# Novel chromatographic process for the recovery and purification of hydroxy acids from alkaline spent pulping liquors

Heinonen Jari, Sainio Tuomo

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# HIGHLIGHTS

- Recovery and purification of hydroxy acids from alkaline black liquors is studied.
- Hydroxy acids are efficiently purified with a sequential chromatographic process.
- The process enables the recycling of lignin and spent pulping chemicals as such.
- The separation materials used have a low fouling tendency.

# NOVEL CHROMATOGRAPHIC PROCESS FOR THE RECOVERY AND PURIFICATION OF HYDROXY ACIDS FROM ALKALINE SPENT PULPING LIQUORS

Jari Heinonen*, Tuomo Sainio

School of Engineering Science

Lappeenranta University of Technology
Skinnarilankatu 34, FIN-53850 Lappeenranta, Finland

*Corresponding author. Tel: +358-40-127 2920, e-mail: jari.heinonen@lut.fi

## ABSTRACT

In this study, an efficient sequential chromatographic process for recovering hydroxy acids (HAs) from soda and kraft black liquors (BLs) has been developed. Lignin and pulping chemicals are also recovered and can be recycled back to the pulping process. A weak cation exchange resin in $Na^+$ form separates lignin from BL. Up to 95% lignin yield was obtained, with over 50% yield for HAs as Na salts. A cellulose-based resin is used to separate HAs from NaOH. Complete separation, and thus 100% yield for HAs and NaOH, was achieved. The HAs in soda BL are liberated by ion exchange. In case of kraft BL, the solution is acidified with $H_2SO_4$ and subjected to ion exchange and ion exclusion chromatography to recover the remaining pulping chemicals. It was found that fouling, which limits the efficiency of membrane-based processing of BLs, is avoided with the appropriate choice of chromatographic separation materials.

Keywords: black liquor; hydroxy carboxylic acids; lignin; pulping chemicals; chromatographic separation

# 1 INTRODUCTION

Aliphatic carboxylic acids are valuable platform chemicals (Holladay et al., 2007; IEA, 2011; Jang et al., 2012). Hydroxy carboxylic acids (HAs), such as lactic acid and glycolic acid, are of particular interest because they contain, in addition to carboxyl group(s), one or more hydroxyl groups (Bhalla et al., 2011; Dusselier et al., 2013; Dusselier and Sels, 2014; Kornhauser, 2010). Thus, HAs can undergo reactions typical of both carboxylic acids and alcohols (McMurry, 2008). Potential applications of HAs include fine chemicals (Dusselier et al., 2013; Werpy and Petersen, 2004), biodegradable polymers and plastics (IEA, 2011; Mehtiö et al., 2012; Wang and Huang, 2008), tissue engineering (Barralet et al., 2005), cosmetics (Draelos, 2000; Kessler et al., 2008), and metal chelating agents (Ekberg et al., 2004; Shaw et al., 2012; Svensson et al., 2007; Vercammen et al., 1999).

Some HAs, such as lactic acid and glycolic acid, can be produced by fermentation (e.g. Ghaffar et al. (2014), Koivistoinen et al. (2013)). However, alkaline spent pulping liquors (i.e. black liquors; BLs) formed during chemical pulping of wood are a potential source of a wide variety of HAs. BLs contain almost 100 different HAs, predominantly glycolic acid, lactic acid, glucoisosaccharinic acids (GISA; α and β forms), xyloisosaccharinic acid (XISA), 2,5-dihydroxypentanoic acid (2,5-DHPA), and 2-hydroxybutanoic acid (2-HBA) (Niemelä and Alén, 1999).

During pulping, wood biomass is delignified and pure cellulose fibers are produced. HAs (and formic acid and acetic acid) are formed during the pulping owing to alkaline degradation of cellulose and hemicelluloses (Gustafsson et al., 2011). Two methods (with modifications) can be used for chemical pulping under alkaline conditions: the kraft method and the soda method. The kraft method is the dominant method, owing to the stronger fibers produced. In the soda method, NaOH is the sole active pulping chemical, whereas in the kraft method the main active chemicals are NaOH and $Na_2S$, with possible small amounts of $Na_2CO_3$, $Na_2SO_4$, $Na_2S_2O_3$, NaCl, and $CaCO_3$ (Gustafsson et al., 2011). Annually, almost 200 Mt of BL as dry solids is produced worldwide (IEA, 2015; Vähä-Savo, 2014; Vakkilainen, 2007). The BLs compose of lignin (30%), carboxylic acids (20% HAs, 10% formic acid and acetic acid), spent pulping chemicals (22%), Na bound to organics (11 %), and other organics (7 %)  (Niemelä and Alén, 1999). Thus, approximately 40 Mt/a HAs and 20 Mt/a formic acid and acetic acid are formed.

BLs with HAs (hereafter, the term HA also encompasses formic and acetic acids) are currently combusted in the recovery boilers of pulp mills for energy. The acids have low calorific values in comparison with lignin, and thus their share of the energy production is small (Van Heiningen, 2006). On the other hand, recovery of HAs from BLs prior to combustion would open up a huge source for platform chemicals. However, industrial scale recovery of HAs has not yet been implemented. This is a challenging problem, as HAs exist as Na salts and thus are among the most polar components in BLs.

Several methods have been investigated for the recovery of HAs from BLs as a mixture. In most of the proposed methods, the BLs are first acidified directly with $H_2SO_4$ (to pH 2.5) (Alén et al., 1990; Alén and Sjöström, 1981; Kumar and Alén, 2015) or after carbonation (to pH 8.5) (Alén and Sjöström, 1980a; Kumar and Alén, 2014). Acidification is done to liberate HAs (conversion of $Na^+$ salts to free acids) and to precipitate lignin from the solution. Ion exclusion (Alén et al., 1990), crystallization (Alén and Sjöström, 1980a), distillation under vacuum (Alén and Sjöström, 1981, 1980b), electrodialysis (Kumar and Alén, 2014), and esterification of HAs and subsequent distillation (Kumar and Alén, 2015) have been used to further purify the acid mixture. Mänttäri et al. (2015) used ultrafiltration prior to acidification to remove approximately 75% of lignin for recycling. After acidification, further HA purification was done by cooling crystallization and nanofiltration (Mänttäri et al., 2015). Although the aforementioned methods produce rather pure HA mixtures, they are uneconomical owing to high chemical consumption, low or moderate lignin recycling levels, and excessive salt generation (mainly $Na_2SO_4$). Recycling of large amounts of salts in the pulping process would disturb the Na/S balance of the process and, thus, is not an option.

Recently, Hellstén et al. (2013b) presented a technique for HA recovery from soda BL that does not require acidification or other chemical additions. First, 80% of lignin is removed by ultrafiltration. Then HAs are separated from NaOH, using size exclusion gel Sephadex G-10 as separation material. As the final step, HAs are liberated and the remaining $Na^+$ ions in the solution are removed by ion exchange with a cation exchange resin in $H^+$ form. This approach enables the recycling of NaOH and lignin from soda BL. However, fouling of the membranes used for lignin separation is a problem. Moreover, the separation material used in the NaOH separation has a pH limit of 13, which is lower than the typical pH of alkaline BLs (13–14) (Kumar and Alén, 2015, 2014; Mänttäri et al., 2015). In addition, this approach has only been tested for soda BL, although the majority of BLs are produced by the kraft process.

Here, we propose a novel sequential chromatography-based process (Fig. 1) for the recovery of HAs as free acids from both kraft and soda BLs in such a way that lignin and spent pulping chemicals can be recycled back to the pulping process. Besides recycling, the lignin could also be further processed into various monomeric and polymeric products (e.g. Gomes et al., 2018; Lignimatch, 2010; Mota et al., 2016; Silva et al., 2009; Upton and Kasko, 2016).

Hydrophilic weak acid cation exchange (WAC) resins in $Na^+$ form were used for the chromatographic separation of lignin from the BLs. NaOH separation was carried out using a similar chromatographic method to that described by (Hellstén et al., 2013b), but the use of a more durable separation material was studied. Recovery of the other inorganic salts in kraft BL was also investigated. The final product was a pure mixture of HAs produced from lignin and NaOH free BLs via ion exchange, chromatography, and acidification. The feasibility of the process was demonstrated with batchwise separation experiments. Process optimization was not done.

<<Figure 1 around here>>

## 2 MATERIALS AND METHODS

### 2.1 Chemicals and separation materials

Ultrapure water (produced with a CENTRA R 60/120; ELGA LabWater), analysis grade sodium hydroxide (≥ 99.0%, pellets for analysis, Merck KGaA), sulfuric acid (95–97%, pro analysis, Merck KGaA), and ethanol (100%; AnalaR Normapur, VWR) were used in the experiments. Commercially available chemicals were acquired and used for the identification and quantification of HAs: formic acid (98–100%, for analysis, Merck KGaA), acetic acid (99–100% glacial, chemically pure, VWR), glycolic acid (99%, Acros Chemicals), succinic acid (≥99.5%; AnalaR Normapur, VWR), lactic acid (90% aqueous solution, chemically pure, VWR), sodium salt of 2-hydroxybutyric acid (97%, Sigma-Aldrich, CAS 5094-24-6), calcium salt of α-glucoisosaccharinic acid (calcium α-D-isosaccharinate, 98%, Alfa Aesar, CAS 16835-77-1), lactone of xyloisosaccharinic acid (2,4-dihydroxy-2-hydromethylbutanoicacid-1,4-lactone; ≥ 97%; Carbosynth, CAS 19444-86-1). Blue dextran 2000 (GE Healthcare) was used for the resin bed porosity measurements. Authentic hardwood soda and kraft BLs (obtained from a Finnish pulp and paper company) were used as feed solutions (Table 1).

The separation materials used in this study and their properties are listed in Table 2. WAC resins were shipped in $Na^+$ form. Conversion of the strong acid cation exchange (SAC) resins into $H^+$ form was done with 1 mol/L HCl using standard methods.

<<Table 1 around here>>

<<Table 2 around here>>

## 2.2 Chromatographic fractionation

Chromatographic separation experiments were carried out at 50 °C with top-down flow. The column loading ($V^F$) was 0.1–0.3 BV, and the flowrate ($Q$) was 1–2 BV/h. The chromatography unit consisted of two high-performance liquid chromatography (HPLC) pumps attached to a glass column with water heating jacket via a fluid degasser and injection valve. Columns with approximately 120 mL ($d_{\mathrm{bed}} = 1.5$ cm, $h_{\mathrm{bed}} = 70$ cm) and 900 mL ($d_{\mathrm{bed}} = 5$ cm, $h_{\mathrm{bed}} = 45$ cm) bed volumes were used. The column outlet stream was monitored with an online conductivity detector, a refractive index (RI) detector, and an ultraviolet (UV) detector. A fraction collector was also connected to the column outlet. Valve control and data collection were performed with LabView software (National Instruments). Purified water and NaOH solutions (0.05 mol/L and 0.2 mol/L, respectively) were used as eluents.

