



U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND ARMAMENTS CENTER

Modeling the Mass Transfer Limited Nitration of Dense Cellulose Materials
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PROBLEM STATEMENT / OBJECTIVE



- **The traditional approach to nitrocellulose (NC) manufacturing relies on recipe-based methods for selecting raw materials and operating conditions for NC production**
 - Nitration diagrams, feed recipes, limited qualified sources of raw materials, etc.
 - These methods are used to correlate an expected degree of nitration in the resulting NC with a given mixed acid composition and acid to cellulose ratio
- **A lack of predictive tools results in extensive trial and error when considering changes to raw materials or nitration conditions**
 - Cellulose (source, physical form, moisture content, etc.)
 - Mixed acids (composition, oxides, etc.)
 - Processing conditions (temperature, acid to cellulose ratio, residence time, etc.)
- **Establishment of a model capable of describing the nitration of cellulose for a wide range of cellulose raw materials and reaction conditions would provide improved flexibility and reduce the reliance on these traditional methods**
 - Accurate prediction of the observed kinetics of nitration for cellulose feeds ranging from linters to wood pulp slivers or chips for various processing conditions

SOLUTION APPROACH



Measure Cellulose Characteristics and Perform Experiments and Statistical Analyses to Identify Critical Parameters for Cellulose Nitration

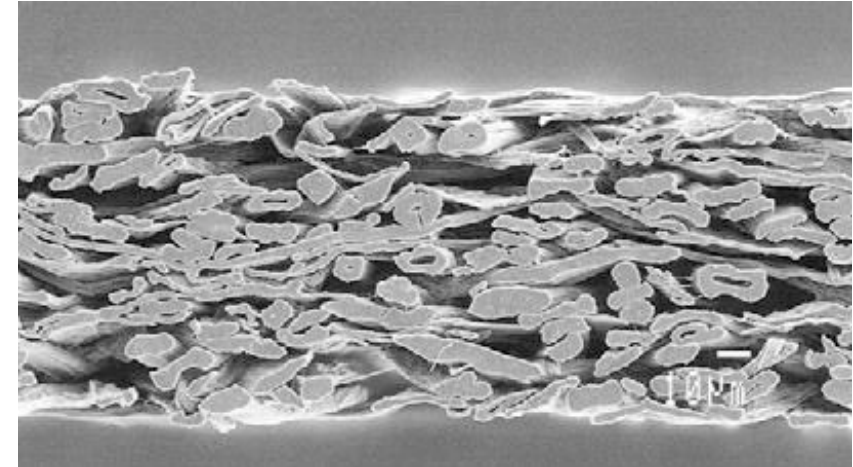
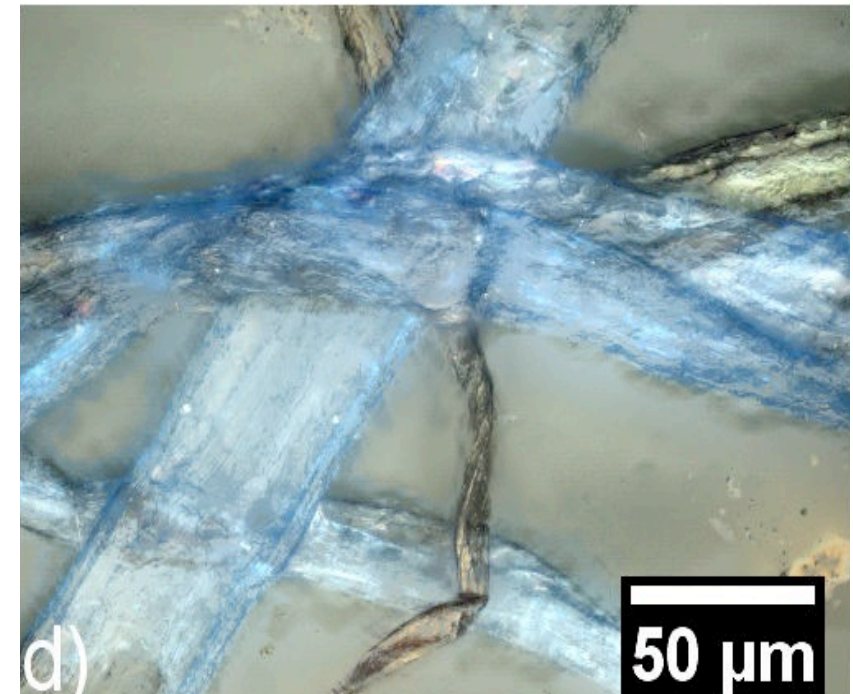
- Cellulose Characteristics
 - Wood pulp sliver (WPS) dimensions, density, porosity, morphology, purity, etc.
- Processing Conditions
 - Reactor temperature, initial acid compositions, acid to cellulose ratio, agitation, reaction time, etc.

Establish Range of Raw Materials and Reaction Conditions to Evaluate in PDE and FEM Models

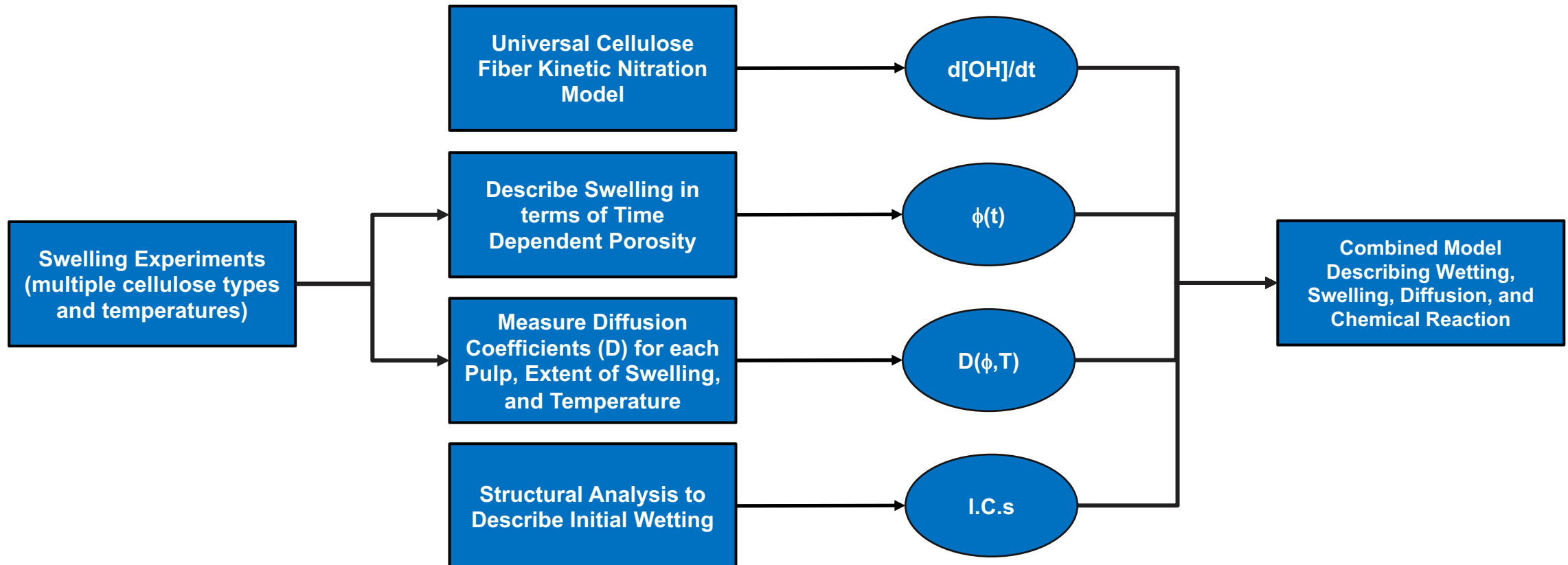
- Range determined based on assay of material properties for multiple cellulose sources and documented variation in manufacturing process conditions

