

Approximate solution of the autocatalytic hydrolysis of cellulose

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Abstract Depolymerization of cellulose in homogeneous acidic medium is analyzed on the basis of autocatalytic model of hydrolysis with a positive feedback of acid production from the degraded biopolymer. The normalized number of scissions per cellulose chain, $S(t)/n^{\circ} = 1 - C(t)/C_0$, follows a sigmoid behavior with reaction time t , and the cellulose concentration $C(t)$ decreases exponentially with a linear and cubic time dependence, $C(t) = C_0 \exp[-at - bt^3]$, where a and b are model parameters easier determined from data analysis.

Keywords Cellulose · Depolymerization · Acid hydrolysis · Ageing · Autocatalytic kinetics

Introduction

The understanding of the kinetics of the chemical degradation of cellulose is an important requirement in many industrial activities related to the processing of this biomaterial. Additionally, that understanding is critical in applications in which materials containing cellulose fibers need to be preserved for long

times. On the other hand, the enzymatic degradation of cellulosic materials, producing carbohydrates, has attracted much attention recently in connection with the production of biofuels.

The complexity of the chemical degradation of cellulose by acid or base catalysis is inherent to the complex nature of the chemical reactions of the macromolecular chain scission process, and there are differences between hydrolysis kinetics in homogeneous and in the presence of solid state fibres (Stephens et al. 2008) containing amorphous and crystalline parts. Several phenomenological models have been suggested to describe the degradation kinetics of cellulose (Ekenstam 1936; Emsley and Stevens 1994; Emsley et al. 1997; Zervos and Moropoulou 2005; Ding and Wang 2008; Calvini et al. 2007, 2008). The simple one is the Ekenstam model where initial cellulose degradation is considered a pseudo-zero order process. However, experimental results have indicated that advanced stage of the degradation process departs from zero order kinetics and in this case even pseudo-first order kinetics may fail, existing clear evidences that an autocatalytic step may occur based on the sigmoid or S-shape of the depolymerization yield as a function of time, especially for reaction in sealed vessels without pH control (Zervos and Moropoulou 2005; Calvini et al. 2007, 2008).

Recently, Calvini et al. (2007, 2008) have worked under the assumption that hydrolytic cellulose degradation mechanism contains a positive feedback of acid production from the degraded cellulose. The

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simple mechanism proposed explain most of the experimental data by introducing an autocatalytic branch in a simple but consistent model that contains only two rate constants. However, the nonlinearity of the kinetic scheme does not allow an analytical solution in a close form, and only approximate solutions have been worked out, or special cases were considered (Calvini et al. 2007, 2008). In this contribution, the autocatalytic model is analyzed and a second-order approximation that carries important figures of the kinetics is presented. Moreover, some strategies on how to recovery the kinetic parameters of the model from experimental data analysis is also addressed.

Cellulose degradation kinetics with autocatalysis

Following the model proposed by Calvini et al. (2007, 2008), the mechanism of hydrolytic cellulose degradation is represented by,



where C represents the starting or undegraded cellulose chains, H an acid catalytic agent, P the degraded cellulose chains, and k is the second order rate constant of this main reaction step. A positive feedback is then introduced by the assumption that degraded cellulose chains may undergo further chemical rearrangements producing more acidic compound which should accelerate the degradation of C, as given by,



where A represents the rearranged product of degradation, α the excess of produced acidity H, and k_a is the first order rate constant of this reaction step. Processes 1 and 2 provide the following system of rate equations for C, P and H concentrations,

$$\frac{dC}{dt} = -kHC \quad (3)$$

$$\frac{dP}{dt} = kHC - k_a P \quad (4)$$

$$\frac{dH}{dt} = \alpha k_a P \quad (5)$$

where the initial conditions are usually $C(0) = C_0$, $P(0) = 0$, and $H(0) = H_0$.

The feedback or autocatalysis ascribed to Eq. 5 turns the system nonlinear, which precludes analytical solution. However, there are integrated forms that under interactive substitution yields a second order approximation to $C(t)$, that will be called here as $C_2(t)$. Thus, Eq. 3 has solution on the form,

$$C(t) = C_0 \exp \left[-k \int_0^t H(\tau) d\tau \right]. \quad (6)$$

In the same way, the solution of Eq. 5 is given by,

$$H(t) = H_0 + \alpha k_a \int_0^t P(\tau) d\tau. \quad (7)$$

In order to derive an approximate solution of $C(t)$, it is assumed $H(t) = H_0$ to calculate the first order approximation $C_1(t)$ from Eq. 6 as,

$$C_1(t) = C_0 \exp[-kH_0 t]. \quad (8)$$

Under these two later conditions, a first order approximation of $P(t)$ in terms of solution of Eq. 4 is related to the following convolution integral,

$$P_1(t) = k \exp[-k_a t] \otimes H_0 C_1(t) \quad (9)$$

Where \otimes represents the convolution operator.

