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Performance evaluation of a recycle-integrated process for the production and purification of monosaccharides from lignocellulosic biomass

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ABSTRACT

Performance of a recycle-integrated process for producing monosaccharides from lignocellulosic biomass was investigated. The process combined continuous concentrated sulfuric acid hydrolysis of hemicellulose extract in a plug-flow reactor with single-column batchwise chromatographic fractionation of the resulting hydrolysates via sulfuric acid recycling. A pseudo-first order model with rate constants depending on proton and bisulfate concentrations was derived and successfully used to describe the hydrolysis kinetics. Sulfuric acid concentration was found to affect the process significantly. At a constant level of monosaccharide production rate, the hydrolysis reactor volume was found to decrease by 90% and the separation column volume increase by 76–130%, depending on the amount of monosaccharides in the feed, when sulfuric acid concentration was increased from 0.5 to 2.5 mol/L. However, at the same time, the difference between the equipment volumes decreased. The maximum monosaccharide productivity in the chromatographic separation decreased by 40%, and eluent consumption at the operating points giving these maxima increased by 33%, when the sulfuric acid concentration was increased from 0.5 to 2.5 mol/L. On the basis of the results, the studied process should be operated with 1.0–1.5 mol/L sulfuric acid.

1. Introduction

Monosaccharides are valuable platform chemicals that can be converted into a wide variety of products either by bio- or thermochemical means [1–3]. These products include alcohols (e.g., ethanol, butanol), carboxylic acids (e.g., succinic acid, lactic acid, levulinic acid), amino acids, aldehydes, ketones, esters, ethers, polymers, alkanes, alkenes (e.g., isobutene), and furans (e.g., furfural, hydroxymethyl furfural) [2,4–8].

Cellulose and hemicelluloses in lignocellulosic biomasses are potential raw materials for monosaccharide production [9–11]. In forest biorefineries that integrate the production of chemicals, heat, and energy with traditional pulp production from lignocellulose, only cellulose is utilized for pulp and paper making. Thus, the hemicelluloses can be used, for example, in the production of monosaccharides [12].

Hemicelluloses are separated from wood chips with pressurized hot water extraction prior to the pulping process [13]. This is a well-known technique. In the case of lignocellulose, the extraction is carried out in relatively mild conditions in order to prevent the degradation of cellulose fibers [14,15]. The resulting extracts contain, in addition to hemicelluloses, lignin, extractives, and organic acids [16,17]. These are valuable products, but also affect the processing of the hemicelluloses. Thus, purification of the hemicelluloses is required. This can be accomplished by ultrafiltration [12]. Sainio et al. [12] investigated the separation of hemicelluloses from hot water extracts with a two-step ultrafiltration process. First, hemicelluloses were separated from lignin based compounds with a loose ultrafiltration membrane (cut-off 30 kg/mol) with 80% yield. Then, a tighter ultrafiltration membrane (cut-off 5 kg/mol) was used to separate the hemicelluloses from smaller compounds in the extract with 50% yield [12].

Efficient production of monosaccharides from the purified hemicelluloses can be accomplished via hydrolysis with concentrated sulfuric acid [12]. On the contrary to the hydrolysis of solid lignocellulosic biomasses [18,19], the hydrolysis of hemicelluloses rich extracts can be accomplished in a single step with complete conversion [12]. Only small amount of by-products (acetic acid, furfural, hydroxymethyl furfural (HMF)) are generated during the concentrated acid hydrolysis [9,11,18,19]. Acetic acid is the most significant byproduct. Its formation in the hydrolysis results from the unavoidable cleavage of the acetyl groups in the hemicellulose molecules [12,19]. On the other hand, the formation of furfural and