Evaluate Effects of These Parameters on Extent and Uniformity of Nitration

- Develop 3-D structure for sheeted wood pulp cut into slivers
- Perform simulations to evaluate significance of parameters/interactions on hydroxyl/nitrate ester gradients within structures and calculate mass-average degree of nitration



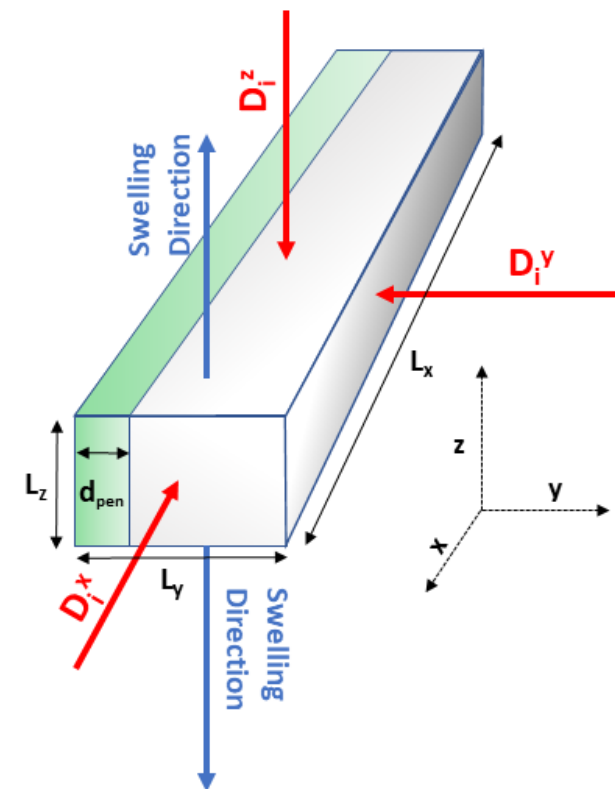
SOLUTION APPROACH



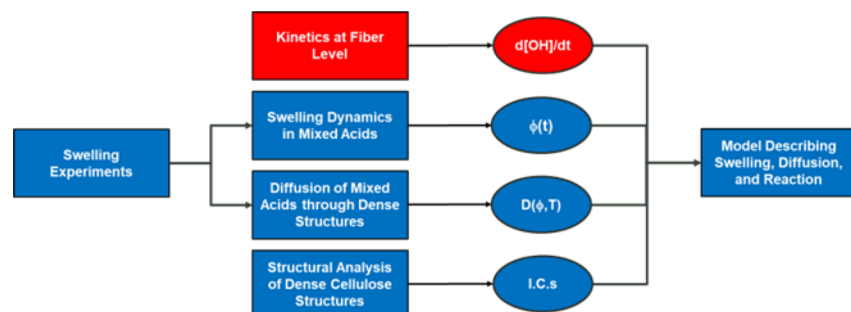
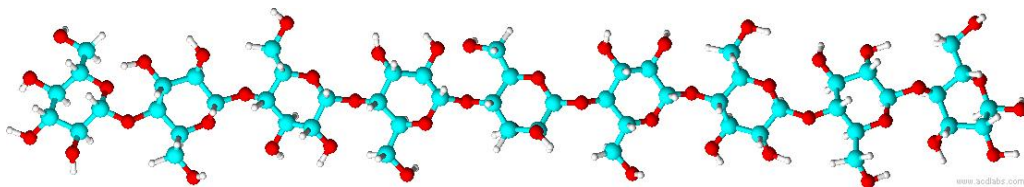
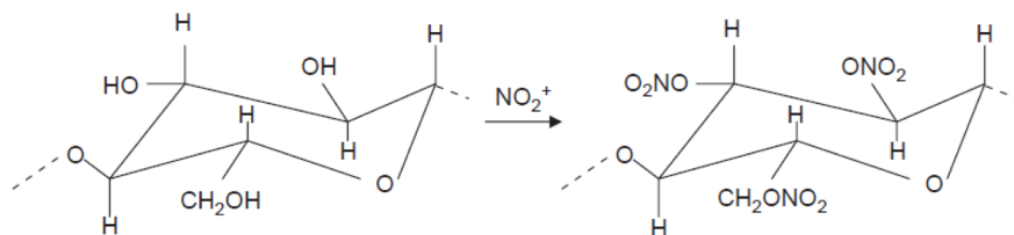
CONCEPTUAL MODEL OF DENSE CELLULOSE NITRATION

Model cellulose sliver cut from sheeted wood pulp or cotton linters as a parallelepiped with length L_x , width L_y , and height (thickness) L_z with the nitration reaction proceeding according to the following steps after the sliver is immersed in mixed acid:

1. The exterior surfaces and rapidly wetted portions of the wood pulp sliver begin to react immediately upon immersion in the mixed acids.
2. Mixed acid species penetrate the wood pulp sliver structure through diffusion; the wood pulp sliver swells in the dimension of the sheet thickness as acids penetrate the sliver, reacting with available hydroxyl groups and resulting in the net consumption of nitric acid and generation of water.
3. Mixed acid species continue to diffuse through the wood pulp sliver and react with available hydroxyl groups until the system reaches equilibrium. The effective diffusivity of mixed acid species through the sliver is dependent on both temperature and the extent of swelling (or porosity) in the wood pulp sliver.



