Elucidation of associations of ash-forming matter in woody biomass residues using on-line chemical fractionation

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HIGHLIGHTS

► On-line chemical fractionation of ash-forming metals in varied biofuels and ashes.
► Screening results of ash-forming matter delivered to industry in <3 h.
► Assistance in taking decisions on firing/non-firing of biofuels on a short notice.
► Advanced characterization of biomass residues with fractionation, SEM–EDX and XRD.
► Investigation of the selectivity of extractants in sequential extraction procedures.

ABSTRACT

This article reports the application of on-line dynamic chemical fractionation using a stirred-flow chamber for fast characterization of ash-forming metals, *namely*, K, Ca, Na and Mg, and Al as well in woody biomass residues (bark and twigs) and laboratory ashed bark. The chemical fractionation procedure is harnessed to discriminate with minimal operational maintenance those target species associated to the water-soluble, the exchangeable and the acid-soluble fractions as a result of their varying occurrence in the biofuels by resorting subsequently to chemicals of increasing leachability. The final goal is to assist in the evaluation of actual pools of ash-forming elements in industrial boilers.

The proposed technique is able to handle up to 1.0 g of woody biofuels and provide, as opposed to conventional fuel characterization, relevant insight into the amount of leachable elements under worst case scenarios, and real-time quantification of potentially reactive species beside insight into the leaching kinetics of target elements. Screening results can be obtained in less than 3 h instead of more than one week in the batchwise counterpart methods.

For elucidation of metal–biomass/ash associations and investigation of the actual selectivity of extractants, a novel approach has been undertaken by resorting to dynamic fractionation assays in combination with scanning electron microscopy with energy dispersive X-ray fluorescence spectrometry (SEM–EDX) and X-ray diffraction (RXD) assays.

1. Introduction

Biomass is an important source of renewable energy as well as a vital part of the waste management infrastructure. The use of a great variety of biomass fuels and blends thereof as viable alternatives to fossil fuels for power production around the world has launched the quest of novel methods for reliable prediction of the behavior of biofuels in power producing installations. In fact, the introduction of biomass fuels might lead to increased corrosion risks of metal parts in furnaces and boilers, fouling in the convection pass where the heat is recovered from flue gases, bed sintering in fluidized bed boilers and slagging of ash in the furnace [1–6]. The immediate consequence is the deterioration of the efficiency of combustion devices as steam temperatures have to remain much lower in contrast to conventional coal firing. It is thus of utmost relevance to get insight into fuel characteristics when firing biomass fuels or new fuel blends so as to optimize the steam temperatures.

In regards to standard fuel assays [3], the so-called proximate analysis determines the moisture, ash and char/volatiles contents for prediction of burning characteristics. The ultimate analysis

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determines the contents of C, H, O, S, N and Cl for prediction of flue gas composition whilst elemental analysis includes digestion methods for the determination of ash-forming elements for prediction of the ash composition. A standard test method is important to be established for any new, unknown fuel. However, the information retrieved is not sufficient when predicting fuel ash behavior for potential corrosion risks in combustion devices. This holds true for solid biomass fuels of any kind, whereby advanced fuel characterization methods are to be devised for proper evaluation of the chemical associations of ash forming matter prior to the actual industrial use of such fuels [1,3,5,7].

Partitioning of metal species in solid substrates (e.g., soil, sediment, sludge) into operationally defined forms under the sequential action of given leachants with increasing aggressiveness has been recommended by IUPAC [8,9] for distinguishing various forms of metals according to their mode of occurrence, physico-chemical mobility and potential availability [10–15]. The extractants used in sequential extraction procedures (SEPs) are intended to mimic real scenarios promoting the mobilization of metals associated with certain mineralogical phases and organically-bound metals.

Ash-forming matter in fuels has been investigated for more than two decades by resorting to a three-step SEP involving distilled water, ammonium acetate at neutral pH and hydrochloric acid as extractants. The method was originally developed for the characterization of coal [16], modified for the characterization of biomass fuels [17], and further extended to biomass characterization [1,3,18–21]. This method has been harnessed to evaluate how ash-forming elements are bound in the fuel [5,22–25]. Different types of ash-forming matter are discriminated according to their solubility in aqueous solvents. Typical ash-forming components, which are leached out by water include alkali sulfates, carbonates and chlorides. Elements leached out by ammonium acetate are believed to be organically associated via ion exchangeable processes. Hydrochloric acid is leaching carbonates and phosphates of alkaline earth and other metals. Silicates and other minerals remain mainly in the insoluble residue.

