APPLICATION OF A PSEUDO-KINETIC GENERALIZED SEVERITY MODEL TO THE CONCENTRATED SULFURIC ACID HYDROLYSIS OF PINEWOOD AND ASPENWOOD

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The yield of monosaccharides after two-stage concentrated sulfuric acid hydrolysis of softwood (Scots pine) and hardwood (trembling aspen) was modeled using a generalized severity parameter with a time-independent rate constant. The severity parameter, which combines the major operating variables acid concentration, temperature, and reaction time in the decrystallization stage into a single reaction ordinate, was successfully used to describe monosaccharide yields after a standardized hydrolysis stage. Conversion of cellulose to glucose demanded a higher severity to reach maximum glucose yields than the conversion of hemicelluloses to their respective monosaccharides, and the conversion of pine demanded a higher severity to obtain maximum monosaccharide yields as compared to aspen. The results indicate that the generalized severity parameter can be a useful tool for the prediction of sugar yields in a two-stage concentrated sulfuric acid hydrolysis process.

Keywords: Concentrated sulfuric acid; Decrystallization; Generalized severity parameter; Severity parameter; Lignocellulose; Lignocellulosics; Aspen; Trembling aspen; Populus tremula; Pine; Scots pine; Pinus sylvestris; Hydrolysis; Biofuels; Biorefinery

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INTRODUCTION

Concerns about increasing anthropogenic CO_2 emissions and limited availability of petroleum raw materials has increased the interest in the manufacture of liquid fuels and bulk chemicals from renewable resources such as lignocellulosic biomass. A number of different processes are currently being investigated, the main being biomass gasification for syngas-based processes, and biomass saccharification for either fermentative or catalytic conversion of monosugars to fuels and chemicals (Galbe and Zacchi 2007; Knauf and Moniruzzaman 2004; Sun and Cheng 2002).

One of the challenges to the hydrolysis of lignocellulosic biomass into monosaccharides is the recalcitrant nature of these materials towards their breakdown into fermentable sugars (Himmel *et al*. 2007), thus limiting sugar yields and overall process economy. Degradation of sugars during hydrolysis is a problem for acid processes since sugar degradation not only lowers the conversion yields, but it also generates certain byproducts that can inhibit the fermenting microorganisms during the downstream fermentation process, thus jeopardizing sugar-to-ethanol conversion yield and the overall biomass-to-ethanol conversion efficiency (Larsson *et al*. 1998; Sanchez *et al*. 2004; Taherzadeh *et al*. 1997). During hydrolysis in acidic medium, pentoses degrade to furfural, while hexoses degrade to 5-hydroxymethyl furfural (HMF), which degrades further to formic acid and levulinic acid (McKibbins *et al*. 1962).

Unlike dilute acid hydrolysis, hydrolysis of lignocelluloses using concentrated acids achieves near-theoretical sugar yields with fewer degradation products (Miller and Hester 2007; Schell and Duff 1996). The major drawbacks of this process have been consumption of large quantities of concentrated acids, acid recovery constraints, high costs of neutralization, and gypsum disposal problems (Hester and Farina 2000; Sakai 1965; Sherrard and Kressman 1945). However, the development of acid recovery technologies and the high flexibility of this process towards different feedstocks including solid wastes have revived interest in this process (Sheehan and Himmel 1999).

Concentrated sulfuric acid saccharification is a low-temperature high acid concentration process, which is carried out either in three stages (prehydrolysis, main hydrolysis/decrystallization, and posthydrolysis) (Sakai 1965) or in two stages (decrystallization and posthydrolysis) (Bayat-makooi *et al*. 1985; Liao *et al*. 2006). In both cases, decrystallization is an important stage because during the decrystallization stage concentrated acid disrupts the inter- and intra-molecular hydrogen bonding responsible for cellulose crystallinity and renders it amorphous and easily hydrolysable under fairly mild conditions with formation of low levels of degradation products (Wright and Power 1985; Xiang *et al*. 2003). Proper control and management of reaction conditions is important to achieve an effective decrystallization and eventually higher sugar yields (Hon and Shirashi 1991; Sherrard and Harris 1932).

