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A Universal Kinetic Model for the Nitration of Cellulose Fibers in Mixed Acids

Presented by:

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Establish a model capable of describing the nitration kinetics of a wide range of cellulose fibers

- Will enable universal fiber nitration kinetics to be combined with models describing mass transfer and other phenomena to describe the observed kinetics of cellulose feeds ranging from linters to wood pulp slivers or chips

Reduce reliance on recipe-based approaches by providing predictive capability for nitrocellulose (NC) production

- Commercial applications of NC preceded fundamental understanding of the chemistry of cellulose and NC
- To compensate for this, NC producers rely on nitration diagrams and feed recipes to determine the expected degree of nitration in the resulting NC for a given mixed acid composition and acid to cellulose ratio

• Net Equation Describing Nitration (esterification) of Cellulose

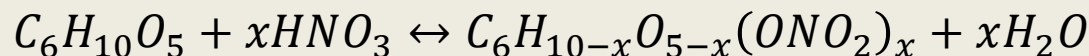
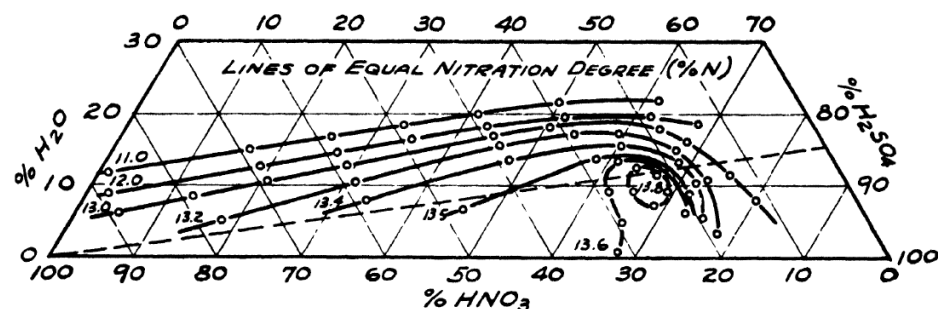


Fig. 6. Effect of spent acid composition on the nitrogen content of nitrocellulose (Berl, Address, and Escales³⁶).

Berl, E., Address, K. R., and Escales, E., *Beiträge zur Kenntnis der Mischsäure*, J. F. Lehman, Munich, 1937

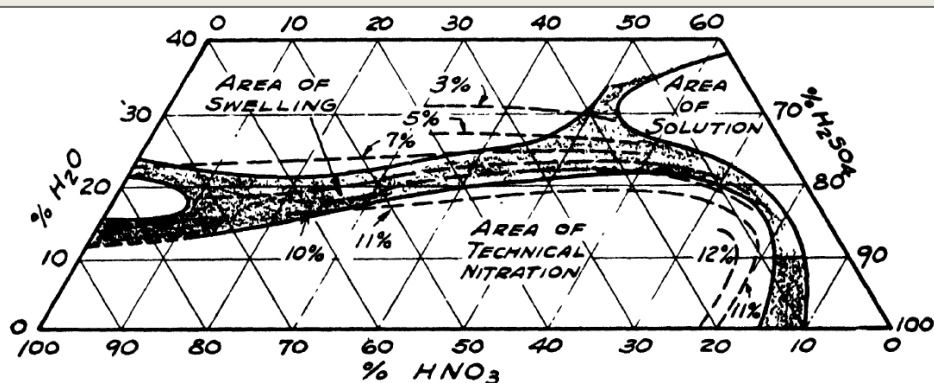
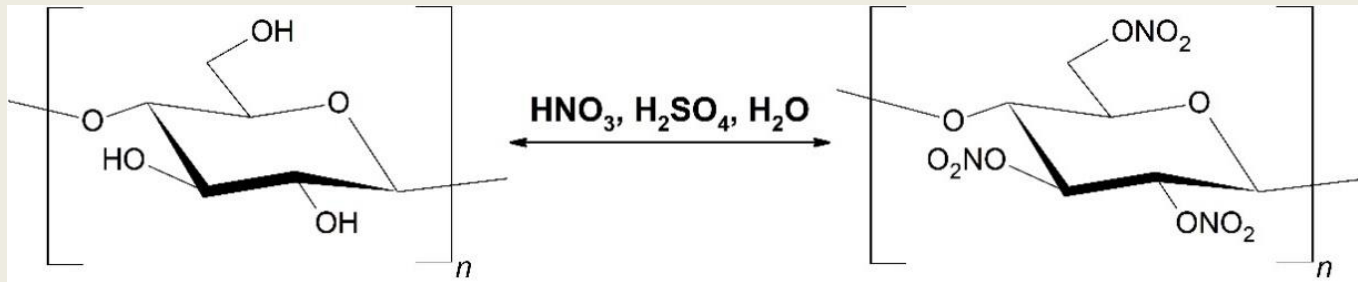


