



Research paper

Rapid X-ray based determination of moisture-, ash content and heating value of three biofuel assortments



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ABSTRACT

Here we demonstrate a new hyphenated X-ray method, qDXA–XRF, for the simultaneous determination of moisture-, ash content and heating value (as received) of biofuels. The method is based on the combination of X-ray transmission imaging and X-ray fluorescence spectroscopy.

The method performance is demonstrated using three biofuel assortments; logging residues, roundwood chips and sawdust, on approximately 3 L samples (~500–1500 g) with a total analysis time of one minute per sample.

Mean absolute errors for the logging residues, roundwood chips and sawdust determinations respectively were; for moisture content MAE = 0.034, 0.026, 0.011 (wet basis mass fraction), for ash content MAE = 0.0015, 0.0015, 0.0049 (dry basis mass fraction), and for heating value (as received) MAE = 0.55, 0.44, 0.17 MJ kg⁻¹.

Furthermore, for the assortment logging residues, the qDXA–XRF determination of heating value decreases the measurement uncertainty from MAE = 1.53 to 0.55 MJ kg⁻¹ (~60% decrease) compared with traditional oven moisture/equation method.

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1. Introduction

Knowledge about the intrinsic properties of biofuels are important because biofuels are increasingly used as fuel for district heat and power generation. Knowing the energy content of biofuels is of great importance both for the trade of the material but also for optimizing the heat-generation processes. The energy content of biofuel is dependent on three factors; 1) the intrinsic energy content of the dry organic components, 2) the moisture content, and 3) the ash content.

Today the determination of energy content, expressed as heating value, can be made using either of two methods; i) by determining the heating value of a dried material using calorimetry and then correct for moisture content (and ash content) or, ii) using a tabulated heating value which is corrected for moisture content (and also possibly corrected for ash content).

The major drawback of both methods is that the sample must be

dried—a process that can take more than 24 h. When also considering the heterogeneity of the biofuels, to estimate the heating/energy value for a shipment (e.g. boat, train or truck load), the combined problem of excessive sampling requirements and time to analyze makes the task of characterizing industrial flows of biofuels challenging, at least in a suitable time frame.

The biofuel moisture content analysis—time problem has previously been addressed with e.g. the following techniques; near infrared and UV spectroscopy (NIR & UV) [1,2], microwaves [3], infrared spectroscopy (IR) [4], low-field magnetic resonance (LFNMR) [5,6]. It should be noted that moisture content determination can also be made using freeze-drying and xylene distillation [7]. A review of moisture measurement in woodchips can be found in Nyström et al. 2004 [8].

This study concerns the characterization of different assortments of solid wood-based biofuels using a fusion of two different X-ray technologies.

Here we have investigated different biofuels with the hypothesis that different intrinsic quality aspects of biofuel viz. moisture content (MC), ash content (AC) and heating value (HV) can be non-invasively and rapidly estimated with a combination of X-ray based techniques—imaging quantitative dual energy X-ray absorptiometry (qDXA) and X-ray fluorescence (XRF) analysis. The

Abbreviations: MAE, mean absolute error; qDXA–XRF, quantitative dual energy X-ray absorptiometry—X-ray fluorescence spectrometry.

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generated X-ray data are processed with multivariate image analysis (MIA), image feature extraction and data fusion—a combination not previously reported for these applications. The qDXA–XRF combination has some attractive features compared with other non-destructive measurement technologies, the most prominent being; speed, ruggedness, insensitivity to sample aggregation state, large measurement volume and possibility for on-line implementation.

Previously, qDXA has been used to quantify the moisture content of clean woodchips [9,10], body composition *i.e.* fat/lean/bone [11,12] and fat content of meat [13–15].

XRF has previously been used to characterize ashes, the majority of the studies aimed at elemental composition not quantifying total amount ash [16–18].

In this study, biofuel samples were collected at different boiler operators in a campaign over approximately 6 months covering three different assortments *viz.* logging residue (GROT), roundwood chips and sawdust at a sampling frequency reflecting the frequency at which the fuel occurs at the selected boiler operators. One challenging aspect of the sample collection was to cover the variations of the selected assortments as good as possible given the natural variation and the sub-optimal sampling scheme that was possible to perform.