## 2.3 Preparation of the final hydroxy acid mixture

After the removal of lignin and NaOH from the BLs, the HAs were converted from sodium salts into free acids (acid liberation). In the case of soda BL, this was done with a SAC resin CS12GC in $H^+$ form in a batch reactor (1/5 solid/liquid ratio). After 30 min equilibration, the pH of the solution was measured and the solution and resin were separated by filtration. This treatment was repeated until the pH of the solution did not change, i.e., all $Na^+$ ions were replaced by $H^+$ ions.

A different approach was used with kraft BL owing to the presence of sodium thiosulfate ($Na_2S_2O_3$) in the solution. Treatment of $Na_2S_2O_3$ with acids results in the formation of solid sulfur, which precipitates. In order to prevent blockage of the pores of the cation exchange resin by sulfur precipitates, the acids from kraft BL were liberated by acidification with 4 mol/L sulfuric acid to pH 1.3. The precipitate was removed by filtration.

After acidification, $Na^+$ ions were removed in a similar way to the HA liberation from soda BL. The resulting solution contained sulfuric acid, which was removed by ion exclusion chromatography (IEC) with SAC resin in $H^+$ form as the separation material in batch mode.

### 2.4 Analyses

Lignin concentrations were determined using UV absorbance. A wavelength of 280 nm was used for the quantification (Brunow et al., 1999). Phenolic compounds in BLs (Faustino et al., 2010; Löwendahl et al., 1978) were treated as part of the lignin and not quantified separately.

The UV absorbance was measured with a Cary 8454 UV/Vis detector (Agilent). The samples were diluted with 20 mmol/L NaOH in order to prevent lignin precipitation. The lignin concentration was calculated from the absorbance with 14 L/(g cm) as the extinction coefficient (birch; Hellstén et al. (2013b).

HAs were quantified with an offline HPLC system (1260 Infinity, Agilent) equipped with a diode array detector (wavelength 205 nm). A Luna Omega Polar C18 column (Phenomenex) was used. The column temperature was 30 °C and the injection volume was 10 µL. A solvent gradient of 0.1% $H_3PO_4$ (A) and methanol (B) was used. The flow conditions were: 0–15.5 min 100% A, $Q = 0.5$ mL/min; 15.5–24.5 min change of eluent to 40% A and 60% B, increase of $Q$ to 1 mL/min; 24.5–26.0 min 40% A, 60% B, $Q = 1$ mL/min; 26.0–29.5 min change of eluent to 100% A, $Q = 1$ mL/min; 29.5–33.5 min

100% A, $Q = 1$ mL/min; 33.5–36.8 min 100% A, decrease of $Q$ to 0.5 mL/min; 36.8–40 min 100% A, $Q = 0.5$ mL/min. The acids were identified by reference to known standards (see above).

The samples were acidified before HPLC analysis with 1 mol/L HCl containing 1.5 g/L succinic acid as an internal standard. The internal standard was required as the acidification results in lignin precipitation and thus a change in the sample volume and concentration.

Sulfate and thiosulfate concentrations were analyzed by ion chromatography (Thermo Fisher ICS-1100) according to standard SFS-EN ISO 10304-2. The column was an IonPac AG22 (4 mm × 50 mm) + AS22 (4 mm × 250 mm), and the eluent was 4.5 mmol/L $Na_2CO_3$ with 1.4 mmol/L $NaHCO_3$.

The alkalinity of the samples containing lignin was evaluated by measuring the pH. Titration with an automatic titrator (T50, Mettler-Toledo) was used for samples free of lignin and Na salts of HAs.

## 3 INDICATORS FOR SEPARATION EFFICIENCY

The separation efficiency was evaluated with respect to the recovery yield of HAs, lignin, and NaOH; and the productivity of the separation process with respect to HAs, and the eluent consumption needed for the production of 1 g of HAs. The recovery yield of component $i$ $Y_i$ (%) was calculated from

$$Y_i = \frac{m_i^{\mathrm{out}}}{m_i^{\mathrm{feed}}} \cdot 100\% \quad , \tag{1}$$

where $m_i$ is the mass of component $i$, and the superscripts “out” and “feed” refer to the component $i$ in the target fraction of component $i$ and feed solution, respectively. Productivity with respect to HAs $Pr_{\mathrm{HA}}$ (g/[L (bed) h]) was calculated with

$$Pr_{\mathrm{HA}} = \frac{m_{\mathrm{HA}}^{\mathrm{out}}}{V_{\mathrm{bed}} t_{\mathrm{cycle}}}, \tag{2}$$

where $V_{\mathrm{bed}}$ is the resin bed volume and $t_{\mathrm{cycle}}$ is the cycle time. The eluent consumption with respect to HAs $EC_{\mathrm{HA}}$ (L/g) was calculated from

$$EC_{\mathrm{HA}} = \frac{Qt_{\mathrm{cycle}} - V^{\mathrm{F}}}{m_{\mathrm{HA}}^{\mathrm{out}}}, \tag{3}$$

where $Q$ is the flowrate and $V^{\mathrm{F}}$ is the feed volume.

# 4 RESULTS AND DISCUSSION

## 4.1 Separation of lignin

### 4.1.1 Selection of separation material and eluent

Separation of lignin should be carried out as the first fractionation step (Fig. 1), as lignin is the component with the highest concentration in BLs. This also minimizes the dilution of the lignin fraction, which is beneficial for pulp mill economics. However, as no optimization of the lignin recovery step was done here, detailed discussion related to topic is out of the scope of this study.

In studies by (Heinonen et al., 2019, 2018b), chromatographic separation of lignin from lignocellulosic hydrolysates was successfully carried out using WAC resins in $Na^+$ form.

Thus, a similar approach was used here, although the feed solution was quite different. It is a well-known fact that such resins are highly selective towards $H^+$ ions and divalent cations. However, $H^+$ concentration in BLs is very small due to high pH. Also exchange of the $Na^+$ ions to other metal cations is highly unlikely due to high $Na^+$ concentration in the feed.

Lignin is a group of large three-dimensional heterogenic aromatic polymers that are strongly hydrophobic. It was thus expected that with BL as the feed solution, lignin (and phenolic compounds in the BLs) would elute first from a column filled with a hydrophilic separation material that had sufficiently small pore size.

Lignin separation was studied with two WAC resins (5.0 wt.% and 8.0 wt.% cross-linked). Separation of lignin from soda BL was achieved with both resins (Fig. 2). On the basis of the elution profiles and separation efficiency, the 5.0 wt.% cross-linked resin yielded better separation of HAs and NaOH from lignin (Fig. 2). For example, for 95% $Y_{\mathrm{lignin,limit}}$ with a single-cut (no waste fraction), 68% $Y_{\mathrm{HA}}$ was obtained with $V^{\mathrm{F}} = 0.1$ BV. For the 8.0 wt.% cross-linked resin, the $Y_{\mathrm{HA}}$ was only 19% (Fig. 2). Increasing $V^{\mathrm{F}}$ from 0.1 BV (Fig. 2) to 0.2 BV (Fig. 3, water eluent) decreased $Y_{\mathrm{HA}}$ with 5.0 wt.% cross-linked resin by more than 20 percentage units ($Y_{\mathrm{lignin,limit}} = 95\%$). However, $Pr_{\mathrm{HA}}$ increased by 85% to 24.2 g/(L(bed) h) and $EC_{\mathrm{HA}}$ decreased by 30% to 0.13 L/g. The improvements in $Pr_{\mathrm{HA}}$ and $EC_{\mathrm{HA}}$ were due to the increased amount of feed treated during one cycle.

<<Figure 2 around here>>

NaOH exhibited strong tailing on the WAC resins in $Na^+$ form (Fig. A1 in the Appendix). This most probably stems from the existence of two types of carboxylate functional groups in these resin. NaOH has strong affinity towards one of these groups and thus strong tailing of NaOH can be observed. However, the existence of such groups in the resin was not confirmed.

To prevent the tailing and thus ensure stable operation of the lignin separation, the use of NaOH eluent was investigated with 5.0 wt.% cross-linked resin (Fig. 3). This was expected to further decrease fouling, as an increase in pH increases the ionization level of lignin (contains weakly acidic OH-groups that are dissociated at high pH (Gustafsson et al., 2011; McMurry, 2008)), resulting in stronger electrostatic repulsion of lignin from the resin. In addition, exchange of the $Na^+$ ions in the resins with other metal cations in the BLs should be even less likely than with water as eluent.

<<Figure 3 around here>>

Use of the NaOH eluent had only a small effect on the elution profiles and thus also on separation efficiency (Fig. 3). With $Y_{\mathrm{lignin,limit}}$ = 95% and $V^F$ = 0.2 BV, $Y_{\mathrm{HA}}$ was appr. 45% with water and 0.05 mol/L NaOH eluents. This value increased slightly (to 50%) when 0.2 mol/L NaOH was used as eluent.

Gel type ion exchange resins swell and shrink when in contact with solution. This causes additional dispersion to the system as a void space is formed at the top of the resin bed. With $V^F$ = 0.1 BV and water as eluent (Fig. 2), the bed height with the 5.0 wt.% and 8.0 wt.% cross-linked resins decreased by 2.6 % and 1.0 %, respectively. With higher loading ($V^F$ = 0.2 BV; Fig. 3), the bed height with the 5.0 wt.% cross-linked resin decreased by 7.3 %. Addition of NaOH to the eluent decreased the extent of the volume changes: the bed height with the 5.0 wt.% cross-linked resin decreased by 6.6 % and 3.1 % with 0.05 mol/L and 0.2 mol/L NaOH eluents, respectively. This results from the partially shrunken state of the resin in NaOH eluent and on the smaller concentration differences between the eluent and the BL feed.

The resin volume changes should not pose problems with resin durability. This is based on the fact that the sweetener industry utilizes ion exchange resins with low cross-linkage (e.g. 5.5–6.0 wt.% cross-linkage) in fractionation of glucose–fructose syrups (appr. 50 wt.% dry solids) (Heinonen et al., 2018a; Purolite 2018; Dow 2018). Resin volume changes in such a separation task are also large, but do not pose problems on resin durability.

On the basis of the results, WAC resin with 5.0 wt.% cross-linkage and 0.05 mol/L NaOH eluent were chosen for subsequent lignin separation experiments.

### 4.1.2 Fouling and separation in large column

The chromatographic lignin separation from both soda and kraft BLs was also studied on a larger scale ($V_{bed}$ = 890 mL) with $V^F$ = 0.15 BV (Fig. 4). The elution profiles were qualitatively similar (Fig. 4), and thus the same processing method is applicable for both BLs.