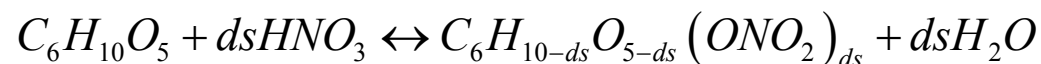
REACTION KINETICS – UNIVERSAL RATE LAW FOR CELLULOSE FIBER NITRATION



Objective: Develop empirical rate law describing the reversible reaction of cellulose with mixed acid species to produce nitrocellulose and water according to the net esterification reaction

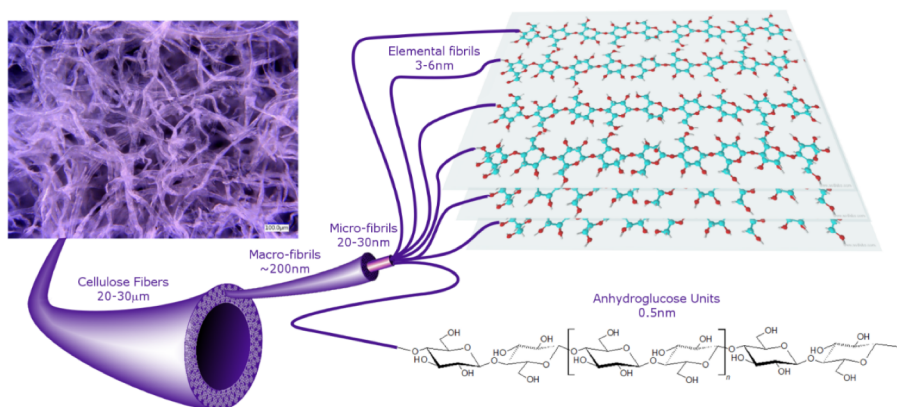
Approach: Study the kinetics of nitration for cellulose materials in a system that is not limited by mass transfer of mixed acid species to reactive sites to identify:

- The nitrating agent
- The denitrating agent
- Factors controlling the rate and extent of reaction
- Form of empirical rate law



REACTION KINETICS – UNIVERSAL RATE LAW FOR CELLULOSE FIBER NITRATION

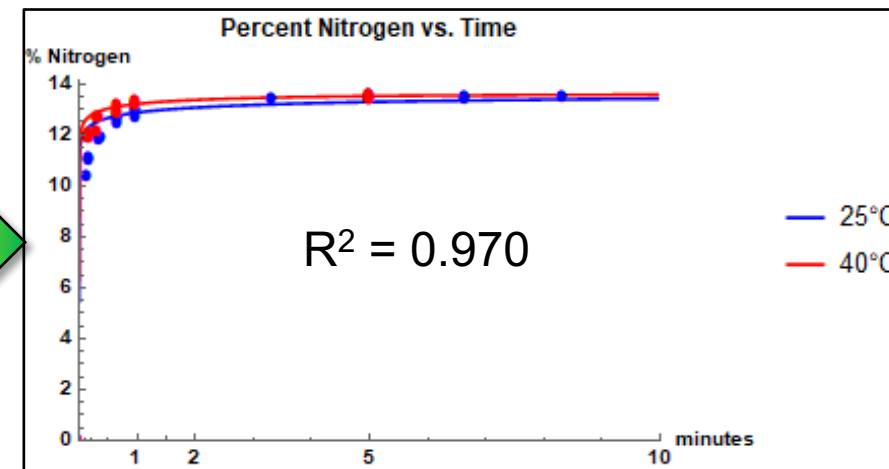
$$\frac{dC_{OH}}{dt} = -A_f e^{-E_{af}/RT} e^{-a_0 \frac{C_{ONO_2}}{C_{OH,0}}} C_{OH} C_{NO_2^+} + A_d e^{-E_{ad}/RT} C_{ONO_2} C_{H_3O^+}$$



Demonstrated that the influence of fiber morphology on the nitration kinetics of high purity cellulose fibers is not significant; all high purity wood pulp derived cellulose fibers exhibit equivalent reactivity

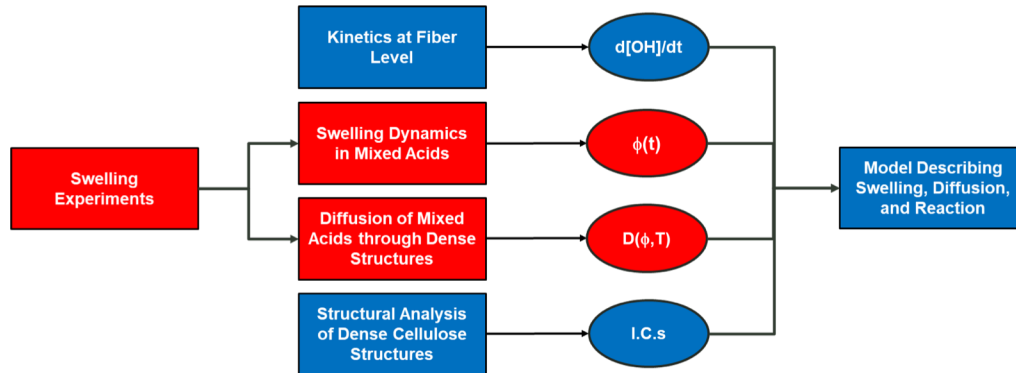
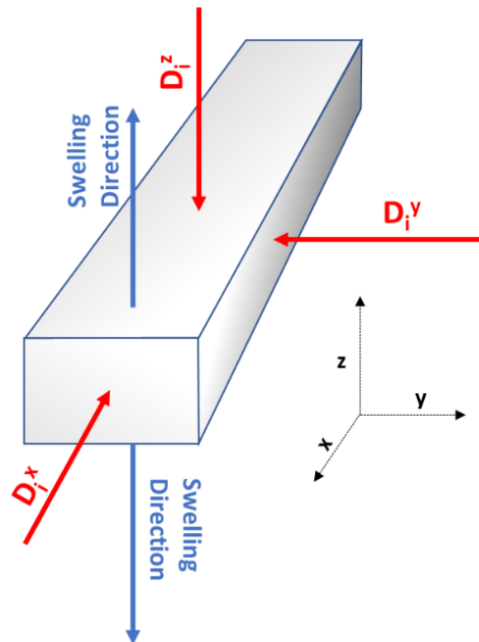
- A **universal kinetic model*** was proposed for describing the reaction kinetics of cellulose fibers

Parameter	Value	Units
A_f	1.430×10^{18}	L/mol·s
E_{af}	68674.7	J/mol
A_d	1108.14	L/mol·s
E_{ad}	46804.4	J/mol
a_0	23.1894	-



*Sullivan F, Simon L, Ioannidis N, et al. Nitration Kinetics of Cellulose Fibers Derived from Wood Pulp in Mixed Acids. *Industrial and Engineering Chemistry Research*. 2018;57(6):1883-1893.

