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KINETIC MODELLING OF CHEMICAL AND ENZYMATIC PROCESSES WITH LIGNOCELLULOSIC FIBER MATERIALS

Greta Radeva, Ivo Valchev, Stoyko Petrin, Ivaylo Gavrilov

University of Chemical Technology and Metallurgy
8 St. Kliment Ohridski Blvd., Sofia 1797, Bulgaria, grradeva@uctm.edu (G.R.); ivoval@uctm.edu (I.V.); stpetrin@uctm.edu (S.P.); igavrilov@uctm.edu (I.G.).

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ABSTRACT

Optimization of pulping, bleaching and biorefining processes requires a good understanding of reaction kinetics. The kinetics of the processes are described by kinetic equations valid for processes taking place at heterogeneous surfaces. The investigation clarifies the influence of operating parameters on the effectiveness of various processes with lignocellulosic fibre materials. The kinetics of oxygen delignification are described by a modified form of the topochemical kinetic equation, while the same kinetic mechanism was found to govern both chlorine dioxide bleaching and xylanase-assisted bleaching. The kinetics of hydrolysis with cellulase complexes is described by an exponential kinetic equation.

Common kinetic expressions were developed to describe the combined effects of reaction time, enzyme concentration, temperature, and other relevant operating parameters on process efficiency.

Keywords: kinetic modelling, lignocellulosic materials, process optimization.

INTRODUCTION

Bleaching can be viewed as an extension of pulping, whereby successive oxidation and extraction stages yields fibers that are nearly free of lignin. In addition to the residual lignin, kraft pulp contains other oxidisable structures, notably hexenuronic acids (HexA) bound to xylan. In both softwoods and hardwoods, xylan chains carry 4-O-methylglucoronic acid substituents at the C-2 position Oxygen delignification removes approximately 40-65 % of the lignin remaining after cooking in softwood pulps and 35-55 % in hardwood pulps [1].

Oxygen delignification proceeds through a heterogeneous system comprising three phases: solid fibres, an aqueous alkaline solution, and gaseous oxygen. Oxygen first dissolves in the aqueous phase and is then transported to the fibre surface. It subsequently diffuses into the fibre wall, where it reacts with lignin and other wood constituents. Studies examining the effect of oxygen pressure on hardwood kraft pulp delignification [1, 2] have shown that raising the pressure from 0.3 to 0.6 MPa lowers both the Kappa number and pulp viscosity while increasing brightness. Investigations of temperature and reaction time have likewise demonstrated that higher temperatures and longer treatment durations promote lignin removal [1, 2].

Most kinetic models of oxygen delignification are empirical and express the delignification rate as a power-law function of residual lignin content, represented by the Kappa number, hydroxide ion concentration, and oxygen pressure. The most widely accepted two-stage kinetic model is that proposed by Olm and Teder, who described the process using pseudo-first-order equations with respect to the Kappa number [3]. However, the empirical nature of these studies limits their ability to fully describe the complex, heterogeneous process of oxygen delignification. An alternative group of kinetic models is based on the topochemical concept, according to which the delignification rate depends on the number of reactive sites generated at the beginning of the process

and on the subsequent growth of the transformed lignin regions originating from these sites [1 - 4].

Since the transition from elemental chlorine bleaching to elemental chlorine-free (ECF) technologies, chlorine dioxide has become the principal bleaching agent in kraft pulp bleaching. The initial chlorine dioxide stage (D_0), followed by an extraction stage reinforced with oxygen and hydrogen peroxide, constitutes the primary delignification sequence. Subsequent chlorine dioxide stages (D_1 and D_2) are mainly employed to increase and stabilise pulp brightness. Chlorine dioxide is a highly selective delignification agent, resulting in effective lignin removal while preserving the carbohydrate fraction and maintaining high pulp yield [5, 6]. It reacts primarily with phenolic lignin end groups through oxidative aromatic ring opening, producing muconic acid derivatives, or through demethylation, leading to quinone structures [7]. These reactions generate modified lignin containing partially oxidised aromatic rings, which are subsequently dissolved and removed during the alkaline extraction stage. The influence of hexenuronic acids removal becomes particularly evident after the D_1 stage, during which chlorine dioxide reacts only slowly with the remaining residual lignin. Simultaneous reactions between chlorine dioxide and the products formed during hexenuronic acids hydrolysis reduce the efficiency of the bleaching process [8, 9]. Applying the power-law kinetic model to hydrolysis with chlorine dioxide indicates that the process proceeds through a chemical reaction at the surface.