Batchwise SEPs have proven however to be tedious and time-consuming. Beside neither are the dynamics of the leaching process of biofuels fully understood, which would be of utmost relevance for optimizing the SEPs aimed at reducing extraction times, and most importantly, analysis expenses. Three additional major problems have been also recognized in batchwise steady-state SEPs for partitioning metals in environmental solids and solid wastes, that is, the lack of selectivity of leaching agents (phase overlapping) for releasing metals associated to a discrete solid phase [9,12,13], which is to be influenced by the extractant exposure time; the re-distribution of target species among phases during extraction [9,12,13], and the impossibility to operate under the nominal pH of extractants for well buffered samples, e.g., fly or bottom ashes [26].

In order to speed-up the entire operational procedure, prevent re-distribution phenomena and gain full knowledge about the kinetics of the metal leaching processes the application of automatic dynamic (non-equilibrium) partitioning is herein proposed for determination of K, Na, Ca and Mg in biofuels and ashes thereof and prediction of ash behavior. In automatic dynamic leaching tests, the solid sample under investigation is loaded in a suitable container, which is exposed continuously to fresh extractant volumes by resorting to flow-based approaches [13,17]. In our case, metered amounts of woody biofuels (twigs and bark) or bark ashes are contained in a stirred-flow chamber (SFC) as a front-end to inductively-coupled plasma atomic emission spectroscopy (ICP-AES) for on-line chemical analysis of the extracts.

Leaching tests, either in manual batchwise or continuous-flow dynamic mode, do not however provide any information as to the actual mobilizable chemical species of the ash-forming matter in biomasses or ashes. To tackle this issue and investigate the actual selectivity (or lack of it) of reagents in the three-step SPE, a novel approach involving the combination of chemical fractionation data with scanning electron microscopy–energy dispersive X-ray fluorescence spectrometry (SEM–EDX) of fuels or ashed fuels [21,28] and X-ray diffraction (RXD) assays of the solid substrates and residues leftover after each step of the dynamic SEP is herein proposed and evaluated.

2. Materials and methods

2.1. Sampling and sample preparation

A ca. 100-year old Scots pine (*Pinus sylvestris* L.) was harvested in the municipality of Kronoby (Midwest Finland). The thinnest branches (<1.0 cm), the so-called twigs, containing both wood and bark, were collected as a whole together with the foliage. In the laboratory, the foliage was separated and the twigs were oven-dried at 105 °C until constant weight. Prior to analysis, the biomass samples were grinded to a particle size less than 1 mm in a bench mill and placed in sealed polyethylene bags in dark storage. A second sample, bark, was provided for by a boiler operator in western Finland. This sample was treated in a similar way as the twigs. Particular attention was paid to ensure a representative test portion for automatic SEPs.

Bark and laboratory prepared bark ashes were chosen as model samples for characterization of metal solid phase associations and the potential overlapping of phases in the SEP. Bark ash was obtained as per BS EN 14775:2009 [29] by heating 1 g of bark in a porcelain crucible from 250 °C (heating rate at 5 °C min^{-1} and held for 60 min) to 550 °C (heating rate at 5 °C min^{-1} and held for 120 min). The amount of ash formed was 4.99 ± 0.30 wt% of the original dry bark, which is in good agreement with earlier reports in the literature [19].

2.2. Characterization of samples

The topology of bark ash particles as well as of the solid residues remaining after each extraction step was examined by Scanning Electron Microscopy (SEM). In addition, the distribution of target elements in the sample structures was explored using Energy Dispersive X-ray Fluorescence Spectrometry (EDX). The main crystalline phases leftover after each extraction step were identified by qualitative X-ray powder diffractometry (XRD) using an X-ray powder diffractometer (Siemens D5000, Washington DC, USA) operating with Cu Kα radiation and a scintillation detector. The identification of compounds was performed through comparison with standard reference patterns.

Raw samples of biomass fuels and ashes (0.5 g bark, 0.15 g twigs and 0.1 g bark ash), and residues leftover after dynamic fractionation were digested in a closed-vessel microwave digestion system (MLS-1200 Mega, Milestone, Italy) for determination of total element concentrations and immobilized metal fractions, respectively. To this end, samples were carefully transferred to PTFE vessels to which 5 mL of concentrated HNO$_3$ (65% w/w) and 3 mL of concentrated H$_2$O$_2$ (30% w/w) were added. A first microwave digestion program composed of seven consecutive steps was utilized as per literature recommendations [30]. After cooling down to room temperature, samples were subjected to a second digestion protocol with further addition of 2 mL of HNO$_3$ and 1 mL of H$_2$O$_2$ [30]. Digests were finally diluted to 50 mL with Milli-Q water.