DIFFUSION AND SWELLING EVALUATION



Objective: Experimentally measure rates of swelling and anisotropic diffusion coefficients for diffusion of mixed acids through wood pulp slivers to consider characteristic relaxation and diffusion times for swelling and diffusion upon immersion of wood pulp slivers in mixed acids

Approach: Conduct swelling experiments to evaluate source dependent rate and extent of swelling at multiple temperatures then measure anisotropic diffusion coefficients at multiple temperatures and extents of swelling in a modified stokes membrane diffusion cell

EVALUATION OF SWELLING DYNAMICS



Wood pulp sliver swelling experiments conducted to measure rate and extent of unidirectional swelling of wood pulps as a function of pulp type and temperature

- Three high purity wood pulps (sulfite softwood, kraft softwood, and kraft hardwood)
- Mixed acid composition consisting of 37.0% HNO₃, 54.6% H₂SO₄, and 8.4% H₂O
- For each experiment, a 5 x 5 array of wood pulp slivers was immersed in mixed acid and extent of swelling was measured as a function of time using handheld digital microscope

Wood pulp sliver thickness was measured at given time intervals to measure time-dependent extent of swelling

- Average dimensionless extent of swelling and porosity calculated for each experimental data point

Characteristic relaxation time, λ , calculated for each wood pulp sliver configuration and temperature

- Used published model for relaxation-controlled volume expansion and experimental swelling data
- Calculated time dependent porosity and time to reach maximum extent of swelling for each wood pulp sliver

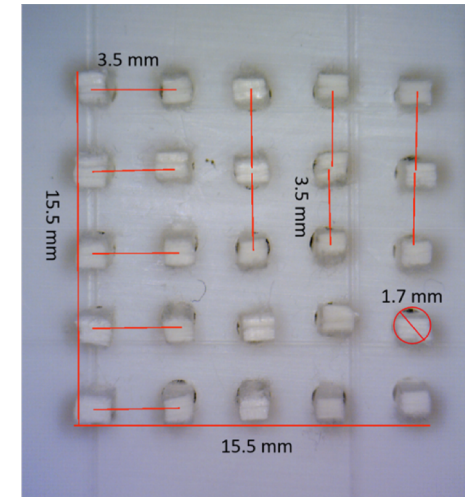
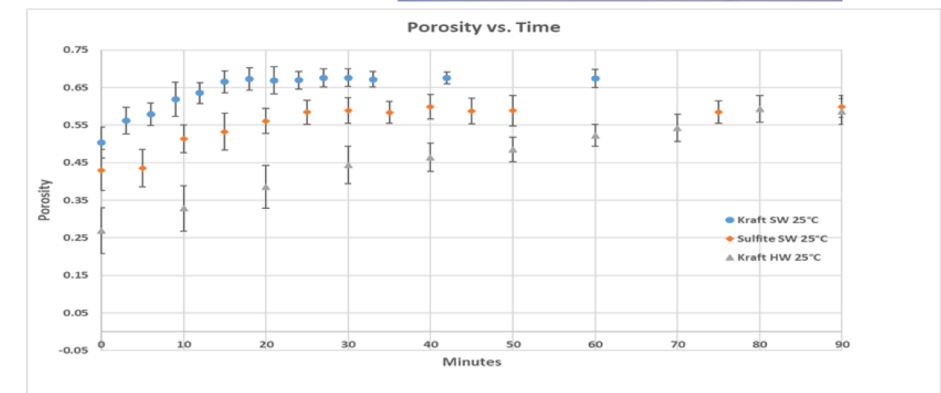
Dimensionless thickness and porosity tend to increase linearly before reaching a maximum value

- Based on this observation, modeled swelling as linear function of porosity using initial porosity, final porosity, and time

Pulp Type	Pulping Method	Sheet Density	Fiber Coarseness	% α -cellulose	Mean Fiber Length
		kg/m ³	mg/m	wt %	m
Softwood	Kraft	720	0.126	98.7	1.58E-03
Softwood	Sulfite	700	0.211	90.9	1.94E-03
Hardwood	Kraft	950	0.092	97.8	8.98E-04

$$\varepsilon = \frac{\Delta l}{l_0}$$

$$\frac{dV_t}{dt} = \frac{V_{eq,t} - V_t}{\lambda}$$



DIFFUSION EVALUATION



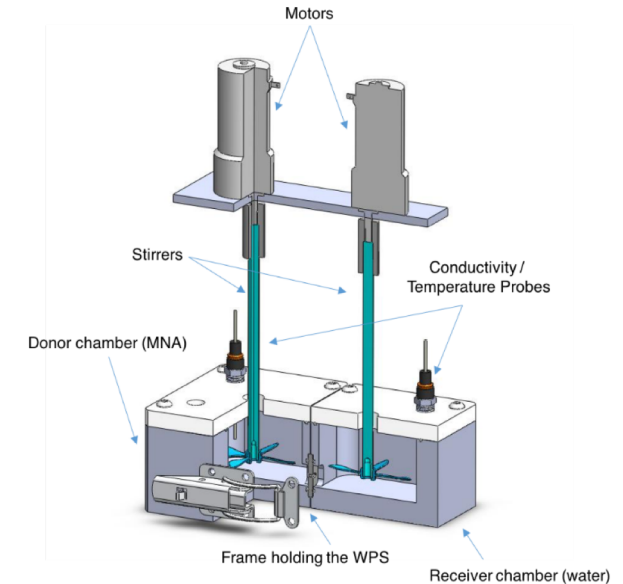
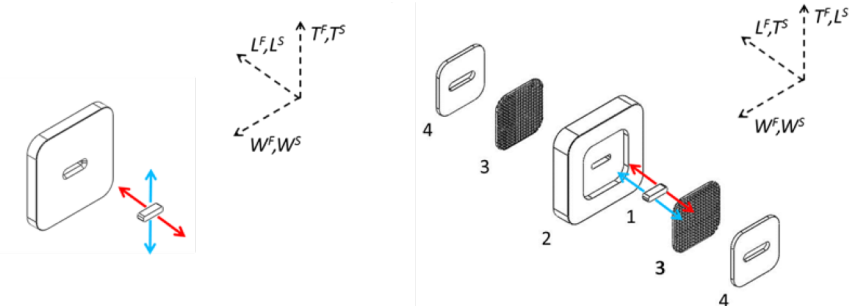
Diffusion experiments conducted using custom membrane diffusion cell and frames to evaluate diffusion of mixed acids through wood pulp slivers at two temperatures and extents of swelling per pulp type

- Three high purity wood pulps (sulfite softwood, kraft softwood, and kraft hardwood)
- Mixed acid composition consisting of 37.0% HNO_3 , 54.6% H_2SO_4 , and 8.4% H_2O
- Diffusion measured in x/y and z directions for initial and swollen states for each pulp type where z is the dimension of the sheet thickness
- Acid concentrations in receiver cell measured using conductivity probe
- Ion chromatography used to analyze S:N ratios in donor and receiver cell

Characteristic diffusion time time, θ , calculated for each wood pulp sliver configuration and temperature

