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#### ABSTRACT

#### MODELING MASS TRANSFER AND CHEMICAL REACTION IN INDUSTRIAL NITROCELLULOSE MANUFACTURING PROCESSES

#### by Francis Sullivan

A series of models are proposed to describe the production of military grade nitrocellulose from dense cellulose materials in mixtures of nitric acid, sulfuric acid, and water. This effort is conducted to provide a predictive capability for analyzing the rate and extent of reaction achieved under a range of reaction conditions used in the industrial nitrocellulose manufacturing process for sheeted cellulose materials. Because this capability does not presently exist, nitrocellulose producers have historically relied on a very narrow range of cellulose raw materials and resorted to trial and error methods to develop processing conditions for new materials. This tool enables nitrocellulose manufacturers to rapidly adapt to changing market conditions, supply disruptions, or normal variation in the quality of cellulose raw materials and provides process engineers with an improved capability for process control and analysis.

This work includes measurement of the kinetics of nitration for cellulose fibers in mixed acids, an evaluation of simultaneous mass transfer and swelling in slivers cut from sheeted cellulose materials, and a structural analysis of slivers cut on industrial rotary cutting machines to consider features that may increase the reactivity of these materials. The kinetics of nitration of all high purity cellulose fibers are demonstrated to be equivalent, and the nitration of dense cellulose materials is shown to be a mass transfer limited process except in the case of small wood pulp slivers in mixed acids used in the production of Grade B nitrocellulose. In addition, it is shown that diffusion and unidirectional swelling occur on similar timescales during the nitration of slivers cut from sheeted wood pulp, resulting in variable diffusivity of mixed acids through the wood pulp sliver structure during the nitration reaction. Finally, delaminated regions or galleries that are formed as a result of the shearing action of the rotary cutting machine used in the industrial nitrocellulose manufacturing process are observed, and the influence of these structural features on the reactivity of the resulting slivers is considered. Based on these findings, generalized models are proposed that can be used to identify optimal processing conditions for new cellulose raw materials to ensure that the resulting nitrocellulose meets quality specifications while avoiding the costs and delays associated with trial and error experimentation.

#### MODELING MASS TRANSFER AND CHEMICAL REACTION IN INDUSTRIAL NITROCELLULOSE MANUFACTURING PROCESSES

by Francis Sullivan

A Dissertation Submitted to the Faculty of New Jersey Institute of Technology In Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Chemical Engineering

> Otto H. York Department of Chemical and Materials Engineering

> > December 2020

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#### **APPROVAL PAGE**

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For my children, Jack, Xavier, and Genevieve. Thank you for motivating and inspiring me - stay inquisitive as you follow your own paths in life.

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#### **CHAPTER 1**

#### FOCUS OF RESEARCH WORK AND INTRODUCTORY MATERIAL

#### 1.1 Objective of Effort and Overview of Research Approach

The objective of this research is to develop a predictive model for describing the production of military grade nitrocellulose from cotton linters and wood pulps. Such a capability provides a valuable tool for evaluating a range of commercially available cellulose pulps for use in nitrocellulose manufacturing. This is accomplished by studying the influence of cellulose pulp characteristics and processing conditions on the nitration and stabilization of these nonwoven, fibrous materials. Independent analyses of reaction kinetics, mass transfer, swelling dynamics, and cellulose structures are performed for a range of cellulose materials under conditions that are relevant to industrial nitrocellulose production. Models are proposed to describe simultaneous mass transport and chemical reaction in wood pulp slivers, and cellulose fiber and sheet structures are analyzed to identify morphological attributes that may affect the reactivity of these materials. These models are validated through both laboratory-scale experiments and analysis of data from industrial scale nitration processes.

An incremental approach (Figure 1.1) is followed in modeling the nitration of cellulose materials in mixtures of sulfuric acid, nitric acid, and water. The kinetics of nitration for cellulosic materials in mixed acids are first obtained by studying the rate of conversion of cellulose to nitrocellulose under conditions where mass transfer due to diffusion of mixed acid species can be neglected. The dynamics of swelling for dense cellulose materials in mixed acids are measured experimentally, and membrane diffusion cell experiments are conducted to measure the diffusion of mixed acids through these

fibrous cellulose structures. By conducting the membrane diffusion cell experiments with cellulose materials at different states of swelling, empirical relationships are considered to relate the effective diffusivity of mixed acids through the cellulose structure to the fiber packing characteristics at a given extent of swelling. A structural analysis of wood pulp slivers is performed to better understand the influence of sheeting and mechanical cutting on the introduction of voids or porous regions in the anisotropic wood pulp sliver structure. The results of these experiments are used to develop models describing the overall nitration kinetics of slivers cut from sheeted wood pulp in nitrating acid mixtures, and simulations are run to predict the performance of these materials under reaction conditions observed in industrial nitration processes.



**Figure 1.1** Incremental process for modeling the nitration of industrially important cellulosic materials. Models increase in complexity as fundamental processes such as mass transfer and chemical reaction are studied in detail.

Models describing the nitration of wood pulp slivers are developed by adding increasing levels of complexity to consider the effects of temperature, swelling, multicomponent diffusion, acid dissociation, and structural characteristics on the rate and extent of nitration achieved for a given wood pulp. The initial models that are developed solve a system of partial differential equations to describe chemical reaction and anisotropic diffusion during the nitration of wood pulp slivers. These models are further enhanced to address other mass transport and chemical reaction phenomena that occur during the nitrocellulose manufacturing process including initial wetting and swelling of wood pulp slivers, diffusion of reactant and product species, and dissociation of mixed acids to ionic species.

A parameterized mathematical model is established to describe the influence of fiber and wood pulp sliver characteristics on diffusion and reaction, and the structures of machine-cut wood pulp slivers are analyzed to develop flexible initial conditions to describe the portion of the wood pulp sliver that is rapidly wetted with mixed acids. Finally, a finite element method model is developed to simulate multicomponent diffusion in a wood pulp sliver structure exhibiting dimensional variation in fiber packing density. This model is used to conduct simulations for various wood pulp types and operating conditions to evaluate the influence of cellulose pulp types and processing conditions on the quality of the nitrocellulose produced under these conditions. The benefit of this approach is the development of a capability that will facilitate rapid process analysis and optimization for new pulps with the measurement of only a few key material properties, providing nitrocellulose manufacturers with the flexibility to select cellulose raw materials based on availability and prevailing market conditions.

#### **1.2 Introduction**

#### **1.2.1** Discovery and Development of Nitrocellulose

Nitrocellulose (NC), or cellulose nitrate, is the first cellulose derivative to be discovered and has been used in industrial and military applications for more than 150 years. This cellulose ester was first produced by Braconnot in 1833 by reacting nitric acid with wood fibers and other plant-based materials, and was subsequently developed into a more highly nitrated material suitable for explosive applications by Schönbein, Böttger, and Otto<sup>1</sup>. These early nitrocellulose materials were produced by reacting cotton in nitric acid or in mixtures of nitric acid and sulfuric acid, resulting in a highly substituted nitrocellulose that saw immediate use as an energetic material. Unfortunately, the stabilization process for this material, which Schönbein named "guncotton", yielded insufficient chemical stability, and several catastrophic explosions occurred during its early manufacture and storage<sup>1</sup>. Abel ultimately developed a process that greatly improved the stability of guncotton by boiling it in water for an extended time followed by mechanical pulping to remove retained acids from the nitrocellulose fibers<sup>2</sup>, leading to the widespread use of nitrocellulose in explosives, films, lacquers, inks, celluloid, and other applications.



**Figure 1.2** Model of cellulose polymer molecule with carbon, oxygen, and hydrogen atoms represented by cyan, red, and white, respectively. Model constructed using ACD Labs 3D Viewer (Freeware) Version 2018.2.1.

#### 1.2.2 The Cellulose Nitration Reaction

Cellulose, the most abundant organic compound on earth, is a naturally occurring polymer (Figure 1.2) consisting of anhydroglucose units with typical degrees of polymerization on the order of 15,000 units for cotton and 10,000 units for wood-based cellulose<sup>3</sup>. The chemical reaction used in nitrocellulose production is a net esterification reaction,

commonly referred to as nitration, that results in the substitution of hydroxyl groups on the cellulose anhydroglucose units with nitrate ester groups (Figure 1.3).



Figure 1.3 Model of nitrocellulose polymer molecule (degree of substitution = 3) with carbon, nitrogen, and oxygen atoms represented by cyan, blue, and red, respectively. Model constructed using ACD Labs 3D Viewer (Freeware) Version 2018.2.1.

Because the cellulose anhydroglucose unit contains three hydroxyl groups that can be substituted during the nitration reaction (Figure 1.4), the degree of substitution (ds) varies between 0 for cellulose and 3 for fully substituted nitrocellulose, or cellulose trinitrate. Nitrocellulose with only a single hydroxyl group substituted per anhydroglucose unit (ds=1) contains 6.76% nitrogen (weight percent), while di-substituted (ds=2) and trisubstituted (ds=3) nitrocellulose contains 11.11% nitrogen and 14.14% nitrogen, respectively.



**Figure 1.4** The reaction of cellulose in mixtures of concentrated nitric acid, concentrated sulfuric acid, and water to produce nitrocellulose.

Like other esterification reactions, the cellulose nitration reaction is a reversible reaction with the equilibrium degree of substitution governed by both the acid composition and the acid to cellulose ratio used in the reaction<sup>2</sup>. In mixed acids, or mixtures of nitric acid, sulfuric acid, and water, this reversible reaction results in the net consumption of nitric acid and generation of water according to Equation  $(1.1)^1$ , where ds represents the degree of substitution of the nitrocellulose. It is also noted that a single anhydroglucose unit is used as a simplified representation of the cellulose molecule in Equation (1.1).

$$C_6H_{10}O_5 + dsHNO_3 \leftrightarrow C_6H_{10-ds}O_{5-ds}(ONO_2)_{ds} + dsH_2O$$

$$\tag{1.1}$$

This reaction, which is sometimes referred to as O-nitration<sup>1</sup> because the nitro group is attached to an oxygen atom to form a nitric ester rather than directly to a carbon atom, has been shown to proceed through a mechanism involving electrophilic attack of the hydroxyl oxygens by the nitronium (NO<sub>2</sub><sup>+</sup>) ion, resulting in proton elimination<sup>4,5</sup>. Mixed acids that exhibit greater dissociation of nitric acid to the nitronium ion generally produce nitrocellulose with a higher degree of nitration than mixed acids with low nitronium ion concentrations, however a degree of substitution of 3 is never reached in practice due to the presence of both the nitrating and denitrating species in the acid mixtures used in industrial NC production. For this reason, higher degrees of nitration are also observed when using larger acid to cellulose ratios because the relative change in the acid composition due to consumption of nitric acid and generation of water is smaller. In batch or continuous processes, the degree of nitration reached is consequently governed by the final composition of the reacted or "spent" acid provided that the system has reached equilibrium.
Due to the widespread use of nitrocellulose products, a variety of cellulose raw materials and nitrating agents have been evaluated since development of the original production processes that relied on reacting cotton with mixed acids or concentrated nitric acid. Cotton linters were historically the primary source of cellulose used for industrial nitrocellulose production because cotton is a naturally occurring, highly pure source of cellulose, but raw material shortages during World War I necessitated development of processing techniques for cellulose feedstocks obtained from wood pulps<sup>1,2</sup>. More recent research has considered hemp<sup>6</sup>, algae<sup>7</sup> and bacteria<sup>8,9</sup> as novel sources of cellulose for the production of nitrocellulose. Similarly, mixtures of concentrated nitric and sulfuric acids, concentrated nitric acid, and other nitric acid solutions<sup>1,10</sup> have been demonstrated as effective nitrating agents for the conversion of cellulose to nitrocellulose. Despite this large number of viable nitrating agents and cellulose materials, mixed acids and cellulose materials sourced from cotton linters or wood pulps remain the most economical and widely used materials for industrial nitrocellulose production.

# 1.2.3 Nitrocellulose Grades and Applications

The unique chemical and physical properties<sup>1</sup> of nitrocellulose make it suitable for use in a diverse range of military and industrial applications. The degree of nitration and molecular weight (measured as viscosity) are generally the two most important characteristics of nitrocellulose that are used to determine its suitability for a given application. The nitrogen content, or weight percent nitrogen, is a useful measure of its energetic properties of nitrocellulose and describes the extent of conversion of hydroxyl groups to nitrate ester groups, while the viscosity is an important characteristic for both processing operations used to convert NC to finished products and for mechanical properties in applications such as coatings.

The strength and elasticity of nitrocellulose containing between 10.7% and 12.3% nitrogen (weight percent) make it suitable for use in protective coatings, films, and binders<sup>2</sup>, while the chemical properties of nitrocellulose containing at least 12.6% nitrogen<sup>11</sup> make it a useful energetic material. The highly nitrated nitrocellulose products that are used most extensively in military applications are Grade B nitrocellulose, or guncotton, which contains a minimum of 13.35% nitrogen, Grade A nitrocellulose, or pyrocellulose, which contains 12.6% nitrogen, and Grade C nitrocellulose, which is a blend of guncotton and pyrocellulose<sup>11</sup>. Other lower nitrated products including Grade D nitrocellulose (12.2% nitrogen), Grade E nitrocellulose (12.0% nitrogen), and Grade F nitrocellulose (11.55% nitrogen) are used in industrial applications such as mining explosives, varnishes, inks, lacquers, and celluloid.

#### 1.3 Background

#### 1.3.1 Industrial Scale Production of Nitrocellulose

The manufacturing process for military grade nitrocellulose involves the reaction of cellulose sourced from cotton or wood pulp in mixtures of sulfuric acid, nitric acid, and water. In industrial nitration reactions, raw cellulose is generally fed in the form of baled cotton linters or slivers cut from sheeted wood pulp due to the inefficiencies associated with transporting, storing, conveying, metering, and wetting loose fibers. Cellulose in the form of bales (cotton linters) or rolls of sheeted cellulose (wood pulp or cotton linters) is either shredded or cut into small slivers before being introduced into a nitration reactor.

Depending on the physical form of the cellulose, a sufficient mass ratio of acid to cellulose is utilized in this nitration step to ensure rapid and complete immersion of the cellulose in the nitrating acid mixture, and the process is designed with adequate residence time to allow the reaction to reach equilibrium.

The nitration step is followed by a centrifugation step in which the resulting nitrocellulose is separated from the acid mixture and washed to remove most of the remaining acid<sup>10,12</sup>. Raw nitrocellulose produced in the nitration reaction is subjected to a series of finishing operations to remove any remaining impurities (acids) that are absorbed in the fibers to achieve suitable stability of the finished material. The first step after centrifugation consists of several boiling and decanting treatments, during which the molecular weight of the cellulose is reduced and most of the residual free acids are removed from the fibers. Following the boiling step, the remaining occluded acids are removed by a mechanical pulping step during which fibers are squeezed and cut into fragments in a slightly alkaline solution. The final poaching step consists of several boiling and decanting and decanting treatments, also under slightly alkaline conditions. The stabilized NC is then processed in a series of blending and dewatering operations depending on the desired product specifications.

The physical state of the cellulose is an important consideration in the nitration, centrifugation, and acidic boiling steps. The transition from baled cotton to cellulose raw materials obtained from wood pulp led to an increased interest in developing processing methods for dense cellulose materials because the web formation, pressing, and drying operations used in wood pulp production generally produce rolls of dense, sheeted material instead of bales of fluffy material. Legacy processing methods for both baled cotton and

sheeted wood pulp use drying and shredding operations to convert the raw cellulose materials into a fluffy mass of fibers before they are introduced into the nitration reactors, however, modern processes have attempted to make use of denser cellulose materials to achieve improved efficiencies. Loose cellulose materials such as baled cotton linters generally result in lower process yields and require larger acid to cellulose ratios to enable the cellulose to be immersed in the mixed acids and to ensure that the slurry can be pumped to downstream stabilization operations. Dense cellulose materials such as slivers cut from sheeted wood pulp generally result in higher process yields and can be completely immersed in acids using smaller acid to cellulose ratios. Mixtures of dense cellulose materials and acids can also be easily pumped to downstream unit operations, but present different challenges due to the less effective mass transfer of mixed acid species into the dense cellulose structures.

# **1.3.2** Previous Attempts to Model the Cellulose Nitration Reaction

Previous attempts to model the nitration kinetics of cellulose in mixed acids have either assumed that the nitration of cellulose fibers is a diffusion controlled process<sup>13</sup> or have used continuous mixtures approaches<sup>14</sup> that require detailed structural descriptions and do not effectively discriminate between kinetic and mass transfer limitations for a given cellulose material. It is also noted that neither of these approaches considers the nitration of cellulose as a reversible, equilibrium-controlled reaction<sup>1,15</sup>, so their applicability to industrial nitrocellulose manufacturing processes that typically have long residence times is very limited.

Atsuki and Ishiwara<sup>13</sup> proposed a model describing the nitration of cotton fibers characterized by diffusion of mixed acid into the fiber followed by progressive nitration of hydroxyl groups. Because this model does not consider the nitronium ion as the active nitrating species, it may only be applicable to nitration reactions carried out under extreme excess acid conditions where the nitronium ion concentration remains relatively constant. This model also fails to consider the nitration of cellulose as a reversible reaction and reported rates of nitration for cellulose fibers that are much slower than have been observed for the nitration of wood pulp fibers in mixed acids<sup>16</sup>, suggesting that diffusion through a dense cellulose structure occurred during these experiments. In addition, the model proposed by Atsuki and Ishiwara assumes that the rate of cellulose fibers is a diffusion limited process, however it has been shown that the characteristic diffusion times for mixed acids through cellulose fibers are orders of magnitude lower than their reaction times<sup>16-18</sup>.

Barbosa et al.<sup>14,19</sup> proposed an alternate model, using a continuous mixtures approach with a distribution function describing molecular weight distribution of cellulose chains within the cellulose fiber. The model also assumed that the rate of reaction is limited by diffusion at the surface of the cellulose fiber while neglecting to treat the nitration of cellulose as a reversible reaction. In addition, this model requires detailed structural analysis through size exclusion chromatography without providing clear evidence that the molecular weight distribution in the cellulose fiber has a significant influence on the rate of nitration. The experimental data reported by Barbosa et al.<sup>19</sup> also demonstrated rates of nitration for cellulose (cotton) that are much slower than have been observed for the nitration of wood pulp fibers in mixed acids<sup>16</sup>, suggesting that that role of interfiber diffusion was once again significant in these experiments. Given these limitations, neither approach describes the nitration of industrially important, dense cellulose raw materials.

A third, more promising approach was proposed by Salmi, et al.<sup>20-22</sup> that used an empirical form of a bimolecular kinetic rate law to describe cellulose substitution kinetics and demonstrated good agreement with experimental results for the carboxymethylation of cellulose. This model was used to describe the substitution kinetics for the hydroxyl groups at each position on the anhydroglucose unit in terms of the hydroxyl group concentrations and the concentration of reacting species (monochloroacetate ion in the reaction modeled). An empirical approach was used to describe the net decrease in reactivity that is known to occur as the reaction proceeds possibly due to steric hindrance, diffusional limitations<sup>21</sup>, or other physicochemical processes<sup>17,18</sup>, enabling cellulose substitution kinetics to be modeled without a complete understanding of the factors responsible for the decreasing reaction rate at high degrees of substitution. A similar approach was used to describe differences in the relative reactivities of the hydroxyl groups on the anhydroglucose unit that have been observed experimentally using Carbon-13 and Proton NMR techniques<sup>23</sup>. This behavior is addressed through incorporating two parameters in the model to describe the decreasing reactivity of hydroxyl groups as the reaction proceeds and to describe the relative reactivities of the hydroxyl groups at each site on the anhydroglucose unit. Finally, it is noted that Salmi et al.<sup>20-22</sup> also did not consider reversibility in their analysis of the cellulose substitution reaction, requiring further enhancement for describing the nitration of dense cellulose materials.

Because of these considerations, there exists substantial opportunity for process optimization based on an enhanced understanding of the influence of cellulose structures on the nitration kinetics of these materials. This can be accomplished through the development of models that can describe the simultaneous chemical reactions and transport processes occurring during the industrial-scale production of nitrocellulose. The incremental approach described in Figure 1.1 was used to first describe the nitration kinetics of cellulose fibers and to then study the transport of mixed acid species through relevant cellulose structures. Preliminary models consisting of sets of time-dependent partial differential equations were developed by coupling chemical reaction and diffusional mass transfer in simplified representations of wood pulp slivers. These models were further enhanced by conducting a detailed structural analysis to consider features of wood pulp slivers cut on industrial processing equipment that may promote or inhibit the transport of mixed acids through the wood pulp sliver structure. To complete the analysis, finite element method models were developed to consider the more complex problem of multicomponent diffusion in these anisotropic, heterogeneous structures, and studies were performed to report findings relevant to industrial scale nitrocellulose manufacturing processes.

#### **CHAPTER 2**

# DEVELOPMENT OF AN EMPIRICAL RATE LAW FOR CELLULOSE NITRATION KINETICS

# **2.1 Introduction**

This chapter is an extension of previously published work<sup>16</sup> that considered the nitration kinetic behavior of cellulose fibers in mixtures of nitric acid, sulfuric acid, and water for the production of Grade B nitrocellulose. This work demonstrated that the nitration of cellulose fibers obtained from wood pulps is not a diffusion limited process, and that the influence of differences in the physical properties of these fibers on their rate and extent of nitration is insignificant. Based on these findings, a universal kinetic model was proposed to describe the reaction kinetic behavior of high purity cellulose fibers obtained from wood pulps using a reversible reaction with the nitronium ion as the nitrating agent. The single cellulose fiber (SCF) kinetic model that was developed yielded excellent agreement with experimental results obtained from bench scale experiments in which Grade B nitrocellulose was synthesized using cellulose fibers from various wood pulp types.

In the present analysis, the model is extended to address some simplifications that were made in the work that was previously reported. Specifically, the previous work assumed a constant nitronium ion concentration because a large acid to cellulose ratio (150:1, weight basis) was used in the bench scale experiments that were performed to obtain kinetic measurements. In addition, water was used as a representative denitrating agent in this initial work because the mixed acid composition was nearly constant due to the large acid to cellulose ratio that was employed. In the present study, the regression is repeated with a broader range of mixed nitrating acid compositions using nitronium ion concentrations calculated with published acid dissociation models and with a more thorough treatment of the denitrating agent. The objective of this work is to extend the kinetic model that was proposed for the nitration of cellulose fibers in the production of Grade B nitrocellulose, to describe the nitration kinetics of cellulose fibers in mixed acids used to produce other nitrocellulose grades (e.g., Grade A) that exhibit lower final degrees of nitration. Using this approach, a kinetic model is proposed that describes the rate and extent of reaction for producing all nitrocellulose grades of military importance.

# 2.1.1 Historical Approaches to Modeling Cellulose Nitration Kinetics

Highly nitrated nitrocellulose containing at least 12.6 percent nitrogen is an important energetic material that has been used extensively in propellants for commercial and military ammunition for well over a century<sup>12</sup>. Because of the commercial successes of guncotton, celluloid, and other early nitrocellulose products, the widespread use of nitrocellulose preceded a fundamental understanding of the chemistry of cellulose and nitrocellulose. To compensate for these limitations, recipe-based approaches using specified acid mixtures and processing conditions have historically been used in the production of nitrocellulose; however, these approaches allow for limited predictability and restrict the ability of process operators to compensate for process and raw material variation. Improved models based on the underlying cellulose chemistry and reaction kinetics can help to overcome these limitations<sup>16</sup>.

Previous attempts to model the nitration kinetics of cellulose in mixed acids have considered the nitration of cellulose fibers as a diffusion controlled process<sup>13</sup> or have used continuous mixtures approaches<sup>14</sup> that require detailed structural descriptions of the

cellulose-acid system and do not effectively discriminate between kinetic and mass transfer limiting conditions. Treatments of the reaction kinetics of cellulose fibers have focused on modeling the molecular weight distribution of cellulose molecules within the fiber structure and have considered diffusional limitations at the fiber surface<sup>19</sup>, without demonstrating that either factor plays a significant role in the observed rate of reaction.

These approaches also fail to consider the nitration of cellulose as a reversible, equilibrium-controlled reaction<sup>1,15</sup>, limiting their applicability to the simulation of industrial nitrocellulose manufacturing processes that are typically characterized by very long residence times. By studying the nitration kinetics of natural cellulose fibers in mixed acids under conditions where mass transfer limitations are negligible, many of these limitations have been addressed. This single cellulose fiber (SCF) kinetic model<sup>16</sup> is an important component of industrial nitrocellulose manufacturing process models because it can be used in conjunction with mass transfer models describing the transport of mixed acid species through cellulose structures to predict the observed nitration kinetics for a variety of cellulose raw materials, physical forms, and processing conditions.

#### 2.1.2 Traditional Approaches to Selecting Reaction Conditions

The chemical reaction most commonly used in industrial scale nitrocellulose manufacturing involves the reaction of cellulose obtained from wood pulps or cotton linters in mixtures of nitric acid, sulfuric acid, and water. This reversible, highly exothermic, multiphase esterification reaction<sup>24</sup> normally occurs in batch or continuous stirred tank reactors and is followed by a series of stabilization operations that are used to separate the mixed acid from the reacted material. Cellulose fibers are typically fed to the reactor in densified form, either as slivers cut from sheeted cotton or wood pulp, or as baled cotton

linters that are shredded before being introduced into the nitration reactors. To account for diffusion of mixed acid species through these cellulose structures, nitrocellulose manufacturing processes are generally designed to exhibit long residence times in the nitration reactors either through a series of continuous stirred tank reactors or by implementing reactor designs that approximate plug flow. These very long residence times (on the order of one hour) help to ensure complete and uniform nitration while preventing regions of poorly nitrated material that can result in unacceptable product solubility.

Nitrocellulose producers have historically selected processing conditions using nitration diagrams that correlate mixed acid compositions to the nitrogen content in the resultant  $NC^{1,10,15}$ . In the absence of models that can be used to predict that rate and extent of nitration for a given acid composition, acid to cellulose ratio, and temperature, these nitration diagrams allow for selection of acid compositions to achieve a desired degree of nitration. Using this approach or other tabulated data, production recipes are selected without the need for a detailed understanding of the underlying chemical reactions and Although this approach has been used extensively in the production of kinetics. nitrocellulose, it presents some shortcomings because the nitration diagrams only relate the equilibrium acid composition to the degree of nitration at a given temperature. This recipebased approach does not consider the influences of cellulose characteristics<sup>10</sup>, heat management, transient process behavior, competing reactions, and the effects of process variation. A predictive kinetic model is thus of great practical interest for supporting rapid process analysis and optimization studies without the need for costly and lengthy experiments.

Because the influence of diffusion is significant in the nitration of wood pulp slivers and shredded material from baled cotton linters, both diffusion and chemical reaction influence the observed kinetics of nitration for these materials and must be considered in developing models for industrial nitrocellulose manufacturing processes. By studying these phenomena separately, it is possible to develop models capable of describing the nitration kinetics of a wide range of cellulose raw materials, physical forms, and processing conditions. Following this approach, the chemical reaction kinetics of cellulose fibers can be studied under nitration conditions that are independent of the mass transfer limitations that govern industrial-scale nitration processes.

## 2.2 Materials and Methods for Establishing SCF Nitration Kinetics

#### 2.2.1 Wood Pulps

The crystallinity and morphology of eleven high purity wood pulps were evaluated to establish the range of crystallinity and wall thickness for softwood and hardwood pulps purified using the sulfite and kraft pulping processes. Fiber dimensional characteristics and coarseness were measured using an OpTest Equipment Inc. fiber quality analyzer conforming to the requirements of TAPPI T271<sup>25</sup>, and crystallinity measurements were measured using x-ray diffraction. Cellulose fibers were obtained from three sources of sheeted wood pulp: a sulfite pulped softwood (northern pine), a kraft pulped softwood (southern pine), and a kraft pulped hardwood for more detailed analysis and reaction kinetics evaluation. These materials were cut from rolls into 1mm x 6mm slivers and were subsequently disintegrated into free cellulose fibers by vigorously agitating the wood pulp slivers in a large volume of deionized water, allowing the fibers to freely disperse in the

water mixture. Loose fiber mats were then formed by filtering a fixed volume of the waterdispersed fiber mixture and drying the resulting fiber mats.

# 2.2.2 Mixed Nitrating Acid Compositions

Mixed acid compositions were prepared using nitric acid (J.T. Baker – Nitric Acid, Fuming, 90%), sulfuric acid (Fisher Scientific – Certified ACS Plus), and deionized water. Two mixed acid compositions were selected to produce Grade B nitrocellulose ( $\geq$ 13.35% nitrogen) in accordance with the quality requirements defined in MIL-DTL-244B<sup>11</sup>. The acid recipes differed by the ratio of sulfuric acid to nitric acid in the mixture and represent mixed acid compositions within the range of mixed acids used in the industrial production of nitrocellulose. The first mixed acid is referred to as a high sulfuric acid recipe and contained 54.6% sulfuric acid, 37.0% nitric acid, and 8.4% water by weight, while the second mixed acid recipe is referred to as a high nitric acid recipe and contained 37.9% sulfuric acid, 54.6% nitric acid, and 7.5% water by weight. Nitronium and hydronium ion concentrations were calculated for each acid composition at 25°C and 40°C using the acid dissociation model published by Albright et al.<sup>26</sup> and are listed in Table 2.1.

Acid	Mass Percentage		[NO2 <sup>+</sup> ] (mol/L)		[H <sub>3</sub> O <sup>+</sup> ] (mol/L)		
Composition	$H_2SO_4$	HNO <sub>3</sub>	H <sub>2</sub> O	25°C	40°C	25°C	40°C
High Sulfuric	54.6	37.0	8.4	1.120	1.003	7.799	7.662
Grade B							
<b>High Nitric</b>	37.9	54.6	7.5	0.742	0.637	5.947	5.811
Grade B							
<b>High Sulfuric</b>	55.96	30.02	14.02	0.150	0.120	9.539	9.373
Grade A							
High Nitric	34.20	52.83	12.97	0.103	0.079	6.883	6.662
Grade A							

 Table 2.1 Acid Compositions Prepared for Single Cellulose Fiber Nitration Experiments

# 2.2.3 Single Cellulose Fiber Nitration Experiments

Single cellulose fiber nitration experiments were conducted by reacting the loose mats of cellulose fibers in the mixed nitrating acid at predetermined reaction times and temperatures. After removing the materials from the reactor, they were filtered, quenched in chilled water, and stabilized in accordance with the procedures described in MIL-DTL-244B<sup>11</sup>.

A full factorial design of experiments (Table 2.2) was developed to study the dependence of reaction kinetics on the source of cellulose fibers and the temperature of the reacting system, with the average degree of nitration as the response variable. Reactions were carried out at 10 seconds, 20 seconds, 40 seconds, 60 seconds, 300 seconds, and 4,200 seconds at each condition with the high sulfuric acid Grade B mixed nitrating acid composition to study both the transient and steady-state behavior of the reacting system.

Table 2.2 Full	l Factorial Experimental E	Design for Single Cellulose	Fiber Reaction Kinetics
	Factor	Levels	

racior	Levels			
Single Cellulose Fiber	3 (sulfite pulped softwood,			
Source	kraft pulped softwood, and			
	kraft pulped hardwood)			
<b>Reaction Temperature</b>	2 (25°C and 40°C)			

A mass ratio of 150 parts mixed acid to 1 part cellulose was used in order to ensure that the concentrations of species in the mixed acid remained effectively constant during the nitration experiment and to promote rapid wetting of the cellulose fibers upon introduction into the mixed nitrating acid. In addition to using excess acid to maintain the concentrations of mixed acid species nearly constant during the reaction, the reactor contents were mixed vigorously and the reaction temperature was controlled using a water bath to maintain nearly isothermal conditions as the exothermic reaction proceeded. A thermocouple and data logger were also used to monitor the temperature in the reactor. Reactions were stopped by quenching the reactor contents in a large volume of chilled, deionized water after the desired reaction time was reached.

## 2.2.4 Raman Spectroscopic Analysis of Mixed Nitrating Acids

A limited analysis was performed using Raman spectroscopy to measure the concentration of nitronium ions in the mixed nitrating acid compositions used in the single cellulose fiber nitration experiments. Raman spectra of the mixed acids and nitronium tetrafluoroborate standard solutions were obtained using a Horiba Scientific XploRA Raman spectrometer, 532nm laser, and a MarqMetrix Optical sensing TouchRaman<sup>TM</sup> immersion BallProbe®. Raman spectroscopy is a suitable technique for detection of the NO<sub>2</sub><sup>+</sup> ion because it exhibits symmetric vibrational stretching that is Raman active but infrared-inactive due to its molecular symmetry<sup>27</sup>. In addition, Raman spectroscopy is largely insensitive to sample size, allowing acid mixture samples to be rapidly examined without the need for sample preparation. Using this method, the relationship between Raman intensity and NO<sub>2</sub><sup>+</sup> ion concentration in acid samples was established from a calibration curve that was developed using the nitronium tetrafluoroborate standards.

#### 2.2.5 Analytical Methods

The nitrogen content of each stabilized nitrocellulose sample was measured using the ferrous ammonium sulfate titration method described in MIL-STD-286C<sup>28</sup> to obtain the average percent nitrogen and degree of substitution for each sample. A minimum of three measurements were recorded for each sample.

Fiber dimensional characteristics and coarseness were measured using an OpTest Equipment Inc. fiber quality analyzer conforming to the requirements of TAPPI T271<sup>25</sup>. Crystallinity measurements were measured using x-ray diffraction, and moisture content was measured for each sample using an Ohaus MB23 moisture analyzer.

## 2.2.6 Data Analysis

Wolfram Mathematica<sup>29</sup> was used to numerically integrate the kinetic rate expression and to estimate the kinetic parameters. The nitration results obtained for reaction times of 70 minutes were considered as steady-state conditions, and non-linear least squares regression was used to estimate the Arrhenius parameters  $A_{f}$ ,  $E_{af}$ ,  $A_d$ ,  $E_{ad}$ , and the activity decay factor, a<sub>0</sub>. Minitab ® Statistical Software, Version 17 was used to perform an analysis of variance on the data to determine the significance of various factors on the nitration behavior of the cellulose fibers.

## 2.3 Experimental Results for Establishing SCF Nitration Kinetics

#### 2.3.1 Experimental Measurement of Wood Pulp Properties

A series of eleven high purity (greater than 90%  $\alpha$ -celluose) wood pulps from different tree species and pulping processes were evaluated to assess the range and variation of crystallinity and fiber widths in a number of wood pulps that were identified as potential candidates for industrial-scale nitrocellulose manufacturing. The total crystallinity varied between 54.4% and 67.7% and the fiber width varied between 14.3 µm and 25.3 µm. Two of the samples (F and J) exhibited higher fractions of the more stable cellulose II allomorph suggesting that these samples were very high purity fibers that underwent some degree of mercerization during the pulping process. The results of this analysis are listed in Table

2.3.

ID	Pulp Type	% Cellulose	%	Total %	Fiber Width
		Ι	Cellulose II	Crystallinity	(µm)
Α	Hardwood	57.6	2.4	60.0	14.4
В	Softwood	58.1	3.3	61.4	23.9
С	Hardwood	59.5	1.9	61.3	15.2
D	Softwood	64.4	3.2	67.7	21.4
Ε	Softwood	65.3	1.9	67.2	25.3
F	Softwood	36.3	19.5	55.8	22.3
G	Hardwood	56.6	2.2	58.9	16.0
Η	Hardwood	57.3	1.7	59.0	14.3
Ι	Softwood	61.1	3.1	64.2	23.8
J	Softwood	33.9	20.5	54.4	22.3
K	Softwood	60.9	2.1	63.0	24.9

 Table 2.3 Crystallinity of Wood Pulps Evaluated

Three samples, a sulfite pulped softwood (Sample D), a kraft pulped softwood (Sample F), and a kraft pulped hardwood (Sample G), were selected from this data set for more extensive analysis and evaluation in lab-scale single cellulose fiber kinetic experiments. The total crystallinity in these samples (Table 2.4) varied between approximately 55% and 68%, and higher quantities of the cellulose II crystalline structure were observed in the kraft pulped softwood sample that exhibited very high purity (greater than 98%  $\alpha$ -cellulose). These three pulps represent a good range total crystallinity, cellulose II content, coarseness, and fiber widths to evaluate the influence of wood pulp characteristics in single cellulose fiber reaction kinetics and to test the applicability of the two conceptual models for the nitration of cellulose fibers.

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		

 Table 2.4 Properties of Single Cellulose Fibers Analyzed

The influence of the fiber structure on the nitration kinetics must not vary considerably among cellulose fibers if a form of empirical rate law is applicable to a range of cellulose fibers. That is, the effects of factors such as crystallinity and fiber dimensions on mass transfer limitations must not play a significant role in the nitration kinetics if the model is to be applicable to a range of fibers. Experiments were designed to test the appropriateness of proposed rate law forms and underlying assumptions. The primary characteristics of interest in the wood pulps were the fiber wall thickness, crystallinity, and fiber morphology. More crystalline materials should react slower according to the micellar heterogeneous model while the crystalline, thinner walled fibers should react faster if the reaction is kinetically limited by intrafiber diffusion. The crystallinity and distribution of crystalline forms varied among the samples with the sulfite pulped softwood the most crystalline material (67.7%) and the kraft pulped softwood the purest and least crystalline (55.8%) material. The kraft pulped hardwood material exhibited the shortest, thinnest-walled, and least coarse fibers. It is noted that the moisture content measurements in Table 2.4 show the opposite trend as the crystallinity measurements, suggesting that the less crystalline materials may also have a greater tendency to accumulate moisture. Because the characteristics of these fibers varied considerably, these materials were used to evaluate the influence of fiber properties on nitration kinetics for high purity (greater than 90%  $\alpha$ -cellulose) wood pulps. It was also noted that the molecular weights of the cellulose molecules in the fibers are very similar, suggesting that the reactivity and viscosity of these fibers would be expected to be nearly identical in solution.

#### 2.3.2 Nitronium Ion Concentration Measurement by Raman Spectroscopy

Raman spectroscopy was used to measure the concentration of nitronium ion in the Grade B (36.0% HNO<sub>3</sub>, 54.6% H<sub>2</sub>SO<sub>4</sub>, 8.4% H<sub>2</sub>O) mixed nitrating acid used in the single cellulose fiber nitration experiments. This was accomplished using a procedure that determines the concentration of the nitronium ion in mixtures of sulfuric acid, nitric acid, and water based on measurement of the area under the band at 1400 cm<sup>-1</sup>. Measurements were obtained 20°C, 30°C, and 40°C yielding nitronium ion concentrations of 1.456, 1.403, and 1.356 moles per liter, respectively. These concentrations are considerably higher than the concentrations predicted by the model published by Albright et al.<sup>26</sup> but do demonstrate that the degree of dissociation of nitric acid to nitronium ion decreases as a function of increasing temperature and that temperature dependence of the nitronium ion concentration

was relatively small over the range of reaction temperatures evaluated. Because development of an acid dissociation model was not the focus of the current effort, the model reported by Albright et al. was used to calculate nitronium ion concentrations and the Raman analysis was used to confirm general trends for the dissociation of nitric acid to the nitronium ion in mixed acid compositions. A more detailed description of the procedure for measuring the nitronium ion concentrations using Raman spectroscopy can be obtained in the thorough treatments provided by Zaman<sup>30</sup> and Edwards et al<sup>27</sup>.

# 2.3.3 Experimental Measurement of Cellulose Fiber Reaction Kinetics

**2.3.3.1 High Sulfuric Acid Grade B Mixed Nitrating Acid Composition.** A series of experiments were conducted using all three fiber types (sulfite pulped softwood, kraft pulped softwood) to evaluate the effect of fiber properties and temperature on the observed rate of nitration of cellulose fibers. Table 2.5 lists the experimental results (average nitrogen percentage) for these single cellulose fiber nitration experiments that were conducted at 25°C and 40°C for each fiber source and nominal reaction time evaluated. The actual acid composition used in the high sulfuric acid Grade B experiments was determined by titration to contain 55.28% sulfuric acid, 37.15% nitric acid, and 7.57% water by weight. Actual reaction times were determined precisely using videos that were recorded to precisely measure the elapsed time between when the fibers were immersed in the mixed nitrating acid and when they were quenched in the deionized water bath.

Nominal Reaction Time	Sulfite I Softw	Pulped vood	Kraft Pulped Kraf Hardwood Soj		Kraft I Softw	raft Pulped Softwood	
(sec)	$T=25^{\circ}C$	$T=40^{\circ}C$	$T=25^{\circ}C$	$T=40^{\circ}C$	<i>T</i> =25° <i>C</i>	$T=40^{\circ}C$	
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	

 Table 2.5 Single Cellulose Fiber Experimental Results (Average Nitrogen Percentage)

Following quenching in deionized water, each sample was stabilized in accordance with the procedures described in MIL-DTL-244B<sup>11</sup>, and the nitrogen content was measured using the potentiometric titration technique described in MIL-STD-286C<sup>28</sup>.

**2.3.3.2** Near Equilibrium Experiments for High Sulfuric Acid Grade B NC. The initial data listed in Table 2.5 indicate that the fibers approached the specification limit for Grade B nitrocellulose (13.35%N per MIL-DTL-244B<sup>11</sup>) at approximately 300 seconds. Consequently, it was determined that additional data points in this region were desired to improve the predictability of the model for near equilibrium conditions. Table 2.6 lists data for additional nitration experiments that were conducted using the high sulfuric acid Grade B mixed acid composition with single cellulose fibers of various sources at 25°C to observe the near-equilibrium behavior of the reacting system. Cotton linters, a highly pure and highly crystalline source of cellulose, and another high purity, kraft pulped softwood wood pulp were evaluated to observe the extent of nitration achieved in these materials.

Cellulose Fiber Source	Moisture	Reaction	Temperature	Percent
	Content	Time (s)		Nitrogen
Kraft Hardwood	5.58%	200	25°C	13.40
Kraft Hardwood	5.58%	400	25°C	13.42
Sulfite Softwood	7.07%	400	25°C	13.40
Sulfite Softwood	7.07%	500	25°C	13.46
Kraft Softwood	12.21%	600	25°C	13.36
Kraft Softwood	12.21%	2300	25°C	13.55
Alternate Kraft Hardwood	2.98%	4200	25°C	13.63
<b>Cotton Linters</b>	2.98%	4200	25°C	13.60

**Table 2.6** Near Equilibrium Single Cellulose Fiber Nitration Experiments for Various

 Wood Pulp Fibers in High Sulfuric Acid Mixed Nitrating Acid Composition

The experimental data for the high sulfuric acid Grade B nitration experiments, including near-equilibrium experiments, were plotted as a function of time (Figure 2.1). Even during short reaction times, it is difficult to distinguish the nitration kinetics of one fiber source from another, but the overall trend of increasing reaction rate with rising temperature is evident.



Figure 2.1 Plot of percent nitrogen vs. time for single cellulose fiber nitration experiments.

**2.3.3.3 High Nitric Acid Grade B Mixed Nitrating Acid Composition.** Because nitrocellulose producers tend to use mixed acid compositions that are either high in nitric acid (greater than 50% HNO<sub>3</sub> by weight) or high in sulfuric acid (greater than 50% H<sub>2</sub>SO<sub>4</sub> by weight), a series of additional experiments were conducted with mixed acid compositions used in the production of Grade B nitrocellulose that are high in nitric acid. This mixed acid composition consisted of 37.9% sulfuric acid, 54.6% nitric acid, and 7.5% water by weight, and reaction times of 20 seconds, 60 seconds, 300 seconds, and 70 minutes were used to evaluate the rate and extent of nitration of the kraft pulped softwood fibers at 25°C and 40°C (Table 2.7). The actual acid composition used in the high nitric acid, Grade B experiments was determined by titration to contain 37.45% sulfuric acid, 55.17% nitric acid, and 7.38% water by weight.

Nominal Reaction Time (sec)	Kraft Pulped Softwood		
	$T=25^{\circ}C$	$T=40^{\circ}C$	
20	12.85	13.36	
60	13.30	13.50	
300	13.50	13.55	
4200	13.62	13.64	

 Table 2.7 Single Cellulose Fiber Kinetic Results for High Nitric Acid Grade B

 Composition

2.3.3.4 Grade A Mixed Nitrating Acid Composition. A final series of experiments were conducted using mixed acid compositions used in the production of Grade A nitrocellulose. Nominal acid compositions consisting of a high sulfuric acid composition (30.02% HNO<sub>3</sub>, 14.02% H<sub>2</sub>O, 55.96% H<sub>2</sub>SO<sub>4</sub>) and a high nitric acid composition (52.83% HNO<sub>3</sub>, 12.97%  $H_2O$ , 34.20%  $H_2SO_4$ ) were prepared and the actual compositions of the mixed acids that were used in these experiments were determined by titration and are listed in Table 2.8. Reactions were conducted using cellulose fibers obtained from the kraft softwood pulp, but the 150:1 acid to cellulose ratio was maintained without diluting the mixed acids to account for the extent of consumption of nitric and generation of water that occurs in the production-scale recipes. Because of this, a degree of nitration significantly higher than 12.6% nitrogen was achieved in these "Grade A" single cellulose fiber nitration experiments (Table 2.8). Nevertheless, because the acid compositions and cellulose characteristics were known, this data can be used in the regression procedure used to generate kinetic parameters to consider the rate of reaction in the more dilute mixed acid compositions used to produce Grade A nitrocellulose.

Acid Composition Used	Temperature	Cellulose Moisture Content	Reaction Time (s)	Percent Nitrogen
52.09% HNO3	25°C	5.03%	20	10.24%
13.12% H <sub>2</sub> O			60	10.55%
34.79% H <sub>2</sub> SO <sub>4</sub>			300	11.99%
			4200	12.48%
	40°C	4.35%	20	11.26%
			60	11.80%
			300	12.70%
			4200	12.96%
34.95% HNO3	25°C	5.54%	20	10.64%
12.92% H <sub>2</sub> O			60	12.21%
52.13% H <sub>2</sub> SO <sub>4</sub>			300	12.99%
			4200	13.46%
	40°C	5.44%	20	11.81%
		·	60	12.93%
			300	13.32%
			4200	13.46%

**Table 2.8** Nitration Results for Kraft Softwood Fibers in Grade A Mixed Nitrating Acid

 Recipes

## 2.3.4 Analysis of Variance (ANOVA) of SCF Nitration Results

The repeatability of the potentiometric titration technique<sup>28</sup> that was used to measure the nitrogen content in reacted samples was very good, exhibiting an overall standard deviation of only 0.023% nitrogen. This implied that the experimental data obtained from the Grade B nitration experiments conducted with cellulose fibers obtained from different pulps could be analyzed to consider sources of variation in the reactivity of these materials. The experimental data from the high sulfuric acid Grade B single cellulose fiber nitration experiments were analyzed at each reaction time to consider the influence of cellulose fiber characteristics and temperature on their rate and extent of nitration. ANOVA was used to partition and compare variation within and between levels and to perform hypothesis testing of the null hypothesis:

$$H_0: \mu_1 = \dots = \mu_k \tag{2.1}$$

that all mean values are equal for a given treatment against the alternate hypothesis that at least one mean value is different from the others. Probabilities were calculated and a confidence level of 95% was applied to determine whether the null hypothesis should be rejected. A General Linear Model procedure was used for the ANOVA analysis with the nitrogen percentage as the response variable and source and temperature as the main effects. Through application of this methodology, the significance of fiber source and temperature were assessed at each reaction time. Table 2.9 lists the factors and levels that were considered in conducting the ANOVA.

**Table 2.9** Factors and Levels for Single Cellulose Fiber Nitration Experiments**ExperimentFactor**Levels

Experiment	Factor		Leve	ls	
Single Cellulose	Source	Sulfite	Kraft Kraft		Kraft
Fibers (SCF)		Pulped	Pulped I		Pulped
		Softwood	Hardw	ood	Softwood
	Temperature	25°C	40		40°C

The results of the ANOVA analysis indicate that temperature is a significant factor in the kinetics of nitration except at equilibrium and near-equilibrium conditions for the nitration of single cellulose fibers in Grade B mixed nitrating acids. Conversely, the ANOVA results suggested that the source of the wood pulp is not a significant factor at all reaction times for the range of fibers evaluated. These results indicate that the data for the three sources of cellulose fibers should be considered together in describing the overall nitration kinetics of single cellulose fibers but that the temperature data should be considered separately.

# 2.4 Discussion of Cellulose Fiber Reactivity and Development of an Empirical Kinetic Model

# 2.4.1 The Nature of the Cellulose Nitration Reaction

Factors that control the rate and extent of nitration of cellulose in mixed acids must be understood to develop an empirical kinetic model for this chemical reaction. To describe the kinetics of reacting cellulose fibers in the absence of diffusional restrictions, insight is required into the nitrating agent, the denitrating agent, and other factors that may limit the rate of this equilibrium-controlled reaction. A considerable amount of research has focused on identifying the nitrating agent in mixtures of nitric acid, sulfuric acid, and water, but comparatively less effort has been devoted to identifying the denitrating agent and the study of factors limiting the rate of reaction in mixed acids. Extensive reviews of previous investigations of the nitrating agent and factors controlling the extent of reaction have been conducted by Urbanski<sup>1</sup>, Fowler<sup>15</sup>, and Short<sup>10</sup>, and offer convincing evidence that the nitronium ion is the nitrating agent in the mixed acids used in industrial scale nitrocellulose production. More recent research by Stovbun et al.<sup>17</sup> has proposed conceptual models for denitration, while Nikolsky et al.<sup>18</sup> have described physical mechanisms that may plan a limiting role in the rate of cellulose nitration. These works are reviewed in detail in the development of an appropriate form for an empirical rate law describing the nitration kinetics of cellulose fibers.

**2.4.1.1 The Nitrating Agent.** The two chemical species which are most often proposed as the active nitrating species in mixtures of nitric acid, sulfuric acid, and water are molecular nitric acid (HNO<sub>3</sub>) and the nitronium ion  $(NO_2^+)$ . Researchers continued to

debate the identity of the nitrating species for many years, partially due to experimental evidence demonstrating that nitration of cellulose can occur in systems in which the presence of the nitronium ion is either undetectable or considered to be unlikely, such as in vapors of nitric acid. Based on this evidence, Miles<sup>31</sup> proposed that the active nitrating agent is either molecular nitric acid or a nitric acid hydrate while others including Chédin<sup>32</sup> proposed that nitration is preceded by dissociation of nitric acid to the nitronium ion, as had been demonstrated by Hughes et al.<sup>33</sup> for aromatic compounds. This debate would persist until the role of the nitronium ion in the nitration of cellulose was ultimately elucidated through two important sets of experiments.

In the first set of experimental work, Klein and Menster<sup>4</sup> demonstrated through experiments conducted with oxygen-18 enriched mixed acids that the nitration of cellulose proceeds through electrophilic attack on the hydroxyl oxygen by the nitronium ion (NO<sub>2</sub><sup>+</sup>) resulting in proton elimination. Bayliss and Watts<sup>34</sup> also performed experiments in which cellulose was reacted in sulfuric acid-potassium nitrate solutions that were selected to achieve dissociation of potassium nitrate to specific ionic species, noting that formation of nitrate esters was only observed in the solutions in which the nitronium ion was present. These findings agree with the results published by Hughes et al.<sup>33</sup> that showed that the nitronium ion is the active species in aromatic substitutions, and provide compelling evidence that the nitronium ion is the nitrating agent for the nitration of cellulose in mixtures of sulfuric acid, nitric acid, and water. Consequently, the nitration of cellulose does not proceed by the elementary reaction described by Equation (1.1), but rather by a reaction mechanism in which the substitution of the cellulose hydroxyl groups is preceded by dissociation of nitric acid to the nitronium ion.

**2.4.1.2 The Denitrating Agent**. Although a fully substituted nitrocellulose exhibiting a degree of substitution equal to 3 (14.14% nitrogen) is theoretically possible, this theoretical limit is never achieved in practice during the industrial manufacture of nitrocellulose. In his review of investigations conducted to explain this behavior, Short<sup>10</sup> noted that two main theories have been proposed to explain why the extent of reaction is limited to some value less than the theoretical maximum extent of nitration when nitrocellulose is prepared using mixed acids. The first theory proposes that the extent of reaction is limited by thermodynamic equilibrium, while the second theory proposes that the reaction extent is limited by the accessibility or availability of reactive hydroxyl groups rather than thermodynamic equilibrium.

In their reviews of prior investigations into the cellulose nitration reaction, Urbanski<sup>1</sup>, Fowler<sup>15</sup>, and Short<sup>10</sup> cited the fact that cellulose and nitrocellulose both tend to reach the same final degree of substitution in a given nitrating acid, regardless of the degree of substitution of the starting material, as evidence of an equilibrium controlled reaction. These early observations suggested that the nitration of cellulose is, indeed, a reversible reaction, that reaches an equilibrium between the nitration reaction and a reverse, denitration reaction. In his review of the topic, Urbanski<sup>1</sup> noted two primary observations regarding the kinetics and equilibrium of nitration and denitration based on these results: the equilibrium degree of substitution is only a function of the acid composition, and the rate of denitration increases with temperature and with the concentration of nitric acid but that little denitration occurs in sulfuric acid or in mixtures with only small amounts of nitric acid. It is noted that this observation is inconsistent with the fact that unstable nitrocellulose is known to exhibit spontaneous decomposition due to occluded acids, primarily sulfuric acid<sup>1</sup>.

While the observation that both nitrocellulose and cellulose reach the same equilibrium degree of substitution when reacted in identical mixed acid compositions is often cited as evidence of the occurrence of denitration, the mechanism of denitration is less clear. Miles<sup>31</sup> proposed the nitration of cellulose occurs through a simple esterification reaction in which an equilibrium exists between acid, alcohol, ester, and water according to Equations (2.2) - (2.5), however this reaction scheme is not consistent with the known nitrating agent, the nitronium ion.

$$C_{6}H_{10}O_{5} + 2dsHNO_{3} \xleftarrow{K_{4}} C_{6}H_{10-ds}O_{5-ds} \left(ONO_{2}\right)_{ds} + dsHNO_{3} \bullet H_{2}O \quad (2.2)$$

$$HNO_3 \bullet H_2O \xleftarrow{K_5} HNO_3 + H_2O \tag{2.3}$$

$$C_6H_{10}O_5 + dsHNO_3 \xleftarrow{K} C_6H_{10-ds}O_{5-ds} (ONO_2)_{ds} + dsH_2O$$
(2.4)

$$K_M = \frac{K_4}{K_5} \tag{2.5}$$

Urbanski<sup>1</sup> noted that while esterification reactions are known to be reversible reactions, the hydrolysis of nitric esters is also known to occur in acidic solutions according to the chemical reaction described in Equation  $(2.6)^1$ .

$$RONO_2 \xrightarrow{[H]} ROH + NH_3$$
 (2.6)

Clark et al.<sup>35</sup> extended the work of previous researchers by using high resolution carbon-13 nuclear magnetic resonance techniques to study the distribution of substituted

groups on the anhydroglucose residues for both cellulose and highly nitrated nitrocellulose in a mixed acid selected to yield an intermediate degree of substitution. This work confirmed that denitration occurs upon immersion of highly nitrated nitrocellulose in a mixed acid composition capable of achieving a lower degree of substitution, but that the distribution of substituted groups on the anhydroglucose residues differs from that of cellulose nitrated in the same mixed acid composition.