Solving Eq. 9, the first order approximation $P_1(t)$ is obtained as,

$$P_1(t) = \frac{C_0 k H_0}{(k H_0 - k_a)} (\exp[-k_a t] - \exp[-k H_0 t]). \quad (10)$$

The next step is to introduce $P_1(t)$ in Eq. 7 to calculate $H_1(t)$, and the resulting expression is,

$$H_1(t) = H_0 + \frac{\alpha C_0}{(k H_0 - k_a)} (k H_0 (1 - \exp[-k_a t]) - k_a (1 - \exp[-k H_0 t])). \quad (11)$$

Using $H_1(t)$ in Eq. 6, $C_2(t)$ is found and represented in logarithm ratio with $C_1(t)$ as,

$$\ln \frac{C_2(t)}{C_1(t)} = \frac{-\alpha k C_0}{(k H_0 - k_a)} \left((k H_0 - k_a) t + \frac{k H_0}{k_a} (\exp[-k_a t] - 1) - \frac{k_a}{k H_0} (\exp[-k H_0 t] - 1) \right). \quad (12)$$

Although cyclic substitution could provide high order approximations of the function $C(t)$, the second

order solution $C_2(t)$ is somewhat consistent and its degree of approximation will be tested against the numerical solution of the rate equation system. Worthwhile, in the limit of $t \rightarrow 0$, $C_2(t)$ converges to $C_1(t)$ as expected, and the approximate solution is in agreement with the Ekenstam model in the first stage of the cellulose degradation kinetics. More interesting, is that the derived expressions has the so called accelerated branch, that is obtained by expanding the exponential terms on the right side of Eq. 12 up to third order in t , since the first and second order are canceled out, and the result obtained is a cubic function of time

$$\ln \frac{C_2(t)}{C_1(t)} \cong \frac{-\alpha k_a k^2 H_0 C_0}{6} t^3. \quad (13)$$

On the other hand, in the limit of long time ($t \rightarrow \infty$), the decay recovers its exponential behavior in time, and the function in Eq. 12 is reduced to,

$$\ln \frac{C_2(t)}{C_1(t)} = \alpha C_0 \left(\left(\frac{k}{k_a} + \frac{1}{H_0} \right) - kt \right). \quad (14)$$

Considering $C_1(t)$ given by Eq. 8, the slope of $C_2(t)$ at long times in logarithm scale is $-(H_0 + \alpha C_0)k$, the maximum of acid compound formed plus the initial value H_0 with both multiplied by the rate constant k . The same rate is straightforward derived from Eq. 11 if one takes the limit of $H_1(t)$ at long time, and introduces it into Eq. 6.

In the analysis of the kinetics of cellulose degradation using $C_2(t)$ or its cubic expansion given by Eqs. 12 and 13, respectively, the normalized number of scissions per cellulose chain, $S(t)/n^\circ = 1 - C(t)/C_0$, is numerically evaluated and plotted against reaction time in arbitrary units. This normalized coordinate is in agreement with a random scission model of the cellulose chain by hydrolysis in which $C_0 = n^\circ$ (number of scissile glycosidic bonds of number-average cellulose chain).

Simulation of the process

The numerical result obtained by integration of the rate equation system using fourth order Runge-Kutta method is compared with approximated solutions derived. The time evolution of $S(t)/n^\circ$ for different set of model parameters is plotted in Fig. 1.