- Used equation for 1-D diffusion through sheet of thickness, l

$$\theta = \frac{l^2}{D_{eff}}$$



DIFFUSION EVALUATION



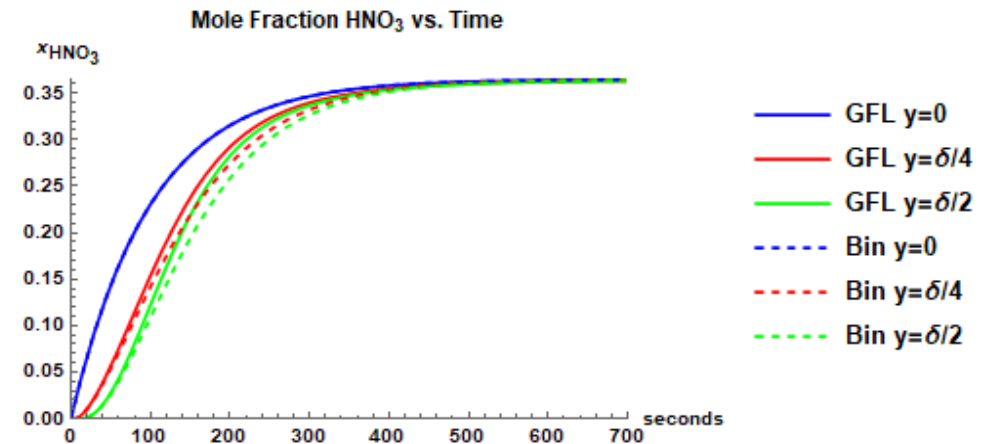
Effective diffusivity measured at 25°C and 40°C for each pulp type, temperature, and extent of swelling

Analysis of multicomponent diffusion based on inversion of Maxwell-Stefan equations conducted to consider error associated with measurement of overall effective diffusivity and a single binary diffusion coefficient, D_{AB}

- Diffusion through stagnant layer and equimolar counter-diffusion considered
- Percent difference in mole fractions of acidic species compared for the two diffusion models:
 - < 7% for stagnant film case, < 1% for equimolar counter-diffusion case

Source	Temperature	Diffusivity $\times 10^{10}$ (m ² /sec)			
		unswollen		swollen	
		xy	z	xy	z
Sulfite Softwood	25°C	2.37 $\pm$ 0.16	0.63 $\pm$ 0.09	2.40 $\pm$ 0.10	5.00 $\pm$ 0.65
	40°C	3.22 $\pm$ 0.62	1.47 $\pm$ 0.32	2.18 $\pm$ 0.09	2.59 $\pm$ 0.33
Kraft Softwood	25°C	2.13 $\pm$ 0.42	1.61 $\pm$ 0.40	107 $\pm$ 17	2.43 $\pm$ 0.25
	40°C	4.12 $\pm$ 0.32	1.57 $\pm$ 0.29	163 $\pm$ 28	3.03 $\pm$ 0.87
Kraft Hardwood	25°C	1.02 $\pm$ 0.12	0.37 $\pm$ 0.12	3.18 $\pm$ 0.24	1.00 $\pm$ 0.08
	40°C	3.87 $\pm$ 0.35	1.50 $\pm$ 0.30	3.65 $\pm$ 0.34	3.14 $\pm$ 0.33

$$D_{eff} = \frac{D_{AB}\phi}{\tau}$$



DIFFUSION EVALUATION



Calculated dimensionless Deborah number (ratio of characteristic relaxation to diffusion times) for each pulp type for diffusion and swelling in z direction

- Diffusion and relaxation occur on similar timescales suggesting that the diffusion coefficients can be modeled as time-dependent diffusivities that are related to the rate of relaxation in the wood pulp slivers
- Specifically, diffusion coefficient can be modeled as a time-dependent function of the porosity in the wood pulp sliver
- Characteristic diffusion times are always 2-5 times higher in the z direction even for large slivers so there is limited benefit to modeling this problem as a moving boundary problem

Empirical diffusion models evaluated to model effective diffusivity as a function of wood pulp sliver porosity

- Direct use of pulp-specific effective diffusivities using linear approximation and three empirical models
- Temperature dependence of diffusion coefficient described using Arrhenius relationship

Sample	$\phi_{\text{unswollen}}$	ϕ_{swollen}	λ_z (s)	θ_z (s)	De	θ_{xy} (s)	θ_z/θ_{xy}
Sulfite-SW	0.52	0.62	862.1	5173.4	0.17	1055.2	4.9
Kraft-SW	0.58	0.71	443.8	2961.7	0.15	1174.7	2.5
Kraft-HW	0.42	0.61	3871.0	5533.5	0.70	2453.4	2.3

$$De = \frac{\lambda}{\theta}$$

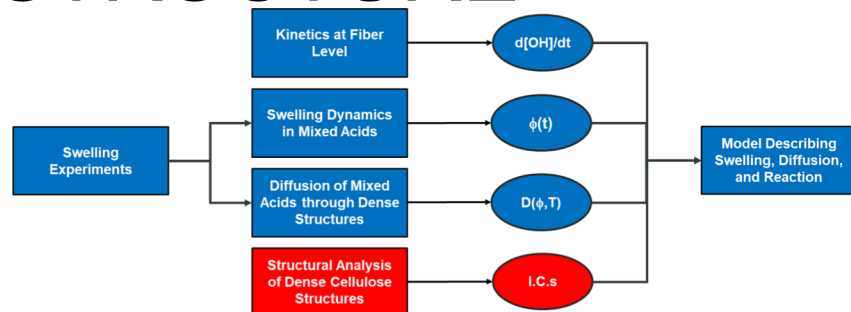
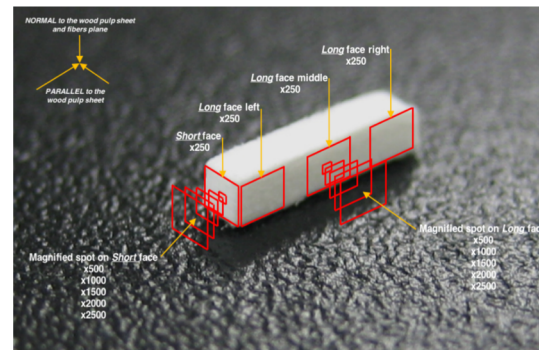
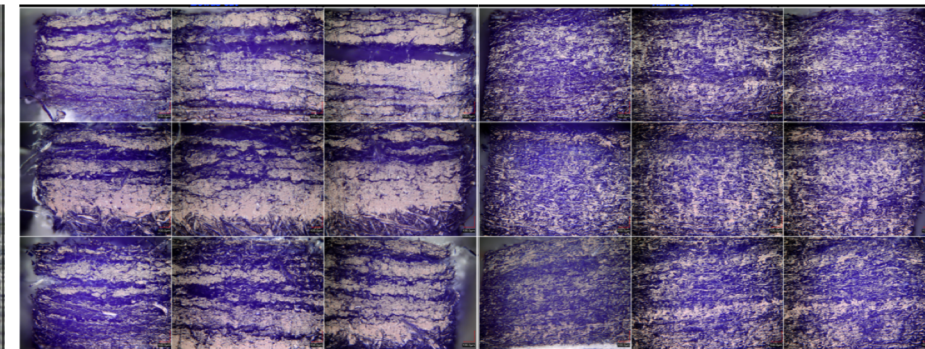
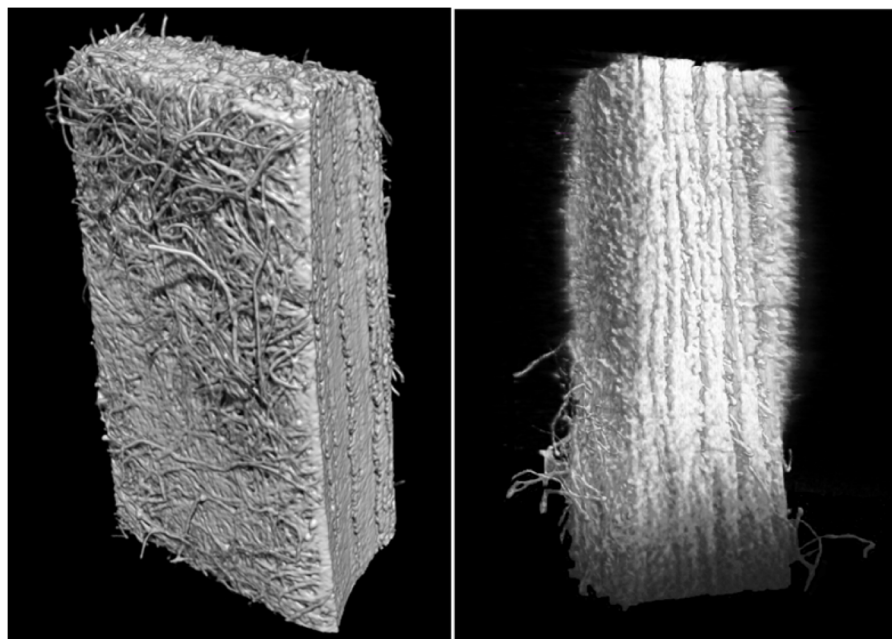
Direct use of Effective Diffusivity

