Chapter 6
Combined Severity Factor for Predicting Sugar Recovery in Acid-Catalyzed Pretreatment Followed by Enzymatic Hydrolysis

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6.1 Introduction

Cellulosic biomass is the only sustainable resource that is sufficiently abundant and low enough in cost to support large-scale, low-cost production of transportation fuels. For instance, biomass costing about $60/ton is equivalent in unit energy cost to petroleum at about $20/barrel (Lynd et al. 1999). In addition, it has been estimated that up to about 1.5 billion tons of biomass could be provided at a cost of less than $60/ton, enough to produce on the order of 100 billion gallons of gasoline equivalent (Langholtz et al. 2016). Furthermore, the polysaccharides that make up cellulose and hemicellulose in cellulosic biomass represent collectively about 65–75% of the mass and can be broken down into sugars that can in turn be fermented to fuels such as ethanol or chemical intermediates such as succinic acid. Biological routes to releasing these pent-up sugars have proven attractive for achieving the high yields that must be realized for cellulosic conversion to fuels to be economically competitive (Lynd et al. 1999). However, cellulosic biomass has built up a natural resistance to breakdown to sugars in order to survive in nature, and this recalcitrance must be overcome for biological conversion to be economically viable (Lynd et al. 1999). Introduction of a pretreatment step prior to

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enzymatic hydrolysis reduces recalcitrance sufficiently to allow enzymes to access the remaining polysaccharides more effectively (Yang and Wyman 2008). Treatment with dilute sulfuric acid has been shown to be very effective in favoring breakdown of hemicellulose to its constituent sugars with high yields while leaving behind glucan-enriched solids that enzymes can then attack (Lloyd and Wyman 2005). The result is a two-step operation in which biomass is first pretreated and the resulting glucan-enriched solids are digested by enzymes to realize high yields of sugars from the hemicellulose and cellulose fractions. A subsequent fermentation step can then convert the sugars to ethanol or other products (Humbird et al. 2011).

An alternative is to use only thermochemical operations for biomass deconstruction, with use of dilute acid at moderate temperatures favored. In this case, cellulose is much more recalcitrant than hemicellulose, and strictly thermochemical processes typically employ a two-step approach in which most of the hemicellulose is depolymerized in a first stage followed by thermochemical breakdown of the glucan-rich solids in a second stage (Wright and Wyman 1988). This sequence allows both operations to focus on applying two different combinations of time, temperature, and acid concentration to maximize total sugar yields from hemicellulose and cellulose combined. Hemicellulose sugar yields will be maximized in the same way as would be applied for pretreatment followed by enzymatic hydrolysis. However, because glucose yields from the more recalcitrant cellulose are limited for thermochemical conversion with dilute acid, focus has shifted from converting glucan to glucose for fermentation to ethanol or other products to breaking down glucose to 5-hydroxymethylfurfural and levulinic acid that can be catalytically converted into fuels that are fungible with conventional hydrocarbons (Cai et al. 2014; Li et al. 2011).

High yields of final products are a necessary, although not sufficient, condition for economic competitiveness in that high yields distribute costs over more product. In order to meet this metric, high yields of intermediates must first be achieved. Thus, it is vital to tune reaction conditions to maximize sugar yields from both hemicellulose and cellulose. Although it would be ideal if kinetic models could accurately predict reaction conditions that realize high yields a priori, the variability in biomass composition and recalcitrance makes it necessary to experimentally establish optimal reaction conditions (Jacobsen and Wyman 2000). However, it is expensive and extremely time-consuming to conduct numerous experiments to clearly define conditions that maximize yields. The development of the severity parameter that combines time and temperature in a simple variable by Chornet and Overend (Overend et al. 1987) made it possible to translate from a reaction time that gave the highest yields at one temperature to the time required to give corresponding yields at a different temperature, thereby dramatically reducing the amount of experimentation needed. Chum et al. and Abatzoglou et al. extended the utility of the severity factor approach to dilute acid hydrolysis of the hemicellulose in biomass by including the effect of acid concentration in addition to time and temperature (Abatzoglou et al. 1992; Chum et al. 1990).

This chapter will review the development of the combined severity factor and describe its relationship to kinetic models that have been developed to relate hemicellulose hydrolysis performance to reaction conditions. Illustrations will show the relationship of sugar yields from hemicellulose hydrolysis to the combined severity factor over a range of reaction conditions. Results from enzymatic hydrolysis of solids produced by dilute acid pretreatment of biomass will then be related to the combined severity factor. A summary of a recent adjustment in the combined severity factor to describe dilute acid hydrolysis of hemicellulose oligomers will conclude the chapter.

6.2 Dilute Acid Pretreatment of Cellulosic Biomass

Although hydrothermal pretreatment with just hot water improved the digestibility of the glucan-enriched solids produced through removal of much of the hemicellulose, it was found that adding dilute acid improved hemicellulose sugar yields substantially while also making the bulk of the glucan left in the solids highly digestible. As summarized in a dilute acid pretreatment chapter authored by Trajano and Wyman (2013), the development of dilute acid pretreatment progressed from initial research by Han and Callihan on a two-stage pretreatment of sugarcane bagasse with 10–50% H_2SO_4 for 15 min at 121 °C followed by dilution to 0.5–2% H_2SO_4 and holding the mixture at 121 °C for 15 min to 2 h (Han and Callihan 1974). Although their results led them to conclude that acid pretreatment was not as effective as alkali pretreatment, others showed that batch pretreatment with 0.9 w/w% H_2SO_4 at 100 °C for up to 5.5 h enhanced yields from enzymatic hydrolysis of such agricultural residues as wheat straw, barley straw, rice straw, sorghum straw, and corn stover (Sciamanna et al. 1977). Next, Grethlein and Converse applied a continuous plug flow reactor to pretreat a wide variety of materials including newsprint, corn stover, oak, white pine, poplar, and mixed hardwoods with sulfuric acid concentrations of 0.4–1.2% at 160–220 °C and reactor retention times of 6.6–13.2 s (Grethlein and Converse 1991; Knappert et al. 1980). They hypothesized that the increased susceptibility of the various materials they tested such as corn stover and oak to enzymatic hydrolysis could be attributed to increased pore size and surface area. A number approaches to dilute acid pretreatment were patented including an early invention by Foody in which lignocellulosic biomass was treated with 0.15–1 w/w% H_2SO_4 (Foody 1985). Although the initial focus was on achieving high glucose yields from enzymatic digestion of the pretreated solids, the objective shifted to maximizing recovery of as much sugar as possible from the hemicellulose and cellulose from pretreatment combined with enzymatic hydrolysis following genetic engineering of organisms to ferment both five and six carbon sugars that began in 1990 (Lloyd and Wyman 2005).