In his analysis of denitration, Fowler<sup>5</sup> also observed that it is difficult to describe the denitration of nitrocellulose mechanistically under the reaction scheme in which the nitronium ion is the nitrating agent according to Equations (2.7) and (2.8). This net reaction bears some similarities to the acid hydrolysis mechanism discussed by Urbanski<sup>1</sup> but neither reaction is mechanistically consistent with acid dissociation reactions responsible for the formation of the nitronium ion such as Equation (2.7), where hydronium ions (H<sub>3</sub>O<sup>+</sup>) rather than hydrogen ions (H<sup>+</sup>) would be present. Fowler<sup>15</sup> proposed additional denitration experiments using nitrogen-15 labelled nitric acid to provide additional insight into the denitration mechanism, but was ultimately unable to obtain a nuclear magnetic resonance spectrum for nitrogen-15 labeled nitric acid.

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+$$

$$(2.7)$$

$$C_{6}H_{10}O_{5} + dsNO_{2}^{+} \to C_{6}H_{10-ds}O_{5-ds}(ONO_{2})_{ds} + dsH^{+}$$
(2.8)

Lure et al.<sup>36</sup> discussed the reaction of nitrocellulose in aqueous sulfuric acid, noting that both denitration and degradation reactions occur in this media, contrary to the observations of Miles<sup>31</sup>. Based on these findings, it was proposed that acid hydrolysis is the primary mechanism responsible for both reactions, with degradation characterized by hydrolysis of the ether bond in the cellulose chain and denitration characterized by hydrolysis of the nitrate ester groups. The mechanism proposed by Lure et al.<sup>36</sup> was formulated for a system in which denitration and degradation occur in aqueous sulfuric acid. This mechanism has been modified in Equations (2.9)–(2.12) to propose a reaction mechanism in which the nitronium ion acts as the nitrating agent and the hydronium ion, through acid hydrolysis, acts as the denitrating agent.

• Step 1: Dissociation of nitric acid to nitronium ion:

$$HNO_3 + H_2SO_4 \xleftarrow{Ka} NO_2^+ + HSO_4^- + H_2O$$

$$(2.9)$$

• Step 2: Reaction of cellulose hydroxyl group with nitronium ion to form intermediate

$$C_6H_7O_2(OH)_3 + NO_2^+ \xleftarrow{Kb} C_6H_7O_2(OH)_2OHNO_2^+$$
(2.10)

• Step 3: Reaction of intermediate with water to form nitrocellulose

$$C_6H_7O_2(OH)_2OHNO_2^+ + H_2O \xleftarrow{\kappa_c} C_6H_7O_2(OH)_2ONO_2 + H_3O^+ \quad (2.11)$$

• Step 4: Regeneration of sulfuric acid

$$HSO_4^- + H_3O^+ \xleftarrow{Kd} H_2SO_4 + H_2O \tag{2.12}$$

This mechanism can be further simplified by applying the pseudo steady state hypothesis to require that the active intermediate, the product of Equation (2.10), is highly reactive and is thus consumed as fast as it is formed. This assumption allows for the rate law to be expressed in terms of concentrations of species described by the acid dissociation reactions and the net cellulose nitration reaction, and provides a basis for choosing potential forms of the empirical rate law to be used in evaluating kinetic data. A preliminary analysis of these elementary reactions suggests that the concentrations of hydroxyl groups, nitronium ions, nitrate ester groups, hydronium ions, and water should be considered in developing a semi-empirical rate law describing the reversible cellulose nitration reaction.

**2.4.1.3** The Dissociation of Mixed Acids to Ionic Species. Because nitric acid first dissociates to ionic species including the nitronium ion before reacting with available cellulose hydroxyl groups during the nitration of cellulose in mixtures of sulfuric acid, nitric acid, and water, it is necessary to calculate or measure the concentration of nitronium ions in a given mixed acid. Albright et al.<sup>26</sup> proposed a set of dissociation reactions (2.13) -(2.15) and equilibrium constants ( $K_1$ ,  $K_2$ , and  $K_3$ ) to model the dissociation of nitronium ion concentration data published by Zaman<sup>30</sup>, where  $x_i$  is the mole fraction of species i. The Raman spectroscopic techniques that were used by Zaman<sup>30</sup> to measure dissociation of nitric acid dissociation reactions (2.13) -(2.15) to calculate equilibrium constants (Table 2.10) that can be used to model the nitronium ion concentration in mixtures of nitric acid, sulfuric acid, and water.

$$HNO_3 + H_2SO_4 \longleftrightarrow NO_2^+ + HSO_4^- + H_2O$$

$$(2.13)$$

$$H_2SO_4 + H_2O \xleftarrow{K_2} H_3O^+ + HSO_4^-$$
(2.14)

$$HNO_3 + H_2O \xleftarrow{K_3} H_3O^+ + NO_3^-$$
(2.15)

$$K_{1} = \frac{\left(x_{NO_{2}^{+}}\right)\left(x_{HSO_{4}^{-}}\right)\left(x_{H_{2}O}\right)}{\left(x_{HNO_{3}}\right)\left(x_{H_{2}SO_{4}}\right)}$$
(2.16)

$$K_{2} = \frac{\left(x_{H_{3}O^{+}}\right)\left(x_{HSO_{4}^{-}}\right)}{\left(x_{H_{2}SO_{4}}\right)\left(x_{H_{2}O}\right)}$$
(2.17)

$$K_{3} = \frac{\left(x_{H_{3}O^{+}}\right)\left(x_{NO_{3}^{-}}\right)}{\left(x_{HNO_{3}}\right)\left(x_{H_{2}O}\right)}$$
(2.18)

Reaction **Temperature** 20°C 30°C 40°C (2.13)0.067 0.055 0.045 (2.14)65 59 67 0.2 0.19 0.16 (2.15)

Table 2.10 Equilibrium Constants Reported by Albright et al.<sup>26</sup>

The equilibrium constants (K<sub>1</sub>, K<sub>2</sub>, and K<sub>3</sub>) listed in Table 2.10 that were reported by Albright et al.<sup>26</sup> on a mole fraction basis were converted to a concentration basis (K<sub>1</sub><sup>\*</sup>, K<sub>2</sub><sup>\*</sup>, and K<sub>3</sub><sup>\*</sup>) using the density,  $\rho_{acid}$ , and average molecular mass, MW<sub>acid</sub>, of the acid mixture according to Equations (2.19)-(2.21), where *[i]* is the concentration of species i expressed in moles per liter.

$$K_1^* = K_1 \frac{\rho_{acid}}{MW_{acid}} = \frac{[NO_2^+][HSO_4^-][H_2O^*]}{[HNO_3^*][H_2SO_4^*]}$$
(2.19)

$$K_{2}^{*} = K_{2} = \frac{[H_{3}O^{+}][HSO_{4}^{-}]}{[H_{2}SO_{4}^{*}][H_{2}O^{*}]}$$
(2.20)

$$K_{3}^{*} = K_{3} = \frac{[H_{3}O^{+}][NO_{3}^{-}]}{[HNO_{3}^{*}][H_{2}O^{*}]}$$
(2.21)

In modeling the dissociation of mixed acids to ionic species, it was assumed that the rate of acid dissociation is very fast when compared to the rate of cellulose nitration, implying that the acid dissociation reactions are locally at equilibrium in the reacting mixture (concentrations are functions of spatial coordinates and time), with the mole fractions of mixed acid species described by Equations (2.19)-(2.21). Reaction stoichiometry is used to relate equilibrium concentrations of sulfuric acid, nitric acid, and water ( $[H_2SO_4]$ ,  $[HNO_3]$ , and  $[H_2O]$ , respectively) in the dissociated acid mixture to the initial concentrations of undissociated acid species ( $[H_2SO_4]_0$ ,  $[HNO_3]_0$ , and  $[H_2O]_0$ ) using Equations (2.22)-(2.24), and the nitrate ion concentration,  $[NO_3^-]$ , is replaced using Equation (2.25).

$$[H_2SO_4] = [H_2SO_4]_0 - [HSO_4^-]$$
(2.22)

$$[HNO_3] = [HNO_3]_0 - 2[NO_2^+] - [H_3O^+] + [HSO_4^-]$$
(2.23)

$$[H_2O] = [H_2O]_0 + [NO_2^+] - [H_3O^+]$$
(2.24)

$$[NO_{3}^{-}] = [H_{3}O^{+}] - [HSO_{4}^{-}] + [NO_{2}^{+}]$$
(2.25)

Using this approach, the dissociation of nitric acid, sulfuric acid, and water to ionic species was described by a set of algebraic equations according to Equations (2.26)-(2.28).

$$K_{1} \frac{\rho_{acid}}{MW_{acid}} = \frac{[NO_{2}^{+}][HSO_{4}^{-}]([H_{2}O]_{0} + [NO_{2}^{+}] - [H_{3}O^{+}])}{([HNO_{3}]_{0} - 2[NO_{2}^{+}] - [H_{3}O^{+}] + [HSO_{4}^{-}])([H_{2}SO_{4}]_{0} - [HSO_{4}^{-}])} (2.26)$$

$$K_{2} = \frac{[H_{3}O^{+}][HSO_{4}^{-}]}{([H_{2}SO_{4}]_{0} - [HSO_{4}^{-}])([H_{2}O]_{0} + [NO_{2}^{+}] - [H_{3}O^{+}])} (2.27)$$

$$K_{3} = \frac{[H_{3}O^{+}]([H_{3}O^{+}] - [HSO_{4}^{-}] + [NO_{2}^{+}] - [H_{3}O^{+}])}{([HNO_{3}]_{0} - 2[NO_{2}^{+}] - [H_{3}O^{+}] + [HSO_{4}^{-}])([H_{2}O]_{0} + [NO_{2}^{+}] - [H_{3}O^{+}])} (2.28)$$

An alternate approach to modeling the dissociation of mixed acids during the nitration of cellulose involves assuming that the rate of acid dissociation is at least an order

of magnitude faster than the cellulose nitration reaction. Forward and reverse rate constants for the acid dissociation reactions are described by Equations (2.29)-(2.31), where  $k_f$  is the forward rate constant for the cellulose nitration reaction.

$$K_1 = \frac{k_1}{k_{-1}}; \quad k_1 \gg k_f$$
 (2.29)

$$K_2 = \frac{k_2}{k_{-2}}; \quad k_2 \gg k_f$$
 (2.30)

$$K_3 = \frac{k_3}{k_{-3}}; \quad k_3 \gg k_f$$
 (2.31)

Overall reaction rates can then be calculated for each species by considering the generation and consumption of species in the cellulose nitration reaction and the acid dissociation reactions described by Equations (2.13)-(2.15). This procedure is described in detail in the model implementation section of this chapter.

# 2.4.2 The Structure of Cellulose Fibers

Because nitrocellulose is produced from naturally occurring fibers (primarily cotton linters and wood pulps), the influence of the cellulose fiber structure (Figure 2.2) on the rate of nitration of these materials must be considered. The hollow wood pulp fiber ultrastructure consists of a three-layered<sup>37</sup>, hierarchical fibrillar structure with highly ordered cellulose present in the secondary wall and disordered cellulose present in the primary cell wall<sup>3,38</sup>. Orientation also exists in the substructures with polymer chains exhibiting a helical arrangement in the elemental fibril structures<sup>18,38</sup>, and with highly oriented crystalline regions on the order of 2-20nm in width and 2-20 nm in thickness<sup>3</sup>. O'Sullivan<sup>3</sup> noted that while covalent bonds, hydrogen bonds, and van der Waals forces generally govern the cellulose ultrastructure, the degree of polymerization and morphological characteristics
vary with the source of natural fibers. It was reported that for smaller microfibrils such as those found in wood, which generally contain between 30 and 200 cellulose chains, the surface area is approximately equivalent to the amorphous content. Given this, it is likely incorrect to consider amorphous regions in cellulose as analogous to amorphous regions in other polymers, as they still are likely to exhibit a high degree of order and may have a significant influence on the accessibility and reactivity of cellulose<sup>38</sup>.



Figure 2.2 Hierarchical fibrillar structure of a cellulose fiber.

Ott et al.<sup>2</sup> noted that the two main concepts that have been developed to describe the nitration of natural cellulose fibers are a micellar heterogeneous reaction and a homogeneous or permutoid reaction. Under the micellar heterogeneous reaction model, the nitrating species penetrates the amorphous regions between the cellulose micelles and the reaction proceeds as the nitrating species diffuses through the micelles as they are nitrated progressively from the outside to the interior regions. Conversely, the homogenous reaction model describes the nitrating species as penetrating uniformly through all regions of the cellulose fiber and all cellulose molecules nitrating at approximately the same time. In discussing these models, Ott et al.<sup>2</sup> reported that the available experimental results at the time of his publication overwhelmingly favored the homogeneous theory, citing fractionation experiments by others that failed to find significant variation in the nitrogen content of nitrocellulose specimens while also failing to find regions of cellulose trinitrate in partially nitrated samples. This finding contradicts both the heterogeneous reaction model and the theory of inaccessible regions controlling the extent of reaction in cellulose fibrils and can be tested by performing experiments with cellulose fibers with different crystallinities. Because the amorphous regions of cellulose probably still exhibit a high degree of order<sup>3</sup>, the differences in diffusion rates through the amorphous and crystalline regions in cellulose fibers also may not differ by as much as has been previously assumed.

Through careful selection of cellulose fibers and experimental conditions, the validity of these two conceptual models for the nitration of cellulose fibers were evaluated. Fibers exhibiting a range of crystallinities and characteristic dimensions should exhibit different rates of nitration if the reaction is governed by either the rate of diffusion of mixed acid species into crystalline regions or by diffusion of mixed acids into the fiber. This was accomplished by considering these two nitration models in analyzing single cellulose fiber nitration data and in assessing the suitability of kinetic models for describing the reaction of single cellulose fibers in mixed acids. By testing models that consider the nitronium ion and hydronium ion as the nitrating and denitrating agents, respectively, the reaction mechanism (micellar heterogeneous vs. homogeneous) and factors controlling the extent of reaction (chemical equilibrium vs. accessibility) were evaluated through experimental design.

Considerable uncertainty exists in much of the published literature for cellulose reactivity in mixed acids because researchers often neglected to report the physical state of the cellulose raw materials evaluated. Dense cellulose materials were most likely used in these studies because they are the cellulose raw material most commonly used in industrial nitrocellulose manufacturing processes, but they are also known to exhibit mass transfer limitations and are thus not suitable materials for reaction kinetic studies. To avoid the complexity associated with simultaneous mass transfer and chemical reaction in dense cellulose structures, it was necessary to conduct experiments in an environment in which kinetics can be studied independent of the effects of mass transfer associated with these densified forms. This was accomplished by considering cellulose reaction kinetics at the smallest practical scale for this multiphase reaction where interfiber diffusion is absent: single cellulose fibers dispersed in mixed nitrating acids. Under these conditions, only the effects of intrafiber diffusion need be considered in our treatment of reaction kinetics.

The influence of intrafiber diffusion on the nitration of cellulose fibers can be estimated by considering the fiber geometries and diffusivities of mixed acid species through the wall of the cellulose fiber. Because vigorous mixing is generally maintained in cellulose nitration processes, fibers with different surface area to volume ratios provide some insight into whether mass transfer at the fiber surface plays a limiting role. Similarly, the significance of intrafiber diffusion can be considered by estimating the time required for the mixed acid species to diffuse through the cellulose fiber wall. This diffusion time was estimated using Equation (2.32), where  $t_D$  is the diffusion time,  $\delta$  is the fiber wall.

$$t_D \approx \frac{\delta^2}{2D} \tag{2.32}$$

Foston et al.<sup>39</sup> reported diffusivities on the order of  $5.49 \times 10^{-10}$  m<sup>2</sup>/s for the diffusion of dilute acids through the walls of plant derived cellulose fibers that can be used to estimate characteristic diffusion times during the nitration of cellulose fibers. The diffusion times were calculated using Equation (2.32) for fiber wall thicknesses varying between 3.5 $\mu$ m (hardwood fibers) and  $5\mu$ m<sup>37</sup> (softwood fibers) resulting in very small (~0.02s) diffusion times. This result was also independently reached by Nikolsky et al.<sup>18</sup> in their treatment of factors controlling the rate of nitration in cellulose fibers by considering representative diffusion coefficients through solids and crystalline polymers. Given the magnitude of these characteristic diffusion times, diffusion can be neglected in estimating the reaction kinetics of cellulose fibers, which have been reported to exhibit reaction times on the order of minutes<sup>13</sup>. This observation is consistent with the homogeneous reaction model for cellulose nitration in which the nitrating media penetrates through all regions of the fiber at approximately the same time. Because the effects of intrafiber mass transfer are expected to be negligible for single cellulose fibers dispersed in mixed nitrating acids, it is proposed that cellulose fibers represent a suitable experimental system for studying the kinetics of cellulose nitration. The fact that diffusion through the fiber wall is so rapid also suggests that immersing the reacting fibers in chilled water should be an effective means of ceasing the nitration reaction.

#### 2.4.3 Empirical Rate Law for Cellulose Nitration Kinetics

The empirical rate law that was developed to describe the nitration of cellulose was based on an empirical form of a bimolecular rate law that was proposed by Salmi, et al.<sup>22</sup> to describe the kinetics of cellulose substitution reactions. This form of rate law demonstrated good agreement with experimental results for the carboxymethylation of cellulose and can be adapted to describe the reversible nitration of cellulose.

$$\frac{dC_{OH,i}}{dt} = -k_0 e^{-a_0 ds} \alpha_i C_{OH,i} C_{HA} \quad (i = 2, 3, 6)$$
(2.33)

Equation (2.33) was used to describe the substitution kinetics for the hydroxyl groups at the C<sub>2</sub>, C<sub>3</sub>, and C<sub>6</sub> positions (Figure 2.3) in terms of the dimensionless concentrations of the hydroxyl groups,  $C_{OH,i}$ , at each position, and the concentration of the monochloroacetate ion,  $C_{HA}$ . To describe the decreasing reactivity of hydroxyl groups as the reaction proceeds, the model features two parameters: an activity decay factor,  $a_0$ , to describe the decreasing reactivity of hydroxyl groups as the reaction proceeds, and a proportionality coefficient,  $\alpha_i$ , for each reaction to describe the relative reactivities of the hydroxyl groups at the C<sub>2</sub>, C<sub>3</sub>, and C<sub>6</sub> sites. The degree of substitution (ds) is a parameter that varies between 0 and 3 depending on the extent of reaction.



**Figure 2.3** Cellulose repeating unit with carbon positions on anhydroglucose ring numbered. Reactive hydroxyl groups are located on the C2, C3, and C6 carbons.

This model<sup>22</sup> describes the decreasing reactivity of hydroxyl groups as the reaction proceeds empirically by assuming that the decrease in reactivity,  $\Delta k_i$ , is proportional to the change in the degree of substitution,  $\Delta ds$ .

$$\Delta k_i = -a_0 k_i \Delta ds \tag{2.34}$$

Equation (2.34) can be integrated by allowing the changes in the degree of substitution to become infinitesimal and applying the condition that the initial reactivity,  $k_i$ , is equal to  $k_o$  in unsubstituted cellulose:  $k_i = k_o$  when ds = 0.

$$k_{i} = -k_{0}e^{-a_{0}ds} ag{2.35}$$

Using this approach, an empirical parameter is introduced to describe the net decrease in reactivity that is known to occur as the cellulose nitration reaction proceeds. This phenomenon has been attributed to complex processes that limit the accessibility of available reaction sites, possibly due to untwisting of cellulose nanofibrils<sup>17,18</sup> or breaking hydrogen bonds in crystalline regions of the cellulose fiber<sup>38</sup>. The temperature dependence of the rate parameter,  $k_0$ , is described by an Arrhenius relationship, where A and  $E_a$  are the frequency factor and activation energy, respectively.

$$k_0 = A e^{-E_a/RT}$$
(2.36)

An expression describing the net rate of substitution of cellulose was obtained by summing (2.33) over the three reactive hydroxyl group sites and combining terms.

$$\frac{dC_{OH}}{dt} = -k_0 e^{-a_0 ds} \left( \alpha_2 C_{OH,2} + \alpha_3 C_{OH,3} + \alpha_6 C_{OH,6} \right) C_{HA}$$
(2.37)

The fact that a denitration reaction occurs implies that the degree of substitution achieved when nitrating cellulose is equilibrium controlled rather than limited by the accessibility or availability of reactive hydroxyl groups. This is consistent with the finding that all wood-pulp derived, single cellulose fibers exhibit similar reactivity<sup>16</sup>, as differences in the structure of the fibers would have resulted in different kinetics if accessibility were a significant factor. This is also consistent with the experimental observation that the degree of substitution depends only on the final composition of the mixed acid used to nitrate the cellulose. Given this, it is possible to describe the nitration of cellulose in terms of the generation and consumption of hydroxyl groups (or nitrate ester groups) as the reaction proceeds. The equilibrium degree of substitution is then characterized by the point at which the rates of generation and consumption of hydroxyl groups are equal, or the net rate of formation of nitrate ester groups is equal to zero.

To further modify this equation to describe the equilibrium controlled nitration of cellulose, a term was added to describe the reverse reaction, or denitration, and monochloroacetate was replaced with the nitronium ion,  $NO_2^+$ , as the nitrating species.

$$\frac{dC_{OH}}{dt} = -k_0 e^{-a_0 \frac{C_{ONO_2}}{C_{OH,0}}} \left( \alpha_2 C_{OH,2} + \alpha_3 C_{OH,3} + \alpha_6 C_{OH,6} \right) C_{NO_2^+} + k_d C_{ONO_2} C_{H_3O^+}$$
(2.38)

The degree of substitution has been expressed in terms of the nitrate ester concentration and initial hydroxyl concentration while allowing the coefficient to be absorbed into the activity decay factor.

$$ds = 3 \frac{C_{ONO_2}}{C_{OH,0}}$$
(2.39)

A final simplification was made by considering the experimental observations by  $Wu^{23}$  and Fowler and Clark<sup>40</sup> regarding the reactivity of the hydroxyl groups at the C<sub>2</sub>, C<sub>3</sub>, and  $C_6$  sites. Wu<sup>23</sup> reported that the  $C_6$  site is the most reactive site and generally is substituted first during nitration while Fowler and Clark<sup>40</sup> noted that a nitrated C<sub>6</sub> site is generally the last site to react during denitration, suggesting that nitration of the C<sub>6</sub> site may result in a lower free energy state than nitration of the C<sub>2</sub> or C<sub>3</sub> sites in addition to being less sterically hindered. Fowler and Clark<sup>35</sup> also observed that during nitration, the presence of another nitrated group in an anhydroglucose unit tends to activate the remaining unsubstituted hydroxyl groups in that anhydroglucose unit, and demonstrated experimentally that the kinetics of denitration are much slower than the kinetics of nitration. Urbanski<sup>1</sup> suggested that the rate of denitration may be slower than the rate of nitration because of the relative accessibility of reacting groups in cellulose and nitrocellulose, noting that the crystal structure of nitrocellulose remains even after the material has denitrated to a lower degree of substitution. Given that the kinetics of the denitration reaction were observed to be much slower than the kinetics of the nitration reaction, the denitration reaction was modeled as an elementary, bimolecular reaction.

In consideration of these observations and the fact that the specific substitution site is not of practical interest for a kinetic model describing industrial-scale bulk nitration, the proportionality coefficients were eliminated to allow the activity decay factor,  $a_0$ , to address the net decline in reactivity of remaining hydroxyl groups as the reaction proceeds. Incorporation of these assumptions results in a reaction model (2.40) for an equilibrium controlled reaction describing the net conversion of hydroxyl groups to nitrate ester groups in the presence of the nitronium ion and hydronium ion. This assumption allows for the rate law to be expressed in terms of concentrations of species described by the acid dissociation reactions proposed by Albright et al.<sup>26</sup>, and considers the nitronium ion and hydronium ion as the active nitrating and denitrating agents, respectively.

$$\frac{dC_{OH}}{dt} = -A_f e^{-E_{af}/RT} e^{-a_0 \frac{C_{ONO_2}}{C_{OH,0}}} C_{OH} C_{NO_2^+} + A_d e^{-E_{ad}/RT} C_{ONO_2} C_{H_3O^+}$$
(2.40)

The temperature dependence of the nitration and denitration reactions are both described by Arrhenius relationships with the nitration reaction frequency factor and activation energy denoted by  $A_f$  and  $E_{af}$ , and the denitration reaction frequency factor and activation energy denoted by  $A_d$  and  $E_{ad}$ , resulting in a five-parameter model. Through treating the reaction as an equilibrium reaction, the final degree of nitration achieved after long reaction times (70 minutes) can be treated as a steady-state condition in the parameter estimation procedure.

## 2.4.4 Analysis of Single Cellulose Fiber Nitration Kinetic Data

For each single cellulose fiber nitration experiment, the initial hydroxyl concentration,  $[OH]_0$ , was determined using Equation (2.41), where  $m_{cell}$  is the mass of cellulose fibers, mc is the moisture content of the cellulose fibers (mass percentage basis),  $m_{acid}$  is the mass of the mixed acid,  $\rho_{acid}$  is the density of acid, and  $\rho_{cell}$  is the density of cellulose. Because the cellulose fibers evaluated all contained at least 90%  $\alpha$ -cellulose, there was little error associated with assuming that the impurities (hemicelluloses) contained approximately the same hydroxyl content by weight as cellulose. The densities of mixed acids were calculated using a density model adapted from the model published by Martin et al.<sup>41</sup> (see Appendix C) that was generated by measuring the densities of a large range of mixed acid compositions using an Anton Paar DMA 5000M density meter, and a density of 1.46 g/cm<sup>3</sup>

was used as the density of cellulose based on results published by Sun<sup>42</sup>. It is also noted that all cellulose fiber nitration experiments were conducted using a large excess of mixed nitrating acid (150 grams of acid per gram of cellulose fibers), minimizing the effect of any density variation in the cellulose fibers.

$$\left[OH\right]_{0} = \frac{m_{cell} \times \left(1 - \frac{mc}{100}\right) \times \frac{3}{162} \times 1000}{\frac{m_{cell}}{\rho_{cell}} + \frac{m_{acid}}{\rho_{acid}}} \frac{moles}{L}$$
(2.41)

It was assumed that the volume change during the reaction was negligible, allowing the conservation of species for hydroxyl and nitrate ester groups to be represented by Equation (2.43). This assumption is reasonable because a large excess of acid was used for the single cellulose fiber experiments, the reacting system consists of fibers uniformly dispersed in a liquid (mixed acid), and the experiments were conducted under isothermal conditions. The concentrations (moles/liter) of hydroxyl and nitrate ester groups were then calculated for each time and nitrogen percentage data point using Equations (2.42) and (2.43) where 14 is the atomic mass per nitrogen atom, 162/3 is the cellulose molecular weight per hydroxyl group, and 297/3 is the nitrocellulose molecular weight per nitrate ester group.

$$\%N = \frac{[ONO_2] \times 14 \times 100\%}{[ONO_2] \times \frac{297}{3} + [OH] \times \frac{162}{3}}$$
(2.42)

$$\left[OH\right]_{0} = \left[OH\right] + \left[ONO_{2}\right] \tag{2.43}$$

Using the known total number of moles of hydroxyl groups that were converted to nitric ester groups at each reaction time and extent of nitration, the concentrations of nitric

acid and water were calculated using reaction stoichiometry from Equation (1.1) to account for consumption of nitric acid and generation of water in the overall nitration reaction (see Appendix A). Concentrations of ionic species were then calculated using the concentrations of nitric acid, sulfuric acid, and water using the acid dissociation model published by Albright et al.<sup>26</sup> Using this approach (Figure 2.4), a tuple was established for each experimental data point consisting of the reaction time (t), initial hydroxyl concentration *[OH]*<sub>0</sub>, hydroxyl concentration *[OH]*, nitrate ester concentration *[ONO*<sub>2</sub>], nitronium ion concentration *[NO*<sub>2</sub><sup>+</sup>], and hydronium ion concentration *[H*<sub>3</sub>*O*<sup>+</sup>], arranged as (t, [OH]<sub>0</sub>, [OH], [ONO<sub>2</sub>], [NO<sub>2</sub><sup>+</sup>], [H<sub>3</sub>O<sup>+</sup>]).



**Figure 2.4** Process for converting single cellulose fiber reaction data to tuples of reaction times, initial hydroxyl concentrations, hydroxyl concentration, nitrate ester concentration, nitronium ion concentration, and hydronium ion concentration for use in nonlinear least squares regression routine.

The processed data was then grouped so that the kinetic parameters  $A_f$ ,  $A_d$ ,  $E_{af}$ ,  $E_{ad}$ , and  $a_0$  from Equation (2.40) could be estimated using a numerical integration and nonlinear least squares regression routine. A full list of processed data is included in Appendix B.

#### 2.4.5 Evaluation of Single Cellulose Fiber Nitration Kinetic Behavior

The data in Tables 2.5-2.8 indicate that nitration reaction for cellulose fibers is extremely rapid, as degrees of substitution in excess of 2.0, or 11.11% nitrogen, were reached within 20 seconds of exposure of the cellulose fibers to the mixed acids in all of the Grade B single cellulose fiber nitration experiments. The rate of reaction of cellulose fibers in mixed acids used for producing Grade A nitrocellulose was also very rapid, exceeding 10% nitrogen within 20 seconds of immersion of the fibers in mixed acid. Even given these very rapid rates of reaction, the nitration of cellulose fibers does not appear to be a diffusion limited process due to the extremely small (~0.02s) characteristic diffusion times for mixed acid species through the fiber wall.

The influences of the fiber type and temperature were considered using an ANOVA that considered the influence of these factors on the kinetics of nitration for the single cellulose fiber kinetic experiments that were performed with mixed acids high in sulfuric acid used to produce Grace B nitrocellulose. The results of this ANOVA suggest that the reaction kinetics of the cellulose fibers studied were indistinguishable from one another and that the equilibrium degree of substitution was independent of both the temperature and the source of the cellulose fibers under these reaction conditions. This finding is inconsistent with diffusion-limited models that would predict different rates of nitration for cellulose fibers with significant differences in wall thickness or dense crystalline regions, as were evaluated in this study. Given this finding, it is proposed that all high purity (high  $\alpha$ -cellulose content), wood-pulp derived, cellulose fibers exhibit equivalent reactivity in mixed nitrating acid compositions.

Because high purity cellulose fibers exhibit equivalent reactivity in mixed nitrating acid compositions, it is proposed that a universal kinetic model can be developed to describe their rate of reaction in mixed acids. The finding that cellulose fiber nitration kinetics are independent of the source of the fibers also has implications that are of consequence to the selection of materials and the design of processes for industrial-scale nitrocellulose production. Because all highly pure (> 90%  $\alpha$ -cellulose) cellulose fibers derived from wood pulp exhibit equivalent reactivity, it follows that the tree species from which the fibers were obtained and the pulping process used to produce the fibers are also insignificant within the range of fibers considered in this evaluation. Thus, the reactivity of high purity hardwood and softwood fibers produced from the kraft pulping process is expected to be equivalent to the reactivity of softwood fibers produced from the sulfite pulping process that have traditionally been used as a raw material for nitrocellulose production. Because advances in pulping technology have increased the availability of high purity cellulose fibers, a much broader range of suitable materials exist as potential feedstock for industrial scale nitrocellulose manufacturing operations than have historically been used for this application.

The equivalent reactivity exhibited by these fibers in Grade B mixed acids also provides insight into the nature of the cellulose nitration reaction. In addition to the heterogeneous micellar and homogeneous models described by Ott et al.<sup>2</sup>, Munro et al.<sup>5</sup> and Short et al.<sup>43</sup> noted that both thermodynamic equilibrium and the presence of inaccessible regions within the cellulose fibers have been proposed as factors limiting the extent of reaction. The micellar heterogeneous model predicts differences in the nitration kinetics of fibers with significantly different characteristic dimensions and crystallinity, a result not observed in the single cellulose fiber nitration experiments. Conversely, the homogeneous model describes the kinetic behavior as occurring through a mechanism where wetting of the fibers is very rapid, and all regions of the fiber react at approximately the same time. The experimental data clearly demonstrate that significant source-dependent differences are not observed in the transient nitration behavior of the fibers analyzed, consistent with the homogeneous nitration model. This result is also in agreement with the estimated times for the acids to diffuse through the fiber wall that suggest that the effect of fiber geometry is insignificant over the range of fibers analyzed.

The single cellulose fiber nitration experiments also provide insight into factors controlling the extent of reaction. If the extent of reaction is controlled by the presence of inaccessible regions in the fibers, then the fiber morphology, in particular the amount and distribution of crystalline and amorphous regions in the fiber, would be expected to produce an effect on the equilibrium degree of nitration achieved. Alternatively, equilibrium control would be described by the system reaching a minimum free energy state, and the influence of morphological characteristics such as crystallinity would be much less pronounced when compared to the contributions from the Gibbs energies of the species produced and consumed in the chemical reaction. The experimental data supports the latter theory, as the same degree of substitution was reached for all three types of fibers despite significant differences in morphology. These findings are further supported by the two additional experiments that were performed with cotton fibers (a highly pure and highly crystalline material) and wood pulp fibers from a random source, which also yielded the same equilibrium degree of nitration as the three wood pulp fibers evaluated under this study. In This provides further evidence that the equilibrium degree of substitution is,

indeed, thermodynamically limited rather than limited by inaccessibility of regions within the cellulose fiber. Collectively, these findings provide a strong case for the use of a universal kinetic model describing the rate of reaction of cellulose fibers in mixed acids.

# 2.4.6 Kinetic Parameters and Sensitivity Analysis

Kinetic parameters were estimated by numerically integrating the unsteady state mass balance for hydroxyl groups represented by Equation (2.40), and performing nonlinear least squares regression of an objective function designed to calculate the total error between the numerical solution and the experimental data points. Because the ANOVA failed to identify significant differences in the reactivity of the three wood pulp fibers that were evaluated, a single set of kinetic parameters was used to describe the nitration kinetics of all of data from the single cellulose fiber nitration experiments. Because the experimental data points recorded for reaction times of 70 minutes were considered to be steady-state values, the rate of change of the hydroxyl concentration was set to zero and one of the kinetic parameters was expressed in terms of the other four parameters using Equation (2.44), where the concentrations are evaluated at 4200 seconds.

$$A_{f}e^{-E_{af}/RT}e^{-a_{0}\frac{C_{ONO_{2}}(4200)}{C_{OH,0}}}C_{OH}(4200)C_{NO_{2}^{+}}(4200) = A_{d}e^{-E_{ad}/RT}C_{ONO_{2}}(4200)C_{H_{3}O^{+}}(4200)$$
(2.44)

Kinetic parameters were estimated using the NMinimize<sup>29</sup> global optimization routine embedded in a Monte Carlo algorithm that was used to generate the initial guesses for the kinetic parameters. Using this approach, the kinetic parameters listed in Table 2.11 were generated and are proposed as universal kinetic parameters describing the nitration of cellulose fibers in mixed acids. This model yielded a correlation coefficient of 0.970 for the full set of 76 single cellulose fiber nitration experiments.

Parameter	Value	Units
$\mathbf{A_{f}}$	$1.430 \times 10^{18}$	L/mol·s
Eaf	68674.7	J/mol
Ad	1108.14	L/mol·s
Ead	46804.4	J/mol
ao	23.1894	-

**Table 2.11** Universal Single Cellulose Fiber Nitration Model Kinetic Parameters

A sensitivity analysis was performed to assess the influence of the kinetic parameters on the overall model correlation coefficient. The influence of parameters on the correlation coefficient was evaluated by slightly changing individual parameters while keeping the other parameters at the nominal values and computing the correlation coefficient, R<sup>2</sup>. Using this approach, the influence of changes to the kinetic parameters on the fit of the model was evaluated. Each parameter's influence on the correlation coefficient was quantified by calculating the rate of change of the correlation coefficient using the five-point derivative rule:

$$\frac{\partial R^2}{\partial p_i} = \frac{R^2 \left( p_i - 2\Delta p_i \right) - 8R^2 \left( p_i - \Delta p_i \right) + 8R^2 \left( p_i + \Delta p_i \right) - R^2 \left( p_i + 2\Delta p_i \right)}{12\Delta p_i} (2.45)$$

where  $\Delta p_i$  is a small change in the parameter  $p_i$ .

The correlation coefficient was monitored while making small changes to the kinetic parameters to calculate the rate of change in correlation coefficient in response to a change in the kinetic parameters (Table 2.12). The parameter,  $\gamma$ , was varied from 0.1 to 0.0001 to verify the accuracy of the five-point derivative rule, with the change in parameter  $p_i$  equal to  $\gamma * p_i$ . This analysis demonstrated that the activity decay factor,  $a_0$ , and the frequency factors for the nitration and denitration reactions,  $A_f$  and  $A_d$ , have the most

significant effect on the fit of the model to the experimental data. The activity decay factor, which was introduced to describe the phenomenon of decreasing reactivity of remaining hydroxyl groups as the reaction proceeds, is also needed to describe the very rapid initial kinetics for this reaction. Conversely, the activation energy for the nitration reaction,  $E_{af}$ , exhibited the least significant effect on the fit of the model to the experimental data.

Parameter	γ			
	0.1	0.01	0.001	0.0001
$A_f$	-1.48E-05	-1.48E-05	-1.48E-05	-1.48E-05
Eaf	-1.17E-07	-1.17E-07	-1.17E-07	-1.17E-07
$A_d$	-1.48E-05	-1.48E-05	-1.48E-05	-1.48E-05
Ead	6.61E-06	6.60E-06	6.60E-06	6.60E-06
ao	-2.69E-03	-2.68E-03	-2.68E-03	-2.68E-03

**Table 2.12** Sensitivity Analysis to Estimate the Influence of Kinetic Parameters on Correlation Coefficient ( $\Delta p_i = \gamma^* p_i$ )

### 2.4.7 Explanations for Observed Kinetic Behavior

Additional discussion is warranted given the observation that three wood pulps with significantly different characteristics exhibited effectively identical kinetic behavior. These results appear to be inconsistent with both the heterogeneous reaction mechanism and with the suggestions by Miles<sup>31</sup> and Urbanski<sup>1</sup> that diffusion in the crystalline regions of cellulose fibers may be either slow or incomplete. The differences in crystallinity of these fibers are of interest because the total crystallinity was approximately 15%-20% higher in the sulfite pulped softwood fibers than in the other two fibers while the percentage of the more stable cellulose II allomorph was an order of magnitude higher in the kraft pulped softwood fibers than in the other two fibers. Some insight can be gained by

considering the structure of cellulose fibers and the meaning of crystalline and amorphous regions within the context of this fibrillar structure.

The question of whether the equilibrium degree of substitution is limited by inaccessibility of crystalline regions within the cellulose fiber can be addressed by considering the experimental results at very long (4200s) reaction times. These data demonstrate that all fibers reached the same equilibrium degree of substitution in a mixed acid composition regardless of the total crystallinity or distribution of crystal allomorphs in the fibers. This same result was repeated for both cotton linters (a highly pure and highly crystalline natural source of cellulose) and for another kraft pulped softwood pulp. In addition, Short<sup>43</sup> and Wu<sup>23</sup> demonstrated using carbon-13 NMR that no unsubstituted primary hydroxyl groups (position C6) remained in nitrocellulose samples with a degree of substitution as low as 2.3 that were prepared using mixed acids. Because all the primary hydroxyl groups in these samples were substituted, all regions of the cellulose fiber were necessarily accessible to the nitrating agent. There is thus no evidence that inaccessible regions of cellulose I or cellulose II crystals within the cellulose fiber limit the equilibrium degree of substitution for nitration of cellulose fibers in the mixed acid evaluated.

Although the crystalline regions of the cellulose fibers are clearly accessible to the nitrating agent, this does not explain why the degree of crystallinity in the samples did not exhibit a measurable effect on the nitration kinetics of the fibers as suggested by Prask and Choi<sup>44</sup>. This question can be addressed by considering the ability of the mixed nitrating acid to penetrate the fiber, and by considering the influence of the morphology of the cellulose fiber ultrastructure. Short<sup>10</sup> reported that sulfuric acid is able to cause interfibrillar swelling but that nitric acid is able to cause both interfibrillar and intrafibrillar

swelling. This behavior was attributed to the planar shapes of nitric acid and the nitronium ion which can penetrate the crystalline lattice structure and suggests that all acid species may not diffuse into the crystalline regions of the fiber.

Miles<sup>31</sup> also presented experimental data that demonstrated that the cellulose I crystal structure is not converted to the nitrocellulose crystal structure until the material is nearly fully substituted, suggesting that complete reaction of the interior of the crystalline regions and disruption of the cellulose I crystalline structure may not occur until all of the amorphous regions and crystal surface regions have been nitrated. Clark and Stephenson<sup>45</sup> reported similar results in a study monitoring the d(110) spacing as a function of the degree of nitration in both nitrated and denitrated samples noting that the crystal structure changes considerably between 13.5% nitrogen and a fully substituted material (14.14% nitrogen). This suggests that even in the high degrees of nitration achieved in this study (~13.6% nitrogen) the influence of the crystalline structure may have been minimal, as this is only the very beginning of the region where large changes in crystal structure were reported for incremental increases in nitrogen content<sup>46</sup>.

Additional insight can be gleaned by considering the morphology of the cellulose fiber. O'Sullivan<sup>3</sup> noted that while covalent bonds, hydrogen bonds, and van der Waals forces generally govern the cellulose ultrastructure, the degree of polymerization and morphological characteristics vary with the source of natural fibers. It was reported that for smaller microfibrils such as those found in wood, which generally contain between 30 and 200 cellulose chains, the surface area is approximately equivalent to the amorphous content. Given this, it is probably incorrect to think of amorphous regions in cellulose as analogous to amorphous regions in other polymers, as they likely still exhibit a relatively high degree of order. Because the amorphous regions of cellulose probably still exhibit a high degree of order, the differences in diffusion rates through the amorphous and crystalline regions in cellulose fibers also may not differ by as much as has been previously assumed.

O'Sullivan<sup>3</sup> also noted that two polymorphs, cellulose I $\alpha$  and celluose I $\beta$ , have been shown to exist in native cellulose and suggested that regions of cellulose I $\alpha$  may be the site of initial reaction in fibrils where both phases coexist, due to the fact that the cellulose I $\alpha$ is a metastable phase. Differences in the ratio of cellulose I $\alpha$  to cellulose I $\beta$  in samples as well as the characteristic dimensions of microfibrils could thus offer a possible explanation for why samples with significantly different crystallinity might exhibit identical reactivity. Indeed, Liitiä et al.<sup>47</sup> reported that cellulose I $\alpha$  is at least partially converted to cellulose I $\beta$ during kraft pulping due to the elevated temperature and caustic conditions employed in this process. Furthermore, Åkerholm et al.<sup>48</sup> reported that this conversion of cellulose I $\alpha$ to cellulose IB is observed in wood pulps produced using the kraft pulping process, but not in wood pulps produced using the sulfite pulping process. This suggests that the crystalline regions in the kraft pulped samples may have contained a higher ratio of the more stable cellulose I\u03c3 polymorph even though the total crystallinity was lower in these samples, possibly explaining why these samples with lower total crystallinity exhibited equivalent kinetics of nitration.

# 2.4.8 Modeling the Rate of Nitration for Single Cellulose Fibers

The kinetic parameters listed in Table 2.11 can be used to construct a universal kinetic model for the nitration of high purity cellulose fibers that accounts for the mixed acid

composition, acid to cellulose ratio, reaction temperature, and the cellulose moisture content. This model effectively simulates the equilibrium-controlled cellulose nitration reaction by coupling cellulose fiber nitration kinetics with acid dissociation reactions to dynamically adjust the acid composition as the reaction proceeds. To implement this model, the equilibrium constants proposed by Albright et al.<sup>26</sup> (Table 2.10) to describe acid dissociation reactions were converted to a molarity basis from mole percentage basis, and the acid dissociation reactions were assumed to proceed at a rate that is an order of magnitude faster than the forward rate constant cellulose nitration reaction. The forward rate constant for the cellulose nitration reaction is expressed using an Arrhenius relationship using the kinetic parameters for the frequency factor ( $A_f$ ) and activation energy ( $E_{af}$ ) according to Equation (2.46), where R is the universal gas constant and T is the absolute temperature. Forward and reverse rate constants were defined for the acid dissociation reactions according to Equations (2.47)-(2.55).

$$k_f = A_f e^{\frac{E_{af}}{RT}}$$
(2.46)

$$HNO_3 + H_2SO_4 \xleftarrow{k_{1f}} NO_2^+ + HSO_4^- + H_2O$$
(2.47)

$$H_2SO_4 + H_2O \xleftarrow{k_{2f}}{k_{2r}} H_3O^+ + HSO_4^-$$
(2.48)

$$HNO_3 + H_2O \xleftarrow{k_{3f}}{k_{3r}} H_3O^+ + NO_3^-$$
(2.49)

$$k_{1f} = 10k_f \tag{2.50}$$

$$k_{1r} = \frac{10k_f}{K_1} \tag{2.51}$$

$$k_{2f} = 10k_f \tag{2.52}$$

$$k_{2r} = \frac{10k_f}{K_2} \tag{2.53}$$

$$k_{3f} = 10k_f \tag{2.54}$$

$$k_{3r} = \frac{10k_f}{K_3} \tag{2.55}$$

If the system is assumed to be well mixed, then the concentrations of mixed acid species in Equations (2.26)-(2.28) are only functions of time and are independent of the spatial coordinates in the reacting mixture.

Unsteady state mass balances were written for each reacting species in the system according to Equation (2.56), where  $r_{ij}$  represents the rate of reaction of species *j* in reaction *i*. Consumption and generation terms for the cellulose nitration reaction were written using the net cellulose reaction, Equation (1.1), and the acid dissociation reactions, Equations (2.47)-(2.49). The rate of consumption and generation of species in Equation (1.1) was described according to Equation (2.40), the empirical rate law for the nitration of cellulose fibers, with the nitronium ion as the nitrating agent and the hydronium ion as the denitrating agent.

\_ \_

$$r_{ij} = \frac{d[j]}{dt} = \sum_{i} r_j \tag{2.56}$$

$$\frac{d[H_2SQ_4]}{dt} = -k_{1f}[H_2SQ_4][HNQ_3] + k_{1r}[NQ_2^*][HSQ_4^*][H_2Q] - k_{2f}[H_2SQ_4][H_2Q] + k_{2r}[H_3Q^*][HSQ_4^*] \quad (2.57)$$

$$\frac{d[HNQ_3]}{dt} = -k_{1f}[H_2SQ_4][HNQ_3] + k_{1r}[NQ_2^*][HSQ_4^*][H_2Q] - k_{2f}[HNQ_3][H_2Q] + k_{2r}[H_3Q^*][NQ_3^*] - k_{2e}e^{-\frac{d(NQ_3)}{dH}}[OH][NQ_2^*] + k_{d}[ONQ_3][H_3Q^*] \quad (2.58)$$

$$\frac{d[H_2Q]}{dt} = +k_{1f}[H_2SQ_4][HNQ_3] - k_{1r}[NQ_2^*][HSQ_4^*][H_2Q] - k_{2f}[H_2SQ_4][H_2Q] + k_{2r}[H_3Q^*][HSQ_4^*] - k_{3f}[HNQ_3][H_2Q] \quad (2.59)$$

$$\frac{d[H_3Q^*]}{dt} = +k_{1f}[H_2SQ_4][HNQ_3] - k_{1r}[NQ_3^*] - k_d[ONQ_3][H_3Q^*] \quad (2.60)$$

$$\frac{d[H_3Q^*]}{dt} = +k_{2f}[H_2SQ_4][HNQ_3] - k_{2r}[H_3Q^*][HSQ_4^*] + k_{3f}[HNQ_3][H_2Q] - k_{3r}[H_3Q^*][NQ_3^*] \quad (2.61)$$

$$\frac{d[NQ_3^*]}{dt} = +k_{1f}[H_2SQ_4][HNQ_3] - k_{1r}[NQ_4^*] + k_{3f}[H_3Q^*][NQ_3^*] \quad (2.62)$$

$$\frac{d[HSQ_4^*]}{dt} = +k_{1f}[H_2SQ_4][HNQ_3] - k_{1r}[NQ_4^*] + k_{3f}[H_3Q^*] \quad (2.64)$$

$$\frac{d[NQ_4^*]}{dt} = -k_{2f}[H_2SQ_4][HNQ_3] - k_{1r}[NQ_2^*] + k_{4}[ONQ_2][H_3Q^*] \quad (2.64)$$

$$\frac{d[OH]}{dt} = -k_{2f}e^{-e^{\frac{(NQ_3)}{(OH)_{1}}}} \quad (2.64)$$

This set of coupled ordinary differential equations represents a combination of the single cellulose fiber nitration kinetic model, acid dissociation model, and mixed acid density model, and can then be solved using only the known mixed acid composition, temperature, acid to cellulose ratio, and cellulose moisture content. This model is described as a universal kinetic model for the nitration of wood pulp derived, single cellulose fibers in mixed acids because it has been demonstrated to accurately describe the kinetics of nitration for cellulose fibers obtained from significantly different wood pulps. The model parameters are also in reasonable agreement with the nitration activation energy (~46 kJ/mol) published by Stovbun et al.<sup>17</sup>, although it must be noted that a different (zeroth order) rate law was assumed in calculating those parameters. Figure 2.5 shows that the model accurately predicts the degree of nitration as a function of time for the three wood pulps evaluated and at both temperatures evaluated.



**Figure 2.5** Single cellulose fiber kinetic model results versus experimental data for Grade B high sulfuric acid mixed nitrating acid composition.

Only the temperatures and reaction times of the experimental data are distinguished in Figure 2.5 because the reaction kinetics of the three different fiber types were determined to be statistically equivalent. Because the experimental results that were obtained at long reaction times (70 minutes) were imposed as a steady-state condition in the parameter estimation algorithm that was used, the model does sacrifice some accuracy in the predicting the rate of nitration at very short reaction times in order to achieve good agreement with the equilibrium degree of nitration (Figure 2.6).



**Figure 2.6** Single cellulose fiber kinetic model results versus experimental data for Grade B high sulfuric acid mixed nitrating acid composition at long reaction times.

The SCF model is applicable to high purity (greater than 90%  $\alpha$ -cellulose) wood pulp fibers obtained from either the kraft or sulfite pulping processes. The ability of the model to accurately predict the nitration kinetics of cotton (a highly pure, highly crystalline cellulose fiber) have not been demonstrated under this effort, but the model has been shown to accurately predict the equilibrium degree of nitration in cotton fibers. The model is also capable of describing the nitration kinetics of pulps obtained from both hardwood and softwood tree species as the diffusion times of mixed acids through the fiber wall has been shown to be very fast compared to the time required for the nitration reaction to reach completion. Finally, the model has been demonstrated to accurately predict the nitration kinetics of wood pulp fibers over the temperature range of 25°C to 40°C, which is typically employed in industrial nitration processes. One would need to verify that competing reactions do not become favorable outside of this temperature range to use the model at significantly higher or lower temperatures.

Using this model, simulations can be rapidly run for any combination of mixed acid composition, cellulose, acid to cellulose ratio, and moisture content to estimate the rate and extent of nitration for cellulose fibers. This is demonstrated using a mixed acid consisting of 30.18% HNO<sub>3</sub>, 54.67% H<sub>2</sub>SO<sub>4</sub>, and 15.15% H<sub>2</sub>O (weight percent) that yielded nitrocellulose containing 12.67% nitrogen in the industrial process where a reaction temperature of 27°C was maintained using an acid to cellulose ratio of 23:1. The model under these same conditions predicts an equilibrium degree of nitration of 12.71% nitrogen (Figure 2.7), which is very reasonable considering that there is usually a small amount of denitration that occurs when the acid laden slivers are rinsed with water in the centrifuge.



**Figure 2.7** Model predictions for nitration of cellulose fibers in mixed acid composition used in industrial process to produce Grade A nitrocellulose resulting in an equilibrium degree of nitration of 12.6% nitrogen.

The universal SCF model predicts that the reaction of single cellulose fibers in Grade B mixed acids proceeds very rapidly, reaching a degree of nitration of 13.35% nitrogen in 206 seconds at 25°C and in only 62 seconds at 40°C. Thus, the model agrees with the experimental results that demonstrated that the degree of nitration associated with Grade B nitrocellulose (13.35% nitrogen) was generally achieved within five minutes of immersion of the cellulose fibers in the mixed acid. This suggests that the required residence time in the industrial scale process could be reduced considerably from the current average residence time of 70 minutes during the production of Grace B nitrocellulose if measures are taken to improve mass transfer in the densified structures or to fiberize the cellulose feed materials.

The model predicts a slower rate of reaction when conditions representative of those used in the production of Grade A nitrocellulose are used. In the simulation run with a mixed acid composition consisting of 32.88% HNO<sub>3</sub>, 51.96% H<sub>2</sub>SO<sub>4</sub>, and 15.16% H<sub>2</sub>O

(weight percent), at a reaction temperature of 27°C with an acid to cellulose ratio of 32:1, the model predicts that are reaction time of 675 seconds is required to reach a degree of nitration of 12.5% nitrogen, the lower specification limit for Grade A nitrocellulose. This suggests that long residence times may be required to achieve complete nitration of dense cellulose materials used in the production of Grade A nitrocellulose, where reaction conditions may be limited by mass transfer. The required reaction time decreases to approximately 220 seconds if the reaction temperature is increased to 40°C, suggesting that increased reaction temperatures may be desirable in the production of Grade A nitrocellulose to accelerate reaction rates and to overcome mass transfer limitations.

