}{\partial \tau} = -\frac{1}{3}\phi\gamma C_A^* C_B^*$$

where $t = \frac{R^2\tau}{D_{AC}}, x = \frac{r}{R}$ $C_A^* = \frac{C_A}{C_{Ao}}$ $and\ C_B^* = \frac{C_B}{C_{Bo}}$

B.C: $\frac{\partial C_A^*}{\partial x}(x = 0, \tau) = 0$ $C_A^*(x = 1, \tau) = 1$

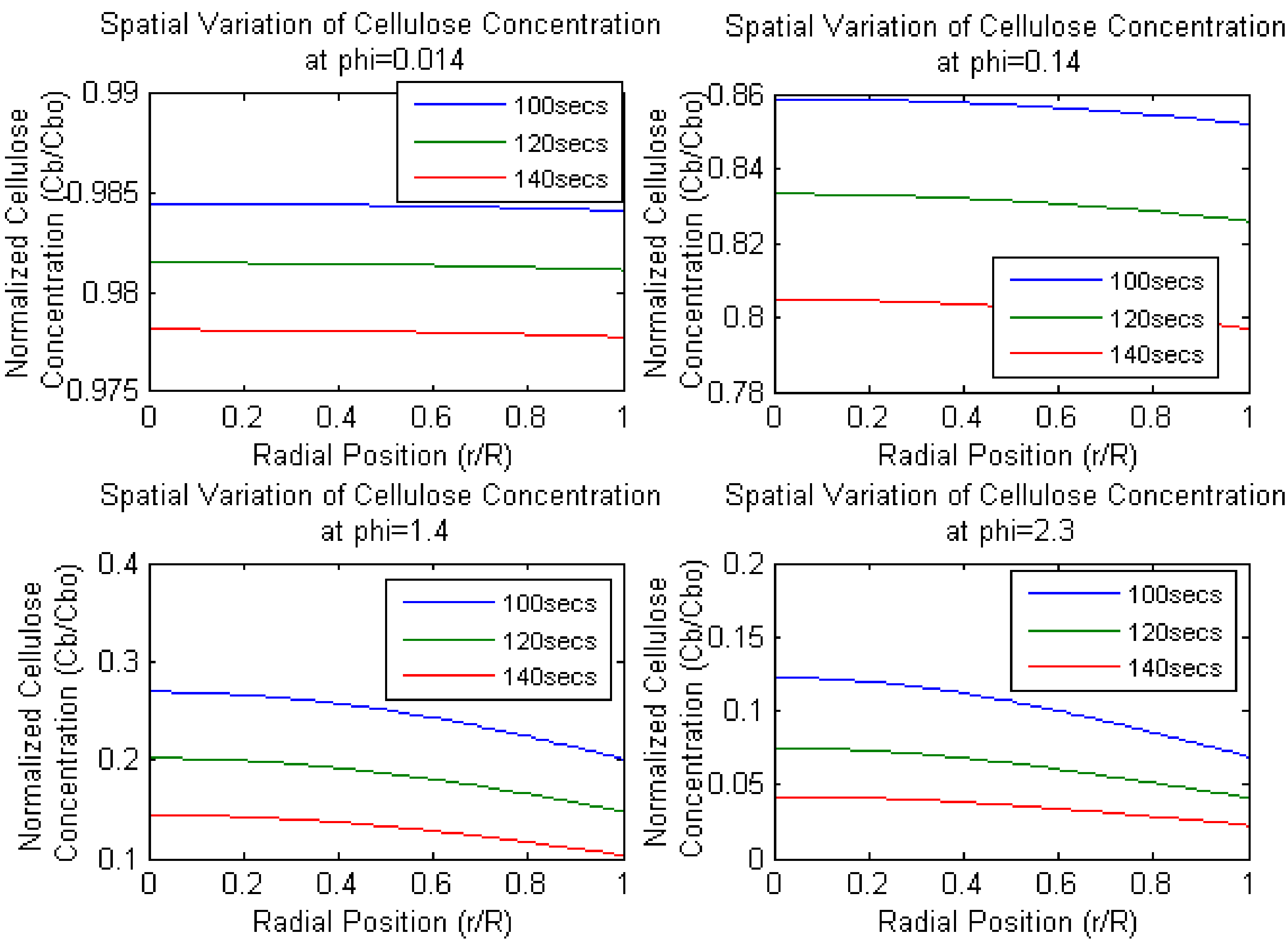
I.C: $C_A^*(x, \tau = 0) = 0$ $C_B^*(x, \tau = 0) = 1$

The coupled partial differential equations are dimensionalized, where φ is the Damkohler number that characterizes the strength of chemical reaction and γ is the saturation ratio of acid concentration with respect to cellulose.

