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# Chromatographic separation of wood model constituents—Mathematical modeling and parameter estimation

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## ABSTRACT

A mathematical model of the hydrophobic adsorption chromatographic separation of wood model constituents has been developed. Veratryl alcohol was selected to illustrate a lignin molecule and salicin was selected to illustrate a lignin–carbohydrate complex. A variety of available experimental methods in combination with parameter fitting was used to estimate the parameters of packed bed porosity, axial dispersion, film mass transfer, diffusivities and adsorption equilibria with a phenylic silica stationary phase. The model was verified to simulate the separation to within an accuracy of 95%. The model was, however, unable to predict the phenomenon of elution curve *fronting*, caused by the channeling of the packed bed.

*Keywords:* Wood constituents; Chromatography; Parameter estimation; Modeling; Biorefinery; Lignin-carbohydrate complex

## 1. Introduction

The dominant species of the large Scandinavian forests is Norway spruce (*Picea abies*), and it is presently utilized in traditional applications, such as paper products, sawn timber, and dissolving pulps. However, major changes in consumer patterns and the need for renewable resources to replace petroleum-based material have led to the need for novel products and processes based on biomass, such as spruce. The development of such products requires different wood components in relatively pure forms. At the Wallenberg Wood Science Center (WWSC), methods for the pretreatment and extraction of wood components have been developed (Azhar et al., 2011). Therefore, in biorefinery concepts, the selective liquid-phase fractionation of different wood components is highly interesting – a process which chromatographic techniques are suitable for.

A number of new material applications of wood polymers have been described and are under development. Examples of uses are hydrogels (Lindblad et al., 2001) and gas barrier films for food packaging produced both with the hardwood-abundant xylan (Grondahl et al., 2004) and softwood-abundant galactoglucomannans (GGM) (Hartman et al., 2006). Besides the hemicelluloses and lignin there are investigations into the applications of lignin–carbohydrate complexes (LCCs). Uraki et al. (2006) have investigated the amphiphilic properties of LCCs and has suggested their potential use as a polymeric surfactant or as a substance carrier in pharmaceuticals. The method presented by Oinonen et al. (2011), where LCC polymers are cross linked between aromatic side groups by enzymatic synthesis, has shown the potential of producing a wide selection of bio-polymer-based materials for a wide range of applications, by controlling the frequency of cross linking.

The development of new materials and other uses of the bio-polymer feed stock are sufficient to motivate the investigation of the full production line. The bottle neck of actual production of such material at this point is obtaining bio-polymers in pure form, regarding molecular weight and the number of aromatic side groups. Today, the separation of these constituents is mainly performed by means of membrane-separation (Persson et al., 2010; Leppänen et al., 2010) and/or precipitation (Lawoko et al., 2006). The obvious drawback of both these processes is their limited specificity, and that the precipitative means might also have a chemical modification

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effect on the constituents. Westerberg et al. (2012) and Takahashi et al. (1982) have investigated the chromatographic separation of wood constituents. Takahashi et al. (1982) used hydrophobic interaction chromatography (HIC) on an aromatic sorbent to separate LCCs and found that the order of elution was determined by the relative amount of aromatic contents. Westerberg et al. (2012) combined cross flow filtration and two stages of hydrophobic adsorption chromatography to separate hot-water-extracted spruce into lignin, LCCs and hemicelluloses. The method described by Westerberg et al. (2012) has the advantage that all three fractions are treated as products, while the comparable methods of filtration and precipitation only aim for one product fraction and thus have large losses in the process. The method used by Westerberg et al. (2012) also showed limitations. The exact composition of the products could not be determined due to the complexity of the inlet stream, and as a consequence, the factors influencing the separation could not be evaluated.

The present work aims to evaluate the factors limiting the chromatographic separation of wood constituents with a simplified model system. Two commercially available molecules were selected as models of lignin and LCC. The sorbent used was a granular silica with phenylic ligands, which have shown a specific affinity for lignin molecules, with a particle diameter suitable for preparative-scale separation with regard to pressure drop. The physical parameters describing the course of migration of an analyte in hydrophobic adsorption chromatography were estimated in high-pressure liquid chromatography (HPLC) experiments combined with mathematical modelling. The findings are intended to be used to estimate the optimal operating conditions for and the restrictions on a preparative unit operation for the chromatographic separation of wood constituents.