The model can also be used to estimate the degree of nitration that would be achieved in an equilibrium reaction carried out with a 30:1 ratio of acid to cellulose. Under these conditions, the model predicts that a final degree of nitration of 13.52%N is achieved at 25°C and a final degree of nitration of 13.62%N is achieved at 40°C for the high sulfuric acid Grade B mixed acid composition. Similarly, the model predicts that a final degree of nitration of 13.47%N is achieved at 40°C for the high nitric acid Grade B mixed acid composition. Similarly, the model predicts that a final degree of nitration of 13.47%N is achieved at 40°C for the high nitric acid Grade B mixed acid composition. This result is significant given that the high nitric acid Grade B acid recipe that was used in this evaluation is one that is used in production to achieve a 13.35%N degree of nitration when a 30:1 acid to cellulose mass ratio is maintained. Under these conditions, it takes the single fibers approximately 15 minutes to reach a degree of nitration of 13.35%N at 25°C and approximately 4 minutes to reach a degree of nitration of 13.35%N at 40°C. Because of this, the acid to cellulose ratio and reaction temperature may be even more critical for mixed acid compositions that are high in nitric acid.

Establishment of this model provides a key building block for the simulation of industrial nitrocellulose manufacturing processes. The introduction of a term to describe an elementary denitration reaction allows the model to describe the nitration of cellulose fibers as an equilibrium-controlled process, consistent with the generally accepted understanding of the cellulose nitration reaction. Through describing the nitration of wood pulp fibers using a universal kinetic model, it is only necessary to describe mass transfer in densified cellulose structures to completely model the effective nitration kinetics of industrially used cellulose feedstocks. This will greatly expand the capability of process engineers to conduct process optimization and economic analyses by providing a much greater predictive capability than the nitration diagrams that have historically been employed.

In addition, the finding that a broad range of cellulose fibers exhibit equivalent reactivity in Grade B mixed acids is also an important result. This implies that nitrocellulose manufacturers should have much greater flexibility in selecting sources of raw materials in response to shifting market conditions or supply disruptions and need not be limited to the relatively small range of cellulose materials that have traditionally been used in nitrocellulose production. It is particularly significant that high purity, kraft pulped wood pulps demonstrated equivalent reactivity to sulfite pulped wood pulps because this ensures a continued supply of viable raw materials as the availability of sulfite pulps declines due to environmental constraints and market conditions.

#### **2.5 Recommendations**

The kinetic model for single cellulose fiber nitration could be further improved by conducting additional experiments to increase the capability of the model for describing the nitration of single cellulose fibers under a broad range of nitration conditions. These experiments should be performed to study the reaction kinetics of other acid compositions that exhibit sufficient equilibrium nitronium ion concentration to produce other grades of nitrocellulose including Grades A, D, and F. This work could also help to address the observations noted by Ott et al.<sup>2</sup>, Urbanski<sup>1</sup>, and Hoggett et al.<sup>49</sup> suggesting that the rate of nitration is dependent on the concentrations of nitric acid, sulfuric acid, and water in the mixed acid. The work performed in this study suggested that these differences in nitration rates can be attributed to differences in the concentrations of nitronium and hydronium ions in these mixed acids, as the relative change in the nitronium ion concentration is more significant as the reaction proceeds in mixed acids that are high in nitric acid. By performing additional nitration experiments in conjunction with experimental measurement of nitronium ion concentrations, it can be determined if these observed effects can be better described as the result of changing the nitronium ion concentration in the acid mixture.

Additional complexity and capability can be included in the model by considering the dissociation of the mixed acid components to ionic species. Given that acid dissociation reactions generally occur very rapidly, the acid dissociation reactions were assumed to occur at a rate that is an order of magnitude faster than the nitration reactions in this effort. Alternatively, it should be possible to assume that the acid dissociation reactions are instantaneous, and that the mixed acid species are always at equilibrium in the reacting mixture instead of calculating the equilibrium concentration of species in the mixed acid dynamically as individual species are produced and consumed in the main nitration reaction. Measurement of nitronium ion concentrations for many mixed acid compositions and at multiple temperatures would allow for better estimation of equilibrium constants for a given set of dissociation reactions, enabling the model to dynamically adjust the water and nitronium ion concentrations as the reaction proceeds.

# **2.6 Conclusions**

A model has been developed that is capable of accurately describing the nitration kinetics of wood pulp-derived, single cellulose fibers in mixed nitrating acids used to produce nitrocellulose grades used in military applications. This model describes the nitration of cellulose fibers as occurring through a reaction mechanism that is approximated as a homogeneous, equilibrium-controlled reaction, and can be incorporated as a generation/consumption term in partial differential equations describing unsteady-state mass transfer and chemical reaction in the nitration of densified cellulose forms. Acid dissociation and an empirical density model were incorporated into the universal single cellulose fiber nitration model to improve the accuracy and predictive capability of the model for simulating a range of reaction conditions. The model differs from those published by other researchers due to the fact that it: (1) is a universal model that has been demonstrated to accurately describe the nitration kinetics of a wide variety of wood pulp derived cellulose fibers, and (2) correctly describes the nitration of cellulose as an reversible reaction with the nitronium ion as the nitrating agent and the hydronium ion as the denitrating agent.

Experiments were conducted with additional cellulose fibers (cotton and a randomly selected kraft wood pulp) to validate the ability of the model to predict the equilibrium degree of nitration for these materials. A series of near-equilibrium experiments were also conducted to improve the accuracy of the model for describing near-equilibrium kinetics and to confirm the finding that crystalline regions in the fibers do not result in differences in the nitration kinetics for different fibers in this region. Finally, experiments were conducted with the more dilute mixed acids used in the production of Grade A nitrocellulose to ensure that the model is capable of predicting both the rate of nitration and extent of nitration for cellulose fibers reacted in these mixed acid compositions.

Evidence was presented to support the finding that the reaction kinetics of single fibers do not depend on the source of the cellulose fibers, and an explanation for this behavior was proposed based on the nature of the amorphous regions of the fiber and changes in fiber crystallinity resulting from the pulping process. It was also noted that the effects of crystallinity on nitration kinetics may not play a significant role even at the high degree of nitration achieved under this study. The finding that a wide range of wood pulps exhibit equivalent reactivity in nitration is an important result that suggests that the relationship between densified structural forms and mass transfer is of more significant interest that pulp source. This suggests that a broad range of cellulose materials can be considered as potential feed materials for industrial nitrocellulose manufacturing based on prevailing market conditions and densified forms.

# **CHAPTER 3**

# EVALUATION OF DIFFUSION AND SWELLING IN WOOD PULP SLIVER (WPS) STRUCTURES

## 3.1 Introduction

## 3.1.1 Considerations for the Nitration of Dense Cellulose Materials

The objective of this work described in this chapter is to establish relationships between the swelling and diffusion behavior that occurs during the nitration of dense cellulose materials and the properties of these dense cellulose materials. This chapter extends previously published work<sup>50</sup> that was conducted to evaluate the phenomena of simultaneous swelling and diffusion that occurs during the nitration of wood pulp slivers in mixed acids. In the last chapter, it was noted that the rate of nitration of cellulose fibers is not limited by diffusion; however, this is generally not true for dense cellulose materials. The reacting system of uniformly dispersed, single cellulose fibers in mixed nitrating acid was approximated as a homogeneous system and it was demonstrated that the kinetics of nitration of cellulose fibers is not dependent on diffusion of acids through the cellulose fiber wall or into crystalline regions of the cellulose fiber. This was supported by experimental results that showed that the rate of nitration is equivalent in cellulose fibers with significant differences in wall thickness and crystallinity. It was also shown that the characteristic diffusion times for mixed acids through the cellulose fiber walls are several orders of magnitude less than the experimentally measured reaction times for cellulose fibers in mixed acids.

Because the rate of reaction of cellulose fibers in mixed acids is known to be very rapid<sup>16-18</sup>, it is expected that mass transfer may significantly affect the rate of nitration of dense cellulose materials, suggesting that the assumption of a homogeneous reacting system is not applicable for these materials. The observed kinetics of nitration for dense cellulose materials such as slivers cut from sheeted wood pulp that are used in industrial nitrocellulose manufacturing processes are influenced by both mass transfer due to diffusion of mixed acid species through these nonwoven, fibrous structures, and by the kinetics of nitration for cellulose fibers. Wood pulp slivers are also known to exhibit unidirectional, interfibrillar swelling in the dimension of the sheet thickness (the direction that fibers are deposited during sheet formation) as the acids penetrate the fibrous structure and disrupt hydrogen bonding between fibers (Figure 3.1). The influence of this behavior on the reactivity of wood pulp slivers is significant because the void fraction, or interfiber porosity, of wood pulp slivers increases as the slivers swell, potentially facilitating mass transfer of acids in the structures. Understanding the influence of this behavior on the reactivity of wood pulp slivers is critical to modeling the dynamics of wood pulp sliver nitration.



**Figure 3.1** Conceptual model of swelling and anisotropic diffusion during the nitration of wood pulp slivers where  $D_i^x$ ,  $D_i^y$ , and  $D_i^z$  are the diffusivities of mixed acid species in the x, y, and z directions.

The swelling behavior observed for wood pulp slivers in mixed acids is not unique to wood pulps, as cellulose raw materials sourced from cotton have also been reported to swell in mixed acid compositions<sup>1</sup>. In his review of this behavior, Short<sup>10</sup> reported that individual mixed acid species may be responsible for different swelling behavior in cellulose materials, with sulfuric acid able to cause interfibrillar swelling and nitric acid able to cause both interfibrillar and intrafibrillar swelling. The intrafibrillar swelling that primarily occurs in concentrated nitric acid mixtures and may also result in partial dissolution of the cellulose fibers<sup>1</sup> is not of interest for industrial nitrocellulose production because these acid mixtures generally do not produce high degrees of substitution. Mixed acid compositions that cause interfibrillar swelling, however, are of much greater interest because the effective diffusivity of a solvent through a porous membrane is known to depend on both the porosity and the tortuosity of the material. The rate of diffusion also increases with temperature, suggesting that mass transfer in dense cellulose materials can potentially be optimized by utilizing elevated reaction temperatures and by selecting materials with greater characteristic rates and extents of swelling in mixed acids. The use of materials and reaction conditions that optimize mass transfer should result in increased reactivity and uniformity of nitration in industrial nitrocellulose manufacturing processes.

# 3.1.2 Evaluation of Swelling and Diffusion in Industrial NC Processes

The mass transfer of a solute in swellable polymer systems can be characterized by the relative rates of penetrant diffusion and polymer swelling in the system. In systems where the swelling or relaxation phenomena occurs at either a much faster or much slower rate than diffusion, Fickian diffusion predominates, while similar rates of swelling and diffusion describe non-Fickian (anomalous) transport<sup>51,52</sup>. Analysis of swelling and diffusion during the nitration of dense cellulose materials allows for comparison of fiber reaction times with characteristic diffusion and swelling times to consider the relative influences of relaxation and mass transfer phenomena on the reactivity of these dense cellulose structures. By independently measuring the rates of swelling and diffusion for a range of pulps and at multiple temperatures, mass transfer during the nitration of wood pulp slivers is characterized and models are developed to describe the range of reaction conditions that exist in industrial nitrocellulose manufacturing processes. An analysis of the relative rates of diffusion and swelling of wood pulp slivers in mixed acids is used to determine whether the dynamics of wood pulp sliver nitration are limited by diffusional mass transfer or by the rate of relaxation of the cellulose fiber matrix. Using this information, models are developed to describe the simultaneous diffusion and swelling in
the three-dimensional wood pulp sliver structure during production of nitrocellulose from dense cellulose raw materials.

To compensate for mass transfer limitations in the nitration of dense cellulose materials, industrial nitrocellulose manufacturing processes are typically designed with very long residence times (approximately one hour) in the nitration reactors. Processing equipment including shredders and hammer mills have also been utilized to open dense cellulose materials to promote the penetration of mixed acids into these structures. While these processing techniques are effective methods for increasing the rate of reaction for dense cellulose materials, they may limit the capacity or efficiency of nitrocellulose manufacturing operations, typically require high acid to cellulose ratios in the nitration reactors, and utilize mixtures of acids and nitrocellulose that can be difficult to pump to downstream operations. For these reasons, it is advantageous to process dense cellulose materials if an acceptable extent and uniformity of nitration can be achieved. Very little research has been published on the effects of simultaneous swelling and diffusion during the production of nitrocellulose using dense cellulose materials, so this work should be of particular interest as nitrocellulose producers make more extensive use of wood pulps due to changing market conditions and dwindling supplies of cotton linters.

## 3.2 Materials and Methods

#### **3.2.1** Experimental Approach

Swelling and mass transfer were evaluated independently under conditions that are relevant to the industrial nitrocellulose manufacturing process. Swelling was analyzed first to understand the nature and extent of swelling that occurs during the nitration of dense cellulose materials over the range of temperatures and reaction times maintained in the NC manufacturing process. The results of these swelling experiments were used to design a custom membrane diffusion cell and experimental conditions to study the diffusivity of mixed acids in wood pulp slivers over the same range of temperatures and reaction times. Wood pulps were characterized to identify structural attributes of wood pulp slivers such as density and porosity that may influence the diffusion of mixed acids through these materials.

## 3.2.2 Wood Pulps and Mixed Acid Compositions Evaluated

Three high purity wood pulps were evaluated that differed by pulping method, pulp type, purity, and sheet density (Table 3.1). The pulping method describes the process used to purify the wood pulps, and the pulp type describes the tree species and fiber properties of the pulp. In addition to the pulping method, the sheet density was the main characteristic of interest in this evaluation with the kraft-pulped softwood, sulfite-pulped softwood, and kraft-pulped hardwood pulps exhibiting sheet densities of 0.72 g/mL, 0.70 g/mL, and 0.95 g/mL, respectively. These sheeted materials were hand-cut into  $6 \times 1.4$ mm<sup>2</sup> slivers for the diffusion and swelling experiments.

Pulp Type	Pulping Method		Sheet Density	Fiber Coarseness	% α- cellulose	Mean Fiber Length
			kg/m <sup>3</sup>	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

**Table 3.1** Properties of Wood Pulps Evaluated

Mixed acid compositions were prepared using nitric acid (J.T. Baker – Nitric Acid, Fuming, 90%), sulfuric acid (Fisher Scientific – Certified ACS Plus), and deionized water. A mixed acid composition containing 54.6% sulfuric acid, 37.0% nitric acid, and 8.4% water by weight (suitable for production of Grade B<sup>11</sup> nitrocellulose) was prepared for all diffusion and swelling experiments.

## 3.2.3 Experimental Measurement of Swelling of Wood Pulp Slivers in Mixed Acids

Swelling experiments were conducted to measure the rate of unidirectional swelling in wood pulp slivers upon immersion in the nitrating acid mixture under temperaturecontrolled conditions. An array of 25 wood pulp slivers was affixed to a Teflon plate (Figure 3.2) in an agitated vessel containing mixed acids and was oriented to allow the cross section of the wood pulp slivers to be observed using a digital microscope. The wood pulp slivers were inserted into holes in the swelling fixture so that the free ends of the wood pulp slivers swelled in an unconstrained manner as the acids penetrated the wood pulp sliver structures. The vessel was immersed in a water bath to control the temperature of the acid and wood pulp slivers during the swelling experiments. The thickness of the free end of each wood pulp sliver was measured as a function of time to calculate the rate and extent of swelling for the different wood pulp types. Images were obtained using a Dino-Lite AM3111T handheld digital microscope at specified time intervals during the swelling experiment for dimensional analysis of the wood pulp slivers.



Figure 3.2 Teflon plate with holes spaced in a 5 x 5 grid to affix wood pulp slivers for optical analysis during swelling experiments.

## 3.2.4 Experimental Measurement of Diffusivities Using a Membrane Diffusion Cell

A diffusion diaphragm cell (Figure 3.3) was used to measure the unidirectional diffusion of mixed species acids through dense cellulose structures. Using this approach, effective diffusivities of mixed acids through wood pulp slivers were measured under various experimental conditions, including at different temperatures, acid compositions, and degrees of swelling to evaluate the influence of sheet and fiber characteristics on the diffusion of acid species through the sliver.



**Figure 3.3** Conceptual design of diffusion diaphragm cell with porous membrane dividing donor and receiver cells.

The diffusion diaphragm cell consists of two well mixed compartments with different concentrations of diffusing species separated by a porous membrane. The diffusivity is calculated by measuring the change in concentration of the solute in the receiver cell as a function of time, where  $V_D$  is the volume of the donor cell,  $V_R$  is the volume of the receiver cell,  $C_D$  is the concentration of solute in the donor cell, and  $C_R$  is the concentration of solute in the receiver cell. The governing equations for the diffusion diaphragm cell are obtained by performing mass balances on the donor and receiver cells and solving for the effective diffusivity (D/ $\tau$ ), or the ratio of the diffusivity to the tortuosity.

Mass Balance on Donor Cell:

$$V_D \frac{dC_D}{dt} = -\frac{DA}{\tau} \frac{\left(C_D - C_R\right)}{\delta}$$
(3.1)

Mass Balance on Receiver Cell:

$$V_{R}\frac{dC_{R}}{dt} = \frac{DA\left(C_{D} - C_{R}\right)}{\tau \delta}$$
(3.2)

Subtracting (3.2) from (3.1) and simplifying:

$$\frac{\frac{d}{dt}(C_D - C_R)}{(C_D - C_R)} = -\frac{DA}{\tau\delta} \left(\frac{1}{V_D} + \frac{1}{V_R}\right)$$
(3.3)

Integrating between  $t_i$  and  $t_f$  and solving for  $D/\tau$ :

$$\frac{D}{\tau} = \frac{1}{\beta \left( t_f - t_i \right)} \ln \left( \frac{C_D^i - C_R^i}{C_D^f - C_R^f} \right)$$
(3.4)

where:

$$\beta = \frac{A}{\delta} \left( \frac{1}{V_D} + \frac{1}{V_R} \right)$$
(3.5)

The cell constant,  $\beta$ , is calculated using Equation (3.5), where V<sub>D</sub> and V<sub>R</sub> are the known volumes of the donor and receiver cells, A is the cross-sectional area of the membrane (wood pulp sliver), and  $\delta$  is the diffusion length of acid through the membrane (wood pulp sliver). Equation (3.4) is then used to calculate the effective diffusivity of a solvent through a membrane using the initial and final concentrations of the diffusing species in the donor and receiver cells and the elapsed time between the initial and final concentration measurements.

# 3.2.5 Design of Diffusion Cell for Measuring Diffusion of Mixed Acids in Wood Pulp Slivers

A custom diffusion diaphragm cell (Figure 3.4) was designed to evaluate the diffusion of mixed acids through wood pulp slivers. This apparatus contains two chambers, each with ports for mixing impellers and temperature and conductivity probes. The diffusion cell was designed with frames that maintain the wood pulp sliver between the donor and receiver cells both in a fixed orientation and with a fixed extent of swelling. The donor and receiver cells were agitated to ensure that the solutions in these chambers were well mixed, and the temperature was controlled by submerging the sealed system in a water bath. Frames were designed for each material and temperature in the initial and swollen states to measure the diffusion of mixed acids through wood pulp slivers in the x/y direction

(fiber orientation is similar in x and y directions) and the z direction, where z is the direction of the sheet thickness as shown in Figure 3.1. The chambers were sealed together using a gasket that mates against the frame and aperture containing the wood pulp sliver.



Figure 3.4 Custom diaphragm cell for measuring diffusion of acids through wood pulp slivers.

The frames with apertures (Figure 3.5) were designed to maintain the crosssectional area and diffusion length for each diffusion experiment. Because the wood pulp slivers only swell in the direction of the sheet thickness during nitration, additional frames with screens were necessary to restrict swelling of the slivers when measuring diffusion in the z direction.



**Figure 3.5** Diffusion diaphragm cell frames and for measuring diffusion thorough wood pulp slivers in the x/y direction (left) and through the z direction (right). Red arrows indicate direction of diffusion and blue arrows indicate direction of swelling.

Mixed acid diffusivities were measured experimentally under temperaturecontrolled conditions using the membrane diffusion cell and frames. Frames were designed to measure the diffusivity of mixed nitrating acid (MNA) species through the three different types of pulps in the initial and swollen states at 25°C and 40°C.

A limited number of ion chromatography experiments were conducted to determine whether the diffusional rates of the mixed acid species differed significantly. Samples collected from the receiver cell and diluted samples of the mixed acid that was initially charged in the donor cell were analyzed to compare the ratio of sulfuric acid to nitric acid in both cells.

## 3.2.6 Measurement of Mixed Acid Concentrations in Membrane Diffusion Cells

The concentration of mixed acid species in the receiver cell was measured as a function of time using a Fisherbrand<sup>TM</sup> Accumet<sup>TM</sup> AB200 pH/conductivity benchtop meter. Conductivity measurements were converted to total concentrations of mixed nitrating acid species using a calibration curve that was prepared by adding known masses of mixed nitrating acid to deionized water and measuring the resulting conductivity of the solution.

The conductivity was then measured as a function of time during the diffusion experiment and the measured conductivity values were converted to concentrations in the donor and receiver cells using the calibration curves.

#### 3.2.7 Data Analysis

The JMicroVision<sup>53</sup> image analysis suite was used to measure the thicknesses of wood pulp slivers from images obtained in the swelling experiments. Wolfram Mathematica<sup>29</sup> was used to consider the effect of multicomponent diffusion during the nitration of wood pulp slivers.

#### 3.3 Results

## 3.3.1 Swelling Experimental Results

Swelling experiments were conducted at 25°C for the three wood pulps that were evaluated. Sheeted wood pulps were cut into 6mm × 1.4mm slivers, affixed to a plate (Figure 3.6), and immersed in mixed acid for 70 minutes while the thickness of each wood pulp sliver was recorded. Uniaxial swelling was observed to occur uniformly over the wood pulp sliver width for all three wood pulps. The extent of swelling in the kraft-pulped softwood and sulfite-pulped softwood samples reached peak values at approximately 18 minutes and 25 minutes, respectively, however the kraft-pulped hardwood sample continued to swell over the duration of the experiment.

Swelling experiments were also conducted for all three pulps over a 240-minute interval at 25°C, and the swelling behavior of the kraft-pulped hardwood sample was evaluated over this interval at two elevated temperatures (40°C and 50°C). The extent of swelling observed in the extended duration test for the kraft-pulped softwood and sulfite-

pulped softwood samples was the same as was observed in the 70-minute test, but the kraftpulped hardwood sample continued to swell over the 240-minute duration of the test at all temperatures evaluated.

a	Kraft Softwood	b		d	
a	Kraft Hardwood	b	C	d	e
a	Sulfite Softwood	b	C	d	e

**Figure 3.6** Slivers mounted on the Teflon plate and submerged into Grade B acid at  $25^{\circ}$ C, from top to bottom: kraft-pulped softwood, kraft-pulped hardwood and sulfite-pulped softwood, (a)@ 0 min dry, (b)@ 0 min (wet), (c)@ 1 hr., (d) @ 2 hr., (e)@ 4 hr.

The dimensionless swelling of wood pulp slivers in mixed acids was evaluated by calculating the ratio of the change in the wood pulp sliver thickness to the initial wood pulp sliver thickness according to Equation (3.6) where  $\varepsilon$  is the dimensionless wood pulp sliver thickness,  $\Delta l$  is the change in thickness, and  $l_0$  is the original wood pulp sliver thickness.

$$\varepsilon = \frac{\Delta l}{l_0} \tag{3.6}$$

The dimensionless swelling was plotted as a function of time (Figure 3.7) for the sulfite-pulped softwood, kraft-pulped softwood, and kraft-pulped hardwood samples at 25°C to evaluate the differences in the swelling behavior of these three materials.



**Figure 3.7** Dimensionless swelling of wood pulps in mixed acid at 25°C (SW-Kraft = kraft-pulped softwood, SW-Sulfite = sulfite pulped softwood, HW-Kraft = kraft-pulped hardwood).

An analysis of means of the degree of swelling in the kraft-pulped hardwood slivers confirmed that these samples continued to swell as a function of immersion time in the acid over the duration of the experiment.

#### 3.3.2 Relationship Between Conductivity and Mixed Acid Concentration

Calibration curves (Figure 3.8) were established for the mixed acid and water system at 25°C and 40°C by adding known masses of mixed acids to deionized water and measuring the resulting conductivity under temperature-controlled conditions. Mixed acids containing 54.6% H<sub>2</sub>SO<sub>4</sub>, 37.0% HNO<sub>3</sub>, and 8.4% water (the same mixed acid composition

used in the swelling and diffusion experiments) were added to a vessel containing deionized water in a temperature-controlled bath and allowed to reach thermal equilibrium before the conductivity was recorded.



**Figure 3.8** Calibration curve relating conductivity to concentration of mixed acid species at 25°C and 40°C using a second order polynomial function.

Three replicates were performed for the experiments that were conducted to generate the calibration curves at 25°C (Figure 3.8) and repeatability of the measurement technique was verified.

#### 3.3.3 Results of Diffusion Cell Experiments

Effective diffusivities (Table 3.2) were measured for each wood pulp type, at two temperatures (25°C and 40°C), and at two states (initial and swollen). To measure the change in diffusivity as the slivers swell during the nitration reaction, frames were designed

for the initial state and for the extent of swelling resulting after immersion of the wood pulp slivers in the mixed acids for 70 minutes. Five replicates of the membrane diffusion cell experiment were performed for each configuration that was evaluated. The effective diffusivities generally increased with increasing temperature and as the sliver became more porous due to swelling.

**Table 3.2** Experimentally Measured Diffusivities of Mixed Acids Through Wood Pulp

 Slivers

Source	Temperature	Diffusivity $\times$ 10 <sup>10</sup> (m <sup>2</sup> /sec)				
		unsw	vollen	swollen		
		xy	Z	xy	Z	
Sulfite	25°C	$2.37\pm0.16$	$0.63\pm0.09$	$2.40\pm0.10$	$5.00\pm0.65$	
Softwood	40°C	$3.22\pm0.62$	$1.47\pm0.32$	$2.18\pm0.09$	$2.59\pm0.33$	
Kraft	25°C	$2.13\pm0.42$	$1.61\pm0.40$	$107\pm17$	$2.43\pm0.25$	
Softwood	40°C	$4.12\pm0.32$	$1.57\pm0.29$	$163\pm28$	$3.03 \pm 0.87$	
Kraft	25°C	$1.02\pm0.12$	$0.37\pm0.12$	$3.18\pm0.24$	$1.00\pm0.08$	
Hardwood	40°C	$3.87\pm0.35$	$1.50\pm0.30$	$3.65\pm0.34$	$3.14\pm0.33$	

The effective diffusivities that were measured in the xy direction for the kraftpulped softwood samples in the swollen state are both at least an order of magnitude larger than published binary diffusion coefficients for nitric acid-water<sup>54-56</sup> and sulfuric acidwater<sup>55-57</sup> systems, indicating that convective mass transfer occurred during these experiments. This suggests that the sliver structure had opened enough to allow for convection through the slivers due to the agitation of the cells and the high porosity of the swollen kraft pulped softwood.

## 3.3.4 Ion Chromatography Experiments

Ion chromatography analysis was conducted to determine whether significant differences in the rates of diffusion of sulfuric acid and nitric acid through the cellulose matrix were observed. Samples were collected from the receiver chamber of the membrane diffusion cell (in experiments that did not show evidence of convection) and were compared with diluted samples of acids initially charged to the donor cell in the membrane diffusion cell. Receiver cell samples were collected at the end of three independent diffusion experiments to determine whether there were systematic differences in the measured ratios of sulfuric acid to nitric acid ratio in the donor and receiver cells. There was considerable variability in the ion chromatography results (Table 3.3) but no general trends were observed that would suggest that the diffusivity of one species was significantly greater than another. Measured differences in the mixed acid component ratios in the donor and receiver compartments that were not consistent with the concentration gradient across the wood pulp sliver might have been indicative of interactions between some of the mixed acid species and the cellulose matrix.

Sample source	Conductivity	NO <sub>3</sub>	SO <sub>4</sub>	SO <sub>4</sub> /NO <sub>3</sub>
		ppm	ppm	
Acids mixture - reference	Ref	360	580	1.61
Diluted reference acid mixture	160	10	15	1.50
Diffusion experiment I	270	15	25	1.67
Diffusion experiment II	550	30	60	2.00
Diffusion experiment III	1930	120	170	1.42

**Table 3.3** Ion Chromatography Results (Mass Basis) for Mixed Acid Samples Collected

 from Diffusion Cell Experiments After Long Diffusion Time

For the mixed acid composition used in the diffusion cell experiments, the mass ratio of sulfuric acid to nitric acid was 1.476, or a molar ratio of 0.948. The ion chromatography technique tended to report higher sulfuric acid to nitric acid ratios than the known donor cell acid ratio as seen in the reference and diluted reference acid mixture samples in Table 3.3. Because this same result (higher sulfuric acid to nitric acid ratios than the known ratio in the donor acid mixture) was observed in both the reference (donor) and receiver cell acid compositions, no apparent trend was observed that would suggest that there were large differences in the rates of diffusion of the mixed acid species (Figure 3.9). Given that the initial concentration gradients for nitric acid and sulfuric acid across the wood pulp sliver were nearly identical for the mixed acid composition studied, this also suggests that the diffusion coefficients of sulfuric acid and nitric acid are similar. The ion chromatography results exhibited too much variability for this method to be used as a primary method for measuring concentration of total mixed acid species in the receiver cell, but it is a useful verification that diffusion of both mixed acid species through the wood pulp sliver occurs at similar rates.



**Figure 3.9** Sulfuric acid to nitric acid ratio measured using ion chromatography (solid line) compared to known sulfuric acid to nitric acid ratio in donor cell mixed acid composition (dotted line) with high variability but no apparent trend observed. Donor Cell and Diluted are samples of known concentration and sulfuric acid to nitric acid ratio while Exp1-Exp3 are samples collected from the receiver cell of the diffusion experiment after long diffusion times.

#### 3.4 Discussion

## 3.4.1 Analysis of Swelling Behavior in Wood Pulp Slivers

Wood pulp swelling data was analyzed to consider relationship between the time to reach the maximum extent of swelling and the time dependent porosity for each wood pulp and temperature. Because differences were observed in the swelling behavior and time to reach maximum extent of swelling for the kraft pulped softwood pulp, sulfite pulped softwood pulp, and kraft-pulped hardwood pulp, the porosity in each sample was estimated as a function of swelling by using the initial density of the wood pulp samples and density of cellulose<sup>42</sup>. Equation (3.7) was used to estimate the porosity of the wood pulp sliver for each sample and swelling measurement to consider the change in porosity for each wood pulp sliver as a function of the extent of swelling, where  $V_{sl}$  is the volume of the sliver and  $V_{cell}$  is the volume of cellulose in the sliver.

$$\phi = \frac{V_{void}}{V_{total}} = \frac{V_{sl} - V_{cell}}{V_{sl}}$$
(3.7)

The volume of cellulose in the wood pulp sliver,  $V_{cell}$ , was estimated using the initial wood pulp sliver dimensions,  $V_{sl,i}$ , the sheet density,  $\rho_{sl}$ , and the density of cellulose,  $\rho_{cell}$ .

$$V_{cell} = \frac{m_{cell}}{\rho_{cell}} \approx \frac{\rho_{sl} V_{sl,i}}{\rho_{cell}}$$
(3.8)

This approximation considers the total initial mass of the initially dry wood pulp sliver to be cellulose and does not differentiate between the interfiber void regions and the void regions in the hollow cellulose fibers. A more sophisticated analysis is necessary to estimate interfiber porosity, but this approach does enable a preliminary analysis of the time-dependent overall porosity of the wood pulp slivers as they swell in mixed acids (Figure 3.10).



**Figure 3.10** Porosity time relationship for three pulps evaluated at 25°C with standard deviation indicated in error bars. Final porosity values all approach range of 0.6-0.7.

These results suggest that at some final porosity value, all the interfiber hydrogen bonds have been disrupted and the wood pulp sliver no longer continues to swell. Indeed, the estimated final porosity that was achieved with the kraft pulped softwood sample at 25°C and the kraft pulped hardwood sample at 50°C were 0.674 and 0.676, respectively. A more detailed analysis of interfiber porosity using micro tomography is discussed in Chapter 5.

# 3.4.2 Analysis of Characteristic Diffusion and Swelling Times During the Nitration of Wood Pulp Slivers

The relative influences of swelling and diffusion of mixed acids through dense cellulose materials must be considered in developing approaches for modeling the nitration of wood pulp slivers. An initial evaluation was performed by applying the assumption that all mixed acid species in the nitrating acid mixture diffuse at similar rates. While this was not confirmed by the ion chromatography experiments that were performed, it is evident that the rate of diffusion of mixed acid species did not differ by an order of magnitude as the average sulfuric acid to nitric acid ratio for samples collected from the receiver cell are similar to the measured sulfuric acid to nitric acid ratio in the known donor cell mixed acid species to enable a preliminary assessment of the relative rates of swelling and diffusion of wood pulp slivers in mixed acids.

The analysis of simultaneous swelling and diffusion can be aided by research focused on other applications involving mass transfer in materials that exhibit swelling and relaxation behavior as a penetrant diffuses into a structure. One such application is swellable polymers that are used extensively in extended release drug delivery applications<sup>58-60</sup>. In these pharmaceutical dosage forms, a tablet consisting of a polymer matrix swells in response to a penetrant (solvent) diffusing into it, releasing a solute (pharmaceutical ingredient) as the polymer matrix transitions from a glassy matrix to a rubbery gel. Although the swelling of cellulose during nitration is characterized by the disruption of interfiber hydrogen bonds instead of a transition from a glassy to a rubbery

region, these techniques can be used to consider the relative influence of swelling during the nitration of wood pulp slivers.

Ségot-Chicq and Peppas<sup>51</sup>, Davidson III and Peppas<sup>52,61</sup>, and Lustig and Peppas<sup>60</sup> have proposed approaches for describing diffusion in these swellable polymer systems that can be adapted for modeling diffusion and swelling during the nitration of wood pulp slivers. These approaches introduce the diffusional Deborah number, De, as a dimensionless number indicative of the coupling between transport and relaxation phenomena according to Equation (3.9), where  $\theta$  is the characteristic diffusion time and  $\lambda$ is the characteristic relaxation time. In analyzing diffusion and swelling in wood pulp slivers, the characteristic diffusion time can be calculated using the effective diffusivity, D<sub>eff</sub>, and the sliver width in the diffusion direction according to Equation (3.10), where the diffusion length, l, is half the sliver width because acids diffuse into the sliver from both sides. The characteristic relaxation time,  $\lambda$ , can be calculated for each sliver configuration using experimental swelling measurements following an approach described by Lustig and Peppas<sup>60</sup>. Using this approach, Equation  $(3.11)^{60}$  was proposed to model relaxation controlled volume expansion where  $V_{eq,t}$  and  $V_t$  are the equilibrium and instantaneous differential specific volumes.

$$De = \frac{\lambda}{\theta} \tag{3.9}$$

$$\theta = \frac{l^2}{D_{eff}} \tag{3.10}$$

$$\frac{dV_t}{dt} = \frac{V_{eq,t} - V_t}{\lambda}$$
(3.11)

Integration of Equation  $(3.11)^{60}$  between the initial state (t = 0, V<sub>t</sub> = V<sub>0</sub>) and the equilibrium state yields Equation (3.12) which can be used directly to calculate the characteristic relaxation time using time dependent volume measurements obtained from swelling experiments.

$$\ln\left[\frac{V_{eq,t} - V_t}{V_{eq,t} - V_0}\right] = -\frac{1}{\lambda}t$$
(3.12)

Table 3.4 lists the initial and final porosities, the characteristic diffusion times, relaxation times, and Deborah numbers for diffusion and swelling in the z-direction for each wood pulp sliver configuration at 25°C. Characteristic relaxation times and Deborah numbers were not calculated for the x and y directions because swelling only occurs in the z direction, where z is the dimension of the sheet thickness.

**Table 3.4** Characteristic Relaxation and Diffusion Times for Wood Pulp SliverConfigurations Evaluated in Diffusion Cell Experiments at 25°C

Sample	Sample $\phi_{unswollen}$		$\lambda_z$	θz	De	θxy	$\theta_z/\theta_{xy}$
			(s)	(s)		(s)	
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

The characteristic diffusion and swelling times listed in Table 3.4 can be used to make simplifying assumptions for modeling swelling and variable diffusivity during the nitration of wood pulp slivers in mixed acids. The Deborah numbers listed in Table 3.4 indicate that the diffusion and swelling phenomena 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. In particular, the diffusivity can

be modeled as a time dependent function of the porosity,  $\phi$ , or the polymer weight fraction,  $\omega_p$ , as acids penetrate the wood pulp sliver. For the range of wood pulp sliver sizes that are of industrial interest (less than 1.6mm wide), mass transfer in the z direction can be considered without the added complexity of simulating a moving boundary due to swelling because the characteristic diffusion times (Table 3.2) for mixed acids in the wood pulp slivers are much smaller in the xy direction than in the z direction. For this reason, incorporation of a moving boundary in the z direction to describe the transport of mixed acids in the wood pulp sliver adds unnecessary complexity without significantly affecting the overall concentration of mixed acid species in the wood pulp sliver. This simplification is also reasonable because the diffusivities in the z direction (Table 3.2) increase as the wood pulp slivers swell, partially compensating for the change in diffusion length due to swelling.

#### 3.4.3 Multicomponent Diffusion in the H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, H<sub>2</sub>O Ternary System

Although it was assumed that the diffusivities of all mixed acid species are approximately equal in the evaluation of characteristic swelling and diffusion times, some additional analysis of this system is necessary before models describing swelling dependent diffusion coefficients can be developed. In a ternary system such as the nitric acid, sulfuric acid, and water system under consideration, the interactions between diffusing species must be considered. Curtiss and Bird<sup>62</sup> reviewed the two primary models that have been developed to describe mass flux in multicomponent diffusion and considered the relationships between the diffusivities used in these models. The first model, the Fick's Law model, expresses the mass flux as a linear combination of concentration gradients<sup>62</sup> and is well suited for use in computational fluid dynamic routines<sup>63</sup>. The second, more comprehensive

model, the Maxwell-Stefan model, expresses the concentration gradient as a linear combination of mass fluxes<sup>62</sup> using concentration dependent diffusivities and is based on a balance between driving and drag forces to describe individual species velocities<sup>64,65</sup> according to Equation (3.13) <sup>66</sup>. In Equation (3.13),  $x_i$  is the mole fraction of species i,  $c_i$  is the molar concentration of species i, c is the total molar concentration,  $D_{ij}$  is the binary diffusion coefficient for the i-j system,  $v_i$  is the velocity of species i, and  $N_i$  is the molar flux of species i with respect to stationary coordinates. Equation (3.13) is a simplification, as the Maxwell-Stefan equations more generally describe a gradient in chemical potential resulting from activity driving forces.

$$\nabla x_i = \sum_{j=1}^n \frac{c_i c_j}{c^2 D_{ij}} \left( v_j - v_i \right) = \sum_{j=1}^n \frac{1}{c D_{ij}} \left( x_i N_j - x_j N_i \right)$$
(3.13)

Despite its limitations, the Fick's law model is used more extensively, and diffusion coefficients are generally reported only for the Fick's law model. These limitations can be overcome using a form of Generalized Fick's Law (GFL) that was proposed by Curtiss<sup>67</sup> based on inversion of the Maxwell-Stefan equations. Using this approach, Curtiss<sup>67</sup>, and later Curtiss and Bird<sup>62</sup> calculated a set of symmetric ( $\tilde{D}_{ij} = \tilde{D}_{ji}$ ) Maxwell-Stefan diffusion coefficients for a multicomponent system as described by Equation (3.14) where  $\tilde{D}_{ij}$  are the Maxwell-Stefan diffusivities,  $\tilde{C}_{ij}$  are multipliers defined to have units of time/length<sup>2</sup>,  $\delta_{ij}$  is the Kronecker delta function,  $\omega_i$  is the mass fraction of species i, and  $\nu$  is the number of components in the multicomponent system. For a ternary system, Equation (3.14), which is Equation (6.1) in Curtiss and Bird<sup>62</sup>, results in the system of equations described by Equation (3.15).

$$\sum_{k \neq i} \left( \tilde{C}_{ik} + \frac{\omega_k}{\omega_i} \sum_{n \neq i} \tilde{C}_{in} \right) \tilde{D}_{kj} = -\delta_{ij} + \omega_i \quad i, j = 1, 2, 3, \cdots, \nu$$

$$\begin{bmatrix} 0 & \tilde{C}_{12} + \frac{\omega_2}{\omega_1} \left( \tilde{C}_{12} + \tilde{C}_{13} \right) & \tilde{C}_{13} + \frac{\omega_3}{\omega_1} \left( \tilde{C}_{12} + \tilde{C}_{13} \right) \\ \tilde{C}_{12} + \frac{\omega_1}{\omega_2} \left( \tilde{C}_{12} + \tilde{C}_{23} \right) & 0 & \tilde{C}_{23} + \frac{\omega_3}{\omega_2} \left( \tilde{C}_{12} + \tilde{C}_{23} \right) \\ \tilde{C}_{13} + \frac{\omega_1}{\omega_3} \left( \tilde{C}_{13} + \tilde{C}_{23} \right) & \tilde{C}_{23} + \frac{\omega_2}{\omega_3} \left( \tilde{C}_{13} + \tilde{C}_{23} \right) & 0 \end{bmatrix} \begin{bmatrix} \tilde{D}_{11} & \tilde{D}_{12} & \tilde{D}_{13} \\ \tilde{D}_{12} & \tilde{D}_{22} & \tilde{D}_{23} \\ \tilde{D}_{13} & \tilde{D}_{23} & \tilde{D}_{33} \end{bmatrix} = \begin{bmatrix} \omega_1 - 1 & \omega_1 & \omega_1 \\ \omega_2 & \omega_2 - 1 & \omega_2 \\ \omega_3 & \omega_3 & \omega_3 - 1 \end{bmatrix}$$

$$(3.15)$$

Curtiss<sup>67</sup>, Condiff<sup>68</sup>, and Curtiss and Bird<sup>62</sup> solved this system of equations to obtain expressions for the  $\tilde{D}_{ij}$  in terms of  $D_{ij}$  using an alternate approach involving reducing the order of the matrix by that multiplies the  $\tilde{D}_{ij}$  matrix by one to obtain solutions for  $\tilde{D}_{ij}$ .

Equations (3.16) - (3.18) represent the set of equations developed by Curtiss and Bird<sup>62</sup> to describe diffusion in a ternary system, and coefficients not listed in Equations (3.16) - (3.18) were be obtained by permutation of the indices as described by Curtiss and Bird<sup>62</sup>. Equations (3.19) - (3.22) in combination with Equations (3.16) - (3.18) form a set of equations that satisfy the condition of Equation (3.23) as described by Curtiss<sup>62</sup>.

$$\Delta_3 = \tilde{C}_{12}\tilde{C}_{13} + \tilde{C}_{12}\tilde{C}_{23} + \tilde{C}_{13}\tilde{C}_{23}$$
(3.16)

$$\tilde{D}_{11} = \left[\omega_3^2 \tilde{C}_{12} + \omega_2^2 \tilde{C}_{13} + (\omega_2 + \omega_3)^2 \tilde{C}_{23}\right] / \Delta_3$$
(3.17)

$$\tilde{D}_{12} = \left[\omega_3^2 \tilde{C}_{12} - \omega_2 (\omega_1 + \omega_3) \tilde{C}_{13} - \omega_1 (\omega_2 + \omega_3) \tilde{C}_{23}\right] / \Delta_3$$
(3.18)

$$\tilde{D}_{22} = \left[\omega_1^2 \tilde{C}_{23} + \omega_3^2 \tilde{C}_{12} + (\omega_1 + \omega_3)^2 \tilde{C}_{13}\right] / \Delta_3$$
(3.19)

$$\tilde{D}_{33} = \left[\omega_1^2 \tilde{C}_{23} + \omega_2^2 \tilde{C}_{13} + (\omega_1 + \omega_2)^2 \tilde{C}_{12}\right] / \Delta_3$$
(3.20)

$$\tilde{D}_{13} = \left[\omega_2^2 \tilde{C}_{13} - \omega_3 (\omega_1 + \omega_2) \tilde{C}_{12} - \omega_1 (\omega_2 + \omega_3) \tilde{C}_{23}\right] / \Delta_3$$
(3.21)

$$\tilde{D}_{23} = \left[\omega_1^2 \tilde{C}_{23} - \omega_3 \left(\omega_1 + \omega_2\right) \tilde{C}_{12} - \omega_2 \left(\omega_1 + \omega_3\right) \tilde{C}_{13}\right] / \Delta_3$$
(3.22)

$$\sum_{j} \omega_{j} \tilde{D}_{jk} = 0 \quad j = 1, 2, 3 \tag{3.23}$$

This form of GFL model has been evaluated by Gandhi<sup>63</sup> for the case of a ternary system and has been shown to be suitable for modeling multicomponent diffusion under a range of scenarios. The Generalized Fick's Law (GFL) model, which is equivalent to the inverted Maxwell-Stefan Equation, is expressed in molar concentrations and mole fractions according to Equation (3.24). Equation (3.25) is used to describe the  $C_{ij}$  values where  $x_i$  and  $x_j$  are the mole fractions of species i and j, respectively, to recast the multicomponent diffusivities  $\overline{D}_{ij}$  into a mole fraction basis according to Equations (3.26) - (3.32).

$$J_{i}^{*} = -C_{i} \sum_{j} \overline{D}_{ij} d_{j}, \quad \sum_{i} y_{i} \overline{D}_{ij} = 0, \quad i, j = 1, 2, \dots \nu$$
(3.24)

$$C_{ij} \equiv \frac{x_i x_j}{D_{ij}} \tag{3.25}$$

$$\overline{\Delta}_3 = C_{12}C_{13} + C_{12}C_{23} + C_{13}C_{23}$$
(3.26)

$$\overline{D}_{11} = \left[ x_3^2 C_{12} + x_2^2 C_{13} + \left( x_2 + x_3 \right)^2 C_{23} \right] / \overline{\Delta}_3$$
(3.27)

$$\overline{D}_{12} = \left[ x_3^2 C_{12} - x_2 \left( x_1 + x_3 \right) C_{13} - x_1 \left( x_2 + x_3 \right) C_{23} \right] / \overline{\Delta}_3$$
(3.28)

$$\overline{D}_{22} = \left[ x_1^2 C_{23} + x_3^2 C_{12} + \left( x_1 + x_3 \right)^2 C_{13} \right] / \overline{\Delta}_3$$
(3.29)

$$\overline{D}_{33} = \left[ x_1^2 C_{23} + x_2^2 C_{13} + \left( x_1 + x_2 \right)^2 C_{12} \right] / \overline{\Delta}_3$$
(3.30)

$$\overline{D}_{13} = \left[ x_2^2 C_{13} - x_3 \left( x_1 + x_2 \right) C_{12} - x_1 \left( x_2 + x_3 \right) C_{23} \right] / \overline{\Delta}_3$$
(3.31)

$$\overline{D}_{23} = \left[ x_1^2 C_{23} - x_3 \left( x_1 + x_2 \right) C_{12} - x_2 \left( x_1 + x_3 \right) C_{13} \right] / \overline{\Delta}_3$$
(3.32)

This set of coupled, partial differential equations can be solved using published binary diffusion coefficients to evaluate diffusion in the ternary system. For aqueous systems of nitric acid at a temperature of 298 K, Nisancioglu and Newman<sup>54</sup> reported

diffusion coefficients between  $2.92 \times 10^{-9}$  m<sup>2</sup>/s and  $3.11 \times 10^{-9}$  m<sup>2</sup>/s, while Chapman and Newman<sup>55</sup> reported a diffusion coefficient of  $3.31 \times 10^{-9}$  m<sup>2</sup>/s. Chapman and Newman<sup>55</sup> also reported a diffusion coefficient of  $2.86 \times 10^{-9}$  m<sup>2</sup>/s for aqueous sulfuric acid at 298 K, while Klenø<sup>69</sup> reported a diffusion coefficient of  $2.13 \times 10^{-10}$  m<sup>2</sup>/s for the nitric acid/sulfuric acid system at 298 K. These diffusion coefficients can be used in Equations (3.25)-(3.32) to describe diffusion in the ternary mixed acid system and to compare these results with simpler Fick's Law models that utilize binary diffusion coefficients and neglect some interactions.

## 3.4.4 Evaluation of Multicomponent Diffusion in Simple Systems

Two simple examples were considered to evaluate the differences between multicomponent diffusion using the inverted Maxwell-Stefan equations and a simplified Fick's law model that neglected interactions between nitric acid and sulfuric acid in the mixed acid system. To evaluate the significance of interactions in the ternary system, onedimensional models were developed to compare the diffusion of mixed acid species through both sides of a film of thickness,  $\delta$ , at 25°C using the multicomponent Generalized Fick's Law model described in Equations (3.25)-(3.32), and a simplified Fick's Law diffusion model assuming no interactions and using binary diffusion coefficients for aqueous nitric acid and aqueous sulfuric acid. Models were developed to consider unidirectional diffusion under the simplified cases of diffusion through a stagnant water phase and for equimolar counter diffusion resulting in no net flux of acid species through the film. Nitric acid is denoted as species 1, sulfuric acid as species 2, and water is denoted as species 3 in the equations that follow for the purpose of conciseness. **3.4.4.1 Diffusion Through a Stagnant Water Layer.** Diffusion through the stagnant water layer was considered using the simplified Fick's law model by neglecting the interactions between nitric acid and sulfuric acid. Using this approach, the results of two, independent binary systems (nitric acid in water and sulfuric acid in water) were compared with the results for the multicomponent system for diffusion of the mixed acid species through a stationary water phase. For diffusion in one direction, the unsteady-state mass balance for species i is described by Equation (3.33).

$$\frac{\partial C_i}{\partial t} = \frac{\partial (Cx_i)}{\partial t} = -\frac{\partial N_{iz}}{\partial z}$$
(3.33)

The total molar flux of species i,  $N_i$ , is expressed as the sum of the diffusive flux,  $J_i^*$ , and the flux due to bulk flow of species i in the mixture according to Equation (3.34)<sup>66</sup>, where  $N_T$  is the total molar flux in the mixture.

$$N_{i} = J_{i}^{*} + x_{i} N_{T}$$
(3.34)

For the two binary systems, the total flux is equal to the flux of species i, so Equation (3.34) simplifies to Equation (3.35) where Fick's first law of diffusion can be used to express the diffusive flux of A in the binary AB system according to Equation  $(3.36)^{66}$ .

$$N_i = \frac{1}{1 - x_i} J_i^*$$
(3.35)

$$J_A^* = -CD_{AB} \nabla x_A \tag{3.36}$$

Combining Equations (3.33), (3.35) and (3.36) yields Equations (3.37) and (3.38) which describe binary diffusion of nitric acid through stagnant water and sulfuric acid through stagnant water, respectively.

$$\frac{\partial x_1}{\partial t} = \frac{\partial}{\partial z} \left( \frac{D_{13}}{1 - x_1} \frac{\partial x_1}{\partial z} \right)$$
(3.37)

$$\frac{\partial x_2}{\partial t} = \frac{\partial}{\partial z} \left( \frac{D_{23}}{1 - x_2} \frac{\partial x_2}{\partial z} \right)$$
(3.38)

In the case of a ternary mixture with a stagnant water phase, the total molar flux,  $N_T$ , can be expressed in terms of the diffusional flux of water by making use of the fact that the total molar flux of water is equal to zero according to Equation (3.39).

$$N_3 = 0 = J_3^* + x_3 N_T \tag{3.39}$$

This expression can be rearranged to express the total molar flux in the mixture in terms of the diffusive flux of water and mole fraction of water according to Equation (3.40).

$$N_T = -\frac{J_3^*}{x_3}$$
(3.40)

The molar flux of species i,  $J_i^*$ , in a ternary system can be defined using more generally by the molar concentration,  $C_i$ , and driving force,  $d_i$ , according to Equation  $(3.41)^{63}$ .

$$J_{i}^{*} = C_{i} \sum_{j=1}^{3} \overline{D}_{ij} d_{j}, \quad \sum_{i=1}^{3} x_{i} \overline{D}_{ij} = 0, \quad i, j = 1, 2, 3$$
(3.41)

Using this approach, Equations (3.33), (3.40), and (3.41) can be combined to yield the unsteady mass balance in Equation  $(3.42)^{63}$ , which describes transient diffusion in a ternary system with a stagnant phase using the inverted Maxwell-Stefan equations.

$$\frac{\partial x_i}{\partial t} = \frac{\partial}{\partial z} \left( x_i \sum_{j=1}^{j=3} \left( \tilde{D}_{ij} - \tilde{D}_{3j} \right) \frac{\partial x_j}{\partial z} \right), \quad i = 1, 2$$
(3.42)

For the ternary nitric acid, sulfuric acid, water system, Equations (3.43) and (3.44) describe the multicomponent diffusion of nitric acid and sulfuric acid through a stagnant water phase.

$$\frac{\partial x_1}{\partial t} = \frac{\partial}{\partial z} \left[ x_1 \left( \left( \overline{D}_{11} - \overline{D}_{31} \right) \frac{\partial x_1}{\partial z} + \left( \overline{D}_{12} - \overline{D}_{32} \right) \frac{\partial x_2}{\partial z} + \left( \overline{D}_{13} - \overline{D}_{33} \right) \frac{\partial x_3}{\partial z} \right) \right]$$
(3.43)

$$\frac{\partial x_2}{\partial t} = \frac{\partial}{\partial z} \left[ x_2 \left( \left( \overline{D}_{21} - \overline{D}_{31} \right) \frac{\partial x_1}{\partial z} + \left( \overline{D}_{22} - \overline{D}_{32} \right) \frac{\partial x_2}{\partial z} + \left( \overline{D}_{23} - \overline{D}_{33} \right) \frac{\partial x_3}{\partial z} \right) \right] \quad (3.44)$$

This system of partial differential equations can be solved using Equations (3.25)-(3.32) and by substituting for the water mole fraction using Equation (3.45).

$$x_1 + x_2 + x_3 = 1 \tag{3.45}$$

Simulations were run assuming unidirectional diffusion through two sides of a 1.4mm thick film with Dirichlet boundary conditions describing the concentrations of at the surfaces of the film and assuming that no acid was initially present in the film. Transient diffusion results were plotted from the initial condition (t=0s) until approximately twice the characteristic diffusion time (t=700s) for the system to illustrate differences in the concentration of nitric acid in the film as a function of time. Figure 3.11 illustrates the mole fraction of nitric acid at the surface, <sup>1</sup>/<sub>4</sub> width, and center (x = 0, x =  $\delta/4$ , x =  $\delta/2$ ) of the film as a function of time for these symmetric diffusion models.



