Fuel 142 (2015) 283–288

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Sampling procedure in a willow plantation for chemical elements important for biomass combustion quality

Na Liu [a,*], Henrik Kofoed Nielsen [b], Uffe Jørgensen [a], Poul Erik Lærke [a]

[a] Department of Agroecology, Aarhus University, Blichers Allé 20, 8830 Tjele, Denmark
[b] Department of Engineering Sciences, University of Agder, Serviceboks 509, N-4898 Grimstad, Norway

HIGHLIGHTS

- We assessed the distribution of twelve elements and ash content within willow shoots.
- Large spatial variation of most elements exists along the length of the willow shoots.
- We revealed the relationship between shoot diameter and distribution of elements.
- A smaller stem section can be used to roughly estimate biomass quality for combustion.

ARTICLE INFO

Article history:
Received 2 July 2014
Received in revised form 29 September 2014
Accepted 5 November 2014
Available online 18 November 2014

Keywords:
Salix
Short rotation coppice
Nutrients
Heavy metals
Vertical distribution

ABSTRACT

Willow (*Salix* spp.) is expected to contribute significantly to the woody bioenergy system in the future, so more information on how to sample the quality of the willow biomass is needed. The objectives of this study were to investigate the spatial variation of elements within shoots of a willow clone 'Tordis', and to reveal the relationship between sampling position, shoot diameters, and distribution of elements. Five Tordis willow shoots were cut into 10–50 cm sections from base to top. The ash content and concentration of twelve elements (Al, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, P, Si, and Zn) in each section were determined. The results showed large spatial variation in the distribution of most elements along the length of the willow shoots. Concentrations of elements in 2-year old shoots of the willow clone Tordis were fairly stable within the range of 100–285 cm above ground and resembled the mean concentration of the whole stem (from 86% to 108%, except for Mg, Na, Al and Fe). For practical reasons it is recommended to sample 10 cm sections at the breast height (125–135 cm) to minimise labour costs.

1. Introduction

Bioenergy is a possible solution to mitigate the energy crisis and greenhouse gas emission from fossil fuels [1]. Combustion is an efficient way to utilize biomass for energy production [2] and it is economical and convenient to convert conventional heat and power plants from fossil fuel to biomass.

Considerable attention is given to Short Rotation Coppice (SRC) crops, such as willow, as a potential feedstock for bioenergy production. Based on the advantages of its rapid growth, high annual yields, low labour needs and low nitrate leaching, willow is an ideal candidate for commercial energy farming [3,4]. In addition, willow is able to grow on contaminated soil and with waste water, but this may also increase the concentration of heavy metals such as Cd and Zn of the harvested biomass [4].

Biomass is a complex and a difficult feedstock compared to conventional fossil fuels. Its diversity of chemical composition results in different fuel properties, which can raise technical challenges such as slagging, fouling, agglomeration, and corrosion in combustion facilities [1,5–7]. This may reduce energy conversion efficiencies or even cause physical damage to boilers and bioreactors [8,9]. High content of some elements (e.g. Si, K, and Na) lower the ash melting temperature [1,5] and high content of K, Si, Mg and P have a tendency to produce more slagging [10]. Cd pollution from willow combustion may also raise environmental concerns for the waste products [11–13].

Characterising composition of the woody feedstock provides the basis for improved crop management and to assess fuel properties. The high yielding willow clone Tordis is currently the most promising clone for SRC in terms of productivity in Denmark [14]. Therefore, developing faster sampling procedures to evaluate raw

* Corresponding author. Tel.: +45 8715 4785; fax: +45 8715 4798.
E-mail addresses: Na.Liu@agrsci.dk (N. Liu), henrik.kofoed.nielsen@uia.no (H.K. Nielsen), Uffe.Jorgensen@agrsci.dk (U. Jørgensen), PoulE.Laerke@agrsci.dk (P.E. Lærke).

http://dx.doi.org/10.1016/j.fuel.2014.11.020

feedstock quality of Tordis in SRC plantations would be of special interests for large scale biomass production. Sampling is usually conducted by shredding whole shoots and then taking subsamples. However, mature SRC willow shoots are usually 6–7 m high, which makes it costly and time-consuming to process the whole shoot on-site, so an alternative method which relies on a small portion of the stem would be useful.

Evaluation and prediction methods typically include parameters that are easy to measure, such as shoot diameter. Sander and Ericsson [15] illustrated the vertical distribution of elements by stratified sampling (taking 5-cm pieces at 1-m vertical intervals from willow shoots). However, less is known regarding the accuracy of using only one small stem section for prediction of the quality of the whole willow shoot. Therefore, although the fuel properties of willow have been well documented in literatures, a better understanding of the distribution of chemical elements in the willow shoots is required to allow easy and representative sampling of a standing willow crop.

The objectives of this study were, (1) to investigate the spatial variation of twelve elements Al, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, P, Si, and Zn within 2-year old shoots of the willow clone Tordis, (2) to reveal the relationship between concentration of elements in stem sections, diameters of stem sections and mean concentration of elements in the whole stem, and (3) to suggest an efficient and suitable sampling method for prediction of the mean concentration of elements in the whole stem of the willow clone Tordis and thus the fuel quality of raw feedstock before harvesting.

