Estimation of Kinetic and Mass-Transfer Parameters for Cellulose Nitration

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When nitrocellulose is used in the production of gun powders and rocket/missile propellants, rigid control of the cellulose nitration reaction is necessary. Nitrogen content is, by far, the most important parameter to be controlled and only off-line measurements can be performed for that. Although cellulose is a natural polymer whose characteristics may vary, the final product must have its nonuniformities compensated by blending of different batches. In this work, kinetic and mass-transfer parameters are nonlinearly fitted using typical nitration experiments. The required mathematical modeling is carried out using a continuous mixtures approach, which depends only on structural descriptions of the cellulose. The model leads to an algebraic-integro-differential population balance system of equations, solved with an approximant built with block-pulse functions. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 3549–3554, 2006

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Introduction

Nitrocellulose, or cellulose nitrate, has been used in a wide range of products.[1] Of particular interest are smokeless gun powders and propellants for rocket and missiles, in which a rigid product quality control must be implemented, given that ballistic behavior profoundly depends on nitrocellulose characteristics. However, this is a difficult task because cellulose nitration can be monitored only by off-line measurements. Therefore, products of different batches must be blended to achieve some predefined ballistic behavior, on a mean basis, because with the mentioned off-line nitrogen measurements, it is almost impossible to achieve a reliable reaction monitoring. Besides, cellulose is a natural polymer and its characteristics may vary depending on its geographic origin and season of the year. Even if a rigid reaction protocol is followed, slight differences in molecular weight distributions of the reactant can lead to products with a completely diverse ballistic behavior.

Therefore, a reliable predictive model would be of great assistance. Such a model cannot depend on the reactant, which is common in lumped models.[2] A good alternative is the usage of continuous models, built with structural descriptions of the cellulose molecule, which tend to exhibit parameters that are independent of the cellulose or sulfonitric mixture used. Once parameters are fitted and cellulose molecular weight distribution is measured by size-exclusion chromatography (SEC),[3-6] the ideal batch time can be defined.

The mentioned continuous models arise when the reactional mixture is assumed to be composed of a homologous series of molecules, deferring one from the other by a typical functional group. Availability of such a group is related to an index whose continuity is assumed. Therefore, molar concentration C_i of each species A_i of the mixture is replaced by $f(x)dx$, which is the molar concentration of material with an index in the $(x, x + dx)$ interval. Function $f(x)$ is known as the mixture concentration distribution function (CDF) in mol/m^3. In the present approach, more than one index is used to completely characterize the continuum of species, where x is a vector of n continuous indexes. The molar concentration of species with indexes in the region $(x_1, x_1 + dx_1) \times (x_2, x_2 + dx_2) \times \cdots \times (x_n, x_n + dx_n)$ is given by the analogous expression $f(x)d^nx$.

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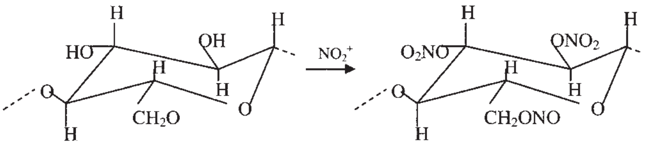

Figure 1. Cellulose nitration.

Material balances in such approaches lead to n-dimensional integro-differential equations whose solutions have been traditionally accessed by numerical methods. A comprehensive list of typical mathematical approaches for this class of problems can be found in the related literature.[1]

For the cellulose nitration, even if no diffusional effects are considered, all reactants and products belong to the same double-index continuous series, which increases the mathematical complexity of the problem; as described in previous works, this leads to balances expressed by integro-differential equations. However, if mass-transfer effects are taken into account, algebraic-integro-differential systems must be solved because the concentration profile on the fiber surface must be calculated at each simulation time. An efficient mathematical strategy for solution of this problem is the main original feature of the present work, which used a block-pulse expansion,[7] in conjunction with the integration of the resulting algebraic-differential system.

The developed model is based on a structural description of cellulose and nitrocellulose, and kinetic and diffusion parameters were fitted using an experimental protocol of cellulose nitration reactions, standard maximum likelihood criteria, and also standard nonlinear optimization methods.[1,2,8,9] Diffusion aspects required the calculation of the number of moles of nitronium ions available at each simulation time.

