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 (eg. isolated from a kraft black liquor), and containing more or less contaminants.

A list of analytical services related to lignin is appended.

Contact persons
Jerk Rönnols
Tel: +46 768 7124
Email: jerk.ronnols@ri.se

Fredrik Aldaeus
Tel: +46 768 676 7188
Email: fredrik.aldaeus@ri.se

Anna Jacobs
Tel: +46 768 676 7152
Email: anna.jacobs@ri.se

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 Schöniger 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 Schöniger 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 Schöniger combustion.

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

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

Condensation degree
The condensation degree is determined using periodate oxidation followed by gas chromatography

Diffusion coefficient
The diffusion coefficient is determined NMR spectroscopy.

Hydroxyl groups (phenols) content
We employ three different methods. The total phenolic content may either be determined using aminolysis or by using a Folin-Ciocalteu method with spectrophotometric detection. For the determination of aliphatic, phenolic and carboxylic hydroxyl groups, we use 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.

ID: 111

RISE RESEARCH INSTITUTES OF SWEDEN
Division Bioeconomy

ADDRESS
Drottning Kristinas Väg 61
Box 5604, SE-114 86 Stockholm, Sweden

CONTACT
+46 8 676 70 00
info@ri.se, www.ri.se