6.3   Simple First-Order Kinetic Models of Dilute Acid Hydrolysis of Biomass Hemicellulose

To help understand the basis for the combined severity factor, it is useful to first review selected kinetic models that have been applied to describe the breakdown of polysaccharides in biomass and recovery of the sugars produced. However, in light of previous reviews of these models, only key features relevant to the combined severity factor will be noted here (Jacobsen and Wyman 2000). To start with, early kinetic models of these reactions mostly focused on breakdown of cellulose to form glucose for fermentation to ethanol (Saeman 1945). This emphasis on cellulose instead of hemicellulose was likely motivated by the inability to ferment the xylose component that dominates hemicellulose in many types of biomass to ethanol, while the glucose from cellulose could be converted to ethanol by conventional yeast. For these early models, cellulose breakdown to glucose and glucose losses to 5-hydroxymethylfurfural (5-HMF) and other products were taken as proceeding according to the following series reaction (Saeman 1945):

$$\text{Cellulose} \xrightarrow{k_1} \text{Glucose} \xrightarrow{k_2} \text{Degradation products} \qquad (6.1)$$
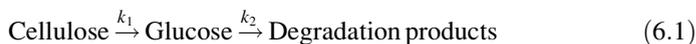
in which k_1 and k_2 are the rate constants for cellulose and glucose breakdown, respectively, while the degradation products refer to 5-HMF, levulinic acid, and other products that result from the glucose reaction. Furthermore, each step in the overall reaction sequence was assumed to be first order in the concentration of the reacting species, and the reactions were treated as if they were all homogeneous. Thus, according to these assumptions, the rate of disappearance of cellulose and rate of accumulation of glucose were described by the following expressions, respectively:

$$\frac{dC_\text{c}}{dt} = -k_1 C_\text{c} \qquad (6.2)$$

$$\frac{dC_\text{G}}{dt} = +k_1 C_\text{c} - k_2 C_\text{G} \qquad (6.3)$$

in which C_c and C_G are the concentrations of cellulose and glucose, respectively, and t is the reaction time. The kinetic rate constants were assumed to follow the following Arrhenius dependence on temperature:

$$k_i = k_{i,0} C_\text{a}^n \exp\left[\frac{-E_i}{RT}\right] \qquad (6.4)$$

in which $k_{1,0}$ is the frequency factor for rate constant k_i, C_a is the concentration of the acid catalyst that is assumed to remain constant, n is a power that is usually taken to be 1, E_i is the activation energy for the reaction, R is the universal gas constant, and T is the absolute temperature.

Most kinetic models for describing hemicellulose deconstruction have also been built from this framework of (1) simple series reaction, (2) first-order kinetics, (3) homogeneous concentrations, and (4) Arrhenius dependence of the rate constant on temperature. Furthermore, for hardwoods, grasses, and agricultural residues that are rich in xylan, the models often focus on just that portion due to its predominance coupled with difficulties in accurately measuring the other components in hemicellulose. On these bases, hemicellulose breakdown to xylose and other constituent sugars is pictured to proceed by the following series reaction:

$$\text{Hemicellulose} \xrightarrow{k_3} \text{Xylose} \xrightarrow{k4} \text{Degradation products} \qquad (6.5)$$
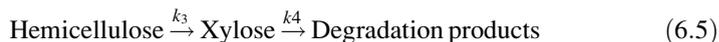
And the kinetic rate expressions to describe hemicellulose breakdown to xylose followed by xylose degradation to furfural and other compounds not of interest become

$$\frac{dC_H}{dt} = -k_3 C_H \qquad (6.6)$$

$$\frac{dC_X}{dt} = +k_3 C_H - k_4 C_X \qquad (6.7)$$

with C_H and C_x representing the concentrations of hemicellulose (usually just taken as xylan) and xylose, respectively, and k_3 and k_4 being the first-order rate constants for hemicellulose and xylose breakdown, respectively, per Eq. (6.5). The rate constants are assumed to follow the Arrhenius expression in Eq. (6.4).

Several points are noteworthy about these kinetic models. First, even though the polysaccharides cellulose and hemicellulose are insoluble in water while the sugars are soluble, the reactions are assumed to occur as if all components are dissolved. In addition, the acid concentration is assumed to stay virtually unchanged so that it can be combined with the rate constant. However, there are also some important differences in the implication of these models for maximizing yields of the sugars that comprise cellulose and hemicellulose. In the case of cellulose, glucose yields increase with increasing temperature to a maximum of about 70% of theoretical at about 260 °C but are restricted to under 50% for lower temperatures that would substantially reduce formation of tars and other degradation products that foul equipment and challenge extended operation. This drop-off in yields with lower temperatures results from the activation energy for cellulose hydrolysis being greater than that for glucose degradation. On the other hand, xylose yields from hemicellulose hydrolysis can reach about 85–90% of the theoretical maximum and remain nearly constant over the range of temperatures of commercial interest. The virtual constant maximum xylose yield over a range of temperature results from the ratio of k_3 to k_4 remaining nearly constant.

6.4 Derivation of Combined Severity Factor from Simple First-Order Kinetic Models

The severity factor relationship developed by Chornet and Overend trades off temperature against time to predict conditions that result in similar yields from the breakdown of hemicellulose to its component sugars according to the following relationship (Overend and Chornet 1987):

$$R_0 = t \exp\left\{\frac{(T - 100)}{14.75}\right\} \tag{6.8}$$

in which R_0 is the severity factor, t is the time in minutes, and T is the temperature in °C. The exponential term is consistent with the heuristic that the reaction rate will double for every 10 °C increase in temperature. Thus, Eq. (6.8) predicts that the value of R_0 will remain the same if the time t is cut in half for every 10 °C increase in temperature. Furthermore, once a particular combination of time and temperature has been identified to give a target yield, Eq. (6.8) can be used to quickly project how long to carry out the reaction for a different temperature. Equation (6.8) has some similarities to the following H factor equation that was developed to relate time and temperature for delignification in kraft pulping (Rydholm 1985):