Modeling

Cellulose is a linear polymer consisting of β-1,4-linked D-glucopyranose units[1] and its nitration to nitrocellulose follows the scheme in Figure 1.

Therefore, a typical nitrocellulose molecule can be represented as $[C_6H_{10\text{-}3x}O_{5\text{-}6x}N_{3x}]_z$ and denoted by $P(x, z)$, where $z \in R^+$ stands for the number of monomeric units and $x \in [0, 1]$ is the fraction of nitration points that was effectively nitrated. So, in $P(x, z)$, there are $3z$ nitration points from which $3xz$ were effectively nitrated and $3z(1 - x)$ are still to be nitrated. The CDF is then denoted by $f(x, z, t)$ and a normalization condition is given by

$$\int_0^\infty \int_0^1 f(x, z, t)dxdz = C(t) \tag{1}$$

where $C(t)$ is the total concentration in mol/m^3 of cellulose.

The initial condition for $f(x, z, t)$ can be represented as

$$f(x, z, 0) = C_0 g_0(z)\delta(x) \tag{2}$$

where C_0 is the initial concentration in mol/m^3 of cellulose, $\delta(x)$ is the Dirac delta function, and $g_0(z)$ is the normalized initial concentration distribution function (NICDF), which will be chosen to be a Pearson type III distribution[10]:

$$g_0(z) = \frac{\varepsilon^{\eta+1} z^\eta \exp(-\varepsilon z)}{\Gamma(\eta + 1)} \tag{3}$$

The fraction of molecules with indexes (y, z) that are nitrated to produce molecules with indexes (x, z), where $x > y$, is given by the stoichiometric coefficient distribution function (SCDF)[1]:

$$v(x, y) = B\,\frac{(1 - x)^m (x - y)^m}{(1 - y)^{2m+1}} \tag{4}$$

with

$$B = \frac{\Gamma(2m + 2)}{[\Gamma(m + 1)]^2} \tag{5}$$

to address the obvious normalization.

To establish the rate of consumption of $P(x, z)$, some balances must be performed. Denoting by $c_s(t)$ the concentration of nitronium ions at the surface of the cellulose fiber, one can assume the following rate of "consumption" of nitrable sites:

$$r(x, z, t) = Kc_s(t)C_0 g(x, z, t) \tag{6}$$

where K is the specific reaction rate or velocity constant (an adjustable kinetic parameter) and $g(x, z, t) = f(x, z, t)/C_0$ is the normalized concentration distribution function NCDF.

It can be easily seen that the bulk concentration of nitronium ions is given by

$$c(t) = c_0 - \int_0^\infty \int_0^1 3xzC_0 g(x, z, t)dxdz \tag{7}$$

because one mole of nitronium ions reacts with one mole of nitration points. Once the concentration of nitration points of molecules with indexes in the region $[x, x + dx] \times [z, z + dz]$ is given by $3z(1 - x)f(x, z, t)dxdz$, $c_s(t)$ can be calculated, at each time, by equaling the rate of NO_2^+ consumption at the surface of the fiber to the rate of diffusion of the ion from the solution to the fiber:

$$\int_0^\infty \int_0^1 \int_0^x 3Kz(x - y)v(x, y)c_S(t)C_0 g(y, z, t)dydxdz = \alpha_d[c(t) - c_S(t)] \tag{8}$$

where α_d is a diffusional adjustable parameter given by $\alpha_d = DA/\delta$, in which A is the total surface area (in m^2), D is a diffusion coefficient (in s^{-1} m^{-1}), and δ is the thickness of the diffusion film (in m).