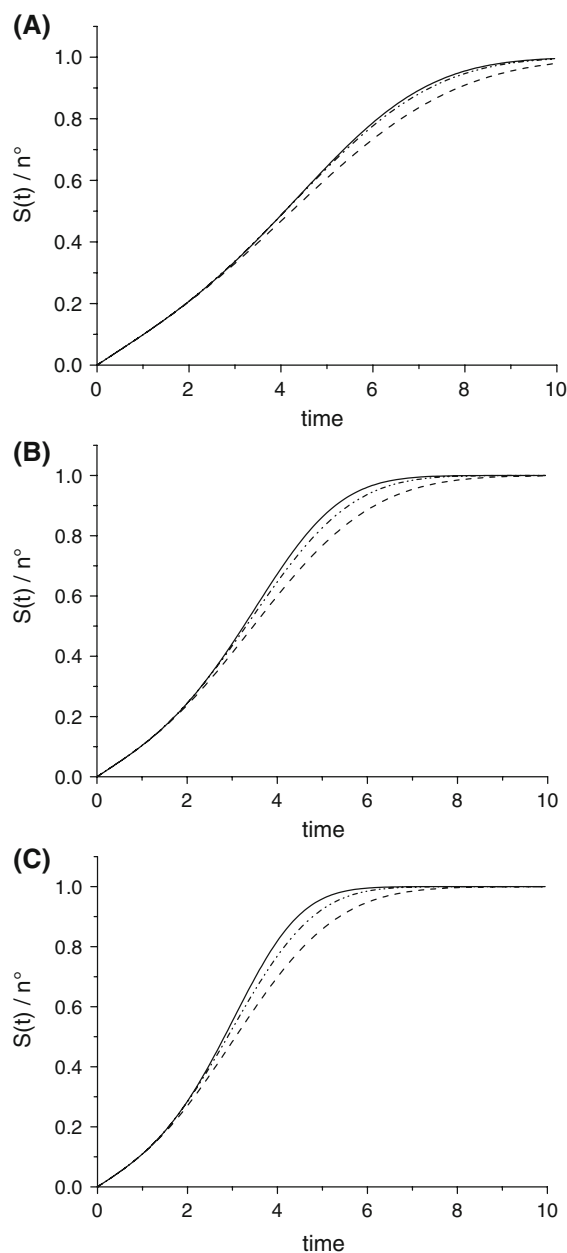


Fig. 1 Time evolution of the normalized number of scissions per cellulose chain. Continuous line is the numerical result while (---) is the $C_2(t)$ approximation and (- · -) is the cubic expansion given by Eq. 13. Constant parameters are $H_0 = 1.0$; $C_0 = n^\circ = 50$; $k = 0.1$ and $\alpha = 1$. The rate constant k_a is changed from 0.05 (a); 0.12 (b) and 0.2 (c)

The unexpected result is that the cubic expansion given by Eq. 13 is a better approximation to the numerical results, while the functional $C_2(t)$ is only a good approximation for the initial evolution of the

kinetics, or in the situation of $kH_0 \gg k_a$ where the S-shaped plot is practically lost. On the other hand, the increase of k_a compared to kH_0 enhances the difference between numerical result and approximations used, but nevertheless the cubic function still describes in reasonable form the time evolution up to half degradation of the cellulose, that is a very important region for experimenters. This convenient result using Eq. 13 provides a way to estimate the lifetime $t_{1/2}$ of the cellulose material by solving the cubic equation in the condition of $C_2(t) = C_0/2$.

$$t_{1/2}^3 + \frac{6}{\alpha k_a k C_0} t_{1/2} = \frac{6 \ln 2}{\alpha k_a k^2 C_0 H_0}. \quad (15)$$

In order to compare the lifetime $t_{1/2}$ calculated using the expression above with the time in which $C(t) = C_0/2$ from the numerical integration, the plot of these two values is comparatively shown in Fig. 2. There is a very good agreement between the numerical value and that predicted by using Eq. 15, although a small difference is somewhat recognized in the region of high k_a/kH_0 values.

The exponential factor $-(H_0 + \alpha C_0)kt$ that appears in the long time limit of Eq. 14 has been also found by Calvini et al. (2008) when solving analytically the kinetics in the condition of $k_a \gg kH_0$, a situation that holds when the initial acid concentration H_0 is very low (it means that the rate determining step is the slow hydrolysis given by Eq. 1). In this case, the rate equation follows a logistic type differential equation with proper

