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Stochastic modelling of polysaccharide hydrolysis

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Abstract. A stochastic model was selected and developed to describe polysaccharide hydrolysis kinetics. This model can accurately predict the hydrolysis kinetics and covers the limitations of some classical kinetic models (*e.g.*, complexity of mathematical models, large number of parameter estimations, change in parameters with a change in hydrolysis conditions, etc.). One of the main advantages of the stochastic mathematical model approach is represented by the fact that the polysaccharide structural characteristics and operating parameters can be separately incorporated into the model. The stochastic process characterizing the model considers that the breakdown of a polysaccharide by hydrolysis is a random process based on the cleavage of a parent macromolecule within a molecular mass range into two descendants within lower molecular mass ranges. The model description and its implementation in the hydrolysis of a hypothetical polysaccharide were presented.

Keywords: stochastic model, kinetic model, cellulose hydrolysis, polysaccharide hydrolysis, transition probability.

1. Introduction

Lately, several papers have been published on the chemical or thermal degradation of some polymers, including biopolymers such as cellulose, starch or other low

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molecular mass polysaccharides [1-7]. In a considerable part of these studies, many parallel and consecutive chemical reactions are considered. This fact determines patterns and models that are often not so easy for solving. For example, in a study on the thermal degradation of halogenated polymers, a kinetic mechanism taking into account 38 species involved in 190 chemical reactions was proposed [8]. In another study referring to the thermal degradation of polyvinyl chloride, 40 species and 250 chemical reactions were considered [9]. Mathematical models based on a random scission of linear polymer chains [10] and a polymer degradation with chain-end scission [11] were reported. For classical polymers as well as for biopolymers, the experimental measurements are used to justify the depolymerization (degradation) models. Accordingly, for depolymerization of polymer chains in a polymer solution, e.g., PMMA in toluene, at different temperature values, the experimental kinetics can be described by discrete decay pattern models [12]. There are also models based on a chemical bond breaking mechanism at a random position in the polymer chain. This mechanism is supported by many cases where the rate of decomposition of the polymer depends on the length of the chain [13]. In such models, the random positioning of the polymer chain breakdown is done by means of a pseudo-random generation number. In the case of acid hydrolysis of cellulose, the random distribution of biopolymer breakage position gives an appropriate coverage of data obtained by experimental investigation of process kinetics. Acid hydrolysis of cellulose was better explained by assuming a mechanism with systematic breakage of cellulose chains [14]. For enzymatic and acid hydrolysis of cellulose, the use of the stochastic models with Markov description of transition probabilities was attempted [15]. Distribution of the length of cellulose descendants during the hydrolysis was obtained by applying this model type. Moreover, the use of Markov type stochastic models to describe a large number of processes in chemical engineering is a current practice [16]. Applications of this modelling pathway are also encountered in all engineering fields where elementary processes with random evolution cause dynamic changes in a population [17]. However, for hydrolysis of cellulose (major component of vegetal biomass used as a basic material in the hydrolysis), simple phenomenological models are generally adopted [13,18-20].

This paper proposes a mathematical model based on particularization of random breakdown of the polymer chain, which can describes the simultaneous hydrolysis of several polysaccharides, as is the case of algal material, where other polysaccharides are found besides cellulose [21].

2. Model description

It has been found that the molecular masses of the partial hydrolysates obtained by hydrolysis of a vegetal material or of a cellulose type can be controlled during the treatment. Since the molecular mass distribution of species produced by the hydrolysis of a polysaccharide is influenced by its degradation mechanism, the description of dynamics of this mechanism can determine the dynamics of polysaccharide hydrolysis yield. Extending this problem to all polysaccharides from a vegetal material subjected to hydrolysis, the overall hydrolysis yield could be expressed. In order to develop a stochastic model describing the dynamics of hydrolysis of polysaccharides from a vegetal material, the following assumptions have been considered:

- (i) the material processed by hydrolysis contains a finite number of hydrolysable polysaccharides with known concentration and molecular mass of each species $(M_0^1, M_0^2...M_0^S)$;
- (ii) the polysaccharide breaking into several macromolecules is a random process based on splitting a parent macromolecule into two descendants; the probability for producing this event depends on polysaccharide chemical structure, on energy state inside the system, and on interactions of the molecules with the hydrolysis medium; some influencing factors include concentration of reagents and catalysts, temperature, pH, and agitation conditions; in principle, the stochastic model considered does not require preliminary or accurate knowledge of the effects of these factors;
- (iii) since the polysaccharide is a long carbohydrate, the location of a bond rupture is random, *i.e.*, the breaking of the carbohydrate chain into fragments of different lengths can happen with different probabilities;
- (iv) the large number of molecules involved in the hydrolysis process determines a distribution of species molecular masses corresponding to a continuous process; however, the division of this distribution into discrete intervals is possible because the discrete dynamics of the molecular mass distribution can be expressed by a histogram that can accurately approximate the continuous dynamics;
- (v) due to fragmentation of molecular masses in intervals, it is considered that a macromolecule within a molecular mass range breaks into two macromolecules within lower molecular mass ranges;
- (vi) the transitions from a given molecular mass range to other ranges depend only on the state of momentary distribution of hydrolysate molecular masses; accordingly, the older molecular mass distributions reported to current time have no influence on momentary transitions; as a consequence, the process of molecular fragmentation by hydrolysis is a homogeneous Markov process [15,16];
- (vii) all polymer chains within a molecular mass range break as if they were single;
- (viii) the hydrolysis breakdown process of each *s* species of polysaccharides must respect any time the species and total balance;
- (ix) no coupling process (*e.g.*, dimerization, trimerization) occurs between the fragments resulted in the hydrolysis process.

The stochastic principle of hydrolysis of a polysaccharide species (s) is illustrated in Fig. 1. It is noticed the division into molecular mass groups of the hydrolysis fragments and is shown how the macromolecule having an initial molecular mass M_0^s splits into one within the molecular mass class M_1^s and another within the molecular mass class M_N^s . Moreover, it is illustrated how the macromolecule within the molecular mass class M_1^s continues the process. It should be noted that in Fig. 1 is presented only one case of many other possible for starting and continuing the hydrolysis. For the transition probability P_{mk}^s in Fig. 1, superscript *s* refers to the polysaccharide species (*s*=1, 2...*S*), whereas *k* and *m* subscripts correspond to the molecular mass ranges before and after breaking, respectively.

The probability of breakage by hydrolysis of macromolecules within the molecular mass range M_i^s at the current time is p_i^s . Since the system has a large number of molecules, the law of large numbers can be considered to be applicable for its characterization. Consequently, for the molecular mass range M_i^s , the above probability gives the expected proportion of macromolecules that will be broken (hydrolyzed) in the time period $\Delta \tau$. The mass balance corresponding to the breaking (hydrolysis) of macromolecules within the molecular mass range M_k^s into ones within the molecular mass ranges M_l^s and M_m^s can be expressed by Eq. (1), where m_k^s is the mass of *s* species parent macromolecules within the molecular mass range M_k^s , whereas m_l^s and m_m^s represent the masses of descendants within the molecular mass ranges M_l^s .

$$m_k^s = m_l^s + m_m^s$$



(1)

Fig. 1. The principle of hydrolysis of a polysaccharide in stochastic terms.

Because at a time τ the parent macromolecule breaks into two parts, then the probability of birth of each part is equal to the probability of breaking (hydrolysis) of the parent, as shown by Eq. (2).

$$p_k^s = P_{lk}^s = P_{mk}^s \tag{2}$$

Breaking probability referring to the molecular mass range M_i^s , *i.e.*, p_i^s , can be determined depending on the transition probabilities P_{ji}^s $(j=1, 2...N, j\neq i)$ for $\Delta \tau$ using Eq. (3), whereas hydrolysis missing probability associated with M_i^s , *i.e.*, P_{ii}^s (i=1, 2...N), is expressed by Eq. (4).