Among bleaching enzymes, xylanases are the most extensively applied in the pulp and paper industry. Their beneficial effect on pulp brightness is attributed both to the removal of xylan from the fibre surface and to the degradation of lignin-carbohydrate complexes within the fibre wall. Overall, the effect of xylanase treatment on peroxide bleaching has been reported to be approximately twice as great as that of oxygen treatment alone [10]. Xylanase pretreatment improves the efficiency of subsequent delignification and bleaching stages by increasing the accessibility of the fibre structure to chemical bleaching agents such as hydrogen peroxide, chlorine dioxide, and ozone, thereby directing their action primarily toward lignin chromophoric groups [11, 12]. According to our previous study, xylanase pretreatment increased the brightness of peroxide-bleached pulp by approximately 4 % ISO while reducing the Kappa number by about one unit with a simultaneous 10 % reduction in hydrogen peroxide consumption [10]. Kinetic investigations of xylan degradation catalysed by different xylanases have demonstrated that the modified topochemical equation adequately describes the reaction kinetics [13 - 16]. Application of the modified Prout-Tompkins equation indicates that enzymatic xylan degradation is associated with a continuous change in the reaction surface, governed by the xylan chain structure and the lignin–carbohydrate linkages.

Agricultural residues such as wheat straw represent abundant renewable resources for lignocellulosic bioconversion. Wheat straw is particularly attractive because of its relatively low lignin content (less than 20 % w/w) and high carbohydrate content, comprising approximately 50 % hemicellulose and 30 % cellulose [17]. Enzymatic hydrolysis using appropriate cellulolytic enzymes is considered one of the most effective methods for converting lignocellulosic biomass into fermentable sugars, predominantly glucose. However, the enzymatic hydrolysis of lignocellulosic materials is inherently complex because these substrates are heterogeneous and insoluble, resulting in limited enzyme accessibility and reaction efficiency [18]. Consequently, the classical Henri-Michaelis-Menten equation is generally unsuitable for describing the kinetics of enzymatic hydrolysis in heterogeneous systems [19 - 21]. Instead, the heterogeneous nature of the wheat straw-cellulase system permits the application of heterogeneous catalytic reaction models to describe the kinetics of enzymatic hydrolysis.

EXPERIMENTAL

Oxygen delignification

Unbleached kraft pulp from beech and oak, of Kappa number 17.9, brightness 33.1 % ISO and viscosity 965 $dm^3 kg^{-1}$ was used. The kinetics of the process was studied at temperatures of 85, 95, 102 and 110°C and reaction times varying from 10 to 80 min. The oxygen pressure was varied from 0.3 to 0.6 MPa, the sodium hydroxide charge from 2.0 to 3.5 % and the pulp consistency from 8 to 14 %. The Kappa number, brightness and viscosity were measured according to SCAN methods (SCAN-C 1:77, SCAN-CM 38:87 and SCAN 15:02) [2].

Chlorine dioxide bleaching

Delignification stage D_0: ClO_2 charge 10 - 20 kg t^{-1}; pH 2.3 - 3.5; Temperature 50°C to 70°C; Retention time 20 - 60 min; Pulp consistency 10 % to 12 %. Brightness stages D_1 and D_2: ClO_2 charge 5 - 10 kg t^{-1}; pH 3.5 - 5.5; Temperature 85°C to 110°C; Retention time 120 min; Pulp consistency 10 % to 12 %. The Kappa number, brightness and viscosity were measured according to SCAN methods (SCAN-C 1:77, SCAN-CM 38:87 and SCAN 15:02). Spectroscopic method was used for Hexenuronic acid amount TAPPI Standard Method (T 282 / Chai's Method) [8, 9].

Xylanase bleaching

Xylan decomposition from unbleached pulp was investigated with the enzyme preparation Pulpzyme HC produced by Novozymes A/S. Pulpzyme HC contains endo-1, 4-beta-D-xylanase activity (E.C. 3.2.1.8), and is virtually free of cellulase activity. The product is standardized to 0.3 - 1 XU g^{-1}. Retention time up to 120 min; Temperature about 55 - 65°C, pH of 8.0 - 9.0. The Kappa number, brightness and viscosity were measured according to SCAN methods (SCAN-C 1:77, SCAN-CM 38:87 and SCAN 15:02). The amount of reducing sugars was determined using the DNS method [22].

Cellulase hydrolysis

The investigations were performed on wheat straw. The enzyme cellulase complex NS 50013 and β-glucosidase NS 50010 of Novozymes A/S were used. The enzyme charge of NS 50013 was 5 %, while that of NS 50010 was 0.5 %, both based on the dry mass of wheat straw. Cellulase hydrolysis was investigated at 30°C, 40°C and 50°C, at a substrate consistency of 10 %, pH 4.6 - 5.0 reaction time of 1 - 24 h and enzyme concentration 1 %, 2 %, 3 % and 5 %. The amount of reducing sugars was determined using the DNS method [22]. The experimental procedure and kinetic evaluation have been described previously [23, 24].

RESULTS AND DISCUSSION

Kinetics of oxygen delignification

Oxygen delignification is an effective pre-bleaching process that reduces residual lignin content, decreases bleaching chemical consumption and costs, lowers the formation of chlorinated organic compounds AOX, and improves the environmental and economic performance of kraft pulp bleaching while maintaining pulp quality.

