Volumes 106, Number 1 - 3 Spring 2003, ISSN: 0273–2289

Applied Biochemistry and Biotechnology

Biotechnology for Fuels and Chemicals

The Twenty-Fourth Symposium

Editors

Brian H. Davison

James W. Lee

James D. McMillan

Mark Finkelstein

HUMANA PRESS

0273-2289/03/105-108/0451/$20.00

Simplistic Modeling Approach to Heterogeneous Dilute-Acid Hydrolysis of Cellulose Microcrystallites

Pär O. Pettersson,[*,1] Robert W. Torget,[2] Robert Eklund,[3] Qian Xiang,[4] Y. Y. Lee,[4] and Guido Zacchi[5]

[1]Mid Sweden University, 891 18 Örnsköldsvik, Sweden, E-mail: par.pettersson@mh.se; [2]National Renewable Energy Laboratory, Golden, CO; [3]Umeå University, 90187 Umeå, Sweden; [4]Auburn University, Auburn, AL; and [5]Lund University, 22100 Lund, Sweden

Abstract

The classic kinetic model for cellulose hydrolysis is often referred to as *pseudo-homogeneous*, a term revealing the insight that the process is actually heterogeneous. During the past 10–15 yr, the shortcomings of this model have been demonstrated in various studies and the interest in the heterogeneous aspects has increased. The present work presents a simplistic model in which the intrinsic, heterogeneous hydrolysis and transport rates are coupled by the assumption of a constant glucosidic surface concentration. The mechanisms affecting these two rates are largely unknown, but the model serves as a guideline for further exploration of the process.

Index Entries: Dilute-acid hydrolysis; kinetic model; heterogeneous model.

Introduction

The model presented here deals with glucan hydrolysis alone, ignoring sugar degradation. The model is simplistic, and its validity is discussed following its presentation.

Model and Simulation Procedure

In this heterogeneous model, the total (T) surface concentration of glucopyranose rings is assumed constant. It is further assumed that these glucopyranoses are parts of either glucan (G) or sugar (S):

$$C_T = C_G + C_S \ (\mathrm{kg/m^2}) \tag{1}$$

*Author to whom all correspondence and reprint requests should be addressed.

By sugar we mean all mono-, di-, or oligomers that are solvable. The mass change owing to hydration is ignored for simplicity. The hydrolysis step does not leave the sugar solubilized, but attached to the surface. Once the sugar is solubilized (i.e., released from the surface), an underlying glucan unit is revealed, thereby keeping the total surface concentration C_T constant. The two processes of hydrolysis (h) and transport (t) (≈solubilization) are assumed to be first order:

$$r_h = k_h \cdot C_G \left(\text{kg}/[\text{m}^2\text{s}]\right) \tag{2}$$

$$r_t = k_t \cdot C_S \left(\text{kg}/[\text{m}^2\text{s}]\right) \tag{3}$$

in which k_h and k_t are rate constants. We use the term *transport* for the entire escape of the hydrolyzed sugar from the domain of the solid surface. Note that the rate of transport is assumed independent of the sugar concentration in the bulk. Since the sugar is a mix of mono-, di-, and oligomers, the rate constants are lumped entities, averaging a set of hydrolysis and transport mechanisms.

The surface concentration of sugar (C_S) is then determined from the rate:

$$\frac{dC_S}{dt} = r_h - r_t = k_h \cdot (C_T - C_S) - k_t \cdot C_S \tag{4}$$

With the initial condition $C_S(t) = 0$, $C_S(t)$ becomes

$$C_S(t) = \frac{k_h C_T}{k_h + k_t}\left(1 - e^{-(k_h + k_t)t}\right) \tag{5}$$

If we assume that the experimental data on remaining glucan include also the sugar at the surface (which is hydrolyzed but not solubilized), we are interested in the simulated amount of all material that has not been transported away. This amount (mass) m is given by Eq. 6:

$$\frac{dm}{dt} = -A \cdot r_t = -A \cdot k_t \cdot C_S(t) = -A \cdot k_t \frac{k_h C_T}{k_h + k_t}\left(1 - e^{-(k_h + k_t)t}\right) \tag{6}$$