So, with all this elements, a typical normalized population balance equation can be written for species $P(x, z)$:

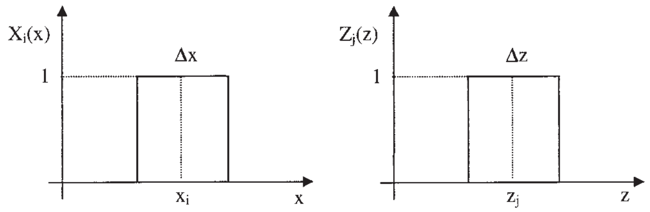

Figure 2. Block-pulse functions.

$$\frac{\partial g(x, z, t)}{c_s(t)\partial t} = -3Kz(1 - x)g(x, z, t) + \int_0^x 3Kz(1 - y)v(x, y)g(y, z, t)dy \quad (9)$$

The left-side term in Eq. 9 is an accumulation one; on the right side, there is a disappearance term and an integral term that takes into account the contribution of all species with $y < x$ that form $P(x, z)$ after nitration.

The initial condition for Eq. 9 is given by

$$g(x, z, 0) = g_0(z)\delta(x) \quad (10)$$

Equation 9 must be solved in conjunction with Eq. 8 because of the presence of $c_s(t)$, differently from other approaches found in literature.[1]

Numerical Solution

The following approximant for the NCDF is proposed:

$$\tilde{g}(x, z, t) = \sum_i \sum_j g_{ij}(t) X_i(x) Z_j(z) \quad (11)$$

where $X_i(x)$ and $Z_j(z)$ are block-pulse functions,[7] respectively, built around x_i and z_j, which are, at their time, the ith and the jth discretization points of each domain, according to Figure 2.

The approximant is substituted in Eq. 9 and the series in Eq. 11 is truncated on $i = nx$ and $j = nz$, resulting in a residue. The Galerkin method is then used, forcing this residue to be orthogonal to every function of the base expansion, for instance $X_l(x)$ and $Z_s(z)$, leading to

$$\frac{dg_{ls}(t)}{c_s(t)dt} \Delta x \Delta z = p_s v_l g_{ls} + Bp_s \sum_{i=1}^{l-1} A_{li} g_{is} \quad (12)$$

where

$$p_s = 3K\xi_s \qquad \text{with } \xi_s = \left.\frac{z^2}{2}\right|_{z_s-(\Delta z/2)}^{z_s+(\Delta z/2)} \quad (13)$$

$$v_l = \chi_l - \Delta x \qquad \text{with } \chi_l = \left.\frac{x^2}{2}\right|_{x_1-(\Delta x/2)}^{x_l+(\Delta x/2)} \quad (14)$$

and

$$A_{li} = \begin{cases} \displaystyle\int_{x_l-(\Delta x/2)}^{x_l+(\Delta x/2)} \int_{x_i-(\Delta x/2)}^{x_i+(\Delta x/2)} \frac{(1 - x)^m (x - y)^m}{(1 - y)^{2m}} dydx & \text{if } i < 1 \\ 0 & \text{if } i \geq 1 \end{cases} \quad (15)$$

With the previous entities, it is also possible to calculate $c(t)$ in Eq. 7:

$$c(t) = c_0 - 3C_0 \underline{\chi}^t \underline{\underline{G}}\ \underline{\xi} \quad (16)$$

where $(\underline{\underline{G}})_{ls} = g_{ls}$, and $c_s(t)$ in Eq. 8:

$$c_s(t) = \frac{c(t)}{\left[\dfrac{-3KBC_0B_2\underline{\mathrm{v}}_1^t\ \underline{\underline{G}}\ \underline{\xi}_{\mathrm{j}}}{\alpha_d} + 1\right]} \quad (17)$$

where the superscript t indicates matrix transposition and

$$B_2 = \left[\frac{\Gamma(m + 2)\Gamma(m + 1)}{\Gamma(2m + 3)}\right] \quad (18)$$

Equation 12 can be written as

$$\frac{d\underline{G}_s(t)}{dt} = c_s(t)\underline{\underline{M}}\,\underline{G}_s(t) \quad (19)$$

where $\underline{G}_s$ is the sth column of $\underline{\underline{G}}$ and

$$\underline{\underline{M}} = \frac{p_s}{\Delta x \Delta z}[\underline{\underline{\mathrm{Diag}}}(\underline{v}) + B\underline{\underline{A}}] \quad (20)$$

where

$$\underline{\underline{\mathrm{Diag}}}(\underline{v}) = \begin{bmatrix} v_1 & 0 & \cdots & 0 \\ 0 & v_2 & \cdots & 0 \\ \cdots & \cdots & \cdots & 0 \\ 0 & \cdots & 0 & v_{nz} \end{bmatrix} \quad (21)$$