Fig. 7. Effect of dipping acid composition on the nitrogen content of nitrocellulose (Miles and Milbourn³⁸).

Miles, F. D., *Cellulose nitrate: the physical chemistry of nitrocellulose, its formation and use*. Published for Imperial Chemical Industries by Oliver and Boyd: 1955

- The historical approach using ternary plots or recipes correlating acid compositions to resulting degree of nitration is very limited:
 - Does not account for cellulose characteristics or mass transfer limitations
 - Relates equilibrium acid composition to resulting degree of nitration
 - Does not address kinetics, temperature dependence, or process dynamics
 - Generally does not provide degree of insight required for process control or to respond to changes in raw materials



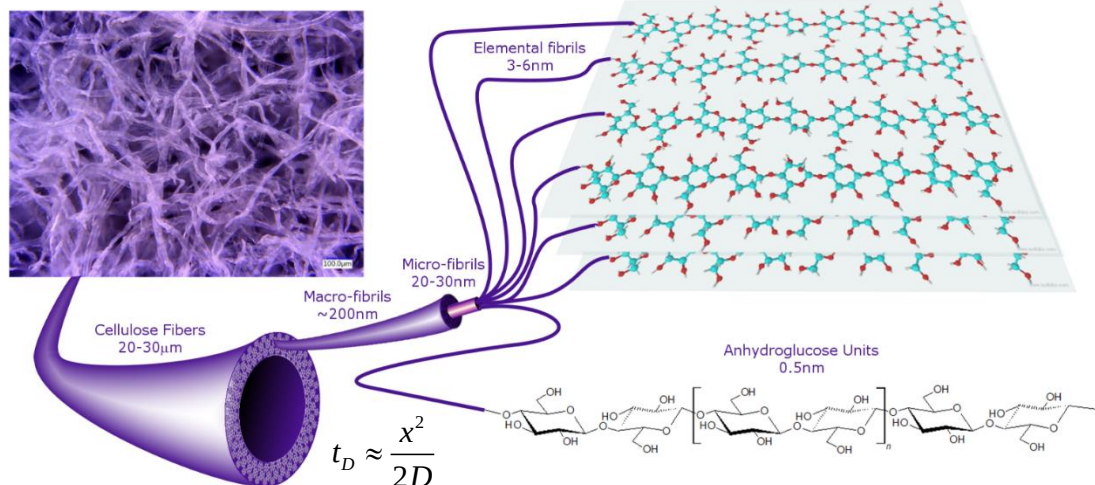
- Factors that must be considered in developing a universal kinetic model for the nitration of cellulose fibers:
 - The nitrating agent
 - Influence of fiber characteristics on the rate of reaction
 - Influence of fiber characteristics on the extent of reaction
- Can answer these questions through a combination of experimentation and review of previous work
- Mass transfer also plays an additional role in industrial-scale NC production, particularly for dense materials such as wood pulp slivers or chips



$$\frac{dC_{OH}}{dt} = -A_f e^{-E_{af}/RT} e^{-a_0 \frac{C_{ONO_2}}{C_{OH,0}}} C_{OH} C_{NO_2^+} + A_d e^{-E_{ad}/RT} C_{ONO_2} C_{H_2O}$$

- Empirical model describing the net conversion of hydroxyl groups to nitrate ester groups in the presence of nitronium ions and water
- Equilibrium-controlled reaction with nitronium ion (NO_2^+) as nitrating agent
- Utilizes activity decay factor* to describe the decreasing reactivity of remaining hydroxyl groups as reaction proceeds
- Denitration modeled as an elementary bimolecular reaction
- Can test the validity of this model through analysis and controlled nitration experiments