**Figure 3.11** Mole fraction of nitric acid vs. time for Generalized Fick's Law Model (GFL) and Simplified Binary Diffusion Model (Bin) for diffusion of mixed acids through stagnant water layer at 25°C. Solid lines represent results for multicomponent diffusion model based on inversion of Maxwell-Stefan equations while dashed lines represent results from a simplified binary diffusion model. Results illustrate mole fractions at the outer surface, <sup>1</sup>/<sub>4</sub> width, and center of the film.

A comparison of the results indicates that the maximum error associated with using the simpler model with no interactions was approximately 7% at a diffusion time of 160 seconds and rapidly dissipated to nearly zero at a diffusion time of 450 seconds (Figure 3.12).



**Figure 3.12** Squared error versus time for nitric acid mole fraction in stagnant water layer when comparing Generalized Fick's Law model with simple binary diffusion model. Error reaches a maximum value at approximately 160 seconds and rapidly reduces to zero by approximately 450 seconds.

The influence of interactions on the overall rate of diffusion in this system may be relatively small because the reported diffusion coefficient for nitric acid in sulfuric acid is an order of magnitude lower than the reported diffusion coefficients of aqueous nitric acid and aqueous sulfuric acid. This suggests that the concentration gradients in the system will be primarily driven by the diffusivities of mixed acid species in water. Given that the effects of interactions among diffusing species are relatively small for the mixed acid system in the case where water is a stagnant phase, the simplified binary Fick's Law diffusion model can be used to make simple predictions while reducing computation time and complexity without introducing significant error into models describing the nitration of wood pulp slivers under these conditions.

**3.4.4.2 Equimolar Counter Diffusion in an Aqueous Film.** A second case described by equimolar counter-diffusion of mixed acid species in a film was considered to compare the

error associated with using simple binary diffusion models with multicomponent diffusion models. The binary diffusion model again consisted of the results of two, independent binary systems (nitric acid in water and sulfuric acid in water) and were compared with the results for the multicomponent system for equimolar counter diffusion in the ternary mixed acid system.

In the case of equimolar counter diffusion, the total molar flux in the system  $(N_T)$  is equal to zero so the binary, unsteady mass balances for nitric acid and sulfuric acid simplify to Equations (3.46) and (3.47), respectively.

$$\frac{\partial x_1}{\partial t} = D_{13} \frac{\partial^2 x_1}{\partial z^2}$$
(3.46)

$$\frac{\partial x_2}{\partial t} = D_{23} \frac{\partial^2 x_2}{\partial z^2}$$
(3.47)

In the case of unidirectional, equimolar counter diffusion in a multicomponent system, the unsteady mass balance is described by Equation (3.48).

$$C\frac{\partial x_i}{\partial t} = -\frac{\partial J_i^*}{\partial z}$$
(3.48)

Combining Equations (3.41) and (3.48) yields the unsteady mass balances for diffusion in one direction of nitric acid and sulfuric acid in the multicomponent system, where the mole fraction of water can again be expressed in terms of the other two species using Equation (3.45).

$$\frac{\partial x_1}{\partial t} = \frac{\partial}{\partial z} \left( x_1 \left( \overline{D}_{11} \frac{\partial x_1}{\partial z} + \overline{D}_{12} \frac{\partial x_2}{\partial z} + \overline{D}_{13} \frac{\partial x_3}{\partial z} \right) \right)$$
(3.49)

$$\frac{\partial x_2}{\partial t} = \frac{\partial}{\partial z} \left( x_2 \left( \overline{D}_{12} \frac{\partial x_1}{\partial z} + \overline{D}_{22} \frac{\partial x_2}{\partial z} + \overline{D}_{23} \frac{\partial x_3}{\partial z} \right) \right)$$
(3.50)

This system of partial differential equations was also solved using Equations (3.25) -(3.32) to model the scenario of diffusion through two sides of a 1.4mm thick film with Dirichlet boundary conditions describing the concentrations of nitric acid and sulfuric acid at the surfaces of the film and assuming that no acid was initially present in the film. Transient diffusion results were again plotted from the initial condition (t=0s) until approximately twice the characteristic diffusion time (t=700s) for the system to illustrate differences in the concentration of nitric acid in the film as a function of time. Figure 3.13 illustrates the mole fraction of nitric acid at the surface, <sup>1</sup>/<sub>4</sub> width, and center (x = 0,  $x = \delta/4$ ,  $x = \delta/2$ ) of the film as a function of time for these symmetric diffusion models.



**Figure 3.13** Mole fraction of nitric acid vs. time for Generalized Fick's Law Model (GFL) and Simplified Binary Diffusion Model (Bin) for equimolar counter diffusion of mixed acids in water layer at 25°C. Solid lines represent results for multicomponent diffusion model based on inversion of Maxwell-Stefan equations while dashed lines represent results from a simplified binary diffusion model. Results illustrate mole fractions at the outer surface, <sup>1</sup>/<sub>4</sub> width, and center of the film.

For the mixed acid system, the error between models is much smaller in the case of equimolar counter diffusion, as the maximum error in the nitric acid mole fraction associated with using the simpler model with no interactions was approximately 0.8% at a diffusion time of 440 seconds and approaches zero at long diffusion times (Figure 3.14).



**Figure 3.14** Squared error versus time for nitric acid mole fraction when comparing Generalized Fick's Law model with simple binary diffusion model for case of equimolar counter diffusion. Error reaches a maximum value at approximately 440 seconds and reduces to zero at long diffusion times.

The influence of interactions on the overall rate of diffusion in this system is even smaller in the case of equimolar counter diffusion. Diffusion proceeds at a faster rate in the limiting stagnant film case because the overall mass flux is into the film in this scenario. In the stagnant film case, it takes approximately 180 seconds for the mole fraction of nitric acid in the center of the sliver to reach 0.25 while it takes approximately 220 seconds to reach a nitric acid mole fraction of 0.25 in the center of the film in the equimolar counter diffusion case. Because the overall rate of mass transfer is generally lower in equimolar counter diffusion case than in the case of diffusion through the stagnant film, the influence of interactions between nitric acid and sulfuric acid is also minimized under this scenario. Consequently, similar to diffusion through a stagnant water phase, the simplified binary Fick's Law diffusion model can be used to make preliminary predictions without introducing significant error into models describing the nitration of wood pulp slivers under conditions that can be approximated by equimolar counter diffusion.

## 3.4.5 A Simple Linear Model for Describing Simultaneous Swelling and Diffusion Using Experimentally Measured Effective Diffusivities

The wood pulp sliver swelling experiments indicated that wood pulp slivers tend to swell linearly before reaching a maximum extent of swelling, suggesting that a linear relationship is suitable for describing the change in effective diffusivity due to swelling. This is consistent with simple equations that have been developed to relate bulk diffusivities,  $D_{AB}$ , to effective diffusivities,  $D_{eff}$ , in porous materials. One such relationship is Equation (3.51) <sup>70</sup> which relates the bulk diffusivity to the effective diffusivity using the porosity,  $\phi$ , constriction factor,  $\sigma$ , and tortuosity,  $\tau$ , of the porous material. In this expression, the porosity is the ratio of the void volume to the total volume of the material and the tortuosity is a factor that describes ratio of the actual distance that a solvent molecule travels between two points to the shortest distance between those points. The constriction factor is a factor that accounts for variation in the cross-sectional area in the direction normal to diffusion, for example to account for narrow regions in porous channels.

$$D_{eff} = \frac{D_{AB}\phi\sigma}{\tau}$$
(3.51)

Using this approach, the time-dependent effective diffusivity for each wood pulp was modeled by assuming that the effective diffusivity varies linearly between the experimentally measured effective diffusivities for the initial and swollen states according to Equation (3.52) as the wood pulp sliver swells. This assumption implies that the effective diffusivity varies as a linear function of the extent or swelling, or porosity in the wood pulp sliver.

$$D_{eff}(t) = D_{eff}(t_{sw}) - \frac{\left(D_{eff}(t_{sw}) - D_{eff}(0)\right)}{t_{sw}}(t_{sw} - t)u(t_{sw} - t)$$
(3.52)

In this expression,  $t_{sw}$  is the time to reach the maximum extent of swelling,  $D_{eff}(t_{sw})$  is the effective diffusivity at the swollen state, and  $D_{eff}(0)$  is the effective diffusivity at the initial or unswollen state. A unit step function,  $u(t_{sw}-t)$ , is again employed to prevent the diffusivity from increasing after the maximum extent of swelling is reached. This pulp-specific effective diffusivity,  $D_{eff}(t)$ , can be used to describe the swelling-dependent effective diffusivity of mixed acids through the wood pulp sliver structure for a given pulp type and temperature. One notable disadvantage of this model is that it is not a generalized model and requires both swelling and diffusion data for a given wood pulp. Swelling experiments are easily performed but membrane diffusion cell experiments require fabrication of custom diffusion cells and frames to maintain the wood pulp sliver in a given orientation and state of swelling.

## 3.4.6 Evaluation of Generalized Diffusion Models

To increase the utility of the swelling and diffusion data for analyzing the nitration of wood pulp slivers, models were considered that relate the effective diffusivity to the bulk diffusivities and other the easily measured attributes of wood pulp slivers. Generalized approaches that have been developed to model the diffusion of solvents through porous membranes can also be adapted to describe the diffusion of mixed acid species in the fibrous wood pulp sliver structure. If the wood pulp sliver acts as a porous membrane, the effect of the dense wood pulp sliver structure is to hinder the diffusion of mixed acid species by requiring the acids to take a more tortuous path through the structure. Uniform, unidirectional swelling of the wood pulp slivers in the direction of the sheet thickness has the effect of increasing the porosity ( $\phi$ ) term and potentially reducing the tortuosity ( $\tau$ ) term in Equation (3.53), which is Equation (3.51) without the constriction factor

$$D_{eff} = \frac{D_{AB}\phi}{\tau}$$
(3.53)

To generalize the effect of swelling on the diffusivity of mixed acid species through the wood pulp sliver, the mixed acid species diffusivities,  $D_{AB}$ , can be used to estimate the tortuosity for a given wood pulp sliver configuration, porosity, and effective diffusivity,  $D_{eff}$ , using Equation (3.53). Using this approach, the effective diffusivity of mixed acid species through the wood pulp sliver structure can be modeled as a function of the initial wood pulp sliver density, fiber packing characteristics, and the time dependent degree of swelling in the wood pulp sliver structure.

Because the error associated with using binary diffusion models instead of multicomponent diffusion models was shown to be small for the ternary mixed acid system, the simplified Fick's Law diffusion model was used to calculate the overall diffusivity of mixed acid species,  $D_{AB}$ , for the mixed acid composition used in the diffusion experiments, yielding net diffusion coefficient of  $2.88 \times 10^{-9}$  m<sup>2</sup>/s at 25°C and . Tortuosity values were calculated using the experimentally measured effective diffusivities, the known wood pulp
sliver porosities, and the net diffusion coefficient for mixed acid species. Two empirical tortuosity models proposed by Koponen et al.<sup>71,72</sup> were evaluated to describe the relationship between the wood pulp sliver tortuosity ( $\tau$ ) and the porosity ( $\phi$ ). Equation (3.54) is a simpler, linear model while Equation (3.55) is a nonlinear, two-parameter model that describes the tortuosity as a monotonously decreasing function of porosity, where p, q, and m are empirical parameters and  $\phi_c$  is a percolation threshold that is approximately equal to 0.33.

$$\tau = p\left(1 - \phi\right) + 1 \tag{3.54}$$

$$\tau = 1 + q \frac{(1 - \phi)}{(\phi - \phi_c)^m}$$
(3.55)

For the diffusion experiments conducted at 25°C, best-fit values of 13.721, 4.992, and 0.563 were obtained for p, q, and m, respectively, using a nonlinear least squares regression routine. The 25°C data set was used to eliminate the influence of temperature on the calculated tortuosity values because binary diffusion coefficients were reported for all mixed acid species at this temperature. It is noted that a larger set of binary diffusion coefficients is required to test the applicability of these models over the range of concentrations and temperatures that are relevant to industrial scale NC manufacturing. Nevertheless, these models were evaluated in the wood pulp sliver nitration model to attempt to generalize the model for describing the nitration kinetics of a range of wood pulps for which only the sheet density and swelling time are known.

An alternate approach based on free volume theory describes the dependence of the self-diffusion coefficient, D, on the polymer (cellulose) weight fraction,  $\omega_p$ , using an exponential relationship according to Equation (3.56).<sup>73</sup> In this expression, D<sub>o</sub> is the

diffusion coefficient at infinite dilution and  $\beta$  is a constant used to represent the tendency of the cellulose to inhibit mass transfer. Ferrero et al.<sup>73</sup> have also demonstrated that this expression can be applied for the study of aqueous systems in modeling drug release from hydrophilic matrices consisting of cellulose ethers. The set of diffusion experiments that were conducted at 25°C were again used to eliminate the effect of temperature on the diffusion coefficients, and a best-fit value of 6.425 was obtained for  $\beta$ .

$$\ln D = \ln D_o - \beta \omega_n \tag{3.56}$$

In all three diffusion models, a linear rate of swelling is assumed as seen in Figure 2.8 so that the porosity increases from an initial value,  $\phi_0$ , to the final value in the fully swollen state,  $\phi(t_{sw})$ , at the characteristic swelling time,  $t_{sw}$ , for each wood pulp according to Equation (3.57). A unit step function,  $u(t_{sw}-t)$ , is again used to prevent the porosity from continuing to increase after the maximum extent of swelling is reached at  $t_{sw}$ .

$$\phi(t) = \phi(t_{sw}) - \frac{(\phi(t_{sw}) - \phi_o)}{t_{sw}} (t_{sw} - t) u(t_{sw} - t)$$
(3.57)

The linear tortuosity model, Equation (3.54), and the exponential model, Equation (3.56), yielded better agreement with the experimental data than the nonlinear twoparameter tortuosity model, Equation (3.55). The linear tortuosity model provided a better fit to the experimental data evaluated for various degrees of swelling at 25°C, but the exponential model has the advantage of approaching the limiting value of the net diffusion coefficient for the mixed acid species as the porosity approaches unity. Given this behavior, the linear tortuosity model is proposed to be a good predictor of the diffusion coefficient of mixed acids that swell similarly to the wood pulps evaluated under this effort, and the exponential model is likely more appropriate for wood pulps that swell to porosities in excess of 0.75 should this situation be observed.



**Figure 3.15** Comparison of experimentally measured diffusivities with three models evaluated at 25°C and 40°C over a range of porosities. In general model predictions were within one standard deviation of experimental results at 25°C but agreement was not as good at 40°C, possibly due to anomalous experimental results.

Considerable variation was observed in the diffusion cell experiments as seen in Figure 3.15. This may be due to nonhomogeneous regions in sheeted wood pulp yielding slivers with significant differences in structural characteristics. Anomalous behavior was also observed in some of the experimentally measured diffusivities, particularly in the swollen state (high porosity) experiments that were conducted at 40°C. The three models that were evaluated generally fell within one standard deviation of the experimental results for the diffusivities that were measured at 25°C, but the fit to the data was not as good at 40°C. This is partially because binary diffusion experiments were not available for the concentrated aqueous nitric acid and aqueous sulfuric acid over the temperature range studied to allow for modeling the temperature dependence of the binary diffusion

coefficients. Instead, an Arrhenius relationship was used by calculating an activation energy for the sulfuric acid system over another concentration and temperature range and using extrapolation to calculate the binary diffusivities of aqueous nitric acid and aqueous sulfuric acid at 40°C. A more extensive set of diffusion coefficients would allow for detailed interpretation of diffusion cell results over the full temperature range studied. The suitability of these models can also be better assessed by evaluating a broader range of wood pulps at multiple degrees of swelling; however, this was beyond the scope of the current effort.

### **3.5 Findings and Recommendations**

The generalized diffusion models that were evaluated are suitable for conducting preliminary assessments of the diffusion limited reaction of dense wood pulps in mixed nitrating acid compositions. This investigation provided key insight into the relative rates of swelling and mass transfer during the nitration of slivers cut from sheeted wood pulp and the diffusion of mixed acids through the wood pulp sliver structure. Independent experiments were conducted to study the dynamic swelling behavior, diffusional mass transfer, and the influence of machine cutting, and lab-scale nitration experiments were performed to observe the net effect of these factors on the nitration kinetics for several wood pulp sliver configurations and reaction temperatures. Through considering the influence of these phenomena under conditions relevant to industrial nitrocellulose manufacturing, models were developed and evaluated to establish a predictive capability for describing the mass transfer of mixed acids in wood pulp slivers during the industrial manufacture of nitrocellulose.

Swelling and diffusion experiments demonstrated that unidirectional swelling of wood pulp slivers ensues upon immersion of the slivers in mixed nitrating acids, and that the associated relaxation and mass transfer phenomena occur on similar timescales during the nitration of wood pulp slivers. The diffusivity of mixed nitrating acid species through the wood pulp sliver structure was found to be a function of both temperature and of the extent of swelling, or porosity, of the wood pulp sliver. Anisotropic effective diffusion coefficients were measured in the direction of the wood pulp sheet thickness (through the sheet) and in the plane of the wood pulp sheet (parallel to the sheet) at two different temperatures and extents of swelling for each pulp type that was evaluated. Diffusion in the plane of the sheet was determined to occur at a much faster rate than diffusion through the sheet thickness, leading to simplifying assumptions for describing diffusion of mixed acids through wood pulp slivers cut from sheeted wood pulp. Based on this analysis, it was proposed that the effective diffusion coefficient in the plane of the wood pulp sheet should vary as a function of swelling but that the changes in the diffusion length and diffusivity through the thickness of the sheet could be neglected for the wood pulp sliver geometries that were studied under this effort.

A series of models was evaluated to describe the change in the effective diffusivity of mixed acids through the wood pulp sliver as it swells, and generic models were proposed to describe the relationship between the extent of swelling and the effective diffusivity of mixed acid species through the wood pulp sliver. An analysis of multicomponent diffusion was performed for the ternary mixed acid system using a Generalized Fick's Law model based on inversion of the Maxwell Stefan relations to quantify the error associated with using binary diffusion coefficients to describe the diffusion of mixed acid species through the wood pulp sliver. Overall diffusivities for the mixed acid system were used to calculate tortuosity in wood pulp slivers using the effective diffusivity values measured experimentally in the diffusion cell experiments. These tortuosity and effective diffusivity results were then related to the wood pulp sliver structure using known porosity values and characteristic swelling times. In addition to a linear model that utilized the experimentally measured effective diffusivities directly to describe the change in effective diffusivity of mixed acids through the wood pulp sliver as it swells, two generalized models (the linear tortuosity model and the exponential diffusivity model) also provided reasonable agreement with experimentally measured effective diffusivities.

The ability of the model to predict diffusion of mixed acid species through the wood pulp sliver could be improved by utilizing a more robust set of binary diffusion coefficients for mixed acid species over the temperature and concentration ranges of interest to the industrial cellulose nitration reaction. A limited set of binary diffusion coefficients was available for the mixed acid species, and diffusion coefficients for the aqueous nitric acid system at 40°C were notably absent from the published literature. This required extrapolation of the binary nitric acid-water diffusion coefficients to describe diffusion at temperatures above 25°C. The analysis of effective diffusivities of mixed acid species through the wood pulp sliver structure could be extended by analyzing a greater number of swelling states and by making more extensive use of ion chromatography to better characterize diffusion of individual species in the multicomponent nitrating acid mixture. By analyzing more samples under varied degrees of swelling, it might be possible to establish a better empirical relationship between the effective diffusivity and extent of swelling observed in wood pulp slivers. Swelling experiments with different mixed acid compositions could also be conducted to study the effect of the mixed acid composition on the relaxation time and maximum extent of swelling in wood pulps. The evaluation of effective diffusivities for mixed acids through wood pulp slivers could also be improved by conducting a structural analysis to provide a more detailed characterization of the porous regions in the wood pulp sliver by excluding the void volume inside the hollow cellulose fibers to consider only the effect of interfiber porosity on the diffusion of mixed acids through the wood pulp sliver.

# **3.6 Conclusions**

The influences of swelling and multicomponent diffusion were considered in developing a set of simplifying assumptions for modeling the complex, multiphase reaction that occurs during the nitration of dense cellulose materials to produce nitrocellulose. The swelling behavior of wood pulp slivers in mixed nitrating acids was studied, and characteristic relaxation times were calculated for each of the wood pulps that were evaluated in this study. Effective diffusivities of mixed acid species through the porous wood pulp sliver structure were also measured using a custom membrane diffusion cell, and a dimensionless analysis was performed using the characteristic diffusion and relaxation times to develop a reasonable approach for modeling these simultaneous phenomena. Relationships between the wood pulp sliver porosity and the corresponding effective diffusivity were evaluated to develop a generalized form of the wood pulp sliver nitration model that does not require experimental measurement of effective diffusion coefficients to predict the nitration kinetics for a given wood pulp. These expressions can be combined with the single cellulose fiber kinetic model in partial differential equations describing mass transfer

and chemical reaction in dense cellulose structures to describe the observed kinetics of nitration for industrially relevant cellulose materials.

#### **CHAPTER 4**

# EXPERIMENTAL MEASUREMENT OF OBSERVED NITRATION KINETICS OF WOOD PULP SLIVERS

## 4.1 Introduction

Experimental data describing the kinetics of nitration for a range of industrially relevant dense cellulose materials and nitration conditions is necessary to evaluate the validity of models describing the observed kinetics of nitration for these materials. This can be accomplished through performing lab-scale nitration and stabilization experiments with a range of wood pulp slivers under controlled nitration conditions. These experimental results obtained using different mixed acid compositions, temperatures, and acid to cellulose ratios can also be compared with production data (final degree of nitration and solubility) for the same reaction conditions to confirm that the lab-scale experimental configuration is predictive of the industrial nitrocellulose manufacturing process. The work described in this chapter is an extension of previously published work<sup>50</sup> that considered the nitration kinetic behavior of a range of wood pulp slivers in mixed acid compositions suitable for the production of Grade B nitrocellulose.

# 4.1.1 The Industrial Process for Producing Military Grade Nitrocellulose

The general processing steps for producing military grade nitrocellulose (Figure 4.1) are described in MIL-DTL-244B<sup>11</sup>. Although this specification was later revised (MIL-DTL-244C) to place more emphasis on nitrocellulose quality attributes and to allow for wider implementation of modern manufacturing methods, it provides useful guidelines for developing lab-scale nitrocellulose synthesis and stabilization processes that replicate the

performance observed in legacy nitrocellulose manufacturing operations. In particular, processing conditions and treatment times are prescribed for atmospheric boiling and poaching Grades A, B, D, and E nitrocellulose (Grade C is a blend of Grades A and B). By replicating these conditions in lab-scale nitration equipment, it is possible to achieve reproducibility between lab-scale and industrial scale nitration processes.



**Figure 4.1** General processing steps in nitrocellulose manufacturing with drying, preliminary boil, pulping, poaching, washing, and screening steps described in MIL-DTL-244B<sup>11</sup>

The drying operation described in MIL-DTL-244B consists of drying cotton cellulose at 110°C or rapid dying of sheeted wood pulp cellulose (sulfate or sulfite) at temperatures less than 175°C and not exceeding 165°C for more than 15 minutes. These drying operations are only required when producing Grades D and E nitrocellulose in batch nitration processes, presumably to prevent dilution of the mixed nitrating acids with moisture in the cellulose, resulting in a shift in the equilibrium degree of nitration. Lab nitration processes are generally batch processes, suggesting that the moisture content of the cellulose materials must be lowered through drying or accounted for in the selection of mixed acid recipes for these experiments.

The cutting or shredding operation employed depends on the physical form of the cellulose material. Baled materials are shredded into loose masses of fibers while sheeted materials are either shredded into loose fibers or cut into small slivers. The method of cutting or shredding and the nitration reactor configuration determine the range of acid to cellulose ratios that can be employed in the process. Because cut or shredded cellulose material can readily be obtained from the industrial nitrocellulose manufacturing process, variation can be eliminated by performing lab nitration experiments with these cut or shredded cellulose materials.

The nitration reaction is conducted using either a batch reactor, a series of continuous stirred tank reactors, or a reactor train consisting of a continuous stirred tank reactor followed by reactors that approximate plug flow. Turbulent mixing is maintained in the batch reactor and all continuous stirred tank reactors to promote efficient transfer of mixed acids into the cellulose structures. Turbulent mixing is particularly important in the initial reactor of a nitration train to ensure that cellulose materials are rapidly wetted and immersed in mixed acids as they are fed to the nitration reactor to prevent hot spots due to the heat generated by the nitration reaction. Temperature control is generally only maintained through controlling the temperature of the mixed acid fed to the process. The nitration reactor train is designed with sufficient residence time to allow the mass transfer limited nitration of dense cellulose materials to reach equilibrium.

Following nitration, acids are rapidly separated from the nitrocellulose and washed to remove residual acid from the raw nitrocellulose. In most modern nitrocellulose manufacturing processes this is accomplished using one or more countercurrent centrifuges. The reacted, or "spent" acid is removed from the nitrocellulose in the first stage of the centrifuge, and fresh water is used to wash the nitrocellulose at the last stage before exiting the centrifuge. The equipment is configured to run in a countercurrent manner such that the liquid stream exiting the fresh water wash at the last stage of the centrifuge is used to wash the mildly acidic nitrocellulose at the second-to-last stage, and so on. There is generally no rinse stream in the first stage of the centrifuge as the spent acids are removed and recovered from this stage for refortification and reuse in the nitration reactors. Temperature control in the centrifuge is maintained by controlling the temperature of the fresh water that is fed to the last stage of the centrifuge.

The preliminary boil is described in MIL-DTL-244B as consisting of a preliminary boil in acidic water not less than 0.05% acidity calculated as sulfuric acid and preferably falling within the limits of 0.05% to 0.50% acidity. Two more boiling treatments are conducted during the preliminary boil with a change of water between each boiling treatment. The boiling times depend on the grade of nitrocellulose being processed and are listed in Table 4.1. During the preliminary boiling treatment, the viscosity of the nitrocellulose is lowered due to hydrolysis of the nitrocellulose chains and residual acids not removed during centrifugation are partially removed from the cellulose fibers.

NC Grade	First Boil (hr)	Second Boil (hr)	Third Boil (hr)
Grade A	20	5	5
Grades D and E	15	5	5
Grade B	40	5	5

**Table 4.1** Boiling times (hours) by Nitrocellulose Grade for Preliminary Boiling Treatment

Following the preliminary boil, a poaching step is performed in slightly alkaline water to grind the nitrocellulose fibers to the desired degree of fineness (measured using a volumetric settling test) while removing occluded acids from the fibers. Decanting and rinse treatments may be performed during pulping to maintain alkaline conditions in the pulping tank, and to remove impurities released from the fibers. The objective of the pulping operation is to identify operating conditions (time and pulping intensity) such that the desired level of residual acidity and fineness are reached simultaneously after a defined pulping treatment. Generally, pulping conditions that are not optimized for the specific nitrocellulose material being stabilized result in a material that reaches the fineness limit significantly before the desired reduction in residual acidity is achieved.

After pulping, the nitrocellulose is washed and decanted before poaching is conducted with fresh water containing a maximum of 10 lbs. of sodium carbonate per 2000 lbs. of nitrocellulose. Mechanical agitation is used in the poaching vessel and direct steam injection is used to maintain the temperature in the poaching vessel above 95°C. The poaching treatment consists of four cycles (Table 4.2) with a settling and decanting step between each cycle that consists of removing and replacing at least 30% of the liquid phase with fresh water.

Poaching Step	Time (hr)	Conditions
1	4	Can use sodium carbonate
2	2	Without sodium carbonate
3	1	Without sodium carbonate
4	1	Without sodium carbonate

**Table 4.2** Poaching Cycles Described in MIL-DTL-244B<sup>11</sup>

The poaching step is followed by at least two cold water washing steps that consist of agitating the nitrocellulose in fresh water for at least 30 minutes before settling and decanting at least 30% of the rinse water. After washing the nitrocellulose is screened to remove agglomerates or bundles of fused nitrocellulose fibers and then the nitrocellulose may be blended with other batches of nitrocellulose to achieve the desired nitrogen content for a given end use.

## 4.1.2 Developing A Lab Scale Process

The general processing steps used in industrial nitrocellulose manufacturing processes and described in MIL-DTL-244B can be adapted to a series of lab-scale processing steps that yield the same extent and uniformity of nitration as the industrial-scale processes. Using this approach, it is possible to conduct lab-scale nitration experiments that are representative of the expected performance in industrial-scale nitrocellulose manufacturing processes. Each unit operation in the manufacturing process imparts characteristics or quality attributes in the nitrocellulose using known operating ranges and controls. By identifying these characteristics, operating ranges, and controls, these unit operations can be adapted to lab-scale processing equipment.

The cutting or shredding step governs the size of densified cellulose materials (slivers or bundles of shredded fibers) obtained from either sheets or bales of cellulose and may also affect changes to the internal structure of these materials. Although wood pulp slivers could easily be hand cut to match the size of wood pulp slivers cut in the industrial cutting equipment, the effect of structure is best captured by using materials cut on the industrial processing equipment. This is important because hand-cut slivers are known to exhibit decreased reactivity when compared to wood pulp slivers cut on industrial cutters<sup>50</sup>.

The nitration unit operation ensures that the nitration reaction is conducted under controlled acid to cellulose ratio, temperature, and mixing conditions while the centrifugation unit operation rapidly removes the nitrocellulose from the spent acid and washes the nitrocellulose with water. These operations can be combined by performing the nitration reaction in a temperature controlled, agitated, lab-scale batch reactor and by immediately filtering the nitrocellulose fibers and quenching them in chilled water after the desired reaction time is reached. A lab process must be designed to rapidly remove the nitrated material from the spent acid and to wash the nitrated fibers in chilled water to emulate the performance of the centrifuges used in the industrial nitration process and to ensure that reaction times can be tightly controlled.

Lab-scale stabilization processes can in many cases be performed similarly to the industrial nitration process following the criteria established in MIL-DTL-244B. These preliminary boiling times and decanting cycles can be followed precisely in the lab-scale nitration process to maintain consistency with the nitrocellulose manufacturing process, and residual acidity measurements can be performed to confirm that the acidity is within the range described in MIL-DTL-244B. In lab-scale nitration experiments where the resulting nitrocellulose is not used for propellants, a more aggressive pulping step can be employed, using a benchtop homogenizer, to ensure that trapped acids are released even though this may result in a very fine nitrocellulose material. Like the preliminary boiling step, the poaching (Table 4.2) and the final wash steps can also easily be performed under the same conditions as are used in the industrial NC process.

For nitrocellulose produced in lab-scale nitration experiments that will not be used in propellants, the final wash step is the last step of the nitrocellulose process that is necessary to evaluate the reactivity of given cellulose materials and to assess their suitability for use in industrial nitrocellulose manufacturing processes. The lab-scale nitration and stabilization process is described in Figure 4.2. The primary differences are the quenching and rinse process that is used instead of centrifugation and the lab-scale homogenization step that is used to replace the pulping step employed in the manufacturing process.



Figure 4.2 Lab-scale process for nitrating cellulose materials cut on industrial cutting/shredding equipment.

These experiments can be used to measure the observed kinetics of nitration for a range of dense cellulose materials and cutting configurations to qualify new sources of cellulose for use in nitrocellulose production and to validate predictive models describing the nitrocellulose manufacturing process.

## 4.2 Materials and Methods

### 4.2.1 Experimental Approach

Four sheeted wood pulps that differed by the pulping method (sulfite versus kraft) and tree species (softwood versus hardwood) were evaluated. The pulping method describes the method used to purify the wood pulps, and the tree species from which the pulps were obtained primarily differentiates fiber qualities. Mixed acid compositions used in the production of Grades B and A nitrocellulose were evaluated to study the influence of the wood pulp sliver structure on the observed kinetics of nitration for these dense cellulose materials. Using this approach, the pulp properties and reaction conditions were controlled variables and the degree of nitration was the response variable for each reaction time that was evaluated.

For each nitration experiment, the sheet characteristics, fiber properties, sliver dimensions, acid composition, acid to cellulose ratio, and reaction temperature were controlled, and the degree of nitration was measured after a prescribed reaction time. A design of experiments (Table 4.3) was prepared to evaluate the reactivity of wood pulp slivers for the same wood pulps and acid compositions (37.0% HNO<sub>3</sub>, 54.6% H<sub>2</sub>SO<sub>4</sub>, and 8.4% H<sub>2</sub>O) that were used in the single cellulose fiber nitration kinetic experiments and in the diffusion cell experiments.

**Table 4.3** Design of Experiments for Wood Pulps and Grade B Mixed Acid Composition

 Used in Fiber Kinetics and Diffusion Experiments

Factor	Levels					
Source	Sulfite Softwood	Kraft So	ftwood	Kraft Hardwood		
Size	6.0mm x 0.8mm		6	5.0mm x 1.8mm		
Temperature	25°C		40°C			

A Taguchi L9 array (Table 4.4) was used instead of a full factorial design of experiments to test the significance of wood pulp sliver (WPS) source, reaction temperature, and WPS size on extent or nitration achieved (percent nitrogen) for each reaction time that was evaluated. The temperature and wood pulp sliver size were confounded to reduce the number of experiments that needed to be performed and because the influence of temperature is understood through both the single cellulose fiber kinetic work and the theoretical influence of temperature on the rate of diffusion.

Experiment	Factors / Levels						
	WPS Source	Temperature	WPS Sliver	Temp*WPS			
			Size	size			
1	Sulfite	25°C	S	low			
	Softwood						
2	Sulfite	25°C	L	med			
	Softwood						
3	Sulfite	40°C	L	high			
	Softwood						
4	Kraft	25°C	S	low			
	Hardwood						
5	Kraft	40°C	S	med			
	Hardwood						
6	Kraft	40°C	L	high			
	Hardwood						
7	Kraft Softwood	25°C	S	low			
8	Kraft Softwood	25°C	L	med			
9	Kraft Softwood	40°C	L	high			

**Table 4.4** Taguchi L9 Array used to Evaluate Influence of Pulp Type, Wood Pulp Sliver Size, and Temperature at Each Reaction Time Evaluated

Additional wood pulp sliver nitration experiments (Table 4.5) were conducted with other high purity wood pulps using different sliver sizes and mixed acid compositions for model validation and pulp reactivity assessment. These experiments were conducted over the same range of temperatures and using the same acid to cellulose ratio as the samples that were evaluated in the design of experiments for the Grade B mixed acid composition to enable comparison of the measured rates of nitration in these experiments. Two mixed acid compositions were identified for each nitrocellulose grade – one containing greater than 50% nitric acid (mass basis) and the other containing greater than 50% sulfuric acid (mass basis) and the other containing greater than 50% sulfuric acid and mixed acid compositions that are rich in sulfuric acid are both known to be suitable for the production of nitrocellulose<sup>1</sup>.

Source	Size	Acid	Temperature
		Composition	
Kraft softwood	6.0mm x 1.4mm	High HNO <sub>3</sub>	40°C
		Grade A	
Kraft softwood	6.0mm x 1.4mm	High H <sub>2</sub> SO <sub>4</sub>	40°C
		Grade A	
Kraft softwood	6.0mm x 1.0mm	High HNO <sub>3</sub>	25°C
		Grade B	
Kraft softwood	6.0mm x 1.5mm	High HNO <sub>3</sub>	25°C
		Grade B	
Alternate Kraft	6.0mm x 1.0mm	High HNO <sub>3</sub>	25°C
softwood		Grade B	

**Table 4.5** Additional Wood Pulp Sliver Nitration Experiments with Varying Pulps, Sliver

 Sizes, Acid Compositions, and Temperatures

These experiments include sufficient variation to evaluate the influence of pulp type, wood pulp sliver size, temperature, and mixed acid composition on the nitration kinetics of industrially relevant dense cellulose materials. Reaction times of 30 seconds, 60 seconds, and 4200 seconds were used to study the rate and extent of reaction in these materials. A more extensive set of reaction times including 60 seconds, 300 seconds, 600 seconds, 1800 seconds, 2400 seconds, and 4200 seconds was used to establish a kinetic profile for various wood pulp configurations and reaction conditions to better understand the influence of processing conditions on the rate and uniformity of nitration achieved in the industrial nitrocellulose manufacturing process.

# 4.2.2 Mixed Acid Compositions

Mixed acid compositions were prepared using nitric acid (J.T. Baker – Nitric Acid, Fuming, 90%), sulfuric acid (Fisher Scientific – Certified ACS Plus), and deionized water. Two mixed acid compositions used in the production of Grade B nitrocellulose and two mixed

acid compositions used in the production of Grade A nitrocellulose were prepared (Table

4.6) for the lab scale nitration experiments.

Acid Composition	HNO3	H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O
High HNO3 Grade B	54.6	37.9	7.5
High H2SO4 Grade B	37.0	54.6	8.4
High HNO3 Grade A	52.83	34.20	12.97
High H2SO4 Grade A	30.02	55.96	14.02

 Table 4.6 Nominal Mixed Acid Compositions Used in Wood Pulp Sliver Nitration

 Experiments

The mixed acid composition containing 54.6% sulfuric acid, 37.0% nitric acid, and 8.4% water by weight is identical to the mixed acid composition that was used in the diffusion, swelling, and cellulose fiber nitration experiments, and was used in the design of experiments for the sulfite softwood, kraft softwood, and kraft hardwood pulps. The acid compositions that were selected for producing Grade A nitrocellulose were estimated compositions based on compositions that were reported to have been used in production trials designed to identify processing conditions for wood pulp cellulose materials. The actual mixed acid compositions were verified by potentiometric titration prior to conducting nitration experiments.

# 4.2.3 Wood Pulps

The high purity wood pulps that were selected for the nitration kinetic experiments differed by pulping method, pulp type, sheet density, and sheet thickness, and purity. The primary characteristics of interest in the nitration kinetic experiments were the sheet density and sheet thickness (Table 4.7) as these characteristics would be expected to affect the effective diffusivity and diffusion length of acids through the wood pulp sliver. Fiber dimensional characteristics and coarseness were measured using an OpTest Equipment Inc. fiber quality analyzer conforming to the requirements of TAPPI T271<sup>25</sup>. Crystallinity measurements were measured using x-ray diffraction, and moisture content was measured for each sample using an Ohaus MB23 moisture analyzer.

**Table 4.7** Properties of Sheeted Wood Pulps Evaluated in Wood Pulp Sliver Nitration

 Experiments

Pulp	Sheet Density	% α-cellulose	Sheet Thickness
	kg/m <sup>3</sup>	wt %	mm
Kraft softwood	720	98.7	1.15
Sulfite softwood	700	90.9	1.11
Kraft hardwood	950	97.8	0.79
Alternate kraft softwood	570	96.3	1.24

# 4.2.4 Wood Pulp Sliver Nitration Experiments

Lab-scale wood pulp sliver nitration experiments were conducted at controlled temperatures and predetermined reaction times by reacting 5 grams of wood pulp slivers in mixed acids using an acid to cellulose ratio of 30:1 (mass basis). After the desired reaction time was reached, the nitrated wood pulp slivers were filtered, quenched in chilled, deionized water, and then stabilized in accordance with the procedures described in MIL-DTL-244B<sup>11</sup>. Reactions were conducted at 25°C and 40°C for 30 seconds, 60 seconds, and 70 minutes to study the transient and steady state behavior of the wood pulp sliver nitration reaction. A water bath, thermocouple, and data logger were used to measure and

control the reaction temperature, and the reactor contents were mixed vigorously to ensure uniform temperature in the reactor.

The exact reaction times, especially for short duration reactions were determined using videos taken of each reaction to precisely determine the elapsed time between sample immersion in mixed acid and sample quenching in an ice-cold excess water wash. Specially designed wire-mesh baskets (Figure 4.3) were fabricated to facilitate rapid immersion of wood pulp slivers in mixed acids and removal of the slivers from the nitrating acid after the desired reaction time was reached. At the start of each experiment, the wood pulp slivers were placed inside the basket and submerged in the nitrating acid. The slivers were stirred with stainless steel tongs for a predefined amount of time after which the basket containing the reacted cellulose was removed from the reactor and submerged in a bath containing one liter of chilled water. The basket contents were then immediately transferred to a Buchner funnel and rinsed with an additional one liter of chilled water. The sample was then placed in 100ml of deionized water and staged for later acid boiling and stabilization.



**Figure 4.3** Wire mesh baskets and Teflon plunger assembly used to rapidly immerse wood pulp slivers in mixed nitrating acid and to remove slivers from mixed acid after designated reaction time.

Nitrated wood pulp slivers were stabilized immediately after the end of the nitration reaction. Following stabilization, the nitrogen content of each stabilized nitrocellulose sample was measured using the ferrous sulfate titration method described in MIL-STD- $286C^{28}$ . This procedure involves release of the nitrate in the sample by strong H<sub>2</sub>SO<sub>4</sub>, forming HNO<sub>3</sub>, which is the titrated with FeSO<sub>4</sub>. The titration is monitored by glass and platinum electrodes which read the change in millivolt output from a range of 500-600 mv to a preselected mv endpoint. The change is measured in volume of FeSO<sub>4</sub> necessary to produce this change. The accuracy achieved was  $\pm 0.02\%$ N with measurements performed in triplicate.

## 4.2.5 Data Analysis

Minitab<sup>®</sup> Statistical Software, Version 18, was used to perform an analysis of variance on the lab-scale nitration data to determine the significance of temperature, wood pulp sliver size, and pulp type on the nitration behavior of dense cellulose materials.

# 4.3 Results

## 4.3.1 Analysis of Mixed Acid Compositions

The compositions of the acid mixtures used in the wood pulp sliver nitration experiments were verified by potentiometric titration (Table 4.8). While the actual acid compositions were generally close to the nominal acid compositions, the actual high H<sub>2</sub>SO<sub>4</sub> Grade A composition was a significantly more concentrated acid mixture than the nominal high H<sub>2</sub>SO<sub>4</sub> Grade A composition, and consequently would be expected to yield an equilibrium degree of nitration higher than 12.6% nitrogen. The effect of this difference between the nominal and actual acid composition is addressed in the discussion of the experimental results.

Acid Composition	HNO3	H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O
High HNO3 Grade B	54.86	37.24	7.90
High H2SO4 Grade B	37.12	55.24	7.64
High HNO3 Grade A	52.08	34.78	13.14
High H2SO4 Grade A	34.94	52.12	12.94

**Table 4.8** Potentiometric Titration Results for Mixed Acid Compositions Used in Wood

 Pulp Sliver Nitration Experiments

# 4.3.2 Wood Pulp Sliver Nitration Results for High H<sub>2</sub>SO<sub>4</sub> Grade B Mixed Acid Composition

Percent nitrogen analysis was performed on three samples from each reaction that was conducted in the high H<sub>2</sub>SO<sub>4</sub> Grade B nitration experiments. Reaction times of 30 seconds, 60 seconds, and 70 minutes were evaluated to consider the transient and steady-state behavior of wood pulp slivers while varying the pulp type, sliver size (width), and reaction temperature (Table 4.9).

**Table 4.9** Percent Nitrogen Results for Wood Pulp Sliver Nitration Experiments with HighH2SO4 Grade B Mixed Acid Composition

Reaction Time (s)	Sulfite Softwood			te Softwood Kraft Hardwood			Kraft Softwood		
	25°C	25°C	40°C	25°C	40°C	40°C	25°C	25°C	40°C
	0.8mm	1.8mm	1.8mm	0.8mm	0.8mm	1.8mm	0.8mm	1.8mm	1.8mm
0	0	0	0	0	0	0	0	0	0
30	7.47	5.19	6.54	6.30	8.12	6.57	6.90	6.42	7.34
60	8.78	6.66	7.57	7.72	9.14	7.26	8.19	6.80	9.00
4200	13.51	13.03	13.33	13.40	13.53	13.40	13.46	13.10	13.48

# 4.3.3 Wood Pulp Sliver Nitration Results for Other Mixed Nitrating Acid Compositions

Percent nitrogen analysis was performed on three samples from each reaction that was conducted in the alternate mixed acid composition and wood pulp nitration experiments. Reaction times of 60 seconds, 300 seconds, 600 seconds, 1800 seconds, 2400 seconds, and 70 minutes were evaluated to obtain a comprehensive reaction kinetic profile under each set of reaction conditions (Table 4.10). These reactions were not structured for the purpose of ANOVA but were instead designed to enable comparison of model predictions for when reactions approach NC specification limits with experimental data. In some instances,

experimental data points were obtained for the sole purpose of comparing differences in final degree of nitration achieved at 70 minutes (the residence time characteristic of the industrial NC manufacturing process) for different wood pulps, sliver sizes, and temperatures.

Time	High HNO3 Grade A		High I Grae	High H <sub>2</sub> SO <sub>4</sub> Grade A		High HNO3 Grade B			
	Kraft Softwood		Kraft Softwood		Kraft Softwood		Alt Kraft Softwood		
<b>(s)</b>	1.8mm,	1.4mm,	1.8mm,	1.4mm,	1.8mm,	1.0mm,	1.5mm,	1.0mm,	
	25°C	40°C	40°C	40°C	40°C	25°C	25°C	40°C	
0	0	0	0	0	0	0	0	0	
30	-	7.57	-	6.20	-	-	-	-	
60	-	8.97	-	8.08	-	10.88	9.97	11.09	
300	-	-	-	-	-	12.87	12.03	12.75	
600	-	-	-	-	-	13.16	12.54	13.20	
1800	-	-	-	-	-	13.42	13.32	13.51	
2400	-	-	-	-	-	13.50	13.41	13.54	
4200	12.31	12.47	12.37	13.00	12.77	13.44	13.42	13.56	

**Table 4.10** Percent Nitrogen Results for Wood Pulp Sliver Nitration Experiments with

 Alternate Mixed Acid Compositions and Wood Pulps

## 4.4 Discussion

## 4.4.1 General Observations of Wood Pulp Sliver Nitration Results

In the experiments that were conducted with the high sulfuric acid Grade B nitrating acid composition, it was noted that an average degree of nitration greater than 6.0% nitrogen was reached very rapidly as the surfaces of the wood pulp slivers reacted. The specification limit for Grade B nitrocellulose (13.35% nitrogen) was approached at long reaction times, except under low temperature and high reaction time conditions. For wood pulp slivers

that were identical in size, more rapid nitration was observed at elevated temperature, and the rate of nitration of larger slivers was slower than the rate of nitration of smaller slivers.

The reactions that were conducted with alternate mixed acid compositions and wood pulps suggested that mixed acid compositions that are rich in nitric acid may more rapidly penetrate the wood pulp sliver structure, as higher initial degrees of nitration were reached at 60 seconds for the high nitric acid Grade A and Grade B mixed acid compositions when compared with the results obtained with the same wood pulp sliver sizes and reaction temperatures with the high sulfuric acid mixed nitrating acid compositions.

Initial concentrations of nitronium and hydronium ions (Table 4.11) were calculated using the acid dissociation model published by Albright et al.<sup>26</sup> to consider potential causes of the more rapid initial rate of nitration observed in the samples reacted with high nitric acid mixed acid compositions. It is noted that both the initial nitronium ion and hydronium ion concentrations are lower for these acid compositions when compared with the high sulfuric acid mixed nitrating acid compositions, suggesting that the higher rate of nitration might be due to either more effective initial penetration of the wood pulp slivers with mixed acids or more effective mass transfer in the mixed acid compositions that are rich in nitric acid.

Acid Composition	[NO <sub>2</sub> <sup>+</sup> ] mol/L		[H <sub>3</sub> O <sup>+</sup> ] mol/L	
	25°C	40°C	25°C	40°C
High HNO3 Grade B	0.631	0.533	6.019	5.880
High H <sub>2</sub> SO <sub>4</sub> Grade B	1.394	1.268	7.547	7.408
High HNO3 Grade A	0.100	0.076	6.966	6.744
High H <sub>2</sub> SO <sub>4</sub> Grade A	0.197	0.157	8.894	8.728

**Table 4.11** Initial Nitronium Ion and Hydronium Ion Concentrations for Mixed Acid

 Compositions Evaluated

The nitronium ion and hydronium ion concentrations illustrate the influence of these species on the equilibrium degree of nitration achieved and appear to be consistent with the proposed model that considers the nitronium ion as the nitrating agent and hydronium ion as the denitrating agent. While the high nitric acid compositions for producing Grades A and B nitrocellulose exhibit lower nitronium ion concentrations, the also exhibit lower hydronium ion concentrations according to the acid dissociation model, suggesting that a similar equilibrium degree of substitution may be achieved.

The nitration reactions that were conducted with mixed acids selected to produce Grade A nitrocellulose all failed to meet the specification limit (12.6 +/- 0.15% nitrogen<sup>11</sup>) for Grade A nitrocellulose. The actual acid composition that was made for the nitric acid rich mixed acid for Grade A NC was slightly more dilute than the specified mixed acid composition, while the actual mixed acid composition that was made for sulfuric acid rich mixed acid composition for Grade A NC was significantly more concentrated than the specified mixed acid composition. As a result, the wood pulp slivers that were nitrated in

the nitric acid rich mixed acid composition all resulted in final nitrogen contents that fell below the Grade A nitrocellulose specification limit while the wood pulp slivers that were nitrated in the sulfuric acid rich mixed acid composition resulted in final nitrogen contents that exceeded the Grade A nitrocellulose specification limit.

Despite this failure to meet the specification limit for Grade A nitrocellulose, it was generally noted that smaller slivers exhibited a higher extent of nitration than larger slivers when nitrated under the same reaction conditions. A slight temperature effect was also evident in these samples as slivers of equal size that were nitrated at 40°C reached a higher degree of nitration than wood pulp slivers that were nitrated at 25°C. Although these samples failed to meet the specification limit for Grade A nitrocellulose, the data generated in these experiments is still useful for identifying factors affecting the rate and extent of nitration, and for validating models describing the observed kinetics of nitration for dense cellulose materials in mixed acids capable of producing Grade A nitrocellulose.

The lab nitration results for the high nitric acid mixed acid composition used in the production of Grade B nitrocellulose indicate that the specification limit for Grade B nitrocellulose (13.35% nitrogen<sup>11</sup>) is reached after a reaction time of between 600 seconds and 1800 seconds for small (1.0mm x 6.0mm) slivers and between 1800 seconds and 2400 seconds for large slivers (1.5mm x 6.0mm). Because the final degrees of nitration that were achieved in these materials were significantly higher than the specification limit for Grade B nitrocellulose, it is still expected that there is significant non-uniformity in the extent of nitration at the center of the wood pulp sliver at this point. This non-uniformity would be evident in the acetone and ether-alcohol solubility of the nitrocellulose, for which quality limits are also specified in MIL-DTL-244B.

#### 4.4.2 ANOVA of Grade B, High H<sub>2</sub>SO<sub>4</sub> Nitration Results

Experimental design was used in developing the list of wood pulp sliver nitration experiments to maximize the information obtained for the kinetics of wood pulp sliver nitration within the available number of experiments. In performing this experimental design, reaction conditions were identified to enable measurement of the effect on a dependent variable (nitrogen percentage) based on manipulation of independent variables (pulp type, temperature, wood pulp sliver size).

The experimental data was analyzed at each reaction time to determine which factors affect the rate of nitration or kinetic behavior and which factors affect the final degree of nitration or equilibrium behavior of the reacting system. Analysis of Variance (ANOVA) was used to partition and compare variation within and between levels and to perform hypothesis testing of the null hypothesis:

$$H_0: \mu_1 = \dots = \mu_k \tag{4.1}$$

that all mean values are equal for a given treatment against the alternate hypothesis that at least one mean value is different from the others. The experimental data was grouped by factor and analyzed for each reaction time (Table 4.12). Factors for the wood pulp sliver experiments were wood pulp type, temperature, and wood pulp sliver size. Probabilities were calculated and a significance level of 5% was applied to determine whether the null hypothesis should be rejected. Through application of this methodology, the significance of wood pulp type, temperature, and wood pulp sliver size were assessed at various reaction times.

Facto	rs / Levels	Response			
Pulp Type	Temperature	Sliver	Percent Nitrogen		
		Size	t=30s	<i>t=60s</i>	t=70min
Sulfite Softwood	25°C	0.8mm	7.47	8.78	13.51
Sulfite Softwood	25°C	1.8mm	5.19	6.66	13.03
Sulfite Softwood	40°C	1.8mm	6.54	7.57	13.33
Kraft Hardwood	25°C	0.8mm	6.30	7.72	13.40
Kraft Hardwood	40°C	0.8mm	8.12	9.14	13.53
Kraft Hardwood	40°C	1.8mm	6.57	7.26	13.40
Kraft Softwood	25°C	0.8mm	6.90	8.19	13.46
Kraft Softwood	25°C	1.8mm	6.42	6.80	13.10
Kraft Softwood	40°C	1.8mm	7.34	9.00	13.48

**Table 4.12** High H<sub>2</sub>SO<sub>4</sub> Grade B Wood Pulp Sliver Nitration Data Grouped by Factors and Levels

A General Linear Model procedure was used for the ANOVA, however, the interaction terms were discarded because the experiments were performed without replicates resulting in insufficient degrees of freedom to distinguish the interaction terms from the standard error term. Consequently, only main effects were considered in performing the ANOVA analyses of the lab-scale experimental data.

The General Linear Model for the wood pulp sliver nitration experiments is written as:

$$Y_{ijk} = \mu + \alpha_i + \beta_j + \gamma_k + \alpha \beta_{ij} + \alpha \gamma_{ik} + \beta \gamma_{jk} + \alpha \beta \gamma_{ijk} + \varepsilon_{ijk}$$
(4.2)

Where the response variable  $Y_{ijk}$  is nitrogen percentage,  $\mu$  is the population mean,  $\alpha$  is the source effect,  $\beta_j$  is the temperature effect,  $\gamma_k$  is the size effect, and  $\varepsilon_{ijk}$  is the random error. The simplified model containing only main effects is then:

$$Y_{ijk} = \mu + \alpha_i + \beta_j + \gamma_k + \varepsilon_{ijk}$$
(4.3)

where source, temperature, and size are the three independent variables considered.

Table 4.13 summarizes the ANOVA results for the SCF and WPS experiments. A confidence level of 95% was applied in conducting this analysis and it was noted that the effect variation due to actual reaction times is manifested in the random error term of the model. P-values were calculated for each factor to determine whether the null hypothesis (that the means within a treatment are equal) could be rejected, suggesting that the effect of a factor is insignificant.