The initial condition for Eq. 19 can be found in a similar way, applying the same expansion and the Galerkin method:

$$G_{ls}(0) = \begin{cases} \displaystyle\int_{z_s-(\Delta z/2)}^{z_s+(\Delta z/2)} \frac{g_0(z)dz}{\Delta x \Delta z} & \text{for } l = 1 \\ 0, & \text{for } l \neq 1 \end{cases} \quad (22)$$

Integrals on Eq. 22 are accessed by standard quadrature methods and Eq. 19 is integrated by the Euler method

$$\underline{G}_s(t^{n+1}) = \underline{G}_s(t^n) + \left.\frac{d\underline{G}_s(t)}{dt}\right|_{t^n} \Delta t \quad (23)$$

Table 1. Results of Kinetic Parameters Regression

Parameter	Value (Unit)
K	$(3.7 \pm 0.5) \times 10^{17} \left[\dfrac{\text{mol}_{P(x,z)}/\text{s} \cdot \text{m}^3}{(\text{mol}_{\text{NO}_2^+}/\text{m}^3)_\text{s}\text{mol}_{\text{nitration points}}/\text{m}^3}\right]$
m	$(1.0 \pm 0.2) \times 10^{-4}$
α_d	$(3.5 \pm 0.3) \times 10^{-36}$ (s^{-1})
S_y^2	$0.0004715 \left(\dfrac{\text{g}_\text{N}^2}{\text{g}_\text{cellulose}^2}\right)$
$\underline{\underline{\text{COV}}}$	$\begin{bmatrix} 2.47 \times 10^{33} & 1.05 \times 10^{12} & 1.5 \times 10^{-20} \\ 1.05 \times 10^{12} & 4.13 \times 10^{-10} & 7.1 \times 10^{-42} \\ 1.5 \times 10^{-20} & 7.1 \times 10^{-42} & 9.7 \times 10^{-74} \end{bmatrix}$

to define the state matrix of the system, $\underline{\underline{G}}(t)$ with size $nx \times nz$. The required values for $c(t)$ and $c_s(t)$ are calculated, in each time, using Eqs. 16 and 17 and the previous value of $\underline{\underline{G}}$.

Equation 23 shows, as expected, that each z-indexed entity has its own "history" of nitration, which is independent of the other z'-indexed entities (where $z \neq z'$). This is explained by the fact that the model presented here is a special case of a population balance in which a distribution is necessary entirely because the initial condition is distributed. However, given that every $g(x, z, t)$ must be calculated to elucidate the time evolution of the total nitrogen content (which is measured), the whole matrix $\underline{\underline{G}}$ must be updated. Besides, one could think of a warped timescale for each z ($\tau = zt$) in Eq. 9, but, for the lumped procedure required in each experimental time, it would be of no use.

Experimental

Cotton cellulose weight distributions were elucidated by SEC and the results were used to estimate NICDF parameters (ε, η). The complete procedure was described previously,[1] although, briefly, it involves the dissolution with dimethylimidazolidinone (DMI) and LiCl. A standard gel permeation chromatography system was applied using, as the mobile phase, a 0.5% LiCl in DMI solution. Values for the number-average molecular weight (M_n), weight-average molecular weight (M_w), peak molecular weight, and polydispersity were produced.

The nitration involved a sulfonitric mixture prepared with 63.5% H_2SO_4, 22% HNO_3, and 14.5% H_2O, similarly to the one used in the industrial plant.[1] Samples of 5 g of cellulose were nitrated in different stirred vessels and, at each 2 min, the content of a particular vessel was poured into a large amount of distilled water and vigorously stirred, to stop the reaction; stabilization procedures were also performed.