The influence of temperature and treatment duration on kraft pulp properties during oxygen delignification was investigated [1, 2].

Fig. 1 indicates that the treatment times and temperatures enhance lignin removal. As it's seen when the temperature raise from 90°C to 110°C produces an effect equivalent to doubling the reaction time.

Oxygen delignification takes place in a complex three-phase heterogeneous system consisting of solid fibres, an aqueous alkaline solution, and gaseous oxygen. The topochemical kinetic model follows the concept, that the delignification rate is governed by the number of reactive sites established at the onset of the process and the rate at which lignin transformation progresses from these sites.

As a kinetic variable is used a dimensionless variable α, which accounts the fraction of oxidized and dissolved lignin.

$$v = \frac{d\alpha}{dt} = k'\chi\alpha^{\frac{\chi-1}{\chi}}(1-\alpha)^{\frac{\chi+1}{\chi}} \quad (1)$$

where $Kappa_{in}$ is initial Kappa number and Kappa is Kappa number at time (t).

The process is described using a modified Prout-Tompkins topochemical equation [1, 2, 4], where the reaction rate depends on the changing interface between reacted and unreacted lignin.

$$v = \frac{d\alpha}{dt} = k'\chi\alpha^{\frac{\chi-1}{\chi}}(1-\alpha)^{\frac{\chi+1}{\chi}} \quad (2)$$

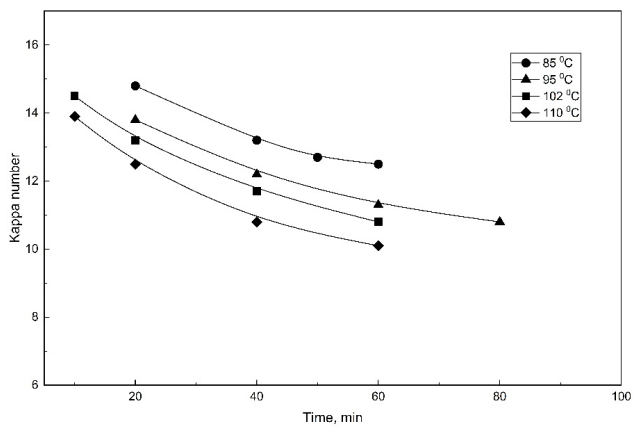


Fig. 1. Kinetic curves of Kappa number at different temperatures.

According to this model, the rate of delignification v is a function of the amount of oxidised lignin that subsequently becomes soluble α, and of the amount of residual undissolved lignin at any time (1 - α).

The power factors $\frac{\chi-1}{\chi}$ and $\frac{\chi+1}{\chi}$ determine the relative contributions by the dissolved and undissolved parts of lignin, respectively, on the rate of delignification.

The integrated form of Eq. (2) used for the description of the experimental data is:

$$\frac{\alpha}{1-\alpha} = (kt)^{\chi} \quad (3)$$

where $k = \frac{k'}{\chi}$ is an apparent rate constant and χ is a power factor.

After rearrangement of this Eq. (3) and with the inclusion of the Arrhenius temperature dependency of the apparent rate constant k, a new Eq. (4) is obtained.

$$Kappa = Kappa_{in}\left\{1 - \left[1 + \left(5x10^4 e^{\left(-\frac{5833}{T}\right)t}\right)^{-0.59}\right]^{-1}\right\} \quad (4)$$

In a mill with relatively constant pulping conditions and wood supply, the activation energy and the coefficient χ is constant 0.59. The activation energy E is 48.2 kJ mol^{-1} and depends only on the nature of the unbleached pulp. The obtained ratio of the activation energy of the process to the universal gas constant, E/R, is 5833 K. The preexponential factor, A, includes the effect of all steric factors on the process (charge of reagents, their mixing, the pressure in the system accessibility of surface and so on) and was found to be constant 5 x 10^4 min^{-1}. This Eq. (4) can be used for process control of the Kappa number.

Inclusion of the effect of oxygen pressure P and alkali charge C on the process properties leads to new more full equation (5):

$$Kappa = Kappa_{in}\left\{1 - \left[1 + + \left(2.16x10^4 e^{\left(-0.175C+0.8P-\frac{5833}{T}\right)t}\right)^{-0.59}\right]^{-1}\right\} \quad (5)$$

where C is the alkali charge in % and P is the oxygen pressure in MPa.

The generalised Eq. (5) allows the Kappa number to be predicted at any point during oxygen delignification as a function of temperature, oxygen pressure and alkali charge. This can help optimize temperature and treatment time parameters, as well as control oxygen pressure and alkali charge in real time during the process.

Kinetic analysis of chlorine dioxide bleaching

Chlorine dioxide (ClO_2) has emerged as the principal agent used in kraft pulp bleaching. The D_0 stage, followed by oxygen- and peroxide-reinforced extraction, provides the primary delignification, while the D_1 and D_2 stages mainly increase and stabilize pulp brightness. Due to its high selectivity for lignin, ClO_2 preserves carbohydrate yield. Hexenuronic acid (HexA) removal becomes most evident after the D_1 stage, when the residual lignin content is low.