$$D_{\text{eff}}(t) = D_{\text{eff}}(t_{\text{sw}}) - \frac{(D_{\text{eff}}(t_{\text{sw}}) - D_{\text{eff}}(0))}{t_{\text{sw}}}(t_{\text{sw}} - t)u(t_{\text{sw}} - t)$$

Empirical Models

$$\tau = 1 + q \frac{(1 - \phi)}{(\phi - \phi_c)^m} \quad \ln D = \ln D_o - \beta \omega_p \quad \tau = p(1 - \phi) + 1$$

CHARACTERIZE AND MODEL PULP STRUCTURE



Objective: Analyze hand-cut and machine-cut wood pulp slivers to identify features that may promote rate and uniformity of nitration; develop approaches for modeling the influence of these features

Approach: Evaluate wood pulp slivers structures using a combination of optical microscopy and micro CT to identify differences between hand-cut slivers which are known to exhibit poor reactivity and machine-cut slivers which are known to exhibit improved nitration performance

CHARACTERIZE AND MODEL PULP STRUCTURE

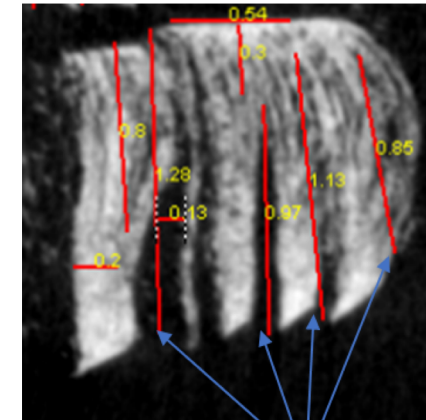


Because these delaminated and fused regions were observed, a more detailed analysis of the wood pulp sliver structures was conducted using Xray microtomography

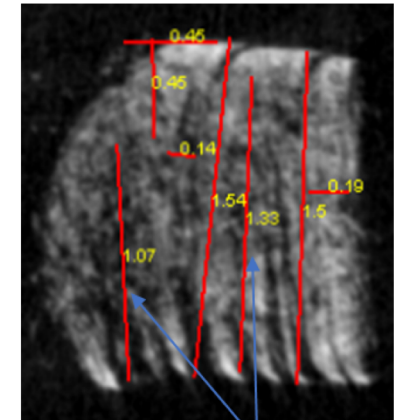
- 4 pulp types: sulfite softwood, kraft softwood, alternate kraft softwood, sheeted cotton
- Multiple lots enabled limited evaluation of sheet characteristics
- 6 sliver sizes: 0.5mm, 0.8mm, 1mm, 1.25mm, 1.5mm, 1.8mm
- 3 cutter configurations: R, N, and M

12 slivers were scanned for each sliver/cutter/size combination and the number and extent of delaminated regions were measured in cross sections taken every $\frac{1}{2}$ mm over the 6mm length of the sliver

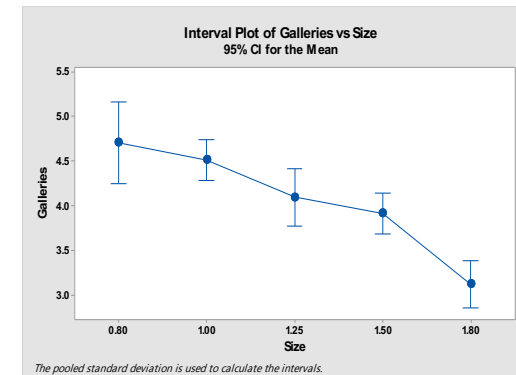
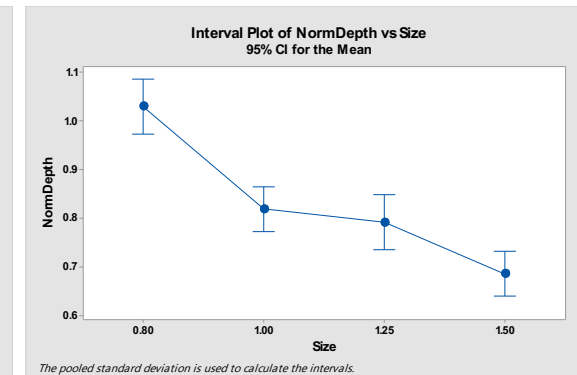
- A preliminary analysis of this data appeared to show correlations between the volume in the delaminated regions of the sliver and the overall cross section of the sliver, with smaller slivers exhibiting a greater relative porous volume
- A cutter effect was also observed for cutters that differed by the design of the rotary cutting tool