$$p_{i}^{s} = \sum_{\substack{j=1\\j\neq i}}^{N} P_{ji}^{s}$$
(3)

$$P_{ii}^{s} = 1 - p_{i}^{s} = 1 - \sum_{\substack{j=1\\j\neq i}}^{N} P_{ji}^{s}$$
(4)

Because the hydrolysis of *s* species can be considered a Markov homogenous stochastic process, the transition probability P_{ji}^{s} is given by Eq. (5), where α_{ji}^{s} is the transition frequency, and the transition probability in mass expression is determined by Eq. (6). Time variation of mass fraction of *s* species within the molecular mass range M_{i}^{s} , expressed by Eq. (7), was obtained by species mass balance.

$$P_{ji}^s = \alpha_{ji}^s \Delta \tau \tag{5}$$

$$P_{ji}^{s,m} = \frac{M_j^s \alpha_{ji}^s}{\sum\limits_{k=1}^{N} M_j^s \alpha_{ji}^s}$$
(6)

$$\frac{\Delta \omega_i^s}{\Delta \tau} = \sum_{\substack{k=1\\k\neq i}}^N P_{ik}^{s,m} \omega_k^s - \omega_i^s \sum_{\substack{j=1\\j\neq i}}^N P_{ji}^{s,m}$$
(7)

3. Model implementation

A hypothetical hydrolysis of a polysaccharide having the molecular mass of 3600 g/mole (decasaccharose or decacellobiose) was studied. 10 uniformly distributed molecular mass ranges were considered (Fig. 2) as follows: M_0^1 =3600 g/mole, M_1^1 =3240 g/mole, M_2^1 =2880 g/mole... M_8^1 =720 g/mole, M_9^1 =360 g/mole. It was assumed that the fragment consisting in saccharose or cellobiose (M_9^1 =360 g/mole) was decomposed into glucose (M_{10}^1 =180 g/mole). Schema shown in Fig. 2 was proposed based on the fact that in the cellulose and in other low molecular mass polysaccharides, the repeating structural unit is the β -cellobiose disaccharide [22]. Other studies referring to the cellulose hydrolysis suggested a similar schema [23]. According to Fig. 2, the mass fractions of hydrolysable species within the molecular mass ranges M_0^1 , $M_1^1...M_{10}^1$ are described by the probability vector given by Eq. (8), where τ_n is the current time and *n* the number of steps (sequences) considered in the evolution of hydrolysis process. Initial condition expressed by Eq. (9) corresponds to hydrolysis starting ($\tau = \tau_0$), *i.e.*, when in the system there are only macromolecules within the molecular mass range M_0^1 .

$$p^{1}(\tau_{n}) = [p_{0}^{1}(\tau_{n}) \ p_{1}^{1}(\tau_{n}) \ p_{2}^{1}(\tau_{n}) ... p_{8}^{1}(\tau_{n}) \ p_{9}^{1}(\tau_{n}) \ p_{10}^{1}(\tau_{n})]$$
(8)

$$p^{1}(\tau_{0}) = [p_{0}^{1}(\tau_{0}) \ p_{1}^{1}(\tau_{0}) \ p_{2}^{1}(\tau_{0}) \dots p_{8}^{1}(\tau_{0}) \ p_{9}^{1}(\tau_{0}) \ p_{10}^{1}(\tau_{0})] = [1 \ 0 \ 0 \dots 0 \ 0 \ 0]$$
(9)

Similar to Markov stochastic cellular models [15], the transition probabilities P_{ji}^{1} defined by Eq. (5) are arranged in the transition probability matrix P^{1} given by Eq. (10), where the diagonal elements (P_{ii}^{1} , *i*=0, 1...10) correspond to the hydrolysis absence. The value $P_{99}^{1}=1$ indicates that hydrolysis ends in the molecular mass

range M_{9^1} . The transition from M_9 (cellobiose) to M_{10^1} (glucose), occurring with probability P_{109^1} , is the only possible process.