<<Figure 4 around here>>

Some differences were observed (Fig. 4) in the shapes of the lignin profiles of soda and kraft BLs. These most probably stem from the presence of different lignin compounds in the BLs owing to the different pulping conditions used; kraft BL contains, in addition to NaOH, NaHS, $Na_2CO_3$, $K_2CO_3$, $Na_2SO_4$, $Na_2S_2O_3$, $Na_2SO_3$, $Na_2S_x$, and NaCl (Vakkilainen, 2008). Elution of the inorganic salts was monitored with respect to online electrical conductivity at the column outlet. The conductivity "profile" for kraft BL was wider and had a smaller maximum value than that obtained for soda BL (Fig. 4). This can be attributed to differences in the retention and electrical conductivity of the different salts.

The separation efficiency was slightly higher with soda BL than with kraft BL (Fig. 4). For example, with $Y_{\mathrm{lignin,limit}} = 95\%$, the $Y_{\mathrm{HA}}$ was 47% for soda BL and 39% for kraft BL. The lower $Y_{\mathrm{HA}}$ value with kraft BL was due to stronger overlapping of the lignin and HA profiles. The $Y_{\mathrm{HA}}$ for soda BL with $V^{\mathrm{F}} = 0.15$ BV was approximately same as that obtained using the small column and $V^{\mathrm{F}} = 0.2$ BV. Thus, the separation efficiency with the large column was lower than with the small column, mainly owing to the 36% shorter bed and the consequent lower number of theoretical plates (NTP) in the large column.

Process stability and resin fouling were evaluated on the basis of 35 cycles long runs (appr. 5 L of feed) with both soda and kraft BLs. The operating conditions given in the caption of Fig. 4 were used. Three fractions were produced (Fig. 4): lignin (fraction 1), main HA fraction (fraction 2), and fraction containing tail of HAs and the pulping chemicals (fraction 3). A design constraint $Y_{\mathrm{lignin,limit}} = 95\%$ was set, which defined the beginning of the HA fraction. Fraction 2 ended (and fraction 3 began) at the point at which the HA concentration decreased below 10 g/L. Fraction 3 ended when the conductivity signal reached the baseline. The feeding interval was chosen such that collection of lignin product started immediately after fraction 3 of the previous cycle ("touching bands" mode).

No changes in the elution profiles were observed during the cyclic runs (Fig. A2 in the Appendix). This clearly indicates that resin fouling was not an issue, although the resin color was slightly darker at the end than at the beginning owing to sorption of some lignin compounds. Similarly, fouling of WAC resin in $Na^+$ form was not an issue in the separation of lignin from lignocellulosic hydrolysates (pH = 6) (Heinonen et al., 2019). Here, the situation was even better owing to the higher feed pH, which resulted in higher electrostatic repulsion of lignin from the resin.

In total, an approximately 3.4 L fraction 2 was produced in the cyclic runs from both BLs. The compositions of the collected fractions are given in Table 1. $Y_{\mathrm{lignin}}$ and $Y_{\mathrm{HA}}$ were 91% and 34%, respectively, for soda BL and 96% and 34% for kraft BL. $Pr_{\mathrm{HA}}$ and $EC_{\mathrm{HA}}$ for soda BL were 6.02 g/[L(bed) h] and 0.11 L/g; and for kraft BL they were 4.6 g/[L(bed) h] and 0.17 L/g, respectively. $Y_{\mathrm{lignin}}$ obtained by the chromatographic method was considerably higher than that obtained by ultrafiltration of a more dilute soda BL (approximately 80% for hardwood soda BL) by Hellstén et al. (2013a). Fouling of the membranes by lignin compounds was also found to be a major issue (Hellstén et al., 2013a). It can be thus concluded that the chromatographic method is a better option for lignin separation than ultrafiltration. Here the lignin separation was performed using a batch process that offered comparatively low separation efficiency (low HA yield, dilution of the product fractions). This can be improved with more advanced process schemes such as the simulated moving bed process (SMB) or steady state recycling chromatography (SSR, e.g. Heinonen et al., 2019).

## 4.2 Separation of sodium hydroxide

### 4.2.1 Selection of separation material

Chromatographic separation of HAs and NaOH in lignin-free soda BL has been achieved with Sephadex G-10 as the separation material (Hellstén et al., 2013a, 2013b). Although good separation efficiency was obtained, the separation material has a pH limit of 13 and may not be stable in alkaline conditions. Here, we investigated the use of an alternative separation material, porous cellulose-based Cellufine GH-25, for the separation of NaOH and HAs in lignin-free BLs. This material has a pH limit of 14 making it well suited to alkaline conditions.

G-10 and GH-25 were compared with respect to the separation of HAs and NaOH from lignin-free soda BL (main HA fraction from the lignin separation step) (Fig. 5A,B). Both materials were found to separate HAs and NaOH qualitatively similarly; HAs eluted first and NaOH last. No separation between individual HAs was achieved.

<<Figure 5 around here>>

NaOH showed relatively strong sorption with both separation materials. Both separation materials consist of glucose units. These are bound together by α-D-glycosidic bonds in G-10 (dextran) and β-D-glycosidic bonds in GH-25 (cellulose). The hydroxyl groups on the glucose units are weakly acidic (glucosidic OH groups in cellulose have p$K_a$ value of 13.7 (Motomura et al., 1998)) and can thus dissociate in the presence of a strong base such as NaOH. This can be interpreted as binding of NaOH to the glucose unit. However, owing to the weak acid strength of the OH groups, NaOH binding is easily reversible and resulted in the elution profiles seen in Fig. 5A,B, with self-sharpening front and diffuse rear. A more detailed discussion of this mechanism can be found in Laatikainen et al. (2018).

The HAs (Na-salts) had weaker sorption than NaOH (Fig. 5A,B). This is because there are no attractive interactions between HAs and the OH-groups in the resin matrix owing to the low local pH which prevented dissociation of the OH-groups. This situation was similar to the separation of $Na_2MoO_4$ and NaOH with GH-25 (Laatikainen et al., 2018). The elution profile of HAs was also completely different than that of NaOH. In addition, differences in the HA profiles with G-10 and GH-25 were observed. With G-10 (Fig. 5A), the HA profile had a diffuse front and sharp rear. This was caused by ion exclusion due to the small charge of the carboxylic groups on the Sephadex separation material (Hellstén et al., 2013a; Neddermeyer and Rogers, 1968).

With GH-25 (Fig. 5B), the HA profile had a diffuse front at low concentrations, but developed a “self-sharpening” front at higher concentrations. The rear of the profile was diffused at high concentrations, but shock-like at low concentrations. The shape of the profile at low concentrations most probably stemmed from ion exclusion, as in the case of G-10. However, GH-25 probably has fewer carboxylic groups than G-10 (4 µeq/g (dry gel) (Neddermeyer and Rogers, 1968)), and the ion exclusion effect thus disappeared with increasing HA concentration, resulting in the changes observed in the HA profile at higher concentrations.

Although the separation of HAs and NaOH from lignin-free soda BL could be achieved with both separation materials, the separation was significantly better with GH-25 (Fig. 5A,B). For $Q = 2$ BV/h and $V^F = 0.3$ BV (Fig. 5), complete separation could be obtained with GH-25. With G-10, the HA and NaOH profiles overlapped to some extent and, with the design constraint $Y_{\text{NaOH,limit}}$ = 100%, $Y_{\text{HA}}$ was 70%, $Pr_{\text{HA}}$ was 23.9 g/(L(bed) h), and $EC_{\text{HA}}$ was 0.051 L/g. With GH-25 (100% $Y_{\text{NaOH,limit}}$), $Y_{\text{HA}}$ was 100%, $Pr_{\text{HA}}$ was 22.8 g/(L(bed) h) and $EC_{\text{HA}}$ was 0.065 L/g. The slightly lower $Pr_{\text{HA}}$ and $EC_{\text{HA}}$ with GH-25 were due to approximately 50% longer cycle time.

Although its $Pr_{\text{HA}}$ was slightly lower (same $Q$ and $V^F$), the higher $Y_{\text{HA}}$ makes GH-25 a better option for the separation of HAs (Na salts) and NaOH. Moreover, GH-25 showed a lower fouling tendency from residual lignin in the feed compared with G-10. After six pulse experiments, G-10 had a considerably darker color than GH-25 (Fig. A3 in the Appendix).

### 4.2.2. Recovery of pulping chemicals from kraft BL

The use of GH-25 for the recovery of pulping chemicals from kraft BL was also investigated. As shown in Fig. 5C, the separation of HAs and NaOH was excellent, but no separation between HAs and the other inorganic salts could be obtained ($Na_2SO_4$ and $NaS_2O_3$ were quantified). This was because the anions of the inorganic salts had weaker attractive interactions than NaOH with the OH-groups of GH-25. Thus, an additional step is required for the separation of these compounds from the HAs. With a feed volume of $V^F$ = 0.3 BV, $Pr_{HA}$ and $EC_{HA}$ for this step (recovery of NaOH) were 21 g/(L(bed) h and 0.071 L/g, respectively. These values were close to those obtained for soda BL with GH-25.

### 4.2.3 Fouling and separation in large column

Stability and fouling of the GH-25 resin was studied by fractionating approximately 3.2 L of lignin-free soda and kraft BLs ($V_{bed}$ = 890 mL; $Q$ = 1 BV/h; $V^F$ = 0.15 BV) into HA and NaOH fractions (Fig. 5D). In total, 48 cycles were performed. No changes in the elution profiles were observed (Fig. A4 in the Appendix). This confirmed the low fouling tendency of the GH-25 and thus the suitability of GH-25 for this separation task.

Three fractions were collected (Fig. 5D). Fraction 1 (Table 1) contained 100% of the HAs (and inorganic salts other than NaOH with kraft BL). The other two fractions contained 100% of NaOH. $Pr_{HA}$ and $EC_{HA}$ for soda BL were 3.63 g/(L(bed) h) and 0.24 L/g. For kraft BL, the values were 2.93 g/(L(bed) h) and 0.3 L/g. $Pr_{HA}$ and $EC_{HA}$ values are not comparable with those of the small column experiments because lower, and thus suboptimal, feed volume and flow rate ($V^F$ = 0.15 BV; $Q$ = 1 BV/h) were used.

## 4.3 Liberation of hydroxy acids from soda black liquor

After the separation of lignin and NaOH from the soda BL, the HAs must be converted from Na salts into free acids to obtain the final product mixture. This can be done either using mineral acids or by ion exchange with a SAC resin. The latter option was used here as it simultaneously removes $Na^+$ ions (and other possible metal cations) from the solution. The acid liberation was carried out in a batch reactor.

Three batchwise ion exchange cycles were sufficient for the complete conversion of the Na salts of HAs into free acids. The composition of the final product mixture is given in Table 1. On an industrial scale, this acid liberation step should be carried out in a column for higher efficiency. Also, regeneration of the exhausted resin in $Na^+$ form is straightforward in a column. However, the feed solution should be free of residual lignin as lignin might precipitate due to pH decrease and thus eventually block the column.