Reaction<br/>TimeP-ValuesPulp<br/>TypeTemperature<br/>0.031Size30s0.3170.0310.027

Table 4.13 ANOVA Results for High H<sub>2</sub>SO<sub>4</sub> Grade B Wood Pulp Sliver Nitration

Experiments

 
 Time
 Pulp Type
 Temperature
 Size

 30s
 0.317
 0.031
 0.027

 60s
 0.207
 0.023
 0.013

 4200s
 0.583
 0.032
 0.017

The wood pulp sliver nitration results suggest that the wood pulp source is not a significant factor over the range of reaction times analyzed but that the temperature and wood pulp sliver size are significant factors. The ANOVA results indicate that the null hypothesis that all means are equal for the pulp type treatment can be rejected with a confidence level of 95%; thus it cannot be concluded that the effect of wood pulp type is significant at the reaction times that were evaluated. The results also indicate that the null hypotheses that all means are equal for the temperature treatment and that all means are equal for the size treatment cannot be rejected with a confidence level of 95%; thus we can conclude that the effects of temperature and size are significant over the range of reaction times studied.

Importantly, the pulp type plays an insignificant role in determining the final degree of nitration achieved. The distinction between these factors must also be considered in evaluating these results. In this analysis, the pulp type has been considered as a qualitative factor (sulfite softwood, kraft hardwood, and kraft softwood) as has size (small sliver and large sliver). As the analysis shifts to studying the effects of sliver morphology on nitration due to dynamic effects such as delamination or the development of diffusional barriers, the analysis must consider whether these effects are truly source dependent or whether they can be considered as size attributes that begin to play an important role in nitration as the sliver size increases. For the high sulfuric acid Grade B mixed acid composition and wood pulps that were evaluated, this data may suggest that these issues can be effectively overcome by the range of sliver sizes that were tested in the lab scale experiments, regardless of source.

# 4.4.3 Applicability of Bench Scale Wood Pulp Sliver Nitration Results to Model Development and Validation

The experimentally measured wood pulp sliver nitration data is suitable for both the purposes of model design and model validation. The finding that both wood pulp sliver size and reaction temperature are significant factors in the observed nitration kinetics of wood pulp slivers suggest that predictive models describing the nitration behavior of industrially relevant dense cellulose materials must include capability to consider both of these factors for a reacting system. Because data has been collected for several acid compositions, pulp types, sliver sizes, and temperatures, this data set can be used to validate models describing the observed kinetics of nitration for high purity, dense cellulose

materials and to consider the applicability of generalized models that can be used to identify processing conditions for new cellulose raw materials.

The effect of temperature can be considered both in terms of the influence of temperature on the rate of diffusion of mixed acids through the cellulose structure and on the rate of nitration of cellulose fibers. These phenomena have been modeled to describe the temperature dependence using an Arrhenius relationship, allowing the influence of temperature and wood pulp sliver size to be effectively decoupled. The influence of wood pulp sliver size can be described directly in models, as the sliver size primarily affects the diffusion length of mixed acids through the porous wood pulp sliver structure. This approach allows the wood pulp sliver size to be considered on a continuum that approaches the reaction kinetics of single cellulose fibers as the wood pulp sliver size becomes negligible. The transient wood pulp sliver nitration data points will allow for effective model validation and consideration of initial and boundary conditions by evaluating initial wetting and reactions at the surface of the wood pulp sliver.

## **4.5 Findings and Recommendations**

Lab-scale nitration reactions demonstrated that the reaction of wood pulp slivers cut from sheeted wood pulp is very rapid, reaching a degree of substitution of one (6.67% nitrogen) within one minute of immersion in the mixed nitrating acid composition. These reactions were conducted over a range of temperatures and at an acid to cellulose ratio (30:1 mass basis) that is relevant to industrial-scale nitrocellulose manufacturing with dense cellulose materials. These lab-scale reactions also demonstrated that wood pulp slivers tend to react

more rapidly in mixed acid compositions that are rich in nitric acid, likely due to more effective mass transfer through the dense cellulose structures.

Experiments that were conducted with mixed acids that were representative of acid recipes used for producing Grade A nitrocellulose demonstrated that the equilibrium degree of nitration for Grade A nitrocellulose is very sensitive to the mixed acid composition, particularly at the acid to cellulose ratios maintained in the industrial manufacturing process. A slightly dilute (excess water) nitric acid rich mixed acid composition yielded nitrocellulose with nitrogen content below the Grade A nitrocellulose specification limit while a slightly strong (excess acid) sulfuric acid rich mixed nitrating acid composition yielded nitrocellulose with nitrogen content in excess of the Grade A nitrocellulose specification limit. This failure to meet the specification limit did not preclude use of the data for evaluating factors affecting the rate or extent of nitration for dense cellulose materials or for validating models describing the industrial production of Grade A nitrocellulose, but additional experiments could be conducted to determine the sensitivity of the final degree of nitration to the mixed acid concentration for lower nitrated nitrocellulose grades such as Grades A, D, E, and F (commercial NC containing 11.55% nitrogen).

Temperature and the size of the wood pulp sliver were found to be significant factors in the degree of nitration achieved during the nitration of dense cellulose materials. These factors could be further explored by conducting a follow-on design of experiments exploring the sensitivity of the nitration reaction to temperature and wood pulp sliver size by evaluating several levels for each factor to establish a response surface. It would be expected that the influence of the wood pulp sliver size on the final degree of nitration
(after a reaction time of 70 minutes) is insignificant below some limit describing the largest sliver configuration where complete and uniform nitration is achieved. Mapping this response surface would be of great practical importance for nitrocellulose producers working with a given wood pulp type as it would reduce the amount of cutting and associated wear to cutting machines in the industrial nitrocellulose process. Cutting is also known to generate fines or dust that are not effectively captured in downstream stabilization equipment and consequently decrease process yield.

A final set of nitration experiments could also be conducted to generate larger quantities of nitrocellulose sufficient to support solubility analysis. This data would be useful to understand whether differences in the final degree of nitration achieved for wood pulp slivers based on sliver size and reaction temperature are significant in terms of the quality of the resulting nitrocellulose. These experiments require a significantly larger bench-scale batch size because several grams of dried nitrocellulose are required for each solubility test<sup>11</sup>.

## **4.6 Conclusions**

Lab-scale wood pulp nitration experiments were conducted to identify factors affecting the rate and extent of nitration of dense cellulose materials under reaction conditions that are relevant to the industrial manufacture of nitrocellulose. An ANOVA was conducted on the results of nitration reactions that were performed in a sulfuric acid rich mixed acid composition used for producing Grade B nitrocellulose that concluded that both the wood pulp sliver size and the reaction temperature were significant factors in both the rate and extent of nitration for these materials. Additional experiments were conducted with

alternate wood pulp types and mixed acid compositions to study the nitration of wood pulp slivers under these reaction conditions and to generate data to be used for the validation of models describing the industrial manufacturing of nitrocellulose from dense cellulose materials. These experiments demonstrated that wood pulps reacted in nitric acid rich mixed acid recipes tend to exhibit a higher rate of reaction than wood pulps that were reacted in sulfuric acid rich mixed acid recipes. A sufficient data set was generated to support design and validation of models describing the rate of nitration of high purity wood pulps.

#### **CHAPTER 5**

## CHARACTERIZATION OF WOOD PULP SLIVER STRUCTURES

## **5.1 Introduction**

In the industrial nitrocellulose manufacturing process, dense cellulose materials are either cut from sheeted wood pulp using rotary cutting machines or shredded into loose fiber bundles using shredding machines. The rotary cutting machine cuts the pulp into slivers that are approximately 6mm long and 1mm wide that can be effectively nitrated and pumped to downstream processing operations even while using acid to cellulose ratios on the order of 30 parts acid to one part cellulose (weight basis). The sheeted wood pulp used in this process is shipped in large rolls from pulp mills and is produced to designated quality attributes (purity, basis weight, Mullen burst strength, etc.) relevant to end-use applications for a specific wood pulp product line. In the case of nitrocellulose manufacturing, the purity, density (or sheet thickness and basis weight), Mullen burst strength (a measure of sheet cohesiveness), moisture content, and cellulose fiber source are considered to be important factors that can be used to ensure consistency in batches of nitrocellulose produced using the same manufacturing process and operating parameters. The industrial cutting machines used in the nitrocellulose manufacturing process are designed such that the rolls of sheeted wood pulp can be fed directly into the machines.

In this sheet forming process used by the wood pulp manufacturer, a machine called a Fourdrinier is used to produce a continuous paper web from a slurry of fibers and water. The slurry is sprayed onto a conveyor belt, called a wire, and a series of pressing and drying operations are used to drain the water from the pulp slurry and to form the fibers into a continuous sheet of paper. The wood pulp slivers that are obtained from these sheets are anisotropic as the fibers exhibit a degree of orientation resulting from the shear stresses that result as the pulp slurry is sprayed onto the moving wire. Fibers are generally oriented in the length and width dimensions of the sheet and are stacked to form a fibrous mat with the desired sheet thickness. The effect of this orientation is evident in the anisotropic diffusion of mixed acids through the wood pulp sliver structure that was observed in the diffusion cell experiments.

Both the size and the structure of wood pulp slivers are expected to influence their observed rate of nitration during the production of nitrocellulose. It was previously reported that all high purity cellulose fibers derived from wood pulp exhibit equivalent rates of nitration despite significant differences in fiber morphology and crystallinity<sup>16</sup>, but it was also shown that the wood pulp sliver size is a significant factor in the rate and extent of nitration for dense cellulose materials. In addition, the wood pulp sliver structure may be a relevant factor when developing initial conditions for modeling the nitration of dense cellulose materials. Given these considerations, an analysis of wood pulp sliver structures is performed with an emphasis on the relationship between the structural characteristics of wood pulp slivers and the sliver size, pulp type, and industrial cutter configuration.

#### 5.1.1 Influence of Wood Pulp Structure on Rate and Extent of Reaction

The wood pulp sliver structure is expected to influence both the rate and extent of reaction of wood pulp slivers during nitration in mixed acids. Differences in the effective surface area of the wood pulp sliver are expected to influence the initial kinetics of nitration while differences in the diffusion length, or size of the wood pulp sliver, are expected to influence the extent of reaction reached at longer reaction times. Structural characteristics that increase the effective surface area of the wood pulp sliver are expected to have a significant effect on both the initial wetting of the wood pulp sliver with mixed acids and on the observed rate of nitration, evidence by the fact that wood pulp slivers reached an average degree of substitution of one (~6.67% nitrogen) within 30 seconds of immersion of the wood pulp slivers in mixed acids. It is not expected that diffusion alone can explain this rapid initial rate of nitration under the assumption that the wood pulp sliver is a homogeneous rectangular parallelepiped.

One plausible explanation for the rapid initial rate of nitration is that the cutting process and nonwoven fibrous structure of the wood pulp slivers results in a much larger effective surface area for initial contact between cellulose fibers and mixed acids upon immersion of the wood pulp slivers in the nitrating acid mixtures. This is to be expected given that the wood pulp sliver is a microporous material consisting of layers of cellulose fibers. It has been shown that the diffusivity of mixed acids through the wood pulp sliver structure increases as the extent of swelling or porosity of the wood pulp sliver increases but this finding was finding was based on the preliminary assumption that the porosity is distributed uniformly throughout the volume of the wood pulp sliver structure. The introduction of large voids or channels in the wood pulp sliver structure could further increase the initial rate of reaction by providing channels to facilitate convective flow of mixed acids into the wood pulp sliver. This is not seen in the nitration of hand-cut wood pulp slivers<sup>50</sup>, which have been shown experimentally to exhibit much slower observed kinetics of nitration, and even regions of incomplete nitration, when compared with machine-cut wood pulp slivers.

# 5.1.2 Overview of Sheet Cutting Processes

The industrial cutting machine used to cut sheeted wood pulp into slivers for the nitrocellulose manufacturing process consists of a stationary bed knife that cuts the sheet into 6mm strips followed by a rotary cutter that cuts the wood pulp slivers to the desired width (Figure 5.1). The width is controlled by regulating both the speed of the rotary cutter and the speed at which the sheet is fed into the cutter. Because of the design of the rotary cutter, shear forces are applied both through the cross section of the sheet and in the plane of the sheet, resulting in partial delamination of the sheet and an uneven cut surface. Understanding the influence that wood pulps, processing conditions, and manufacturing equipment have on the formation of these characteristics can lead to identification of wood pulps with enhanced reactivity in the nitrocellulose manufacturing process for dense cellulose materials. An evaluation of these characteristics can also lead to identification of initial and boundary conditions for models that can more accurately describe the nitration of machine cut wood pulp slivers.



Figure 5.1 Photo of industrial cutting equipment showing bed knife and rotary cross cutter.

## 5.1.3 Analysis of Cellulose Structures

Several techniques have been applied to the analysis of sheeted cellulose fiber structures microscopy<sup>74</sup>, microscopy<sup>37</sup>, including light scanning electron and x-ray microtomography<sup>74,75</sup>. These techniques can provide insight into both fiber structure characteristics and attributes of nonwoven fiber macrostructures. In examining dense cellulose structures, light microscopy can be used to generate three-dimensional images of wood pulp slivers to study features such as fusing of fibers at cutting surfaces, delaminated fiber layers, and regions of densely entangled fibers or bundles. X-ray microtomography is a nondestructive technique that can be used to measure structural attributes of wood pulp slivers including the size and distribution of porous regions in the slivers, and the number and extent of delaminate regions or galleries that are formed in the sliver upon cutting. Image analysis tools can be used to measure characteristics and to make comparisons over many samples to consider the significance of pulp or cutting equipment on structural attributes of wood pulp slivers. Through performing this analysis, representative initial and boundary conditions can be identified for modeling the nitration behavior of a wide range of slivers cut from sheeted wood pulp.

#### 5.2 Materials and Methods

## 5.2.1 Cellulose Materials, Sliver Sizes, and Cutter Configurations Evaluated

Optical microscopy analysis was performed on the kraft pulped softwood, kraft pulped hardwood, and sulfite pulped softwood pulps using both machine-cut and hand cut samples. This purpose of this preliminary analysis was to determine whether there were structural differences in materials cut on industrial cutting machines when compared with hand-cut materials. It was expected that features may be formed during machine cutting that enhance the reactivity of these materials, as it was previously observed that machine-cut slivers tend to react faster and to a greater extent of nitration than hand cut wood pulp slivers<sup>50</sup>.

A more comprehensive analysis of cellulose pulp sliver structures was conducted using four sheeted cellulose pulps that were cut to six sliver sizes using three different cutter configurations. The cellulose pulps that were evaluated consisted of three wood pulps (two kraft softwood and one sulfite softwood) and one sheeted cotton linter sample. One of the kraft pulped softwood samples and the sulfite pulped softwood sample were the same materials that were evaluated in the single cellulose fiber nitration, diffusion, and wood pulp sliver nitration studies. The other two materials were a kraft pulped softwood pulp that has been considered for use in industrial nitrocellulose manufacturing operations and a sheeted cotton linter pulp that is currently used as a feedstock for nitrocellulose production. Samples of from different lots of material were obtained for each pulp and were cut to multiple sliver sizes to consider the influence of sliver size on defects or delaminated regions in the slivers that are formed during cutting. Samples were also grouped by the Mullen burst strength (Table 5.1), as this attribute was identified as a likely predictor of pulps that would nitrate effectively<sup>44</sup>, possibly due to the formation of cutter induced delaminated regions when processed on industrial cutting machines.

Pulp	Levels				
	Mullen (kPa)	Sliver Width (mm)	Cutter		
Kraft Pulped	570, 640, 680, 800	0.80, 1.00, 1.25,	M, R		
Softwood		1.50, 1.80			
Sulfite Pulped	550, 700, 740	0.80, 1.00, 1.25,	M, R		
Softwood		1.50			
Alternate Kraft	910	0.50, 0.80, 1.00,	Ν		
Pulped Softwood		1.25, 1.50			
Cotton Liner Pulp	295	0.50, 0.80, 1.00,	N		
		1.25, 1.50			

 Table 5.1 Pulps, Mullen Burst Strengths, and Slivers Sizes Evaluated

The sheets of cellulose pulps were cut on three different industrial cutting machines (identified as cutter N, cutter M, and cutter R) with slight differences in cutting blade designs to evaluate the effect of the cutter type on the resulting wood pulp sliver morphology. Experiments were designed to evaluate whether the cutter configuration had a significant influence on the formation of structural attributes of machine-cut wood pulp sliver slivers but not to evaluate the specific effect of cutter design features.

# 5.2.2 Light Microscopy Measurements

Light microscopy images were obtained using a Keyence VHX-5000 digital microscope. The structure of cellulose pulp sliver samples was preserved by immersing the machinecut slivers in microscopy grade EpoThin 2 epoxy system and cured overnight at 60°C. After curing the samples were cut into 0.2mm thick slices using a diamond saw to produce cross sections perpendicular to the long (6mm) dimension of the cellulose pulp slivers.

An additional analysis was performed to evaluate cutting surface features at different locations on the wood pulp sliver (Figure 5.2). This analysis was performed to determine the extent to which fusing of the edges occurs during cutting and to determine whether this occurs to an extent that would inhibit nitration. General features were

observed at 250x magnification while more detailed structural features were examined at up to 2500x magnification at the middle of each cut surface as shown in Figure 5.2.



Figure 5.2 Analysis of cut surfaces on machine-cut and hand-cut wood pulp slivers

## 5.2.3 X-Ray Microtomography Measurements

X-Ray Microtomography scans were performed using a Bruker SkyScan 1275 Micro-CT scanner. Images were obtained using 50 millisecond exposure time, 45 kV voltage and 200 µA current, and an array of twelve slivers was mounted to a scanning stage to scan multiple slivers simultaneously. By scanning multiple slivers simultaneously, a greater amount of structural data was obtained during each scan. Micro CT scans were obtained for all four cellulose pulps and an analysis was performed to determine whether relationships exist between structural features that may promote more uniform and rapid nitration and the sliver sizes, pulp types, and cutter designs. Images were reconstructed using Bruker's NRecon software, and dimensional analysis of the reconstructed images was performed using Bruker's CTan software.

## 5.2.4 Data Analysis

The JMicroVision<sup>53</sup> image analysis suite was used to measure the structural features of cellulose pulp slivers in optical microscopy images. Minitab<sup>®</sup> Statistical Software, version 18, was used to perform analyses of variance on the structural attributes to consider factors affecting the number and extent of delaminated regions in the cellulose pulp slivers. Feature dimensions and porosity measurements were obtained using the CTAN 3D image analysis tool of the Bruker 3D.SUITE software package for reconstruction, inspection, visualization, and analysis of internal object structures.

## 5.3 Results

# 5.3.1 Optical Microscopy Analysis

A qualitative analysis was performed using optical microscopy for both hand-cut and machine-cut wood pulp slivers to identify characteristics formed in the internal structure of wood pulp slivers during machine cutting that may influence the reactivity of the wood pulp slivers. It was noted that machine cut wood pulp slivers exhibit uneven cut surfaces due to the radial cutting action of the rotary cutter, and that the shear component of this cutting action results in partial delamination of the wood pulp sliver (Figure 5.3). The quantity and extent of these delaminated regions in the wood pulp sliver is an important consideration in modeling the nitration of wood pulp slivers. A more detailed investigation of these features was performed using Xray microtomography.



**Figure 5.3** Cross section of machine cut wood pulp sliver cast in epoxy depicting radial cut surface (top and bottom) and delaminated regions resulting from shearing in the plane of the wood pulp sheet during cutting.

An additional qualitative analysis was performed to study the influence of cutting methods on the cut surfaces of machine-cut and hand-cut wood pulp slivers at the locations shown in Figure 5.2. This analysis suggested machine-cut slivers tend to exhibit alternating compressed and delaminated regions (Figure 5.4) propagating from the cut surface formed by the action of the rotary cutter that in many instances span the entire width of the wood pulp sliver. This feature is not observed in hand-cut wood pulp slivers, which tend to exhibit a more uniform distribution of cellulose fibers at the cut surface (Figure 5.4).



**Figure 5.4** Optical microscopy images (250x) of machine-cut wood pulp slivers (left) and hand-cut wood pulp slivers (right) exhibiting delaminated regions and compressed regions in machine-cut slivers at the surface formed by the rotary cutter that are not observed in hand-cut samples.

Machine-cut and hand-cut wood pulp slivers were also examined at the short face of the wood pulp sliver (Figure 5.2) that is formed by the action of the bed knife in the industrial cutting machine. At this surface, the machine-cut wood pulp slivers do not exhibit the same compressed and delaminated regions over the face of the cut surface due to the lack of shearing forces in the plane of the sheet resulting from the action of the bed knife (Figure 5.5).



**Figure 5.5** Optical microscopy images (250x) of machine-cut wood pulp slivers (top) and hand-cut wood pulp slivers (bottom) that do not show evidence of delaminated regions and compressed regions in machine-cut slivers at the surface formed by bed knife of the industrial cutting machine.

A final analysis was conducted to investigate fused regions resulting at the wood pulp sliver surface formed by the rotary cutter of the industrial cutting machine and to compare these regions with dense regions formed in hand-cut wood pulp slivers upon cutting with a sharp razor. Dense regions at the long cut surface of the wood pulp sliver (Figure 5.2) were evaluated at up to 2500x magnification to consider the nature of the dense regions in both machine-cut and hand-cut wood pulp slivers. Figure 5.6 demonstrates that these fused regions are much more prevalent in the surface of machine-cut wood pulp slivers that is formed by the action of the rotary cutter, and that these compressed regions do, indeed, appear to consist of fused ends of fibers.



**Figure 5.6** Optical microscopy images (500x - 2500x magnification) of dense regions in machine-cut (top) and hand-cut (bottom) wood pulp slivers exhibiting a greater prevalence of fused fiber regions resulting from the action of the rotary cutter in the industrial cutting machine.

# 5.3.2 Micro CT Analysis

A total of 408 machine-cut cellulose pulp slivers were scanned using micro CT and were analyzed to measure the number of delaminated regions in the slivers and the extent to which the delaminated regions penetrate the width of the slivers. Slivers were scanned using 6µm and 9µm voxel sizes and were filtered to eliminate continuous regions less than 7 voxels in volume so that porosity in the hollow regions of the fibers was not considered in the overall porosity of the wood pulp sliver that is expected to affect mass transfer of acids through the nonwoven fibrous sliver. This porosity analysis was performed using the CTAN 3D image analysis tool to measure the size and distribution of interfiber porous regions in machine cut cellulose pulp slivers. This analysis also demonstrated that machine-cut samples tend to exhibit delaminated regions in the cellulose pulp slivers to form interstices that are not observed in the hand-cut samples (Figure 5.7).



**Figure 5.7** Micro-CT scans of hand-cut (left) and machine-cut (right) wood pulp slivers exhibiting delaminated regions in machine-cut samples.

A preliminary volumetric analysis was conducted to evaluate the dependence of the volume of delaminated regions or interstices that are formed during machine-cutting of cellulose pulp slivers on the sliver size, cutter type, and mullen burst strength of the pulp. This analysis was performed by scanning 12 slivers for each experimental condition and analyzing the number of delaminated regions and the depth of each delaminated region at cross sections located every ½ mm along the length of the sliver. The cross sections (Figure 5.8) were analyzed using the JMicrovision image analysis suite to calculate the average volume of the delaminated region for each experimental condition.



**Figure 5.8** Method for estimating volume fraction of delaminated regions in wood pulp sliver according to Equation (5.1). The number and depth (A) of delaminated areas is measured and multiplied by the width (B) of the delaminated areas.

The void fractions of the delaminated regions,  $\phi_d$ , were estimated by multiplying the number of delaminated regions (N<sub>d</sub>) by the average depth (h<sub>d</sub>) and width (w<sub>d</sub>) of the delaminated regions in each sliver and by dividing by the overall volume (w<sub>s</sub>×h<sub>s</sub>) of the cellulose pulp sliver according to Equation (5.1).

$$\phi_d = \frac{N_d w_d h_d}{w_s h_s} \tag{5.1}$$

This analysis appeared to show correlations between the void fraction of the delaminated regions and both the sliver size (Figure 5.9) and the cutter type (Figure 5.10). A clear correlation with the mullen burst strength was not apparent, possibly because the mullen burst strength is confounded with many other properties of the sheeted wood pulp.



**Figure 5.9** Plot of normalized void fraction of delaminated regions versus nominal sliver width demonstrating decreasing relationship between volume fraction of delaminated regions and sliver width.



**Figure 5.10** Plot of normalized void fraction of delaminated regions versus cutter type showing influence of cutter type on volume fraction of delaminated regions.

Based on these preliminary results, an ANOVA was performed to consider the influence of the pulp type, sliver size, and cutter type on both the quantity of delaminated regions formed in the sliver and the extent that the delaminated regions penetrate the width of the sliver. The ANOVA (Table 5.2) was configured with the number and extent of

delaminated regions in the slivers as response variables to test the significance of the cellulose pulp source, sliver size, and cutter configuration in the formation of these features.

Factor	Levels			
Pulp Type	Kraft Softwood, Alt. Kraft Softwood, Sulfite Softwood,			
	Cotton Linters			
Sliver Size (mm)	0.5, 0.8, 1.0, 1.25, 1.5, 1.8			
<b>Cutter Configuration</b>	N, M, R			

 Table 5.2 Factors and Levels for ANOVA Analysis of Micro CT Data

Subsets grouped by cellulose pulp source and cutter were first analyzed to evaluate the significance of these factors on structural characteristics, and these observations were used to develop an ANOVA for the overall data set. This approach was necessary because the available data set did not represent a balanced ANOVA design, primarily because the cutters were located at different facilities around the world preventing the same pulps from being cut at all three locations. A one-way ANOVA was employed for each of the cellulose pulp source and cutter subgroups and a post-hoc (Tukey test) was conducted for all significant factors. Findings at the subgroup level were then extended to the overall data set using a general linear model. While it was possible to evaluate the significance of the mullen burst strength factor in some of the subgroups, it was not possible to evaluate this factor in the overall data set because it was not independent from the source factor. That is, the pulps that were evaluated did not all show a similar range of mullen burst strength values that would suggest that the mullen burst strength is truly independent from the pulp type.



Figure 5.11 Approach used to measure  $N_d$  and  $\xi_d$  in cross sections located at fixed intervals within the wood pulp sliver.

The response variables for the ANOVA were the average number delaminated regions or galleries,  $N_d$ , in each cross-section and the average extent that the delaminated regions or galleries,  $\xi_d$ , penetrate the width of the sliver cross section (Figure 5.11). The average number of delaminated regions or galleries per cross section is calculated using Equation (5.2), while the average extent of delaminated regions or galleries is calculated using Equation (5.3), where  $n_c$  is the number of cross sections analyzed for each sliver.

$$N_d = \frac{\sum_{n_c} Galleries}{n_c}$$
(5.2)

$$\xi_{d} = \frac{\sum w_{d}}{\sum Galleries}_{W_{s}}$$
(5.3)

The ANOVA results for the significance of factors affecting the number of delaminated regions and the extent that the delaminated regions penetrate the cellulose sliver structure are listed in Tables 5.3 and 5.4, respectively. The mullen burst strength

was evaluated only within the kraft softwood and sulfite softwood subgroups because

samples with multiple mullen burst strength values were only available for these two pulps.

**Table 5.3** ANOVA Results for Average Number of Delaminated Regions in Cellulose Pulp Sliver Cross Section Grouped by Pulp Type, Cutter Type, Sliver Size, and for Overall Data Set

Factors and Levels		P Values				
		Source	Size	Cutter	Mullen	
Source	Cotton Linter Pulp	-	0.489	-	-	
	Alt Kraft Softwood	-	0.023	-	-	
	Kraft Softwood	-	< 0.001	0.162	0.376	
	Sulfite Softwood	-	< 0.001	0.375	< 0.001	
Cutter	М	< 0.001	< 0.001	-	-	
	R	< 0.001	0.002	-	-	
	Ν	< 0.001	0.027	-	-	
	Overall	< 0.001	< 0.001	0.002	-	

**Table 5.4** ANOVA Results for Average Extent that Delaminated Regions Penetrate Cellulose Pulp Sliver Grouped by Pulp Type, Cutter Type, Sliver Size, and for Overall Data Set

Factors and Levels		P Values				
		Source	Size	Cutter	Mullen	
Source	Cotton Linter Pulp	-	< 0.001	-	-	
	Alt Kraft Softwood	-	< 0.001	-	-	
	Kraft Softwood	-	0.021	0.611	0.478	
	Sulfite Softwood	-	< 0.001	< 0.001	< 0.001	
Cutter	М	< 0.001	0.055	-	-	
	R	0.006	< 0.001	-	-	
	Ν	0.070	< 0.001	-	-	
	Overall	< 0.001	< 0.001	< 0.001	-	

Porosity analysis was conducted for both hand-cut wood pulp slivers and for the four cellulose pulp slivers that were evaluated for structural characteristics using optical microscopy and micro CT (Table 5.1). Population distributions of dense regions (Figure 5.12) and porous regions (Figure 5.13) in the slivers were obtained to analyze the influence of machine-cutting on the wood pulp sliver structure. Filters were applied to exclude the

porosity associated with the hollow cellulose fibers and to only include the interfiber porosity in the cellulose pulp sliver structure.



**Figure 5.12** Population distribution of dense cellulose regions in hand-cut wood pulp sliver exhibiting total porosity of approximately 43% of sliver volume.



**Figure 5.13** Population distribution of porous regions in hand-cut wood pulp sliver exhibiting initial total porosity of approximately 43% of sliver volume.

#### 5.4 Discussion

# 5.4.1 ANOVA of Machine-Cut Cellulose Pulp Slivers

The ANOVA analyses of factors influencing the number and extent of delaminated regions in the cellulose pulp sliver structure formed during machine cutting were conducted for each of the cellulose pulp sliver source subgroups and for the overall data set. The significance of each of the factors listed in Table 5.3 was evaluated within each subset, and these results were extended to a more generalized analysis of the factors influencing formation of these characteristics in the overall set of sheeted cellulose pulps that were cut on industrial cutting machines. Because material was only available from a single lot of material (only one mullen burst strength) for the sheeted cotton linter pulp and alternate kraft pulped softwood materials, and because these materials were only cut on one type of cutter, only the size factor could be evaluated for these subsets. The data for the kraft pulped softwood and the sulfite pulped softwood subsets enabled evaluation of the size, cutter type, and mullen burst strength for these materials.

**5.4.1.1 ANOVA of Machine-Cut Cellulose Pulp Slivers** – **Source Subgroups.** ANOVAs were conducted for each of the four source subgroups to consider the influence of sliver size, cutter type, and mullen burst strength on the number and extent of delaminated regions formed in the wood pulp sliver during machine cutting. Not all factors were evaluated for all pulp types due to limitations in the available experimental data. In these instances, statistical significance was only evaluated for factors represented in the available data set.

The ANOVA for the sheeted cotton linter pulp indicated that the effect of the sliver size on the mean number of delaminated regions or galleries in the sliver cross section was

not statistically significant (ANOVA (F(4,55)=0.87, p=0.489), but that the effect of the sliver size on the mean extent that the delaminated regions penetrated the sliver structure was statistically significant (ANOVA (F(4,55)=6.18, p<0.001)). This suggests that the number of delaminated regions formed in the sliver during machine cutting of sheeted cotton linter pulp may be independent of the sliver size over the range evaluated, but that the extent or depth of penetration of delaminated regions into the sliver structure is likely a function of the sliver size.

The analysis of the alternate kraft softwood pulp material indicated that the size of the wood pulp sliver is a significant factor in both the number and extent of delaminated regions formed during machine cutting. The ANOVA for the alternate kraft pulped softwood material indicated that the effect of the sliver size is statistically significant for both the mean number of delaminated regions or galleries (ANOVA (F(4,55)=3.08, p=0.023) and the mean extent that the delaminated regions penetrated the sliver structure (ANOVA (F(4,55)=16.20, p<0.001). Figure 5.14 illustrates this effect for the influence of sliver size on the number of delaminated regions in the alternate kraft pulped softwood material. It is noted that the sheeted cotton linter pulp and the alternate kraft softwood pulp represent the extremes in terms of the mullen burst strength of the materials evaluated, possibly suggesting that the number of delaminated regions formed in the sliver cross section only increases after some threshold sheet cohesiveness level that enables efficient transfer of shear forces between layers in the sliver.



**Figure 5.14** Interval plot of number of delaminated regions in wood pulp sliver cross section versus wood pulp sliver size (width) for alternate kraft pulped softwood material showing decreasing relationship between the number of delaminated regions and the size of the sliver.

A broader range of experiments was conducted for the sulfite pulped softwood and kraft pulped softwood materials, allowing the influences of sliver size, cutter type, and mullen burst strength on the average number and extent of delaminated regions in the cross section of machine cut slivers to be considered for these materials. The ANOVA of the sulfite pulped softwood material indicated that the effects of the sliver size (ANOVA (F(3,116)=11.98, p<0.001) and mullen burst strength (ANOVA (F(2,117)=23.48, p<0.001) were statistically significant for the number of delaminated regions observed in wood pulp slivers, but that the effect of the cutter type on the number of delaminated regions was not statistically significant (ANOVA (F(1,118)=0.79, p=0.375).

In the analysis of factors affecting the extent of delaminated regions in the wood pulp sliver, the effects of all three factors were found to be statistically significant. The ANOVA of the sulfite pulped softwood material indicated that the effects of sliver size (ANOVA (F(3,116)=29.55, p<0.001), mullen burst strength (ANOVA (F(2,117)=17.86,

p<0.001), and cutter type (ANOVA (F(1,118)=27.82, p<0.001) on the extent of delaminated regions observed in wood pulp sliver cross sections were all statistically significant. Figure 5.15 illustrates the relationship between the sliver size and the extent of delaminated regions formed in the sulfite pulped softwood material.



**Figure 5.15** Interval plot of extent of delaminated regions in wood pulp sliver cross section versus wood pulp sliver size (width) for sulfite pulped softwood material showing decreasing relationship between the extent of delaminated regions and the size of the sliver.

The kraft pulped softwood material exhibited slightly different behavior than the sulfite pulped softwood material, as the cutter type and mullen burst strength did not appear to have a significant effect on the number and extent of delaminated regions formed in this material. The ANOVA of the kraft pulped softwood material indicated that only the effect of sliver size was found to be statistically significant for both the number of delaminated regions (ANOVA (F(4,163)=18.34, p<0.001) and the extent that the delaminated regions penetrate the wood pulp sliver cross section (ANOVA (F(4,163)=2.96, p=0.023). This material has been noted to exhibit extensive "puffing" or opening of the sliver structure upon cutting, possibly due to differences in how the material is formed into a sheet. One

possibility is that the puffing mechanism that releases energy stored in the sheet is more significant than the influence of shear forces imparted by the cutter that may be responsible for the formation of delaminated regions in the sliver.

**5.4.1.2 ANOVA of Machine-Cut Cellulose Pulp Slivers – Cutter Subgroups.** Because the effect of the cutter type on the extent of delaminated regions formed in the wood pulp sliver upon cutting was found to be statistically significant for the sulfite pulped softwood material, ANOVAs were conducted for each cutter subgroup to investigate the effect of pulp source and sliver size on the number and extent of delaminated regions formed during cutting (Table 5.4). The effects of the pulp source and the sliver size on the number of delaminated regions formed in the wood pulp were found to be statistically significant for all three cutters that were evaluated. The results for factors affecting the extent that delaminated regions penetrate the cellulose sliver structure were not as consistent, as the effect of the pulp source was found to be statistically significant only for cutters N and R. In aggregate, this analysis suggests that the different pulp types and sliver sizes will result in different amounts of cutter-induced damage for a given cutter configuration.

**5.4.1.3 ANOVA of Overall Data Set for Machine-Cut Cellulose Pulp Slivers.** Because the effects of the cellulose pulp sliver size, cutter type, and mullen burst strength were found to be statistically significant for the number and extent of delaminated regions formed during cutting, these factors were included in a general linear model that was used to conduct an ANOVA of the overall machine-cut sliver data set. In this analysis, the mullen burst strength was lumped into a more general cellulose pulp source factor because the mullen and pulp source are not independent factors in this data set and because there

may be other attributes of pulps that are responsible for formation of this cutter-induced damage. Capturing all of the pulp characteristics in a common "source" term is a more conservative approach that can help to avoid reaching erroneous conclusions about the factors that contribute to cutter induced damage that may increase the nitration performance of these materials.

The ANOVA that was performed on the overall data set indicated that the effects of the cellulose source, sliver size, and cutter were statistically significant for both the number and extent of delaminated regions formed during machine cutting. This analysis showed that different pulps and cutters can result in differences in the number and extent of delaminated regions formed during machine cutting. The analysis also showed that both the number and extent of penetration of delaminated regions tend to decrease with increasing sliver size (Figure 5.16). Figure 5.16 also illustrates the influences of the cutter and the wood pulp type on the number of delaminated regions or galleries formed during cutting. Given these observations, it is noted that smaller wood pulp slivers are likely exhibit faster rates of nitration both because of the smaller diffusion length of acids through the wood pulp sliver and because of the formation of delaminated regions that allow for mixed acids to rapidly penetrate the wood pulp sliver structure.



**Figure 5.16** (Clockwise from top left) Effect of sliver size on average number of delaminated regions in sliver cross section, effect of sliver size on extent of penetration of delaminated regions in sliver cross section, effect of cutter on number of delaminated regions in sliver cross section, and effect of pulp source on number of delaminated regions in sliver cross section.

## 5.4.2 Implications of Significance of Source, Cutter, and Size Factors

The finding that the pulp type, sliver size, and cutter configuration play significant roles in the formation of attributes during machine cutting that are expected to increase the reactivity of dense cellulose materials in mixed acids is important. This result can be exploited for the design of nitrocellulose manufacturing processes and can be used to establish optimized processing parameters to achieve a uniform degree of nitration and a desired level of solubility in acetone and ether-alcohol solvents. This behavior is also important for modeling the nitration of industrially relevant dense cellulose materials, as the presence of features not observed in hand-cut slivers must be accounted for in models describing the rate of nitration of machine-cut slivers exhibiting structural features formed during machine cutting.

The presence of delaminated regions or galleries in the cellulose sliver structure is expected to promote wetting of the sliver with mixed acids. In addition, galleries or voids in the sliver structure may enable the convective flow of mixed acids into these regions of the sliver, increasing the effective surface area of the sliver and decreasing the effective diffusion length of acids through the adjacent dense regions in the sliver. Both increased surface area and decreased diffusion lengths in the sliver would result in an increase in the observed rate of nitration for wood pulp slivers. These void regions or interstices may also promote the diffusion of water formed during the nitration reaction out of the wood pulp sliver. This is an important consideration given that the mixed acid composition governs the equilibrium degree of nitration in the nitrocellulose<sup>2</sup>, so water trapped in the sliver would have the effect of diluting the mixed acid composition in the sliver and resulting in a lower degree of nitration and associated solubility in those regions of the sliver.

In three dimensional models describing the nitration of wood pulp slivers exhibiting this cutter induced damage, assumptions can be made to the initial and boundary conditions to approximate rapid wetting of delaminated regions of wood pulp slivers with mixed acids and to consider changes to the effective diffusion length of mixed acids through the wood pulp sliver structure. More complex models considering the effective surface area of the wood pulp slivers or the distribution of void and dense regions in the wood pulp sliver can also be considered based on a more detailed structural analysis of the wood pulp slivers. Generalized approximations of the number and extent of delaminated regions in the wood pulp sliver are particularly useful because they allow for the simulation of a range of processing conditions based on factors such as the sliver size and pulp type.

# 5.4.3 Approach to Modeling Initial and Boundary Conditions Based on Structural Analysis Results

The structural analysis that was performed for machine-cut cellulose pulp slivers can be used inform the selection of initial and boundary conditions to describe the effect of delaminated regions and increased void space in the slivers. This analysis of factors affecting the number and extent of delaminated regions in machine-cut wood pulp slivers suggested a linear relationship between the width of the sliver and the depth that the interstices formed during cutting penetrate the wood pulp sliver for a given pulp type. Figure 5.17 illustrates the relationship between the interstices formed during cutting (bottom of left image) and the normalized depth (void depth divided by nominal sliver width) that these resulting interstices extend into the width of the wood pulp sliver for the sulfite pulped softwood material. This behavior was observed for the overall set of pulps, sliver sizes, and cutter variations that were evaluated in this effort but the extent of puffing up and formation of interstices during cutting is likely to exhibit dependence on both the cutter and the specific wood pulp.



**Figure 5.17** Cross section of wood pulp sliver showing void areas created by mechanical cutting (left) and relationship between depth of interstices and sliver width (right) for the sulfite pulped softwood material.

The effect of these delaminated regions or interstices on promoting transport of mixed acids into the wood pulp sliver, can be estimated by measuring the amount of puffing, or introduction of void space into the sliver, that results upon cutting. The dimensionless degree of puffing can then be used to estimate the extent that these interstices penetrate the width of the wood pulp sliver according to Equation (5.4). The wood pulp sliver dimensions listed in Table 5.5 that were used in the lab-scale wood pulp sliver nitration experiments using the high sulfuric acid Grade B mixed acid composition demonstrate this effect, as the narrow slivers tended to exhibit greater puffing (initial sliver thickness) in the dimension of the sheet thickness than the wider slivers.

Source	Temperature	Initial Sliver Dimensions			Percent Nitrogen		
		(mm)					
		length	width	thickness	30s	60s	4200s
Sulfite	25°C	6.22	0.83	1.44	7.47	8.78	13.51
Softwood	40°C	6.31	1.62	1.32	6.54	7.57	13.33
Kraft	25°C	6.16	0.76	1.42	6.30	7.72	13.40
Hardwood	40°C	6.16	0.76	1.42	8.12	9.14	13.53
	40°C	6.06	1.77	1.10	6.57	7.26	13.40
Kraft Softwood	25°C	6.16	0.78	1.50	6.90	8.19	13.46
	40°C	6.21	1.64	1.31	7.34	9.00	13.48

 Table 5.5 Wood Pulp Sliver Nitration Results for Experiments Conducted with High

 H<sub>2</sub>SO<sub>4</sub> Mixed Acid Composition

Because the sheet thickness before cutting is known, Equation (5.4) provides a simple relationship that allows for estimation of the penetration depth of the interstices  $(d_{pen})$  using the measured thickness of the cut wood pulp slivers  $(L_z)$ , the known initial thickness of the sheeted wood pulp  $(L_{z,0})$ , and the width of the wood pulp sheet,  $L_y$ .

$$d_{pen} = L_y (0.35 + 0.55 \frac{L_z - L_{z,0}}{L_{z,0}})$$
(5.4)

This expression<sup>50</sup>, which was developed based on structural and dimensional analysis of approximately 400 machine-cut cellulose pulp slivers, can be used to develop initial conditions to describe rapid partial wetting slivers cut from sheeted wood pulp or cotton linters with mixed acids. Using this expression, the initial conditions used in the models describing nitration of dense cellulose materials can be adjusted so that the wood pulp sliver is rapidly wetted only to a depth,  $d_{pen}$ , in the dimension of the sliver width with no acids initially present in the remainder of the wood pulp sliver ( $L_y - d_{pen}$ ). This assumption is physically consistent with the asymmetric puffing of the wood pulp sliver that is seen at leading and trailing edges (Figure 5.17) of the wood pulp sliver as they enter the rotary cutter.

This "variable wetting" approach allows the model to be initialized under a condition of partial wetting that is consistent with the opening of the wood pulp sliver structure that has been observed experimentally for machine-cut wood pulp slivers. It is reasonable to assume that these interstices that form upon machine cutting promote the transport of mixed acids into the open regions of the wood pulp slivers upon immersion in mixed nitrating acids. A more sophisticated model describing how these interstices are formed in the sliver upon machine cutting could be developed after performing structural analysis of a larger number of wood pulps and sliver sizes to allow for consideration of other pulp characteristics that may influence the extent of cutting-induced damage in wood pulp slivers.

# 5.4.4 Use of Porosity Distributions in Wood Pulp Sliver Reaction Models

The use of three-dimensional structural analyses can add an additional degree of accuracy to models describing the nitration of dense cellulose structures by enabling the porosity in the sliver to be represented as a function of the spatial coordinates,  $\phi(x,y,z,t)$ . Using this approach,  $\phi_0$  and  $\phi(t_{sw})$  in Equation (3.57) can be represented as functions of the spatial coordinates so that to describe the variation in porosity through the wood pulp sliver and to allow the diffusivity to also be represented as a function of spatial coordinates according to Equation (3.53). This structural information could also be directly imported into a finite element method (FEM) modeling package as stp/step or igs/iges files, or the information obtained from population distributions could be used to define representative structures for use in FEA modeling packages. To minimize computational complexity, the latter approach will be evaluated for modeling the nitration of machine cut wood pulp slivers in mixed acids using porous media models.

Population distributions were obtained for porous and dense regions in the cellulose sliver by eliminating porous regions below 42 $\mu$ m for the 6 $\mu$ m voxel resolution scan and 63 $\mu$ m for the 9 $\mu$ m voxel resolution scan. The scans that were performed using a 6mm voxel size produced better results, indicating that the open porosity in hand-cut slivers was approximately 43% which compares well with the estimated total porosity of 49.5% that can be calculated using the sheet density and density of pure cellulose<sup>42</sup> and includes porous regions inside the hollow fibers. This porosity value is also in reasonable agreement with the total porosity value that is calculated using Equation (5.5)<sup>76</sup>, where G is the cellulose sheet basis weight, L<sub>z0</sub> is the sheet thickness, and  $\rho_{fiber}$  is the density of the cellulose fiber, which is reported<sup>77</sup> to be 1610 kg/m<sup>3</sup>.

$$\phi = 1 - \frac{G}{L_{z0}\rho_{fiber}} \tag{5.5}$$

These population distributions can be used to calculate various transport properties of the porous wood pulp sliver structure including the hydraulic radius, permeability, and diffusivity, including using the Kozeny-Carman equation<sup>75,76</sup> to estimate the permeability of the sliver and using the porosity and tortuosity to estimate the effective diffusivity of fluids through the fiber space<sup>75</sup>. The application of these techniques are considered in the development of finite element method models describing the rate of nitration of wood pulp slivers in mixed acids.

#### 5.5 Findings and Recommendations

Optical microscopy was used to evaluate cross sections of hand-cut and machine-cut wood pulp slivers to identify differences in these materials given the previous observation that machine-cut slivers generally exhibit enhanced reactivity during nitration when compared with hand-cut slivers. This analysis identified the presence of delaminated regions or galleries in the machine-cut slivers that are not observed in hand-cut slivers. Subsequent structural analysis of machine-cut slivers demonstrated that machine-cutting of sheeted cellulose materials results in the formation of these defects, or delaminated regions that are not observed in hand-cut sheeted cellulose materials. Given the nature of these delaminated regions, or galleries, that are formed as a result of a shear component in the plane of the sheet by the rotary cutting blade of the cutting machine for sheeted cellulose pulps, it is expected that they may promote more rapid and uniform nitration of wood pulp slivers. Consequently, an analysis was conducted to investigate factors that may have a significant effect on the number and extent of penetration of these delaminated regions that are formed during cutting.

The analysis of structural attributes of slivers cut from sheeted cellulose pulps on three different industrial cutting machines indicated that the pulp type, sliver size, and cutter all have statistically significant effects on the number and extent of delaminated regions formed in the resulting slivers. Importantly, the number and the depth of penetration of delaminated regions in the slivers increased as the size of the sliver decreased, suggesting that smaller slivers are advantageous not only because they present smaller diffusion lengths for mixed acids but also because they exhibit important structural characteristics that may aid the transport of mixed acids into the sliver structure. While it
was possible to glean a significant amount of information from this analysis, it was not possible to evaluate a number of factors that are characteristics of the sheeted pulp because the pulps that were evaluated were not able to be cut to all of the sizes and on each of the cutters that was evaluated. This analysis could be expanded by conducting a more comprehensive set of experiments using a wider range of pulps with each pulp was cut to the same range of sliver sizes and on each cutter that evaluated under carefully controlled conditions (feed speeds, cutting rates, etc.). Such an analysis would enable pulp-specific factors such as the mullen burst strength, fiber morphology, density, and pulp purity to be evaluated to help to identify specific attributes of pulps that may make them more suitable for use in nitrocellulose manufacturing process for dense cellulose materials.

This analysis could also be expanded by considering other factors that are relevant to industrial scale nitrocellulose manufacturing including the generation of fines during cutting and wear to the blades of the industrial cutting machine. Quantifying the small cellulose particles or fines generated as a function of pulp type and sliver size would provide useful information for nitrocellulose manufacturers because these fines are generally lost in the spent acid stream during centrifugation and result in lower process yields. Similarly, the influence of cutting conditions on cutter blade life should be investigated to help to understand the maintenance impact (life of cutting surfaces) associated with a given set of cutting conditions. Finally, the influence of blade wear on the resulting sliver structure should be investigated to help to understand the process impacts (e.g., incomplete nitration) associated with extensive wear to the cutting surfaces.

Microtomography was shown to be a useful, nondestructive technique for investigating the structure of machine-cut cellulose pulp slivers. Samples were analyzed

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to obtain porosity distributions that can be used to estimate the permeability and effective diffusivity of wood pulp slivers during the nitration reaction. This method can rapidly provide a tremendous amount of structural data for machine-cut slivers for consideration by process operators when evaluating new pulp materials or processing conditions. This technique also may show great promise as a process monitoring tool that could be used to detect changes in the morphology of machine-cut slivers due to raw material variation or blade wear in the industrial cutting machines. As micro CT machines continue to become more compact and affordable, this technique may become a suitable standard method used by quality control groups in nitrocellulose manufacturing plants to perform these assessments.

### **5.6 Conclusions**

Optical microscopy and micro CT analyses were conducted to evaluate structural characteristics of hand-cut and machine-cut cellulose slivers. These analyses identified delaminated regions formed during machine-cutting of slivers from sheeted cellulose pulps that may promote more rapid and uniform nitration and are not observed in slivers that are hand-cut from cellulose pulp sheets. An ANOVA that was conducted to evaluate factors affecting the number and extent of these delaminated regions in the sliver cross section found that the influences of the pulp type, sliver size, and cutter configuration are all statistically significant for the formation of these features. Importantly, the number and extent of these delaminated regions gliver size.

An empirical approach was proposed for estimating the extent of penetration of these delaminated regions in the wood pulp sliver cross section based on the amount of puffing or change in thickness that results in the pulp sliver upon cutting. This approach was proposed for establishing initial and boundary conditions for modeling the nitration of wood pulp slivers under conditions relevant to industrial nitrocellulose manufacturing. More sophisticated methods based on using the spatially dependent porosity to estimate the permeability and effective diffusivity as a function of position in the pulp sliver were also discussed.

### **CHAPTER 6**

## MATHEMATICAL MODELING OF WOOD PULP SLIVER NITRATION

## **6.1 Introduction**

This chapter is an extension of previously published work<sup>50</sup> that proposed predictive models describing the rate and extent of nitration of dense cellulose materials used in industrial nitrocellulose production. This work demonstrated that generalized models consisting of sets of partial differential equations describing simultaneous mass transfer and chemical reaction during the nitration of dense cellulose materials can be used to predict the nitration behavior of industrially important cellulose raw materials. Model predictions were compared with experimental results for a range of wood pulps and sliver sizes that were nitrated in a mixed acid composition that was rich in sulfuric acid. Based on this work, it was concluded that generalized models can be used to assess the suitability of new cellulose raw materials with only limited information regarding the tendency of the materials to swell upon immersion in mixed acid compositions.

In the present analysis, the model is extended to consider a broader range of mixed acid compositions, wood pulps, and wood pulp sliver sizes than were previously reported. Specifically, the nitration kinetics of wood pulp slivers in mixed acids used in the production of Grade A nitrocellulose and in mixed acid compositions rich in nitric acid that are used in the production of Grade B nitrocellulose are studied in greater detail. In addition, considerations are discussed for extending this approach to describe the nitration of nonhomogeneous dense cellulose structures. The objective of this work is to extend the reaction model that was proposed for the production of Grade B nitrocellulose using dense cellulose materials to describe the observed kinetics of nitration for wood pulps in mixed acids used to produce other nitrocellulose grades (e.g., Grade A) that exhibit lower final degrees of nitration. Using this approach, a model is proposed that describes the rate and extent of reaction for producing all nitrocellulose grades of military importance using dense cellulose materials.

# 6.1.1 Phenomena to be Considered in Modeling the Nitration of Dense Cellulose Materials

To establish a generalized model capable of describing the nitration kinetics of cellulose feedstocks ranging from cotton linters to slivers cut from sheeted wood pulp, it is necessary to consider mass transfer and chemical reaction independently. A conceptual model that also considers the effects of simultaneous diffusion and swelling has been developed to describe the unidirectional, interfibrillar swelling<sup>10</sup> that sheeted cellulose materials are known to exhibit in the dimension of the sheet thickness when immersed in mixed acids. The role of this swelling behavior on the nitration kinetics of dense cellulose materials is important because it has been shown experimentally to facilitate mass transfer of acids into the sliver structure as the void fraction, or interfiber porosity, increases.<sup>50</sup> By combining the phenomena of mass transfer, chemical reaction, and polymer relaxation or swelling, it is possible to describe the nitration dynamics of dense cellulose materials in mixed acids.

# 6.1.2 Benefits and Applicability of the Model

A predictive capability for modeling the observed kinetics of nitration for dense cellulose materials does not presently exist, limiting the opportunity to perform process design and residence time optimization based on variation in cellulose raw materials. This is complicated by the fact that much of the published cellulose nitration kinetic data neglects to provide details of the physical state of the cellulose or the influence of mass transfer on the kinetics of nitration. For example, Urbanski<sup>1</sup> describes the significance of diffusion in discussing the nitration kinetics of cellulose, but only with respect to the rate of diffusion of acids into the cellulose fibers while neglecting to address the physical form of the cellulose. Other researchers<sup>13,18</sup> have reported significantly slower rates of nitration than those observed for single cellulose fibers<sup>16</sup>, suggesting that mass transfer is playing a limiting role in much of the published experimental work due to the diffusion of acids into regions of densely packed cellulose fibers. As a result, much of the published cellulose nitration data is of limited utility to nitrocellulose producers seeking to evaluate alternate cellulose raw materials or to achieve improved process control.