Two methods can be used to determine the hydrolysis dynamics. The first one consists in establishing the time evolution of probability of hydrolysis in each molecular mass range (Eq. (11)). The second method is based on Eq. (12), which was obtained from Eq. (7), where the probabilities (p_i^s) were used instead of the mass fractions (ω_i^s) . Considering the molecular mass ranges M_0^s , $M_1^s \dots M_N^s$ (*s*=1, 2...*S*) the distribution of p_i^s or ω_i^s can be determined by solving a system of *SN* differential equations.

$$p^{1}(\tau_{n}) = p^{1}(\tau_{0}) \left[P^{1,m} \right]^{n}$$
(11)

$$\frac{dp_i^s}{d\tau} = \sum_{\substack{k=1\\k\neq i}}^{N} P_{ik}^{s,m} p_k^s(\tau) - p_i^s(\tau) \sum_{\substack{j=1\\j\neq i}}^{N} P_{ji}^{s,m}$$
(12)

Hydrolysis dynamics expressed as mass fractions of hydrolysable species at four time sequences (n=0, 4, 8, and 10), which were predicted assuming equal transition probabilities, are presented in Fig. 3. In this case the transition probabilities have a uniform stochastic distribution given by Eq. (13).

$$pp_{ji}^{1} = \begin{bmatrix} \frac{1}{N} & \text{if } i < j \\ 0 & \text{otherwise} \end{bmatrix}, \qquad P_{ij}^{1} = \begin{bmatrix} \frac{1}{N+1} & \text{if } i = j = 0 \\ 1 & \text{if } i = j = N \\ pp_{ij}^{1} & \text{if } i \neq j \\ 1 - \sum_{j=1}^{N} pp_{ij}^{1} & \text{otherwise} \end{bmatrix}$$
(13)

Hydrolysis dynamics are presented in Fig. 4 for a uniform progressive distribution of transition probabilities (Fig. 4a) and a normal distribution with highest breaking probabilities in the centre of $M_0^1 - M_{10}^1$ range (Fig. 4b). Mathematical expressions of transition probability distributions depicted in Fig. 4 are given by Eqs. (14) and (15), where m=5.5 and $\sigma=3.45$.



Fig. 2. Hydrolysis structure and transition probabilities of a polysaccharide with a molecular mass (M_0^1) of 3600 g/mole.



Fig. 3. Transition probability matrix with equal transition probabilities (P_{ij}^{-1}) and mass fractions of *i* hydrolysable species $(M_0^1, M_1^1 \dots M_{10}^1)$, ω_i^{-1} (g_i/g_{cel}), at different time sequences (n=0, 4, 8, and 10).





Fig. 4. Transition probability matrix (P^1) and dynamics of *i* hydrolysable species $(M_0^1, M_1^1 \dots M_{10}^1)$, ω_i^1 (g_i/g_{cel}), for transition probabilities with: (a) uniform progressive distribution and (b) normal distribution.

Based on Eq. (5) and Fig. 4, where $\Delta \tau = 100$ s, Eqs. (14) and (15) can be used for determining the process transition frequencies (α_{ji}). Plots in Fig. 4 highlight 2 stages in the capitalization of experimental data by means of this stochastic model. The first one consists in establishing the distribution of transition probabilities which covers the best the experimental time evolution of final hydrolysis product. The second one is to establish the value of time frame which determines the complete covering of time evolution of final hydrolysis product.

4. Results and discussions

Cellulose is a biopolymer with a wide variability, which is determined by its polymerisation degree (*PD*). Data summarized in Table 1 reveal that the values of *PD* (100-15000) depends on cellulose source and processing [24,25]. Mass fractions of hydrolysable species at different time sequences for hydrolysis of cellulose with *PD*=200 and *PD*=1000, respectively, are presented in Figs. 5 and 6. Depicted data indicate that the species having high molecular mass disappear relatively quickly. It suggests that the hydrolysis of species with low molecular mass determines the process rate. This observation is in line with studies in the related literature, which consider the cellulose hydrolysis as a homogeneous kinetic process described by Eqs. (16)-(19) [26-29].

