

AN2301: AF4-MALS as a Promising Tool for Industrial Lignosulfonate Analysis

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Summary

Lignin is a renewable compound with great commercial potential. A cheap starting material which is readily available as a byproduct of common chemical pulping processes, it can replace fossil-based raw materials in a variety of products. Its conversion into value-added products promises huge economic benefits.

Currently numerous research institutions, in collaboration with industrial companies, are evaluating lignin utilization pathways. With new production strategies, the demand for suitable analytical procedures is growing rapidly.

Standard lignin analysis can be impeded due to contamination of the recovered material with various low molecular weight impurities. Thus, the search for robust, simplified means to analyze lignin is a topic of great interest. The present work represents an original approach to measure the molar mass of technical lignosulfonates by means of AF4-MALS. The method does not require labor-intensive sample purification steps; it is fast and easy to implement in industrial laboratories. AF4-MALS provides reliable data in a short time and is therefore highly attractive from an economical point of view.

Introduction

The pulp and paper industry utilizes various chemical methods to separate cellulose from lignin. As a result, large quantities of by-products with different characteristics are produced. Part of the separation and purification process involves the removal of lignin from the spent industrial liquor. The chemical conversion of lignin to other products holds great economic promise, especially when compared with its conventional conversion to fuel. The total product value is expected to increase from 0.18 US \$/kg to 1.08 US \$/kg [1].

Lignosulfonate (LS) obtained during sulphite pulping only accounts for around 10% of all lignin production, yet it is the most widely utilized form of lignin with respect to value-added products [2]. The broad spectrum of commercial applications originates from its structural characteristics, in particular from the presence of sulfonate groups, which ensure its solubility in water and impart unique colloidal properties [3].



Photo: https://en.wikipedia.org/wiki/Black_liquor.

The functional properties of LS are tightly linked to molar mass, and so establishing a method for rapid and accurate molar mass analysis is imperative. Gel permeation chromatography (GPC) is the traditional approach for polymer molar mass characterization. However, the presence of various impurities in sulphite spent liquor (SSL), such as residual inorganic salts and low molecular weight organic compounds including sugar monomers, sugar oligomers and phenolic extractives, presents a major risk of damage to the GPC column.

The total fraction of these compounds varies but usually accounts for around 50% of the total mass of SSL [4, 5].

Hence, analysis by GPC requires significant and costly purification of LS prior to analysis. The removal of these impurities by ultrafiltration or adsorption techniques does allow for sample analysis by GPC, but these processes are costly in terms of equipment, energy and times.

Asymmetric flow field-flow fractionation (AF4) coupled with multi-angle light scattering (MALS) offers an alternative approach to LS analysis which combines aspects of purification and analytical separation. In the present study we have tested AF4-MALS as an alternative approach for LS molar mass analysis. Separation in a channel minimizes the risk of adverse sample interaction with the column's stationary phase, and therefore may lead to a greatly simplified sample preparation procedure, which is easy to implement directly in industrial laboratories.

Materials and Methods

Lignosulfonate samples were received from industrial partners as unpurified liquor from commercial pulping processes. The following setup was applied for AF4 analysis: Dionex DG-1210 online degasser; Agilent Technologies 1260 Infinity pump; Agilent Technologies G1367C auto sampler; Wyatt Technology Eclipse® AF4 separation system; Detectors: Knauer 101 UV detector at 280 nm, Wyatt Technology DAWN®, ($\lambda = 658$ nm laser) multi-angle light scattering detector with band pass filters installed on all even numbered detectors and Wyatt Optilab® T-rEX RI detector. Separation was accomplished in a long separation channel (275 mm long) with a 350 μm spacer and a 5 kDa regenerated cellulose membrane (Millipore). The mobile phase was 0.1M NaNO_3 (+250 ppm NaN_3).