In a previous paper (Janga *et al*. 2012), the individual and synergistic effects of the major operating variables (reaction temperature, acid concentration, and residence time) in the decrystallization stage, and their influence on the sugar recovery and subsequent sugar degradation was investigated systematically. This was accomplished by employing statistical modeling with design of experiment (DOE) to correlate the effect of decrystallization reaction conditions (independent variables) on sugar yields (dependent variables or responses) in a two-stage concentrated sulfuric acid hydrolysis of softwood (Scots pine) and hardwood (aspen).

The DOE modeling approach showed good correlation between obtained data and the simple quadratic models employed. However, combining the effect of time, temperature, and acid concentration into one single parameter, a “severity factor”, would facilitate easy characterization of the extent of reaction. While the severity factor approach previously has been applied for other reaction systems such as autohydrolysis, dilute acid hydrolysis, and delignification kinetics (Abatzoglou *et al*. 1992; Garrote *et al*. 2002; Martínez *et al*. 1997; Montané *et al*. 1993, 1994, 1998), it has not, to the authors’ knowledge, been applied to the concentrated acid hydrolysis process. The scope of this work has thus been to investigate the applicability of the severity factor concept to the concentrated acid hydrolysis process.

THEORY

The generalized severity parameter (R_{OH}), developed by Abatzoglou *et al*. (1992) for first-order depolymerization and solubilization reaction kinetics of lignocellulosic biomass polymers like cellulose and hemicelluloses, is given in Equation 1.

$$R_{OH} = \int_0^t \exp\left(\frac{C - C_{ref}}{\lambda C_{ref}}\right) \exp\left(\frac{T - T_{ref}}{\omega}\right) dt \qquad (1)$$

For an isothermal reaction, R_{OH} in equation 1 becomes,

$$R_{OH} = \exp\left(\frac{C - C_{ref}}{\lambda C_{ref}}\right) \times \exp\left(\frac{T - T_{ref}}{\omega}\right) \times t \qquad (2)$$

where C and C_{ref} are the acid concentration and the reference acid concentration in mol/L or % w/w, T and T_{ref} are the temperature and the reference temperature in K, λ is a parameter expressing the acid effect in the conversion, ω expresses the temperature influence in the conversion and is related to the average activation energy, and t is the reaction time in minutes (Chum *et al*. 1990). The reference conditions (C_{ref} and T_{ref}) have been reported to have an insignificant influence on the severity analysis and the fitted optimal values of the model parameters (Montané *et al*. 1994) and can therefore be chosen at the middle of the data sets.

When fitting the parameters of the generalized severity parameter R_{OH}, it is necessary to choose an appropriate function for the behavior of yield with respect to treatment severity. For hemicellulose solubilization, a simple exponential function has been used (Montané *et al*. 1994); however this function is not particularly suitable for analyzing final yields in a system where the product undergoes significant degradation leading to yield loss, as is the case for acid hydrolysis of polysaccharides. Assuming that the system consists of at least two consecutive reactions (biomass decrystallization/hydrolysis followed by acid-catalyzed degradation of the sugars to various degradation products), the general shape of the yield-R_{OH} function f should be an increase to a maximum, followed by a decrease towards zero yield. A second-order polynomial in R_{OH} can therefore be used to semi-quantitatively describe the behaviour of yield (Y) with respect to severity:

$$Y = a + b \cdot R_{OH} + c \cdot {R_{OH}}^2 \qquad (3)$$

The R_{OH} parameter in Equation 2 is the reaction ordinate used as the severity index for decrystallization and hydrolysis since it is a function of the main operating variables time, temperature, and acid concentration. The severity factor for concentrated sulfuric acid decrystallization and hydrolysis, CSF_{CSA}, was defined as the logarithm of the R_{OH} parameter:

$$CSF_{CA} = \ln\left(R_{OH}\right) \qquad (4)$$

EXPERIMENTAL

Raw Materials (Substrates)

The raw materials were dry wood chips from trembling aspen (*Populus tremula*) and Scots pine (*Pinus sylvestris*) of Nordic provenance. The chips were milled in a hammer mill and screened, and the fraction between 3 mm and 7 mm was retained. Size distributions obtained by analytical screening of the 3 mm to 7 mm fractions are given by Janga *et al*. (2012).

