



Lignin: Recent advances and emerging applications



Magnus Norgren*, Håkan Edlund*

Fibre Science and Communication Network (FSCN), Mid Sweden University, SE-851 70 Sundsvall, Sweden

ARTICLE INFO

Article history:

Received 12 May 2014

Received in revised form 20 August 2014

Accepted 24 August 2014

Available online 4 September 2014

Keywords:

Lignin

Self-aggregation

Colloidal stability

Lignin surface chemistry

Carbon fibers

ABSTRACT

In this paper, we focus on the recent advances on the physical chemistry of lignin. Emerging trends of incorporating lignin in promising future applications such as controlled release, saccharification of lignocelluloses, bioplastics, composites, nanoparticles, adsorbents and dispersants, in electro-chemical applications and carbon fibers, are also reviewed. We briefly describe the complexity of the lignin structure that influences the solution behavior, both as a macromolecule and a colloid, as well as the potential of being a renewable precursor in the development of high-value applications. Special attention is paid on summarizing the present knowledge on lignin colloidal stability and surface chemistry.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Lignin is the second most abundant natural polymer after cellulose, and it is mainly found in the cell wall of woody tree species. The main source of lignin readily available for use on a larger scale comes from spent pulping liquors and chemical liberation of wood fibers from the pulp and paper industries, and the global production of lignin-based materials and chemicals exceeds 50 million t per annum. Lignin has not yet been converted into high-value products on a large-scale and today lignin is mainly used for energy recovery at the pulp mills. However, as the price of oil increases, the demand for sustainable and renewable resources consequently increases. A huge opportunity for securing vast quantities of this raw material at economically viable rates is from the pulp and paper industry. This could be seen in light of the ongoing discussion about the development of biorefineries and the integration of biomass conversion processes to produce power, heat, biofuels, materials and value-added chemicals from biomass [1–3].

The ambition in the present paper has been to focus on and summarize the recent advances in surface and colloid chemistry of lignin, as well as the emerging trends of incorporating lignin in new applications. In Section 2, we present the lignin macromolecule as a biomaterial resource and the possibilities and constraints in colloidal chemistry. Section 3 is describing the self-association of lignin in solution into aggregates and particles, as well as the solid lignin surface chemistry. In Section 4, some ongoing development of lignin into applications of higher values is discussed. The paper is concluded in Section 5.

2. Lignin molecule architecture

Lignin is a highly branched and amorphous biomacromolecule with variable composition dependent on the plant source [4,5]. Lignin is unique as a plant cell wall biopolymer due to its heterogeneity, lack of defined primary structure and aromatic functionality. However, lignin can be rationalized as the polymerized product of the three basic phenylpropane monomers as repeating units known collectively as “monolignols”: *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.

These three monolignols account for the majority of the repeating units making up the lignin polymer molecules; however, other lignols may be present in smaller quantities. The proportion of different monomers in lignin varies considerably depending upon the type of plant material and there are many possible inter-connecting patterns between individual units giving an additional complexity to the final molecule. A representation of molecular fragment kraft lignin, the most common technical lignin, illustrating different important linkages is shown in Fig. 1.

It must be noticed that naturally occurring lignin in its unaltered form is still beyond the realms of possibility to directly study. The isolation of lignin from native sources results in chemical modification of the three-dimensional network through the cleavage of bonds between different lignin monomers, or the covalent attachments to polysaccharides, creating differently sized lignin fragments. However, numerous analyses of different isolated lignin samples over the past decades have led to extensive knowledge of the prevalence of different covalent linkages.

As mentioned earlier, the main source of lignin readily available for use on a larger scale comes from spent pulping liquors after chemical liberation of wood fibers. By far, the most important pulping methods

* Corresponding authors.

E-mail addresses: magnus.norgren@miun.se (M. Norgren), hakan.edlund@miun.se (H. Edlund).

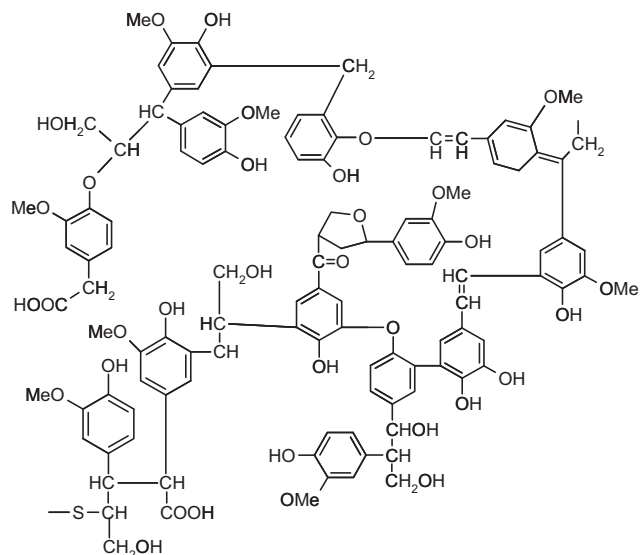


Fig. 1. A structural model of a technical lignin fragment (kraft lignin) showing examples of important intra-molecular linkages [6].

are kraft and sulfite cooking. The content of the most important functional groups present in the lignin materials, such as the phenolic hydroxyl, carboxyl and sulfonate groups varies with the pulping process applied. Kraft lignin is usually isolated by precipitation that remains after cooking through acidification and protonation of phenolic groups. Depending on the pH value to which the spent liquor (black liquor) is acidified, a different composition and yield of the lignin is obtained. A hydrosoluble form of lignin that contains a large number of charged groups, the lignosulfonates, is prepared from the by-products of the sulfite pulping process where the lignins are sulphonated, degraded and solubilized. The organosolv process is a pulping process using aqueous organic solvents with the lignocellulosic biomass separating the lignin fragment via solubilization. The homogeneity of the organosolv processed lignin is higher than that of kraft lignins and lignosulfonates.