## 2. Materials and experimental setup

### 2.1. Experimental setup

All breakthrough and pulse injection experiments were performed in a high performance liquid chromatography (HPLC) setup consisting of a (Waters, Milliford) model 600 gradient pump, an inline degasser, a model 717 autosampler, and an external column temperature controller. For detection a 2487 dual wavelength detector and a 2424 evaporative light scattering detector (ELSD) were used.

### 2.2. Model compounds and solvents

The model system in this work is intended to resemble the separated species found by Westerberg et al. (2012) to as great an extent as possible. To be able to distinguish the effect of various parameters, the model compounds must be in pure fractions. Obtaining hemicelluloses with a mono dispersed degree of polymerization (DP) and with an exact number of aromatic side groups is difficult, especially if a higher DP is desired. In order to overcome this obstacle, the effect of DP on the retention mechanism was neglected and instead focus was on the aromatic/hydrophobic character of the model compounds.

Salicin is a flavanoid and was chosen as a model compound due to its similarities to LCCs: a sugar monomer with an aromatic side group. Veratryl alcohol was used as a model compound of lignin in this study. Veratryl alcohol is soluble in water and methanol, and has a more strongly hydrophobic character than salicin. Westerberg et al. (2012) observed that acetonitrile was the best suited organic solvent, while the model compounds used in this work displayed higher solubility in methanol. Therefore, methanol was used throughout the work as an organic modifier instead of acetonitrile.

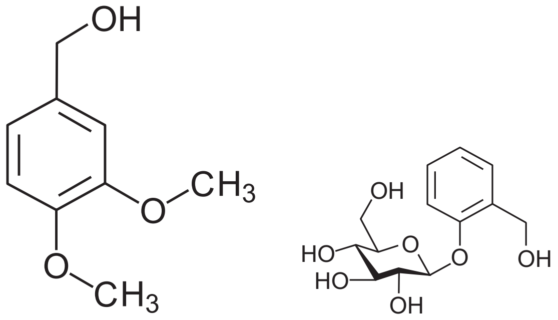

**Fig. 1 – Left: veratryl alcohol, right: salicin.**

Milli-Q water was produced in the lab using a Millipore 50 filter setup. All other solvents were of analytical grade. Analytical grade Blue dextran (Mw 2000 kDa), cellubiose, 3,4-Dimethoxybenzyl alcohol (veratryl alcohol) and salicin were obtained from Sigma. The chemical structures of the compounds are illustrated in Fig. 1.

### 2.3. Resins and columns

Westerberg et al. (2012) used both a polymeric hydrophobic resin consisting of large granules (0.3 mm), and a hydrophobic resin of phenylic silica consisting of spherical particles in μm dimensions. In this work, a compromise was made between the high specificity, low transport resistance and the high hydrophobicity of the phenylic silica, which has a higher price, and the large dimension of the polymeric sorbent, which has a lower price. The advantage of using large particle sorbents is a reduced pressure drop that allows a higher production rate in preparative separation.

Granular silica was obtained from Sorbent Technologies (Norcross, GA, USA) with and without phenyl ligands. Table 1 lists the characteristics of the silica that had been measured by the supplier. A 4.6 mm × 250 mm column was loaded with approximately 2.84 g dry resin. A vibratory device was used to assist close particle packing. The column had been washed in water and acetone in steps including a sonic bath and using a pipe cleaner. The frits of the column were washed in 0.5 M alkali at an elevated temperature (90 °C) to remove any organic contaminants.

A second column of the dimensions 4.6 mm × 75 mm was prepared using the same procedure with about 0.867 g of the same resin.

The particle size distribution was measured with laser diffraction using a Malvern Instruments Mastersizer 2000.

**Table 1 – Granular silica characteristics.**

| Item | Lot data | Unit |
|---|---|---|
| Carbon content | 16.5 | wt% |
| Surface area | 528 | $m^2/g$ |
| Pore volume | 73 | vol% |
| Particle size Avg [38–75 μm] | 91.7 | wt% |

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