$$H = \int_0^t \exp(43.2 - 16,115/T)dt \tag{6.9}$$

The combined severity factor was developed by Chum et al. and Abatzoglou et al. to combine the effects of temperature, time, and acid concentration on hemicellulose release from biomass and facilitate trade-offs among these three operational parameters; more details of its derivation are presented in those references (Abatzoglou et al. 1992; Chum et al. 1990). Alternatively, integrating Eq. (6.6) gives the following result to describe the breakdown of xylan in biomass hemicellulose:

$$\ln\left(\frac{C_H}{C_{H,0}}\right) = -k_3\, t \tag{6.10}$$

in which $C_{H,0}$ is the initial concentration of xylan prior to reaction. Although Eq. (6.10) could be used to predict how the concentration C of xylan drops with time t if k_3 is known, it can also be recast to include temperature and acid concentration based on Eq. (6.4) as

$$\frac{C_H}{C_{H,0}} = \exp\left(k_{3,0}\, C_a\, \exp\left(\frac{-E_3}{RT}\right)t\right) \tag{6.11}$$

in which n has been set equal to 1 in Eq. (6.4). This relationship clearly shows that the value of $C_H/C_{H,0}$ can have the same value over a range of combinations of acid concentration, time, and temperature as long as $k_{3,0}$ and E_3 remain unchanged. Thus, we can use Eq. (6.11) to correlate the effects of time, temperature, and acid concentration. Furthermore, integration of Eq. (6.7) results in the following expression to predict the concentration of xylose sugars left in solution as a result of the series reaction expression of Eq. (6.5):

$$\frac{C_X}{C_{H,0}} = \frac{k_3}{k_4 - k_3}\{\exp(k_3 t) - \exp(k_4 t)\} \tag{6.12}$$

Substituting the Arrhenius expression from Eq. (6.4) into Eq. (6.12) results in

$$\frac{C_X}{C_{H,0}} = \frac{k_{3,0}\,C_a\,\exp\left(\frac{E_3}{RT}\right)}{k_{4,0}\,C_a\,\exp\left(\frac{E_4}{RT}\right) - k_{3,0}\,C_a\,\exp\left(\frac{E_3}{RT}\right)}$$
$$\times \left\{\exp\left(k_{3,0}\,C_a\,\exp\left(\frac{E_3}{RT}\right)t\right) - \exp\left(k_{4,0}\,C_a\,\exp\left(\frac{E_4}{RT}\right)t\right)\right\} \tag{6.13}$$

Furthermore, if k_3 is much greater than k_4 so that a substantial fraction of hemicellulose H is converted to xylose X before an appreciable fraction of X can degrade, Eq. (6.13) can be simplified to

$$\frac{C_X}{C_{H,0}} = \left\{\exp\left(k_{3,0}\,C_a\,\exp\left(\frac{E_3}{RT}\right)t\right) - \exp\left(k_{4,0}\,C_a\,\exp\left(\frac{E_4}{RT}\right)t\right)\right\} \tag{6.14}$$

Because the reaction of hemicellulose to xylose is so much more rapid than the breakdown of xylose for the first-order reaction sequence of Eq. (6.5) and the activation energies of the two reactions are similar, Eqs. (6.11) and (6.14) are able to relate both hemicellulose deconstruction and xylose yield data to combinations of time, temperature, and acid concentration.

Expression (6.14) can be further rearranged to

$$\frac{C_X}{C_{H,0}} = \exp\left(k_{3,0}\,C_a\,\exp\left(\frac{E_3}{RT}\right)t\right)$$
$$\times \left\{1 - \exp\left\{\left[k_{4,0}\,C_a\,\exp\left(\frac{E_4}{RT}\right) - k_{3,0}\,C_a\,\exp\left(\frac{E_3}{RT}\right)\right]t\right\}\right\} \tag{6.15}$$

Thus, it is possible to combine the effects of time, temperature, and acid concentration into the following two parameters that are imbedded in Eqs. (6.14) and (6.15):

$$P_H = k_{3,0}\,C_a\,\exp\left(\frac{E_3}{RT}\right)t = \ln\left(\frac{C_H}{C_{H,0}}\right) \tag{6.16}$$

$$P_X = k_{4,0} \, C_a \exp\left(\frac{E_4}{RT}\right) t \qquad (6.17)$$

Equations (6.11) and (6.14) could be used to relate yield data easily for various combinations of time and acid concentration, but including the effects of temperature would require determining the activation energy of each reaction. Although it is certainly possible to determine activation energies that fit data on hemicellulose deconstruction at several temperatures, doing so would greatly limit the utility of the severity parameter. However, it is possible to substitute the 10-degree Celsius rule for the activation energy term to arrive at

$$\ln\left(\frac{C_H}{C_{H,0}}\right) \propto C_a t \exp\left(\frac{T - 100}{14.75}\right) = C_a R_0 \qquad (6.18)$$

$$\ln\left(\frac{C_X}{C_{H,0}}\right) \propto C_a t \exp\left(\frac{T - 100}{14.75}\right) = C_a R_0 \qquad (6.19)$$

Although use of the acid concentration in these expressions is pragmatic for quickly identifying conditions that give similar performance, the acid catalyst mechanism is more accurately represented by substitution of the hydrogen ion concentration for C_a in the above derivations. In that case, Eqs. (6.18) and (6.19) become

$$\ln\left(\frac{C_H}{C_{H,0}}\right) \propto C_{H^+} \, t \exp\left(\frac{T - 100}{14.75}\right) = C_{H^+} R_0 = \mathrm{CS} \qquad (6.20)$$

$$\ln\left(\frac{C_X}{C_{H,0}}\right) \propto C_{H^+} \, t \exp\left(\frac{T - 100}{14.75}\right) = C_{H^+} R_0 = \mathrm{CS} \qquad (6.21)$$

in which CS is the combined severity factor. Taking advantage of the definition of pH allows Eqs. (6.20) and (6.21) to be rewritten as

$$\log \mathrm{CS} = \log R_0 - \mathrm{pH} \qquad (6.22)$$

We have found the combined severity factor CS developed by Chum et al. and Abatzoglou et al. as well as the severity factor R_0 developed by Chornet and Overend, to be very valuable for comparing data sets collected at different temperatures, times, and acid concentrations and for translating from one set of reaction conditions to another that should give similar results (Abatzoglou et al. 1992; Chum et al. 1990). However, it is important to realize that the factor may not always be able to accurately make such projections. For instance, the following kinetic model developed by Kobayashi and Sakai that employed two rate constants to represent hemicellulose deconstruction has often predicted changes in concentrations with time better than the simple first-order expression of Eq. (6.6), suggesting that