Chemical composition was analyzed as described by Janga *et al*. (2012), and the analysis results are given in Table 1. Further details about the raw materials are given by Janga (2011).

From the raw material composition data, and accounting for the addition of one mole of water added per mole of monosaccharide liberated during hydrolysis, the maximum theoretical yields of glucose were 48.4 and 50.6 g/100 g o.d. wood for pine and aspen, respectively.

Table 1. Composition of Scots Pine and Aspen Feedstocks (g per 100 g o.d. wood)

	Pine		Aspen	
	Values	Totals	Values	Totals
Glucan	43.6		45.6	
Mannan	11.3		1.8	
Galactan	1.5		1.7	
Hexosans		*56.4*		*49.1*
Xylan	6.4		17.9	
Arabinan	0.9		0.5	
Pentosans		*7.3*		*18.4*
(Carbohydrate polymers)		*(63.7)*		*(67.5)*
Acid insoluble lignin	26.1		18.6	
Acid soluble lignin	0.3		0.6	
Total lignin		*26.4*		*19.2*
Extractives	2.3		3.1	
Ash	0.5		0.5	
Low molecular mass compounds		*2.8*		*3.6*
Unaccounted*	7.1	7.1	9.7	9.7
Total	100.0	100.0	100.0	100.0

* Based on literature data, most of the material unaccounted for is believed to be uronic acids and acetyl content in hemicelluloses.

Table 2. Initial Experimental Design for the Decrystallization Stage, Coded and Actual Factor Levels

Variables	Coded levels		
	Low -1	Middle 0	High 1
Temperature, θ (^{o}C)	35	52.5	70
Reaction time, T (min)	60	120	180
Acid concentration, C (wt. %)	65	72.5	80

Experimental Design

Yield data were taken from a previous study (Janga *et al*. 2012), where a response surface methodology (RSM) technique was used to investigate the effects of the three independent variables (temperature, acid concentration, and time) on sugar yields and degradation (dependent/response variables) during decrystallization. The two levels/ three factors CCF experimental design consisted of 17 ($2^k + 2k + n_c$) experiments with 8 runs at the corner or cube points (2^k), 6 axial points ($2k$), and 3 repeats at the center point (n_c), where k is the number of factors. The DOE design is described in more detail by Janga *et al*. (2012)

The upper and lower limits of the conditions used in the CCF study (Table 2) were chosen based on information in the literature (Bayat-makooi *et al*. 1985; Camacho *et al*. 1996; Goldstein 1980; Harris 1949; Hon and Shirashi 1991; Sherrard and Kressman 1945; Xiang *et al*. 2003). Additional experiments were selected and added to cover a large range of temperatures up to 20 °C outside the original design matrix, increasing the total number of datapoints to 27 for each of the two raw materials.

Validation Experiments

For a tentative validation of the obtained severity factor model, 12 additional datapoints were obtained for each of the raw materials, using a simple OVAT (one variable at the time) approach. Five datapoints for each raw material were obtained by varying the acid concentration, while 7 were obtained by varying the decrystallization temperature.

Table 3. Reaction Parameters for the Validation Experiments

	Reaction time T (min)	Temperature θ (^{o}C)	Acid concentration C (wt. %)
Pine, acid conc.	60	35	{66, 68, 72.5, 75, 79}
Pine, temperature	60	{22, 27, 38, 48, 58, 66, 75}	72
Aspen, acid conc.	60	35	{66, 68, 72.5, 75, 79}
Aspen, temperature	60	{22, 27, 38, 48, 58, 66, 75}	67

Saccharification

The saccharification was performed in two stages, the decrystallization stage and the hydrolysis stage.

