

Characterization of Raw Material Properties

Properties of wood can be divided to physical and chemical properties. Physical properties are measurable, for example temperature, moisture and particle size. Chemical composition on the other hand, cannot be determined just by viewing or touching the substance. A tree consists of mainly four chemical components: cellulose, hemicellulose, lignin in addition to relatively small amount of extractable small molecules i.e. extractives.

CHARACTERIZATION OF PHYSICAL PROPERTIES

Moisture content determination

Moisture content of solid biofuels is determined by a standard method (EN 14774-1:2009). A sample with the minimum mass of 300 g is dried at a temperature of 105 ± 2 °C and in which the air atmosphere changes between 3 and 5 times per hour, until constant mass is achieved. The moisture content as per cent is calculated from the loss in sample mass through drying.

Heating value determination

Determination of a fuel's heating value is carried out at constant volume and at a reference temperature of 25 °C using a bomb-type calorimeter according to a standard procedure (EN 14918).

In measuring gross calorific value using this method, the gaseous H_2O formed from combustion products is condensed to a liquid. In this case, the heating value is called the gross heating value of the fuel.

Ash content determination

The ash content of organic materials is determined by a standard method for solid biofuels (EN 14775:2009). The ash content (expressed as per cent) is calculated from the mass of the residue remaining after a sample of the material is heated in air controlled conditions (i.e. combusted) for a specific time 550 ± 10 °C.

Particulate analysis

The particle size distribution (PSD) of a powdered or granular material is determined by a standard method for solid biofuels (EN 15149-1:2010).

The method uses an oscillating screen and sieves to separate a particulate material into groups based on particle diameter. PSD gives information about the relative particle size differences that exist in a sample or pile of a material.



CHARACTERIZATION OF CHEMICAL COMPOSITION

Extractives

The spruce bark extractives were obtained with accelerated solvent extractor (ASE) from freeze dried spruce bark. The material was extracted first with n-hexane, then with UHQ-water. During the hexane and the UHQ-water extraction, the solvent temperature was 120 °C, the pressure was 1500 Psi, and 10 min static cycle was applied.

The extractives were first determined gravimetrically. Then the extractive groups, and individual free and esterified extractives were analyzed quantitatively via GC-FID (Örså and Holmbom 1994) and qualitatively via GC-MS. Some phenolic extractives were also analyzed with LC-DAD-MS/MS.

Carbohydrates and lignin

The extractives-free bark was analysed for its carbohydrate (cellulose and hemicellulose) and acid insoluble lignin content using acid hydrolysis and acidic methanolysis. Cellulose and lignin content were determined by acid hydrolysis and hemicellulose content determined via acidic methanolysis.



For acid hydrolysis the carbohydrates in the bark samples were hydrolyzed and solubilized by sulfuric acid. The acid-insoluble lignin (Klason lignin) was filtered off, dried and weighed (TAPPI T 222 om-02). The acid-soluble lignin was determined from the filtrate via UV/Vis-spectrophotometer. at 215 and 280 nm.

The hydrolyzate was analysed for its monosaccharide content by high performance anion exchange chromatography (HPAEC) using Dionex IC25 ion chromatograph equipped with PA-1 column. Water and NaOH were used as solvents with eluent flow of 1,0 ml/min, and postcolumn solvent was mixture of 100 mM NaOH and 300 mM of CH₃COONa with eluent flow of 0,2 ml/min.

Acid methanolysis was performed with 2 ml of 2 M anhydrous HCl/MeOH according to the produce of Bertaud et al. 2002. Neutralisation, derivatisation and gas chromatographic (GC) analysis was performed by modifying a method by Sundberg and co-workers (1996).

Spectrophotometric assays

The hydrophilic extractives were analyzed spectrophotometrically for their antioxidative activity and tannin evaluation by using 280 nm UV-Vis, Folin-Ciocalteu³, and HCL-Butanol^{4,5} assays.

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More information on raw material characterization:

- [1] Antoine, L.M.; Simon, C.; Pizzi, A. UV spectrophotometric method for polyphenolic tannin analysis. *Journal of Applied Polymer Science* 2004, 91, 2729–2732.
- [2] Bertaud, F., A. Sundberg, and B. Holmbom. "Evaluation of acid methanolysis for analysis of wood hemicelluloses and pectins." *Carbohydrate Polymers* 48.3 (2002): 319-324.
- [3] Charrier, B., Haluk, J.P., Metche, M. Characterization of European oakwood constituents acting in the brown discoloration during kiln drying, *Holzforshung* 49 (1995) 168–172.
- [4] Hagerman, A. 2002, Acid Butanol Assay for Proanthocyanidins
- [5] Porter, L. J., Hrstich, L. N. and Chan, B. G. "The Conversion of Proanthocyanidins and Delphinidins to Cyanidin and Delphinidin," *Phytochemistry*, Vol. 25, No. 1, 1986, pp. 223-230.
- [6] Sundberg, A., Sundberg, K., Lillandt, C., & Holmbom, B. (1996). Determination of hemicelluloses and pectins in wood and pulp fibres by acid methanolysis and gas chromatography. *Nordic Pulp and Paper Research Journal*.
- [7] TAPPI standard T 249 cm-00 Carbohydrate composition of extractive-free wood and wood pulp by gas-liquid chromatography
- [8] TAPPI standard T 222 om-02 Acid-insoluble lignin in wood and pulp
- [9] Örså, F. and Holmbom, B. (1994): A convenient method for the determination of wood extractives in papermaking process waters and effluents. *J. Pulp Pap. Sci.*, 20:12, p. 361.