2. Materials and methods

2.1. Sample collection

Willow shoots were harvested December 11–15, 2011, from a willow plantation with an initial planting density of 16,700 cuttings ha^{-1} on a sandy soil in Dømmesmoen, Grimstad (58°35′N, 8°58′E), Norway. The stand has been fertilized with 75 kg nitrogen ha^{-1} year^{-1}. Soil pH in the harvest area was 5.9–6.1. Five living willow shoots of the clone 'Tordis' (2nd-year shoots from the 4th rotation, 7 years old root stocks) were chosen from three neighbouring stools in a row representing the range in diameter at breast height of all shoots in the plot. The shoots were cut at 10 cm above ground and held horizontally to obtain the position of its geometric centroid (GC). Each shoot was divided into stem and branches. The main stem was defined as the longest living part of the shoot and all other parts of the shoot were collected as branches. The main stem was sheared into maximum 15 sections with the lengths of 10, 25, 40, 50 cm and a top section of varying length (Table 1). The lengths of the five shoots were 758, 650, 459, 725, 726 cm, respectively. For shoots exceeding the height of 585 cm the top section is equivalent to section 15 and for shoot shorter than 585 cm the top section was section 12. The branches were removed from the main stem and separated in two groups according to their diameter and defined as section 16 (<10 mm) and section 17 (>10 mm). Dead materials from each stool were collected as a separate sample (section 18). The fresh and dry weight of each section of all shoots and their GCs were recorded. The diameters were measured at the base (section 1), at 1 m height above ground level (section 4), at breast height (1.3 m above ground level, section 5), and at GC.

2.2. Sample preparation

All sections and branches of the willow shoots were cut into pieces of maximum 10 cm length and dried at 60 °C till constant weight. The dried sections were chipped using a Bosch AXT 25 TC, Turbine Cut System (Robert Bosch GmbH, Germany) and subsequently ground to fine powder using a 8–82-K water-cooled Tekemas Christy mill (Chelmsford, UK) mounted with a 0.8 mm sieve.

2.3. Elemental and ash content analysis

7394 g subsamples from 83 willow stem sections and branches were pre-digested by a new high-throughput method using only micro volumes of hydrofluoric acid [16]. The concentrations of twelve elements (Al, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, P, Si, and Zn) in the samples were determined using a Thermo Scientific iCAP 6000 Series Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Thermo Fisher Scientific, Waltham, MA, USA). Total ash content was determined by ignition at 450 °C for 4 h.

2.4. Calculation and statistical analysis

Statistical analyses were performed using the MIXED procedure in SAS 9.2 (SAS Institute, Inc., Cary, NC, USA). Before analysis of data, the five individual shoots were grouped according to the position of GC: GC6 (1 shoot, with GC in section 6), GC7 (1 shoot, with GC in section 7), and GC8 (3 shoots, with GCs in section 8).

The data of sections 12–17 were excluded from analysis because of missing data as this height was not reached by all the analysed shoots. The data of sections 1 and 11 were included in the test run of model 1, but it showed that concentrations of most elements of sections 1 and 11 were much higher than the mean concentration of the complete stem (Table 2). Sections 1 and 11 also introduced considerably more variation and was thus excluded from the final model run giving a better test of the remaining sections. Later on section 1 was statistically tested by model 2. Thus, only data of shoot sections 2–10 were analysed by the following mixed model:

$$Y_{ij} = \mu + \text{Section}_i + \text{GC}_j + \text{Section}_i \times \text{GC}_j + e_{ij} \quad (1)$$

where Y_{ij} is the concentration of elements in section i; μ is the overall mean; Section$_i$ is the fixed effect of the ith section (i = 2–10); GC$_j$ is the corresponding group j of the geometric centroid (j = 6, 7, and 8) and e_{ij} is the undescribed error term.

For the four sections, for which the diameter was measured, effect of diameter was included in the analysis. Inspired by Sander and Ericsson [15], who used the surface area to volume ratio ($2\pi rh/\pi r^2 h = 2/r$) of a shoot to describe the relation of bark proportion to

Table 1
Sampling sections of willow shoots.

Materials	Section no.	Height (cm)	Length (cm)	Note
Stump	–	0–10	10	
Stem	1	10–20	10	Base
Stem	2	20–60	40	
Stem	3	60–100	40	
Stem	4	100–125	25	
Stem	5	125–135	10	Breast height
Stem	6	135–185	50	
Stem	7	185–235	50	
Stem	8	235–285	50	
Stem	9	285–335	50	
Stem	10	335–385	50	
Stem	11	385–435	50	
Stem	12	435–485	50	
Stem	13	485–535	50	
Stem	14	535–585	50	
Stem	15	585–top		Top
Branches	16			Diameter < 10 mm
Branches	17			Diameter > 10 mm
Dead materials	18			