*Salmi, T.; Valtakari, D.; Paatero, E.; Holmbom, B.; Sjöholm, R., Kinetic study of the carboxymethylation of cellulose. *Ind. Eng. Chem. Res.* **1994**, 33 (6), 1454-1459



Diffusion Times for Wood Pulp Fibers

<i>Fiber Type</i>	<i>Fiber Diameter</i>	<i>Wall Thickness</i>	<i>Diffusion Time</i>
	(μm)	(μm)	(s)
Sulfite-Pulped Softwood	21.4	4.9	0.02
Kraft Pulped Softwood	22.3	4.2	0.02
Kraft Pulped Hardwood	16.0	3.5	0.01
$D = 5.49E-10 \text{ m}^2/\text{s}^*$			

*Foston, M.; Ragauskas, A. J., Changes in the structure of the cellulose fiber wall during dilute acid pretreatment in Populus studied by 1H and 2H NMR. *Energy Fuels* **2010**, 5677-5685

- Single Cellulose Fibers (SCF) represent smallest practical scale for evaluating industrial nitration kinetics:
 - Studies measuring the diffusivity of acids through the walls of plant-derived cellulose fibers indicate that fibers are wetted very rapidly
 - This suggests that mass transfer may be insignificant in the nitration kinetics of cellulose fibers



Cellulose Fiber Types Evaluated

Characteristic	Cellulose Fiber Source		
	Sulfite Softwood	Kraft Softwood	Kraft Hardwood
% α -cellulose	90.9	98.7	97.8
% Moisture	3.99%	5.12%	4.01%
% Cellulose I	64.4	36.3	56.6
% Cellulose II	3.2	19.5	2.2
% Total Crystallinity	67.7	55.8	58.9
Fiber length (mm)	1.578	1.936	0.898
Coarseness (mg/m)	0.126	0.211	0.092
Fiber width (μm)	21.4	22.3	16
Fiber wall thickness (μm)	4.9	4.2	3.5
Mn (kDa)	245.2	284.2	288.3
Mw (kDa)	409.5	423.5	445.3
Polydispersity	1.7	1.6	1.5

Mixed Acid Evaluated

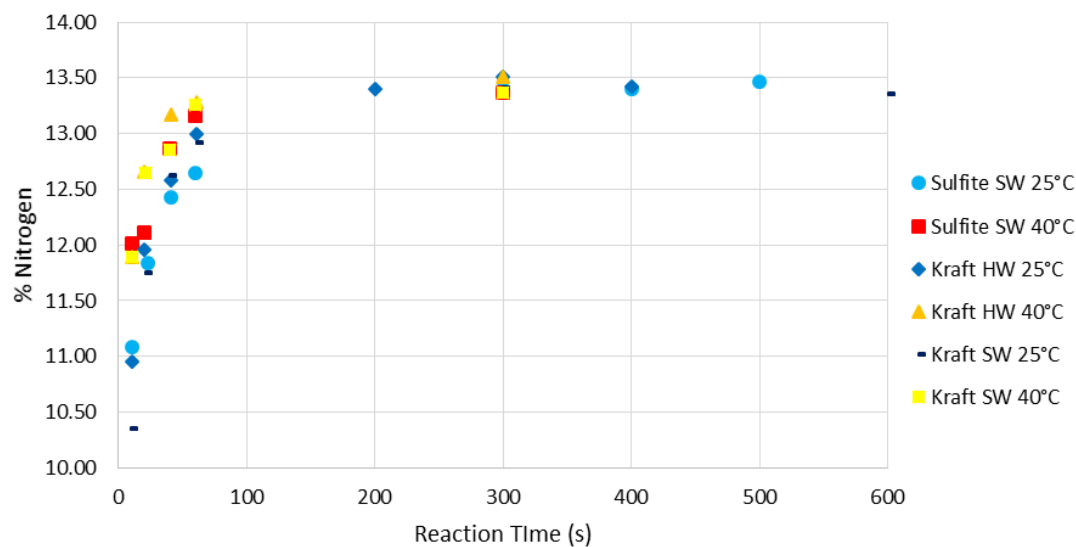
Species	Initial Composition mass %	Equilibrium Composition	
		30:1 mass %	150:1 mass %
HNO_3	37.0%	34.3%	36.5%
H_2SO_4	54.6%	56.0%	54.9%
H_2O	8.4%	9.7%	8.7%
$[\text{NO}_2^+] @ 25^\circ\text{C}^*$	1.08	0.78	1.02
$[\text{NO}_2^+] @ 40^\circ\text{C}^*$	0.97	0.68	0.91
Nitronium ion concentrations (mol/l) estimated using equilibrium model published by Albright et. al.			

