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Size-exclusion chromatographic separation of hydroxy acids and sodium hydroxide in spent pulping liquor

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ABSTRACT

In this work, chromatographic recovery of hydroxy acids and cooking alkali (NaOH) from spent pulping liquor using size-exclusion chromatography (SEC) is investigated. Ultrafiltered black liquors from soda cooking of hardwood and softwood were used as feed and Sephadex G-10 as the stationary phase. Hydroxy acids were successfully separated from sodium hydroxide and the lignin content of the product fraction was reduced significantly. Fouling did not reduce the separation capability of the separation medium in extended runs with more than 40 consecutive injections. High column loadings, up to 25% of the bed volume, were found applicable for separation of authentic solutions without compromising the resolution. This was attributed to size-exclusion of individual ions which leads to co-operative sorption of NaOH in the presence of the sodium salts of hydroxy acids. The proposed mechanism was verified using data from experiments with model solutions.

1. Introduction

Black liquor is the spent cooking liquor of pulping. It contains the inorganic cooking chemicals used in pulping but also alkaline degradation products of lignin and wood carbohydrates. These degradation products include salts of hydroxy carboxylic acids [1–3], which could be widely utilised in the synthesis of various chemicals and polymeric materials [4–6]. However, separation of these hydroxy acids from the inorganics and lignin of black liquor is challenging. Various separation methods for recovering hydroxy acids and other valuable compounds from black liquor have been proposed, including precipitation [7,8], ultrafiltration [9–11], electrodialysis [12], distillation [13], cooling crystallization [9], and chromatography [14]. In this paper, the focus is on chromatographic separation.

Alén et al. utilised ion-exclusion chromatography for separating hydroxy acids from the inorganic compounds of black liquor [14]. This separation technique requires that black liquor is first neutralized [14]. If the feed contains NaOH, several problems are encountered. For example, use of a strong-acid cation exchange resin in Ca^{2+} form under alkaline conditions may lead to precipitation of calcium hydroxide inside the resin which is consequently converted to Na^{+} form. The same precipitation reaction may also occur for resins in other salt forms, as the solubility product of many metal hydroxides is low. As a consequence of hydroxide precipitation, pH of the liquid phase decreases leading to precipitation of lignin, which may cause blockage of the column.

In a recent paper, sodium salts of hydroxy acids were successfully separated from sodium hydroxide (NaOH) of soda black liquor using size-exclusion chromatography (SEC) as a part of a multistep separation process for recovering hydroxy acids from black liquor [15]. A well-established size-exclusion gel, Sephadex G-10 with an exclusion limit of 700 g/mol, was used as the separation medium. The acids were recovered as their sodium salts under alkaline conditions, which enables a straightforward recovery of the cooking chemicals and thus facilitates integration of the process to a pulp mill. However, the separation process based on SEC was not optimised. The target of the present work is to achieve better understanding on the separation mechanisms and on the long-term performance of the separation medium to facilitate the optimisation the process.

The main application area of SEC is protein purification [20]. The separation task in the recovery of hydroxy acids is similar to desalting of proteins, but the difference in molecular sizes of the components to be separated is smaller.

Davankov and coworkers [21–23] have shown that SEC is also applicable for separation of electrolytes with a minor difference in size. They found out that the separation selectivity is determined not only by the size but also by the concentration of ionic species, and observed self-concentration of the separated electrolytes. It is possible that similar phenomena are also present in the case of separating NaOH and sodium salts of hydroxy acids. A better understanding of the separation mechanism is needed for selection of optimal separation material and process parameters. Therefore, the separation mechanism in the separation of sodium salts of hydroxy acids from NaOH on a size-exclusion gel is investigated

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in the present work. In addition, the influence of column loading on process performance is discussed.

In addition to the recovery of hydroxy acids, also other biorefinery applications for SEC have been recently proposed, including fractionation of lignosulphonates [16], and recovery oligosaccharides from biomass hydrolysates [17,18] and from steam-treated wood [19]. However, the feasibility of size-exclusion gels in long-term use at the relatively harsh conditions of biorefinery is not well-established.

Black liquor contains various wood-derived compounds which may cause fouling of the separation medium and thus decrease the separation performance in a long-term use [24]. For example, flux decline due to fouling has been found a major challenge in the design of membrane filtration processes for black liquor [25]. The major foulant in black liquor is decomposed lignin [24]. Considering chromatographic separation, anion exchange resins, which were applied for chromatographic fractionation of hydroxy carboxylic acids already in the 1960s [26], are easily fouled by organic matter [27], which makes their utilisation in processing of raw black liquor challenging. Fouling tendency of size-exclusion gels and its effect on the separation performance is not well known. Palm and Zacchi [19] observed adsorption of lignin on a dextran-polymer-based size-exclusion gel during the recovery of oligosaccharides from a wood extract. Similar behaviour was also found in the processing of black liquor [15]. The effect of this fouling on the separation selectivity is therefore investigated here.

In addition to fouling, the chemical stability of the separation medium is also an important issue when considering its long-term performance in processing of black liquor. NaOH may cause decomposition of the dextran polymer matrix of Sephadex [28]. Therefore, the stability of Sephadex G-10 under alkaline conditions is also studied in this paper.