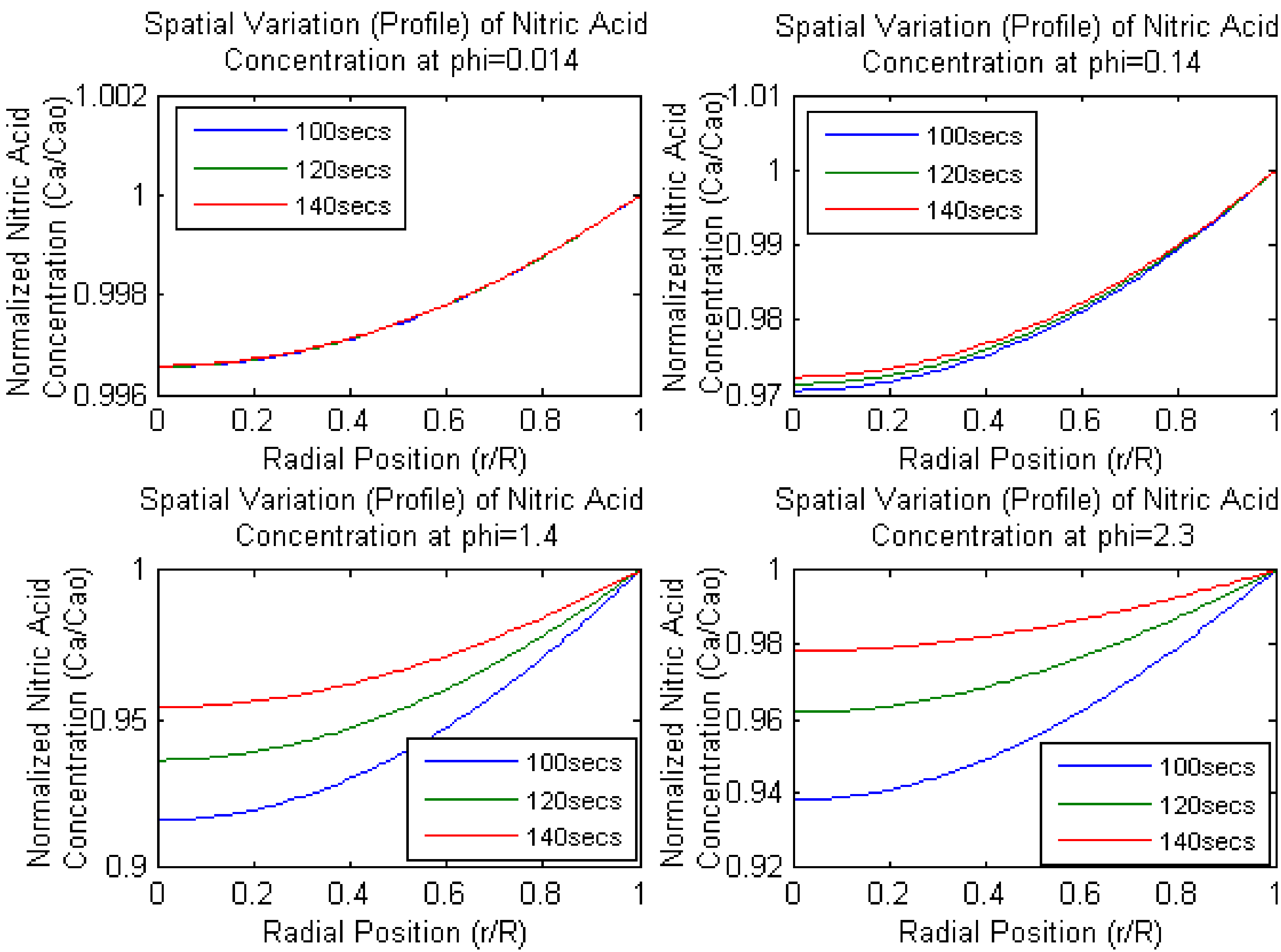
$$\phi = \frac{R^2 K C_{Bo}}{D_{AC}}$$

$$\gamma = \frac{C_{Ao}}{C_{Bo}}$$