CS could have a limited range of application in some situations (Kobayashi and Sakai 1956):

$$\begin{array}{c} \text{Fast hemicellulose} \searrow k_f \\ \xrightarrow{\qquad} \text{xylose} \xrightarrow{\; k_d \;} \text{degradation products} \\ \text{Slow hemicellulose} \nearrow k_s \end{array} \qquad (6.23)$$
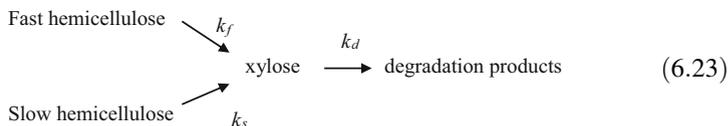
In Eq. (6.23), k_f is the rate constant for the breakdown of a more easily hydrolyzed portion of hemicellulose (typically about 65% of the total), k_s is the rate constant for breakdown of the more recalcitrant fraction (about 35% of the total), and k_d is the rate constant for degradation of xylose. The two parameter models can be hypothesized to account for the multiple bond types in hemicellulose that would be expected to have different activation energies and therefore not be represented as a homogeneous material. Nonetheless, although it is important to recognize the limitations of the combined severity factor, it still provides a very valuable tool with which to rapidly project performance based on one combination of temperature, time, and acid concentration to performance built around a different combination of time, temperature, and acid level.

Against this background, the next two sections of this chapter review the application of the combined severity factor to correlating xylan removal and xylose yields from various types of biomass. In addition, data will be presented to illustrate the applicability of the combined severity factor to relating enzymatic release of glucose from solids produced by dilute acid pretreatment of different cellulosic materials. Finally, a slight modification of the combined severity factor will be shown to relate yields from deconstruction of xylooligomers produced by hydrothermal pretreatment of biomass.

6.5   Correlation of Pretreatment Xylose Yields to Combined Severity Factor

The pretreatment severity $\log R_0$ has been widely applied to a broad range of pretreatment methods, including hydrothermal and dilute acid pretreatments. On the contrary, $\log CS$ gained less attention in reported research although it easily incorporated acid concentration into the time and temperature accounted for by $\log R_0$. This situation may result from $\log CS$ applying to just dilute acid pretreatment, while results using $\log R_0$ can be readily compared across hydrothermal and dilute acid pretreatments (Yang and Tucker 2013; Yang and Wyman Charles 2009). Thus, limited references were published based on $\log CS$, and even fewer applied both $\log R_0$ and $\log CS$. To compare applications of $\log R_0$ and $\log CS$, Fig. 6.1 shows the correlation of these two pretreatment severity parameters with data for yields of xylose, xylan oligomers, and the sum of the two (total xylan) as well as xylan removal collected from dilute acid steam
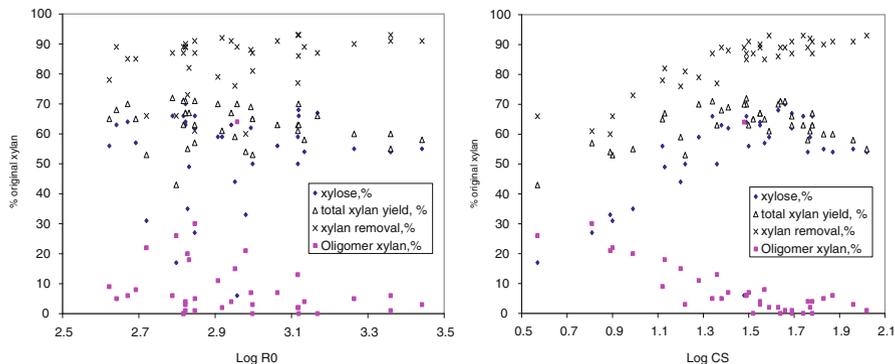
Fig. 6.1 Xylan removal and yields vs. log R_0 and log CS for dilute sulfuric acid steam explosion pretreatment (Schell et al. 2003)

explosion (Schell et al. 2003). It indicated that xylan removal increased with log CS, while total soluble xylan yield increased until about log CS = 1.5 before it dropped as degradation of dissolved xylan increased faster than formation at more severe conditions. The xylose monomer yield followed a similar trend as the total xylan yield with increasing log CS increased and then dropped as values increased further. Although about a 30% xylan oligomer yield was realized at log CS less than 0.9, it dropped to nearly zero for log CS = 1.5. However, no clear trend of xylan yields or removal was found when using the pretreatment severity log R_0 that does not include the acid concentration. Therefore, log CS is more valuable in terms of evaluating pretreatment involving dilute acid than log R_0.

Figure 6.2 shows xylan yields and removal vs. log CS over a log CS range from 0.4 to 3.1 for dilute acid pretreatment in closed batch tubes and in a continuous steam explosion reactor. Continuous steam explosion was conducted in a plug flow reactor that was fed corn stover and softwood forest thinning wastes as feedstocks, while the batch dilute acid pretreatment data were determined with a tubular reactor with corn stover (Lloyd and Wyman 2005; Nguyen et al. 2000; Schell et al. 2003). The data indicated that the highest xylan yields could be achieved at log CS between 1.2 and 1.7 for dilute acid steam explosion pretreatment. The majority of recovered xylan in the hydrolysate was as monomeric xylose, while the oligomeric xylan yield followed a bell-shaped curve with increasing log CS. Xylan removal increased with increasing log CS to nearly 100%. However, as log CS increased above 1.5, xylan degradation became more and more significant. Batch dilute acid pretreatment achieved somewhat greater total dissolved xylan yields than continuous acid steam explosion at the same log CS.

