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Downscaled method using glass microfiber filters for the determination of Klason lignin and structural carbohydrates

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ABSTRACT

The analysis results of Klason lignin and structural carbohydrates determined by downscaled analysis methods using 50 mg and 5 mg biomass and glass microfiber filters for the filtration of acid-insoluble lignin, were compared to a conventional method using 300 mg biomass and ceramic crucibles. The usage of microfiber filters reduces space requirement in oven and furnace to a minimum and speeds up the filtration of Klason lignin about three-fold. Furthermore, tedious cleaning of crucibles is unnecessary which additionally increases the number of samples that can be analyzed in a given time frame. The analysis of 5 feedstocks comprising herbaceous, hard- and softwood, revealed no significant differences of hemicellulosic sugars between the 50 mg microfiber and the 300 mg crucible method. The 50 mg microfiber method resulted in Klason lignin values in the range of −6.1% to +4.0% (relative) and glucan values in the range of −0.8% to +3.7% (relative) of the values obtained with the 300 mg crucible method. The 50 mg microfiber method was highly reproducible with relative standard deviations (RSD%) of 0.27–0.56% (average 0.38%) for Klason lignin and 0.54%–1.46% (average 1.01%) for glucan. Compared to the 50 mg microfiber method, the 5 mg microfiber method resulted in similar deviations of Klason lignin and glucan from the 300 mg method values. However, the reproducibility was slightly lower. Overall, the 50 mg and 5 mg microfiber method reflected the actual biomass composition with sufficient accuracy and are therefore recommended as alternative methods or when downscaling of the analysis is required.

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1. Introduction

Lignocellulosic biomass is essentially composed of the polysaccharides cellulose and hemicellulose and the polyphenolic macromolecule lignin. Analyzing this composition is required when assessing biomass characteristics and properties, e.g. before and after pretreatment, extraction or conversion steps.

Due to the complex and irregular structure of lignin, a variety of analytical methods have been developed to quantify lignin levels in different plant species. Examples include spectrophotometric methods such as UV, IR and NMR with and without lignin solubilization, indirect methods such as the consumption of permanganate ("kappa number") and gravimetric methods such as the acid-detergent lignin (ADL) and Klason lignin procedure (for overview and comparison see e.g.

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Ref. [1]) as well as pyrolysis MS [2]. All these methods give different lignin amounts even when applied to the same feedstock and often one method is preferred for a given feedstock.

At the beginning of the last century, Peter Klason of the Royal Institute of Technology in Stockholm, Sweden, described the isolation of lignin by the removal of carbohydrates with 72% sulfuric acid (for a brief overview of early sulfuric acid wood lignin methods, see Ref. [3]). This Klason lignin procedure is now one of the most widespread methods for lignin determination since it can be combined with the determination of structural polysaccharides. The procedure essentially consists of a 72% sulfuric acid incubation step for de-crystallization of the cellulose and a subsequent hydrolysis at a lower acid concentration in order to completely hydrolyze the carbohydrates. The acid-insoluble residue is collected and corrected for ash and protein content to give the Klason lignin content. However, the Klason lignin can significantly overestimate the true lignin value of a feedstock because other acid-insoluble compounds such as waxes, suberin and cutin can be present [4].

For biomass and feedstock analysis, the Klason lignin procedure is described in the TAPPI 222 official test method "Acid-insoluble Lignin in Wood and Pulp" [5] and the NREL standard biomass laboratory analytical procedure "Determination of Structural Carbohydrates and Lignin in Biomass" [6]. In both cases, the collection of the acid-insoluble residue is done by filtration through ceramic filter crucibles, either with or without glass microfiber filter inserts. The use of ceramic crucibles is recommended in order to minimize the need for quantitative transfers before ashing [7].

Despite widely used, the usage of ceramic crucibles can introduce potential errors and demands accurate weighing of crucibles to constant weight since the ratio of crucible weight and lignin weight is high. Furthermore, cleaning of crucibles after analysis is required. In order to circumvent these obstacles, the lignin can be collected on disposable glass microfiber filters only (without support of crucibles) and subsequently dried and ashed.