To ensure proper separation, a gradual decrease of the cross-flow for 20 min from 4 to 0.1 mL/min was applied followed by a 10 min channel flush with a constant cross-flow of 0.1 mL/min. A washing step without cross-flow was performed for 5 min to ensure complete sample elution from the channel. Other system parameters: 1 mL/min detector flow; 0.2 mL/min injection flow; 5 min total focusing time (including 2 min injection); 55 min total run time. Data evaluation was performed with ASTRA® 6.1 software (Wyatt Technology).

Results and Discussion

In-line purification of LS was accomplished in the AF4 separation channel, depicted schematically in Figure 1. During the focusing step, solvent enters the channel from both ends and exits via the membrane and frit. Low-molecular-weight impurities such as salts and sugars permeate the 5kDa-cutoff membrane and are eliminated. In the elution step, the balance between cross-flow, diffusion and parabolic channel flow separates the biopolymers by size as they are swept towards the outlet and downstream detectors.

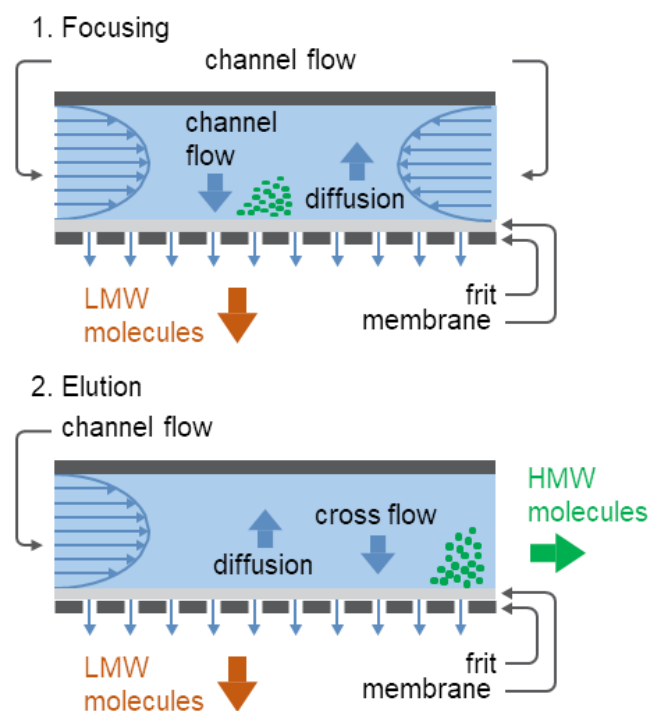


Figure 1. In AF4 separation of crude lignosulfonates, low-molecular-weight molecules such as salts and sugars permeate through the membrane and are eliminated during the focusing step (top), while high-molecular-weight molecules (the lignosulfonates) are separated by size and elute towards the UV, MALS and RI detectors during elution (bottom).

An example of the peak resolution for an unpurified industrial LS sample obtained by AF4-MALS is presented in Figure 2. The system successfully separated the bulk lignosulfonate from inorganic and low molecular weight admixtures, which penetrated the membrane and were removed from the solution in the course of traversing the AF4 channel.

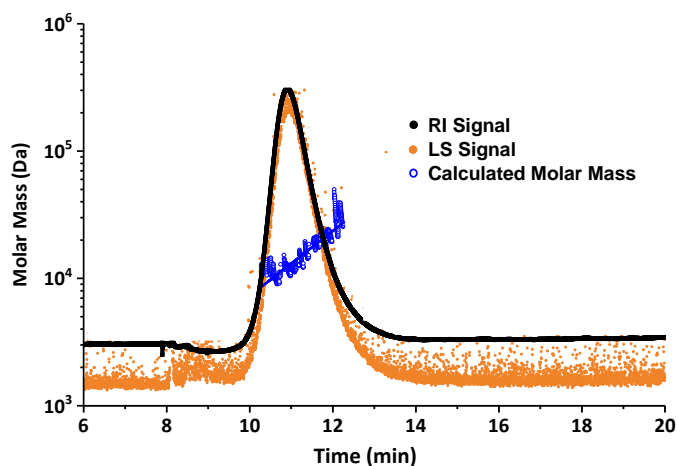


Figure 2. The elution fractogram of an industrial lignosulfonate (LS) sample obtained by AF4-MALS. Molar mass values (blue dots) are calculated at each elution volume by MALS-RI analysis.