Biomass can also be pretreated in a flowthrough reactor in which water with or without addition of acid or other chemicals continuously flows through a stationary bed of lignocellulosic biomass (i.e., cellulose, hemicellulose, and lignin), with the fluid containing dissolved components leaving the reactor before significant degradation or recondensation occurs. For flowthrough pretreatment, flow rate is considered as an important factor in addition to temperature, time, and acid
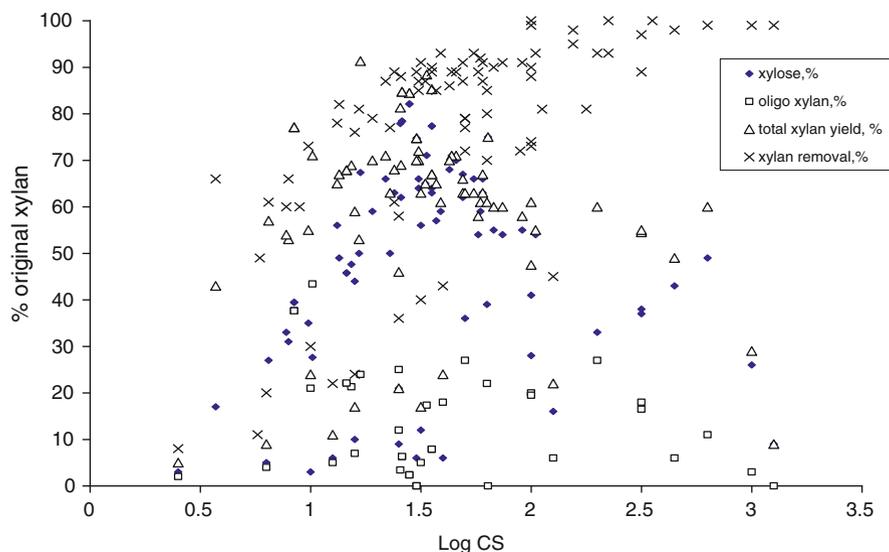
Fig. 6.2 Xylan removal and yields vs. log CS for batch dilute acid and continuous dilute acid steam explosion pretreatments (Lloyd and Wyman 2005; Nguyen et al. 2000; Schell et al. 2003)

concentration whose effects are combined in log CS. When log CS was adopted as shown in Fig. 6.3, xylan removal and xylan yield, including yields of xylose, xylan oligomer, and total xylan (sum of xylose and xylan oligomer) appeared to all correlate well with log CS in acid flowthrough pretreatment of corn stover with very dilute acid (0.05%w/w) (Yan et al. 2014, 2015). Results showed that xylan removal increased as log CS increased and reached nearly 100% for log CS at about 1.8. Total xylan yield was close to xylan removal, indicating that unlike dilute acid steam explosion and dilute acid batch pretreatment, very little xylose degradation occurred (Fig. 6.3). Increasing the flow rate to 62.5 mL/min increased xylan oligomer yields and reduced xylose yields compared to operation at the lower flow rate of 10 mL/min. The gaps between xylan yields were gradually reduced as log CS was increased between flow rates of 62.5 and 10 mL/min. The effects of flow rate on degradation product yields were even greater for fairly low flow rates (data not shown).

On the other hand, although $\log R_0$ for water-only flowthrough pretreatment can be calculated based on a pH measurement of the acidic pretreated hydrolysate, incorporating log CS leads to a very different data interpretation compared to $\log R_0$. As shown in Fig. 6.4, xylan removal and yields from water-only and dilute acid flowthrough pretreatments at the same flow rate of 10 mL/min were compared vs. $\log R_0$ and log CS (Yan et al. 2014). Results based on log CS suggested that water-only flowthrough pretreatment realized greater xylan removal and total xylan yields at a lower severity of log CS than dilute acid flowthrough pretreatments. In addition, water-only appeared to achieve similar xylose yields as dilute acid flowthrough pretreatment at the same pretreatment severity of log CS. $\log R_0$ results
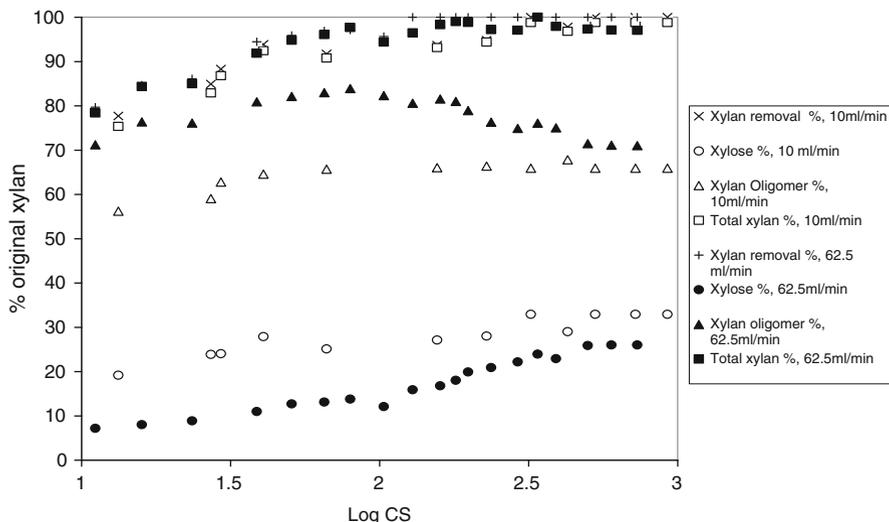
Fig. 6.3 Xylan yield and removal vs. log CS for very dilute acid flowthrough pretreatment of poplar wood (Yan et al. 2014, 2015)

indicated that water-only flowthrough pretreatment required higher pretreatment severity (i.e., higher temperature and/or longer time) to achieve similar xylose, xylan oligomer, and total xylan yields as dilute sulfur acid flowthrough pretreatment. According to mechanisms for water-only and dilute acid pretreatments, sulfuric acid has greater catalytic strength in degrading hemicellulose than water at similar temperature and reaction time. In Fig. 6.4, log R_0 provided a more accurate interpretation of experimental data. Therefore, log R_0 may be more suitable for comparison across different categories of pretreatment, while log CS may be more beneficial for comparison of dilute acid pretreatment results. Because very limited data has been published for application of log CS to hydrothermal pretreatment, further investigation is needed to validate this hypothesis.