The kinetic curves of the Kappa number are represented in Fig. 2. The delignification is very fast in the first 5 min, when the Kappa number falls under 6.0; after that, the process slows down [1, 8, 9].

Hexenuronic acid (HexA) is formed from the 4-O-methyl-D-glucuronic acid substituents of xylan during kraft pulping. Although it contributes to the kappa number, HexA is not lignin and can lead to an overestimation of the residual lignin content. Under the experimental conditions the hexenuronic acids are hydrolysed.

The kinetics of hexenuronic acids (HexA) hydrolysis was studied to determine the optimal conditions and mechanism of pulp bleaching, with chlorine dioxide [25]. The kinetic variable α_H represents the relative change in HexA content. The HexA content was determined spectrophotometrically.

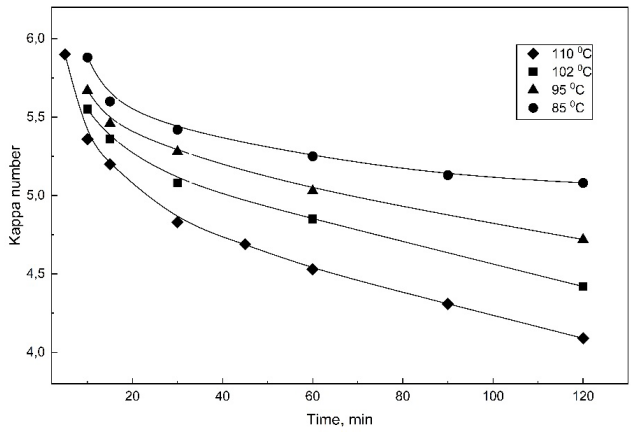


Fig. 2. Kinetic curves of Kappa in D_0 stage at different temperatures.

$$\alpha_H = \frac{HexAs_0 - HexAs_t}{HexAs_0} \quad (6)$$

where $HexAs_0$ is initial and $HexAs_t$ is current hexenuronic acids amount.

Several kinetic models were evaluated to describe the hydrolysis of HexA and the best description has been achieved by the power kinetic equation, which is applied to surface chemical interactions taking place on the exponential uniform surfaces (Eq. (7)).

$$v = \frac{d\alpha_H}{dt} = k_1 \alpha_H^{-\frac{1-\chi}{\chi}} \quad (7)$$

where k_1 is the apparent rate constant and χ is a coefficient of heterogeneity.

The temperature dependence of the rate constant was used to determine the activation energy and the pre-exponential factor. The results showed that the process of a HexA hydrolysis proceeds without changing the activation energy. The slowing of the process is attributed to a decrease in the pre-exponential factor, probably caused by the depletion and reduced accessibility of the reactive groups.

The successful application of the power-law kinetic model indicates that HexA hydrolysis during chlorine dioxide bleaching is governed by surface chemical interactions rather than by topochemical processes. This behaviour is likely related to the relatively low molecular weight of the xylan backbone and the distribution of HexA within the xylan side chains. The proposed kinetic model adequately describes the entire reaction period, including the rapid initial stage.

Fig. 3 illustrates how temperature and reaction time affect brightness during the first stage of chlorine dioxide bleaching [9]. The kinetic curves show that brightness reaches a maximum early in the treatment and subsequently declines. This loss may be attributed to changes in the structure of residual lignin and the formation of new chromophoric groups.

The topochemical kinetic model was found to adequately represent the bleaching process in terms of the light absorption coefficient. As a kinetic variable is used $\alpha_{\frac{k}{s}}$.

$$\alpha_{\frac{k}{s}} = \frac{\frac{k_0}{s} - \frac{k_t}{s}}{\frac{k_0}{s}} = \frac{k_0 - k_t}{k_0} \quad (8)$$

where k/s being the Kubelka-Munk function, k is the light absorption coefficient and s is the scattering coefficient, whose value is constant during bleaching.

Using a modified version of the Prout–Tompkins kinetic equation (Eq. (2)) can be attributed to the non-uniform distribution and varying accessibility of chromophoric groups during bleaching.