## 4.4 Liberation of hydroxy acids from kraft black liquor

The HAs in kraft BL cannot be “liberated” by ion exchange after the separation of lignin and NaOH. Kraft BL contains sodium thiosulfate ($NaS_2O_3$) which could not be separated from the HAs in the NaOH separation step. The thiosulfate anion undergoes disproportionation in acidic conditions

$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow SO_2(g) + S(s) + H_2O(l) \qquad (4)$$

resulting in formation of elemental sulfur, which precipitates. If “acid liberation” with a SAC resin would be done with $S_2O_3^{2-}$ present in the solution, sulfur would precipitate into the pores of the resin, block them and thus render the resin into waste.

No efficient way to separate the Na salts of HAs from the other inorganic salts in kraft BL after the NaOH separation could be found. Thus, a different approach was used for the liberation and final purification of HAs from kraft BL. First, the solution was acidified with sulfuric acid. This was justified at this point, as the solution is free of lignin and NaOH, which results in low $H_2SO_4$ consumption.

The acidification was performed with 4 mol/L $H_2SO_4$ to a final pH of 1.3 (initial pH 9.8). This value was chosen on the basis of the treatment of kraft BL with SAC resin in $H^+$ form. The $H_2SO_4$ consumption was 0.018 g (100% $H_2SO_4$)/g (solution). For direct acidification of native kraft BL, the acid consumption was 1.1 g (100% $H_2SO_4$)/ g (solution). Thus the acid consumption could be decreased by a factor of 60. Precipitates were removed by centrifugation.

During the acidification of kraft BL, sulfur-containing gases and $CO_2$ are also formed. $SO_2$(g) is formed from $Na_2S_2O_3$ (Eq. (4)). Kraft BL may also contain NaHS, $Na_2SO_3$, and $Na_2CO_3$, which form $H_2S$(g), $CO_2$(g), and $SO_2$(g)

$$HS^-(aq) + H^+(aq) \rightarrow H_2S(g) \tag{5}$$

$$SO_3^{2-}(aq) + 2H^+(aq) \rightarrow SO_2(g) + H_2O(l) \tag{6}$$

$$CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l). \tag{7}$$

These gases are also formed as part of normal pulp mill operation during combustion of BL in the recovery boiler, where they form, e.g., $Na_2S$ and $Na_2SO_4$ (Vakkilainen, 2007). Thus, these gases can be fed to the recovery boiler with air. The elemental sulfur formed in reaction of Eq. (4) could also be fed to the recovery boiler where it would react with $O_2$ to form $SO_2$ (g).

The solution from the acidification step contained free HAs, but also $Na^+$ ions and possibly small amounts of other metal cations, and at least $SO_4^{2-}$ ions, which need to be removed. The $Na^+$ ions (and possible metal cations) were removed first by ion exchange with a SAC resin (CS12GC) in $H^+$ form, similarly as the liberation of HAs from soda BL. Four cycles were found to be sufficient to remove all metal cations ions from the solution. The final pH was 0.65. The Na-free solution was then concentrated under reduced pressure (Table 1).

Removal of $SO_4^{2-}$ was performed as the final step. This could be achieved by ion exchange, but this approach would require regeneration of the exhausted anion exchanger. On the other hand, ion exclusion chromatography (Helfferich, 1995) has been successfully used to separate $H_2SO_4$ from concentrated acid lignocellulosic hydrolysates containing monosaccharides and acetic acid (e.g. Heinonen and Sainio, 2014, 2010). In IEC, regeneration of the ion exchange resin is not required, as no ion exchange occurs. Therefore, IEC was chosen for sulfate removal.

Two SAC resins with different cross-linkages were tested for IEC (Fig. 6). The elution behavior with these was qualitatively similar, with $H_2SO_4$ eluting first owing to ion exclusion, and HAs eluting last. The elution profiles of $H_2SO_4$ were typical for IEC, with breakthrough at the void volume of the resin bed. The HAs are not affected by IEC, as dissociation of HAs is prevented by the high proton concentration in the resin. Thus HAs are adsorbed to the resin more strongly than $H_2SO_4$ and separation between these is obtained.

<<Figure 6 around here>>

The separation efficiency was found to increase with decreasing resin cross-linkage (Fig. 6). This was due to the weaker size exclusion of HAs from the less cross-linked resin. For example, with $Y_{\mathrm{H2SO4,limit}} = 100\%$, the $Y_{\mathrm{HA}}$ values were 95% and 76% for 5.5 wt.% and 8.0 wt.% cross-linked SAC resins, respectively. $Pr_{\mathrm{HA}}$ and $EC_{\mathrm{HA}}$ ($Y_{\mathrm{H2SO4,limit}} = 100\%$) with 5.5 wt.% cross-linked resin were 5.2 g/(L(bed) h) and 0.34 L/g, respectively, while those for 8.0 wt.% cross-linked resin were 5.2 g/(L(bed) h) and 0.32 L/g. $Pr_{\mathrm{HA}}$ and $EC_{\mathrm{HA}}$ were approximately same in the two cases, as the cycle time for the 8.0 wt.% cross-linked resin was 30% shorter than for the 5.5 wt.% cross-linked resin.

The final HA product mixture from kraft BL was obtained using CS11GC as the separation material (Table 1). The recovered $H_2SO_4$ can be used for regeneration of the SAC resin used in $Na^+$ removal or acidification of the HA mixture after NaOH separation. The resin regeneration generates $Na_2SO_4$, which could be treated in the recovery boiler to form $Na_2S$ (Vakkilainen, 2007). Thus, in principle, no additional waste streams will be generated.

## 5 CONCLUSIONS

A novel chromatographic method for the recovery of pure HAs as a mixture from alkaline spent pulping liquors was presented. The feasibility of the process was demonstrated by batchwise experiments. HAs were recovered from kraft and soda BLs in such a way that lignin and spent pulping chemicals could be recycled to the pulping process. Throughput of the chromatographic process did not decrease owing to fouling as it does in membrane filtration-based processing. The final purification of HAs was more complicated in the case of kraft BL than that of soda BL, but was accomplished efficiently. Only chemicals already used in pulp mills were needed, and waste generation was not increased.

Optimization of the separation steps with respect to operating conditions and process schemes was not done in this study, but should be carried out in order to realize industrial scale application. In addition, the removal of $Na^+$ ions was carried out here in a batch reactor. However, ion exchange in a column results in higher efficiency and the regeneration of the exhausted resin is straightforward. Therefore a detailed investigation of the ion exchange step should be done.

The proposed process enables the production of pure HAs as a mixture. In most applications, pure individual HAs would most likely be preferred. Thus efficient production of individual HAs from HA mixtures should be investigated. Use of chromatographic separation to achieve this will be addressed in future studies by the authors.

## Acknowledgements

Financial support from the Academy of Finland (grant SA/298548) is gratefully acknowledged.

## Appendix

Supplementary figures.

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## Appendix – Supplementary figures

Elution of pure NaOH (0.25 mol/L) pulse from a chromatographic column filled with WAC resin in $Na^+$ form is shown in Fig. A1.

<<Figure A1 around here>>

Online conductivity signals during various cycles of lignin separation from soda and kraft BLs with WAC resin in $Na^+$ form as separation material are shown in Fig. A2.

<<Figure A2 around here>>

Sephadex G-10 and Cellufine GH-25 size exclusion materials after HA–NaOH separation experiments is shown in Fig. A3.

<<Figure A3 around here>>

Online conductivity signals during various cycles of NaOH separation from soda and kraft BLs with WAC resin in $Na^+$ form as separation material are shown in Fig. A4.

<<Figure A4 around here>>

**Figure captions**

Figure 1. Sequential chromatographic process for the production of pure hydroxy acid mixture from soda and kraft BLs.

Figure 2. Chromatographic separation of lignin from soda BL with gel-type WAC resins in $Na^+$ form. $Q$ = 2 BV/h; $V^F$ = 0.1 BV; $T$ = 50 °C; $h_{bed}$ = 70 cm; $d_{bed}$ = 1.5 cm. Symbols: black circles = lignin; blue diamonds = NaOH red squares = total HAs; triangles = individual HAs (green = glycolic acid, pink = formic acid, cyan = GISA, grey = XISA, brown = lactic acid, dark green = acetic acid, dark blue = 2-HBA). Lines: in the upper subfigures are provided to guide the eye.

Figure 3. Effect of eluent composition on the separation of lignin with 5 wt.% cross-linked WAC resin in $Na^+$ form. $Q$ = 2 BV/h; $V^F$ = 0.2 BV; for other conditions, see caption to Fig. 1. Symbols: see caption to Fig. 1. Lines in left hand subfigures: lignin concentration based on color intensity at 400 nm from online UV/Vis detector; other lines are presented to guide the eye.

Figure 4. Lignin separation from soda and kraft BLs with 5.0 wt.% cross-linked WAC resin in $Na^+$ form and 0.05 mol/L NaOH eluent. $Q$ = 2 BV/h; $V^F$ = 0.15 BV; $T$ = 50 °C; $h_{bed}$ = 45 cm; $d_{bed}$ = 5 cm. Symbols and lines: blue dashed line, electrical conductivity; vertical dashed lines, fractionation cut points; for others; see caption to Fig. 1. Fractions: 1, lignin; 2, HAs; 3, pulping chemicals.

Figure 5. Separation of NaOH from HAs with Sephadex G-10 (A) and Cellufine GH-25 (B-D). Only conductivity is shown for kraft BL in D. $V_{bed}$: A-C, 120 mL; D, 890 mL. $T$ = 50 °C; A-C, $Q$ = 2 BV/h, $V^F$ = 0.3 BV; D, $Q$ = 1 BV/h, $V^F$ = 0.15 BV. Symbols and lines: green circles = total amount of $Na_2SO_4$ and $NaS_2O_3$; blue dashed line, conductivity with kraft BL; vertical dashed lines, fractionation cut points; vertical dotted line, 2nd cut point with kraft BL; for others, see caption to Figs 1 and 3. Fractions: 1, HAs; 2, NaOH; 3, NaOH.

Figure 6. Separation of $H_2SO_4$ from HAs with gel-type SAC resins in $H^+$ form. $Q$ = 2 BV/h, $V^F$ = 0.1 BV, $T$ = 50 °C, $h_{bed}$ = 70 cm, $d_{bed}$ 1.5 cm. Symbols and lines: solid purple = $H_2SO_4$ based on online conductivity signal; for others, see caption to Fig. 1.

Figure A1. Elution of a pulse of 0.25 mol/L NaOH through a bed filled with a 5.0 wt.% cross-linked WAC resin in $Na^+$ form. Experimental conditions: $Q$ = 2 BV/h; $V^F$ = 0.1 BV; $h_{bed}$ = 72.5 cm; for other conditions, see caption of Fig. 1.