Dealing with fluorescence

Lignins are known to exhibit fluorescence which may affect light scattering measurements and result in overestimated molar mass values [6]. However, band pass filters placed on the MALS detectors when analyzing LS sufficiently eliminate the fluorescence yield while transmitting scattered photons, providing reliable data for LS molar mass determination [7, 8]. To block fluorescent photons in the measured light scattering signal, band pass filters were installed on the even-numbered detectors.

Data from odd-numbered detectors (without filters) were used for comparison with those photodiodes having fluorescence filters. The data comparison on a Zimm plot demonstrated clear differences in the values obtained, as shown in (Figure 3). The light scattering signals and therefore the calculated molar masses were constantly higher when filters were not applied than with filters in place, as expected.

Molar mass distributions

An example of a molecular weight distribution of the industrial LS is presented in Figure 4. The smooth distribution obtained shows no indication of any significant quantity of low molecular weight impurities, additionally confirming efficient sample purification during the separation step.

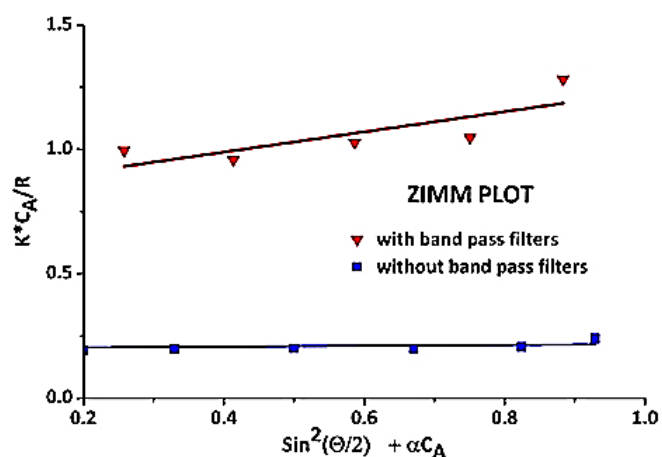


Figure 3. Comparison of Zimm plots obtained with and without band pass filters.

Previously, the investigations of isolated fractions of industrial LS were performed by means of GPC with conventional and universal calibration [9], as well as light scattering techniques [7]. The molar mass values obtained by these methods are in good correlation with the data obtained by light scattering with AF4.

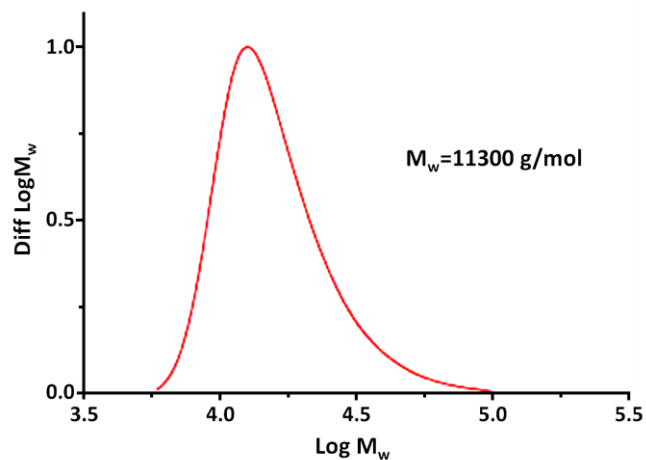


Figure 4. Molecular weight distribution of lignosulfonates obtained by AF4-MALS. No evidence for low-molecular-weight impurities is present.