Accounting for the temperature dependence of the rate constant yielded a simplified equation for determining the light absorption coefficient at any given time:

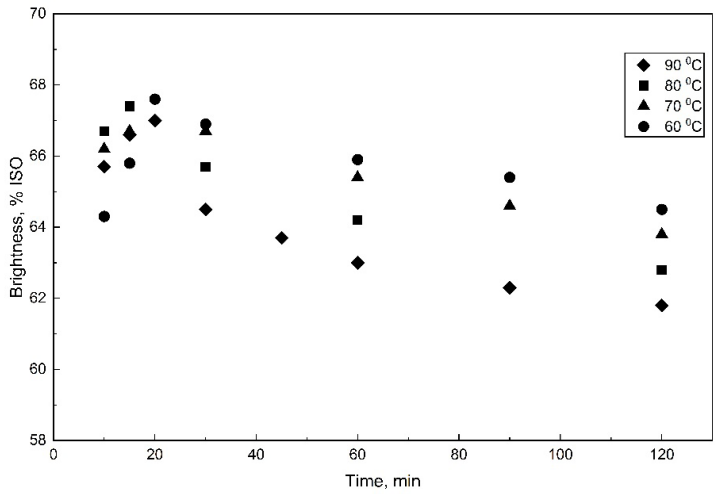


Fig. 3. Evolution of pulp brightness with time during the first stage of chlorine dioxide bleaching at temperatures studied.

$$k = k_0 \left\{1 - \left[1 + \left[\left(20x10^6 . e^{-\frac{6531}{T}}\right)t\right]^{-0.15}\right]^{-1}\right\} \quad (9)$$

where k_0 and k denote the initial and instantaneous absorption coefficients, respectively, χ is equal to 0.15, the value of the pre-exponential factor A is 20 x 10^6 min^{-1} and the value of the attitude E/R is 6531 K.

Eq. (9) provides a practical tool for controlling the bleaching process because it accounts for the combined effects of temperature and reaction time on the bleaching rate.

Kinetics of xylanases in pulp bleaching

Xylanases are the most widely used enzymes in pulp bleaching. The beneficial effect of hemicellulases on pulp brightness is attributed to the removal of xylan from the fibre surface and the degradation of xylan-lignin complexes located within the inner layers of the pulp matrix. Overall, the effect of xylanase pretreatment on subsequent peroxide bleaching is approximately twice that of oxygen delignification alone [14].

Treatment with xylanase improves the brightness of peroxide-bleached pulp by approximately 4 % ISO and lowers the Kappa number by about one unit (Fig. 4) [10].

It was found that the optimal bleaching is attained with a low enzyme dosage and relatively limited xylan conversion. It should also be noted that, pulp yield and strength properties remain largely unchanged [26].

The dimensionless kinetic variable α was defined as the ratio of the amount of reducing sugars that are solubilised (*Rs*) at any moment of the process to the maximum amount of reducing sugars Rs_{max}.

$$\alpha = \frac{Rs}{Rs_{max}} \quad (10)$$

The kinetic variable α therefore represents the degree of xylan conversion. Monitoring the release of reducing sugars allows real-time estimation of α and, consequently, prediction of the remaining reaction time.

Because of the heterogeneous distribution of xylan within the pulp fibres and the structural variations of xylan throughout the pulp matrix, the classical Michaelis-Menten equation does not adequately describe the kinetics of enzymatic xylan degradation. Therefore, several kinetic models have been evaluated to account for the heterogeneous nature of the process. Investigations of xylan hydrolysis have demonstrated that the modified Prout–Tompkin's equation (Eq. (3)) describes the reaction kinetics with good agreement [13-16].

Application of this equation to xylanase action on pulp indicates that the process is connected with a continuous change of reaction area, which is determined by the xylan chain structure and the lignin-carbohydrate bonds. The values of the coefficient χ ($0 < \chi < 1$) are approximately 1 and show that the amount of xylan in the pulp has a decisive effect on the enzyme action rate. The decrease of the rate *v* during the process is mainly

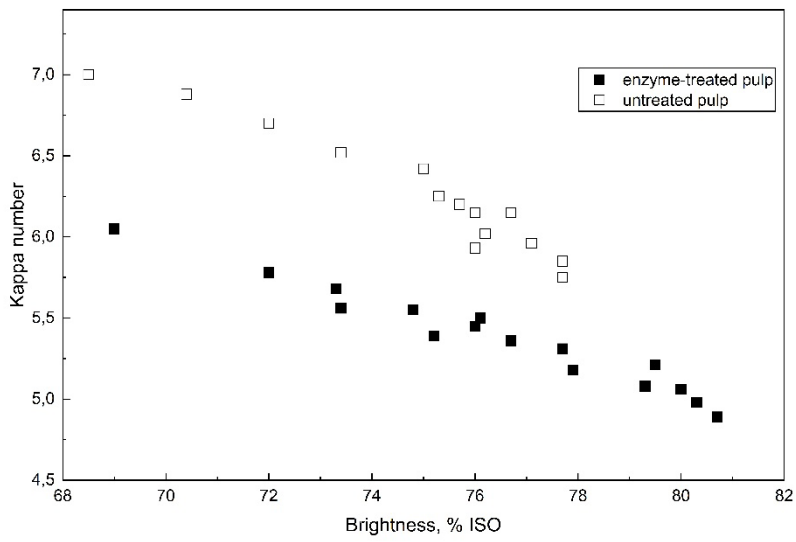


Fig. 4. Brightness as a function of the Kappa number.

due to exhaustion of the xylan, being mainly affected by the amount of unreacted xylan in the pulp (1- α).