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Nomenclature

A_{col}	column cross-sectional area (m^2)
C	liquid phase concentration (mol/L)
C_{A0}	initial concentration of A (mol/L)
C_{Acetyl}	concentration of acetyl groups in the hemicelluloses (mol/L)
C_{AcOH}	acetic acid concentration (mol/L)
C_H	hemicellulose concentration (mol/L and g/L)
C_{H^+}	proton concentration (mol/L)
$C_{HSO_4^-}$	bisulfate concentration (mol/L)
C_m^{feed}	monosaccharide concentration in the feed stream to the column (mol/L)
C_i^{in}	concentration of i at the column inlet (mol/L)
D_{ax}	axial dispersion coefficient (m^2/s)
D_i^P	diffusion coefficient (m^2/s)
d_{col}	column diameter (m)
d_p	particle diameter (m)
E_a	activation energy (J/mol)
EC	eluent consumption (L/mol)
ΔH_S	temperature dependence factor (kJ/mol)
h_{bed}	column height (m)
K_2	second dissociation constant of H_2SO_4 (–)
K_S	promoting factor for species containing sulfur (L/mol)
k_H	rate constant of hemicellulose hydrolysis reaction (1/min)
k_{H^+}	acid factor in rate constant of hemicellulose hydrolysis reaction (L/(mol min))
k_{H_2O}	solvent factor in rate constant of hemicellulose hydrolysis reaction (1/min)
k_D	rate constant of monosaccharide degradation reaction (1/min)
$k_{m,i}$	intraparticle mass transfer coefficient (1/s)
L	flow path length (m)
n_m	mole amount of monosaccharides (mol)
$n_{H_2SO_4}$	mole amount of sulfuric acid (mol)
n_i^{out}	mole amount of i in the target fraction (mol)
PR_m	production rate of monosaccharides (mol/h)
Pr_m	productivity with respect to monosaccharides (mol/(m^3(resin) h))
Δp	pressure drop (bar or Pa)
q	solid phase concentration (mol/L)
q_i^*	solid phase concentration of *i* at equilibrium with liquid phase concentration C_i (mol/L)
$\bar{q}_i$	average solid phase concentration of *i* (mol/L)
R	gas constant (J/(mol K))
r_{AcOH}	formation rate of acetic acid (mol/(L min))
r_m	formation rate of monosaccharides (mol/(L min))
T	temperature (K)
T_{mean}	reference temperature (K)
t	time coordinate (s)
t_{cycle}	cycle time (min or h)
V_{bed}	resin bed volume (m^3)
V_{feed}	volume of feed pulse (m^3)
V_R	reactor volume (m^3)
$\dot{V}_{col}$	eluent flow rate (BV (bed volumes)/h)
$\dot{V}_R$	volumetric flow rate in hydrolysis (plug flow) reactor
VRF	volume reduction factor (–)
v	superficial velocity (m/s)
X_A	conversion of A (–)
X_H	hemicellulose conversion in concentrated acid hydrolysis (–)
Y_i	recovery yield of *i* (–)
z	spatial coordinate (m)

Greek letters

α	constant
β	constant
ε	local bed porosity (–)
θ	extent of resin shrinking (–)
κ	isotherm constant
μ	dynamic viscosity of the fluid (kg/(m s) (=Pa s))
ρ	density of the fluid (kg/m^3)
τ	space–time (min)
Φ_S	sphericity factor of solid particles (–)
ψ_p	volume fraction of polymer (–)

Subscripts and superscripts

i	initial
f	final
m	monosaccharides
ref	reference state
θ	resin shrinking

HMF is very slow in the conditions of the concentrated acid hydrolysis ($T < 100$ °C, $p = 1$ atm). For example, according to Sainio et al. [12], after complete conversion of hemicelluloses with 21 wt.% sulfuric acid at 80 °C temperature, the concentrations of furfural and HMF (in [g/L]) were approximately only 1% and 0.2%, respectively, of that of the monosaccharides.

Prior to the utilization of the monosaccharides obtained in concentrated acid hydrolysis, separation of the monosaccharides from sulfuric acid and the by-products (acetic acid) should be carried out. This can be accomplished with electrolyte exclusion chromatography with gel type strong acid PS–DVB cation exchange resins in acid (H^+) form [20–27]. The chromatographic separation enables the recovery of sulfuric acid in such a way that it can be reused in the hydrolysis, thus minimizing the acid consumption in the hydrolysis. Over 95% of sulfuric acid needed in the hydrolysis can be recycled via both batchwise [23] and continuous chromatographic separation processes [25,26]. In addition, monosaccharide and acetic acid fractions with high purity are obtained [23,25,26].

The performance of the chromatographic separation unit in fractionation of concentrated acid hydrolysates of lignocellulose has been investigated in detail prior to this study [23–27]. However, investigation of the sole separation unit in cases in which one or more product streams are recycled to the preceding process steps gives a conservative impression of the separation performance. The process steps coupled with the separation unit should be taken into account in order to obtain a more realistic picture of the performance. This is also the case with the chromatographic fractionation of acidic hydrolysates. Here, a recycle-integrated process connecting concentrated acid hydrolysis of hemicellulose extract with chromatographic fractionation of the resulting hydrolysates via sulfuric acid recycle stream is investigated numerically. The aim of this study is to produce novel information regarding the effect of sulfuric acid concentration on the hydrolysis kinetics and separation performance, and on the required equipment volumes (hydrolysis reactor and separation column). The effect of the sulfuric acid concentration on the performance of the studied process has not been investigated prior to this work. A continuous plug flow reactor (PFR) is used for the hydrolysis. The hydrolysis kinetics in the PFR are modeled using a pseudo-first order rate model. Although the fractionation of the hydrolysates resulting from the