2. Materials and methods

2.1. Feed black liquor

Softwood (SW) and hardwood (HW) soda black liquors were prepared at VTT (Technical Research Centre of Finland, Espoo, Finland) in laboratory-scale cooking of pine and birch chips at temperature of 170 °C or 165 °C, respectively. The liquor to wood ratio (W/D) was 4:1 and the amount of effective alkali was 5.5 mol/kg. The cooking was continued until H-factor of 1936 for SW or 1324 for HW was reached. The total dry solids content of the SW black liquor was 14.3 wt% and that of HW black liquor 14.0 wt%.

The black liquors were pre-treated by ultrafiltration using DSS LabStak M20 filter unit (Alfa Laval, Nakskov, Denmark) and GR95PP membrane (Alfa Laval, Nakskov, Denmark) with molecular weight cut-off of 2000 Da at temperature of 60 °C and pressure of 10 bar. The dry solids (d.s.) content of the permeate was approximately 10 wt%. To study the effect of feed concentration on the chromatographic separation, part of the solution was concentrated to 25 wt% using a rotary evaporator.

The compositions of the feed solutions to chromatographic separation are presented in Table 1. The amount of NaOH in the feed solutions was determined by measuring the residual effective alkali by titration [29], as in soda black liquor NaOH is the only component responsible for effective alkali. The samples were diluted to ¼ with purified water (Millipore) and titrated with 1 M HCl (Titrisol®, Merck KGaA, Darmstadt, Germany) using an automated titrator (Mettle DL 25, Mettler-Toledo, Greifensee, Switzerland). Hydroxy acids and other carboxylic acids were analysed at VTT (Espoo, Finland) using capillary electrophoresis as described in [9,30]. The following acids were included in the analysis: oxalic acid, formic acid, acetic acid, glycolic acid, lactic acid, 2-hydroxy butanoic acid (2-HBA), 2,5-dihydroxy pentanoic acid (2,5-DHPA), xyloisosaccharinic acid (XISA), and glucoisosaccharinic acid (GISA). The apparent absence of oxalic acid before the concentration of the black liquor (Table 1) is due to the limited sensitivity of the analysis for very small concentrations.

As the experiments were done at alkaline conditions, the ultrafiltered black liquor was used without further pre-treatment. For comparison, in one experiment the pH of the SW black liquor feed was first reduced to 8.5 by adding 95% sulphuric acid (Merck KGaA, Darmstadt, Germany) and the precipitated lignin was separated by centrifugation (3000 rpm, 10 min).

2.2. Chromatographic separation of hydroxy acids

Sephadex G-10 (GE Healthcare Bio-Sciences, Uppsala, Sweden) was rinsed with purified water prior to use. Experiments were done in a laboratory scale glass column (ECO SR 25/200, Kronlab, Sinsheim, Germany, H_{bed} = 20 cm, D_{bed} = 2.5 cm). The bed porosity was determined to be 0.39 by using Blue Dextran 2000 (Amersham Biosciences, Uppsala, Sweden). The total hold-up volume of the column was measured with a 1 mL injection of deuterium oxide (99.9% atom-% D, Sigma Aldrich, Oakville, ON, Canada) to the column using a flow rate of 0.8 mL/min and a value of 0.81 bed volumes (BV) was obtained.

The column was thermostated at 50 °C with a heating jacket and a water circulation thermostat (Lauda C6C5, Lauda-Königshofen, Germany). Eluent was purified water. Both the eluent and the feed were introduced into the column with a flow rate of 1 mL/min using an HPLC pump (Waters 515, Waters Corporation, Milford, MA, USA), equipped with a degasser (DG-4400, Phenomenex Degassex, Torrance, CA, US). The valves were operated using LabView software (National Instruments, Austin, TX, USA). The column outlet was monitored online using conductivity detector (Conductivity Monitor, Pharmacia Biotech, Uppsala, Sweden), refractivity detector (RI 2000 Schambeck SFD GmbH, Bad Honnef, Germany) and UV-detector (Waters 2487 dual λ Absorbance Detector with 3 mm semiprep flow cell, Waters Corporation, Milford, MA, USA) on wavelengths of 280 and 350 nm. Samples were collected from the column outlet using an automated fraction collector (Frac-100, Pharmacia LKB, Uppsala, Sweden).

HW and SW soda black liquors in concentrations of 10 and 25 wt% d.s. prepared as described in Section 2.1 were used as feed.

Table 1
Composition of black liquors used in the chromatographic fractionation experiments. The concentration of lignin was determined based on UV absorbance at 280 nm, NaOH concentration based on titration, and acid concentrations based on CE analysis.

Black liquor	d.s. (wt%)	Lignin (g/L)	NaOH (g/L)	Oxalic acid (g/L)	Formic acid (g/L)	Acetic acid (g/L)	Glycolic acid (g/L)	Lactic acid (g/L)	2-HBA (g/L)	2,5-DHPA (g/L)	XISA (g/L)	GISA (g/L)
HW	10	18.3	8.00	0.00	3.50	11.50	1.02	1.98	4.08	0.00	3.50	2.97
SW	10	13.9	9.10	0.00	3.85	3.81	1.37	3.45	1.12	0.92	2.72	9.06
HW	25	64.6	9.60	1.41	13.00	39.46	3.26	7.05	16.40	0.00	12.70	10.50
SW	25	42.1	28.4	1.08	10.7	10.77	3.75	9.22	2.89	2.25	7.42	24.56