By integrating Eq. (9), the required retention time for a desired degree of conversion can be calculated.

$$\int_0^{\alpha} \frac{d\alpha}{\alpha^{\frac{\chi-1}{\chi}}(1-\alpha)^{\frac{\chi+1}{\chi}}} = kt \quad (11)$$

This information is useful for sizing industrial enzyme-treatment towers and optimizing residence time.

The activation energy and pre-exponential factor are determined from the temperature dependence of the apparent rate constant, k, using the Arrhenius equation over the temperature range of 20 - 50°C.

The activation energy remains essentially constant throughout the reaction, with a value of $E = 47.0$ kJ mol^{-1}, indicating that the enzyme interacts predominantly with a specific fraction of xylan during the entire process [16]. This observation suggests that the energetic characteristics of the xylan-enzyme interaction remain unchanged as hydrolysis progresses. In contrast, the pre-exponential factor A decreases with increasing α, reflecting the gradual reduction in the reaction rate during xylan conversion.

$$A = \lambda\alpha^{\frac{\chi-1}{\chi}}(1-\alpha)^{\frac{\chi+1}{\chi}} \quad (12)$$

The pre-exponential factor can be interpreted as a measure of the size and accessibility of the reactive xylan surface. At the beginning of the process, enzymatic hydrolysis occurs primarily on the readily accessible fibre surface. As the reaction progresses, the enzyme penetrates the internal capillary structure of the pulp matrix, where substrate accessibility becomes increasingly restricted. Consequently, enzyme access to the remaining xylan is progressively hindered, leading to a decrease in the reaction rate.

The developed kinetic model enables prediction of xylan conversion and bleaching performance under various operating conditions, including temperature, enzyme dosage, and treatment time. Consequently, the model can be incorporated into bleaching process simulations to estimate chemical savings and improvements in pulp quality. Furthermore, it provides a foundation for the development of automatic process control strategies aimed at maintaining consistent bleaching performance while minimizing chemical consumption.

Kinetics of cellulase action in biorefining

Bioconversion of wheat straw is favoured because of its relatively low lignin content (less than 20 % w/w) and high carbohydrate content (approximately 50 % hemicellulose and 30 % cellulose). Enzymatic hydrolysis using appropriate cellulolytic enzymes is considered one of the most effective methods for releasing fermentable sugars from lignocellulosic materials.

The dimensionless quantity α used as a kinetic variable is defined as the relative change in the amount of reducing sugars [23, 24].

$$\alpha = \frac{Rs}{Rs_{max}} \quad (13)$$

The time dependence of glucose formation was investigated at different temperatures and enzyme loadings of 1 %, 3 %, and 5 % (w/w, based on the dry mass of wheat straw) is shown in Fig. 5.

The heterogeneous nature of the wheat straw-cellulase system allows the application of kinetic models developed for heterogeneous catalytic reactions to describe the enzymatic hydrolysis process. The exponential kinetic model for reactions on uniformly heterogeneous surfaces provided the best description of the enzyme hydrolysis kinetics [27 - 29]:

$$v = \frac{d\alpha}{dt} = v_0 e^{-a\alpha} \quad (14)$$

where v_0 is the initial rate of cellulase hydrolysis and v is the current rate of the process. The coefficient a represents the kinetic heterogeneity of the system.

At the beginning of hydrolysis, the readily accessible cellulose is rapidly converted into soluble sugars. As the reaction proceeds, the remaining cellulose becomes progressively less accessible because crystalline regions become exposed, lignin restricts enzyme penetration, pore diffusion limitations increase, and the number of productive enzyme adsorption sites decreases.

The current rate decreases during the process, following the dependence:

$$v = ke^{(bc_E - a\alpha)} \quad (15)$$

where k is the apparent rate constant, while b is a coefficient equal to 0.23 (it does not depend on the temperature and the enzyme concentration).

The kinetic coefficient of heterogeneity, a, reflects

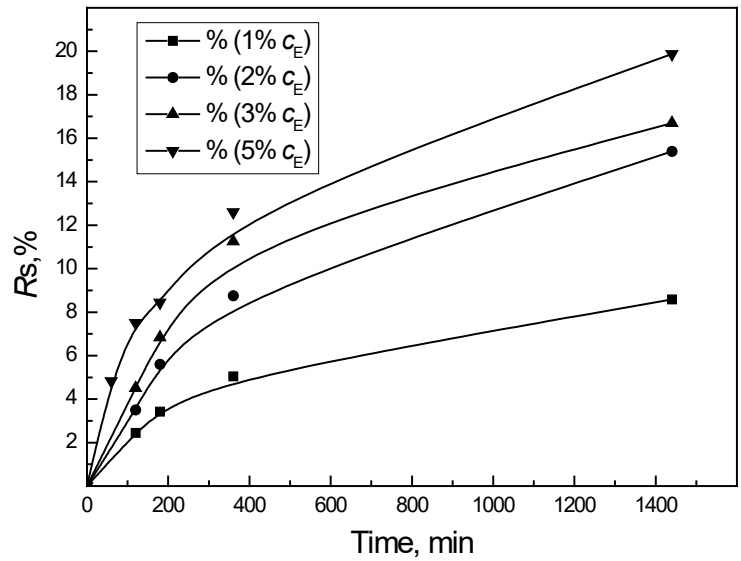


Fig. 5. Kinetic curves for reducing sugars, R_S, referring to the different enzyme concentrations at 40°C.