Nitrogen content of each sample was measured by automatic potentiometry with $FeSO_4$ standard solution under stirring.[1]

Parameter Estimation

Size-exclusion chromatography of cotton was performed that measured the M_n and M_w values of cellulose. These entities can be related to moments of $g_0(z)$ in Eq. 3, which are given by

$$M^n = \int_0^\infty z^n g_0(z)dz = \frac{\Gamma(\eta + n + 1)}{\varepsilon^n \Gamma(\eta + 1)} \tag{24}$$

From this, expressions for M_w and M_n are given by

$$M_w = 162\,\frac{\eta + 2}{\varepsilon} \qquad M_n = 162\,\frac{\eta + 1}{\varepsilon} \tag{25}$$

The numerical values of M_w and M_n (found by SEC) were used to calculate ε and η.

For the estimation of K, m, and α_d, a nonlinear least-square estimation was used.[11] Simulation of the complete time evolution of the system is carried out by the integration in Eq. 23. Then, the values of $\underline{\underline{G}}$ corresponding to each kth experimental batch time (t_k) are used to calculate the related nitrogen content ($\text{N}_{\text{calc}\ k}$), using

$$N\text{calc}_k = \frac{42\underline{\chi}^t\underline{\underline{G}}(t_k)\underline{\xi}}{(135\underline{\chi}^t + 162\Delta x\underline{l}^t)\underline{\underline{G}}(t_k)\underline{\xi}} \tag{26}$$

Each correspondent experimental nitrogen content ($\text{N}_{\exp\ k}$) is used to build a sum of squares of deviations, given by

$$\min_{\{K,m,\alpha_d\}} \sum_{k=1}^{10} (\text{N}_{\exp\ k} - \text{N}_{\text{calc}\ k})^2 \tag{27}$$

which is a (highly) nonlinear function of K, m, and α_d. The minimization in Eq. 27 was conducted using a standard secant optimization method with a BFGS approximant for the Hessian matrix.[12] In this quasi-Newton method, the stationary points of the objective function gradient are found, in an automatic and iterative way. The Taylor series expansion of the gradient is conducted, up to the first-order terms and forced to be null, resulting in a set of recurrence equations for the parameters. In this procedure, second derivatives (Hessian matrix) are needed, which are accessed empirically (BFGS approximation). The detailed procedure can be found in the related literature.[12]

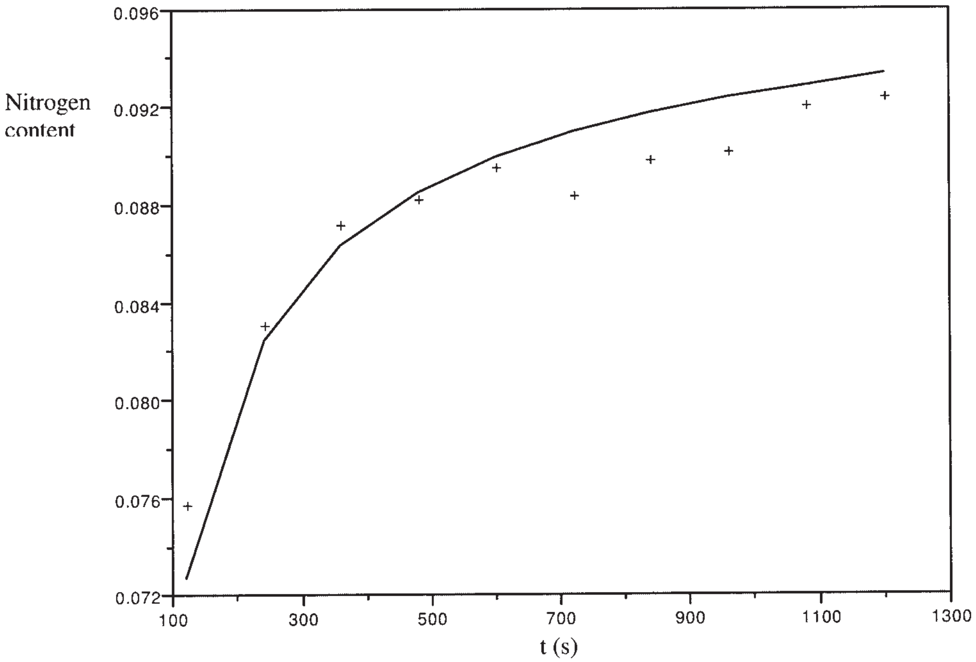

Figure 3. Nitrogen content at each batch time.