6.6 Correlation of Enzymatic Hydrolysis Glucose Yields to Combined Severity Factor

A substantial portion of the glucan originally in raw biomass generally remains in the solid residues from various dilute acid pretreatments, including single-stage batch, flowthrough, and acid- or SO_2-catalyzed steam pretreatment with or without explosion. Thus, most of the cellulose is left for conversion into fermentable glucose in a second enzymatic hydrolysis stage. The cellulose-rich pretreated solids most likely contain some residual hemicellulose as well as various fractions of the lignin depending on pretreatment methods and conditions. Therefore, sugars
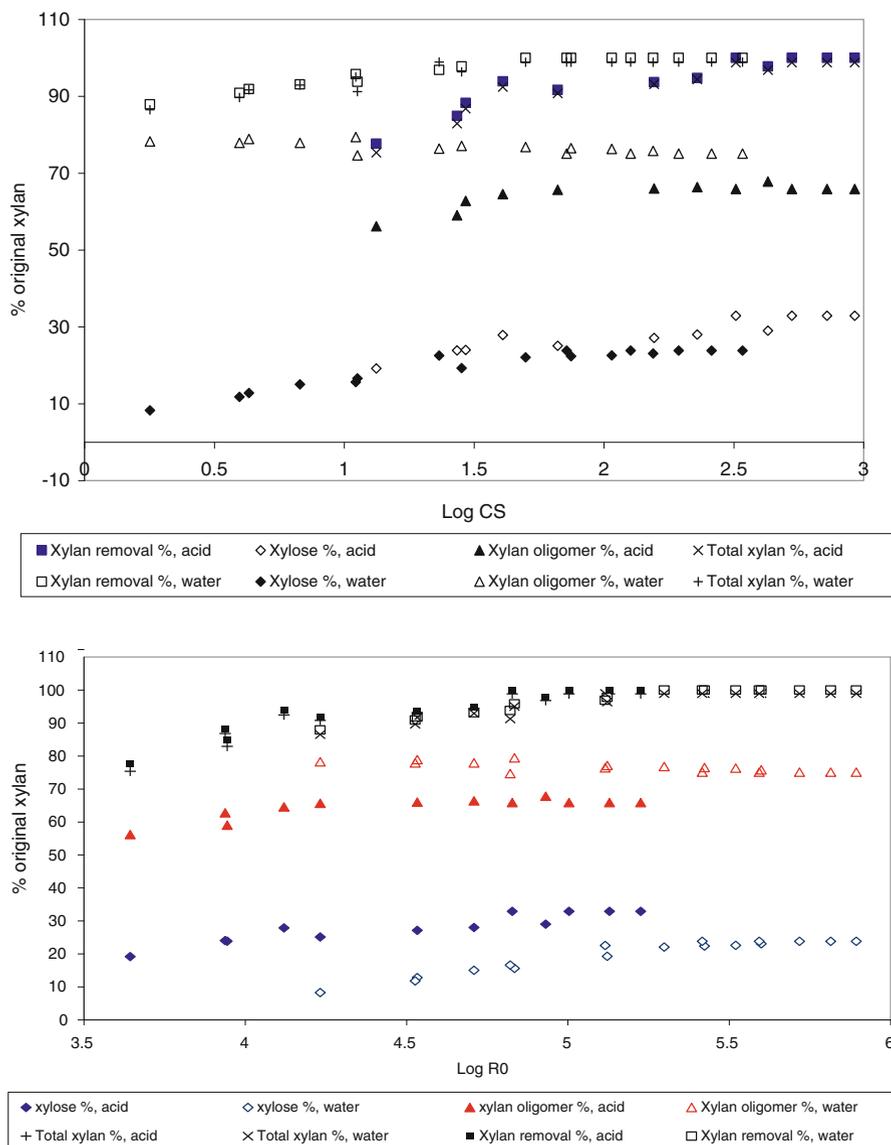
Fig. 6.4 Comparison of xylan yields and removal vs. log R_0 and log CS for water-only and dilute acid flowthrough pretreatments of poplar wood at a flow rate of 10 mL/min (Yan et al. 2014, 2015)

released by cellulose digestion by enzymes dominate the overall solubilized glucan yield. In turn, cellulose digestibility depends strongly on a number of factors, including chemical and structural characteristics of the pretreated solids, enzymatic hydrolysis mode (solely enzymatic hydrolysis or simultaneous saccharification and fermentation (SSF)), and enzymatic hydrolysis conditions, such as solids loading,
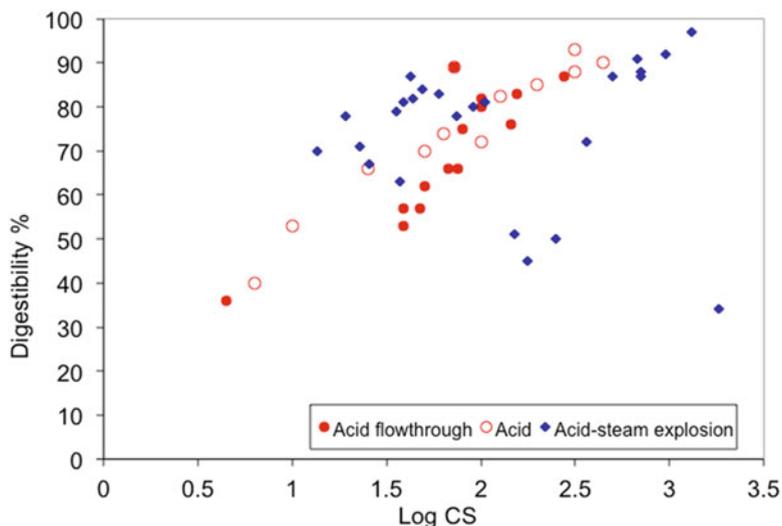
Fig. 6.5 Enzymatic digestibility (glucose yield) as a percent of the maximum possible from solid residues produced by dilute acid pretreatment of various biomass species vs. the adjusted combined severity parameter (Lloyd and Wyman 2005; Nguyen et al. 2000; Yang and Wyman 2004; Schell et al. 2003)

cellulase type, supplementation with β-glucosidases or/and xylanases, enzyme loading, duration of enzymatic hydrolysis or SSF, and microorganisms used in SSF. Because digestibility data reported in the literature has generally been developed at different combinations of these conditions, i is difficult to accurately compare such data across different research groups to evaluate the effectiveness of pretreatment methods and conditions. Nevertheless, based on assuming the results reflect the maximum possible glucose yields from pretreated solids by enzymes, Fig. 6.5 shows the correlation between enzymatic hydrolysis glucose yield from different biomass species and the adjusted combined severity parameter log CS (Lloyd and Wyman 2005; Nguyen et al. 2000; Yang and Wyman 2004; Schell et al. 2003). The data show that glucose yields from enzymatic hydrolysis increased with combined severity log CS and that a glucose yield of over 80% was achieved when the log CS was greater than 2 for dilute acid batch pretreatment (labeled as Acid), a result similar to that for dilute acid flowthrough pretreatment. For dilute acid steam explosion, a lower log CS of about 1.5 was sufficient to achieve a glucose yield of 80% by enzymatic hydrolysis, although the data fluctuates for log CS between 2 and 3; this result may reflect the influence of factors other than just pretreatment severity.