The total solids area A is dependent on the conversion. Assuming that the particles are long microcrystallites of size $3 \times 3 \times 100$ nm (corresponding to 6×6 strands of glucan), we can consider the length to be constant in comparison to the crystallite width r, so that

$$A(r) = 4Lr \left(\text{m}^2\right) \tag{7}$$

$$V(r) = Lr^2 \ \left(\text{m}^3\right) \tag{8}$$

in which L is the total length of all particles. The assumption of a constant particle length is not merely a mathematical convenience but is largely supported by experiments *(1)*. We can now describe the area dependence on the remaining mass m:

$$A = 4rL = 4\sqrt{LV} = 4\sqrt{Lm/\rho} = 4\frac{\sqrt{m_0 m}}{\rho r_0} \tag{9}$$

in which ρ is the density, and the subscript zero denotes initial values. Inserting Eq. 9 into Eq. 6, and dividing both sides by m_0, we arrive at

$$\frac{d\,(m/m_0)}{dt} = -Q\sqrt{\frac{m}{m_0}} \cdot \varphi\,(t) \tag{10}$$

in which

$$Q = \frac{4\,C_T}{r_0\rho}\,\frac{k_h k_t}{k_h + k_t}\ \text{(overall rate constant, s}^{-1}\text{)} \tag{11}$$

$$\varphi(t) = 1 - e^{-(k_h + k_t)t} \tag{12}$$

Parameter values used in our simulations are ρ = 2000 kg/m^3, C_T = 10^{-6} kg/m^2, $r_0 = 3 \times 10^{-9}$ m. Some values of k_h and k_t are given in the next section. MATLAB's ode-solver *ode45* was used to simulate $m(t)/m_0$, which has a real-value solution only up to a critical time t_c with $m(t_c) = 0$. If φ(t) were equal to 1 (it actually starts off at 0 and approaches 1 exponentially), the analytical solution would be given by Eq. 13, and t_c would then be equal to $2/Q$. Since φ(t) is *not* constantly 1, t_c is somewhat bigger than this value. Numerically, there is a breakdown around $m(t) = 0.01m_0$.

$$\frac{m(t)}{m_0} = \left(1 - \frac{Q}{2}\,t\right)^2 \tag{13}$$

This numerical limitation does not limit the use of this model, since we have plenty of reasons to mistrust the model at high conversion anyway.

Discussion

The model invariably yields glucan profiles with a certain curvature, but the overall rate is determined by the parameter Q (Eq. 11). In Fig. 1, two simulations are shown, in which a 12-fold difference in the value of k_t yields different overall rates. Figure 1 also shows two experimental data sets, one for batch and one for percolation. These data were presented earlier *(2)*, as were the experimental procedures *(3)* under which they were produced. As can be seen in Fig. 1, the simulations coincide, to some extent, with the experimental data. This is just a simple example to show the fundamental applicability of the model. The observed difference between two reactors could, in this example, be qualitatively explained by a hypothesized difference in transport efficiency.

In fact, the notational distinction between hydrolysis and transport may be short on physical significance, since the two processes are linked in a more complicated way than the model describes. Hydrolysis itself infers steric changes that alter the structure of the surrounding solvation shell, which is the beginning of solvation.

The two so-called rate constants k_h and k_t are hardly constant, and we therefore refer to them hereafter as rate *parameters*. Not only are temperature, pH, and flow likely to influence the rate parameters, but conversion

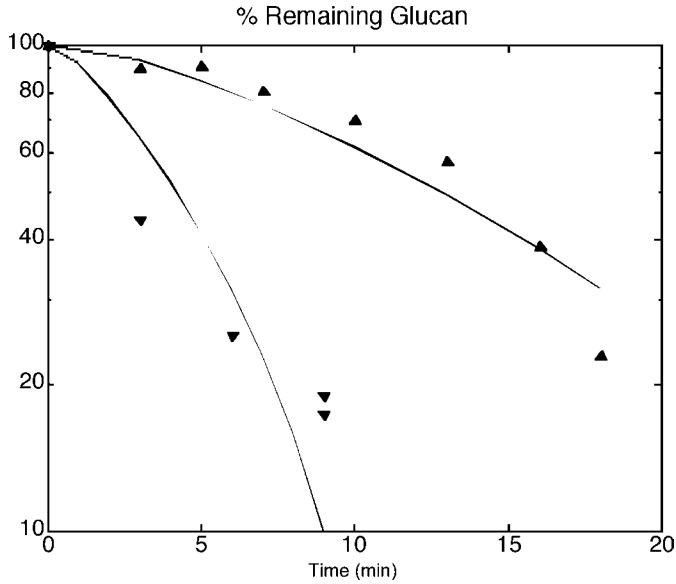

Fig. 1. Measured hydrolysis profiles for pretreated yellow poplar in (▲) batch and (▼) percolation at 225°C, 0.07% (w/w) *(2)*. The lines are simulations, in which k_h = 4.93×10^{-3} in both cases, but k_t differs 12-fold (1.97×10^{-3}) for the upper profile, (23.68×10^{-3} for the lower).

could have a great impact as well. A dependency on conversion would influence the curvature of the profiles, whereas the other three factors only affect the overall rate. Quantitative—and even qualitative—descriptions of these dependencies are hard to come by with current experimental procedures, since we cannot observe one rate parameter in isolation from the other.