*Albright, L. F.; Sood, M. K.; Eckert, R. E., Modeling Nitronium Ion Concentrations in HNO_3 - H_2SO_4 - H_2O Mixtures. ACS Symp. Ser. **1996**, 623, 201-213.

- Broad range of cellulose fiber properties (purity, crystallinity, morphology, etc.) to evaluate effects of fiber characteristics on rate and extent of reaction
- Significant differences in wall thickness, crystallinity, and coarseness to confirm hypothesis that mass transfer is insignificant
- Large acid to cellulose ratio (150:1) used to ensure rapid wetting and to maintain nearly constant nitration conditions

Time (sec)	Sulfite Pulped Softwood		Kraft Pulped Hardwood		Kraft Pulped Softwood	
	T=25°C	T=40°C	T=25°C	T=40°C	T=25°C	T=40°C
10	11.08	12.01	10.96	11.89	10.35	11.89
20	11.84	12.12	11.96	12.66	11.76	12.64
40	12.42	12.87	12.58	13.17	12.62	12.86
60	12.65	13.16	12.99	13.28	12.93	13.26
300	13.40	13.36	13.51	13.51	13.41	13.37
4200 (70 min)	13.60	13.58	13.61	13.63	13.55	13.62

Percent Nitrogen vs. Time



- Materials stabilized per MIL-DTL-244B
 - Reactions rapidly quenched prior to stabilization
 - Videos recorded to allow for precise measurement of reaction times
 - Reactions conducted at 25°C and 40°C to measure effect of temperature
 - ANOVA employed to evaluate significance of fiber “source” and temperature



- Nitration reaction proceeds very rapidly, reaching a DOS of ~2.0 within 10s
- Fiber characteristics were not a significant factor in SCF nitration kinetics
 - Reaction kinetics of cellulose fibers studied were indistinguishable from one another
 - This may be explained by considering the rod-like nature of the cellulose polymers (amorphous regions still exhibit a high degree of order) and the presence of more stable crystalline polymorphs in less crystalline, kraft-pulped samples
- Temperature was a significant factor in SCF nitration kinetics
 - Rate of nitration reaction increases with increasing temperature
- Equilibrium degree of nitration was independent of both cellulose source and temperature
- **This suggests that the a broad range of cellulose fibers are suitable for producing NC and that their nitration kinetics can be described by a universal kinetic model**



Time (sec)	WPS Source	Moisture Content	Temperature	%N
200	Kraft Pulped Hardwood	5.58%	25°C	13.40
400	Kraft Pulped Hardwood		25°C	13.42
400	Sulfite Pulped Softwood	7.07%	25°C	13.40
500	Sulfite Pulped Softwood		25°C	13.46
600	Kraft Pulped Softwood	12.21%	25°C	13.36
2300	Kraft Pulped Softwood		25°C	13.55
4200	Random wood pulp	6.97%	25°C	13.63
4200	Cotton	2.98%	25°C	13.60

Pulp Type	% Cellulose I	% Cellulose II	Total % Crystallinity	Fiber Width (μm)
Hardwood	57.6	2.4	60	14.4
Softwood	58.1	3.3	61.4	23.9
Hardwood	59.5	1.9	61.3	15.2
Softwood	64.4	3.2	67.7	21.4
Softwood	65.3	1.9	67.2	25.3
Softwood	36.3	19.5	55.8	22.3
Hardwood	56.6	2.2	58.9	16
Hardwood	57.3	1.7	59	14.3
Softwood	61.1	3.1	64.2	23.8
Softwood	33.9	20.5	54.4	22.3
Softwood	60.9	2.1	63	24.9