Figure A2. Signal from online conductivity detector during cyclic lignin separation runs. Lines: solid, soda BL; dashed, kraft BL. Colors: black, 1st cycle; blue, 20th cycle; red, 35th cycle. For other details, see caption to Fig. 4.

Figure A3. Sephadex-G10 and Cellufine GH-25 after six HA–NaOH separation runs.

Figure A4. Signal from online conductivity detector during cyclic NaOH separation runs. Lines: solid, soda BL; dashed, kraft BL. Colors: black, 1st cycle; blue, 12th cycle; red, 24th cycle. For other details, see caption to Fig. 5.

**Figure1**

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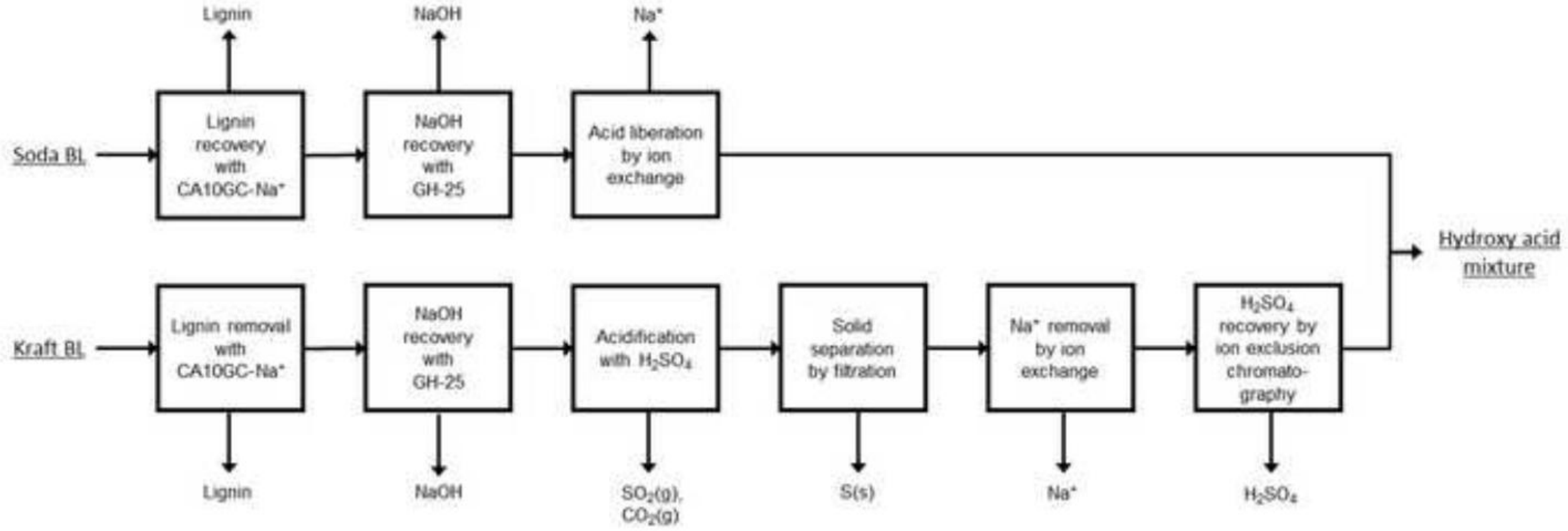

**Figure2**

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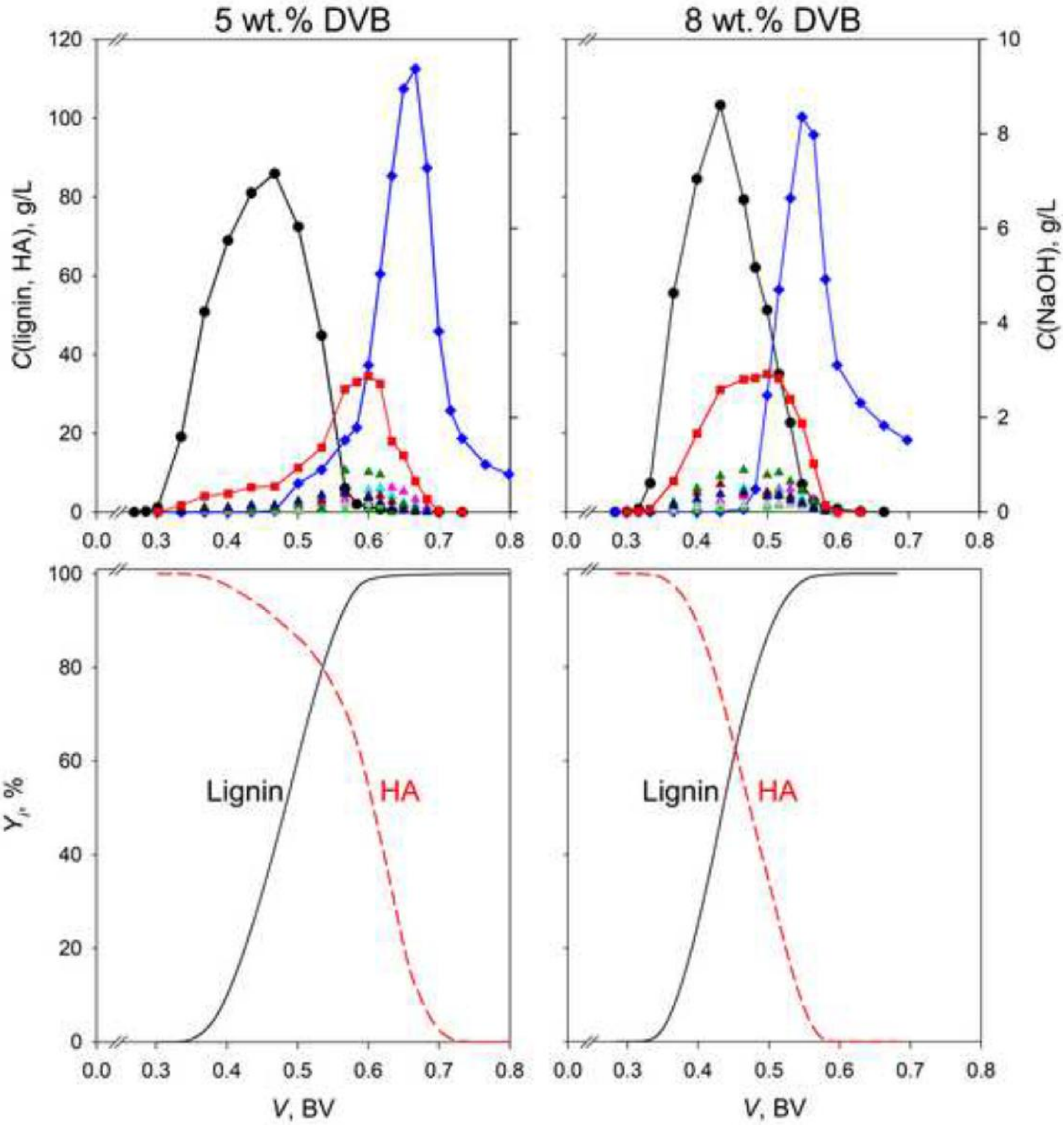
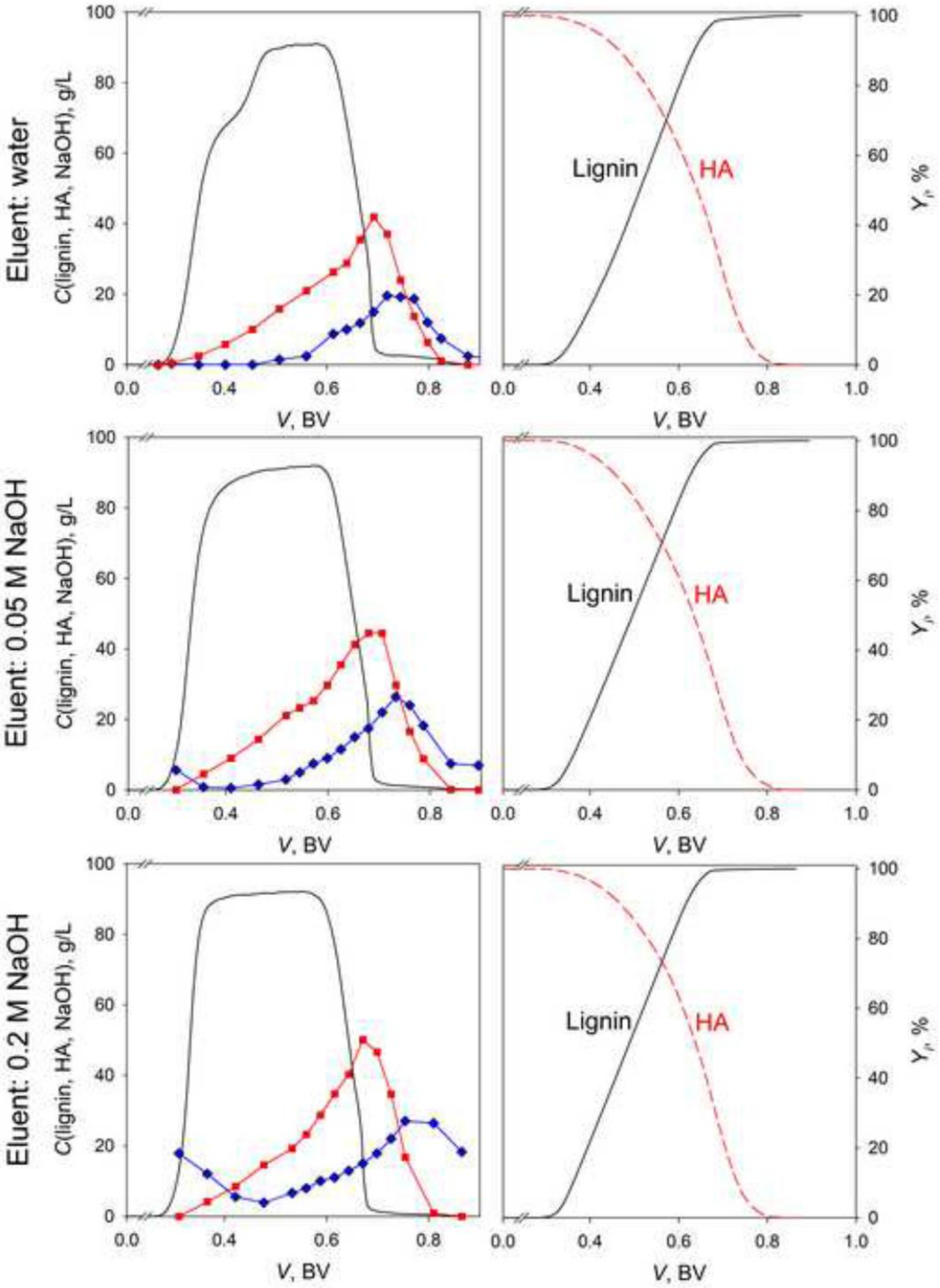