For this reason, predictive models describing the nitration kinetic behavior of various cellulose raw materials are of great interest for the design, operation, optimization, and control of modern nitrocellulose production processes. A model capable of describing the nitration of cellulose to produce military grade NC is expected to be of practical importance for controlling material properties that are critical for propellant blending and manufacturing operations. The focus of this effort is therefore to establish such a model by considering the phenomena of mass transfer and chemical reaction independently to describe the nitration kinetic behavior of machine-cut, wood pulp celluloses used in the production of military grade NC.

# 6.1.3 Approach to Modeling the Nitration of Wood Pulp Slivers in Mixed Acids

The experimentally measured rates of swelling, diffusion, and chemical reaction can be combined with the results of the structural analysis to model the nitration of dense cellulose structures in mixed acids (Figure 6.1).



**Figure 6.1** Approach for combining swelling, diffusion, structural characteristics, and single cellulose fiber nitration kinetics to describe the rate of nitration for dense cellulose structures.

By combining the results of the analyses that were conducted to study the phenomena of swelling, diffusion, and chemical reaction in industrially important cellulose raw materials, a model can be developed to describe the nitration kinetics of wood pulp slivers cut from these materials. Validation of this model can be performed by comparing model predictions with the results of independent lab-scale nitration experiments that were conducted with wood pulp slivers under known reaction conditions.

# 6.2 Materials and Methods

# 6.2.1 Reaction Conditions Evaluated

Models were developed and run using the same wood pulp characteristics, mixed acid compositions, acid to cellulose ratios, and temperatures as were used in the lab scale nitration experiments that were conducted with wood pulp slivers (Table 6.1). All simulations were run using an acid to cellulose ratio of 30:1 (mass basis) and a 5% moisture

content for the wood pulp. The relevant characteristics of the wood pulps (Table 6.2) and the mixed acid compositions (Table 6.3) that were discussed in the context of the lab scale wood pulp sliver nitration experiments in Chapter 4 are repeated here for convenience. The acid compositions used in the wood pulp sliver nitration models were the mixed acid compositions that were verified by the potentiometric titration method rather than the nominal mixed acid compositions (Table 4.6) to ensure that the mixed acids were consistent between the lab scale nitration results and the simulation results.

Source	Size	Acid Composition	Temperature
Sulfite Softwood	6.0mm x 0.8mm	High H <sub>2</sub> SO <sub>4</sub> Grade B	25°C
Sulfite Softwood	6.0mm x 1.8mm	High H <sub>2</sub> SO <sub>4</sub> Grade B	25°C
Sulfite Softwood	6.0mm x 1.8mm	High H <sub>2</sub> SO <sub>4</sub> Grade B	40°C
Kraft Hardwood	6.0mm x 0.8mm	High H <sub>2</sub> SO <sub>4</sub> Grade B	25°C
Kraft Hardwood	6.0mm x 0.8mm	High H <sub>2</sub> SO <sub>4</sub> Grade B	40°C
Kraft Hardwood	6.0mm x 1.8mm	High H <sub>2</sub> SO <sub>4</sub> Grade B	40°C
Kraft Softwood	6.0mm x 0.8mm	High H <sub>2</sub> SO <sub>4</sub> Grade B	25°C
Kraft Softwood	6.0mm x 1.8mm	High H <sub>2</sub> SO <sub>4</sub> Grade B	25°C
Kraft Softwood	6.0mm x 1.8mm	High H <sub>2</sub> SO <sub>4</sub> Grade B	40°C
Kraft Softwood	6.0mm x 1.8mm	High HNO3 Grade A	25°C
Kraft Softwood	6.0mm x 1.4mm	High HNO3 Grade A	40°C
Kraft Softwood	6.0mm x 1.8mm	High HNO3 Grade A	40°C
Kraft Softwood	6.0mm x 1.4mm	High H <sub>2</sub> SO <sub>4</sub> Grade A	40°C
Kraft Softwood	6.0mm x 1.8mm	High H <sub>2</sub> SO <sub>4</sub> Grade A	40°C
<b>Kraft Softwood</b>	6.0mm x 1.0mm	High HNO3 Grade B	25°C
<b>Kraft Softwood</b>	6.0mm x 1.5mm	High HNO3 Grade B	25°C
Alt Kraft softwood	6.0mm x 1.0mm	High HNO <sub>3</sub> Grade B	40°C

**Table 6.1** Reaction Conditions Simulated Using Wood Pulp Sliver Nitration Model

Table 6.2 Wood Pulps and Properties Evaluated in Wood Pulp Sliver Nitration Model

Pulp	Sheet Density	% α-cellulose	Sheet Thickness
	kg/m <sup>3</sup>	wt %	mm
Kraft softwood	720	98.7	1.15
Sulfite softwood	700	90.9	1.11
Kraft hardwood	950	97.8	0.79
Alternate kraft softwood	570	96.3	1.24

Acid Composition	HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O
High HNO3 Grade B	54.86	37.24	7.90
High H2SO4 Grade B	37.12	55.24	7.64
High HNO3 Grade A	52.08	34.78	13.14
High H2SO4 Grade A	34.94	52.12	12.94
Alternate Grade A	30.18	54.67	15.15

**Table 6.3** Mixed Acid Compositions Evaluated in Wood Pulp Sliver Nitration Model

A final set of simulations was run using an alternate Grade A mixed acid composition that has been used to produce Grade A nitrocellulose in the industrial NC manufacturing process. These simulations were primarily run to evaluate the capability of the model for predicting the rate of nitration for dense cellulose feedstocks in the production of Grade A, Type 2 nitrocellulose ( $12.60 \pm 0.15\%$  nitrogen) to assess the suitability of the model as a production support tool.

# 6.2.2 Conceptual Model

A conceptual model was proposed to describe the effects of wetting, swelling, diffusion, and chemical reaction during the nitration of dense cellulose structures. This model describes the nitration of wood pulp slivers as proceeding through the following three steps:

- (1) Wood pulp slivers of known initial dimensions and density are immersed in mixed nitrating acids. The exterior surfaces and rapidly wetted portions (Figure 6.2) of the wood pulp slivers begin to react immediately upon immersion in the mixed acids.
- (2) Mixed acid species penetrate the wood pulp sliver structure through wetting and diffusion; the wood pulp sliver swells in the dimension of the sheet thickness (Figure 6.2) 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 in the wood pulp sliver.



Figure 6.2 Conceptual model of mass transfer and swelling of wood pulp sliver during nitration where  $d_{pen}$  represents region of the sliver that is rapidly wetted with mixed acids.

# 6.2.3 Mathematical Model

The modeling approach described in this section was previously published<sup>50</sup> to describe the nitration of wood pulp slivers, primarily in mixed acids rich in sulfuric acid that are used in the production of Grade B nitrocellulose. The same approach is applied here to extend the model to other acid compositions and to use the revised kinetic parameters that were developed in Chapter 2. The mathematical model describing the reaction of wood pulp slivers in mixed acids consists of a set of coupled, time-dependent partial differential equations derived from the unsteady mass balances of mixed acid species, hydroxyl groups, and nitrate ester groups in the wood pulp sliver. These equations combine acid dissociation, the SCF kinetic model<sup>16</sup>, and unsteady anisotropic diffusion<sup>78</sup> to describe the phenomena of swelling, diffusional mass transfer, and chemical reaction in the threedimensional wood pulp sliver structure (Figure 6.2). The wood pulp sliver is modeled as a parallelepiped with length  $L_x$ , width  $L_y$ , and height (thickness)  $L_z$  to define a region according to Equation (6.1).

$$\Omega = \{(x, y, z) : \frac{-L_x}{2} \le x \le \frac{L_x}{2}; \frac{-L_y}{2} \le y \le \frac{L_y}{2}; \frac{-L_z}{2} \le z \le \frac{L_z}{2}\}$$
(6.1)

Acid dissociation was described using the set of reactions (2.13)-(2.15) and equilibrium constants proposed by Albright et al.<sup>26</sup> that were converted to a molarity basis using the densities of the acid mixtures to model the nitronium ion concentration in mixtures of nitric acid, sulfuric acid, and water. Similar to the approach that was taken in describing the nitration of cellulose fibers, the dissociation of mixed acids to ionic species was assumed to occur at a much faster rate than the cellulose nitration reaction, implying that the acid dissociation reactions are locally at equilibrium in the reacting mixture, with the concentrations of mixed acid species described by Equations (2.26)-(2.28), repeated here as Equations (6.2)-(6.4) for convenience. The assumption of a homogeneous system no longer applies in the case of wood pulp sliver nitration where concentration gradients exist in the sliver, consequently the acid species concentrations depend on both the spatial coordinates and time.

$$K_{1} \frac{\rho_{acid}}{MW_{acid}} = \frac{[NO_{2}^{+}][HSO_{4}^{-}]([H_{2}O] + [NO_{2}^{+}] - [H_{3}O^{+}])}{([HNO_{3}] - 2[NO_{2}^{+}] - [H_{3}O^{+}] + [HSO_{4}^{-}])([H_{2}SO_{4}] - [HSO_{4}^{-}])}$$

$$K_{3} = \frac{[H_{3}O^{+}][HSO_{4}^{-}]}{([H_{2}SO_{4}] - [HSO_{4}^{-}])([H_{2}O] + [NO_{2}^{+}] - [H_{3}O^{+}])}$$

$$K_{4} = \frac{[H_{3}O^{+}]([H_{3}O^{+}] - [HSO_{4}^{-}] + [NO_{2}^{+}] - [H_{3}O^{+}])}{([HNO_{3}] - 2[NO_{2}^{+}] - [H_{3}O^{+}] + [HSO_{4}^{-}])([H_{2}O] + [NO_{2}^{+}] - [H_{3}O^{+}])}$$

$$(6.4)$$

Cellulose fiber reaction kinetics were modeled using the empirical rate law described by Equation (2.40), repeated here as Equation (6.5), and the rate parameters in Table 2.11. This model is used to describe the rate of conversion of hydroxyl groups to nitrate ester groups according to Equation (1.1), where  $[OH]_0$  is the initial concentration of cellulose hydroxyl groups in the reacting mixture. According to Equation (1.1), one molecule of nitric acid is consumed and one mole of water is generated for each hydroxyl group that is converted to a nitrate ester group. This kinetic model also applies in the three-dimensional wood pulp sliver structure where the acid, hydroxyl, and nitrate ester compositions are functions of spatial coordinates and time.

$$r_{OH} = -A_f e^{-E_{af}/RT} e^{-a_0 \frac{[ONO_2]}{[OH]_0}} [OH] [NO_2^+] + A_d e^{-E_{ad}/RT} [ONO_2] [H_3O^+]$$
(6.5)

Equations (6.6)-(6.10) are unsteady mass balances for nitric acid, sulfuric acid, water, hydroxyl groups, and nitrate ester groups, where  $D_{i,j}$  is the diffusion coefficient for species i in the j direction. Nitric acid, sulfuric acid, and water were considered as diffusing species with the rates of generation of water and consumption of nitric acid described by Equation (6.5) and Equation (1.1), the overall stoichiometric equation for the cellulose nitration reaction. The hydroxyl and nitrate ester groups in cellulose and nitrocellulose are immobilized in the wood pulp sliver structure so only generation or consumption due to the nitration reaction is considered in the unsteady mass balances for these species. Equations (6.2)-(6.10) form a set of coupled partial differential equations and algebraic equations that can be used to describe mass transfer and chemical reaction during the nitration of wood pulp slivers.

$$\frac{\partial [H_2 SO_4]}{\partial t} = \frac{\partial}{\partial x} \left( D_{H_2 SO_4, x} \frac{\partial [H_2 SO_4]}{\partial x} \right) + \frac{\partial}{\partial y} \left( D_{H_2 SO_4, y} \frac{\partial [H_2 SO_4]}{\partial y} \right) + \frac{\partial}{\partial z} \left( D_{H_2 SO_4, z} \frac{\partial [H_2 SO_4]}{\partial z} \right) \right)$$

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

$$\frac{\partial [H_2 O]}{\partial t} = \frac{\partial}{\partial x} \left( D_{H_2 O, x} \frac{\partial [H_2 O]}{\partial x} \right) + \frac{\partial}{\partial y} \left( D_{H_2 O, y} \frac{\partial [H_2 O]}{\partial y} \right) + \frac{\partial}{\partial z} \left( D_{H_2 O, z} \frac{\partial [H_2 O]}{\partial z} \right) - r_{OH}$$

$$\frac{\partial [ONO_4]}{\partial t}$$

$$(6.9)$$

$$\frac{\partial [ONO_2]}{\partial t} = -r_{OH} \tag{6.10}$$

**6.2.3.1 Initial and Boundary Conditions.** Initial and boundary conditions must be specified to model the nitration of wood pulp slivers using Equations (6.2)-(6.10), and the relative influences of swelling and diffusion must be considered. Because turbulent mixing is maintained in the nitration reactors of the industrial NC manufacturing process, the boundary condition at the interface between the mixed acids and wood pulp sliver surfaces can be represented using a Dirichlet boundary condition as described by Equation (6.11), where  $[i]_L$  represents the concentration of mixed acid species i (HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, or H<sub>2</sub>O) in the bulk mixed acid outside the slivers. This boundary condition describes ideal mixing in the nitration reactors characterized by the absence of a boundary layer between the bulk acid mixture and the acid composition at the surface of the wood pulp sliver.

$$\left[i\right]\left(\frac{\pm L_x}{2}, y, z, t\right) = \left[i\right]\left(x, \frac{\pm L_y}{2}, z, t\right) = \left[i\right]\left(x, y, \frac{\pm L_z}{2}, t\right) = \left[i\right]_L$$
(6.11)

The wood pulp slivers initially contain no nitrate ester groups, and the cellulose hydroxyl groups,  $[OH]_0$ , are assumed to be uniformly distributed throughout the volume of the wood pulp sliver as described by Equations (6.12) and (6.13). The initial concentrations of acid species in the wood pulp sliver were described using a flexible initial condition that was proposed<sup>50</sup> to describe rapid, partial wetting of the wood pulp sliver with mixed acids to a depth of d<sub>pen</sub>, according to Equation (5.4), such that mixed acids flood the interstices or delaminated regions formed during cutting of the wood pulp sliver. Using this approach, the wood pulp sliver is partially wetted with mixed acids and there are no mixed acids initially present in the remainder of the wood pulp sliver (L<sub>y</sub> - d<sub>pen</sub>) as shown in Figure 6.2. This initial condition allows for evaluation of all cases varying from the limiting cases of very slow wetting (d<sub>pen</sub> = 0), and very rapid, complete wetting (d<sub>pen</sub> = L<sub>y</sub>) of the wood pulp sliver.

The initial concentrations of nitric acid, sulfuric acid, and water in the rapidly wetted regions of the wood pulp sliver are also multiplied by the initial wood pulp sliver porosity,  $\phi_i$ , to account for the fraction of the volume initially occupied by the cellulose fibers. The concentration of water initially present in the wood pulp sliver is equal to the sum of the native moisture content in the wood pulp,  $[H_2O]_0$ , and the concentration of water in the wetted regions of the wood pulp sliver. Equations (6.14)–(6.16) describe these flexible initial conditions for partial wetting of the wood pulp sliver, where a unit step function,  $u(y - L_y/2 + d_{pen})$ , is used to describe the wetted region.

$$[ONO_2](x, y, z, 0) = 0 \tag{6.12}$$

$$[OH](x, y, z, 0) = [OH]_{0}$$
(6.13)

$$[H_2O](x, y, z, 0) = \phi_i [H_2O]_L u(y - \frac{L_y}{2} + d_{pen}) + [H_2O]_0$$
(6.14)

$$[HNO_3](x, y, z, 0) = \phi_i [HNO_3]_L u(y - \frac{L_y}{2} + d_{pen})$$
(6.15)

$$[H_2SO_4](x, y, z, 0) = \phi_i [H_2SO_4]_L u(y - \frac{L_y}{2} + d_{pen})$$
(6.16)

# 6.2.4 Simulation Environment

Wolfram Mathematica<sup>29</sup> was used to numerically integrate the set of partial differential equations and algebraic equations describing the wood pulp sliver nitration reaction and generate results for each set of reaction conditions listed in Table 6.1.

## 6.3 Results

Three different diffusion models were evaluated under the conditions of very slow wetting and rapid partial wetting of the wood pulp sliver with mixed acids. These models used the variable penetration depth initial condition described by Equation (5.4) to enable simulation of the extremes of no initial wetting and rapid volume-wise partial wetting of the wood pulp sliver upon immersion in mixed acids. The results of simulations run using these models and the experimental results obtained from the lab scale wood pulp sliver nitration experiments are listed in Table 6.4. Simulations considered the pulp type, mixed acid composition, wood pulp sliver size, and temperature in describing the nitration of wood pulp slivers under conditions identical to those used in the industrial nitrocellulose manufacturing process. The extent of nitration was calculated at 30 seconds, 60 seconds, and 70 minutes to compare model predictions and experimental results under both transient and steady state conditions. A detailed discussion of these simulation results, diffusion models, and initial conditions follows.

Pulp Type	Acid	Temp	WPS Size	Reaction	Percent Nitrogen					
	Composition		(LxWxH) mm <sup>3</sup>	Time	Experimental	Slow Wetting	Fast Wetting	J	Variable Wett	ing
					Result	Linear Diffusivity	Linear Diffusivity	Linear Diffusivity	Linear Tortuosity	Exponential Diffusivity
Sulfite	High H <sub>2</sub> SO <sub>4</sub>	25°C	6.22 x 0.83 x 1.44	0	0.00	0.00	0.00	0.00	0.00	0.00
Softwood	Grade B			30	7.47	5.19	12.08	7.56	7.50	7.33
				60	8.78	6.65	12.39	8.90	8.83	8.63
				4200	13.51	13.54	13.54	13.54	13.54	13.54
Sulfite	High H <sub>2</sub> SO <sub>4</sub>	25°C	6.31 x 1.62 x 1.32	0	0.00	0.00	0.00	0.00	0.00	0.00
Softwood	Grade B			30	5.19	3.69	11.91	6.29	6.30	6.22
				60	6.66	5.44	12.18	7.24	7.25	7.03
				4200	13.03	13.54	13.54	13.54	13.53	13.53
Sulfite	High H <sub>2</sub> SO <sub>4</sub>	40°C	C 6.31 x 1.62 x 1.32	0	0.00	0.00	0.00	0.00	0.00	0.00
Softwood	Grade B			30	6.54	4.44	12.06	6.84	6.79	6.79
				60	7.57	6.58	12.42	8.24	7.90	7.68
				4200	13.33	13.61	13.61	13.61	13.61	13.61
Kraft	High H <sub>2</sub> SO <sub>4</sub>	25°C	6.16 x 0.76 x 1.42	0	0.00	0.00	0.00	0.00	0.00	0.00
Hardwood	Grade B			30	6.30	3.80	10.84	6.37	6.28	5.88
				60	7.72	5.26	11.06	7.33	7.35	6.72
				4200	13.40	13.53	13.54	13.54	13.53	13.53
Kraft	High H <sub>2</sub> SO <sub>4</sub>	40°C	6.16 x 0.76 x 1.42	0	0.00	0.00	0.00	0.00	0.00	0.00
Hardwood	Grade B			30	8.12	5.93	11.41	8.02	6.93	6.59
				60	9.14	7.94	11.86	9.76	8.24	7.58
				4200	13.53	13.61	13.61	13.61	13.61	13.61

Table 6.4 Comparison of Model and Experimental Results for Various Wood Pulp Types, Reaction Temperatures, Sliver Sizes, and Mixed Acid Compositions

Pulp Type	Acid	Temp	WPS Size Reaction		Percent Nitrogen						
	Composition		(LxWxH) mm <sup>3</sup>	Time	Experimental	Slow Wetting	Fast Wetting	-	Variable Wett	ing	
					Result	Linear Diffusivity	Linear Diffusivity	Linear Diffusivity	Linear Tortuosity	Exponential Diffusivity	
Kraft	High H <sub>2</sub> SO <sub>4</sub>	40°C	6.06 x 1.77 x 1.10	0	0.00	0.00	0.00	0.00	0.00	0.00	
Hardwood	Grade B			30	6.57	4.34	11.06	6.10	5.55	5.24	
				60	7.26	6.19	11.35	7.45	6.85	6.39	
				4200	13.40	13.61	13.61	13.61	13.61	13.60	
Kraft	High H <sub>2</sub> SO <sub>4</sub>	25°C	6.16 x 0.78 x 1.50	0	0.00	0.00	0.00	0.00	0.00	0.00	
Softwood	Grade B			30	6.90	5.25	11.85	7.42	7.25	7.13	
				60	8.19	7.04	12.31	9.19	8.28	7.96	
				4200	13.46	13.54	13.54	13.54	13.54	13.53	
Kraft	High H <sub>2</sub> SO <sub>4</sub>	25°C	6.21 x 1.64 x 1.31	0	0.00	0.00	0.00	0.00	0.00	0.00	
Softwood	Grade B			30	6.42	3.45	11.81	6.08	5.78	5.82	
				60	6.80	5.07	11.99	6.79	6.67	6.36	
				4200	13.10	13.54	13.54	13.54	13.53	13.53	
Kraft	High H <sub>2</sub> SO <sub>4</sub>	40°C	6.21 x 1.64 x 1.31	0	0.00	0.00	0.00	0.00	0.00	0.00	
Softwood	Grade B			30	7.34	4.78	12.32	6.91	6.76	6.60	
				60	9.00	6.82	12.47	8.42	7.92	7.74	
				4200	13.48	13.61	13.61	13.61	13.61	13.61	
Kraft	High HNO <sub>3</sub>	25°C	6.31 x 1.66 x 1.42	0	0.00	0.00	0.00	0.00	0.00	0.00	
Softwood	Grade A			4200	12.31	12.88	12.88	12.88	12.87	12.87	

Table 6.4 Comparison of Model and Experimental Results for Various Wood Pulp Types, Reaction Temperatures, Sliver Sizes, and Mixed Acid Compositions (Continued)

Pulp Type	Type         Acid         Temp         WPS Size			Reaction	Percent Nitrogen					
	Composition		(LxWxH) mm <sup>3</sup>	Time	Experimental	Slow Wetting	Fast Wetting	i	Variable Wetti	ng
					Result	Linear Diffusivity	Linear Diffusivity	Linear Diffusivity	Linear Diffusivity	Linear Diffusivity
Kraft	High HNO <sub>3</sub>	40°C	6.09 x 1.37 x 1.83	0	0.00	0.00	0.00	0.00	0.00	0.00
Softwood	Grade A			30	7.57	4.93	11.72	8.59	8.48	8.26
				60	8.97	6.82	12.03	9.51	9.21	9.34
				4200	12.47	12.94	12.94	12.94	12.94	12.93
Kraft	High HNO <sub>3</sub>	40°C	6.31 x 1.66 x 1.42	0	0.00	0.00	0.00	0.00	0.00	0.00
Softwood	Grade A			4200	12.37	12.94	12.94	12.94	12.94	12.94
Kraft	High H <sub>2</sub> SO <sub>4</sub>	40°C	6.09 x 1.37 x 1.83	0	0.00	0.00	0.00	0.00	0.00	0.00
Softwood	Grade A			30	6.20	4.72	11.45	7.41	7.38	7.22
				60	8.08	6.29	11.64	9.01	8.24	7.99
				4200	13.00	13.03	13.03	13.03	13.03	13.03
Kraft	High H <sub>2</sub> SO <sub>4</sub>	40°C	6.31 x 1.66 x 1.42	0	0.00	0.00	0.00	0.00	0.00	0.00
Softwood	Grade A			4200	12.77	13.03	13.03	13.03	13.03	13.03
Kraft	High HNO <sub>3</sub>	25°C	6.06 x 0.95 x 1.61	0	0.00	0.00	0.00	0.00	0.00	0.00
Softwood	Grade B			60	10.88	6.72	12.38	9.58	9.21	8.88
				300	12.87	12.78	12.96	12.86	12.05	12.00
				600	13.16	13.12	13.17	13.15	12.95	12.94
				1800	13.42	13.35	13.36	13.35	13.33	13.32
				2400	13.50	13.37	13.37	13.37	13.36	13.36
				4200	13.44	13.38	13.38	13.38	13.38	13.38

Table 6.4 Comparison of Model and Experimental Results for Various Wood Pulp Types, Reaction Temperatures, Sliver Sizes, and Mixed Acid Compositions (Continued)

Pulp Type	Acid	Temp	WPS Size	Reaction			Percent Nit	rogen		
	Composition		(LxWxH) mm <sup>3</sup>	Time	Experimental	Slow Wetting	Fast Wetting	-	Variable Wett	ing
				Result	Linear Diffusivity	Linear Diffusivity	Linear Diffusivity	Linear Diffusivity	Linear Diffusivity	
Kraft	High HNO <sub>3</sub>	25°C	6.16 x 1.76 x 1.44	0	0.00	0.00	0.00	0.00	0.00	0.00
Softwood	Grade B			60	9.97	5.34	12.29	8.23	7.67	7.63
				300	12.03	11.02	12.85	11.88	9.86	10.05
				600	12.54	13.03	13.11	12.97	11.27	11.21
				1800	13.32	13.34	13.35	13.34	13.23	13.19
				2400	13.41	13.37	13.37	13.37	13.27	13.24
				4200	13.42	13.38	13.38	13.38	13.36	13.37
Alt Kraft	High HNO <sub>3</sub>	40°C	6.06 x 1.18 x 1.78	0	0.00	0.00	0.00	0.00	0.00	0.00
Softwood	Grade B			60	11.09	8.51	12.75	11.84	10.74	11.44
				300	12.75	13.03	13.23	13.13	13.13	13.08
				600	13.20	13.35	13.38	13.35	13.34	13.29
				1800	13.51	13.44	13.44	13.44	13.44	13.44
				2400	13.54	13.44	13.44	13.44	13.44	13.44
			4200	13.56	13.44	13.44	13.44	13.44	13.44	

**Table 6.4** Comparison of Model and Experimental Results for Various Wood Pulp Types, Reaction Temperatures, Sliver Sizes, andMixed Acid Compositions (Continued)

Pulp Type	Acid	Temp	WPS Size	WPS Size	WPS Size Rea	Reaction	Percent Nitrogen						
	Composition		(LxWxH) mm <sup>3</sup>	Time	Experimental	Slow Wetting	Fast Wetting	J	Variable Wett	ing			
					Result	Linear Diffusivity	Linear Diffusivity	Linear Diffusivity	Linear Diffusivity	Linear Diffusivity			
Kraft	Alternate	25°C	6.06 x 0.95 x 1.61	0	х	0.00	0.00	0.00	0.00	0.00			
Softwood	Grade A			60	х	5.54	11.30	7.50	7.08	6.69			
				300	х	11.86	12.20	12.02	10.08	9.68			
				600	х	12.48	12.53	12.52	12.09	11.82			
				1800	х	12.74	12.74	12.74	12.68	12.69			
			2400	х	12.75	12.75	12.76	12.74	12.74				
				4200	Х	12.76	12.76	12.76	12.76	12.76			
Kraft	Alternate	40°C	6.16 x 1.76 x 1.44	0	х	0.00	0.00	0.00	0.00	0.00			
Softwood	Grade A			60	х	5.66	11.15	7.09	6.91	6.89			
				300	х	10.71	12.32	11.14	10.07	9.70			
				600	х	12.58	12.72	12.57	11.65	11.02			
				1800	х	12.82	12.82	12.82	12.76	12.77			
				2400	х	12.82	12.82	12.82	12.81	12.81			
			4200	х	12.82	12.82	12.82	12.82	12.82				

**Table 6.4** Comparison of Model and Experimental Results for Various Wood Pulp Types, Reaction Temperatures, Sliver Sizes, andMixed Acid Compositions (Continued)

#### 6.4 Discussion

## 6.4.1 Relevant Findings from Analysis of Diffusion and Swelling

The analysis of swelling of wood pulp slivers in mixed acids (see Chapter 3) demonstrated that the wood pulp slivers tend to swell linearly before reaching a maximum extent of swelling. Given this behavior, a linear relationship was suggested for describing the change in porosity as the sliver swells according to Equation (3.57), which is repeated here as Equation (6.17) for convenience.

$$\phi(t) = \phi(t_{sw}) - \frac{(\phi(t_{sw}) - \phi_o)}{t_{sw}} (t_{sw} - t) u(t_{sw} - t)$$
(6.17)

Using this approach, a time dependent porosity was described for each wood pulp type using the experimentally measured swelling data, where  $\phi_0$  and  $\phi(t_{sw})$  are the porosities in the initial and fully swollen states, and  $t_{sw}$  is the time to reach the maximum extent of swelling. A unit step function, u(t<sub>sw</sub>-t), is used to ensure that the porosity does not continue to increase after the maximum extent of swelling is reached.

An initial approximation to describe the change in diffusivity of mixed acids through the wood pulp sliver structure was developed based on the assumption that the diffusivity changes linearly between the experimentally measured diffusivity values at the initial and swollen state for each material according to Equation (3.52), which is repeated here as Equation (6.18) for convenience.

$$D_{eff}(t) = D_{eff}(t_{sw}) - \frac{\left(D_{eff}(t_{sw}) - D_{eff}(0)\right)}{t_{sw}}(t_{sw} - t)u(t_{sw} - t)$$
(6.18)

Equation (6.18) can be used directly in Equations (6.6)-(6.8) to describe the swelling-dependent diffusion of mixed acids through the wood pulp sliver structure for a given pulp. The effective diffusivities for each direction in the initial and swollen states

were calculated at the selected reaction temperature using an Arrhenius equation with the preexponential factor,  $D_{eff,0}$ , and the activation energy,  $Ea_{diff}$ , calculated using the experimentally measured effective diffusivities for each material, direction, and swelling state at 25°C and 40°C.

$$D_{eff}(T) = D_{eff,0} e^{-Ea_{diff}/RT}$$
(6.19)

As discussed in Chapter 3, a disadvantage of this approach is that it requires diffusion and swelling experiments to be conducted for each new material and reaction temperature combination that is evaluated. In particular, the diffusion experiments require the fabrication of custom frames to maintain the wood pulp sliver at a fixed extent of swelling during the diffusion experiment, making this approach unattractive for screening a wide range of candidate materials. Because of this limitation, generalized models were evaluated that do not rely on experimentally measured diffusion coefficients for mixed acids through the cellulose structure.

# 6.4.2 Generalized Diffusion Models

The generalized models that were evaluated in Chapter 3 either use empirical models that relate the effective diffusivity to the porosity and tortuosity in the wood pulp sliver, or relate the diffusivity of mixed acids through the sliver to the polymer (cellulose) weight fraction in the sliver using free volume theory. The first approach uses Equation (3.53) and empirical relationships between the tortuosity and porosity of a material such as Equations (3.54) and (3.55) to define the effective diffusivity of a penetrant through a porous material. The second approach describes the effective diffusivity in terms of the cellulose weight fraction according to Equation (3.56), where the cellulose weight fraction can also be expressed as a function of the porosity.

In addition, two theoretical relationships that directly correlate the tortuosity factors for porous media with their porosity were considered. These relationships have been evaluated for modeling transport phenomena in electrochemical systems<sup>79</sup> and for quantitatively describing the diffusion coefficient in a variety of porous media<sup>80</sup>. These correlations offer the advantage of enabling the effective diffusivity in porous media to be modeled without the need for experimental measurement of effective diffusion coefficients and fitting of parameters to describe diffusion in these porous materials.

**6.2.4.1 Linear Tortuosity Model.** The linear tortuosity model makes use of an empirical relationship proposed by proposed by Koponen et al.<sup>71</sup> in which the tortuosity is described as a linear function of the porosity according to Equation (3.54). Equations (6.17) and (3.54) can then be substituted into Equation (3.53) to express the effective diffusivity in terms of the known porosity of the wood pulp sliver according to Equation (6.20), where p is a parameter that was determined to be 13.721 for the mixed acid and cellulose system based on the analysis of diffusion and swelling results in Chapter 3.

$$D_{eff} = D_{AB} \frac{\phi(t_{sw}) - \frac{(\phi(t_{sw}) - \phi_o)}{t_{sw}} (t_{sw} - t) u(t_{sw} - t)}{p \left(1 - (\phi(t_{sw}) - \frac{(\phi(t_{sw}) - \phi_o)}{t_{sw}} (t_{sw} - t) u(t_{sw} - t))\right) + 1}$$
(6.20)

Using this approach, the effective diffusivity of mixed acid species through the porous wood pulp sliver is described only as function of the porosity and the binary diffusion coefficient of mixed acid species in water.

**6.4.2.2 Exponential Diffusivity Model**. The exponential diffusivity model utilizes Equation (3.56) where the polymer (cellulose) weight fraction,  $\omega_p$ , is defined in terms of the porosity. If wetting of the sliver precedes swelling of the sliver structure, then the

cellulose weight fraction can be estimated at any time if the porosity of the sliver is known and if the change in mass due to the conversion of cellulose to nitrocellulose is neglected. This assumption appears reasonable given that the fibrous structure of cellulose is preserved at a macroscopic level during nitration, although changes in the fibrillar structure<sup>18</sup> and crystallinity are known to occur. Following this approach, effective diffusivity of mixed acids through the wood pulp sliver structure can be described in terms of  $\phi$ ,  $\rho_{cell}$ , and  $\rho_{acid}$ , the porosity of the sliver and the densities of cellulose and the acid mixture, respectively, using Equation (3.56).

$$D_{eff} = D_o e^{-\beta \frac{(1-\phi)\rho_{cell}}{(1-\phi)\rho_{cell} + (\phi)\rho_{acid}}}$$
(6.21)

A consequence of the form of the exponential diffusivity model is that the effective diffusivity of a solvent through the porous structure tends to the binary diffusion coefficient for the diffusing species as the porosity approaches unity. A final simplification can be made by noting that the diffusivity at infinite dilution,  $D_o$ , is the binary diffusivity of mixed acid species in water and by substituting Equation (6.17), the porosity relationship that was developed in Chapter 3 into Equation (6.21).

$$D_{eff} = D_{AB}e^{-\beta \frac{(1 - (\phi(t_{sw}) - \frac{(\phi(t_{sw}) - \phi_o)}{t_{sw}}(t_{sw} - t)u(t_{sw} - t)))\rho_{cell}}{t_{sw}}(t_{sw} - t)u(t_{sw} - t))\rho_{cell} + (\phi(t_{sw}) - \frac{(\phi(t_{sw}) - \phi_o)}{t_{sw}}(t_{sw} - t)u(t_{sw} - t))\rho_{acid}}}$$
(6.22)

This approach enables estimation of effective diffusivities of mixed acid species through the wood pulp sliver structure with only knowledge of the swelling behavior of the sliver and does not require diffusivities to be measured experimentally.

**6.4.2.3 Millington-Quirk Diffusivity Model**. The Millington-Quirk model describes the tortuosity in a porous material as a function of the porosity according to Equation (6.23).

$$\tau = \phi^{-\frac{1}{3}} \tag{6.23}$$

The effective diffusivity of a fluid through a porous material can thus be described by substituting Equation (6.23) into Equation (3.53) to obtain Equation (6.24)<sup>80</sup>.

$$D_{eff} = D_{AB} \phi^{4/3} \tag{6.24}$$

For the specific wood pulps that have been studied under this effort, a final expression, Equation (6.25), is obtained by substituting Equation (6.17), the time-dependent porosity into Equation (6.24).

$$D_{eff} = D_{AB} \left( \phi(t_{sw}) - \frac{(\phi(t_{sw}) - \phi_o)}{t_{sw}} (t_{sw} - t) u(t_{sw} - t) \right)^{\frac{4}{3}}$$
(6.25)

Using this approach, an equation describing the effective diffusivity only as a function of the time dependent porosity of the wood pulp sliver is obtained.

**6.4.2.4 Bruggeman Diffusivity Model**. Derivation of the expression for the Bruggeman model proceeds in a similar fashion with the tortuosity in a porous material described according to Equation  $(6.26)^{79}$ .

$$\tau = \phi^{-1/2} \tag{6.26}$$

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Substituting Equations (6.26) and (6.17) into Equation (3.53) yields, Equation (6.27), the final form of the effective diffusivity equation for transport of mixed acids through the porous wood pulp sliver structure according to the Bruggeman model.

$$D_{eff} = D_{AB} \left( \phi(t_{sw}) - \frac{(\phi(t_{sw}) - \phi_o)}{t_{sw}} (t_{sw} - t) u(t_{sw} - t) \right)^{3/2}$$
(6.27)

Similar to the expression obtained using the Millington-Quirk correlation, Equation (6.27) describes the effective diffusivity only as a function of the time dependent porosity of the wood pulp sliver.

# 6.4.3 Conditions Evaluated and Simulation Results

A series of initial conditions and diffusion models was evaluated using different pulp types, reaction temperatures, and sliver sizes, and these results were compared with experimental results obtained from lab-scale wood pulp nitration experiments. These simulations were used to compare the transient and steady state nitration behavior of wood pulp slivers for a range of pulps and reaction conditions. The acid to cellulose ratio and reaction temperature were considered in calculating the equilibrium degree of nitration achieved for a given set of reaction conditions, but the models do not include a mechanism to limit the extent of nitration reached after very long reaction times to predict the lower extent of nitration generally observed in large wood pulp slivers. Instead, the diffusion and reaction models predict the same equilibrium degree of nitration as the single cellulose fiber kinetic model for a given acid to cellulose ratio and reaction temperature if afforded sufficient reaction time for acids to diffuse through the sliver and reach equilibrium.

Correlation coefficients (Table 6.5) were calculated for the overall data set for each model and set of initial conditions that were evaluated. To consider the performance of the models at different temperatures and for the different mixed acid compositions that were used, correlation coefficients were also calculated for subgroups grouped by temperature and by the dominant acid species (sulfuric acid or nitric acid) in the mixed acid composition. These results show that the variable penetration initial condition yields a better fit to the experimental data than the slow or fast wetting initial conditions for the

empirical models that were evaluated, but that the generalized models based on the Millington-Quirk and Bruggeman models provide very reasonable estimates under the slow wetting initial condition. The model predictions were slightly better for high temperature and acid compositions. The results also suggest that estimates obtained using empirical diffusivity models provided better estimates of the extent of nitration for mixed acid compositions that were rich in sulfuric acid while estimates obtained using theoretical diffusivity models provided better estimates for mixed acids high in nitric acid. This behavior may be a result of the fact that mixed acid compositions that were high in sulfuric acid were used more extensively in the evaluation of single cellulose fiber kinetics in Chapter 2 and in the evaluation of diffusion of mixed acid species through the porous sliver structure in Chapter 3.

**Table 6.5** Correlation coefficients (overall and by subgroup) for Linear Diffusivity (Lin Diff), Millington-Quirk (M-Q), Bruggeman (Brugg), Linear Tortuosity (Lin Tor), and Exponential Diffusivity (Exp Diff) Models and Initial Conditions Evaluated

Subset	Correlation Coefficient											
	Sl	ow Wettin	g	Fast Wetting	Variab	le Penetr	ration					
	Lin	M-Q	Brugg	Lin Diff	Lin	Lin	Exp					
	Diff				Diff	Tor	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 H <sub>2</sub> SO <sub>4</sub>	0.955	0.982	0.984	0.826	0.994	0.991	0.987					
High HNO <sub>3</sub>	0.938	0.989	0.986	0.962	0.990	0.980	0.979					

The model predictions over the range of reaction conditions that were evaluated suggested that partial wetting of the wood pulp sliver likely occurs upon immersion in the mixed acid and that large slivers may present physical barriers that prevent them from reaching the same uniformity and extent of nitration as cellulose fibers or small slivers. The models predict reasonable degrees of nitration for all of the Grade B compositions that were evaluated but tend to predict degrees of nitration that are slightly higher than the specification limit when using mixed acid compositions that are known to be used in the production of Grade A nitrocellulose. This may be partially because some loss of nitrogen through denitration is known to occur in the nitrocellulose stabilization operations but is also likely influenced by the limited number of single cellulose fiber nitration experiments that were conducted in mixed acid compositions used to produce Grade A nitrocellulose. The influence of the reaction temperature on the rate of nitration achieved in wood pulp slivers agreed with experimental results, primarily due to increased rates of mass transfer at elevated temperatures. A discussion of the results for each set of conditions and diffusion models follows.

**6.4.3.1 Analysis of Initial Conditions**. Simulations were run (Table 6.3) using the linear diffusivity model to evaluate the two extremes for describing wetting of the wood pulp sliver with mixed acids and to consider approaches for modeling the initial uptake of acids into the sliver through appropriate selection of initial conditions. The extreme conditions that were modeled consisted of a very slow wetting initial condition in which the wood pulp sliver initially contained no mixed acid species and a very fast wetting initial condition in which the porous regions of the wood pulp sliver were initially saturated with mixed acids. These conditions can be described by setting the depth of penetration of mixed acid species into the wood pulp sliver structure,  $d_{pen}$ , to zero, or more explicitly by using Equations (6.28)-(6.30) for the case of very slow wetting and Equations (6.31)-(6.33) for the case of very rapid, complete wetting.

In the case of very slow wetting, the void regions of the wood pulp sliver only contain the native moisture content of the cellulose, [H<sub>2</sub>O]<sub>0</sub>, and contain no nitric acid or sulfuric acid.

$$[H_2O](x, y, z, 0) = [H_2O]_0$$
(6.28)

$$[HNO_3](x, y, z, 0) = 0 (6.29)$$

$$[H_2SO_4](x, y, z, 0) = 0 (6.30)$$

Conversely, in the case of very rapid, complete wetting of the wood pulp sliver with mixed acids, the void regions of the wood pulp sliver are saturated with mixed acid species at the same concentrations as the water, nitric acid, and sulfuric acid in the bulk region outside of the slivers ( $[H_2O]_L$ ,  $[HNO_3]_L$ , and  $[H_2SO_4]_L$ ). The overall moisture content in the wood pulp sliver in this case is the sum of the native moisture content in the cellulose and the mixed acid moisture content that fills the void regions in the wood pulp sliver according to Equation (6.31).

$$[H_2O](x, y, z, 0) = \phi_i [H_2O]_L + [H_2O]_0$$
(6.31)

$$[HNO_3](x, y, z, 0) = \phi_i [HNO_3]_L$$
(6.32)

$$[H_2SO_4](x, y, z, 0) = \phi_i [H_2SO_4]_L$$
(6.33)

It was noted that neither of these sets of initial conditions provided a suitable prediction of the early nitration kinetics for machine-cut wood pulp slivers for the empirical models that were evaluated. The models that used the slow wetting initial condition consistently underestimated the degree of nitration by an average of 2.2% nitrogen after a reaction time of 30 seconds and 2.1% nitrogen after a reaction time of 60 seconds. In contrast, the models that used the very rapid, complete wetting initial condition overestimated the degree of nitration by an average of 4.9% nitrogen after a reaction time

of 30 seconds and 3.5% nitrogen after a reaction time of 60 seconds. The error in the predicted degree of nitration falls to less than 0.5% after a reaction time of 300 seconds for both models.

The calculated errors in the nitrogen percentage that are on the order of 2% to 5% are very large differences in the extent of nitration given that nitrocellulose with a degree of substitution of one contains 6.67% nitrogen, and nitrocellulose with a degree of substitution of two contains 11.11% nitrogen. For this reason, both the very slow wetting and rapid, complete wetting initial conditions yield relatively poor estimates of the initial rates of reaction for wood pulp slivers. This suggests that wood pulp slivers are partially wetted upon immersion in mixed nitrating acid, but that complete and rapid wetting of the slivers does not occur. Given this observation, the initial condition characterized by partial penetration of mixed acids into the wood pulp sliver structure was further evaluated.

Simulations were run for the three empirical diffusion models described by Equations (6.14)-(6.16) using the partial wetting approach described by Equation (5.4), and each set of simulated data was compared with the experimental results obtained from lab-scale nitration experiments. A full listing of the results comparing simulation predictions with the lab-scale nitration experimental data for each wood pulp type, sliver size, temperature, and reaction time is included in Table 6.3. As expected, all three diffusion models continued to show good agreement with the experimentally measured equilibrium degrees of nitration, but the results for the transient nitration kinetics were also greatly improved.

Although the Millington-Quirk and Bruggeman models did not exhibit very good agreement with the experimentally measured effective diffusivities ( $R^2 \approx 0.7$ ), wood pulp

sliver nitration models that were run using these diffusion models and the slow wetting initial condition yielded good agreement ( $R^2$ =0.985 for both models) with the results of wood pulp sliver nitration experiments. In contrast, both models predicted rates of nitration that were significantly higher than experimental results when using the variable wetting and fast wetting initial conditions. Given this result, the use of these theoretical models for describing the rate of nitration of dense cellulose materials under the slow wetting initial condition is further considered.

6.4.3.2 Linear Diffusivity Model. The linear diffusivity model when coupled with the variable wetting initial condition provided excellent agreement with the experimental results, yielding a correlation coefficient of 0.992 for the range of wood pulps, sliver sizes, acid compositions, and temperatures that were evaluated. This model used the experimentally measured diffusion coefficients directly for each of the wood pulps that were evaluated by applying the assumption that the effective diffusivity of mixed acid species through the wood pulp sliver varies linearly as a function of porosity between the effective diffusivities measured for the unswollen and completely swollen states. Given that this model applies the fewest assumptions and generalizations of the models that were evaluated, it is to be expected that this model would provide the best fit to the experimental data. For this reason, the linear diffusivity model was also the model that was used assess suitability of initial conditions for simulating the nitration of wood pulp slivers. The analysis of correlation coefficients confirms predictive capability of the linear diffusivity model, as the combination of this model and the variable wetting initial condition provided the best fit to the experimental data of the models evaluated.

Some interesting trends are observed in analyzing the correlation coefficients for the reaction temperature and mixed acid composition subgroups. The simulations that were run using the fast wetting initial condition for the mixed acid compositions that were rich in nitric acid yielded a much higher correlation coefficient (0.962) than for any of the other subgroups evaluated under the fast wetting initial condition. This might suggest that acid compositions that are rich in nitric acid are able to penetrate the porous regions of the wood pulp sliver structure more efficiently upon immersion in mixed acids. This may be one possible explanation for the behavior reported by Urbanski<sup>1</sup> suggesting that the rate of reaction of cellulose in mixtures of nitric acid, sulfuric acid, and water decreases with increasing concentration of sulfuric acid. This general behavior was not observed over the range of acid compositions and cellulose forms that were evaluated, but increased penetration of mixed acids rich in nitric acid into the cellulose structure of dense cellulose materials could provide an explanation for this reported behavior.

While the linear diffusivity model demonstrated very good capability for predicting the rate of nitration of dense cellulose materials, it has some disadvantages that may prevent it from seeing widespread use a production aid. One disadvantage of the linear diffusivity model is that it requires diffusion experiments (with fabrication of custom frames) and swelling experiments to be conducted for each new wood pulp type that is evaluated. For NC manufacturing processes that tend to restrict the cellulose feedstocks to only a few qualified sources, the linear diffusivity model may be the most appropriate model for conducting process analysis and optimization studies because frequent swelling and diffusion experiments would not be required. When new sources or cellulose are frequently evaluated or existing sources of cellulose are not maintained within tight specification limits, the amount of experimental data required for this model may be prohibitive.

**6.4.3.3 Linear Tortuosity Model**. The linear tortuosity model when coupled with the variable wetting initial condition also provided good agreement with the experimental results, yielding a correlation coefficient of 0.986 for the reaction conditions that were evaluated. This model combines the estimated diffusion coefficient for mixed acid species in water (see Chapter 3) with the time dependent porosity and an empirical function describing the tortuosity as a linear function of the porosity to describe the effective diffusivity of mixed acid species through the wood pulp sliver structure according to Equation (6.20). As a result, this model is more general in form than the linear diffusivity model because it does not require direct measurement of the effective diffusivities in the initial and swollen states for each wood pulp that is evaluated. As was observed for the linear diffusivity model, the linear tortuosity model generally provided better predictions of the degree of nitration achieved for mixed acid compositions that were high in sulfuric acid, likely due to the fact that these were the primary acid compositions used to generate the cellulose fiber kinetic data and diffusion data.

The generalized nature of the linear tortuosity model offers some advantages over the linear diffusivity model. In addition to the sheeted wood pulp properties and wood pulp sliver dimensions, the linear tortuosity model requires only a single swelling experiment to measure the characteristic time and extent of swelling for a given wood pulp. Because of this, it is only necessary to conduct a swelling experiment to enable calculation of effective diffusivities using the initial porosity of the wood pulp according to Equation (5.5), which can be calculated using data typically found on a manufacturer's certificate of analysis. The model provided a better fit to the experimental data at 40°C ( $R^2 = 0.991$ ) than at 25°C ( $R^2 = 0.982$ ) and also provided a better fit to the experimental data generated using acid compositions that were high in sulfuric acid ( $R^2 = 0.991$ ) than to the data for the acids that were high in nitric acid ( $R^2 = 0.980$ ) but reasonable estimates for the rate and extent of nitration were obtained for all cases that were evaluated. As a result, this model provides a useful tool for conducting process evaluations for new wood pulps without the need for extensive testing.

**6.4.3.4 Exponential Diffusivity Model**. The exponential diffusivity model combines the variable wetting initial condition with an exponential relationship describing the dependence on the effective diffusivity on the porosity of the sliver that is based on free volume theory according to Equation (6.22). This model also provided good agreement with the experimental results, yielding a correlation coefficient of 0.984 for the range of pulp types, sliver sizes, and reaction conditions that were evaluated. The form of the exponential diffusivity model is also more general than the linear diffusivity model and requires only knowledge of the time dependent porosity of the wood pulp sliver to describe the effective diffusivity of mixed acids through the wood pulp sliver as the sliver swells in the mixed acid composition. The behavior of the exponential diffusivity model was similar to that of the linear tortuosity model, as it generally yielded better predictions of the degree of nitration achieved for mixed acid compositions that were high in sulfuric acid and for reactions conducted at 40°C.

Similar to the linear tortuosity diffusion model, the generalized nature of the exponential diffusivity model provides many of the same benefits as the linear tortuosity diffusion model due to the fact that it does not require experimental measurement of

diffusion coefficients to enable evaluation of new materials. Because of the exponential form of the exponential diffusivity model, it exhibits the added benefit of being more suitable for describing diffusion in highly porous cellulose structures, as the effective diffusivity approaches the binary diffusion coefficient as the porosity of the sliver approaches unity. The linear tortuosity diffusion model also requires that the effective diffusivity approaches the binary diffusion coefficient as the porosity approaches unity but in this case the effective diffusivity changes as a linear function of the porosity. Like the linear tortuosity model, the exponential diffusivity model requires only the pulp characteristics and the results of a single swelling experiment to generate predicted nitration kinetics for any given wood pulp type. The capability of these generalized models (linear tortuosity model and exponential diffusivity model) could be further improved by developing a more comprehensive set of diffusion coefficients for the aqueous nitric acid and sulfuric acid systems over a range of temperatures and concentrations.

**6.4.3.5** Millington-Quirk Diffusivity Model. The theoretical tortuosity models represent the most general class of models that were evaluated under this effort as they do not require any regression of experimental data to generate effective diffusivity estimates. Wood pulp sliver nitration models that were run using the Millington-Quirk diffusion model when coupled with the slow wetting initial condition provided good agreement with the experimental results, yielding a correlation coefficient of 0.985 for the range of wood pulps, sliver sizes, acid compositions, and temperatures that were evaluated. This result suggests a nonlinear relationship between the effective diffusivity of mixed acid through the wood pulp sliver and the time-dependent extent of swelling in the wood pulp sliver. Wood pulp sliver nitration model results obtained using the Millington-Quirk diffusion
model differed from the results obtained using the empirical diffusion models because they provided better agreement with experimental results for the transient experiments conducted with mixed acid compositions that were rich in nitric acid. An analysis of residuals suggests that this model tends to predict extents of nitration that average 0.21% higher than experimental results, indicating that the accuracy of these models would not benefit from the use of the variable wetting initial condition.

The wood pulp sliver nitration model using the Millington-Quirk diffusion model is the most general of the models that were evaluated because it does not require the use of any empirical relationships to describe the kinetics of nitration for new cellulose materials. This model only requires the results of a swelling experiment to measure the rate and extent of swelling of candidate wood pulp materials in mixed acids to model the observed rate of nitration for these materials. Like the empirical linear tortuosity and exponential diffusivity models, the effective diffusion coefficient predicted by the Millington-Quirk diffusion model approaches the binary diffusion coefficient as the porosity of the sliver approaches unity. Similar to the other generalized models that were evaluated under this effort, the wood pulp sliver model that uses the Millington-Quirk diffusion coefficients for the aqueous nitric acid and sulfuric acid systems over a range of temperatures and concentrations of interest for industrial nitrocellulose manufacturing processes.

**6.4.3.6 Bruggeman Diffusivity Model**. Wood pulp sliver nitration models that were run using the Bruggeman diffusion model when coupled with the slow wetting initial condition also showed good ( $R^2$ =0.985) agreement with the experimental results from wood pulp sliver nitration experiments. These models are characterized by the same advantages and

behavior as models that were run using the Millington-Quirk diffusion model. Nitration results generated by both models differed from results generated using nitration models that used the empirical diffusion models by providing better agreement with experimental results for the transient experiments conducted with mixed acid compositions that were rich in nitric acid. An analysis of residuals suggests that the wood pulp sliver nitration model that utilizes the Bruggeman diffusion model overestimates the extent of nitration by 0.10% nitrogen when compared to experimental results. This also confirms that the variable wetting initial condition is not required to predict transient nitration kinetics and suggests less bias with respect to the experimental data when compared to results generated using the Millington-Quirk diffusion model.

The wood pulp sliver nitration model using the Bruggeman diffusion model shares the generalized nature, limiting behavior as the porosity approaches unity, and required material property data of the nitration model that uses the Millington-Quick diffusion model. Because this model uses the pure component binary diffusion for the substances diffusing through the porous material, this model could also be improved by developing a more comprehensive set of diffusion coefficients for the aqueous nitric acid and sulfuric acid systems.

# 6.4.4 General Observations and Data Limitations

All three models that were evaluated using the variable wetting initial condition exhibited very good agreement with the experimental results. The generalized models provide the additional benefit of being suitable for evaluating new wood pulp materials or processing conditions without the need for time consuming diffusion cell experiments that require the fabrication of custom hardware. While the models appear to be sufficient for simulating the observed kinetics of nitration for a broad range of wood pulp slivers and reaction conditions, it was noted that these models are not capable of describing phenomena responsible for incomplete nitration of large wood pulp slivers.