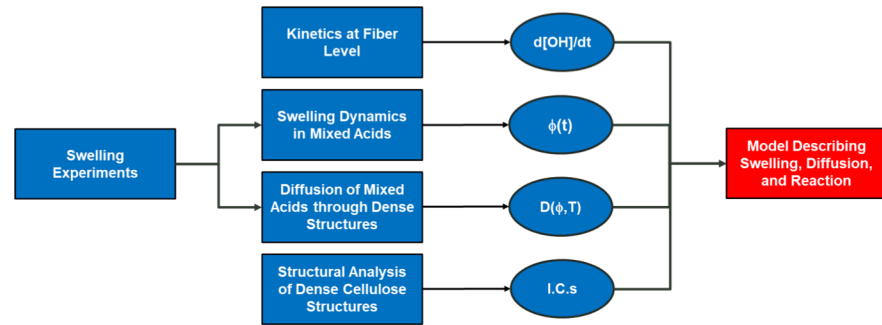
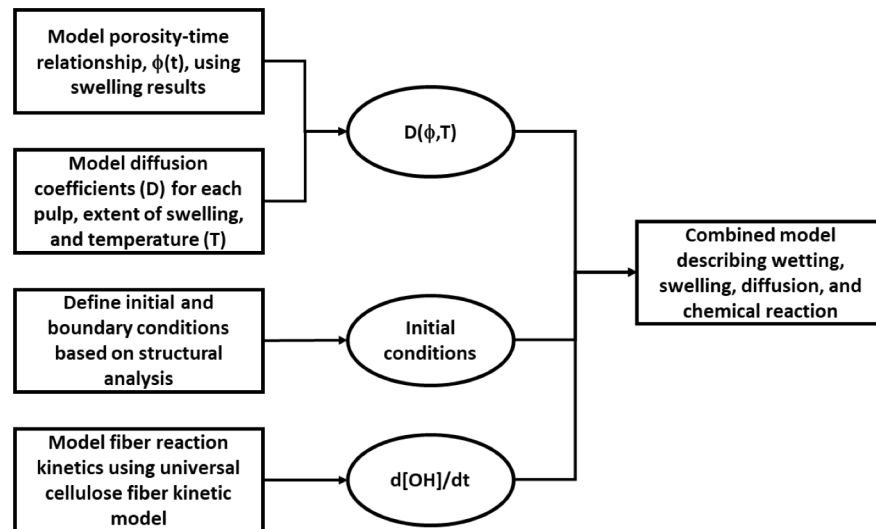
**Number of
Galleries**



**Depth of
Galleries**



MATHEMATICAL MODEL DEVELOPMENT



Objective: Develop models for the nitration of wood pulp slivers in mixed acids that consider the sliver size, mixed acid composition, and acid to cellulose ratio

Approach: Model nitration of wood pulp sliver using systems of unsteady partial differential equations describing generation and consumption of hydroxyl groups, nitrate ester groups, and mixed acid species within a homogenous, three-dimensional representation of a wood pulp sliver

MATHEMATICAL MODEL DEVELOPMENT



Unsteady Mass Balances:

$$\frac{\partial[H_2SO_4]}{\partial t} = \frac{\partial}{\partial x} \left(D_{H_2SO_4,x} \frac{\partial[H_2SO_4]}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_{H_2SO_4,y} \frac{\partial[H_2SO_4]}{\partial y} \right) + \frac{\partial}{\partial z} \left(D_{H_2SO_4,z} \frac{\partial[H_2SO_4]}{\partial z} \right)$$

$$\frac{\partial[HNO_3]}{\partial t} = \frac{\partial}{\partial x} \left(D_{HNO_3,x} \frac{\partial[HNO_3]}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_{HNO_3,y} \frac{\partial[HNO_3]}{\partial y} \right) + \frac{\partial}{\partial z} \left(D_{HNO_3,z} \frac{\partial[HNO_3]}{\partial z} \right) + r_{OH}$$

$$\frac{\partial[H_2O]}{\partial t} = \frac{\partial}{\partial x} \left(D_{H_2O,x} \frac{\partial[H_2O]}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_{H_2O,y} \frac{\partial[H_2O]}{\partial y} \right) + \frac{\partial}{\partial z} \left(D_{H_2O,z} \frac{\partial[H_2O]}{\partial z} \right) - r_{OH}$$

$$\frac{\partial[OH]}{\partial t} = r_{OH}$$

$$\frac{\partial[ONO_2]}{\partial t} = -r_{OH}$$

MATHEMATICAL MODEL DEVELOPMENT



Models were evaluated to consider a range of initial conditions with five different diffusion coefficient models

- Initial Conditions:
 - Very slow wetting where no mixed acids are initially present in the wood pulp sliver structure
 - Fast wetting where the sliver is immediately saturated with mixed acids
 - Rapid, partial wetting where acids penetrate the wood pulp sliver structure to a depth, d_{pen} , that is a function of the puffing or delamination of the wood pulp sliver
- Empirical Diffusion Models:
 - “Linear Diffusivity” – for each pulp type and temperature the experimentally measured effective diffusivity varies linearly between the effective diffusivity at the initial state to the effective diffusivity at the fully swollen state between $t=0$ and $t=t_{swell}$
 - “Linear Tortuosity” – tortuosity varies as an empirical, linear function of porosity
 - “Exponential Diffusivity” – Diffusivity varies as an exponential function of cellulose weight fraction
- Theoretical Tortuosity Models
 - Millington-Quirk Model

$$\tau = \phi^{-1/3} \quad D_{eff} = D_{AB}\phi^{4/3}$$
 - Bruggeman Model

$$\tau = \phi^{-1/2} \quad D_{eff} = D_{AB}\phi^{3/2}$$

MATHEMATICAL MODEL DEVELOPMENT



Porosity was assumed to vary linearly with time for all simulations that were run to capture the effect of swelling

Empirical Diffusion Models

- The empirical models significantly underestimated the extent of nitration at early nitration times when using the slow wetting initial condition and overestimated the extent of nitration at early reaction times when using the fast wetting initial condition
- These models provided reasonable agreement with experimental results when using the variable wetting initial condition with the linear diffusivity model providing the best fit ($R^2=0.992$) and the exponential diffusivity model providing the poorest fit ($R^2=0.984$)

Theoretical Models:

- The theoretical models predict much higher initial effective diffusivities for mixed acid through the wood pulp sliver structure
- Given this, these models provide reasonable agreement ($R^2=0.985$) with the experimental data without considering initial wetting of the wood pulp sliver with mixed acids.