The qDXA–XRF measurements were performed using a laboratory prototype biofuel analyzer (PBA) [19]. In the PBA a 3 L biofuel sample is moved in front of an X-ray fan-beam, sequentially operated at two different peak voltages, whilst recording the transmitted portion of the X-rays in an array-detector (qDXA), resulting in two images. Concurrently the analyzer also records the emitted fluorescent X-rays (XRF) resulting in two additional XRF spectra of the sample.

It is shown that reliable determination of the heating value of GROT, roundwood woodchips and sawdust can be made using the suggested combination of qDXA and XRF. The qDXA–XRF combination realizes the high throughput capabilities of absorption measurements with the multi element capabilities of fluorescence measurements. This combines into a system which can estimate the carbon/oxygen- and the ash content of the sample resulting in a fast and accurate moisture-, ash content and heating value determination.

2. Theory/calculation

2.1. Theory – Quantitative dual energy X-ray absorptiometry (qDXA)

qDXA—theory can, briefly, be summarized as the measurement of the number of X-ray photons that pass through a sample. Moreover, the sample is irradiated with X-ray photons of at least two different mean energies. The difference between the material attenuation characteristics at the two energies, photoelectric attenuation and Compton interaction, makes it possible to measure latent properties in the sample at an atomic level *i.e.* functions of electron density and mass density [20]. Moreover, in the PBA application, the transmitted photons are detected with a multi-pixel line-detector as the sample is traversed in front of the detector resulting in two transmission X-ray images at different energies, see Fig. 1.

A mathematical model for how X-rays interact with matter is the well-known Beer–Lambert relation:

$$I = I_0 \cdot e^{-u(E,M) \cdot d \cdot C_M}$$

where I is the number of photons that pass through the sample and are quantified by the detector and I_0 is the number of photons emitted from the X-ray source prior to interaction with the sample. d is the distance the X-ray beam interacts with the sample (thickness) and $u(E, M)$ is the X-ray energy- and material dependent attenuation constant(s). Finally, C_M is the abundance of material M in the sample. DXA is also known as dual energy X-ray transmission imaging (DE-XRT).

2.2. Theory – X-ray fluorescence (XRF)

XRF theory can, briefly, be summarized as the simultaneous measurement of the abundance and energy of the fluorescent photons that are emitted by atoms when irradiated with X-rays. The fluorescent photons are formed when an X-ray photon knocks out an electron in the electron shell of the irradiated atoms. When the atom fills the electron vacancy with a new electron the electron emits a photon—the atom fluoresces. Emitted photons have energies which exhibit a unique and characteristic pattern for each chemical element so the spectral peaks in XRF constitute “fingerprints” of each and all of the atoms in the periodic table, see Fig. 2. The concentration of an element is proportional to the area under its corresponding peak(s) resulting in that XRF can both quantify and identify the different elements in a sample. Notable is that XRF is the result of photon interactions with the electrons in the nuclei, XRF does not reveal any information about atomic bonds or atomic surroundings—therefore both XRF and qDXA are insensitive to the temperature and aggregation state of the sample.

2.3. Calculations – Development of calibration models

To calibrate the PBA we adopted the hypothesis that each assortment should have separate calibration models for MC, HV and AC. This is notable since the model for heating value in the PBA is directly calibrated with the calorific value calculated from calorimetry/oven moisture content values. The heating value is *not* calculated using a tabulated heating value for wood and corrected with the moisture (and possibly ash) content as is common practice.

Furthermore, some additional calibration problems arise since the qDXA data comes arranged as numbers in two 2D matrices (images) and the XRF comprise two vectors of numbers (spectra). These native numerical representations are not suitable for direct modeling using standard models so some kind of feature extraction must be employed. Also, each model could make use of the collected data in different ways *i.e.* different feature extraction, –combination, –fusion schemes and (MIA) image analysis steps could be possible [21–23]. This data-combinatorial modeling issue makes for an open ended approach to the development of calibration models.

To further complicate the combinatorial aspect of conditioning and arranging the measured data we also have to address the issues of *i)* selection of suitable calibration samples, *ii)* the selection of suitable variables to use in the calibration model and, *iii)* how to ascertain robust calibration models *i.e.* calibration models which are relatively insensitive to measurement noise and overfitting.

Notable, in this context, is that there is no “golden method” to adopt for the above mentioned problems and issues, but a plethora of existing techniques to explore. For issue *i)* there are *e.g.* variance

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