Characterization of kraft lignin

Kraft lignin is nowadays available on a large scale, and consequently utilization of lignin for a number of different applications has gained large interest. The properties of lignin samples are to a great extent influenced by their chemical and molecular structure. This requires reliable and reproducible analytical methods for lignin characterization. The analytical tool providing greatest detail in such measurements is NMR spectroscopy.

We have identified three groups of properties that we need to analyse in order to describe a kraft lignin:

- Purity
- Molecular properties
- Thermal properties.

Purity includes content of lignin, moisture and various impurities (for example carbohydrates, extractives and inorganics). Molecular and thermal properties include molecular mass, functional groups, melting properties, etc.

Lignin is a heterogeneous biopolymer built up by phenylpropanoid units, with different functional groups, and connected by various inter-unit linkages. The structure and polymeric properties of lignins vary depending on origin, i.e. plant species, industrial processing as well as isolation and purification procedure. Technical lignins often contain impurities, that have to be taken into account from an analytical perspective.

By kraft lignin, in the present context, we mean solid matter consisting mainly of degraded lignin isolated from a kraft pulping process (e.g. isolated from a kraft black liquor), and containing more or less contaminants.

A list of analytical services related to lignin is appended.

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There are currently no standardized methods available for lignin samples. Almost all standards were developed for wood, pulp and paper, and may not be directly applicable to lignin samples. We have therefore prepared what we call our ‘Lignin Test Methods’ for lignin analysis. These methods are based on existing methods and ‘best practice’ for wood and pulp, and have been tested and, where necessary, adapted for lignin samples. Repeatability data have also been developed.

The ‘Lignin Test Methods’ can be ordered from our website http://www.innventia.com/en/Our-Ways-of-Working/For-your-labb/Biorefinery-Test-Methods

### Purity

**Lignin content**
We measure the content of acid-insoluble (Klason) and acid-soluble according to our Biorefinery Test Method L2, and deliver the results in mg per g dry sample. 2 g of sample is required.

**Carbohydrate composition**
We measure the carbohydrate content and composition according to our Biorefinery Test Method L2, and deliver the content of glucose, mannose, arabinose, xylose and galactose in mg per g dry sample. 2 g of sample is required.

**Ash content**
We measure the residue (ie. ash) on ignition at 525°C according to our Biorefinery Test Method L3, and deliver the results in percent ash per dry sample. 1 g of sample is required.

**Extractable matter**
We measure the petroleum ether extractable matter or hexane extractable matter (ie. extractives) according to our Biorefinery Test Method L4, and deliver the results in percent extractives per dry lignin sample. 2 g of sample is required.

**Metals/elements content**
A variety of different metals and elements may be measured using atomic emission spectroscopy (ICP-AES), for instance Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Ma, S and P according to our Biorefinery Test Method L5. We deliver the results in mg of each element per g dry sample. 2 g of sample is required.

**Sulfur and sulphate content**
Total sulfur is determined according to SCAN-CM 57 with Schöninger combustion and ion chromatography. Water extractable sulphate is determined according to ISO 9198 with ion chromatography.

**Chlorine and chloride content**
Total chlorine is determined according to SCAN-CM 51 or ISO 11480 with Schöninger combustion and ion chromatography. Water extractable chloride is determined according to ISO 9197 with ion chromatography.

### Molecular Properties

**Molecular mass distribution**
We use two alternative systems for size-exclusion chromatography (SEC) to determine molecular masses and polydispersity of lignin, using organic (THF) or aqueous (NaOH) mobile phase. 0.1 g of sample is required.

**Acidic groups content**
The content of carboxylic acid is measured using conductometric titration according to SCAN-CM 65. The content of sulphonic acid groups is determined by a procedure involving ion chromatography and Schöninger combustion.

**Beta-ether linkages**
The beta-ether linkages are determined using thioacidolysis or NMR spectroscopy.

### Thermal Properties

**Glass transition temperature (Tg) and softening temperature (Ts)**
Using differential scanning calorimetry, properties such as glass transition temperature (Tg) and softening temperature (Ts) is determined.

### Additional Analyses

**Volatile organic compounds**
Using headspace–gas chromatography–mass spectrometry, the content of a range of volatile organic compounds may be determined.

**Two-dimensional NMR spectroscopy**
The atomic framework of lignin molecules in solution can be addressed by two-dimensional NMR spectroscopy methods. Quantifications of different side chain elements and contaminating or added compounds can be performed as well as identification of introduced modifications.