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Steady-state recycling chromatography in the purification of weakly acidic lignocellulosic hydrolysates

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ABSTRACT

Purification of monosaccharides from lignocellulosic hydrolysates using mixed recycle steady-state recycling chromatography (SSR) was studied experimentally on a pilot scale and via simulations. A hydrophilic, weak cation exchange resin was used as separation material, enabling the removal of lignin, formic acid, acetic acid, hydroxymethyl furfural, and furfural in a single step. Lignin concentration had only a minor effect on separation efficiency. The exchange of the Na^+ ions of the resin with Ca^{2+} ions from the hydrolysates was found to decrease separation efficiency. The full recovery of separation efficiency could be obtained via a natrium citrate treatment of the resin. Very strong sorption of some lignin molecules led to coloring of the resin but did not affect separation efficiency. Simulations showed that depending on the monosaccharide concentration of the hydrolysates, the SSR mode yielded 13–20% higher monosaccharide productivity than the batch mode. The experimental investigation of the fractionation on a pilot scale revealed that viscous fingering due to a highly concentrated feed ($\geq$360 g/L) lowered the separation efficiency in single-column batch mode but not in SSR mode. Thus, in practice, SSR is even more efficient than the batch process than was suggested by the simulations.

1. Introduction

While chromatographic separation offers a means of achieving high product purities and yields in many systems, the single-column batch mode often has comparatively low productivity. In binary fractionations, the separation efficiency can be enhanced with more advanced process schemes, such as a simulated moving bed (SMB) process (e.g., [1–3]) or mixed recycle steady-state recycling chromatography (SSR) [4–7]. Of these, SSR is an attractive process option because it can be built easily via small modifications to an existing single-column batch unit. However, it is still a fairly uncommon process as compared to SMB.

In SSR, the unresolved parts of the component profiles are recycled from the column outlet to the column inlet (recycle fraction). This results in high product purities for both product fractions. The resulting recycle fraction is mixed with fresh feed prior to feeding into the column. The process is operated in a cyclic manner because feeding is conducted at fixed intervals, similar to the batch process. However, due to the recycling, the feed concentrations change from cycle to cycle until a cyclic steady-state is reached.

Moreover, SSR has been shown to be superior to the batch process with respect to productivity and eluent consumption [4–7], even in very difficult separation tasks with challenging solute–solute interactions [8]. It has also been shown that the performance advantage of SSR over the batch process increases with increasing dispersion [5]. In addition, according to simulations [9], SSR can be even as efficient as a four-zone SMB with a 1:1:1:1 column configuration.

Monosaccharides are valuable platform chemicals. They can be produced from lignocellulosic biomasses via hydrolysis with acid or enzyme catalysts. These lignocellulose-based monosaccharides must be purified prior to downstream processing. The purification steps depend on the hydrolysis method used. In the case of dilute acid and enzymatic hydrolysis, lignin and hydrolysis by-products must be separated from the monosaccharides [10–12]. In the case of concentrated acid hydrolysis, the acid catalyst, typically H_2SO_4, must be removed [8,13,14].

The removal of lignin from aqueous solutions, such as lignocellulosic hydrolysates, can be performed with a number of methods, including ionic liquids [15,16], membrane filtration [17–19], and adsorption [20–28]. The removal of lignin via adsorption on activated carbon and polymeric adsorbents has been investigated thoroughly [20–28]. Polymeric adsorbents are a more attractive option for this separation task than activated carbon due to their significantly easier desorption of adsorbed lignin. Recently, an adsorption-based method for the removal of lignin from (weakly acidic) lignocellulosic

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Nomenclature

C_i	liquid phase concentration, g/L
D_i^P	diffusion coefficient, m^2/s
EC_m	eluent (water) consumption for the production of 1 kg of monosaccharides, L/kg
F	objective function, –
Pr_m	productivity with respect to monosaccharides, kg/(m^3(bed) h)
Q	Flowrate, mL/min or BV/h
q_i	solid phase concentration, g/L
V_{bed}	resin bed volume, mL or L
V^F	column loading, BV
X_i	undefined fractionation constraint, %
x	weight fraction, wt.%
Y_i	recovery yield of i, %

Greek letters

α_i	isotherm parameter, –
β_i	isotherm parameter, –
δ_i	isotherm parameter, –
φ_i	isotherm parameter, –

Subscripts and superscripts

target	target value

hydrolysates was presented by Heinonen et al. [28]. Eighty percent of lignin could be separated from the hydrolysates, with a 95% monosaccharide yield, using the polystyrene-based XAD-16 N adsorbent. However, other impurities in the hydrolysates (formic acid, acetic acid, hydroxymethylfurfural HMF, and furfural) could not be removed by adsorption. Thus, an additional separation step for the further purification of the monosaccharides is required. In addition, the desorption of lignin from the adsorbent requires the use of 50 wt.% aqueous ethanol solution, which increases the processing costs [28].