The characteristic diffusion times of the large wood pulp slivers that were evaluated in the lab scale nitration experiments were still small enough that the wood pulp slivers should have reached equilibrium within the 70 minute reaction time used in the nitration experiments. Two possible explanations for this incomplete nitration are that denitration occurred during stabilization of the large wood pulp slivers, or that changes in the chemical nature of the cellulose (as it was converted to nitrocellulose) inhibited the diffusion of mixed acids into the center of the wood pulp sliver. It is possible to evaluate the latter possibility by nitrating large slivers in mixed acids then immediately removing the slivers from the nitrating acid mixture and dissolving them in acetone or other suitable solvent to look for evidence of an unreacted (insoluble) core at the center of the sliver; however this was beyond the scope of the present effort.

The data used in the regression that was conducted to generate parameters for the models that were evaluated was primarily generated using mixed acid compositions that were high in sulfuric acid. Given this, it should be confirmed that similar swelling and diffusion behavior is observed for mixed acid compositions that are high in nitric acid. The model was also limited by the available published binary diffusion data for aqueous nitric acid and aqueous sulfuric acid. Limited binary diffusion data was available for the temperature and concentration range of interest for cellulose nitration, potentially restricting the accuracy of the models. As a result, extrapolation was needed to predict the diffusion coefficient of the nitric acid-water system at 40°C.

# 6.4.5 Application of Models to Analyze Reaction Times and Solubility for Various Slivers Sizes and Mixed Acid Compositions

The utility of these models can be demonstrated by considering the uniformity of nitration of nitrocellulose, which is evaluated by measuring its solubility in acetone and etheralcohol solvents per MIL-DTL-244B<sup>11</sup>. Nitrocellulose containing less than 10% nitrogen is generally insoluble in both acetone and ether-alcohol solvents<sup>1</sup>, while nitrocellulose containing greater than 13% nitrogen is also insoluble in ether-alcohol mixtures<sup>1</sup>. Because of this, the solubility of nitrocellulose is used as a practical method for measuring the uniformity of nitration in nitrocellulose, an important quality characteristic for propellant blending and formulation processes.

Simulations can be used to help to determine the maximum size of wood pulp sliver that can be nitrated without exceeding solubility specification limits for a given residence time distribution and wood pulp type by considering the extent of reaction at different regions in the wood pulp sliver. These simulations can also be run to predict the degree of nitration achieved and the amount of acetone or ether-alcohol insoluble material remaining after each stage in the industrial nitration reactor train. To demonstrate this application, two sets of reaction conditions were evaluated to compare results for small and large wood pulp slivers.

Simulations were run for large (1.64mm × 6.21mm × 1.32mm) and small (0.8mm × 6.21mm × 1.44mm) wood pulp slivers using an acid to cellulose ratio of 30:1. Two reaction conditions were evaluated: a Grade B mixed acid composition rich in sulfuric acid (37.0% HNO<sub>3</sub>, 54.6% H<sub>2</sub>SO<sub>4</sub>, and 8.4% H<sub>2</sub>O) at 25°C and a Grade A mixed acid composition rich in sulfuric acid (30.18% HNO<sub>3</sub>, 54.67% H<sub>2</sub>SO<sub>4</sub>, and 15.15% H<sub>2</sub>O) at

 $35^{\circ}$ C, where the acid compositions are expressed in mass percentages. The linear diffusivity model was used for the first set of reaction conditions and the exponential diffusivity model was used for the second set of reaction conditions. The percent insoluble material (mass percent) was calculated by numerically integrating the concentration of hydroxyl and nitrate ester groups in the wood pulp sliver over the total sliver volume and over the region of the sliver containing 10% or less nitrogen, and multiplying by the molecular weights of cellulose and nitrocellulose, where the nitrogen mass fraction,  $w_N$ , is calculated using Equation (6.34).

$$w_{N}(x, y, z, t) = \frac{3 \times 14 \times [ONO_{2}](x, y, z, t)}{162 \times [OH](x, y, z, t) + 297 \times [ONO_{2}](x, y, z, t)}$$
(6.34)

For the simulation that was performed using the Grade B composition rich in sulfuric acid at 25°C, the behavior of the system was evaluated for a reaction time of five minutes, which is average residence time of the first continuous stirred tank reactor (CSTR) used in the industrial nitration process. After a reaction time of five minutes, the large wood pulp sliver (Figure 6.3) exhibits 24.16% residual insoluble material while the small wood pulp sliver exhibits only 4.27% residual insoluble material.



**Figure 6.3** Acetone and ether-alcohol insoluble regions of a 1.64mm × 6.21mm × 1.32mm sulfite-pulped softwood wood pulp sliver showing 10% nitrogen and unreacted surfaces after a reaction time of 5 minutes at 25°C in a Grade B mixed acid composition using the linear diffusivity model and variable wetting initial condition.

This result is important because industrial nitrocellulose manufacturing processes generally consist of either a series of continuous stirred tank reactors or a single continuous stirred tank reactor followed by one or more reactors that emulate plug flow with radial mixing only. In the former case, the material produced by the process will always exhibit a characteristic residence time distribution, and in the latter case the mixing is likely less efficient in the reactor sections that emulate plug flow. In both cases, models that can predict the effect of residence times in different sections of the reactor train can assist process engineers in selecting optimal processing conditions and wood pulp sliver sizes.

The observed rate of reaction is known to be lower in mixed acid compositions used in the production of Grade A nitrocellulose (see Chapter 4). For this reason, simulations were also run to evaluate the amount of residual insoluble material remaining both small and large wood pulp slivers after a reaction time of 5 minutes at a slightly elevated temperature of 35°C. After a reaction time of five minutes, the large wood pulp sliver contains 33.67% residual insoluble material while the small wood pulp sliver still contains 12.03% residual insoluble material. These estimated amounts of residual insoluble material in the wood pulp slivers exiting the first CSTR of the industrial nitration process are considerably higher than were observed for the nitration of wood pulp sliver in the Grade B mixed acid composition.

A reaction time of 10 minutes was also evaluated for the large sliver to estimate the amount of unreacted cellulose remaining in the wood pulp sliver after the material exits the second CSTR in the multiple CSTR process or after an additional 5 minutes of processing in the pseudo plug flow reactor which tightly controls residence time but may exhibit less efficient mixing than the CSTR process. Even after a reaction time of 10 minutes at 35°C, the large wood pulp sliver still contains 15.28% residual insoluble material (Figure 6.4), suggesting that a much more significant fraction of the overall reaction occurs in the secondary nitration reactors of the industrial nitration process for the lower nitrated grades of nitrocellulose. The effect of reaction temperature is also evident, as the large wood pulp sliver still contains 30.00% residual insoluble material after a reaction time of 10 minutes when reacted at 25°C using the same sliver size in the Grade A mixed acid composition.



**Figure 6.4** Acetone and ether-alcohol insoluble regions of a 1.64mm × 6.21mm × 1.32mm kraft-pulped softwood sliver showing 10% nitrogen and unreacted surfaces after 10 minutes at 35°C in a Grade A mixed acid composition using the exponential diffusivity model and variable wetting initial condition.

These results are significant because they demonstrate the challenges associated with producing lower nitrated nitrocellulose products using dense cellulose materials. Because the acid compositions used in the producing of Grade A nitrocellulose, are more dilute than the acid compositions used in the production of Grade B nitrocellulose, the rate of diffusion of mixed acids into the wood pulp sliver is slower. In addition, the driving force for diffusion of water produced during the conversion of hydroxyl groups to nitrate ester groups is also less given the higher concentration of water in the surrounding bulk mixed acid. Because of these considerations, it is likely that smaller sliver sizes are required to consistently meet solubility and nitrogen content when producing Grade A nitrocellulose using dense cellulose materials. Higher reaction temperatures are also advantageous in the production of Grade A nitrocellulose because of the increased rate of mass transfer with increasing temperature.

#### 6.5 Findings and Recommendations

A range of diffusion models and initial conditions were considered to evaluate the ability of models combining mass transfer and chemical reaction to describe the reaction of wood pulp slivers in the mixed acid compositions employed in the production of nitrocellulose. These models generally yielded excellent agreement with experimental data ( $R^2 > 0.98$ ) despite some limitations in the underlying data used to construct the models. Even though these models demonstrated very good accuracy when compared to experimental data, they could be further improved by expanding the set of experimental diffusion and kinetic data that was used to establish reaction kinetic models and generalized diffusion models describing mass transfer of mixed acids through the porous wood pulp sliver structure.

The implementation of generalized binary diffusion models and multicomponent diffusion models was limited by the availability of binary diffusion data for the mixed acid species over the range of temperatures and concentrations that occur during the nitration of wood pulp slivers. An extensive set of binary diffusion data for concentrated aqueous nitric acid systems at elevated temperatures was not available, requiring extrapolation to estimate binary diffusion coefficients for aqueous nitric acid at 40°C. This was discussed in the evaluation of generalized diffusion models in Chapter 3, but it is also relevant here as it may partially explain some of the error observed in estimating the observed rates of nitration for mixed acid compositions that are rich in nitric acid.

Swelling and diffusion experiments could also be conducted with a number of mixed acid compositions to ensure that the relative rates of diffusion and relaxation are similar for mixed acid compositions that are rich in nitric acid and for mixed acid compositions that are rich in sulfuric acid. A broader range of wood pulps at multiple degrees of swelling could also be evaluated to better assess these models; however, this was beyond the scope of the current effort.

## **6.6 Conclusions**

A model has been developed to describe the reaction kinetic behavior of dense cellulose materials used in the industrial manufacture of military grade nitrocellulose. This model considers the effects of diffusional mass transfer and chemical reaction using an unsteady three-dimensional partial differential equation to describe the nitration of slivers cut from sheeted wood pulp in mixtures of nitric acid, sulfuric acid, and water. The influences of swelling, multicomponent diffusion, and the wood pulp sliver structure were considered in developing a set of simplifying assumptions for modeling this complex, multiphase reaction. Relationships between the wood pulp sliver porosity and the corresponding effective diffusivity were evaluated to develop a generalized form of the wood pulp sliver nitration model that does not require experimental measurement of effective diffusion coefficients to predict the nitration kinetics for a given wood pulp.

A range of initial conditions was evaluated to consider wetting of the wood pulp sliver with mixed acids, and wood pulp sliver nitration simulations were run using boundary conditions representing ideal mixing conditions in the nitration reactor. An analysis of initial conditions intended to represent very slow wetting and very fast, complete wetting of the wood pulp sliver upon immersion in mixed acids suggested that rapid, partial wetting of the wood pulp sliver occurs during the nitration of machine-cut wood pulp slivers used in the industrial nitration process. This observation is consistent with the structural analysis of machine cut wood pulp slivers (Chapter 5) that identified interstices, or open regions, in the wood pulp sliver that are generated during machine cutting of sheeted pulps. The empirical relationship that was used to describe the sliver porosity as a function of the characteristic swelling time for a given pulp was used to define a variable wetting initial condition describing rapid, partial wetting of the wood pulp sliver with mixed acids.

Generalized models were proposed that only require sheet properties, wood pulp sliver measurements, and the results of a simple swelling experiment to define "variable wetting" initial conditions and to estimate the observed rates of reaction for new cellulose materials under a given set of reaction conditions. These models can produce good estimates of the required residence times and residual insoluble materials for various reaction conditions without the need for extensive experimentation. Other generalized models based on theoretical correlations between the tortuosity and porosity in porous materials demonstrated reasonable estimates of the transient nitration behavior of wood pulp slivers without the need to consider structural features introduced into the sliver during cutting and their corresponding influence on wetting of the sliver with mixed acids.

Simulations were run to demonstrate the utility of the wood pulp sliver nitration model for evaluating the effects of residence time distributions on the uniformity of nitration, or solubility, of the resulting nitrocellulose. Simulated cases also demonstrated the importance of the size of the wood pulp slivers and the mixing effectiveness in the initial continuous stirred tank reactor used in the industrial nitrocellulose manufacturing process for achieving the desired extent of nitration throughout the wood pulp sliver volume. Finally, a comparison of the rates of nitration for large and small wood pulp slivers with mixed acids used in the production of Grade A and Grade B nitrocellulose demonstrated the importance of the wood pulp sliver size and reaction temperature on the extent and uniformity of nitration, particularly for the lower nitrogen content grades of nitrocellulose.

#### **CHAPTER 7**

# FINITE ELEMENT METHOD MODELING OF WOOD PULP SLIVER NITRATION

### 7.1 Introduction

Computational fluid dynamic (CFD) simulation packages are a useful tool for analyzing complex, multiphase, reactive flows and can be used to provide insight into the phenomena occurring in the nitration reactors used in the production of nitrocellulose from dense cellulose materials. These tools have been used to model similar applications including mixing conditions for multiphase systems in ducts<sup>81</sup> or stirred tanks<sup>82,83</sup> and convective flow in porous, packed beds<sup>84,85</sup>. The finite element method solvers that are implemented in these CFD packages are well suited for modeling reactive flows in porous materials and can be used to develop models describing multicomponent diffusion and chemical reaction during the nitration of wood pulp slivers in mixed acids. Using these techniques, it is possible to model the diffusion of mixed acid species through a structural representation of a porous wood pulp sliver and the subsequent conversion of hydroxyl to nitrate ester groups to describe the observed rate of nitration for industrially relevant cellulose raw materials.

# 7.1.1 Background

Chapters 2-6 established that the nitration of cellulose cut from sheeted pulp can be considered as a complex, multiphase reaction characterized by diffusion of mixtures of nitric acid, sulfuric acid, and water through a dense, cellulose structure followed by rapid, reversible conversion of hydroxyl groups to nitrate ester groups within the fibrillar structure of the cellulose fiber. This reaction is preceded by the dissociation of the mixed acids to ionic species including the nitronium ion and is accompanied by simultaneous swelling of the wood pulp sliver as mixed acid species penetrate the sliver structure. Because diffusive mass transfer and swelling occur on similar timescales, the effective diffusivity of mixed acid species through the wood pulp sliver structure changes as a function of the extent of swelling<sup>50</sup> during the nitration of dense cellulose materials. Empirical relationships and theoretical diffusion models were evaluated to consider the influence of swelling on the diffusion of mixed acids in the wood pulp sliver, and structural analysis of machine-cut wood pulp slivers was performed to establish initial conditions describing wetting that occurs upon immersion of these wood pulp slivers in mixed acids.

Previous models describing the rate of nitration of cellulose materials have either focused on the rate of nitration of cellulose fibers<sup>13,16</sup>, used continuous mixtures approaches<sup>14</sup> that did not differentiate between kinetic and mass transfer limitations, or have only modeled mass transfer within the fiber and the molecular weight distributions in the cellulose fiber<sup>19</sup>. It has also been previously shown<sup>50</sup> that generalized models that approximate the wood pulp sliver as a homogeneous structure using properties of the wood pulp are capable of providing good predictions of the rate of nitration for dense cellulose materials, but these models do not account for attributes that may result in decreased reactivity in large wood pulp slivers.

Other methods have been considered for the general class of problems involving diffusion and heterogeneous reaction in porous materials including upscaling boundary value problems using volume averaging methods for the study of porous catalysts exhibiting Thiele moduli (ratio of rate of surface reaction to rate of diffusion) approaching unity<sup>86</sup> as an alternative to direct numerical solution for these problems. One limitation of

this approach for the present application is the fact that the pores are assumed to be homogeneously distributed over the catalyst volume with constant pore size whereas swelling and significant porosity size distributions are known to exist in wood pulp slivers. In addition, the reactive sites in the dense cellulose structure are consumed in the resulting nitration reaction, necessitating a different approach than the nondimensionalized solution approaches developed to describe mass transfer and chemical reaction in porous catalyst particles.

# 7.1.2 Application of Porous Media Models and Finite Element Methods to Describe Wood Pulp Sliver Nitration Dynamics

Under the present effort, the development of models capable of describing multicomponent diffusion and chemical reaction in porous media has been undertaken. Such models can provide additional insight into the influence of the wood pulp sliver structure and can more accurately describe the diffusion of mixed acid species into the wood pulp sliver and the diffusion of water formed by the net nitration reaction out of the wood pulp sliver. By evaluating preliminary models that implement this capability, a framework can be established to conduct more extensive evaluations of the influence of multiple diffusing species and highly dense and porous regions in the wood pulp sliver.

Functionality can be progressively implemented in models describing the nitration of wood pulp slivers in mixed acids to incrementally improve the capability and sophistication of these models. Preliminary analyses can be conducted by modeling multicomponent diffusion in a homogeneous wood pulp sliver structure. Porous media models can be developed to introduce variable diffusion coefficients and swelling dynamics in the wood pulp sliver nitration model. Structural models can be refined to define distributions of porous regions in the wood pulp sliver and to introduce features including fissures and void regions that promote mass transfer in the wood pulp sliver structure. As a proof of concept for this approach, the objective of this effort is to implement the findings of the previous chapters in finite element solvers to describe phenomena occurring during the nitration of wood pulp slivers in mixed acids and to compare the results of these simulations with experimental results.

## 7.2 Materials and Methods

### 7.2.1 Reaction Conditions Evaluated

Models were developed to simulate the reaction conditions listed in Table 7.1. These conditions include evaluation of two wood pulp types, two sliver sizes, three mixed acid compositions, and three temperatures to represent the range of conditions that were evaluated during the lab scale nitration experiments discussed in Chapter 4. These models used the same wood pulp characteristics, mixed acid compositions, and temperatures as were used in the lab scale nitration experiments that were conducted with wood pulp slivers to enable comparison of model predictions with experimental results. All simulations were run using an acid to cellulose ratio of 30:1 (mass basis) and 5% moisture content for the wood pulp.

Source	Size	Acid	Temperature	
		Composition		
Sulfite	6.22mm x 0.83mm x 1.44mm	37.12% HNO3	25°C	
Softwood		55.24% H <sub>2</sub> SO <sub>4</sub>		
		7.64% H <sub>2</sub> O		
Sulfite	6.31mm x 1.62mm x 1.32mm	37.12% HNO <sub>3</sub>	25°C	
Softwood		55.24% H <sub>2</sub> SO <sub>4</sub>		
		7.64% H <sub>2</sub> O		
Kraft	6.31mm x 1.66mm x 1.42mm	54.86% HNO3	25°C	
Softwood		37.24% H <sub>2</sub> SO <sub>4</sub>		
		7.90% H <sub>2</sub> O		
Kraft	6.06mm x 0.95mm x 1.61mm	54.86% HNO3	25°C	
Softwood		37.24% H <sub>2</sub> SO <sub>4</sub>		
		7.90% H <sub>2</sub> O		
Kraft	6.21mm x 0.80mm x 1.44mm	30.18% HNO <sub>3</sub>	30°C	
Softwood		54.67% H <sub>2</sub> SO <sub>4</sub>		
		15.15% H <sub>2</sub> O		
Kraft	6.21mm x 1.64mm x 1.32mm	30.18% HNO <sub>3</sub>	30°C	
Softwood		54.67% H <sub>2</sub> SO <sub>4</sub>		
		15.15% H <sub>2</sub> O		

Table 7.1 Reaction Conditions Simulated Using Wood Pulp Sliver Nitration Model

Because complete structural analyses were not available for all these wood pulp sliver configurations, the models were only run for select conditions in Table 7.1 to evaluate the overall improvement in the capability of the model associated with increasing complexity.

# 7.2.2 Approaches for Considering Dissociation of Nitric Acid to the Nitronium Ion

Two approaches were used to model the dissociation of mixed acid species to the nitronium ion and other ionic species. The first approach consisted of a simplified diffusion approach that considered nitric acid as the diffusing species and applied a constant dissociation percentage calculated using the equilibrium model proposed by Albright et al.<sup>26</sup> such that a fixed percent of the nitric acid at any point in the system was considered to be available in the form of the nitronium ion. Similarly, concentration of the hydronium ion was

calculated for the acid mixture that was used and it was assumed that the surface concentration of the hydronium ion remained constant during the reaction. It was also assumed that all water formed during the net nitration reaction was immediately converted to hydronium ion through reaction with available sulfuric acid. In this way, only the dissociation of nitric acid and water (ionized to the hydronium) ion were considered as dissociating species with a constant fraction of the nitric acid available as nitronium ion. The concentrations of products of acid dissociation were not modeled explicitly using this simplified approach.

The second approach considered complete dissociation of mixed acid species to ionic species using the set of dissociation reactions and rate constants proposed by Albright et al.<sup>26</sup> This approach utilized Equations (2.50)-(2.55), applying only the assumption that the rate of the dissociation reactions was an order of magnitude faster than the cellulose nitration reaction. This improved implementation of the acid dissociation model enabled dynamic calculation of mixed acid species concentrations at any point in the reacting mixture as nitric acid was consumed and water was generated by the net nitration reaction. While this model was able to predict the concentrations of ionic species in the reacting mixture, it was much more computationally demanding and prone to numerical errors.

### 7.2.3 Model Complexity

Models were developed by incrementally adding functionality to describe the various phenomena that occur during the nitration of cellulose cut from sheeted wood pulp in mixtures of nitric acid, sulfuric acid, and water (Table 7.2).

Functionality	Homogeneous Models		Porous Models		
	Simple	Improved	Simple	Improved	
<b>Chemical Reaction</b>	х	Х	Х	x	
Multicomponent Diffusion	Х	X	Х	X	
Dynamic Acid Dissociation		X		X	
Reaction Rate Scaling		X	х	X	
Variable Diffusivity				X	
Swelling				X	

**Table 7.2** Incremental Approach for Implementing Model Complexity to Describe the

 Nitration of Wood Pulp Slivers in Mixed Acids

This approach was used to evaluate each level of complexity in the models by comparing model predictions with experimental results to determine whether increases in the accuracy and capability of these models justify the associated increases in computational complexity. This is particularly true because the most complex of the models that were evaluated are also very specific to the wood pulp and reaction conditions evaluated. Given this, it may be practical to conduct general evaluations using the simplistic models and to only conduct focused analyses to specific problems in the manufacturing process using the more complex models. Finally, simplifying assumptions were developed to significantly improve computation time and model convergence without adversely affecting the predictive capability of the models.

## 7.2.4 Structural Representation of Wood Pulp Slivers

Two structural representations of wood pulp slivers were evaluated. The first representation consisted of a homogeneous, solid rectangular parallelepiped with the cellulose hydroxyl groups uniformly distributed throughout the wood pulp sliver volume,

as described in Chapter 6. The second representation consisted of a porous, rectangular parallelepiped, again with the hydroxyl groups uniformly distributed throughout the wood pulp sliver volume. The porosity in this second configuration was used to consider theoretical diffusion models and to simulate the swelling, or time-dependent porosity during the nitration of wood pulp slivers.

## 7.2.5 Simulation Environment

COMSOL Multiphysics version 5.3<sup>87</sup> was used to develop models describing the nitration of wood pulp slivers and to generate results the reaction conditions listed in Table 7.1. Models were implemented in the Transport of Diluted Species and Transport of Diluted Species in Porous Media interfaces of the Chemical Species Transport Physics module.

## 7.3 Results

Simulations were run for three of the wood pulp sliver and reaction configurations listed in Table 7.1 using the four variants of wood pulp sliver models listed in Table 7.2 to compare model predictions with experimental results. Functions were written to perform an integration over the wood pulp sliver volume at specific reaction times to compare model predictions with experimental results (Table 7.3). The average nitrogen percentage was also calculated using Equation (6.34) by integrating the concentrations of nitrate ester functional groups and cellulose hydroxyl groups over the wood pulp sliver volume. Concentration probes were used to monitor the concentration of hydroxyl, nitrate ester, and mixed acid species at the center of the wood pulp sliver during the nitration reaction simulation and to calculate the nitrogen percentage in the center of the wood pulp sliver as a function of time.

Pulp Type	Acid Composition	Temperature	WPS Size (LxWxH) mm <sup>3</sup>	Reaction	Percent Nitrogen				
				Time	Experimental	Homogeneous		Porous	
					Result	Simple	Improved	Simple	Improved
Sulfite	37.12% HNO3	25°C	6.22 x 0.83 x 1.44	0	0.00	0.00	0.00	0.00	0.00
Softwood	<b>rood</b> 55.24% H2SO4			30	7.47	8.86	6.32	12.99	7.18
7.649	7.64% H2O			60	8.78	9.86	8.65	13.21	8.75
				4200	13.51	13.54	13.46	13.54	13.61
Sulfite	37.12% HNO3	25°C	6.31 x 1.62 x 1.32	0	0.00	0.00	0.00	0.00	0.00
Softwood	55.24% H2SO4			30	5.19	8.45	5.20	11.66	6.02
7.64% H2O	7.64% H2O			60	6.66	9.03	7.14	13.07	7.61
			4200	13.03	13.54	13.12	13.54	13.61	
Kraft	54.86% HNO3	3 25°C	6.06 x 0.95 x 1.61	0	0.00	0.00	0.00	0.00	0.00
Softwood	ftwood 37.24% H2SO4			60	10.88	10.00	7.35	12.87	11.67
7.909	7.90% H2O			300	12.87	12.69	11.30	13.26	12.38
				600	13.16	13.27	12.11	13.35	12.60
				1800	13.42	13.39	12.34	13.39	12.95
				2400	13.50	13.39	12.43	13.39	13.00
				4200	13.44	13.39	12.63	13.39	13.12

Table 7.3 Experimental and Simulated Results for Various Reaction Conditions Using Homogeneous and Porous Media Structure Models



**Figure 7.1** Concentrations of hydroxyl and nitrate ester groups at center of large wood pulp sliver for simple homogeneous sliver model at 25°C and high sulfuric acid mixed nitrating acid composition.

# 7.4 Discussion

# 7.4.1 General Analysis of Reaction and Diffusion Rates During Nitration of Wood Pulp Slivers in Mixed Acids

Because the rate of reaction of cellulose fibers in mixed acids is described by an empirical rate law that uses an exponential activity decay parameter to describe the decreasing reaction rate as the nitrocellulose reaches higher degrees of substitution, it is worth evaluating the relative rates of reaction and diffusion under these different conditions. Figure 7.2 illustrates the effect of the activity decay parameter on the overall rate of nitration as a function of the extent of conversion,  $\xi$ , of cellulose hydroxyl groups to nitrate ester groups as the reaction proceeds.



**Figure 7.2** Forward rate constant for cellulose nitration reaction as a function of conversion at 25°C. This reaction has previously been shown to proceed very rapidly to a degree of substitution of  $\sim$ 2.0 (11.11% nitrogen) before gradually approaching the equilibrium degree of substitution.

For steady-state diffusion through an infinite slab in one dimension, the ratio of diffusion to reaction can be described according to Equation (7.1).

$$\frac{d^2 C_A}{dx^2} = \frac{k_f C_B}{D_A} C_A \tag{7.1}$$

For a slab of thickness,  $L_0$ , this equation can be nondimensionalized according to Equation (7.2), which can be used to estimate the dimensionless ratios of reaction to diffusion in wood pulp slivers of thickness  $2L_0$ .

$$\frac{d^2 C_A}{d \left(\frac{x}{L_0}\right)^2} = \frac{L_0^2 k_f C_B}{D_A} C_A$$
(7.2)

In the wood pulp sliver the concentration of hydroxyl groups decreases from an initial value of approximately 12,000 mol/m<sup>3</sup> to a final value of approximately 856 mol/m<sup>3</sup>. For a

1.0mm thick wood pulp sliver and an effective diffusivity of  $2.37 \times 10^{-10}$  m<sup>2</sup>/s, the dimensionless ratio of the rate of reaction to diffusion decreases from an initial value of  $1.32 \times 10^5$  to a final value of approximately 0.75. During this process, the reaction transitions from being mass transfer limited to kinetically limited. This implies that below a certain sliver size, the final stages of the nitration reaction are kinetically limited rather than mass transfer limited. This may also imply that a minimum sliver size exists for each grade of nitrocellulose and set of reaction conditions below which there is minimal benefit associated with cutting the slivers to smaller sizes in terms of the required residence time in the nitration reactors. Because the lower nitrated grades of nitrocellulose are characterized by lower degrees of substitution or conversion, it is expected that rate of reaction of wood pulp slivers used in the production of lower nitrated grades of nitrocellulose would be exclusively mass transfer limited.

Because the initial rate of reaction is several orders of magnitude faster than the initial rate of diffusion there are additional challenges for simulating the nitration of wood pulp slivers using finite element methods or numerical solutions. A consequence of the fact that the rate of consumption by chemical reaction is so much greater than the rate of mass transfer by diffusion during the very early stages of the reaction is that the system of differential equations describing the nitration of wood pulp slivers is a stiff system of equations requiring either very small step sizes or suitable approximations to avoid numerical errors. To address this, methods have been proposed to characterize the Dirichlet boundary condition describing the concentration of mixed acid species at the surface of the wood pulp sliver and to describe the initial rates of reaction of mixed acid species in the wood pulp sliver.

#### 7.4.2 General Findings of Models Evaluated

In general, the four models that were evaluated exhibited reasonable agreement with the limited set of wood pulp sliver nitration experimental results that were considered. In addition, the process of building these models leads to practical insight into the significance of the various phenomena occurring during the nitration of dense cellulose structures helps to identify reaction conditions that minimize the influence of conditions that may hinder the rate or extent of reaction achieved in the cellulose nitration reactors.

The significance of acid dissociation within the wood pulp sliver structure was demonstrated by these models. The simplified models that did not consider the dynamic dissociation of mixed acids to ionic species consistently overestimated the extent of nitration achieved for a given set of reaction conditions. The effects of multicomponent diffusion were also demonstrated through implementation of the generalized Fick's law model, as the finite element models that used these multicomponent diffusion models generally demonstrated faster rates of diffusion than were predicted by the simpler binary diffusion models used in the models that were described in Chapter 6. Challenges that were associated with preventing numerical errors in the models prompted an analysis of the relative rates of reaction and diffusion in mixed acid compositions used in the production of Grade B nitrocellulose, leading to a more complete understanding of dominant reaction phenomena during the nitration of wood pulp slivers in these acids.

While the purpose of this study was to explore the relative influences of phenomena occurring during the nitration of wood pulp slivers in mixed acids, the limited validation that was performed showed reasonable agreement between experimental data and the simple homogeneous model ( $R^2 = 0.958$ ) and the improved porous media model ( $R^2 = 0.958$ )

0.991). The improved models showed particularly good agreement for the simulated conditions involving concentrated mixed acid compositions but did not perform as well for the mixed acid composition that is characterized by both lower concentrations of nitronium ion and hydronium ion, suggesting that that numerical errors may exist under these fast reaction and low concentration conditions.

All four models that were developed required special treatment to handle the combination of a very fast reaction rate and an imposed surface concentration initial condition. The surface concentrations were addressed by defining smoothing step functions that eliminated the mathematical discontinuity between the initial conditions specifying that no mixed acid species were present in the sliver and the Dirichlet condition that specified the bulk mixed acid composition concentration at all six surfaces of the sliver. Reaction rate scaling was performed using either a simple ramp function that enabled the concentration profile to establish during model initialization before the reaction rate was increased to the maximum value, or a more complex approach that used a rectangular function and the characteristic diffusion time for the sliver to define a slower initial reaction rate that was still at least two orders of magnitude faster than the rate of diffusion through the wood pulp sliver.

The distribution of hydroxyl groups, nitrate ester groups, and the nitrogen percentage were mapped as a function of position in the sliver for a series of reaction times (Figure 7.3) for each reaction condition that was evaluated. This capability provides a useful tool for visualizing the ether-alcohol and acetone insoluble regions in partially nitrated slivers that can be observed experimentally by nitrated slivers in the appropriate solvent. While not explored under the present effort, these models also facilitate analysis of time-dependent boundary conditions to explore the influence of less turbulent mixing in the secondary nitration reactors of the nitrocellulose process. A detailed discussion of each model developed and overall findings follows.



**Figure 7.3** Percent nitrogen distribution in wood pulp sliver using improved porous model at 30s (left) and 2400s (right) showing uniform nitration at 2400s. (Note scaling values indicated on legends.)

**7.4.2.1 Simple Homogeneous Wood Pulp Sliver Model.** The simple homogeneous wood pulp sliver nitration model was built in the Transport of Diluted Species interface and simulated the diffusion of nitric acid and water in through the wood pulp sliver structure considering hydroxyl groups and nitrate ester groups as immobilized phases. The model was run using the anisotropic effective diffusivity values that were measured (Chapter 3) for each reaction condition and temperature that was evaluated. As described in the Materials and Methods section, the dissociation of nitric acid to the nitronium ion was approximated by calculating the fraction of nitric acid that dissociates to the nitronium ion,  $f_{NO2}$ , using the equilibrium model developed by Albright et al.<sup>26</sup> according to Equation (7.3).

$$[NO_{2}^{+}](x, y, z, t) = f_{NO2} \times [HNO_{3}](x, y, z, t)$$
(7.3)

Of the models that were evaluated, this model provided the second-best fit to the experimental, likely due to the use of experimentally measured diffusion coefficients in this model. It was found that this model is very sensitive to the mesh size selected, particularly for the early nitration data points simulated but also tended to biased toward overestimating the extent of nitration at all reaction times due to the use of the simplified acid dissociation model that generally results in higher than actual nitronium ion concentrations. An example of this is seen in the predicted extent of reaction at 30 seconds that yields 10.32%N when using a mesh consisting of 1027 elements and 8.85%N when using a mesh consisting of 3452 elements. Given these results, further refinement of the mesh and step size are recommended to optimize the performance of this model for use as a predictive tool for nitrocellulose manufacturing. The model was, however, able to predict general performance at longer reaction times as seen in Figure 7.4, a plot of the nitrate ester concentration in the sliver cross-section at 180 seconds for the small wood pulp sliver at 25C using the high resolution mesh.



**Figure 7.4** Nitrate ester concentration in small wood pulp sliver cross section at 180s and 25°C using simple homogeneous model

**7.4.2.2 Improved Homogeneous Wood Pulp Sliver Model.** The improved homogeneous wood pulp sliver nitration model was also built in the Transport of Diluted Species interface and simulated the diffusion and dissociation of all mixed acid species using Equations (2.50)-(2.55). These models were run using the mesh consisting of 1027 elements and used a ramping function to apply a scaling factor of 50 to the equilibrium rate of nitration to ensure that the rate of reaction was maintained at least an order of magnitude higher than the rate of diffusion from the time zero until the characteristic diffusion time was reached. This model shows that optimization of the reaction scaling approach is needed to ensure that the reaction rate of the nitration reaction does not slow before an average degree of substitution of 2 is reached in each region of the wood pulp sliver.

Scaling of the reaction rate was necessary because the combination of the high reaction rate, low rate of diffusion ( $D_{eff} = 2.37 \times 10^{-10} \text{ m}^2/\text{s}$ ), and low concentrations of

products of dissociation of mixed acids resulted non-convergent simulations and numerical errors. This could be addressed by designing an scaling factor that varies with time and space in the wood pulp sliver to prevent the rate of reaction from slowing too much before reaching a suitably high extent of reaction in the center of the wood pulp sliver. Through design of a function that reasonably describes the rate of reaction over the full diffusion timescale, the functionality of the model could be greatly improved. It was noted that the model does predict very good results for the initial rates of nitration for the nitronium ion rich acid compositions, particularly for small wood pulp slivers, emphasizing the benefit of modeling dynamic acid dissociation.

**7.4.2.3 Simple Porous Wood Pulp Sliver Model.** The simple porous wood pulp sliver nitration model utilized the Transport of Diluted Species in Porous Media interface and the Bruggeman model, Equation (6.26), to relate the tortuosity to the porosity in the wood pulp sliver. The rates of diffusion of nitric acid, sulfuric acid, and water were modeled in the porous wood pulp sliver, and the model was run using a constant porosity ( $\phi$ =0.5045 for sulfite softwood and  $\phi$ =0.495 for kraft softwood) that was calculated for each pulp type and reaction condition that was evaluated. Diffusion coefficients of 3.31×10<sup>-9</sup> m<sup>2</sup>/s and 2.86×10<sup>-9</sup> m<sup>2</sup>/s were used for the nitric acid-water system and sulfuric acid-water system, respectively<sup>55</sup>.

The simple porous wood pulp sliver model yielded the poorest results of the four models that were evaluated, likely due to the combination of calculated rates of diffusion that were an order of magnitude higher than the measured effective diffusivities for unswollen wood pulp sliver and due to overestimation of the nitronium ion concentration in the wood pulp sliver due to the use of Equation (7.3) to approximate the concentration of the nitronium ion in the wood pulp sliver based on the local concentration of nitric acid.

7.4.2.4 Improved Porous Wood Pulp Sliver Model. The final model that was developed under this study implemented acid dissociation and swelling (variable porosity) using the Transport of Diluted Species in Porous Media module. Variable swelling was implemented using the known initial and final extent of swelling and the characteristic swelling time for each pulp type according to Equation (3.57) with acid dissociation described by Equations (2.50)-(2.55). The Bruggeman model was used to correlate the tortuosity to the time dependent porosity using Equation (6.26). Finally, a ramp function was used to multiply the equilibrium rate constant value by 1000 to ensure that the initial rate constant was as least three orders of magnitude faster than the rate of diffusion. The relatively short diffusion times associated with the porous media effective diffusivity models made the ramp function provide reasonable approximations for the rate of nitration by applying the scaling factor over the characteristic diffusion time for each sliver size, temperature, and pulp type.

This model showed considerable utility for describing the rate of nitration of wood pulp slivers with little experimental data needed to make reasonable predictions of the rate of nitration for a range of wood pulp sliver sizes. As with the simple homogeneous model, this model would further benefit through the use of a more accurate approximation of the rate constant behavior to capture the combination of very rapid initial kinetics followed by a slower rate of reaction as the system approaches high degrees of substitution. Even using a crude approximation of the rate law for the cellulose nitration reaction, this model provides very reasonable predictions of the nitration kinetic behavior for a range of wood pulp types and reaction conditions (Figure 7.5).



**Figure 7.5** Percent nitrogen versus time for 0.83mm × 6.22mm wood pulp sliver reacted in high H<sub>2</sub>SO<sub>4</sub> mixed acid composition for Grade B NC with equilibrium DOS approached at ~2400s.

A final example was analyzed using the improved porous nitration model to consider the nitration of a 0.95mm × 6.31mm wood pulp sliver in a mixed acid used to produce Grade A nitrocellulose consisting of 30.18% nitric acid, 54.67% sulfuric acid, and 15.15% water (weight percent). The reaction was run for 300s, which is the typical residence time of the pre-nitration reactor, and an isosurface plot was generated to identify the residual material in the wood pulp sliver that would be insoluble in acetone (less than 9% nitrogen) at that point in the reactor train. Figure 7.6 demonstrates that a significant amount of unreacted or partially reacted cellulose remains in the core of the sliver after this combination of reaction time and conditions.

Time=300 s Isosurface: (cOH>COH0/2)



**Figure 7.6** Isosurface plot of partially reacted (<9% nitrogen) region of wood pulp sliver after a reaction time of 5 minutes in Grade A mixed acid composition at 30°C.

#### 7.4.3 Applicability of Models

The data analysis tools implemented in FEM packages enable comprehensive post-analysis of simulation results for the nitration of wood pulp slivers nitrated under a range of reaction conditions. These tools can be used with existing models to consider the relationship between wood pulp type, reaction temperature, sliver size, and the efficiency of mixing in the pre-nitrator and post-nitrator reactors to develop quantitative estimates of the solubility of nitrocellulose produced under these conditions. In particular, the improved porous wood pulp sliver model yielded very good estimates when compared to experimental results and appears to provide suitability accuracy to enable its use in simulations to conduct reaction condition evaluations.

#### 7.5 Findings and Recommendations

Four models exhibiting varying levels of complexity were developed and evaluated to consider mass transfer and chemical reaction during the nitration of dense cellulose materials. Through the development of these models, it was noted that the development of approximate rate laws would be beneficial to enable more efficient simulation of these diffusion and reaction conditions. It was also noted that in the production of Grade B nitrocellulose, reaction conditions likely exist that result in the nitration of slivers cut from sheeted wood pulp transitioning from a diffusion limited reaction to a mass transfer limited reaction.

The application of FEM tools to describe the mass transfer, relaxation, and chemical reaction phenomena occurring during the production of nitrocellulose was successfully demonstrated. These tools can be further utilized to consider more detailed representations of the wood pulp sliver structure to consider the influences of wetting densely packed regions of cellulose fibers, and delaminated regions, or fissures, in the wood pulp sliver that are formed during cutting.

# 7.6 Conclusions

Finite element method models were implemented using Comsol Multiphysics v. 5.3 to describe the nitration of wood pulp slivers in mixed acid compositions used to produce nitrocellulose. These models incorporated functionality to describe the phenomena of chemical reaction, multicomponent diffusion, acid dissociation, swelling, and variable diffusion coefficients to describe the dynamics of simultaneous mass transfer and swelling during the nitration of wood pulp slivers in mixed acids. Simplifying assumptions were

made to handle the stiff set of equations resulting from the extremely high ratio of the reaction rate to the diffusion rate in this system.

The application of these tools and associated analysis packages were demonstrated for the analysis of several wood pulp sliver types and reaction conditions. These tools provide a capability to run simulations for a broad range of reaction conditions and subsequently analyze distributions of nitrated and poorly nitrated regions in the wood pulp sliver. This evaluation demonstrated the significance of the dissociation of mixed acids in the reacting wood pulp sliver on the observed rate of nitration and also suggested that a threshold size exists below which the rate of nitration of wood pulp slivers does not benefit from a reduction in sliver size.

## **APPENDIX** A

# SINGLE CELLULOSE FIBER (SCF) NITRATION EXPERIMENTS - RAW EXPERIMENTAL DATA

Data from the single cellulose fiber nitration experiments were processed to calculate the actual mixed acid composition for each time, percent nitrogen data point using the fiber moisture content and the net cellulose nitration reaction. Equation (1.1) was used to calculate the overall consumption of nitric acid and generation of water for each experimental data point using the acid to cellulose ratio, the initial mixed acid composition, and the cellulose moisture content.

Source	Time	Temp	Fiber Moisture	Percent Nitrogen	Mixed Acid Mass Fractions (adjusted for moisture)			
	(s)	°C	Content (%)	8	HNO <sub>3</sub>	$H_2SO_4$	H <sub>2</sub> O	
Sulfite SW	0.0	25	3.99	0.00	0.3714	0.5527	0.0759	
Sulfite SW	10.9	25	3.99	11.08	0.3676	0.5547	0.0777	
Sulfite SW	23.1	25	3.99	11.84	0.3672	0.5550	0.0779	
Sulfite SW	41.0	25	3.99	12.42	0.3668	0.5552	0.0780	
Sulfite SW	60.6	25	3.99	12.65	0.3667	0.5552	0.0781	
Sulfite SW	300.0	25	3.99	13.40	0.3662	0.5555	0.0783	
Sulfite SW	400.0	25	3.99	13.40	0.3662	0.5555	0.0783	
Sulfite SW	500.0	25	3.99	13.46	0.3661	0.5555	0.0783	
Sulfite SW	4200.0	25	3.99	13.60	0.3660	0.5556	0.0784	
Sulfite SW	0.0	40	3.99	0.00	0.3714	0.5527	0.0759	
Sulfite SW	11.2	40	3.99	12.01	0.3671	0.5550	0.0779	
Sulfite SW	20.7	40	3.99	12.12	0.3670	0.5551	0.0779	
Sulfite SW	40.2	40	3.99	12.87	0.3665	0.5553	0.0782	
Sulfite SW	60.0	40	3.99	13.16	0.3663	0.5554	0.0782	
Sulfite SW	300.0	40	3.99	13.36	0.3662	0.5555	0.0783	
Sulfite SW	4200.0	40	3.99	13.58	0.3661	0.5556	0.0784	
Kraft HW	0.0	25	4.01	0.00	0.3714	0.5527	0.0759	
Kraft HW	10.8	25	4.01	10.96	0.3677	0.5547	0.0776	

 Table A.1 Single Cellulose Fiber Nitration Experimental Data
Kraft HW	20.8	25	4.01	11.96	0.3671	0.5550	0.0779
Kraft HW	40.8	25	4.01	12.58	0.3667	0.5552	0.0781
Kraft HW	60.8	25	4.01	12.99	0.3665	0.5553	0.0782
Kraft HW	200.0	25	4.01	13.40	0.3662	0.5555	0.0783
Kraft HW	300.0	25	4.01	13.51	0.3661	0.5555	0.0784
Kraft HW	400.0	25	4.01	13.42	0.3662	0.5555	0.0783
Kraft HW	4200.0	25	4.01	13.61	0.3660	0.5556	0.0784
Kraft HW	0.0	40	4.01	0.00	0.3714	0.5527	0.0759
Kraft HW	10.8	40	4.01	11.89	0.3671	0.5550	0.0779
Kraft HW	20.2	40	4.01	12.66	0.3667	0.5552	0.0781
Kraft HW	40.8	40	4.01	13.17	0.3663	0.5554	0.0782
Kraft HW	60.8	40	4.01	13.28	0.3663	0.5555	0.0783
Kraft HW	300.0	40	4.01	13.51	0.3661	0.5555	0.0784
Kraft HW	4200.0	40	4.01	13.63	0.3660	0.5556	0.0784
Kraft SW	0.0	25	5.12	0.00	0.3714	0.5527	0.0760
Kraft SW	10.4	25	5.12	10.35	0.3679	0.5545	0.0776
Kraft SW	21.0	25	5.12	11.76	0.3672	0.5549	0.0779
Kraft SW	40.4	25	5.12	12.62	0.3667	0.5552	0.0782
Kraft SW	60.7	25	5.12	12.93	0.3665	0.5553	0.0782
Kraft SW	300.0	25	5.12	13.41	0.3661	0.5555	0.0784
Kraft SW	4200.0	25	5.12	13.55	0.3661	0.5555	0.0784
Kraft SW	0.0	40	5.12	0.00	0.3714	0.5527	0.0760
Kraft SW	10.5	40	5.12	11.89	0.3671	0.5549	0.0779
Kraft SW	21.0	40	5.12	12.64	0.3667	0.5552	0.0782
Kraft SW	40.7	40	5.12	12.86	0.3665	0.5553	0.0782
Kraft SW	60.4	40	5.12	13.26	0.3663	0.5554	0.0783
Kraft SW	300.0	40	5.12	13.37	0.3662	0.5554	0.0784
Kraft SW	4200.0	40	5.12	13.62	0.3660	0.5555	0.0785
Kraft SW	0.0	25	5.03	0.00	0.5207	0.3478	0.1315
Kraft SW	20.0	25	5.03	10.24	0.5178	0.3489	0.1333
Kraft SW	60.0	25	5.03	11.55	0.5173	0.3491	0.1336
Kraft SW	300.0	25	5.03	11.99	0.5170	0.3492	0.1337
Kraft SW	4200.0	25	5.03	12.48	0.5168	0.3493	0.1339
Kraft SW	0.0	40	4.35	0.00	0.5208	0.3478	0.1315
Kraft SW	20.0	40	4.35	11.26	0.5174	0.3491	0.1335
Kraft SW	60.0	40	4.35	11.80	0.5172	0.3492	0.1337
Kraft SW	300.0	40	4.35	12.70	0.5167	0.3494	0.1339
Kraft SW	4200.0	40	4.35	12.96	0.5165	0.3494	0.1340
Kraft SW	0.0	25	5.54	0.00	0.3493	0.5211	0.1295
Kraft SW	20.0	25	5.54	10.64	0.3457	0.5229	0.1314
Kraft SW	60.0	25	5.54	12.21	0.3448	0.5234	0.1318
Kraft SW	300.0	25	5.54	12.99	0.3443	0.5236	0.1321
Kraft SW	4200.0	25	5.54	13.46	0.3440	0.5238	0.1323

Kraft SW	0.0	40	5.44	0.00	0.3493	0.5211	0.1295
Kraft SW	20.0	40	5.44	11.81	0.3450	0.5232	0.1317
Kraft SW	60.0	40	5.44	12.93	0.3443	0.5236	0.1321
Kraft SW	300.0	40	5.44	13.32	0.3441	0.5237	0.1322
Kraft SW	4200.0	40	5.44	13.46	0.3440	0.5238	0.1322
Kraft SW	0.0	25	5.69	0.00	0.5515	0.3744	0.0742
Kraft SW	20.0	25	5.69	12.85	0.5475	0.3761	0.0764
Kraft SW	60.0	25	5.69	13.30	0.5472	0.3762	0.0765
Kraft SW	300.0	25	5.69	13.50	0.5471	0.3763	0.0766
Kraft SW	4200.0	25	5.69	13.62	0.5470	0.3763	0.0766
Kraft SW	0.0	40	6.43	0.00	0.5515	0.3743	0.0742
Kraft SW	20.0	40	6.43	13.36	0.5472	0.3762	0.0766
Kraft SW	60.0	40	6.43	13.50	0.5471	0.3763	0.0766
Kraft SW	300.0	40	6.43	13.55	0.5471	0.3763	0.0767
Kraft SW	4200.0	40	6.43	13.64	0.5470	0.3763	0.0767

#### **APPENDIX B**

# PROCESSED SINGLE CELLULOSE FIBER (SCF) NITRATION DATA FOR NUMERICAL INTEGRATION AND NONLINEAR LEAST SQUARES PARAMETER ESTIMATION ROUTINE

The experimental data in Appendix A were processed to calculate hydroxyl, nitrate ester, and mixed acid species concentrations for each experimental data point. Mixed acid species concentrations were calculated using the acid dissociation model published by Albright et al.<sup>26</sup> and the concentrations of hydroxyl and nitrate ester groups were calculated using the density of cellulose, the acid to cellulose ratio, and the mixed acid density. This data was then in a form that allowed the concentrations of hydroxyl, nitrate ester, nitronium ions, and hydronium ions to be read into the parameter estimate routine.