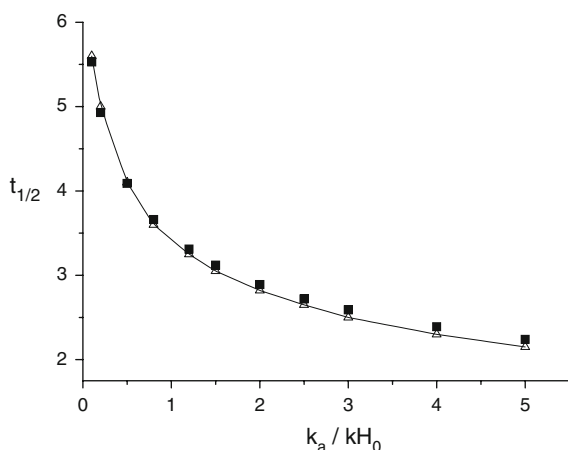


Fig. 2 Lifetime as a function of the ratio k_a/kH_0 . Numerical result (Δ) and value of lifetime $t_{1/2}$ calculated using Eq. 15 (\blacksquare)

parameters, and its exact solution in terms of the number of scissions per cellulose chain, $S(t)$, is given by,

$$S(t) = \frac{n^o(1-y)}{(1+y\alpha n^o/H_0)} \quad (16)$$

where $y = \exp[-k(H_0 + \alpha n^o)t]$.

The classical sigmoid shape of logistic function is recovery by $S(t)$ given by Eq. 16. On the other hand, the limit of $k_a \gg kH_0$ cannot be analyzed here within the scope of the second order approximate solution because large k_a will require high order approximations from Eq. 7, and $C_2(t)$ should work properly on the situation where $kH_0 \geq k_a$. Nevertheless, the approximate solution $C_2(t)$ given by Eq. 12 has twice the term $\exp[\exp(-\tau)]$, which is a classical Gompertz function used in ageing theory (Hallén 2007), as well as in modeling tumor growth (Laird 1964). Moreover, the Gompertz function has been used to describe the biodegradation of cellulose (Hu et al. 2004) as well as the kinetic modeling of hydrogen production from biomass in anaerobic condition (Mu et al. 2006). The sigmoid curve behavior of the kinetics expressed in terms of $S(t)$ with the logistic or Gompertz character is a result of the autocatalytic nature of the mechanism described by Eqs. 3, 4, and 5.

Finally, a protocol of analysis of experimental data is recommended in order to determine the rate constants of the underlined mechanism. The initial

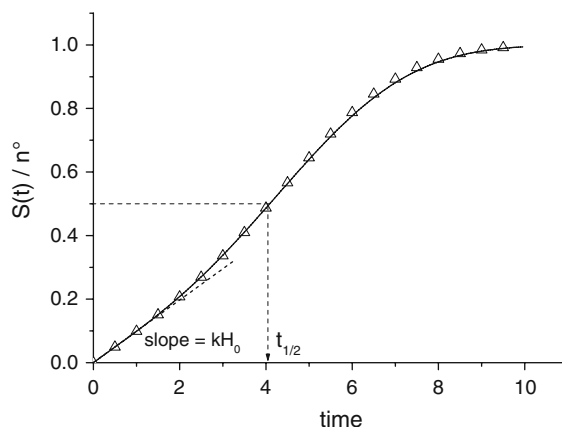


Fig. 3 Scheme of determination of the rate constant parameters from analysis of the initial slope and value of lifetime from the time evolution of $S(t)/n^o$. Numerical result (Δ) and continuous line is the cubic expansion given by Eq. 13. Simulated parameters used are $H_0 = 1.0$; $C_0 = n^o = 50$; $k = 0.1$; $\alpha = 1$; and $k_a = 0.05$; $t_{1/2} = 4.08$

slope of the normalized number of scissions per cellulose chain, $S(t)/n^\circ$ may be a first guess for kH_0 (this is the Ekenstam's approximation), and from the lifetime $t_{1/2}$ the value of k_a (assuming $\alpha = 1$) is straightforward determined from Eq. 15. The protocol is illustrated in Fig. 3. Those initial rate constants can be used in a nonlinear fitting to determine the optimal values for a set of experimental data.

Conclusions

The analysis of the autocatalytic model of acid hydrolysis of cellulose in homogeneous medium has indicated that the time evolution of cellulose concentration $C(t)$ is well described by a simple function of the type,

$$C(t) = C_0 \exp \left[-kH_0 t - \frac{\alpha k_a k^2 H_0 C_0}{6} t^3 \right] \quad (17)$$

where C_0, H_0 is the initial concentration pair of cellulose and acid catalytic agent provided by the experimenter, and k and αk_a are the rate constants of degradation and acid production from product rearrangement, respectively, which are the unknown parameters to be determined from experimental data analysis. The normalized number of scissions per cellulose chain, $S(t)/n^\circ = 1 - C(t)/C_0$ follows a sigmoid shape behavior from which the rate constants are easier evaluated using the proposed model.

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