Figure3



Eluent: water
Eluent: 0.05 M NaOH
Eluent: 0.2 M NaOH
C(lignin, HA, NaOH), g/L
0
20
40
60
80
100
V, BV
0.0
0.4
0.6
0.8
1.0
Y_i, %
Lignin
HA

**Figure4**

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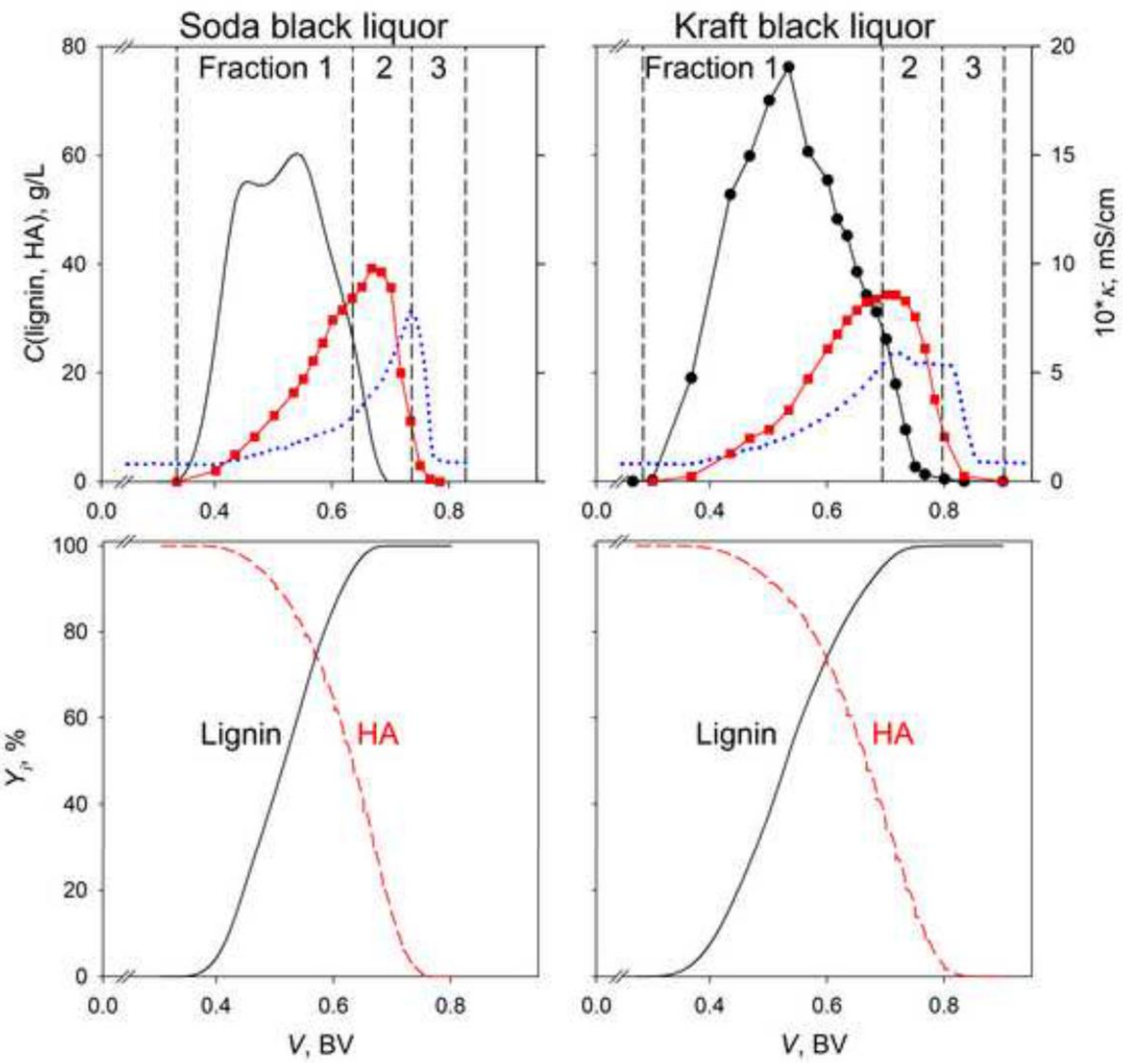

Figure5

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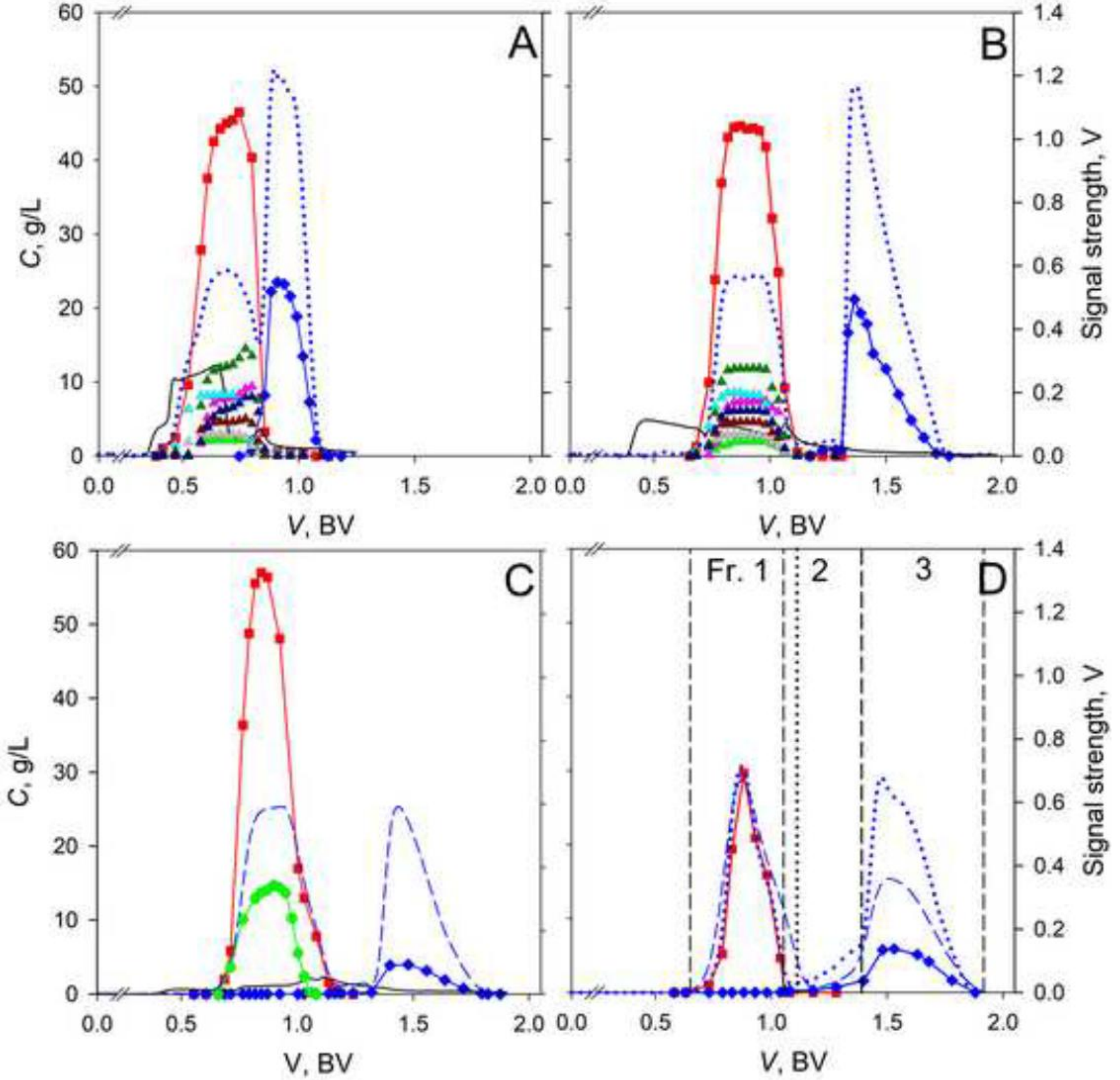