Reaction	Temperature	%N	Mixed A	<b>Mixed Acid Mass Fractions</b>		Density	[OH]	[ONO <sub>2</sub> ]	[NO <sub>2</sub> <sup>+</sup> ]	[H <sub>3</sub> O <sup>+</sup> ]
Time (s)	°C		HNO <sub>3</sub>	$\mathrm{H}_2\mathrm{SO}_4$	H <sub>2</sub> O	g/ml	mol/l	mol/l	mol/l	mol/l
0.0	25	0.00	0.3714	0.5527	0.0759	1.7090	0.2010	0.0000	1.4114	7.5301
10.9	25	11.08	0.3676	0.5547	0.0777	1.7085	0.0676	0.1334	1.3602	7.6203
23.1	25	11.84	0.3672	0.5550	0.0779	1.7085	0.0529	0.1481	1.3546	7.6303
41.0	25	12.42	0.3668	0.5552	0.0780	1.7084	0.0406	0.1604	1.3500	7.6386
60.6	25	12.65	0.3667	0.5552	0.0781	1.7084	0.0357	0.1653	1.3481	7.6419
300.0	25	13.40	0.3662	0.5555	0.0783	1.7084	0.0186	0.1824	1.3415	7.6536
400.0	25	13.40	0.3662	0.5555	0.0783	1.7084	0.0185	0.1825	1.3415	7.6537
500.0	25	13.46	0.3661	0.5555	0.0783	1.7084	0.0170	0.1840	1.3409	7.6547
4200.0	25	13.60	0.3660	0.5556	0.0784	1.7084	0.0137	0.1873	1.3397	7.6569
0.0	40	0.00	0.3714	0.5527	0.0759	1.6895	0.1987	0.0000	1.2845	7.3910
11.2	40	12.01	0.3671	0.5550	0.0779	1.6889	0.0487	0.1500	1.2280	7.4932
20.7	40	12.12	0.3670	0.5551	0.0779	1.6889	0.0466	0.1521	1.2272	7.4946
40.2	40	12.87	0.3665	0.5553	0.0782	1.6889	0.0305	0.1682	1.2212	7.5056
60.0	40	13.16	0.3663	0.5554	0.0782	1.6888	0.0240	0.1747	1.2188	7.5100
300.0	40	13.36	0.3662	0.5555	0.0783	1.6888	0.0191	0.1796	1.2169	7.5133
4200.0	40	13.58	0.3661	0.5556	0.0784	1.6888	0.0140	0.1847	1.2150	7.5169
0.0	25	0.00	0.3714	0.5527	0.0759	1.7090	0.2010	0.0000	1.4114	7.5301
10.8	25	10.96	0.3677	0.5547	0.0776	1.7085	0.0699	0.1311	1.3611	7.6188
20.8	25	11.96	0.3671	0.5550	0.0779	1.7085	0.0504	0.1506	1.3536	7.6320
40.8	25	12.58	0.3667	0.5552	0.0781	1.7084	0.0373	0.1637	1.3486	7.6409
60.8	25	12.99	0.3665	0.5553	0.0782	1.7084	0.0280	0.1729	1.3451	7.6472
200.0	25	13.40	0.3662	0.5555	0.0783	1.7084	0.0185	0.1824	1.3415	7.6537

 Table B.1 Processed Single Cellulose Fiber (SCF) Nitration Data for Parameter Estimation

300.0	25	13.51	0.3661	0.5555	0.0784	1.7084	0.0160	0.1850	1.3405	7.6554
400.0	25	13.42	0.3662	0.5555	0.0783	1.7084	0.0179	0.1830	1.3412	7.6541
4200.0	25	13.61	0.3660	0.5556	0.0784	1.7084	0.0134	0.1876	1.3395	7.6571
0.0	40	0.00	0.3714	0.5527	0.0759	1.6895	0.1987	0.0000	1.2845	7.3911
10.8	40	11.89	0.3671	0.5550	0.0779	1.6889	0.0512	0.1475	1.2289	7.4915
20.2	40	12.66	0.3667	0.5552	0.0781	1.6889	0.0352	0.1635	1.2229	7.5024
40.8	40	13.17	0.3663	0.5554	0.0782	1.6888	0.0237	0.1750	1.2186	7.5103
60.8	40	13.28	0.3663	0.5555	0.0783	1.6888	0.0212	0.1775	1.2177	7.5120
300.0	40	13.51	0.3661	0.5555	0.0784	1.6888	0.0156	0.1830	1.2156	7.5158
4200.0	40	13.63	0.3660	0.5556	0.0784	1.6888	0.0129	0.1858	1.2146	7.5177
0.0	25	0.00	0.3714	0.5527	0.0760	1.7089	0.1986	0.0000	1.4089	7.5326
10.4	25	10.35	0.3679	0.5545	0.0776	1.7085	0.0798	0.1188	1.3628	7.6139
21.0	25	11.76	0.3672	0.5549	0.0779	1.7084	0.0539	0.1448	1.3527	7.6317
40.4	25	12.62	0.3667	0.5552	0.0782	1.7084	0.0359	0.1627	1.3458	7.6440
60.7	25	12.93	0.3665	0.5553	0.0782	1.7084	0.0292	0.1694	1.3432	7.6486
300.0	25	13.41	0.3661	0.5555	0.0784	1.7083	0.0181	0.1806	1.3389	7.6563
4200.0	25	13.55	0.3661	0.5555	0.0784	1.7083	0.0148	0.1839	1.3376	7.6586
0.0	40	0.00	0.3714	0.5527	0.0760	1.6894	0.1964	0.0000	1.2820	7.3936
10.5	40	11.89	0.3671	0.5549	0.0779	1.6889	0.0506	0.1458	1.2265	7.4940
21.0	40	12.64	0.3667	0.5552	0.0782	1.6888	0.0350	0.1613	1.2206	7.5047
40.7	40	12.86	0.3665	0.5553	0.0782	1.6888	0.0304	0.1660	1.2189	7.5079
60.4	40	13.26	0.3663	0.5554	0.0783	1.6888	0.0214	0.1750	1.2155	7.5141
300.0	40	13.37	0.3662	0.5554	0.0784	1.6888	0.0188	0.1776	1.2145	7.5160
4200.0	40	13.62	0.3660	0.5555	0.0785	1.6887	0.0130	0.1834	1.2123	7.5200
0.0	25	0.00	0.5207	0.3478	0.1315	1.5963	0.1858	0.0000	0.0993	6.9680
20.0	25	10.24	0.5178	0.3489	0.1333	1.5958	0.0764	0.1094	0.0950	7.0055

60.0	25	11.55	0.5173	0.3491	0.1336	1.5957	0.0541	0.1317	0.0941	7.0131
300.0	25	11.99	0.5170	0.3492	0.1337	1.5956	0.0460	0.1398	0.0938	7.0158
4200.0	25	12.48	0.5168	0.3493	0.1339	1.5956	0.0365	0.1493	0.0934	7.0191
0.0	40	0.00	0.5208	0.3478	0.1315	1.5763	0.1848	0.0000	0.0762	6.7455
20.0	40	11.26	0.5174	0.3491	0.1335	1.5756	0.0590	0.1258	0.0724	6.7856
60.0	40	11.80	0.5172	0.3492	0.1337	1.5756	0.0494	0.1354	0.0721	6.7887
300.0	40	12.70	0.5167	0.3494	0.1339	1.5755	0.0319	0.1529	0.0716	6.7942
4200.0	40	12.96	0.5165	0.3494	0.1340	1.5754	0.0265	0.1583	0.0714	6.7959
0.0	25	0.00	0.3493	0.5211	0.1295	1.6648	0.1927	0.0000	0.1954	8.8960
20.0	25	10.64	0.3457	0.5229	0.1314	1.6643	0.0725	0.1202	0.1835	8.9505
60.0	25	12.21	0.3448	0.5234	0.1318	1.6641	0.0433	0.1494	0.1808	8.9636
300.0	25	12.99	0.3443	0.5236	0.1321	1.6641	0.0270	0.1657	0.1792	8.9709
4200.0	25	13.46	0.3440	0.5238	0.1323	1.6640	0.0164	0.1763	0.1782	8.9756
0.0	40	0.00	0.3493	0.5211	0.1295	1.6458	0.1907	0.0000	0.1563	8.7302
20.0	40	11.81	0.3450	0.5232	0.1317	1.6454	0.0507	0.1400	0.1449	8.7925
60.0	40	12.93	0.3443	0.5236	0.1321	1.6453	0.0279	0.1628	0.1431	8.8025
300.0	40	13.32	0.3441	0.5237	0.1322	1.6453	0.0193	0.1714	0.1424	8.8063
4200.0	40	13.46	0.3440	0.5238	0.1322	1.6453	0.0162	0.1745	0.1422	8.8077
0.0	25	0.00	0.5515	0.3744	0.0742	1.6408	0.1896	0.0000	0.7464	5.8774
20.0	25	12.85	0.5475	0.3761	0.0764	1.6399	0.0296	0.1601	0.6998	5.9679
60.0	25	13.30	0.5472	0.3762	0.0765	1.6399	0.0196	0.1700	0.6969	5.9735
300.0	25	13.50	0.5471	0.3763	0.0766	1.6399	0.0151	0.1745	0.6957	5.9760
4200.0	25	13.62	0.5470	0.3763	0.0766	1.6399	0.0123	0.1773	0.6949	5.9776
0.0	40	0.00	0.5515	0.3743	0.0742	1.6158	0.1853	0.0000	0.6396	5.7414
20.0	40	13.36	0.5472	0.3762	0.0766	1.6156	0.0180	0.1672	0.5933	5.8384
60.0	40	13.50	0.5471	0.3763	0.0766	1.6156	0.0147	0.1705	0.5924	5.8403

300.0	40	13.55	0.5471	0.3763	0.0767	1.6156	0.0138	0.1715	0.5922	5.8408
4200.0	40	13.64	0.5470	0.3763	0.0767	1.6156	0.0116	0.1737	0.5916	5.8421

## **APPENDIX C**

# MEASUREMENT OF MIXED ACID DENSITIES BY DENSITY / SOUND VELOCITY ANALYSIS

#### **C.1 Introduction**

The densities of mixtures of nitric acid, sulfuric acid, and water are necessary for converting compositions expressed as mass fractions for these systems to molar concentrations. These densities are also needed to convert the nitronium ion concentrations that were reported by Zaman<sup>30</sup> on a mole percentage basis to concentration units, and for using the acid dissociation model published by Albright et al.<sup>26</sup> to predict concentrations of ionic species in mixtures of nitric acid, sulfuric acid, and water. Because these mixed acids are employed in most industrial nitration reactions, a model capable of accurately predicting the density of mixtures of nitric acid, sulfuric acid, and water as a function of composition and temperature is expected to be of significant interest to manufacturers of energetic materials.

One such model was proposed by Martin et al. according to Equation  $(C.1)^{41}$ , where  $\chi$  and  $\phi$  are the weight percentages of sulfuric acid and nitric acid, respectively. The parameters,  $\rho_{i,j}$ , that were estimated by Martin et al. are listed in Table C.1.

$$\rho(x,y) / g \, cm^{-3} = \sum_{i=0}^{4} \sum_{j=0}^{3} \rho_{i,j} \chi^{i} \varphi^{j}$$
(C.1)

ρi,j	j=0	1	2	3
		$\mathbf{T} = \mathbf{293K}$		
i=0	$0.9982 \times 10^{0}$	5.8487×10 <sup>-3</sup>	-2.3873×10 <sup>-5</sup>	7.9815×10 <sup>-7</sup>
1	7.9919×10 <sup>-3</sup>	2.9369×10 <sup>-5</sup>	1.8949×10 <sup>-6</sup>	-3.6905×10 <sup>-8</sup>
2	-7.6431×10 <sup>-5</sup>	2.8093×10 <sup>-6</sup>	-6.4247×10 <sup>-8</sup>	
3	2.2885×10 <sup>-6</sup>	-2.1422×10 <sup>-8</sup>		
4	-1.4651×10 <sup>-8</sup>			
		$\mathbf{T} = \mathbf{253K}$		
i=0	$1.0015 \times 10^{0}$	9.7509×10 <sup>-3</sup>	-1.8340×10 <sup>-4</sup>	2.9113×10 <sup>-6</sup>
1	9.6589×10 <sup>-3</sup>	-3.9433×10 <sup>-5</sup>	3.8149×10 <sup>-6</sup>	-6.3144×10 <sup>-8</sup>
2	-1.1562×10 <sup>-4</sup>	4.3442×10 <sup>-6</sup>	-7.0749×10 <sup>-8</sup>	
3	2.6848×10 <sup>-6</sup>	-3.6871×10 <sup>-8</sup>		
4	-1.6015×10 <sup>-8</sup>			

**Table C.1** Polynomial Expansion Coefficients Proposed by Martin et al.<sup>41</sup> for Modeling Density of H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub>/H<sub>2</sub>O System

This model was obtained using experimentally measured densities of mixed acid systems using a volumetric method for 19 concentrations varying from 5%-65% H<sub>2</sub>SO<sub>4</sub> and from 3%-45% HNO<sub>3</sub> and reported an average versus calculated density deviation of 0.56% for the proposed model. Validation was also performed using data published in Perry's Chemical Engineers' Handbook<sup>88</sup> reporting an average difference of 0.6% and an accuracy of density predictions of 0.0043 g/mL. In evaluating this model it was noted that there were significant differences between densities predicted by the model proposed by Martin et al.<sup>41</sup> and experimentally measured densities for many of the mixed acid compositions that were evaluated for the production of nitrocellulose. This is likely because most of the acid compositions that were evaluated by Martin et al.<sup>41</sup> fall outside the zone of technical interest for industrial nitration reactions, which generally contain less than 15 weight percent water. As a result, extrapolation is needed to predict densities of the mixed acid compositions used in industrial nitration reactions when using this model. Given these limitations of available published models, the collection of highly accurate density data for concentrated mixed acid systems was pursued.

Density and sound velocity analyzers provide a fast and highly accurate method for measuring the density and sound velocity of solutions with a demonstrated reproducibility of 0.000005 g/cm<sup>3</sup> for density measurements. Given the capabilities of this modern instrumentation, it is possible to obtain a comprehensive data set for densities of the ternary sulfuric acid, nitric acid, and water system that are vastly superior to existing published data generated using volumetric methods. Using this approach, a data set that covers the entire concentration range of interest for industrial nitration reactions can be generated and the same form of polynomial expansion can be used for the expanded data set to obtain a more capable model for predicting the density of the ternary mixed acid system.

### C.2 Materials and Methods

### **C.2.1 Mixed Acid Compositions**

Mixed acid compositions were prepared using nitric acid (J.T. Baker – Nitric Acid, Fuming, 90%), sulfuric acid (Fisher Scientific – Certified ACS Plus), and deionized water. One hundred and ninety acid mixtures that varied from 24.33% to 74.94% weight percent sulfuric acid and from 19.57% to 62.62% weight percent nitric acid were prepared for density analysis.

### C.2.2 Density Analysis

Density measurements were performed using an Anton Paar DSA 5000 M density and sound velocity meter. Densities were measured at 25°C and 40°C for each of mixed acid composition that was evaluated.

## C.2.3 Data Analysis

Wolfram Mathematica<sup>29</sup> was used to perform nonlinear least squares regression to fit model parameters to the experimental data set and to calculate the correlation coefficient for the best-fit parameters that were obtained.

# C.3 Results

Table C.2 lists the experimental results for the acid compositions that were evaluated at 25°C and 40°C in addition to the density predictions generated for the models published by Martin et al. and using the improved parameters Table C.3 generated under the present study.

Mas	s Percent	ages	Temperature	D	)ensity (g	/cm <sup>3</sup> )
HNO <sub>3</sub>	$H_2SO_4$	$H_2O$	° <i>C</i>	Exp	Martin	Improved
20.055	74.939	5.006	25	1.796	1.842	1.799
20.110	73.848	6.042	25	1.786	1.832	1.787
20.084	72.819	7.097	25	1.775	1.823	1.776
19.943	72.005	8.052	25	1.766	1.814	1.765
22.662	68.535	8.802	25	1.745	1.790	1.746
20.077	69.806	10.117	25	1.748	1.793	1.741
19.990	68.881	11.129	25	1.735	1.784	1.730
19.983	67.941	12.076	25	1.726	1.774	1.719
19.838	66.211	13.952	25	1.709	1.756	1.698
19.568	65.579	14.854	25	1.698	1.748	1.688
22.466	72.322	5.212	25	1.785	1.824	1.786
22.413	71.478	6.109	25	1.777	1.817	1.776
22.712	70.307	6.981	25	1.760	1.806	1.766
21.877	70.252	7.871	25	1.767	1.804	1.759
22.653	68.344	9.002	25	1.746	1.788	1.744
22.906	66.932	10.162	25	1.734	1.775	1.731
22.356	66.783	10.861	25	1.729	1.772	1.725
22.550	65.456	11.994	25	1.718	1.759	1.712

**Table C.2** Mixed Acid Compositions with Experimentally Measured Densities and

 Predicted Densities for Martin and Improved Models

22.524	64.365	13.111	25	1.707	1.748	1.700
19.748	67.522	12.731	25	1.720	1.769	1.712
22.505	62.269	15.226	25	1.687	1.726	1.677
24.893	70.031	5.076	25	1.779	1.807	1.778
25.051	68.854	6.095	25	1.767	1.797	1.766
24.841	68.101	7.058	25	1.759	1.790	1.757
24.892	67.081	8.027	25	1.749	1.781	1.746
25.109	65.799	9.091	25	1.734	1.769	1.734
24.984	65.026	9.990	25	1.728	1.762	1.726
24.895	64.157	10.948	25	1.714	1.753	1.716
24.251	64.003	11.745	25	1.719	1.750	1.710
25.005	61.955	13.040	25	1.699	1.732	1.694
23.011	63.976	13.014	25	1.706	1.746	1.700
24.852	60.208	14.940	25	1.681	1.714	1.674
27.486	67.381	5.133	25	1.766	1.786	1.767
27.403	66.576	6.021	25	1.758	1.779	1.758
27.392	64.553	8.055	25	1.740	1.761	1.737
27.273	63.493	9.234	25	1.728	1.752	1.726
27.478	61.430	11.092	25	1.708	1.733	1.706
27.445	62.286	10.269	25	1.700	1.741	1.715
27.769	59.117	13.113	25	1.688	1.712	1.685
27.441	58.321	14.238	25	1.679	1.703	1.675
27.454	57.558	14.988	25	1.671	1.696	1.667
29.980	64.985	5.035	25	1.760	1.765	1.760
29.765	63.931	6.304	25	1.760	1.757	1.747
29.816	62.606	7.578	25	1.736	1.746	1.734
29.810	61.977	8.214	25	1.727	1.740	1.728
30.046	60.948	9.006	25	1.720	1.732	1.719
29.704	60.206	10.090	25	1.710	1.725	1.709
30.148	58.865	10.987	25	1.698	1.714	1.699
29.886	58.073	12.041	25	1.690	1.706	1.690
30.359	56.664	12.976	25	1.679	1.694	1.679
29.593	56.581	13.826	25	1.674	1.692	1.673
30.055	55.037	14.908	25	1.662	1.679	1.661
32.278	62.569	5.153	25	1.751	1.744	1.751
32.423	61.551	6.026	25	1.742	1.736	1.741
32.083	60.656	7.261	25	1.729	1.729	1.730
32.551	59.391	8.059	25	1.720	1.719	1.720
32.565	58.329	9.106	25	1.709	1.710	1.710
32.485	57.356	10.159	25	1.699	1.702	1.700
32.491	56.486	11.023	25	1.690	1.695	1.691
32.567	55.431	12.002	25	1.680	1.686	1.682
32.631	54.285	13.084	25	1.671	1.677	1.671

32.616	53.442	13.942	25	1.652	1.669	1.663
33.741	51.231	15.028	25	1.636	1.652	1.649
34.882	59.832	5.286	25	1.739	1.720	1.741
35.047	58.875	6.078	25	1.731	1.713	1.732
35.060	57.954	6.986	25	1.721	1.706	1.722
34.873	56.876	8.252	25	1.708	1.698	1.710
34.834	55.936	9.230	25	1.701	1.691	1.701
35.038	55.038	9.924	25	1.683	1.684	1.693
35.049	54.018	10.933	25	1.682	1.676	1.684
34.949	52.994	12.057	25	1.672	1.668	1.673
34.287	52.911	12.802	25	1.668	1.667	1.668
34.848	51.266	13.886	25	1.656	1.654	1.656
35.128	49.809	15.063	25	1.644	1.642	1.644
37.478	57.104	5.419	25	1.731	1.696	1.730
37.205	56.717	6.079	25	1.725	1.694	1.724
36.818	55.985	7.197	25	1.713	1.690	1.714
37.447	54.547	8.007	25	1.703	1.679	1.704
37.379	53.623	8.999	25	1.694	1.673	1.694
37.362	52.718	9.920	25	1.685	1.666	1.685
37.403	51.620	10.977	25	1.674	1.658	1.675
37.496	50.525	11.979	25	1.664	1.650	1.665
37.537	49.430	13.032	25	1.654	1.642	1.655
37.994	50.905	11.101	25	1.655	1.653	1.672
38.927	54.044	7.029	25	1.723	1.674	1.708
38.865	53.176	7.958	25	1.695	1.668	1.699
39.006	52.025	8.969	25	1.684	1.661	1.688
40.007	49.952	10.041	25	1.676	1.646	1.674
39.999	49.006	10.995	25	1.663	1.640	1.665
39.989	48.008	12.002	25	1.654	1.633	1.656
39.873	47.166	12.961	25	1.645	1.627	1.647
39.727	46.125	14.149	25	1.636	1.620	1.637
41.956	52.396	5.648	25	1.711	1.658	1.712
42.555	51.417	6.027	25	1.705	1.651	1.706
42.655	50.250	7.094	25	1.694	1.645	1.694
42.502	49.454	8.045	25	1.683	1.641	1.685
42.457	48.508	9.035	25	1.673	1.635	1.675
42.394	47.576	10.030	25	1.664	1.630	1.665
42.553	46.475	10.972	25	1.654	1.623	1.656
42.313	45.532	12.155	25	1.644	1.617	1.645
42.632	44.423	12.945	25	1.635	1.610	1.637
42.587	43.419	13.994	25	1.626	1.604	1.627
42.392	42.620	14.988	25	1.619	1.599	1.618
44.953	49.246	5.802	25	1.699	1.635	1.699

44.842	49.082	6.076	25	1.697	1.634	1.696
44.172	48.857	6.970	25	1.686	1.635	1.689
45.079	46.957	7.965	25	1.676	1.624	1.675
44.964	46.062	8.974	25	1.666	1.619	1.666
44.367	45.838	9.795	25	1.659	1.619	1.660
45.032	44.026	10.942	25	1.646	1.609	1.646
44.783	43.224	11.993	25	1.637	1.604	1.637
44.941	41.918	13.141	25	1.626	1.597	1.625
44.979	41.016	14.004	25	1.619	1.592	1.617
45.015	40.013	14.972	25	1.609	1.586	1.608
46.913	47.185	5.902	25	1.691	1.621	1.690
47.359	46.593	6.048	25	1.688	1.618	1.687
47.120	45.905	6.974	25	1.679	1.616	1.678
47.483	44.516	8.000	25	1.666	1.609	1.665
47.322	43.667	9.010	25	1.656	1.606	1.656
47.370	42.535	10.095	25	1.645	1.600	1.645
47.460	41.539	11.000	25	1.636	1.596	1.636
47.246	40.790	11.964	25	1.628	1.592	1.627
47.299	39.501	13.200	25	1.617	1.585	1.615
47.328	38.669	14.004	25	1.609	1.581	1.607
47.486	37.469	15.045	25	1.599	1.575	1.597
49.477	44.489	6.033	25	1.677	1.606	1.678
50.090	43.845	6.065	25	1.674	1.602	1.675
50.079	42.925	6.996	25	1.666	1.599	1.665
50.025	41.951	8.024	25	1.653	1.596	1.655
49.905	41.084	9.012	25	1.642	1.593	1.645
49.363	39.587	11.050	25	1.634	1.587	1.627
50.173	38.868	10.959	25	1.625	1.584	1.625
49.949	38.040	12.011	25	1.616	1.581	1.616
49.748	36.975	13.277	25	1.605	1.576	1.604
49.895	36.059	14.046	25	1.599	1.572	1.597
49.920	35.157	14.923	25	1.591	1.567	1.588
51.675	42.180	6.146	25	1.666	1.594	1.668
52.546	40.480	6.974	25	1.652	1.588	1.656
52.410	39.584	8.006	25	1.645	1.586	1.645
52.411	38.609	8.980	25	1.635	1.583	1.635
52.433	37.586	9.982	25	1.626	1.580	1.625
50.826	38.098	11.076	25	1.617	1.581	1.621
50.886	36.902	12.212	25	1.607	1.576	1.610
50.886	35.935	13.179	25	1.598	1.572	1.601
51.075	34.729	14.196	25	1.585	1.568	1.590
50.691	34.013	15.296	25	1.577	1.564	1.581
54.294	39.427	6.280	25	1.656	1.584	1.656

54.518	39,191	6.291	25	1.653	1.583	1.655
54.999	37.978	7.023	25	1.644	1.580	1.645
55.100	36.913	7.987	25	1.635	1.578	1.635
54.872	36.128	9.000	25	1.625	1.576	1.626
55.044	35.024	9.932	25	1.615	1.573	1.616
55.002	34.013	10.985	25	1.606	1.570	1.606
54.971	33.027	12.002	25	1.598	1.567	1.596
55.045	31.930	13.024	25	1.587	1.564	1.586
54.878	31.143	13.979	25	1.580	1.561	1.578
55.014	29.947	15.038	25	1.570	1.557	1.567
56.744	36.850	6.405	25	1.645	1.577	1.645
60.900	32.482	6.618	25	1.643	1.572	1.629
61.263	31.583	7.154	25	1.634	1.572	1.622
61.204	30.759	8.037	25	1.623	1.571	1.614
61.093	29.990	8.916	25	1.615	1.571	1.606
61.182	28.996	9.822	25	1.603	1.570	1.597
61.108	28.185	10.707	25	1.592	1.569	1.589
60.687	27.774	11.539	25	1.590	1.567	1.583
61.074	26.384	12.543	25	1.579	1.566	1.573
61.138	25.477	13.386	25	1.571	1.564	1.565
61.153	24.586	14.262	25	1.562	1.562	1.557
58.940	34.542	6.518	25	1.635	1.573	1.636
59.468	33.988	6.545	25	1.636	1.573	1.634
59.954	33.045	7.001	25	1.627	1.572	1.628
59.986	31.979	8.034	25	1.614	1.571	1.618
60.047	30.925	9.028	25	1.604	1.570	1.608
60.005	29.960	10.035	25	1.596	1.569	1.598
59.975	29.008	11.017	25	1.588	1.567	1.589
59.923	28.020	12.056	25	1.578	1.565	1.580
60.031	25.971	13.998	25	1.561	1.561	1.562
60.799	24.331	14.870	25	1.551	1.560	1.553
61.600	31.746	6.654	25	1.623	1.572	1.627
62.007	31.319	6.675	25	1.620	1.572	1.625
62.484	30.542	6.974	25	1.616	1.573	1.621
62.624	29.403	7.973	25	1.604	1.573	1.611
62.429	28.595	8.976	25	1.594	1.572	1.602
62.543	27.460	9.997	25	1.585	1.572	1.592
20.055	74.939	5.006	40	1.789	1.829	1.784
20.110	73.848	6.042	40	1.768	1.818	1.772
20.084	72.819	7.097	40	1.757	1.808	1.760
19.943	72.005	8.052	40	1.748	1.799	1.750
22.662	68.535	8.802	40	1.727	1.774	1.729
20.077	69.806	10.117	40	1.730	1.777	1.724

19.990	68.881	11.129	40	1.717	1.767	1.712
19.983	67.941	12.076	40	1.708	1.757	1.701
19.838	66.211	13.952	40	1.691	1.738	1.680
19.568	65.579	14.854	40	1.680	1.730	1.671
22.466	72.322	5.212	40	1.767	1.810	1.769
22.413	71.478	6.109	40	1.759	1.802	1.760
22.712	70.307	6.981	40	1.742	1.792	1.749
21.877	70.252	7.871	40	1.749	1.789	1.743
22.653	68.344	9.002	40	1.728	1.772	1.726
22.906	66.932	10.162	40	1.716	1.758	1.712
22.356	66.783	10.861	40	1.711	1.755	1.707
22.550	65.456	11.994	40	1.700	1.742	1.693
22.524	64.365	13.111	40	1.689	1.730	1.682
19.748	67.522	12.731	40	1.703	1.752	1.694
22.505	62.269	15.226	40	1.670	1.708	1.661
24.893	70.031	5.076	40	1.761	1.793	1.760
25.051	68.854	6.095	40	1.749	1.782	1.748
24.841	68.101	7.058	40	1.741	1.775	1.739
24.892	67.081	8.027	40	1.730	1.765	1.728
25.109	65.799	9.091	40	1.715	1.753	1.716
24.984	65.026	9.990	40	1.710	1.745	1.707
24.895	64.157	10.948	40	1.696	1.736	1.697
24.251	64.003	11.745	40	1.701	1.733	1.690
25.005	61.955	13.040	40	1.681	1.714	1.675
23.011	63.976	13.014	40	1.688	1.728	1.681
24.852	60.208	14.940	40	1.664	1.695	1.658
27.486	67.381	5.133	40	1.748	1.771	1.749
27.403	66.576	6.021	40	1.739	1.764	1.740
27.392	64.553	8.055	40	1.721	1.745	1.718
27.273	63.493	9.234	40	1.710	1.735	1.706
27.478	61.430	11.092	40	1.690	1.715	1.687
27.445	62.286	10.269	40	1.681	1.723	1.695
27.769	59.117	13.113	40	1.670	1.693	1.667
27.441	58.321	14.238	40	1.661	1.685	1.658
27.454	57.558	14.988	40	1.654	1.677	1.651
29.980	64.985	5.035	40	1.741	1.750	1.741
29.765	63.931	6.304	40	1.741	1.741	1.729
29.816	62.606	7.578	40	1.717	1.729	1.715
29.810	61.977	8.214	40	1.708	1.723	1.708
30.046	60.948	9.006	40	1.701	1.714	1.699
29.704	60.206	10.090	40	1.691	1.707	1.689
30.148	58.865	10.987	40	1.680	1.695	1.679
29.886	58.073	12.041	40	1.671	1.688	1.670

30 359	56 664	12 976	40	1 661	1 675	1 660
29 593	56 581	13.826	40	1.656	1.673	1.655
30.055	55 037	14 908	40	1.630	1.679	1.645
32 278	62 569	5 1 5 3	40	1.011	1.009	1.013
32.270	61 551	6.026	40	1.752	1.720	1.752
32.423	60.656	7 261	40	1.723	1.720	1.722
32.003	50 301	8 050	40	1.710	1.712	1.710
32.551	58 320	0.057	40	1.700	1.702	1.701
32.303	57 356	10.150	40	1.690	1.69/	1.690
22.403	56 486	11.022	40	1.000	1.004	1.000
32.491	55 431	12.002	40	1.672	1.67	1.671
22.507	54 285	12.002	40	1.001	1.007	1.002
22.031	52 442	12.042	40	1.033	1.057	1.052
32.010	51 221	15.942	40	1.034	1.030	1.043
33./41	50.822	13.028	40	1.018	1.032	1.032
34.002	59.852	5.280	40	1.720	1.705	1.722
35.047	57.054	0.078	40	1./11	1.090	1./13
35.060	57.954	6.986	40	1.702	1.689	1.703
34.8/3	56.876	8.252	40	1.689	1.680	1.691
34.834	55.936	9.230	40	1.681	1.673	1.681
35.038	55.038	9.924	40	1.663	1.666	1.673
35.049	54.018	10.933	40	1.663	1.657	1.664
34.949	52.994	12.057	40	1.653	1.649	1.654
34.287	52.911	12.802	40	1.649	1.648	1.649
34.848	51.266	13.886	40	1.637	1.634	1.638
35.128	49.809	15.063	40	1.625	1.622	1.627
37.478	57.104	5.419	40	1.711	1.679	1.712
37.205	56.717	6.079	40	1.706	1.677	1.705
36.818	55.985	7.197	40	1.694	1.672	1.695
37.447	54.547	8.007	40	1.683	1.661	1.684
37.379	53.623	8.999	40	1.675	1.654	1.674
37.362	52.718	9.920	40	1.665	1.647	1.665
37.403	51.620	10.977	40	1.654	1.639	1.655
37.496	50.525	11.979	40	1.645	1.631	1.645
37.537	49.430	13.032	40	1.635	1.622	1.636
37.994	50.905	11.101	40	1.636	1.634	1.652
38.927	54.044	7.029	40	1.703	1.656	1.689
38.865	53.176	7.958	40	1.675	1.650	1.679
39.006	52.025	8.969	40	1.664	1.642	1.669
40.007	49.952	10.041	40	1.653	1.627	1.654
39.999	49.006	10.995	40	1.643	1.620	1.645
39.989	48.008	12.002	40	1.635	1.613	1.636
39.873	47.166	12.961	40	1.626	1.607	1.628
39.727	46.125	14.149	40	1.617	1.599	1.618

41.956	52.396	5.648	40	1.691	1.639	1.693
42.555	51.417	6.027	40	1.685	1.632	1.686
42.655	50.250	7.094	40	1.673	1.626	1.674
42.502	49.454	8.045	40	1.663	1.621	1.665
42.457	48.508	9.035	40	1.653	1.615	1.655
42.394	47.576	10.030	40	1.644	1.610	1.645
42.553	46.475	10.972	40	1.635	1.603	1.636
42.313	45.532	12.155	40	1.624	1.597	1.626
42.632	44.423	12.945	40	1.616	1.590	1.617
42.587	43.419	13.994	40	1.607	1.583	1.608
42.392	42.620	14.988	40	1.600	1.578	1.599
44.953	49.246	5.802	40	1.679	1.615	1.678
44.842	49.082	6.076	40	1.676	1.615	1.676
44.172	48.857	6.970	40	1.665	1.615	1.669
45.079	46.957	7.965	40	1.655	1.603	1.655
44.964	46.062	8.974	40	1.645	1.599	1.645
44.367	45.838	9.795	40	1.639	1.598	1.640
45.032	44.026	10.942	40	1.626	1.587	1.626
44.783	43.224	11.993	40	1.617	1.583	1.617
44.941	41.918	13.141	40	1.607	1.575	1.606
44.979	41.016	14.004	40	1.599	1.570	1.598
45.015	40.013	14.972	40	1.590	1.564	1.588
46.913	47.185	5.902	40	1.670	1.601	1.669
47.359	46.593	6.048	40	1.667	1.597	1.665
47.120	45.905	6.974	40	1.659	1.594	1.657
47.483	44.516	8.000	40	1.646	1.587	1.645
47.322	43.667	9.010	40	1.635	1.584	1.635
47.370	42.535	10.095	40	1.624	1.578	1.625
47.460	41.539	11.000	40	1.615	1.573	1.616
47.246	40.790	11.964	40	1.608	1.569	1.607
47.299	39.501	13.200	40	1.597	1.563	1.595
47.328	38.669	14.004	40	1.591	1.558	1.587
47.486	37.469	15.045	40	1.580	1.552	1.576
49.477	44.489	6.033	40	1.656	1.583	1.656
50.090	43.845	6.065	40	1.653	1.580	1.652
50.079	42.925	6.996	40	1.645	1.576	1.643
50.025	41.951	8.024	40	1.632	1.573	1.633
49.905	41.084	9.012	40	1.621	1.569	1.624
49.363	39.587	11.050	40	1.613	1.563	1.607
50.173	38.868	10.959	40	1.604	1.560	1.605
49.949	38.040	12.011	40	1.596	1.556	1.596
49.748	36.975	13.277	40	1.585	1.551	1.584
49.895	36.059	14.046	40	1.579	1.547	1.576

49.920	35.157	14.923	40	1.571	1.543	1.567
51.675	42.180	6.146	40	1.645	1.570	1.644
52.546	40.480	6.974	40	1.630	1.563	1.632
52.410	39.584	8.006	40	1.623	1.561	1.623
52.411	38.609	8.980	40	1.614	1.558	1.614
52.433	37.586	9.982	40	1.605	1.554	1.605
50.826	38.098	11.076	40	1.596	1.557	1.601
50.886	36.902	12.212	40	1.586	1.552	1.590
50.886	35.935	13.179	40	1.578	1.547	1.581
51.075	34.729	14.196	40	1.564	1.542	1.570
50.691	34.013	15.296	40	1.556	1.538	1.559
54.294	39.427	6.280	40	1.634	1.557	1.630
54.518	39.191	6.291	40	1.632	1.556	1.629
54.999	37.978	7.023	40	1.622	1.552	1.620
55.100	36.913	7.987	40	1.594	1.550	1.611
54.872	36.128	9.000	40	1.603	1.548	1.603
55.044	35.024	9.932	40	1.594	1.545	1.595
55.002	34.013	10.985	40	1.585	1.542	1.586
54.971	33.027	12.002	40	1.577	1.538	1.577
55.045	31.930	13.024	40	1.566	1.535	1.566
54.878	31.143	13.979	40	1.560	1.532	1.557
55.014	29.947	15.038	40	1.550	1.528	1.545
56.744	36.850	6.405	40	1.623	1.547	1.617
61.204	30.759	8.037	40	1.601	1.534	1.586
61.093	29.990	8.916	40	1.593	1.533	1.581
61.182	28.996	9.822	40	1.582	1.531	1.575
61.108	28.185	10.707	40	1.571	1.530	1.569
60.687	27.774	11.539	40	1.569	1.529	1.563
61.074	26.384	12.543	40	1.558	1.526	1.554
61.138	25.477	13.386	40	1.550	1.524	1.546
61.153	24.586	14.262	40	1.542	1.522	1.537
58.940	34.542	6.518	40	1.613	1.540	1.605
59.468	33.988	6.545	40	1.614	1.539	1.603
59.954	33.045	7.001	40	1.605	1.537	1.597
59.986	31.979	8.034	40	1.592	1.536	1.590
60.047	30.925	9.028	40	1.582	1.534	1.584
60.005	29.960	10.035	40	1.574	1.533	1.577
59.975	29.008	11.017	40	1.567	1.531	1.569
59.923	28.020	12.056	40	1.557	1.529	1.561
60.031	25.971	13.998	40	1.540	1.524	1.542
60.799	24.331	14.870	40	1.530	1.521	1.530
61.600	31.746	6.654	40	1.600	1.534	1.592
62.007	31.319	6.675	40	1.598	1.533	1.590

62.484	30.542	6.974	40	1.593	1.533	1.587
62.624	29.403	7.973	40	1.582	1.532	1.581
62.429	28.595	8.976	40	1.572	1.531	1.577
62.543	27.460	9.997	40	1.563	1.530	1.570

**Table C.3** Best-Fit Polynomial Expansion Coefficients for Improved Density Model for H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub>/H<sub>2</sub>O System

ρi,j	j=0	1	2	3					
T = 293 K									
i=0	1.0897×10 <sup>-5</sup>	3.4921×10 <sup>-4</sup>	4.2856×10 <sup>-4</sup>	-2.4293×10 <sup>-6</sup>					
1	1.6037×10 <sup>-4</sup>	3.2482×10 <sup>-3</sup>	-5.7128×10 <sup>-5</sup>	2.3503×10 <sup>-7</sup>					
2	6.6719×10 <sup>-4</sup>	-6.3841×10 <sup>-5</sup>	5.7328×10 <sup>-7</sup>						
3	-5.7401×10 <sup>-6</sup>	3.0376×10 <sup>-7</sup>							
4	1.0251×10 <sup>-8</sup>								
	T = 253K								
i=0	-1.6478×10 <sup>-2</sup>	-4.0830×10 <sup>-2</sup>	1.3893×10 <sup>-3</sup>	-7.9541×10 <sup>-6</sup>					
1	-5.2735×10 <sup>-2</sup>	6.8801×10 <sup>-3</sup>	-1.1019×10 <sup>-4</sup>	4.3820×10 <sup>-7</sup>					
2	2.4178×10 <sup>-3</sup>	-1.2811×10 <sup>-4</sup>	1.0375×10 <sup>-6</sup>						
3	-2.5255×10 <sup>-5</sup>	6.2526×10 <sup>-7</sup>							
4	8.3995×10 <sup>-8</sup>								

## C.4 Discussion

The improved density model provides significant improvement over the model published by Martin et al. for the prediction of density for the ternary sulfuric acid, nitric acid, and water system. The correlation coefficient for the complete set of acids analyzed under this study was 0.877 for the Martin model and 0.994 for the improved density model. Figures C.1 and C.2 are comparisons of the models for the density measurements recorded at 25°C and 40°C, respectively, showing excellent agreement between the improved density model and the experimental results.



Figure C.1 Comparison of Martin and Improved Density Models at 25°C with experimentally measured diffusivities.



Figure C.2 Comparison of Martin and Improved Density Models at 40°C with experimentally measured diffusivities.

#### **C.5 Findings and Recommendations**

The improved density model provides significant improvements for the prediction of densities of mixed acid compositions of interest for industrial nitrocellulose manufacturing processes. While this model demonstrated excellent agreement with the experimental data ( $R^2 = 0.994$ ), a sensitivity analysis should be conducted to determine whether the improved density model can either be simplified by removing terms without compromising the accuracy of the model or if additional terms result in a significant improvement to the predictive capability of the model. For the current effort, the model was used in the same polynomial expansion form as the model proposed by Martin et al., but with improved parameters,  $\rho_{i,j}$ , that substantially improve the accuracy of the model for predicting the densities of acid compositions used in the nitration of cellulose.

### **C.6 Conclusions**

An improved density model for the ternary sulfuric acid, nitric acid, and water system was developed to enable more accurate estimation of densities for mixed acid compositions used in industrial nitration reactions. This model used the same polynomial expansion and regression procedure proposed by Martin et al.<sup>41</sup> but with experimentally measured densities for a more expansive set mixed acid compositions that were obtained using a density and sound velocity analyzer. The resulting model provides significantly improved capability for predicting the density mixed acid compositions used in the nitration of cellulose and other energetic materials.

# REFERENCES

- 1. Urbański T. *Chemistry and Technology of Explosives.* New York, NY: Macmillan; 1964.
- 2. Ott E, Spurlin HM, Grafflin MW. *Cellulose and Cellulose Derivatives*. Vol V. 2nd ed. New York, NY: Interscience Publishers; 1954.
- 3. O'Sullivan AC. Cellulose: The Structure Slowly Unravels. *Cellulose*. 1997;4(3):173-207.
- 4. Klein R, Mentser M. The Mechanism of Cellulose Nitration. *Journal of the American Chemical Society*. 1951;73(12):5888-5888.
- 5. Munro HS, Short RD, Fowler AHK. Nitration of Cellulose in Mixed Acids: The Role of the Nitronium Ion. *Polymer Communications Guildford*. 1986;27(8):251-254.
- 6. Golubev AE, Kuvshinova SA, Burmistrov VA, Koifman Ol. Modern Advances in the Preparation and Modification of Cellulose Nitrates. *Russian Journal of General Chemistry*. 2018;88(2):368-381.
- 7. Tarchoun AF, Trache D, Klapötke TM, et al. A Promising Energetic Polymer from Posidonia oceanica Brown Algae: Synthesis, Characterization, and Kinetic Modeling. *Macromolecular Chemistry and Physics.* 2019;220(22):1900358.
- 8. Dong-Ping S, Bo M, Chun-Lin Z, Chang-Sheng L, Jia-Zhi Y. Novel Nitrocellulose Made from Bacterial Cellulose. *Journal of Energetic Materials*. 2010;28(2):85-97.
- 9. Wang Y, Wang X, Xie Y, Zhang K. Functional Nanomaterials Through Esterification of Cellulose: A Review of Chemistry and Application. *Cellulose*. 2018;25(7):3703-3731.
- 10. Short RD. *An Investigation of the Surface and Bulk Nitration of Cellulose* [Ph.D.]. Durham, UK, Durham University; 1986.
- 11. MIL-DTL-244B. In. Vol Detail Specification: Nitrocellulose: Defense Quality and Standardization Office; 1996.
- 12. TM-9-1300-214. In. Vol Military Explosives. Washington, DC: Department of the Army Technical Manual; 1984.
- 13. Atsuki K, Ishiwara M. Studies on Esterification of Cellulose and Cellulose Esters. *Proceedings of the Imperial Academy.* 1928;4(7):382-385.
- 14. Barbosa IVM, Merquior DM, Peixoto FC. Continuous Modelling and Kinetic Parameter Estimation for Cellulose Nitration. *Chemical Engineering Science*. 2005;60:5406-5413.
- 15. Fowler AHK. Some Aspects of the Surface and Bulk Chemistry of Cellulose Nitrates as Studied by ESCA and Other Spectroscopic Techniques [Ph.D.]. Durham, UK, Durham University; 1984.

- 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.
- 17. Stovbun SV, Nikol'skii SN, Mel'nikov VP, et al. Chemical Physics of Cellulose Nitration. *Russian Journal of Physical Chemistry B.* 2016;10(2):245-259.
- 18. Nikolsky SN, Zlenko DV, Melnikov VP, Stovbun SV. The Fibrils Untwisting Limits the Rate of Cellulose Nitration Process. *Carbohydrate Polymers*. 2019;204:232-237.
- 19. Barbosa IVM, Merquior DM, Peixoto FC. Estimation of Kinetic and Mass-Transfer Parameters for Cellulose Nitration. *AIChE Journal*. 2006;52(10):3549-3554.
- 20. Salmi T, Damlin P, Mikkola JP, Kangas M. A Chemical Engineering Approach to Cellulose Substitution Kinetics. *Chemical Engineering Transactions*. 2011;24:151-156.
- 21. Salmi T, Damlin P, Mikkola J-P, Kangas M. Modelling and Experimental Verification of Cellulose Substitution Kinetics. *Chemical Engineering Science*. 2011;66(2):171-182.
- 22. Salmi T, Valtakari D, Paatero E, Holmbom B, Sjöholm R. Kinetic Study of the Carboxymethylation of Cellulose. *Industrial & Engineering Chemistry Research*. 1994;33(6):1454-1459.
- 23. Wu TK. Carbon-13 and Proton Nuclear Magnetic Resonance Studies of Cellulose Nitrates. *Macromolecules.* 1980;13(1):74-79.
- Fernández de la Ossa MÁ, López-López M, Torre M, García-Ruiz C. Analytical Techniques in the Study of Highly-Nitrated Nitrocellulose. *TRaC, Trends in Analytical Chemistry*. 2011;30:1740-1755.
- 25. TAPPI/ANSI T 271 om-12 In. *Fiber Length of Pulp and Paper by Automated Optical Analyzer Using Polarized Light*. Norcross, GA: Technical Association of the Pulp & Paper Industry; 2012.
- 26. Albright LF, Sood MK, Eckert RE. Modeling Nitronium Ion Concentrations in HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O Mixtures. *ACS Symposium Series*. 1996;623:201-213.
- 27. Edwards HGM, Turner JMC, Fawcett V. Raman Spectroscopic Study of Nitronium Ion Formation in Mixtures of Nitric Acid, Sulfuric Acid and Water. *Journal of the Chemical Society, Faraday Transactions*. 1995;91(10):1439-1443.
- 28. MIL-STD-286C. In. Vol Military Standard: Propellants, Solid: Sampling, Examination, and Testing. Picatinny Arsenal, NJ: Department of the Army; 2010.
- 29. *Mathematica* [computer program]. Version 11.3. Champaign, Illinois: Wolfram Research, Inc.
- 30. Zaman MB. *Nitronium Ions in Nitrating Acid Mixtures* [Ph.D.]. Bradford, UK: Postgraduate School of Studies in Chemical Engineering, University of Bradford; 1972.

- 31. Miles FD. *Cellulose Nitrate: The Physical Chemistry of Nitrocellulose, its Formation and Use.* London, UK: Published for Imperial Chemical Industries by Oliver and Boyd; 1955.
- 32. Chedin J, Tribot A. Réactions Topochimiques Sur la Cellulose. Mécanisme de Nitration. *Bulletin des Sociétés Chimiques Belges.* 1948;57(7-9):263-279.
- 33. Hughes ED, Ingold CK, Reed RI. Kinetics of Aromatic Nitration; The Nitronium Ion. *Nature.* 1946;158:448.
- 34. Bayliss NS, Watts DW. The Spectrophotometry of Nitrate Solutions in Aqueous Sulphuric Acid. *Australian Journal of Chemistry*. 1963;16(6):943.
- 35. Clark DT, Fowler AHK, Peeling J. A Carbon-13 N.M.R. Investigation of the Time Dependence of Nitration and Denitration of Cellulosic Materials. *Polymer Communications Guildford*. 1983;24(4):117-119.
- Lure BA, Valishina ZT, Svetlov BS. Kinetics and Mechanism of the Chemical Transformation of Nitrocellulose Under the Action of Aqueous Sulphuric Acid Solutions. *Polymer Science USSR.* 1991;33:99-106.
- 37. Chinga-Carrasco G. Cellulose Fibres, Nanofibrils and Microfibrils: The Morphological Sequence of MFC Components from a Plant Physiology and Fibre Technology Point of View. *Nanoscale Research Letters*. 2011;6(1):417.
- Klemm D, Heublein B, Fink HP, Bohn A. Cellulose: Fascinating Biopolymer and Sustainable Raw Material. *Angewandte Chemie - International Edition*. 2005;44(22):3358-3393.
- Foston M, Ragauskas AJ. Changes in the Structure of the Cellulose Fiber Wall during Dilute Acid Pretreatment in Populus Studied by <sup>1</sup>H and <sup>2</sup>H NMR. *Energy and Fuels*. 2010;24(10):5677-5685.
- 40. Kennedy JF. *Cellulose and its Derivatives: Chemistry, Biochemistry and Applications.* Chichester West Sussex, UK: E. Horwood; 1985.
- 41. Martin E, George C, Mirabel P. Densities and Surface Tensions of H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub>/H<sub>2</sub>O Solutions. *Geophysical Research Letters*. 2000;27(2):197-200.
- 42. Sun C. Communications: True Density of Microcrystalline Cellulose. *Journal of Pharmaceutical Sciences.* 2005;94:2132-2134.
- Short RD, Munro HS. Conclusions Drawn from a Study of Cellulose Nitration in Technical Mixed Acids by X-Ray Photoelectron Spectroscopy and <sup>13</sup>C Nuclear Magnetic Resonance. *Polymer.* 1993;34(13):2714-2719.
- 44. Prask H, Choi C. *The Correlation of Nitrocellulose Properties and Cellulose Feedstock Crystal Structure.* Dover, NJ 07801: ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND;1982. Technical Report ARLCD-TR-82011.

- 45. Clark DT, Stephenson PJ. A <sup>13</sup>C N.M.R. and X-Ray Study of the Relationship Between the Distribution of Nitrate Ester Groups and Interchain d(110) Spacings in a Series of Cellulose Nitrates. *Polymer.* 1982;23(9):1295-1299.
- 46. Trommel J. *The Molecular Arrangement of Cellulose Nitrates.* Nederlandsche Springstoffenfabrieken; 1959.
- 47. Liitiä T, Maunu SL, Hortling B. Effects of Pulping on Crystallinity of Cellulose Studied by Solid State NMR. In: *Cellulosic Pulps, Fibres and Materials.* Elsevier Ltd; 2001:39-44.
- Åkerholm M, Hinterstoisser B, Salmén L. Characterization of the Crystalline Structure of Cellulose Using Static and Dynamic FT-IR Spectroscopy. *Carbohydrate Research*. 2004;339(3):569-578.
- 49. Hoggett JG, Moodie RB, Penton JR, Schofield K. *Nitration and Aromatic Reactivity.* London, UK: Cambridge University Press; 1971.
- 50. 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.
- 51. Ségot-Chicq S, Peppas NA. Solute and Penetrant Diffusion in Swellable Polymers. IV. Semicrystalline, Swelling-Controlled Release Systems of Poly(Ethylene-co-Vinyl Alcohol). Journal of Controlled Release. 1986;3(1-4):193-204.
- 52. Davidson III GWR, Peppas NA. Solute and Penetrant Diffusion in Swellable Polymers. V. Relaxation-Controlled Transport in P(HEMA-co-MMA) Copolymers. *Journal of Controlled Release*. 1986;3(1-4):243-258.
- 53. *JMicroVision: Image Analysis Toolbox for Measuring and Quantifying Components of High-Definition Images* [computer program]. Version 1.3.1.
- 54. Nisancioglū K, Newman J. Diffusion in Aqueous Nitric Acid Solutions. *AIChE Journal.* 1973;19(4):797-801.
- 55. Chapman T, & Newman, J. A Compilation of Selected Thermodynamic and Transport Properties of Binary Electrolytes in Aqueous Solution. Berkeley, CA: Lawrence Berkeley National Laboratory;1968. LBNL Report #: UCRL-17767.
- 56. Plawsky JL. *Transport Phenomena Fundamentals.* 3rd ed. Boca Raton, FL: Taylor & Francis; 2014.
- 57. Leaist DG. Diffusion in Aqueous Solutions of Sulfuric Acid. *Canadian Journal of Chemistry*. 1984;62(9):1692-1697.
- 58. Brazel CS, Peppas NA. Modeling of Drug Release from Swellable Polymers. *European Journal of Pharmaceutics and Biopharmaceutics*. 2000;49(1):47-58.

- 59. Korsmeyer RW, Lustig SR, Peppas NA. Solute and Penetrant Diffusion in Swellable Polymers. I. Mathematical Modeling. *Journal of Polymer Science Part B: Polymer Physics*. 1986;24(2):395-408.
- 60. Lustig SR, Peppas NA. Solute and Penetrant Diffusion in Swellable Polymers. VII. A Free Volume-Based Model with Mechanical Relaxation. *Journal of Applied Polymer Science*. 1987;33(2):533-549.
- 61. Davidson III GWR, Peppas NA. Solute and Penetrant Diffusion in Swellable Polymers. VI. The Deborah and Swelling Interface Numbers as Indicators of the Order of Biomolecular Release. *Journal of Controlled Release*. 1986;3(1-4):259-271.
- 62. Curtiss CF, Bird RB. Multicomponent Diffusion. *Industrial & Engineering Chemistry Research*. 1999;38(7):2515-2522.
- 63. Gandhi KS. Use of Fick's Law and Maxwell-Stefan Equations in Computation of Multicomponent Diffusion. *AIChE Journal*. 2012;58(11):3601-3605.
- 64. Krishna R, Wesselingh JA. The Maxwell-Stefan Approach to Mass Transfer. *Chemical Engineering Science*. 1997;52(6):861-911.
- Bothe D. On the Maxwell-Stefan Approach to Multicomponent Diffusion. In: Escher J, Guidotti P, Hieber M, et al., eds. *Parabolic Problems: The Herbert Amann Festschrift*. Basel, CH: Springer Basel; 2011:81-93.
- 66. Bird RB, Stewart WE, Lightfoot EN. *Transport Phenomena*. Vol 413. New York, NY: John Wiley & Sons; 1960.
- 67. Curtiss CF. Symmetric Gaseous Diffusion Coefficients. *The Journal of Chemical Physics*. 1968;49(7):2917-2919.
- 68. Condiff DW. On Symmetric Multicomponent Diffusion Coefficients. *The Journal of Chemical Physics*. 1969;51(10):4209-4212.
- Klenø JG, Kristiansen MW, Nielsen CJ, Pedersen EJ, Williams LR, Pedersen T. Diffusion Coefficients in Cold Sulfuric Acid Solution. *The Journal of Physical Chemistry A*. 2001;105(37):8440-8444.
- 70. Fogler HS. *Elements of Chemical Reaction Engineering*. 4th ed. Boston, MA: Prentice Hall; 2016.
- 71. Koponen A, Kataja M, Timonen J. Tortuous Flow in Porous Media. *Physical Review E.* 1996;54(1):406-410.
- 72. Koponen A, Kataja M, Timonen J. Permeability and Effective Porosity of Porous Media. *Physical Review E.* 1997;56(3):3319-3325.
- 73. Ferrero C, Massuelle D, Jeannerat D, Doelker E. Towards Elucidation of the Drug Release Mechanism from Compressed Hydrophilic Matrices Made of Cellulose Ethers. I. Pulse-

Field-Gradient Spin-Echo NMR Study of Sodium Salicylate Diffusivity in Swollen Hydrogels with Respect to Polymer Matrix Physical Structure. *Journal of Controlled Release.* 2008;128:71-79.

- 74. Chinga Carrasco G. Microscopy and Computerized Image Analysis of Wood Pulp Fibres Multi-Scale Structures. *Microscopy: Science, Technology, Applications and Education, Formatex, Badajoz.* 2002:2182-2189.
- 75. Ramaswamy S, Gupta M, Goel A, et al. The 3D Structure of Fabric and its Relationship to Liquid and Vapor Transport. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2004;241(1):323-333.
- 76. Nilsson L, Stenström S. A Study of the Permeability of Pulp and Paper. *International Journal of Multiphase Flow.* 1997;23(1):131-153.
- 77. Campbell WB. The Physics of Water Removal. *Pulp and Paper Magazine of Canada*. 1947:103-109, 122.
- 78. Crank J. *The Mathematics of Diffusion*. 2nd ed. Oxford, UK: Clarendon Press; 1975.
- 79. Tjaden B, Cooper SJ, Brett DJL, Kramer D, Shearing PR. On the Origin and Application of the Bruggeman Correlation for Analysing Transport Phenomena in Electrochemical Systems. *Current Opinion in Chemical Engineering*. 2016;12:44-51.
- 80. Ray N, Rupp A, Schulz R, Knabner P. Old and New Approaches Predicting the Diffusion in Porous Media. *Transport in Porous Media*. 2018;124(3):803-824.
- Messa GV, Malavasi S. Computational Investigation of Liquid-Solid Slurry Flow through an Expansion in a Rectangular Duct. *Journal of Hydrology and Hydromechanics*. 2014;62(3):234.
- 82. Torotwa I, Ji C. A Study of the Mixing Performance of Different Impeller Designs in Stirred Vessels Using Computational Fluid Dynamics. *Designs*. 2018;2(1):10.
- 83. Derksen JJ. Numerical Simulation of Solids Suspension in a Stirred Tank. *AIChE Journal*. 2003;49(11):2700-2714.
- Jiang Y, Khadilkar MR, Al-Dahhan MH, Dudukovic MP. CFD Modeling of Multiphase Flow Distribution in Catalytic Packed Bed Reactors: Scale Down Issues. *Catalysis Today*. 2001;66(2):209-218.
- 85. Jafari A, Zamankhan P, Mousavi SM, Pietarinen K. Modeling and CFD Simulation of Flow Behavior and Dispersivity through Randomly Packed Bed Reactors. *Chemical Engineering Journal.* 2008;144(3):476-482.
- 86. Valdes-Parada F, Lasseux D, Whitaker S. Diffusion and Heterogeneous Reaction in Porous Media: The Macroscale Model Revisited. *International Journal of Chemical Reactor Engineering*. 2017.

- 87. *COMSOL Multiphysics* <sup>®</sup> [computer program]. Version 5.3. Stockholm, Sweden: COMSOL AB.
- 88. Green DW, Southard MZ. *Perry's Chemical Engineers' Handbook.* 9th ed. New York, NY: McGraw-Hill Education; 2019.