The weight-averaged molecular weight of the lignosulfonate polymers is typically in the range of 5–400 kDa compared to 1–5 kDa for the kraft lignin and 0.5–3 kDa for the organosolv lignin. The polydispersity for lignosulfonate and kraft lignin is high compared to the organosolv lignin. The watersoluble lignosulfonates are today, by far the most used types of technical lignin polymer and they are utilized in many low-value applications.

Still today, the available technical lignins are always by-products, and the properties of the lignin produced are, thus, substantially dependent on the core process that is mainly dedicated to pulp and paper production. A change is foreseen in the future that an increased and quality improved feedstock of raw material as lignin for biorefinery applications comes from different biorefinery processes.

3. Surface and colloid chemistry of lignin

One fundamental principle about polymers, in general, is that they dissolve spontaneously in a solvent if the free energy of mixing (ΔG_{mix}) is negative. The phase transition is mainly due to the increased configurational entropy of the polymer chain or, for charged polymers, an increase in counterion entropy due to dissociation. The dissociation of weakly acidic functional groups on colloid surfaces is also a prerequisite for sufficient electrostatic double layer repulsion, maintaining stability and reducing self-aggregation in colloidal systems. Knowledge of the surface chemistry of the material is, therefore, highly important. In this section, the abovementioned aspects related to lignin are reviewed and discussed based on the recent advances in lignin physical chemistry.

3.1. Self-association of lignin into aggregates and particles

For polyelectrolytes carrying weakly acidic groups, the dissociation and, thus, the solubility is governed by an increase of the hydroxide ion concentration. This is also the case for, e.g., kraft lignins. The polydispersity of kraft lignins will, of course, also introduce differences in the solubility and colloidal stability characteristics within the macromolecular distribution of the fragments. Numerous studies dealing with the colloidal behavior of kraft lignin derivatives have earlier been presented in the literature [5–19]. Some earlier studies highlighted the physico-chemical characterization of fractionated kraft lignin [20] and the fact that kraft lignin after depolymerization is solubilized mainly through dissociation of phenolic groups [21•]. For decades it has been known that in the presence of high concentrations of monovalent metal ion salts at pH neutral conditions, kraft lignin starts to coagulate and finally precipitate [5]. Moreover, by elevating the temperature in alkaline kraft lignin solutions the dissociation of phenolic groups decreases, sometimes to levels below the threshold of solvency [21•]. From the work of Lindström it was shown that colloidal kraft lignin, in conformity with other colloids, exhibits a strongly marked critical coagulation concentration of added electrolytes (CCC) [9]. More recently, Norgren et al. showed that the experimentally observed phase behavior of colloidal kraft lignin can be described reasonably well by a theoretical approach derived from the DLVO-theory [13•]. Moreover, the colloidal stability of lignin is also strongly affected by specific ions (Hofmeister effects) [15•], and these effects are especially pronounced for anions, e.g. sulfate [16].

During self-aggregation of colloidal particles into larger clusters due to Brownian motion, two well-defined limiting regimes of kinetics have been identified: the rapid diffusion-limited cluster (colloid)–cluster (colloid) aggregation (DLCA) forming loosely jointed and highly disordered structures and the reaction limited aggregation, RLCA, forming somewhat denser aggregates. It has further been shown that the described processes are universal in the sense that they are independent of the detailed nature of the colloid, if the essential physical interactions are the same [22]. The two mentioned classes of aggregation processes and their crossover behaviors are suggested to be sufficient to describe the complete range of kinetic aggregation [22–24]. The DLVO-theory has been a great source of understanding to RLCA. Additional stabilizing effects such as steric stabilization, might, however, also be contributing [25].

By monitoring the kinetics of kraft lignin aggregation using quasi-elastic light scattering (QELS) and through the analysis of the mass fractal dimensions of formed aggregates, Norgren et al. showed that also lignin aggregation follows RLCA and DLCA [14••]. Images of kraft lignin fractal clusters were also obtained by the Cryogenic Transmission Electron Microscopy (CryoTEM). The resemblance between the TEM picture of a DLCA fractal gold colloid cluster with fractal dimension $d_f = 1.75 \pm 0.05$ from Weitz et al. [26] in Fig. 2a, and the obtained DLCA lignin aggregate in Fig. 2b, $d_f \approx 1.9$, determined from quasi-elastic light scattering is striking [11].

Due to the chemical and physical heterogeneity of kraft lignin, self-aggregation in kraft lignin systems is complex. The presence of larger macromolecules is proposed to determine the onset [27]. Depending on the kraft lignin sample composition, nuclei either may be present from the beginning or may be formed due to changes in the solution conditions. Norgren et al. have proposed different modes of kraft lignin aggregation starting from macromolecular kraft lignin and finally reaching fractal kraft lignin clusters [14••]. It has also been shown that it is possible to stabilize kraft lignin and re-dissolve lignin aggregates if proper additives are introduced to the lignin solution [17•]. Introducing bile acid salts to aqueous kraft lignin solutions, new possibilities in controlling the colloidal stability at solution conditions that are otherwise detrimental for keeping kraft lignin soluble or dispersed, are achieved. The interaction between lignin and bile salts is discussed due to association at hydrophobic sites in the lignin structure, which

Download English Version:

<https://daneshyari.com/en/article/10375534>

Download Persian Version:

<https://daneshyari.com/article/10375534>

[Daneshyari.com](https://daneshyari.com)