Decrystallization

In the decrystallization stage, 3.0 g oven dry weight (o.d.w) of pre-steamed wood chips was mixed with deionized water and 96 to 98 wt. % sulfuric acid (p.a. grade) to obtain the predetermined acid concentration at a liquid-to-wood ratio of 15 (w/w). The mixture was put in a shaking water bath (Stuart Scientific SBS 30) preset at the required reaction temperature and a shaking speed of 200 rev/min.

Hydrolysis

The secondary hydrolysis was standardized at the same reaction conditions for all samples. After decrystallization, the suspension was diluted with deionized water to an acid concentration of 20 wt. % and hydrolyzed at 100 ^{o}C for 3 hours in an autoclave (Certoclav, CV-EL 12 L GS) before cooling in an ice bath and vacuum filtration to separate the solid lignin from the acid/sugar solution. The acid/sugar solution was neutralized with solid calcium hydroxide (p.a. grade) to a pH between 5.0 and 6.0, and the solution was again filtered to separate $CaSO_4$ from a yellowish sugar solution. The sugar solution was stored in a refrigerator at 4 °C before monosaccharide and degradation products analysis by HPLC. Further details on the saccharification procedure are given by Janga (2011).

Hydrolysate analysis

Chemical composition of the hydrolyzates was determined by HPLC (Janga *et al.* 2012). All hydrolyzate samples were filtered through a 0.2 μm filter before injection into the HPLC.

For monosaccharide analysis, a Chrompack Carbohydrates Pb column (Varian, Palo Alto, CA, USA) was used with deionized and degassed water as mobile phase and RI detection. Column temperature was 80 °C, and the flow rate was 0.4 mL/min. The analytical column was in line with a cation (H^+)/anion (CO_3^-) deashing guard column (Biorad 125-0118). Mannitol was used as an internal standard in the sugar analyses.

Integration of the chromatograms was performed as described by Janga *et al.* (2012). Sugar yields were calculated as grams of sugar per 100 g o.d. wood. For sugar degradation products analysis an Aminex HPX-87H column (Bio-Rad, Hercules, CA, USA) was used in line with a Cation-H guard column (Biorad 125-0129) and UV absorbance detection. 5-hydroxymethylfurfural (HMF), furfural, and levulinic acid were all detected at 280 nm. The mobile phase was 5 mM sulfuric acid, flow rate was 0.6 mL/min, and column temperature was 65 ^{o}C. Further details on the hydrolysate analyses are given by Janga (2011).

Estimation of Parameters of the Generalized Severity Model for Concentrated Sulfuric Acid, CSF_{CSA}

The yield of monosaccharides from the wood cellulose and hemicelluloses expressed as grams of sugar per 100 grams of oven dry wood (g/100 g o.d. wood) was correlated to the treatment severity during the decrystallization stage. The theoretical maximum hexose yield was 1.11 times the hexosan content, and the theoretical maximum pentose yield was 1.14 times the pentosan content due to the addition of water during hydrolysis.

The yield versus severity factor plots were fitted to a second order polynomial (Equation 5) in a double iteration procedure. The parameters λ and ω in Equation 2 were iterated in an inner loop to obtain an estimated value for the severity factor at each set of conditions before the goodness of fit to a quadratic equation was determined for each set of (λ, ω) values in an outer loop using the non-linear regression function nlinfit in MATLAB®. Thus, the fitting of the quadratic model only served the purpose of investigating how well the yield versus severity factor plot conformed to a general increase to maximum followed by decrease to zero type behaviour. Reference conditions (C_{ref} and T_{ref}) were chosen at the middle of the data set (C_{ref} = 11.9 mol/L, T_{ref} = 315.7K)

RESULTS AND DISCUSSION

As all data have been obtained using a single, standardized secondary hydrolysis stage, the severity parameter analysis performed in this work can only consider changes in reaction conditions during the primary decrystallization stage. Further work will be needed to include secondary hydrolysis conditions in the severity parameter for the concentrated acid hydrolysis process.