Although in the majority of reported acid pretreatments most of the glucan was not broken down during pretreatment but remained in the solid residues, most of the glucan in raw biomass could be removed by dilute acid under certain conditions, especially at higher temperatures. As shown in Fig. 6.6, flowthrough pretreatment with 0.05 wt.% sulfuric acid increased cellulose removal from poplar wood as
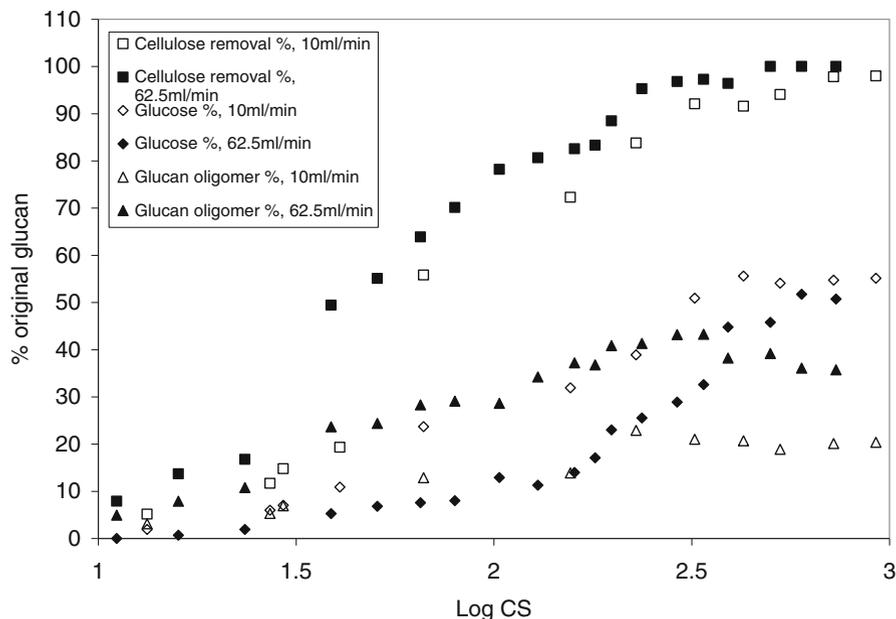
Fig. 6.6 Cellulose deconstruction by very dilute acid flowthrough pretreatment of poplar wood (data adapted from (Yan et al. 2014, 2015)

log CS increased. Furthermore, cellulose removal jumped from less than 20% to over 50% when log CS reached between around 1.6 and 2.5. The glucose yield also increased with increasing log CS, and dropping the flow rate to 10 mL/min resulted in greater glucose yields than operation at a higher flow rate of 62.5 mL/min. Although the glucan oligomer yield measured through post-hydrolysis only revealed low degree of polymerization glucan oligomers, it displayed an increasing trend with log CS in which higher flow rates resulted in higher oligomer yields (Yan et al. 2014, 2015).

6.7 Correlation of Glucose Plus Xylose Yields from Pretreatment Plus Hydrolysis

For biomass conversion processes involving pretreatment (Stage 1) and subsequent enzymatic hydrolysis (Stage 2) by either just enzymes or in SSF, the hemicellulose and cellulose from the raw biomass feedstock can be deconstructed into fermentable sugars, including xylose and glucose. The total sugar (glucose + xylose) yield realized from Stage 1 plus Stage 2 is an essential metric of the effectiveness of a biomass conversion process. In dilute acid pretreatments, acid concentration in addition to temperature and time plays a key role in breakdown of hemicellulose
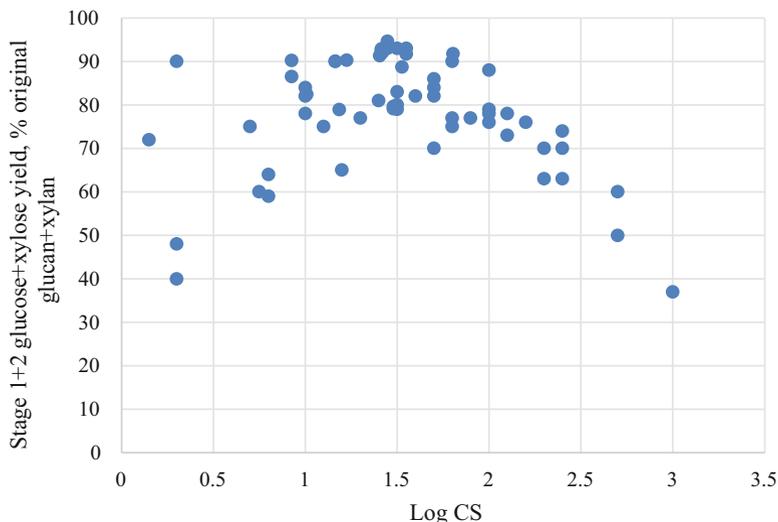
Fig. 6.7 Glucose plus xylose yields from dilute acid pretreatment plus subsequent enzymatic hydrolysis of corn stover and switch grass (Lloyd and Wyman 2005; Shi et al. 2011)

and cellulose into their component sugars through its effect on sugar release during pretreatment and the enzymatic digestibility of the pretreated solid residues. Figure 6.7 shows the correlation of Stage 1+2 glucose + xylose yields with log CS on the basis of original glucan + xylan in raw biomass. These data were collected from a number of different pretreatments, including batch dilute acid pretreatment of switch grass in a tubular reactor (H_2SO_4 0.5–2 wt.%, 140–180 °C) (Shi et al. 2011), batch SO_2 pretreatment of switch grass in a 1 L Parr reactor (SO_2 0–10 wt.% of dry biomass, 180 °C) (Shi et al. 2011), and batch dilute acid pretreatment of corn stover in tubular and Parr reactors (Lloyd and Wyman 2005). The results show that although feedstocks, pretreatment methods, and conditions varied, Stage 1+2 glucose + xylose yields from these acid pretreatments increased as log CS increased, peaked at a log CS of around 1.5, and rapidly dropped when log CS was increased to over 2.