Filters in lignin analysis have been applied previously. Paper filters were used in the analysis of acid-precipitable polymeric lignin (APPL) [8] and neutral and acid detergent fiber [9], glass microfiber filters were used as support inside ceramic crucibles in acid detergent lignin analysis [10] or to collect [4] or remove [11] acid-insoluble lignin, however, without any ashing steps. Furthermore, a direct comparison of the analysis results of glass microfiber filters and ceramic crucibles has not been performed. The purpose of this study was to evaluate the results of Klason lignin and neutral sugar composition of 5 feedstocks (herbaceous, hardwood and softwood) obtained from a downscaled (50 mg) and small scale (5 mg) method using glass microfiber filters and to compare the results to the conventional large-scale method (300 mg) using ceramic crucibles.

2. Materials and methods

Miscanthus (*Miscanthus X giganteus*), corn stover (*Zea mays ssp. mays*), poplar (eastern cottonwood, *Populus deltoides*) and loblolly pine (*Pinus taeda*) were obtained ground by a SM200 cutting mill (Retsch, Haan, Germany) with a 2 mm sieve screen from Energy Biosciences Institute, Urbana–Champaign, IL. Sugarcane bagasse (*Saccharum officinalis*) RM 8491 was obtained from the National Institute of Standards and Technology (NIST). All chemicals were from Sigma Aldrich (St. Louis, MO, USA) unless otherwise specified.

2.1. Biomass extraction

Air-dried plant material was extracted each with water and ethanol at 100 °C using an automated solvent extractor, ASE350 (Thermo Fisher Scientific, Sunnyvale, CA, USA) with the following settings: 150% rinse, 5 min static time per cycle, 3 cycles per solvent, 60 s nitrogen purge after extraction (adapted from Ref. [12]). The extracted biomass was dried at 105 °C for 16 h. In the case of NIST sugarcane bagasse, the biomass was dried at 105 °C for 16 h before extraction and 1 g was weighed in triplicate to the nearest 0.1 mg and extracted as described above. The extracted biomass was quantitatively removed from the cell, dried at 105 °C for 16 h and then weighed again after cooling in desiccator in order to determine the weight loss representing the sum of water and ethanol extractives. This extractives value is needed to correct the analysis results to a "dried, non-extracted biomass" basis as reported in the NIST report of investigation [13]. About 2 g of extracted and dried biomass of each feedstock were ball-milled for 5 min (model 8200, Kleco, Visalia, CA, USA), redried at 105 °C for 16 h, and kept dry in a closed container until further analysis.

2.2. Two-stage acid hydrolysis

For every feedstock, all three hydrolysis scales (300 mg, 50 mg and 5 mg) were performed at the same time in parallel, from the same batch of ball-milled sample, five replicates each. For the crucible method, about 300 mg of biomass were weighed to the nearest 0.1 mg into 100 mL Pyrex glass bottles (Corning, Tewksbury MA, USA). Teflon-coated stirring bars were placed right before adding 3 mL of 72% sulfuric acid. For the microfiber methods 50 mg and 5 mg were weighed to the nearest 0.01 mg and 0.001 mg, respectively, into modified Hungate vials (Chemglass, Vineland, NJ, USA) and Sarstedt tubes (Newton, NC, USA), respectively. All hydrolysis reactions consisted of an incubation step with 72% sulfuric acid in capped vessels at room temperature with mixing of the slurry every 15 min to ensure thorough contact of the biomass and acid. After 60 min, deionized water (28-fold the volume of used 72% sulfuric acid) was added, the vessels were re-capped and the mixture was autoclaved for 60 min (121 °C, liquid cycle) [6].

A sugar recovery standard (SRS) containing all major monosaccharides was prepared in the same acid concentration used during autoclaving. One aliquot was kept at 4 °C and three others with volumes of 1.45 mL, 14.5 mL and 87 mL were autoclaved together with the samples [6]. These SRS can compensate for differences in hydrolysis severity as a result of the different volumes used in the three scales (e.g. the 1.45 mL will heat up faster than the 87 mL reaction and the carbohydrates are therefore exposed to a slightly higher severity).

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