Parameters of the Generalized Severity Model for Concentrated Acid, CSF_{CSA}

The optimization curve for the yield of glucose from pine, which compares experimental values to those predicted from the quadratic model as a function of the reaction ordinate, shows the expected yield increase to a maximum followed by a decline towards zero as treatment severity increases (Fig. 1).

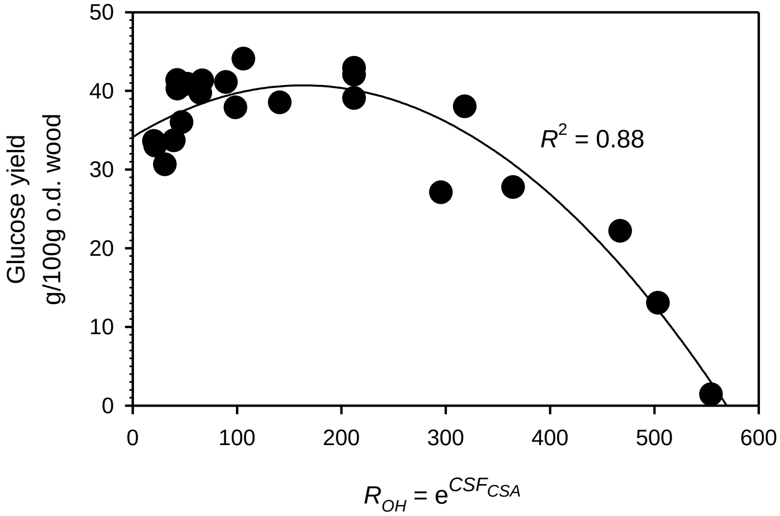

Fig. 1. Glucose yield from pine as a function of the generalized severity parameter (λ= 0.21; ω = 20.26). ●: Datapoints; ———: Model ($Y = a + b \cdot R_{OH} + c \cdot R_{OH}^2$)

The non-linear least squares optimized regression parameters (λ and ω) of R_{OH} in Eq. 2 for monosaccharide yields from cellulose and hemicelluloses in aspen and pine are shown in Table 4. It can be seen that the squared correlation coefficient (R^2) for monosaccharide yields for both aspen and pine was 0.85 or larger, indicating that the fitting of experimental data to the model was adequate, and the residual deviation was of a similar magnitude as the experimental accuracy.

There was a significant variability of the pseudo-kinetic parameters λ and ω, as shown in Table 4 for the two data sets from hardwood (aspen) and softwood (pine). The differences in λ between aspen and pine could be attributed to structural differences between the two wood species, influencing the accessibility of acid to the cell wall components. Such discrepancies in λ have been observed for pentosans from different hardwoods that are structurally considered to resemble each other (Abatzoglou *et al*. 1992; Montané *et al*. 1998). The parameter ω is associated with the activation energy of the reacting system during hydrolysis and hence the temperature effect in the biomass conversion; thus it is linked to the glycosidic bond strength of the reacting polymers (Abatzoglou *et al*. 1992). Being associated with the glycosidic bond cleavage, the ω values for the depolymerization of hexosans or pentosans in a concentrated acid hydrolysis reaction should be expected to be similar.

Table 4. Pseudo-Kinetic Parameters of the Severity Model for the Concentrated Sulfuric Acid Process, and the Coefficient of Determination for the Quadratic Fit of Yield versus Reaction Severity

		Glucose		Xylose		Mannose	
		Pine	Aspen	Pine	Aspen	Pine	Aspen
Individual parameters	λ	0.21	0.12	0.31	0.16	0.15	0.15
	ω	20.26	15.82	15.40	22.52	14.34	33.45
	R^2	0.88	0.84	0.85	0.88	0.92	0.85
Averaged parameters	λ	0.183					
	ω	20.3					
	R^2	0.85	0.82	0.77	0.87	0.92	0.73

However, given experimental error and the inherent variability in the data, the basis for drawing conclusions from the variability in the values for λ and ω is limited. Also, the universality of a severity parameter is limited if the parameter requires one set of values for λ and ω for each raw material and for each reaction product. The arithmetic averages of the pseudo-kinetic parameters (λ = 0.183, ω = 20.3) were therefore chosen for further evaluation of the applicability of the severity factor concept to the concentrated acid hydrolysis process.