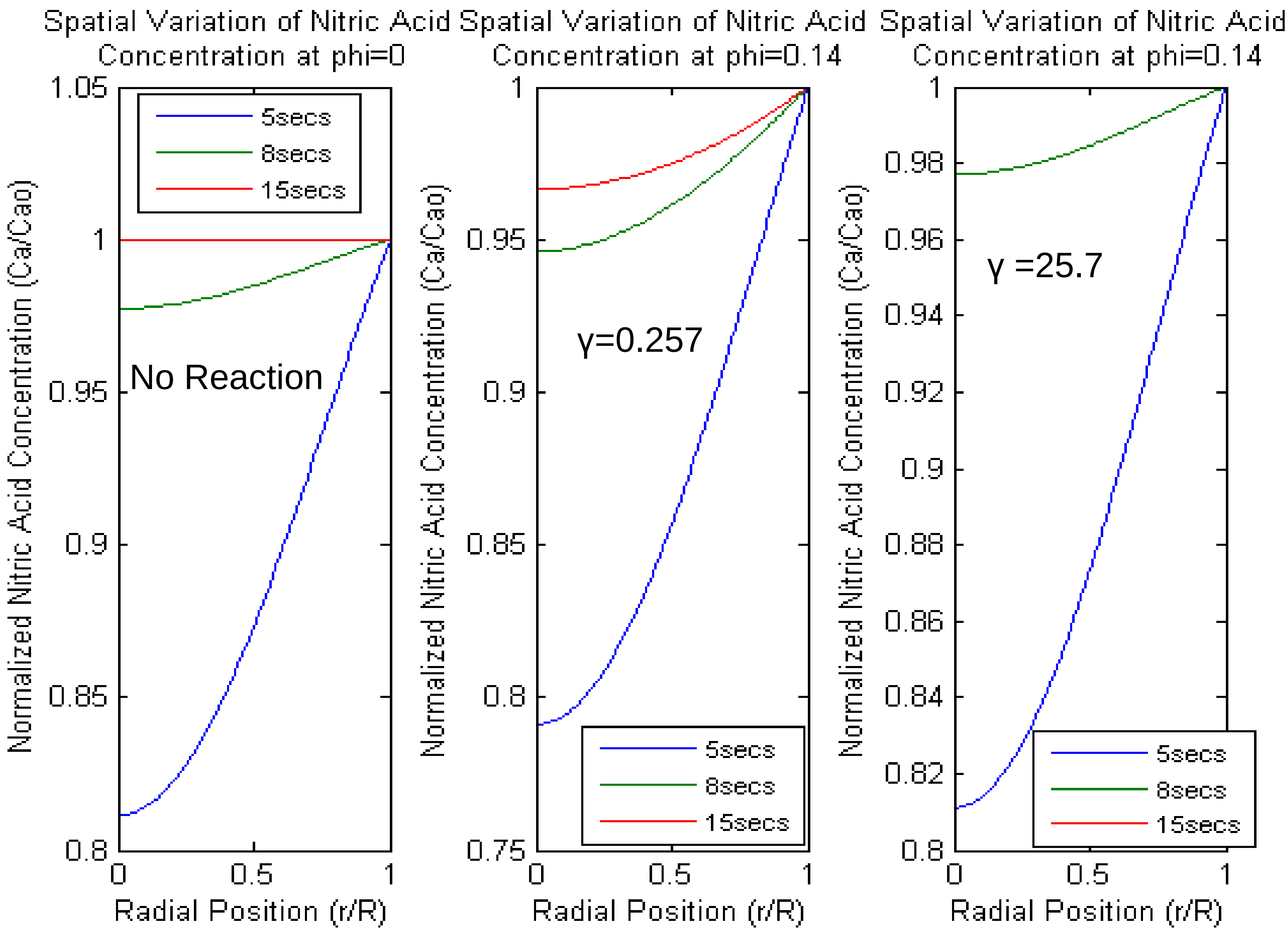
Results: Variation of Damkohler Number (Phi)



Results: Variation of Damkohler Number (Phi)