6.8 Extension of Combined Severity Factor to Dilute Acid Hydrolysis of Xylooligomers

The major portion of the hemicellulose solubilized during hydrothermal pretreatment of cellulosic biomass is in the form of oligomers, mostly xylooligomers for many hardwoods and grasses. However, many organisms cannot ferment these long-chained sugars, and oligomers have also been shown to be very powerful inhibitors of fungal enzymes (Kumar and Wyman 2009; Qing et al. 2010).

Thus, it is vital to hydrolyze the oligomers into fermentable monomers in order to maximize final product yields from both hydrothermal pretreatment and subsequent enzymatic hydrolysis. Post-hydrolysis with dilute sulfuric acid is promising as sulfuric acid is relatively inexpensive and effective. A recent study applied post-hydrolysis to xylooligomers produced at conditions that gave the highest total soluble monomeric and oligomeric xylose yields from hydrothermal pretreatment of corn stover: 14.3 min at 200 °C (Zhang et al. 2015). After testing post-hydrolysis of the liquid fraction from hydrothermal pretreatment with 0.25, 0.50, 0.75, and 1.00% w/w sulfuric acid concentrations at 101, 110, 120, and 130 °C, the highest xylose yield of 99% was achieved for reaction with 0.75% sulfuric acid for 240 min at 110 °C. The combined severity factor CS as defined by Eq. (6.22) was applied to the range of data generated from post-hydrolysis of the xylooligomers in solution from hydrothermal pretreatment to evaluate its ability to relate xylose yields from post-hydrolysis over the range of conditions applied. However, xylose yields were typically greater at higher acid concentrations or temperatures than for lower acid concentrations or temperatures at the same value of the combined severity factor, possibly due to the heterogeneity in bonds among the variety of compounds in hemicellulose oligomers. This possibility was also supported by the differences in log CS that gave the highest yields of monomeric xylose: log CS ~1.3 at 101 °C, ~1.0 at 110 and 120 °C, and ~0.7 at 130 °C.

Next, because the parameters in the conventional CS were determined for hydrothermal pretreatment of hardwood, the parameters were adjusted to better fit the results for post-hydrolysis of xylooligomers over the lower temperature range employed. However, only two constants in the combined severity factor can be adjusted: T_c set at 100 °C in Eq. (6.8) and A that is 14.75 in that same equation. Because T_c only affects the absolute value of CS but does not account for the effects of temperature while parameter A adjusts the CS value at which similar yields are grouped together, A was fit to best correlate xylose yield data for the four temperatures and acid concentrations applied. As illustrated in Fig. 6.8, this approach led to a value of $A = 12.01$ with peak xylose yields at or very near a modified log CS of 2. Nonetheless, lower temperatures resulted in lower yields despite the tight grouping of the yield peaks. Adjusting the value of A meant that rather than the time required to achieve a given yield being cut in half for every 10 °C change in temperature, it now dropped by the same factor for just an 8.35 °C temperature change. Thus, this outcome suggested that dissolved oligomers were more easily deconstructed into monomeric xylose than the hemicellulose in native biomass.

6.9 Conclusions

Detailed kinetic models such as outlined in Eqs. (6.5) through (6.7) can be useful in describing the thermochemical deconstruction of polysaccharides in biomass to sugars followed by the degradation of those sugars. However, at the end of the day, they do not provide a reliable a priori tool for predicting performance in the absence
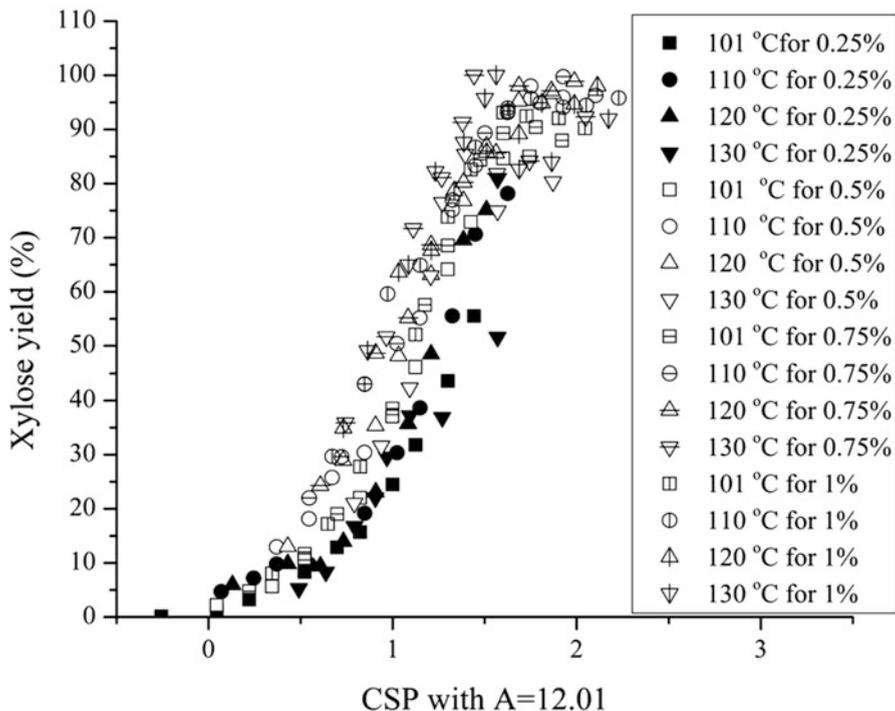
Fig. 6.8 Xylose yields as a percent of the maximum possible from post-hydrolysis of xylooligomers in the liquid fraction produced by hydrothermal pretreatment of corn stover vs. the adjusted combined severity factor over the range of temperatures, sulfuric acid concentrations, and times applied (Zhang et al. 2015)

of data and are not robust in predicting results with different acid concentrations, temperatures, and times for different biomass materials (Jacobsen and Wyman 2000). Rather, they tend to be empirical curve fits with as many parameters employed as needed to describe yields. In addition, these models are not readily employed in the field to estimate trade-off among conditions. On the other hand, the combined severity factor CS developed by Chum et al. (1990) provides a tool that allows quick estimates of new dilute acid pretreatment conditions that can realize performance targets defined at different combinations of temperature, acid concentration, and time. However, although combined severity factor can facilitate identification of conditions to realize targeted performance, we must still recognize the need to validate the outcomes predicted by the combined severity factor.

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