As can be seen from Table 4, there were rather minor changes in the degree of fit for the most abundant monosaccharides (glucose and mannose from pine, and glucose and xylose from aspen), whether unique values were assigned to the different reaction products and raw materials, or whether an average of the pseudo-kinetic parameters was used.

Sugar Yields and Decrystallization Severity

The yield of glucose as a function of decrystallization severity is shown in Fig. 2. It can be seen from Fig. 2 that the glucose yield reached a maximum at a severity factor of approximately 5 for pine, while for aspen the maximum glucose yield appeared at a severity factor between 4 and 4.5. The difference in severity requirements illustrates the higher recalcitrance of softwoods as compared to hardwoods. Overend and Chornet (1987) have previously pointed out that softwoods are less easily treated as compared to hardwoods, and in the dilute acid process softwoods usually need a combined chemical such as SO_2 or H_2SO_4 and steam-aqueous treatment for fractionation.

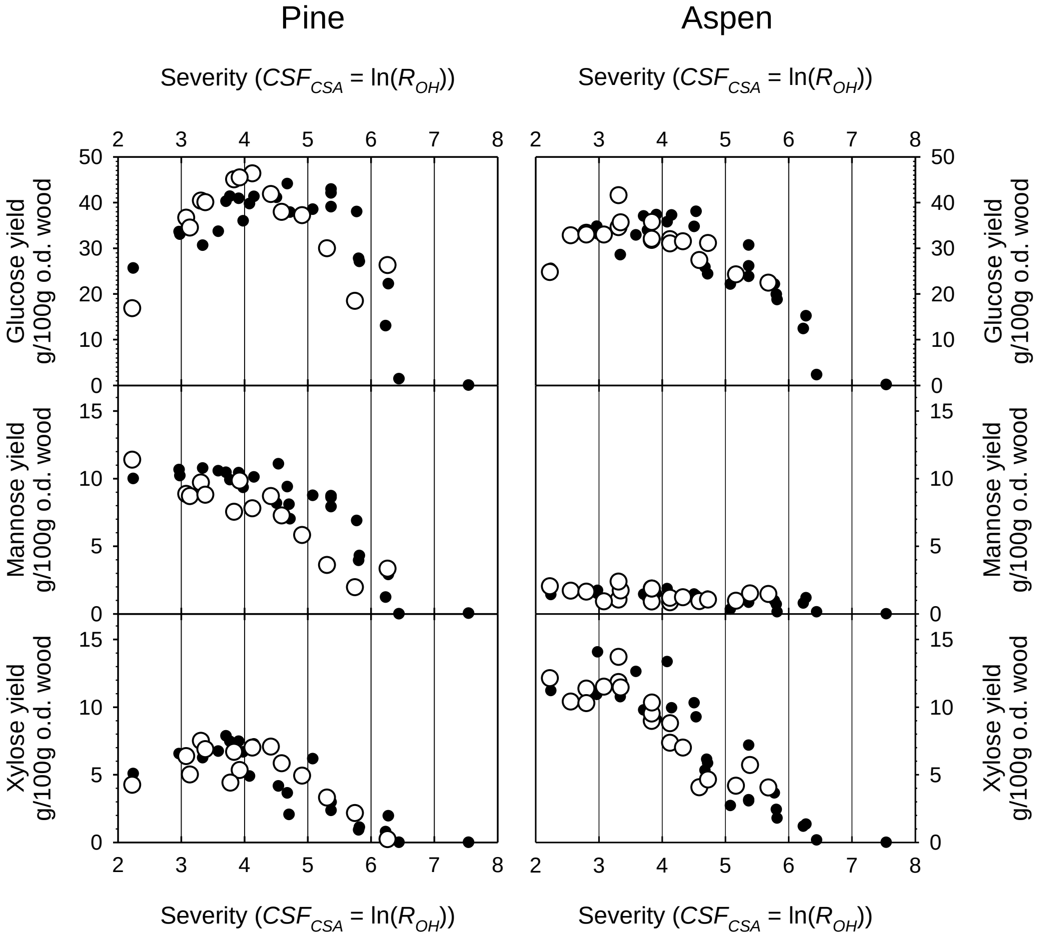

Fig. 2. Effect of decrystallization severity (λ = 0.183; ω = 20.3) on carbohydrate yields from pine (left) and aspen (right). ●: Initial datapoints used for fitting the severity factor parameters; ○: Validation datapoints

The maximum yield of hemicellulose sugars was obtained at lower severities than the maximum yield of glucose (CSF_{CSA} below 4 for mannose and xylose from pine, and CSF_{CSA} below 3 for mannose and xylose from aspen), which agrees with the literature, where hemicellulose sugar yields also have shown maxima at lower severities than glucose yields from cellulose (Liu *et al*. 2009, Montané *et al*. 1993; Overend and Chornet 1987).

As with the severity demand for maximum glucose yield, it can be seen that pine showed a higher severity demand for maximum hemicellulose sugars yield than aspen. This may be attributed to the dominance of a stable glucomannan backbone in softwood hemicelluloses as compared to the glucuronoxylan or xylan backbone in hardwood hemicelluloses (Niemzl *et al*. 2010). The presence of larger amounts of condensed lignin in softwoods, which hinders the swelling of cell wall during hydrolysis (Phaiboonsilpa *et al*. 2009), could also be a possible reason for this difference.