No.	Cellulose source	PD	Observations		
1	Cotton	11000-15000	Cotton leaching, drying, and grinding		
2	Hardwood	9000-11000	Particular separation technology		
3	Softwood	7000-9000	Particular separation technology		
4	Bacterial cellulose	2000-5000	Biosynthesis		
5	Bleached sulphite pulp	1000-1500	Cellulose from sulphite media		
6	Kraft and normal paper	500-1000	Specific processing of cellulose pulp		
7	Viscose regenerated cellulose	100-300	Cellulose via viscose procedure		

Table 1. Polymerization degree (PD) of some cellulose sorts



Fig. 5. Mass fractions of *i* hydrolysable species $(M_0^1...M_{100}^1)$, ω_i^1 (g_i/g_{cel}), at different time sequences (*n*=2, 10, 50, and 100) for hydrolysis of a cellulose (cel) with *PD*=200 (100 units of C₁₂H₂₄O₁₂).



Fig. 6. Mass fractions of *i* hydrolysable species $(M_0^1...M_{500}^1)$, ω_t^{-1} (g_i/g_{cel}), at different time sequences (*n*=10, 50, 100, and 500) for hydrolysis of a cellulose (cel) with *PD*=1000 (500 units of C₁₂H₂₄O₁₂).

$$Cellulose(C) \xrightarrow{k_1} Glucose(G) \xrightarrow{k_2} Hydroxymethylfurfural (HMF)$$
(16)

$$\frac{dc_c}{d\tau} = -k_1 c_c \tag{17}$$

$$\frac{dc_G}{d\tau} = k_1 c_C - k_2 c_G \tag{18}$$

$$\frac{dc_{HMF}}{d\tau} = k_2 c_G \tag{19}$$

A good agreement between the homogeneous kinetic model and stochastic model (for cellulose with PD=200 and uniformly distributed transition probabilities given by Eq. (13)) is revealed by the results presented in Fig. 7. Operating temperature, acid type and concentration strongly influence the dynamics of acid cellulose hydrolysis. Corrections referring to acid strength were considered in the Arrhenius dependences (Eqs. (20) and (21)) expressing characteristic reaction constants of homogenous kinetic model.

$$k_{1} = k_{10} (c_{ad})^{n_{1}} \exp\left(-\frac{E_{1}}{RT}\right)$$
(20)

$$k_2 = k_{20} (c_{ad})^{n_2} \exp\left(-\frac{E_2}{RT}\right)$$
(21)

By analogy with Eqs. (20) and (21), characteristic transition probability frequencies of stochastic model can be determined by Eq. (22), were E_a mean reaction activation energy was considered for all decompositions to glucose and E_G activation energy for transition from glucose (G) to hydroxymethylfurfural (HMF).

$$\alpha_{ji} = \begin{cases} \alpha_{ji}^{0} c_{ad}^{n} \exp\left[\frac{E_{a}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right], & i, j = 0, 1 \dots N - 1\\ \alpha_{ji}^{0} c_{ad}^{n} \exp\left[\frac{E_{G}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right], & i = N - 1, j = N \end{cases}$$
(22)



Fig. 7. (a) Predicted dynamics of *i* hydrolysable species $(M_{97}^1...M_{100}^1)$ concentration, c_i^1 (g_i/L), for acid hydrolysis of a cellulose (cel) suspension (*PD*=200, c_0 =100 g_{cel}/L, $\Delta \tau$ =10 s, uniformly distributed transition probabilities given by Eq. (13));

(b) comparison between stochastic model (line) and homogenous kinetic model (points) for k₁=0.00048 s⁻¹ and k₂=0.0006 s⁻¹;
 (c) as b case for k₁=0.00053 s⁻¹ and k₂=0.00073 s⁻¹.