Here, an efficient monosaccharide purification method based on steady-state recycling chromatography is proposed. With this method, lignin and all other impurities can be removed from lignocellulosic hydrolysates in a single step without additional chemicals (e.g., ethanol). The use of chromatography for the purification of hydrolysate-based monosaccharides has not been studied in academia prior to this work, although such a method for the purification of xylose from spent sulphite pulping liquors has been patented [29–31]. A hydrophilic gel-type weak cation exchange resin in Na^+ form is used as the separation material.

Although the use of SSR for the fractionation of lignocellulosic hydrolysates has been investigated previously, the separation task here is completely different from that discussed, e.g., in [8]. Here, the task is not to separate monosaccharides from sulfuric acid, as in [8], but to separate the monosaccharides from lignin, organic acids, and furans. In addition, the separation material used here is not hydrophobic strong cation exchange resin in H^+ form, as was used in [8].

The use of SSR is studied both experimentally and via simulations, and a comparison with the batch mode is carried out. A pilot-scale SSR unit is utilized in the experiments. The effects of hydrolysate composition and resin fouling on separation efficiency are investigated. In addition, an efficient method of resin regeneration is presented.

2. Experimental methods

2.1. Chemicals and separation materials

Ultrapure water produced with a CENTRA R 60/120 (ELGA LabWater) water purification system was used in all experiments and in the preparation of all solutions. Analysis-grade sodium hydroxide (≥99.0%, pellets for analysis, Merck KGaA) was used in the experiments. Blue dextran 2000 (GE Healthcare) was used in the resin bed porosity measurements.

The gel-type acrylate-based weak acid cation exchange resin CA16GC (Acrylate–DVB matrix; 8.0 wt.% DVB; d_p = 300 µm) in Na^+ form (Finex Oy/Johnson Matthey) was used as a separation material.

2.2. Lignocellulosic hydrolysates

Three slightly acidic authentic hydrolysates of lignocellulose with different compositions were used as feed solutions in the separation experiments (Table 1). The weak cation exchange resin was used in Na^+ form. It is a well-known fact that such resins are highly selective towards H^+ ions. To avoid the exchange of the ionic form of the resin during the experiments with H^+, the pH of the hydrolysates was increased to 6 with 50 wt.% NaOH solution. After pH adjustment, the hydrolysates were filtered using a cord filter to remove precipitates.

2.3. Chromatographic separation

Chromatographic separation experiments were carried out on laboratory and pilot scales at 50 °C with purified water as an eluent. Batchwise laboratory-scale experiments were performed to obtain data for modelling purposes. Duplicate experiments were carried out to address the reproducibility of the experiments. However due to similar

Table 1
Compositions of the hydrolysates used as the feed solution in this work. Determined after the pH adjustment.

	Hydrolysate 1		Hydrolysate 2		Hydrolysate 3	
	C, g/L	x, wt.%[b]	C, g/L	x, wt.%[b]	C, g/L	x, wt.%[b]
Lignin	18.2	3.90	31.6	8.07	8.8	2.42
Monosaccharides[a]	438.1	93.89	343.6	87.77	347	95.38
Formic acid	1.6	0.34	1.1	0.28	1	0.27
Acetic acid	7.8	1.67	13.6	3.47	6.4	1.76
Furfural	0.2	0.04	0.2	0.05	0.2	0.05
HMF	0.7	0.15	1.4	0.36	0.4	0.11
Ca^{2+}	0.4	–	0.9	–	0.2	–
Mg^{2+}	0.1	–	0.23	–	0.05	–
Cu^{2+}	$2.3{\cdot}10^{-4}$	–	$5.0{\cdot}10^{-4}$	–	$1.0{\cdot}10^{-4}$	–
Fe^{2+}	$1.0{\cdot}10^{-2}$	–	$2.6{\cdot}10^{-2}$	–	$3.3{\cdot}10^{-3}$	–

[a] All monosaccharides were treated as one pseudo-component.
[b] Based on the concentrations of the analyzed organic components.