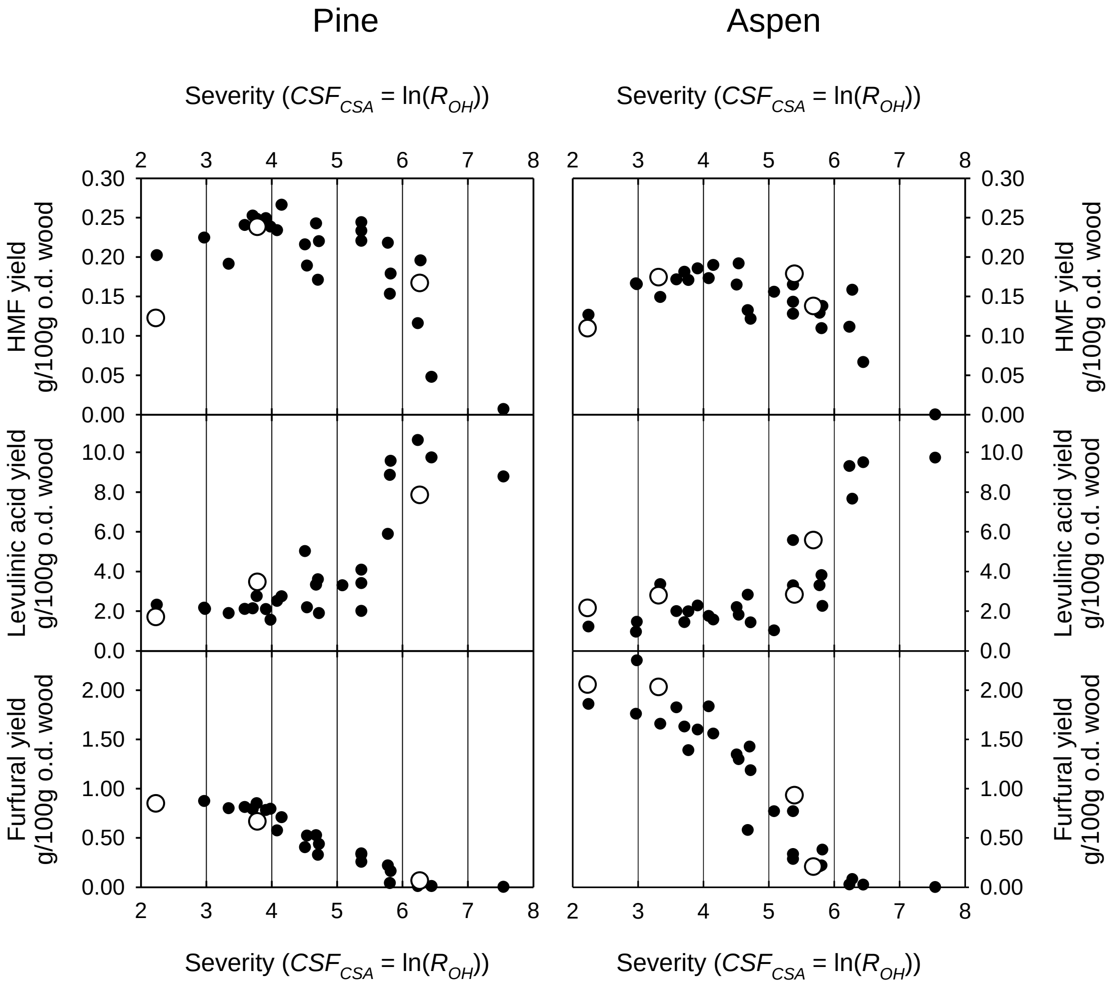

Fig. 3. Effect of decrystallization severity (λ = 0.183; ω = 20.3) on degradation products yields from pine (left) and aspen (right). ●: Initial datapoints used for fitting the severity factor parameters; ○: Validation datapoints

The observed behavior is a strong indication that the severity factor approach to the analysis of the concentrated acid hydrolysis process can be valid for the evaluation and prediction of monosaccharide yields.

Degradation Products (Inhibitors) Yields and Decrystallization Severity

The primary degradation products formed during acid treatment are 5-hydroxymethyl furfural (HMF) formed from hexoses and furfural formed from pentoses. Further degradation of the primary inhibitors gives levulinic acid from HMF and formic acid from both furfural and HMF.

As can be seen from Fig. 3, the yield behavior of HMF and furfural follow the yield behavior of glucose and xylose, respectively, rather closely. The yield of levulinic acid is fairly low at low severities, and increases markedly at severities above approximately 5.5, when the yields of primary degradation products decrease. This is in accordance with the behavior one should expect given the nature of the degradation reactions. It therefore seems that severity factor approach to the analysis of the concentrated acid hydrolysis process can be valid also for the formation of sugar degradation products.

CONCLUSIONS

1. The generalized severity parameter (R_{OH}) and its logarithmic transformation CSF_{CSA} are potentially useful tools for analyzing the extent of the reaction in concentrated acid hydrolysis and can simplify prediction of sugar yields based on the reaction conditions.
2. The trends indicated by the yield-severity factor plots correspond with trends generally acknowledged in the literature, indicating that the severity factor concept is applicable to the concentrated hydrolysis process for manufacture of monosaccharides from lignocellulosic biomass.
3. At the present stage, the severity factor for concentrated acid hydrolysis depends on a single, defined set of reaction conditions during secondary hydrolysis, and further work is needed to incorporate secondary hydrolysis conditions in the severity factor for concentrated sulfuric acid hydrolysis.
4. More experimental data is still needed to incorporate several types of biomass feedstocks, a wider range of decrystallization conditions, variations in secondary hydrolysis conditions, and different mineral acids employed in the concentrated acid hydrolysis process to make the pseudo-kinetic parameters values more universal. However, the fairly good fit obtained for two different feedstocks using one single parameter set for the severity factor is an indication of the applicability of the severity factor also to this reaction system.

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