the energetic and entropic heterogeneity of the substrate. Large values of a (approximately 7.7) indicate a rapid depletion of easily accessible cellulose, pronounced substrate heterogeneity, and a significant decrease in the hydrolysis rate. These results demonstrate that substrate accessibility is the primary factor limiting cellulose conversion [29].

$$\alpha = \frac{1}{a} ln(\lambda at) + \frac{b}{a} c_E - \frac{E}{aRT} \quad (16)$$

where λ is a kinetic parameter connected with the heterogeneity of the system and has the sense of a preexponential factor.

Eq. (16) is of considerable practical importance because it enables prediction of the degree of hydrolysis under predetermined operating conditions, including reaction time, enzyme concentration, and temperature.

Analysis of the hydrolysis rates at a constant degree of conversion shows that increasing the enzyme concentration enhances the reaction rate. For example, increasing the enzyme loading from 2 % to 5 % results in an approximately 23 % increase in the hydrolysis rate. Because the degree of hydrolysis depends logarithmically on reaction time ($\alpha \propto \ln t$), hydrolysis proceeds rapidly during the initial stage but gradually slows as the reaction progresses. Increasing the reaction time from 2 - 20 h increases the logarithmic time term by approximately 2.30, resulting in a corresponding increase in conversion. Temperature exerts an even stronger influence on hydrolysis performance. Raising the temperature from 40 to 50°C significantly increases both the reaction rate and the degree of hydrolysis, indicating that optimization of the reaction temperature is more effective than excessive enzyme addition.

Therefore, this expression provides a simple and reliable tool for monitoring and controlling the enzymatic hydrolysis of wheat straw. It can be applied for process optimization, determination of the optimum enzyme dosage, reduction of hydrolysis time, maximization of sugar yield, and minimization of enzyme consumption, thereby improving the economic feasibility of lignocellulosic bioconversion.

CONCLUSIONS

- A unified kinetic approach based on heterogeneous reaction models successfully describes oxygen delignification, chlorine dioxide bleaching, enzymatic xylanase pretreatment, and cellulase hydrolysis.
- Those processes occur on heterogeneous lignocellulosic surfaces and classical homogeneous kinetic models are often insufficient.
- These models provide valuable tools for predicting

process performance and optimizing industrial pulping, bleaching, and biorefining operations while improving product quality and reducing chemical and energy consumption.

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Author contributions

G.R.: conceptualization, methodology, investigation, writing - original draft, and supervision; I.V.: conceptualization, methodology, validation, and writing - review and editing; S.P.: investigation, formal analysis, and data curation; I.G.: formal analysis, visualization, data curation, and writing - review and editing. All authors have read and approved the final version of the manuscript.