- Because the three pulps that were evaluated exhibited equivalent reactivity, additional experiments were performed to:
 - Obtain additional near-equilibrium data points
 - Evaluate the equilibrium degree of nitration for two additional materials
- This data was used to increase the accuracy of the model for near-equilibrium kinetics
- Additional materials provided further insight into factors controlling extent of reaction; both cotton and another, high α -cellulose wood pulp reached the same equilibrium degree of nitration
- Provided additional evidence that reaction is equilibrium-controlled rather than limited by inaccessible regions



$$\frac{dC_{OH}}{dt} = -A_f e^{-E_{af}/RT} e^{-a_0 \frac{C_{ONO_2}}{C_{OH,0}}} C_{OH} C_{NO_2^+} + A_d e^{-E_{ad}/RT} C_{ONO_2} C_{H_2O}$$

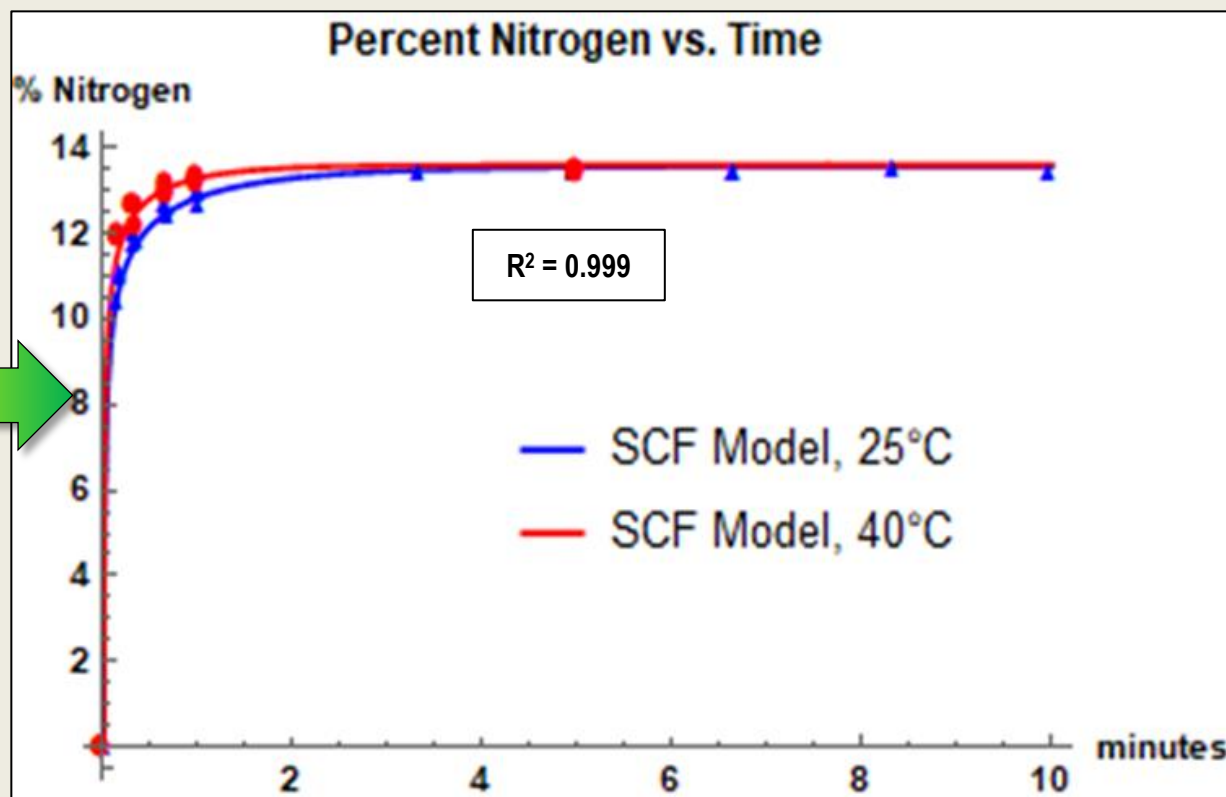
Numerically
integrate
rate law

Estimate
parameters

Evaluate
residuals
and R²

Kinetic Parameters

Parameter	Value	Units
A _f	817729.00	l/mol/s
E _{af}	34774.56	J/mol
A _d	29.56	l/mol/s
E _{ad}	31737.10	J/mol
a ₀	5.0323	const