Subset	Correlation Coefficient						
	Slow Wetting			Fast Wetting	Variable Penetration		
	Lin Diff	M-Q	Brugg	Lin Diff	Lin Diff	Lin Tor	Exp Diff
Overall	0.951	0.985	0.985	0.858	0.992	0.986	0.984
25°C	0.942	0.979	0.979	0.841	0.991	0.982	0.982
40°C	0.961	0.992	0.991	0.875	0.995	0.991	0.988
High H₂SO₄	0.955	0.982	0.984	0.826	0.994	0.991	0.987
High HNO₃	0.938	0.989	0.986	0.962	0.990	0.980	0.979

MATHEMATICAL MODEL DEVELOPMENT

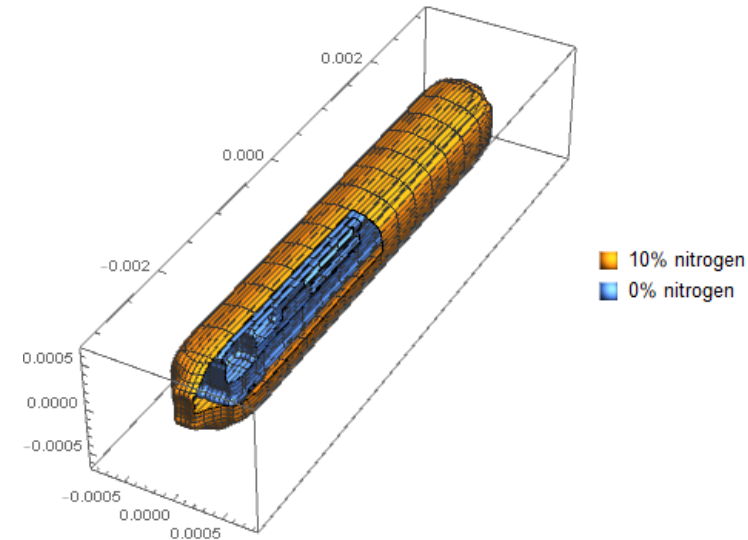
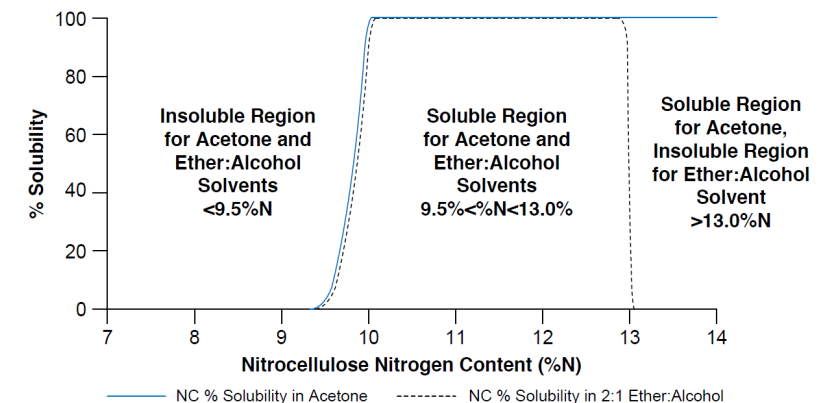


A series of diffusion models and initial conditions were evaluated to solve the system of partial differential equations describing wood pulp sliver nitration

Generalized models were demonstrated that provided reasonable agreement with experimental results; in particular, theoretical models were evaluated that do not require experimental measurement of effective diffusivities or estimation of partial wetting of the wood pulp sliver with mixed acids

These models cannot predict incomplete nitration that is observed in some large wood pulp slivers even after long reaction times; this effect may be a result of denitration in stabilization operations or of high water concentrations in the center of the sliver hindering formation of nitronium ion

These models can be used to predict kinetics, extent of nitration, and resulting solubility of wood pulp slivers for various reaction conditions and residence times



FINITE ELEMENT MODEL IMPLEMENTATION



All four models that were evaluated required special treatment to handle the combination of a very fast initial reaction rate and an imposed surface concentration initial condition:

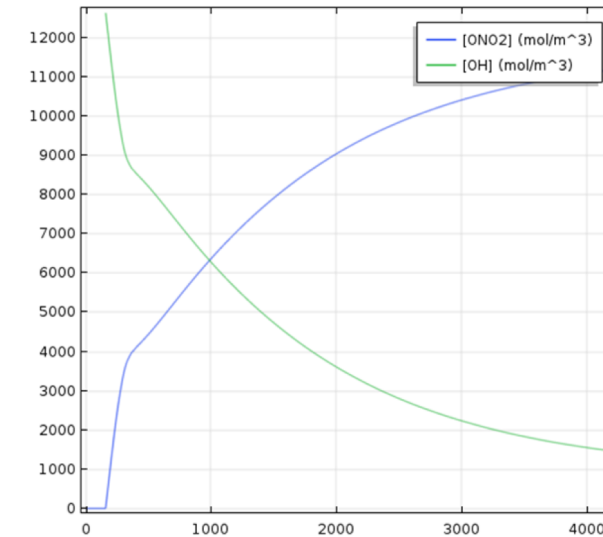
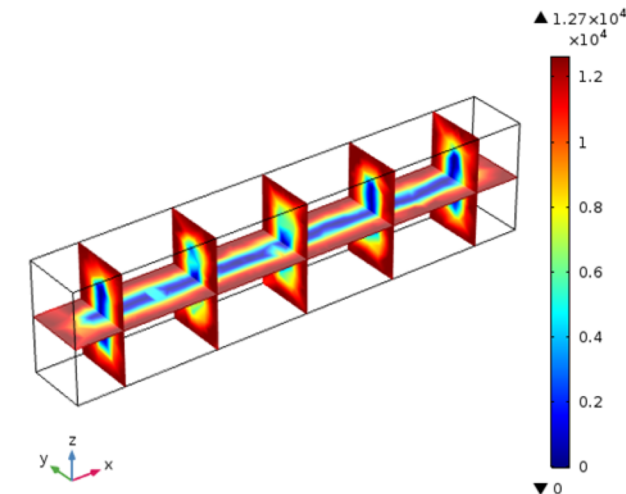
- Smoothing step functions at surface boundary conditions
- Ramp functions for initial reaction rate to prevent numerical errors in concentration gradient calculations

The simple homogeneous model provided comparable results to the PDE models with variable wetting:

- Estimates for extent of nitration achieved at short reaction time with the FEA models appear to be very sensitive to the mesh size.

The improved porous model provided the best agreement with the subset of experimental results that were used for validation

- This model also uses the Bruggeman equation and a user-defined variable porosity



CONCLUSIONS



- **Conducted experimental work to describe various phenomena occurring during industrial-scale nitration of cellulose and to characterize structure of dense cellulose materials**
 - Swelling and diffusion cell experiments
 - Structural analysis (optical microscopy and Micro CT) of “dense” cellulose materials
 - Lab scale nitration with a range of cellulose types, mixed acids, sliver sizes, and temperatures to generate validation data set
- **Demonstrated a model* capable of describing a range of cellulose materials varying from loose cellulose fibers to slivers cut from sheeted cotton linters or wood pulp**
 - Dissociation of mixed acids to ionic species responsible for equilibrium-controlled nitration reaction
 - System of partial differential equations describing wetting, swelling, diffusion, and reaction
 - Theoretical models relating porosity to diffusivity of mixed acids through dense cellulose structures
- **Establishment a model capable of accurately predicting the nitration behavior of a range of raw materials and processing conditions using a first principles approach**
 - Demonstrated practical approach to rapidly establish reaction conditions for new dense cellulose materials based on a simple swelling evaluation and theoretical diffusion models.

*Sullivan F, Simon L, Ioannidis N, et al. Chemical Reaction Modeling of Industrial Scale Nitrocellulose Production for Military Applications. *AIChE Journal*. 2020;66(7):e16234.

ACKNOWLEDGMENTS



- **Co-authors**

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THANK YOU.