For all these unknowns, we still have not addressed the complicated chemistry involved in lignocellulose hydrolysis. Bouchard et al. *(1)* and Mok et al. *(4)* claimed the destruction of some 30% of the glucan, in a way that glucose is never formed. Although these chemical pathways have never been elucidated, it can be assumed that there is more to glucan chemistry than the simple production of sugar. Given the presence of lignin and other compounds, the picture is further obscured. It must therefore be stressed that the complexity of the process is greater than both the model and our understanding. However, much of the complexity can be implicitly accounted for by the two rate parameters.

Xiang et al. *(5)* assumed that at low severity (especially low temperature), the microcrystallites are hydrolyzed at the ends, and the product is glucose. The strong cellulosic structure remains intact. At higher severity, this structure is weakened, and entire glucan chains are dissolved. This idea touches a very important issue: the observed homogeneous kinetics of a presumably heterogeneous process. In the present model, this divide

is represented by the exponent of *m* in Eq. 10. With an exponent of 0.5 (represented by the square root sign in Eq. 10), the process is modeled as entirely heterogeneous, whereas it becomes entirely homogeneous with an exponent of 1. Any intermediate value is plausible, although only the two extremes are easily interpreted. This exponent is probably heavily dependent on conversion and other factors.

This model only concerns the glucan hydrolysis. What happens to the dissolved sugars is a crucial question, and the reader is referred to the works from the laboratory of Dr. Y. Y. Lee *(6,7)*.

Conclusions

There is little reason to assume that heterogenous dilute-acid hydrolysis of cellulose microcrystallites can be adequately described by a simple model with only a few parameters. There is a multitude of interdependent mechanisms, and a comprehensive model is far out of reach. However, insights can be gained by exploring new modelling concepts.

This work has presented a simplistic model in which the intrinsic, heterogeneous hydrolysis rate and the heterogeneous transport rate are coupled by the assumption of a constant glucosidic surface concentration. The mechanisms affecting the hydrolysis and transport rates are largely unknown, but the model serves as a guideline for further exploring the process.

Acknowledgments

We gratefully acknowledge the financial support of the Swedish Energy Agency and the county of Västernorrland.

References

1. Bouchard, J., Abatzoglou, N., Chornet, E., and Overend, R. P. (1989), *Wood Sci. Technol.* **23,** 343–355.
2. Torget, R. W., Kim J. S., and Lee Y. Y. (2000), *Ind. Eng. Chem. Res.* **39,** 2817–2825.
3. Kim J. S., Lee Y. Y., and Torget R. W. (2001), *Appl. Biochem. Biotechnol.* **91–93,** 331–340.
4. Mok, W. S. L., Antal, M. J., and Varhegyi, G. (1992), *Ind. Eng. Chem. Res.* **31,** 94–100.
5. Xiang, Q., Kim, J. S., and Lee Y. Y. (2003), *Appl. Biochem. Biotechnol.* **105–108,** 337–352.
6. Xiang, Q. and Lee, Y.Y. (2001), presented at the *23rd Symposium on Biotechnology for Fuels and Chemicals*, Breckenridge, CO.
7. Lee, Y.Y., Xiang, Q., Zhu, Y., Kim, J.S., and Kim, S.B. (2001), Annual final report to DOE no. DE-FC36-00GO10592, US Department of Energy, Golden Field Office, Golden, CO.

Permission to Use Copyrighted Material

☒ Yes ☐ No

I give the National Renewable Energy Laboratory (NREL) of Golden, Colorado, irrevocable permission to post the following onto its site on the World Wide Web

Name of Document, Report, Article, etc.:

Nine National Biocnergy Center-authored papers in Volumes 105-108 of Applied Biochemstry and Biotechnology, the 24th Symposium on Biotechnology for Fuels and Chemicals

☒ Yes ☐ No

In addition to posting on the Web, I give NREL permission to distribute hard copies of the documentthrough its National Alternative Fuels Hotline in response to requests.

When posting on the Web, NREL will credit the copyright holder thus: "Posted on this site with permission from Humana Press." When distributing hard copies, NREL will label the document "Reprinted with permission from Humana Press.

I deny permission to post the document on the Web or to distribute hard copies, but give permission for the document to be abstracted and cited in NREL's database, along with information about obtaining the document directly from the copyright holder. The document can be obtained by writing:

I represent and warrant that I have the full right and authority to grant the rights herein granted and that no one else's permission is required.

Thomas B. Lanigan

Vice-President Marketing and Sales, Humana Press

Printed name

Thomas B Lanigan

Signed name

Title and company

Thomas B Lanigan

Date

Created February 1997