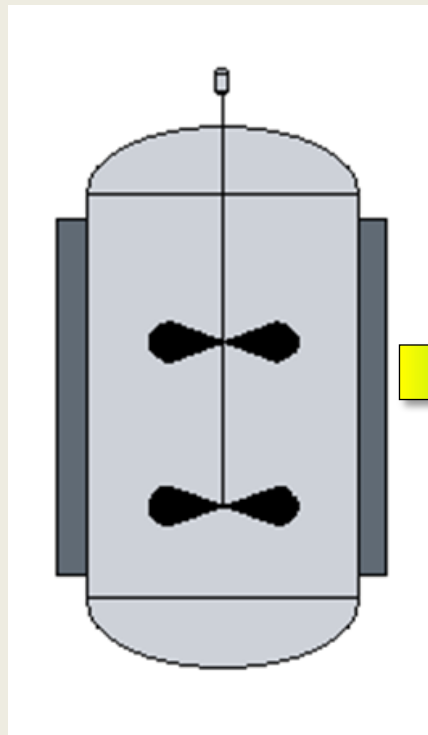
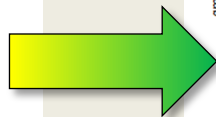
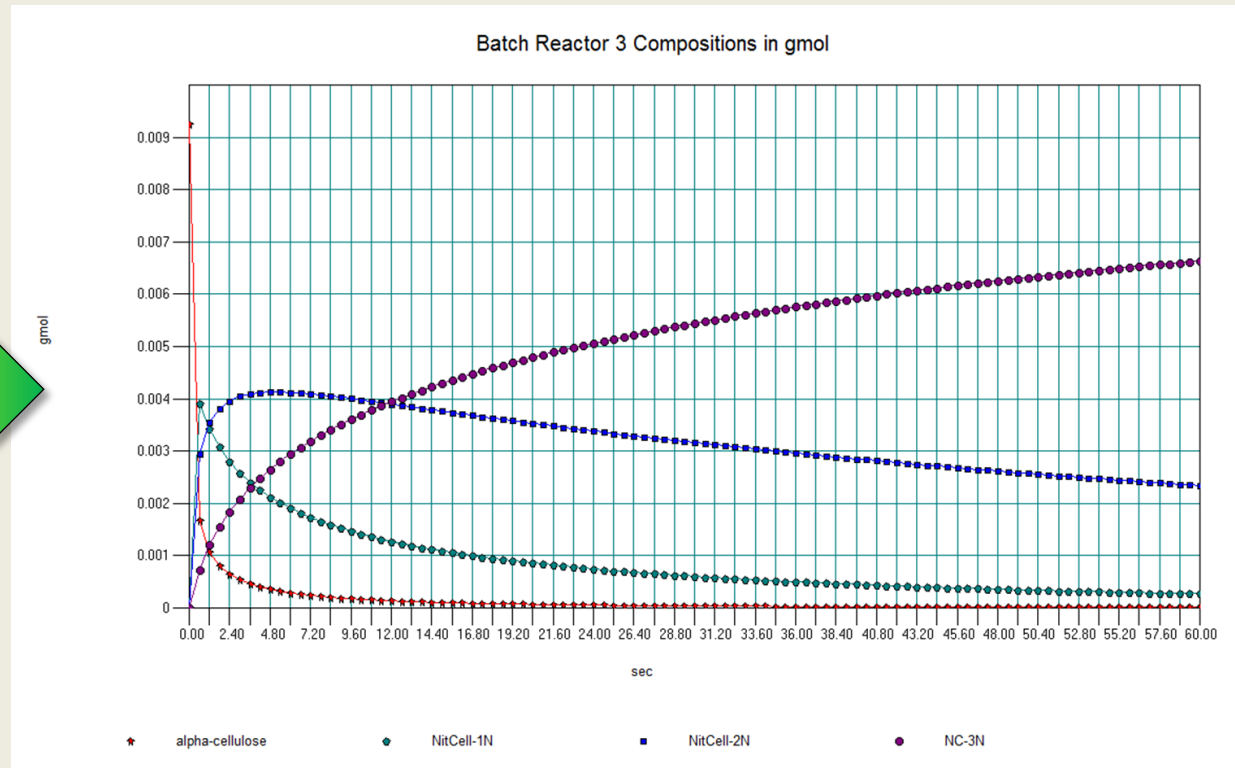