**Figure6**

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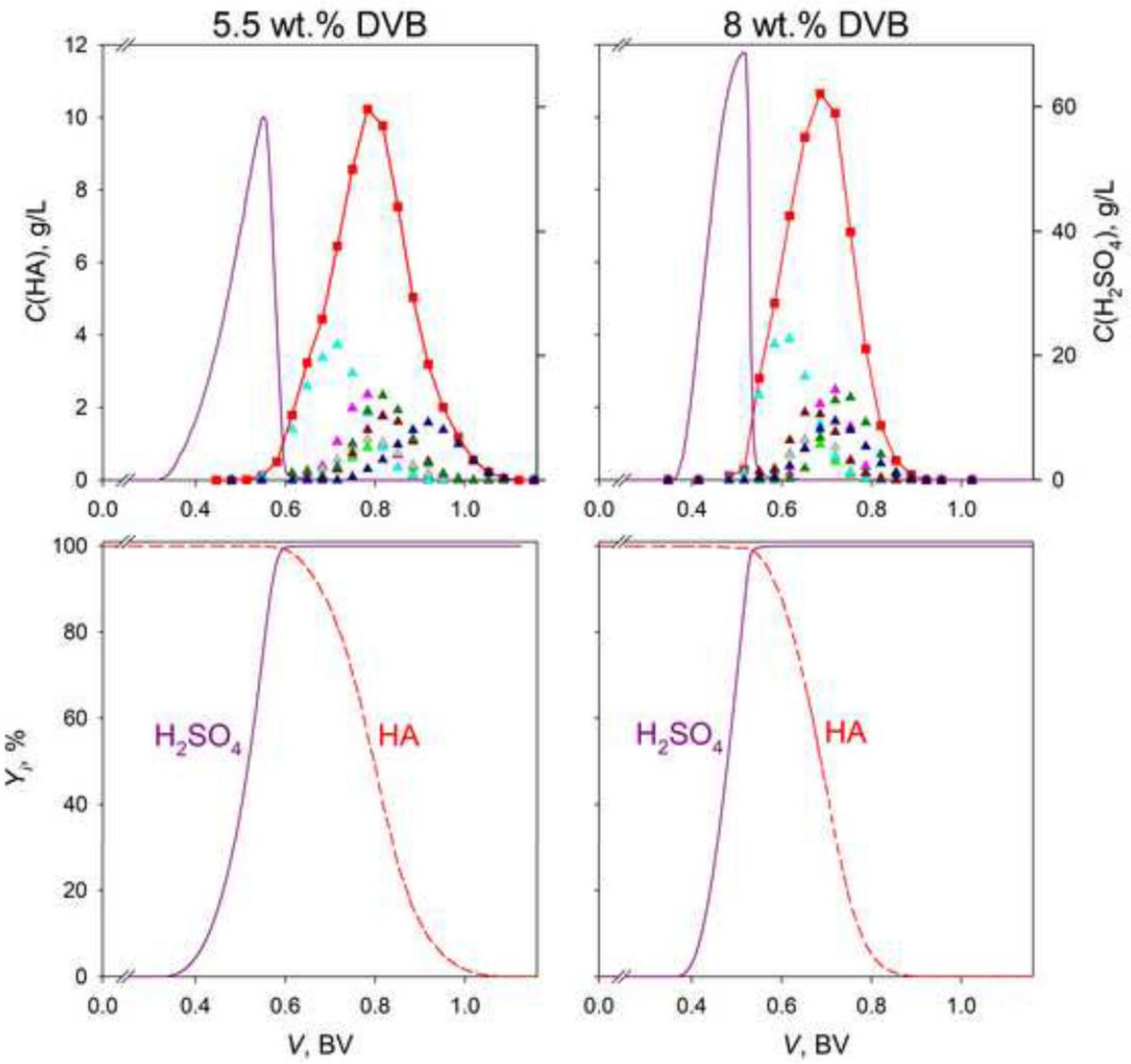
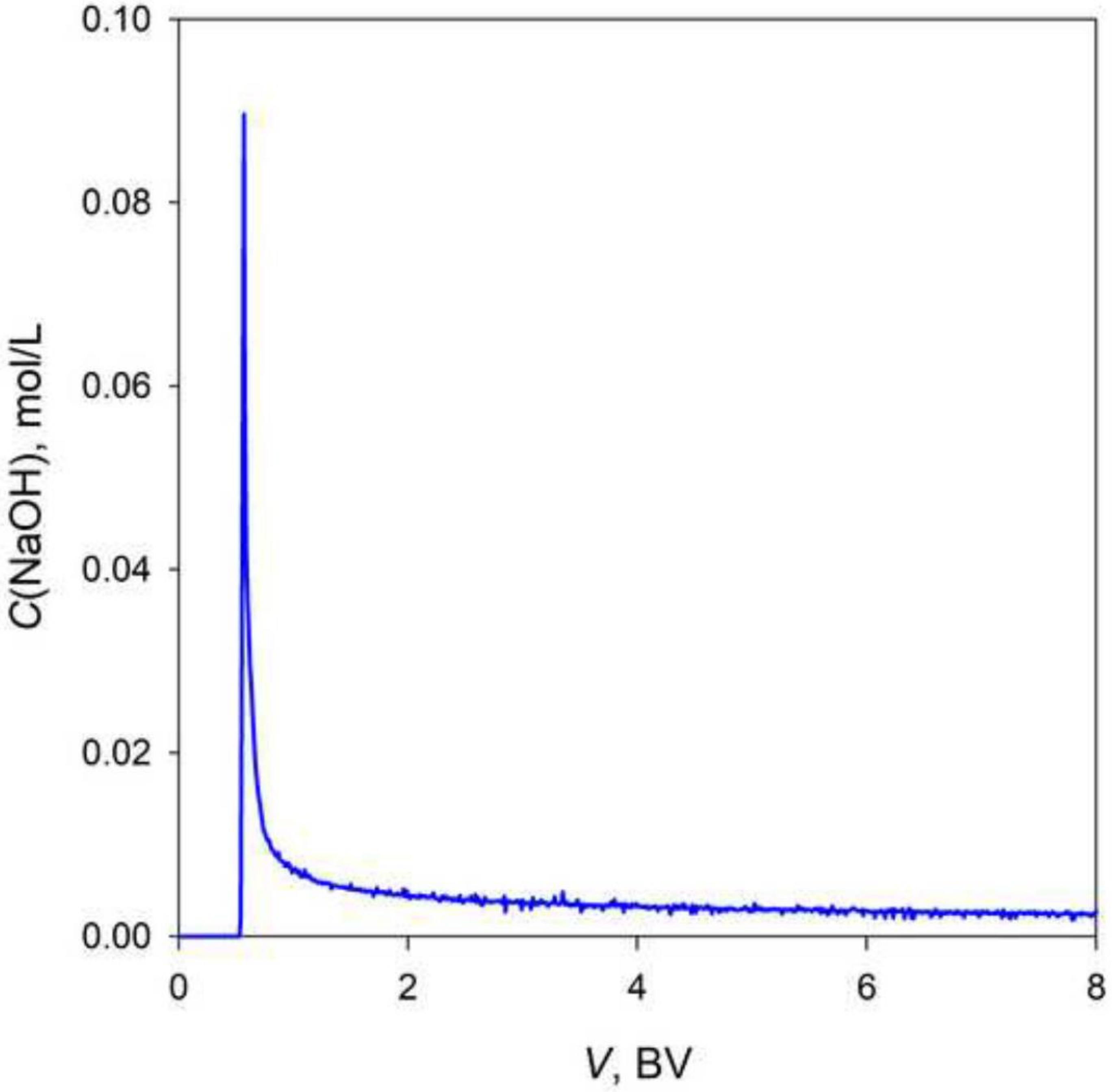


FigureA1



FigureA2

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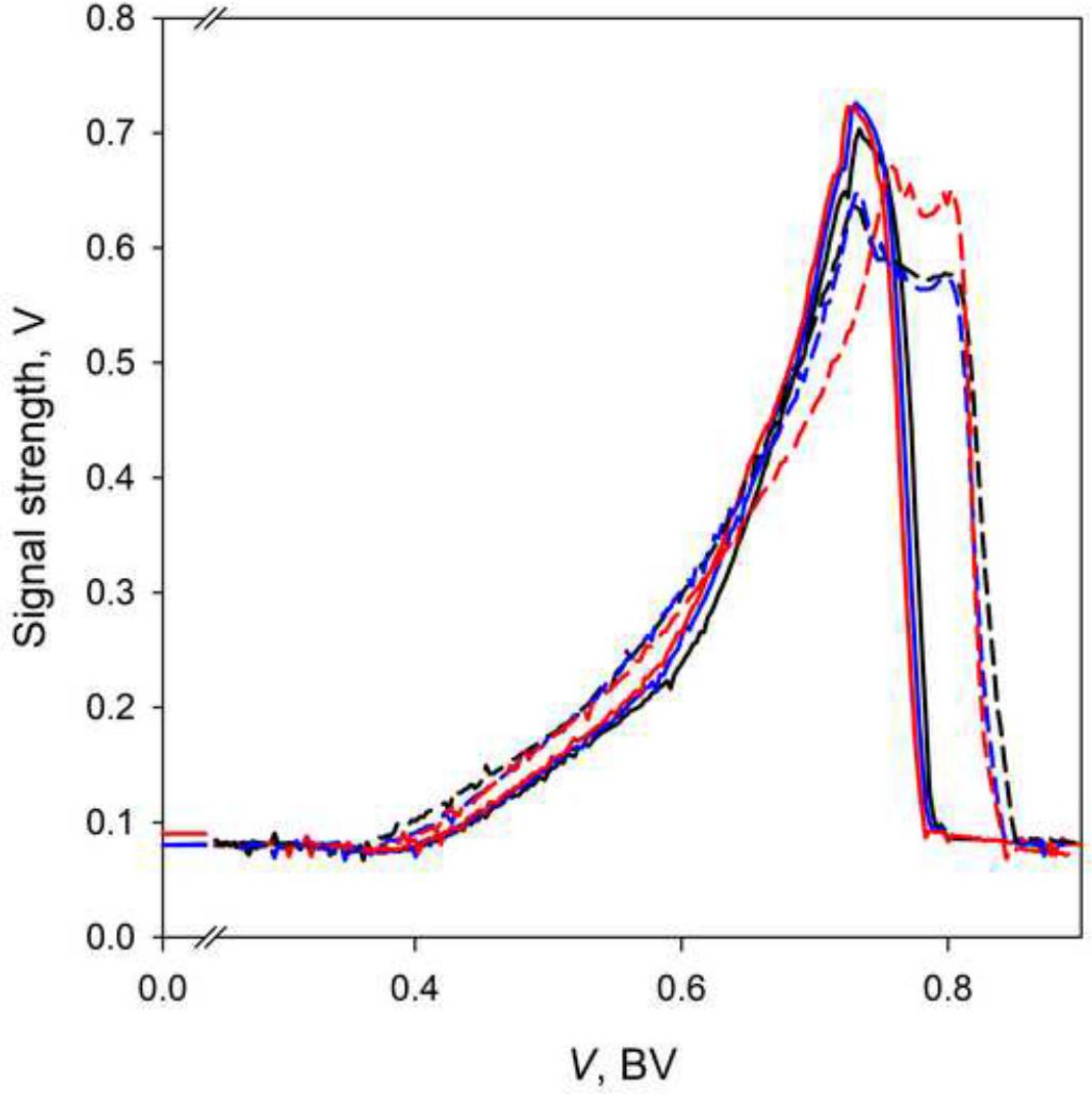
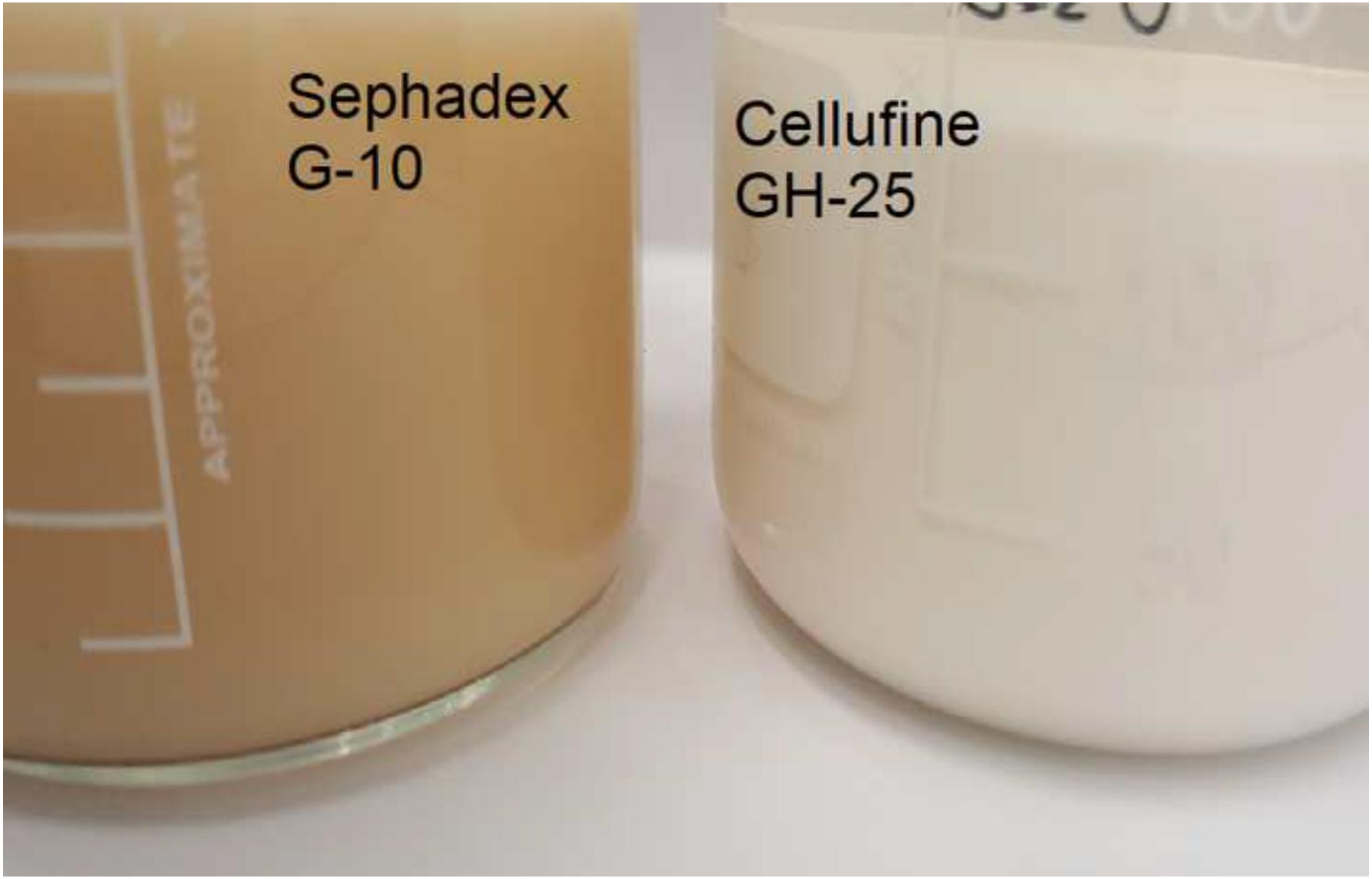