Adherence of the model (continuous line) to experimental data (+).

Results

Cellulose SEC produced $M_n = (53.2 \pm 23.2)$ kg/mol and $M_w = (542.4 \pm 23.2)$ kg/mol, and Eq. 25 gives $\varepsilon = (0.0003 \pm 0.0002)$ and $\eta = (-0.89 \pm 0.07)$. With these results, it is found that $C_0 = 0.295$ mol/m^3 and $c_0 = 5398.95$ mol/m^3.

With these values and the nitrogen content in each sample, the regression of K, m, and α_d was conducted, leading to the results presented in Table 1.

In Table 1, S_y^2 is an estimator of the variance of the model, given by

$$S_y^2 = \frac{1}{7}\sum_{i=1}^{n} (\mathrm{N}_{\exp\,i} - \hat{\mathrm{N}}_{\mathrm{calc}\,i})^2 \tag{28}$$

where $\hat{\mathrm{N}}_{\mathrm{calc}\,i}$ is $\mathrm{N}_{\mathrm{calc}\,i}$ after convergence, and $\underline{\underline{\mathrm{COV}}}$ represents the variances and covariances matrix of the parameters, given by

$$\underline{\underline{\mathrm{COV}}} = S_y^2(\underline{\underline{\mathrm{J}}}^t\underline{\underline{\mathrm{J}}})^{-1} \tag{29}$$

where $\underline{\underline{\mathrm{J}}}$ is the Jacobian matrix (numerically calculated) of Eq. 27 with respect to K, m, and α_d (columns and lines were arranged to follow this exact sequence, which also dictated the variance and covariances in $\underline{\underline{\mathrm{COV}}}$).

Figure 3 represents the adherence of the model to experimental data.

Discussion and Conclusions

A continuous model, based on structural information of cellulose, was built for nitrocellulose production and integrated by standard Euler methods. Using typical nitration protocols and potentiometric and SEC analysis, as well as standard nonlinear least-squares procedures minimized by secant methods, kinetic and mass-transfer parameters could be fitted. With this procedure, fitted parameters do not depend on the initial molecular weight distribution of the cellulose used and can be used to predict the behavior of the reactional systems, if the initial cellulose distribution is known. The parameters and the model exhibited low variances and the model showed good adherence to experimental data.

For comparison purposes, one can find in the literature few works on the same subject as that reported here.[1] Besides, in this work, kinetics depends on fiber surface concentration instead of bulk concentrations,[1] which makes K a rather unique kinetic parameter. Additionally, in previous works, it was indicated that mass-transfer effects must be taken into account but no calculations were performed, including this effect; thus, there is no source for comparison for α_d, as well. Fortunately, $\underline{\underline{\mathrm{COV}}}$ and S_y^2 can be used for comparison and, in this work, smaller relative variances and covariances of the parameters were found. On the other hand, the intrinsic (fundamental) variance of the model increased, without compromising the adherence to experimental data, as can be seen in Figure 3.

The method of optimization used (secant with a BFGS approximant for the Hessian matrix), once it is a quasi-Newton one, tended to be very sensitive to the initial guess for the set of parameters. Because of that, some attempts were not even successful, leading to numerical overflow. So, a test within the routine stocked the last valid parameter set to be used as a new initial guess.

The relatively low value of parameter m (Table 1) induced a test with $m = 0$ (fixed). The time required for the optimization procedure was reduced to one-quarter of the previous one, once only two parameters (K and α_d) were left to be fitted; additionally, convergence was less dependent on the initial guess for the parameters set. However, even though the elements on $\underline{\underline{COV}}$ remained virtually the same, S_y^2 increased 50%; one must decide between low computational time and low model variance to include, or not, parameter m in the optimization set.

The adherence to experimental data shows the degree of predictivity of the model, even though no experimental test was performed to quantitatively ensure this.

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All routines were implemented in the free/open source software Scilab© (INRIA-ENPC; www.scilab.org).

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