Excellent fit for full set of 48 experimental data points



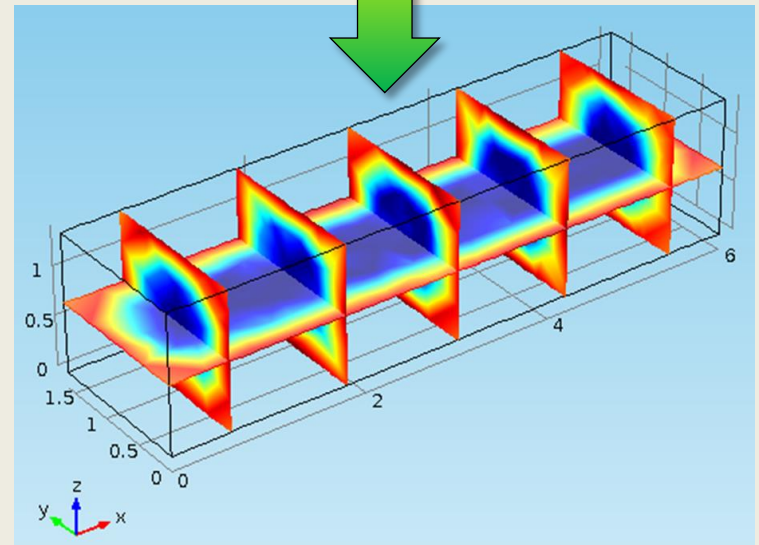
- The specification limit (13.35% Nitrogen) for Grade B (Guncotton) NC is reached very rapidly for cellulose fibers under excess acid (150:1 acid to cellulose) conditions:
 - 132.8 seconds at 25°C
 - 65.9 seconds at 40°C
- For the same mixed acid composition, an equilibrium degree of nitration of 13.40% nitrogen is predicted for an acid to cellulose ratio of 30:1, which is more representative of industrial nitration conditions for dense materials
- Provides good agreement with experimental results demonstrating that Grade B specification limit was reached within 5 minutes of immersion of cellulose fibers in acids
- Demonstrates the importance of the initial acid composition and acid to cellulose ratio for producing lower nitrated products such as Grade A NC or pyrocotton

- Can be coupled with an energy balance to describe the nitration kinetics of loose cellulose fibers or “fluffy” materials
- Can be combined with models of mass transfer phenomena to describe the nitration kinetics of densified cellulose materials
- Can describe transient effects of denitration that occur in centrifugation and stabilization operations





- Extend work to consider other acid compositions:
 - Alternate nitrating acid compositions for Grade A and Grade B NC
 - Acid compositions and temperatures capable of denitrating NC, for example those experienced in centrifugation
- Couple the rate law with acid dissociation reactions to completely describe nitration of cellulose fibers at a given acid to cellulose ratio
- Combine SCF Kinetic Model with mass transfer models to describe nitration of densified cellulose materials





- A model has been developed that accurately describes the nitration kinetics of cellulose fibers used in the production of Grade B NC or guncotton for a broad range of high purity cellulose fibers obtained from wood pulps
- This universal kinetic model treats the nitration reaction as a reversible, equilibrium controlled reaction and uses the nitronium ion as the nitrating agent
- Evidence was presented that indicates that fiber characteristics do not play a significant role in their nitration kinetics, suggesting that a broad range of cellulose materials may be suitable starting materials for industrial nitrations
- For a more detailed discussion of this work, please see:
 - Sullivan, F.; Simon, L.; Ioannidis, N.; Patel, S.; Ophir, Z.; Gogos, C.; Jaffe, M.; Tirmizi, S.; Bonnett, P.; Abbate, P., Nitration Kinetics of Cellulose Fibers Derived from Wood Pulp in Mixed Acids. *Industrial and Engineering Chemistry Research* **2018**, 57 (6), 1883-1893.



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QUESTIONS?