The capacity of stochastic model to predict the influence of temperature and dimensionless acid concentration on cellulose hydrolysis is revealed by Fig. 8, where the matrix of transition probabilities, based on a uniform distribution, was determined according to Eqs. (23)-(25). Data reported in the related literature [4,6,30] were processed based on homogeneous kinetic model described by Eqs. (17)-(21). Values of characteristic parameters of both homogeneous kinetic and stochastic models are summarized in Table 2. The results presented in Fig. 8 highlight an acceptable agreement between the stochastic and homogeneous kinetic models. The stochastic model is much closer to the real process because it considers a large number of elementary processes (*e.g.*, 100 incremental processes per computation sequence in Figs. 7 and 8) involved in the mechanism of hydrolysis. The activation energy associated with these elementary processes is significantly greater than that corresponding to a single process (*E_{am} vs. E*₁ and *E*₂ in Table 2).



Fig. 8. Influence of temperature and dimensionless acid concentration on dynamics of glucose (G) and hydroxymethylfurfural (HMF) concentration for acid (H₂SO₄) hydrolysis of a cellulose (cel) suspension (line: stochastic model, where *PD*=200, *c*₀=100 g_{cel}/L, Δ*τ*=10 s, and transition probabilities are given by Eqs. (23)-(25); points: homogeneous kinetic model, where *k*₁ and *k*₂ are given by Eqs. (20) and (21)): (a) *T*=453 K, *c_{ad}*=1, (b) *T*=453 K, *c_{ad}*=4, (c) *T*=483 K, *c_{ad}*=1, (d) *T*=483 K, *c_{ad}*=4 (*c_{a,ref}=0.1%*).

$$pp_{ji}^{1} = \begin{bmatrix} \frac{1}{N+6} & \text{if } i < j, i < 0.95N, j < 0.95N \\ \frac{1}{N}e_{T}(T)e_{a}(c) & \text{if } i < j, j \ge 0.95N \\ 0 & \text{otherwise} \end{bmatrix}, P_{ij}^{1} = \begin{bmatrix} \frac{1}{N+1} & \text{if } i = j = 0 \\ 1 & \text{if } i = j = N \\ pp_{ij}^{1} & \text{if } i \neq j \\ 1 - \sum_{j=1}^{N} pp_{ij}^{1} & \text{otherwise} \end{bmatrix}$$
(23)

$$e_{T}(T) = \exp\left(\frac{E_{am}}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right)$$

$$e_{a}(c) = \left(\frac{c}{c_{a,ref}}\right)^{n}$$
(24)
(25)

No.	Model	Parameter	Value
1	Stochastic	Mean activation energy of breaking process, E_{am}	26.6 kJ/mole
		Reference temperature, <i>T_{ref}</i>	453 K
		Reference acid concentration, $c_{a,ref}$	0.1% (w/w)
		Power in Eq. (25) , n	0.3
	Kinetic	Constant in Eq. (20), k_{10}	4.93×10 ⁻⁴ s ⁻¹
		Constant in Eq. (21), k_{20}	6.41×10 ⁻⁴ s ⁻¹
2		Activation energy in Eq. (20) , E_1	66.96 kJ/kmole
		Activation energy in Eq. (21) , E_2	82.41 kJ/kmole
		Power in Eq. (20), n_1	0.4
		Power in Eq. (21) , n_2	0.5

Table 2. Values of parameters in Eqs. (2	(20), (21), (24), and (25).
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5. Conclusions

The hydrolysis of cellulose and vegetal biomass, respectively, is a process of high industrial interest. Acid hydrolysis at a temperature higher than 150 °C has been extensively analyzed by experimental studies. Kinetic models, whose relevant parameters can be determined based on experimental data, are widely used to describe the hydrolysis process. A stochastic model assuming a random breaking of some chemical bonds of cellulose polymer chains has been developed in this paper. The model description, the procedure of its implementation, and the use of several types of transition probability matrices have been presented. A uniform distribution of breaking probabilities of cellulose chain was selected in the transition probability matrices applied to predict the hydrolysis dynamics for cellulose with low molecular mass. The effects of temperature and acid concentration have been also evaluated. The results obtained using both kinetic and stochastic models were in a good agreement.

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