



Research paper

Elemental analysis of various biomass solid fractions in biorefineries by X-ray fluorescence spectrometry



Duy Michael Le ^{a, b}, Hanne R. Sørensen ^a, Anne S. Meyer ^{b, *}

^a DONG Energy, Kraftværksvej 53, DK-7000, Fredericia, Denmark

^b Center for BioProcess Engineering, Dept. of Chemical and Biochemical Engineering, Technical University of Denmark, DK-2800, Lyngby, Denmark

ARTICLE INFO

Article history:

Received 15 October 2016

Received in revised form

14 December 2016

Accepted 19 December 2016

Keywords:

Lignocellulose

Pretreatment

Silicon

Aluminium

Calcium

Lignin

ABSTRACT

Elemental analysis by X-ray fluorescence spectrometry (XRF) of solid samples from a biorefinery process was performed to study the behaviour of mineral elements in a process involving hydrothermal pretreatment of biomass (wheat straw, corn stover, sugarcane bagasse, palm oil empty fruit bunches, poplar) followed by enzymatic hydrolysis and fermentation. For all the different biomasses, the biorefinery process concentrated silicon, aluminium, and calcium in the solid fraction, while potassium and magnesium were solubilised in the process and removed from the solid fraction. Sodium concentrations were in general low and they only increased in case of addition during the process. No general tendencies were observed for phosphorus, sulphur, and iron concentrations. A prerequisite for XRF elemental analysis was defining an average chemical formula for the organic matrix of process biomass samples. Based on ultimate elemental analysis of all biomasses, the formula for biomass was $C_6H_{8.4}O_{3.5}$, which was used for all types of samples (raw biomass, pretreated biomass, and lignin residue) and can be used in future XRF analysis of samples of similar process and biomass feedstock as those used in this study.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Developing reliable and efficient biorefinery concepts on lignocellulosic biomass feedstocks requires considerations about mineral elements, since they are present at high concentration in biomasses such as e.g. wheat straw, and sugarcane bagasse [1]. Mineral elements possess practical challenges, notably because the refining process tends to accumulate minerals in various streams causing mineral deposition in reactors and scaling of tubing, e.g. by minerals of calcium, magnesium or silica [2,3]. Minerals are often concentrated in output fractions, which e.g. affect valorisation of cellulose [4] or lignin [5]. Understanding the behaviour of mineral elements in terms of accumulation in biorefinery process is therefore necessary. Elemental analysis of process samples could provide an initial step in reaching this understanding.

Recently, it has been shown that X-ray fluorescence (XRF) spectrometry provide a fast and efficient method for elemental analysis directly of solid biomass samples [6,7]. XRF analysis yielded results comparable to those of the current standard method involving microwave destruction with HF, HNO₃ and H₂O₂ (DS/EN

15290) and quantification of mineral elements using ICP-OES. In those studies, certified reference materials and raw biomass feedstocks were studied, while data from samples from genuine biorefinery processes still have not, to our knowledge, been reported in the literature.

Organic samples with high concentrations of C and O possess a challenge for XRF analysis. These elements cannot be quantified by XRF, but they affect the fluorescence intensity of other elements by the so-called matrix effect [8]. Defining the chemical formula for the organic part of the samples and using this as a balance for calculations of concentrations will solve this challenge, if the chemical formula is defined appropriately.

The purpose of this study was to quantify mineral elements in abundant biomass feedstocks of relevance to lignocellulosic biomass refining and in particular assess their fate during processes to provide a decision-base for biorefinery product upgrading, such as utilization of the lignin residue. The quantitative measurement of elements was done by XRF, and a prerequisite for this analysis was defining the average chemical formula for the biomass samples, so that this could be used as balance for calculations of concentrations.

A wide variety of samples from DONG Energy's Inbicon process [9] were analysed by XRF and compared to values measured by the

* Corresponding author.

E-mail address: am@kt.dtu.dk (A.S. Meyer).

current standard procedure for elemental analysis: ICP-OES. Various biomass sources were analysed, i.e. wheat straw (WS), corn stover (CS), sugarcane bagasse (SCB), palm oil empty fruit bunches (EFB), and poplar (POP). Solid samples were analysed from three locations in the 2nd generation bioethanol process: Before pretreatment (raw biomasses), after hydrothermal pretreatment (pretreated biomass), and after enzymatic hydrolysis and fermentation (lignin residue).

2. Methods

2.1. Sample preparation

All samples were process samples from the Inbicon pilot plant (Skærbæk, Denmark), which had been dried at 50 °C for at least 24 h (to a dry matter content of >95%), milled to <1 mm in an IKA MF10 grinder, and stored in closed containers until further use. Standard values of sodium, magnesium, aluminium, silicon, phosphorus, sulphur, potassium, calcium, iron were determined by FORCE Technology (Vejen, Denmark) by sample destruction (DS/EN 15290) followed by ICP-OES analysis.