REFERENCES

1. I. Valchev, Chemical Pulp Bleaching, in: V.I. Popa (Ed.), Pulp Production and Processing: From Papermaking to High-Tech Products, Smithers Rapra Technology Ltd, Shawbury, 2013, 71-118.
2. S. Nenkova, I. Valchev, G. Simeonova, Possibilities for increasing the effectiveness of oxygen delignification of hardwood kraft pulp, J. Pulp Pap. Sci., 29, 10, 2003, 324-327.
3. L. Olm, A. Teder, The kinetics of oxygen bleaching, Tappi J., 62, 12, 1979, 43-46.
4. I. Valchev, E. Valcheva, E. Christova, Kinetics of oxygen delignification of hardwood kraft pulp, Cellul. Chem. Technol., 33, 3-4, 1999, 303-310.
5. M.J. Joncourt, P. Froment, D. Lachenal, C. Chirat, Reduction of AOX formation during chlorine dioxide bleaching, Tappi J., 83, 1, 2000, 144-148.
6. M.J.M.C. Barroca, P.J.T.S. Marques, I.M. Seco, J.A.A.M. Castro, Selectivity studies of oxygen and chlorine dioxide in the pre-delignification stages of a hardwood pulp bleaching plant, Ind. Eng. Chem. Res., 40, 24, 2001, 5680-5685.
7. B.N. Brogdon, L.A. Lucia, New insights into lignin modification during chlorine dioxide bleaching sequences (III): The impact of modifications in the (EO) versus E stage on the D1 stage, J. Wood Chem. Technol., 25, 3, 2005, 133-147.
8. I. Valchev, G. Simeonova, S. Nenkova, J. Gaidarov, Evolution in hardwood kraft pulp bleaching: A comparison of options, Cellul. Chem. Technol., 39, 1-2, 2005, 105-114.
9. I. Valchev, G. Simeonova, S. Nenkova, E. Valcheva, J. Gaidarov, Evolution of the ECF hardwood bleaching for better chemical efficiency, Balkan Pulp Pap. News, 5, 12, 2004, 25.
10. I. Valchev, I. Dimitrov, E. Valcheva, S. Veleva, Kinetics of pressured peroxide bleaching of hardwood pulp. Part II. Effect of enzyme treatment on pulp, Cellul. Chem. Technol., 38, 1-2, 2004, 67-77.
11. L. Viikari, A. Kantelinen, J. Sundquist, M. Linko, Xylanases in bleaching: From an idea to the industry, FEMS Microbiol. Rev., 13, 2-3, 1994, 335-350.
12. C. Deneault, C. Leduc, J.L. Valade, The use of xylanases in kraft pulp bleaching: A review, Tappi J., 77, 6, 1994, 125-131.
13. I. Valchev, L. Yotova, E. Valcheva, Kinetics of xylanase treatment of hardwood pulp, Bioresour. Technol., 65, 1-2, 1998, 57-60.
14. E. Valcheva, S. Veleva, I. Valchev, I. Dimitrov, Kinetic model of xylanase action on kraft pulp, React. Kinet. Catal. Lett., 71, 2, 2000, 231-238.
15. E. Valcheva, I. Valchev, L. Yotova, Kinetics of enzyme action of Cartazyme NS-10 prior to bleaching of kraft pulp, Biochem. Eng. J., 7, 3, 2001, 223-226.
16. I. Dimitrov, I. Valchev, E. Valcheva, Topochemical kinetics of xylanase action on kraft pulp, Biocatal. Biotransform., 23, 1, 2005, 33-36.
17. F. Alfani, A. Gallifuoco, A. Saporosi, A. Spera, M. Cantarella, Comparison of SHF and SSF processes for the bioconversion of steam-exploded wheat straw, J. Ind. Microbiol. Biotechnol., 25, 4, 2000, 184-192.
18. F. Carrillo, M.J. Lis, X. Colom, M. López-Mesas, J. Valldeperas, Effect of alkali pretreatment on cellulase hydrolysis of wheat straw: Kinetic study, Process Biochem., 40, 10, 2005, 3360-3364.
19. J. Chrastil, Enzymic product formation curves with the normal or diffusion limited reaction mechanism

and in the presence of substrate receptors, Int. J. Biochem., 20, 7, 1988, 683-693.
20. J. Chrastil, Determination of the first order consecutive reaction rate constants from final product, Comput. Chem., 12, 4, 1988, 289-292.
21. J. Chrastil, J.T. Wilson, The effect of chemical and physiological factors on the kinetics for product formation as it relates to enzyme activity and concentration, reaction time and to substrate adsorption and affinity, Int. J. Biochem., 14, 1, 1982, 1-17.
22. G.L. Miller, Use of dinitrosalicylic acid reagent for determination of reducing sugar, Anal. Chem., 31, 3, 1959, 426-428.
23. G. Radeva, I. Valchev, S. Petrin, E. Valcheva, P. Tsekova, Comparative kinetic analysis of enzyme hydrolysis of steam-exploded wheat straw, Cellul. Chem. Technol., 46, 1-2, 2012, 61-67.
24. G. Radeva, I. Valchev, S. Petrin, E. Valcheva, P. Tsekova, Kinetic model of enzymatic hydrolysis of steam-exploded wheat straw, Carbohydr. Polym., 87, 2, 2012, 1280-1285.
25. I. Valchev, G. Simeonova, Kinetic models for investigation and control of the bleaching processes, Proceedings of the 2005 International Pulp Bleaching Conference, Stockholm, Sweden, 14-16 June 2005, 272-274.
26. I. Valchev, P. Tsekova, Xylanase post-treatment as a progress in bleaching processes, Appita J., 63, 1, 2010, 53-57.
27. G. Radeva, I. Valchev, E. Valcheva, Thermodynamics and kinetics of the adsorption of cellulase on bleached and unbleached pulp, in: L. Wang, S. Kuang, Q. Hou, C. Cao, C. Si, H. Zhang (Eds.), Proceedings of the 16th International Symposium on Wood, Fiber and Pulping Chemistry, Tianjin, China, 2011, 516-521.
28. S. Petrin, N. Yavorov, P. Tzvetkov, I. Valchev, G. Radeva, Kinetic aspects of enzyme hydrolysis of cellulose fibre material, Bulg. Chem. Commun., 47, Special Issue A, 2015, 30-33.
29. G. Radeva, I. Valchev, S. Petrin, E. Valcheva, P. Tsekova, Kinetic study of the enzyme conversion of steam-exploded Paulownia tomentosa to glucose, BioResources, 7, 1, 2012, 412-421.