Conclusions

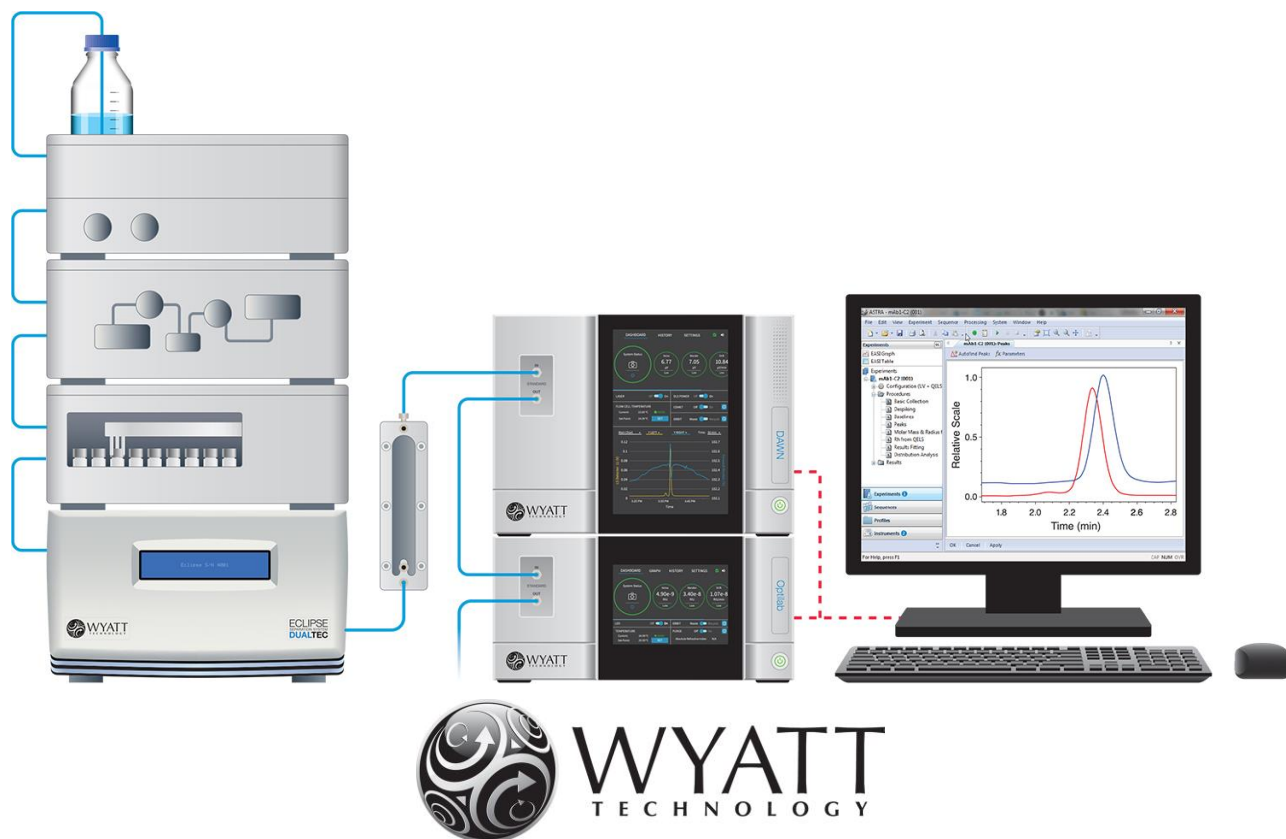
In this application note, we present a novel approach to analyze the molar mass of water-soluble lignosulfonate by means of AF4-MALS. The method allows the direct injection of non-purified industrial samples and provides accurate and precise data about LS molar mass distribution. Fluorescence filters were used to ensure accurate light scattering measurements.

The AF4-MALS method presents a promising alternative to standard GPC analysis. AF4-MALS is a simple, fast technique that eliminates the tedious sample preparation steps required for GPC analysis of lignosulfonates. This method is easy to establish directly at the production site, with great potential for reducing the overall analysis cost.

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