2.2. Chemical composition

All samples were analysed for chemical composition by methods based on the standard NREL analytical procedures [10]. The analysis of all samples included dry matter and ash content determination and strong sulphuric acid hydrolysis (72% H₂SO₄) for structural carbohydrates and lignin.

2.3. Chemical formula

The chemical formula for the organic part of the biomass fractions was determined by measuring carbon, hydrogen, and nitrogen contents using a standardised procedure on a Euro EA 3000 Elemental Analyzer (EuroVector, Pavia, Italy). Oxygen contents in the organic part of samples were calculated by assuming that it constituted the remaining part of the ash-free biomass when carbon, hydrogen, and nitrogen contents had been subtracted. Chemical formulas were scaled to C = 6 for comparison.

2.4. XRF measurements

For XRF analysis, samples were ground in a Mixer Mill MM200 (Retsch, Haan, Germany) in 25 mL PTFE grinding jars with 2 mm grinding balls (PTFE with steel core). Milling was done for 30 min at 25 Hz in two jars simultaneously with 1.5 g sample in each jar to reach a particle size of less than 100 µm to avoid grain size effects. Milled material from the two jars was combined and pressed to pellets of 40 mm in diameter under 20 tons in an Atlas 25T Manual Hydraulic Press (Specac, Orpington, United Kingdom).

XRF spectrometry was performed using a WD-XRF Supermini 200 (50 kV, 200 W Pd-anode, Rigaku, Tokyo, Japan) in helium atmosphere. Initially, a long continuous scan using a LiF(200) crystal at a scan speed of 10°/min was performed to quantify the heavy

elements (Ti to U). All detected elements were automatically annotated, and the net intensities were calculated by subtracting the background intensity (automatically measured in a valley adjacent to the peak) from the peak intensity. Of the heavy elements, only iron concentrations were presented, since the others were not included in this study. The long continuous scans were monitored by separate scans for each of the lighter elements. Silicon, phosphorus, sulphur, chloride, potassium, and calcium were analysed using a PET crystal at a scan speed of 10°/min, aluminium using a PET crystal at a scan speed of 4°/min, and sodium and magnesium using a R×25 crystal at a scan speed of 0.5°/min. Duplicate measurements were made by analysing the pressed pellets on both sides (preliminary work on wheat straw lignin residues had shown that the coefficient of variation of quadruple replicates were <5% across all elements, except for Mg, which due to the very low values recorded, contents of <400 ppm, had coefficient of variation of 7.8%; data not shown). Reproducibility was determined by calculating coefficients of variation, i.e. standard deviation of replicates divided by the average values, and given in percent.

Detection limits, limits of quantification, and analysing depths for XRF analysis on a representative sample are shown in Table 1. The detection limits and analysing depths are in accord with data for XRF analyses on reference samples presented by others [6]; except that there are no suitable biomass reference material for Si, which is of special interest for us.

In ZSX (version 7.42, Rigaku, Tokyo, Japan), Scan Quantitative X (SQX) was utilised to calculate mass% from net intensities for each detected element using a built-in sensitivity library. All measured intensities were corrected for absorption by the helium atmosphere. Absorption/enhancement effects between all measured elements were corrected by the SQX method using built-in correction coefficients. All detected elements were included in these calculations even though only results from sodium, magnesium, aluminium, silicon, phosphorus, sulphur, calcium, potassium, and iron were reported.

As balance for the quantitative estimates of element concentrations, a chemical formula for the organic matrix was defined and used as an average chemical biomass formula (C₆H_{8.4}O_{3.5}) for all samples measured. Calculation of this chemical formula is described later. XRF measurements were compared to ICP-OES standard values by calculation of relative deviations, which is the difference between XRF measured values and ICP-OES standard values divided by the latter and given in percent.

3. Results and discussion

3.1. Chemical composition of biomass

In terms of weight composition of the raw biomasses (Table 2), poplar was different from the others since it had a higher lignin content (29% vs 20–22% for the others), higher glucan content (40% vs 34–38% for the others), lower xylan content (17% vs 21–24% for the others), and lower ash content (2.9% vs 4.6–12% for the others). Raw biomass from SCB and CS had a high ash content (12% and 11%, respectively), while corresponding WS and EFB had a lower ash

Table 1

Detection limits, limit of quantification, and analysing depth as calculated by the software. Values for pretreated WS are here used as a representative example. Detection limits are calculated as 3 times the standard deviation of background measurements in the valley adjacent to each element's peak. Limit of quantification is 3 times the detection limit.

	Sodium	Magnesium	Aluminium	Silicon	Phosphorus	Sulphur	Potassium	Calcium	Iron
Detection limit (ppm)	76.4	32.6	13.1	43.5	10.1	8.5	36.5	26.3	13.2
Limit of quantification (ppm)	229.2	97.8	39.3	130.5	30.3	25.5	109.5	78.9	39.6
Analysing depth (mm)	0.010	0.016	0.025	0.037	0.050	0.070	0.217	0.270	1.338

Download English Version:

<https://daneshyari.com/en/article/4996279>

Download Persian Version:

<https://daneshyari.com/article/4996279>

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