FigureA3



**FigureA4**

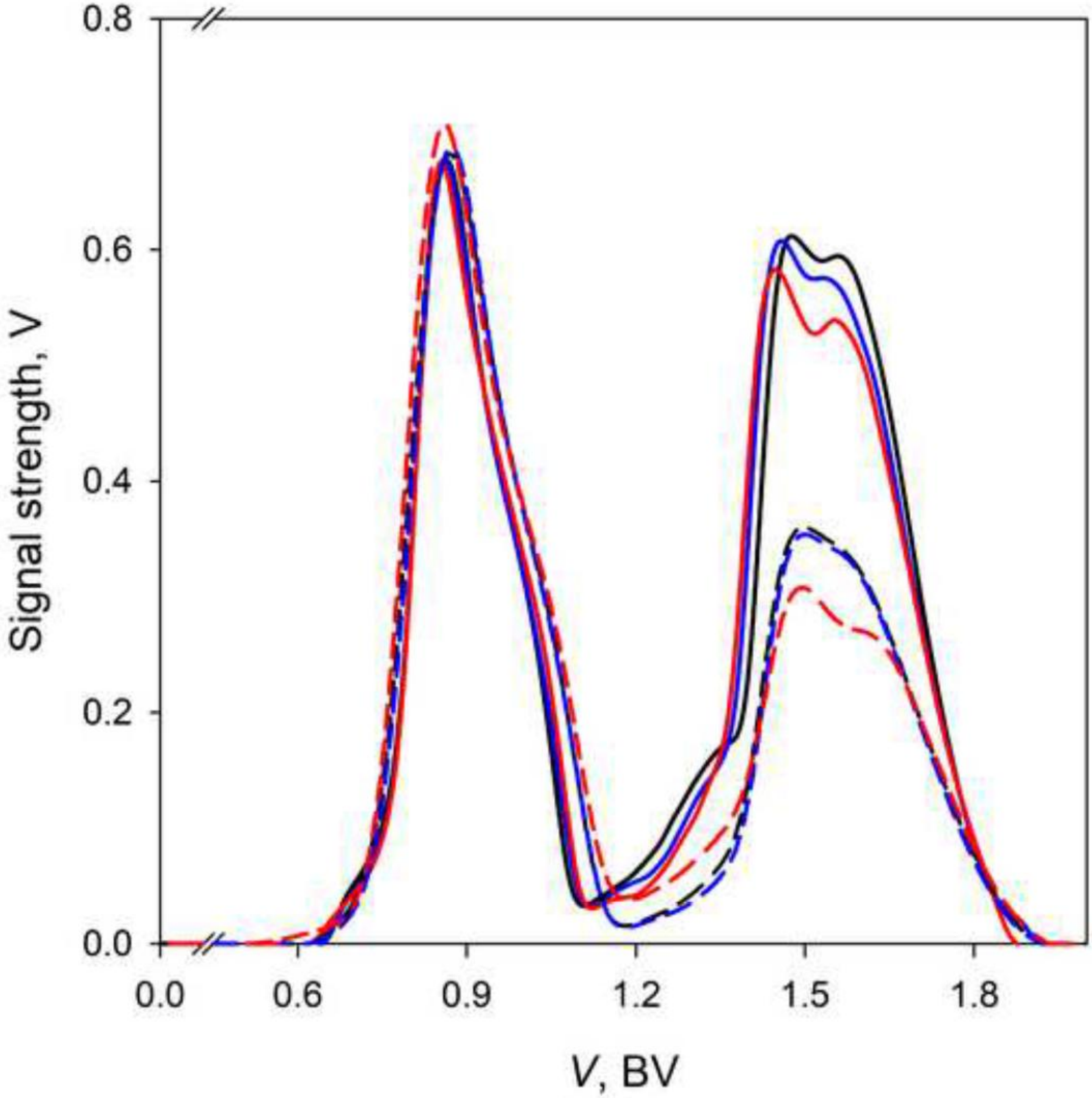


Table 1. Compositions (HAs, lignin, and pH) of the native BLs and the fractions collected during the HA recovery.

| Solution | Concentration, g/L | | | | | | | | | | pH, - |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Lignin | GISA | XISA | Glycolic acid | Lactic acid | 2,5-DHPA | 2-HBA | Formic acid | Acetic acid | Tot. acids | |
| SODA BL | | | | | | | | | | | |
| Native | 113.87 | 12.23 | 3.98 | 2.05 | 6.38 | 3.19 | 6.17 | 7.42 | 16.41 | 57.83 | 13.20 |
| *Lignin separation* | | | | | | | | | | | |
| Frac. 1 (lignin)* | 51.87 | 2.17 | 0.76 | 0.19 | 1.29 | 0.83 | 1.42 | 0.83 | 3.44 | 10.93 | 11.90 |
| Frac. 2 (HA)* | 14.68 | 6.86 | 2.33 | 1.28 | 3.52 | 1.50 | 0.12 | 4.80 | 9.04 | 29.46 | 13.20 |
| Frac. 3 (HA)* | 0.19 | 1.12 | 0.42 | 1.04 | 0.42 | 0.00 | 0.00 | 2.26 | 0.66 | 5.91 | 13.30 |
| *NaOH separation* | | | | | | | | | | | |
| Frac. 1 (HA)** | 2.56 | 4.12 | 1.10 | 0.66 | 1.86 | 0.76 | 1.50 | 2.37 | 4.54 | 16.91 | 8.70 |
| *Acid liberation* | | | | | | | | | | | |
| HA fraction | n.a. | 3.95 | 1.05 | 0.60 | 1.80 | 0.72 | 1.50 | 2.25 | 4.40 | 16.27 | 1.40 |
| KRAFT BL | | | | | | | | | | | |
| Native | 147.04 | 8.90 | 2.90 | 1.32 | 5.43 | 7.81 | 5.49 | 7.07 | 16.29 | 55.23 | 13.00 |
| *Lignin separation* | | | | | | | | | | | |
| Frac. 1(lignin)* | 55.05 | 1.92 | 0.65 | 0.11 | 1.37 | 1.29 | 1.43 | 2.52 | 4.08 | 13.37 | 11.80 |
| Frac. 2 (HA)* | 8.60 | 3.70 | 1.39 | 1.08 | 2.25 | 1.99 | 1.44 | 7.28 | 6.29 | 25.42 | 11.30 |
| Frac. 3 (HA)* | 0.07 | 0.31 | 0.12 | 0.18 | 0.17 | 0.64 | 0.00 | 0.59 | 0.42 | 2.44 | 12.50 |
| *NaOH separation* | | | | | | | | | | | |
| Frac 1 (HA)** | 2.12 | 2.45 | 0.92 | 0.71 | 1.49 | 1.32 | 0.95 | 4.81 | 4.16 | 16.81 | 9.80 |
| *Final purification* | | | | | | | | | | | |
| HA frac. before IEC*** | n.a. | 6.00 | 1.99 | 1.39 | 2.58 | 0.95 | 2.71 | 2.85 | 3.33 | 21.81 | 0.20 |
| HA frac. after IEC | n.a. | 1.08 | 0.39 | 0.29 | 0.53 | 0.20 | 0.56 | 0.59 | 0.67 | 4.32 | 1.20 |

* See Fig. 4.

** See Fig. 5.

*** Fraction concentrated by evaporation under reduced pressure after removal of $Na^+$ ions with CS11GC resin in $H^+$ form.

Table 2. Main properties of the separation materials used in this study. Abbreviations: SAC = strong cation exchange resin; WAC = weak cation exchange resin; SEC = size exclusion resin.

| Separation material | Manufacturer | Matrix | Functional group | DVB/cut-off | Particle size, µm |
|---|---|---|---|---|---|
| CS11GC (SAC) | Finex/Johnson-Matthey | PS-DVB | Sulfonic acid | 5.5 wt.% DVB | 280 |
| CS12GC (SAC) | Finex/Johnson-Matthey | PS-DVB | Sulfonic acid | 6.0 wt.% DVB | 280 |
| CS16GC (SAC) | Finex/Johnson-Matthey | PS-DVB | Sulfonic acid | 8.0 wt.% DVB | 280 |
| CA10GC (WAC) | Finex/Johnson-Matthey | Acrylate-DVB | Carboxylic acid | 5.0 wt.% DVB | 300 |
| CA16GC (WAC) | Finex/Johnson-Matthey | Acrylate-DVB | Carboxylic acid | 8.0 wt.% DVB | 300 |
| Sephadex G-10 (SEC) | GE Healthcare | Cross-linked dextran | – | cut-off 700 g/mol | 55–165 |
| Cellufine GH-25 (SEC) | JNC Corporation | Cross-linked cellulose | – | cut-off 3000 g/mol | 40–130 |