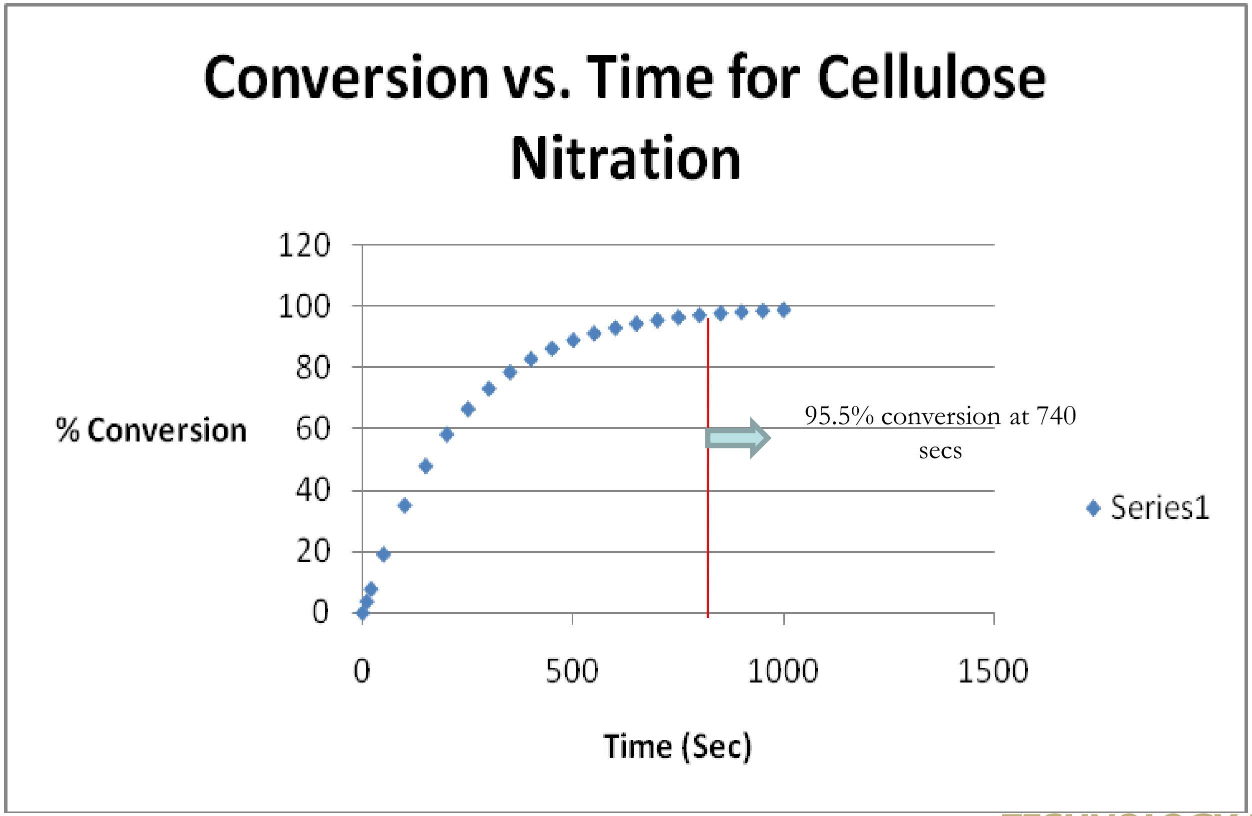
Effect of Saturation Ratio on the Nitric Acid Concentration



D.

Cellulose Conversion

- Manufacturing data
  - Reactor residence time is roughly 740 seconds
  - 96% conversion from cellulose to nitrocellulose
- 95.5% conversion was obtained from the model



Cellulose Conversion

$$X(r,t) = 1 - \frac{C_B(r,t)}{0.008634}$$

Mean Conversion

$$\bar{X}(t) = \frac{\int_0^{2\pi}\int_0^{R} X(r)\,r\,dr\,d\theta}{\int_0^{2\pi}\int_0^{R} r\,dr\,d\theta}$$

Conclusion

- Various characterization techniques are formulated to analyze properties and characteristics of cellulose fibers that can potentially affect the nitration process
- Cellulose concentration at the center of the fiber is typically lower than its surface due to the delay with acid diffusion.
- The diffusion of nitric acid into the cellulose fibers increases with increase in the diffusion coefficients. On the contrary, acid concentration decreases with increase in the rate constants up to a point when reaction is nearly at its completion.
- In the case of slow diffusion, the nitration reaction tends to occur predominantly at the fiber surface.
- Decrease in the reaction rate constant changes the nitration kinetics to reaction-controlled, leading to a more uniform nitration degree inside the fiber.
- Cellulose concentration decreases with time due to reaction while nitric acid increases because equilibrium of nitric acid is never achieved between the surface and the center of fibers whenever there is acid consumption

Thank You !

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