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Research article

Effects of sample preparation on the accuracy of biomass content determination for refuse-derived fuels

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ABSTRACT

A reliable and practical method for characterizing refuse-derived fuels (RDF) with respect to greenhouse gas-relevance (or biomass content) is required by industries and waste management companies. As RDF usually consist of a variety of materials with different physical properties, sampling and sample preparation may represent crucial steps with regard to reliable analysis results. This is particularly valid for analytical methods, which rely on only small test specimens (centigrams), such as the adapted Balance Method (aBM). The aBM was recently developed by the authors and is based on elemental analyses (CHNSO). The investigations focus on elaborating an appropriate sample preparation for the aBM. To this end, two RDF model mixtures are generated out of paper, cardboard and different plastics, and comminuted down to a grain of size of <0.2 mm using two differing mills as finishing step. The results of the aBM (applied for 52 samples) show that the performance of the method in terms of trueness and variation is competitive relative to standardized methods. Deviations between the determined value and the theoretical biogenic mass fraction are below 4.5%rel (at a probability of 95%). Furthermore, the standard deviation for both mixtures is below ±3.0%rel. A nested variance component analysis indicates that the last milling step and the step of drawing the test specimens for analysis contribute most to the observed variability. A consecutive application of two types of mills as a finishing step prior to analysis is proposed in order to facilitate a sufficient grinding of plastics as well as of cellulose fibers.

1. Introduction

Energy recovery from wastes and refuse-derived fuels (RDF) has become of increasing importance for energy-intensive industry branches such as cement manufacturing. In Austria this development has been strongly facilitated by the implementation of the landfill directive in 2009, which bans the disposal of waste with a total organic carbon content larger than 50 g/kg or a lower calorific value above 6.6 MJ/kg waste [1]. Thus, materials of high calorific value present in wastes such as plastics, paper, cardboard or textiles are separated in mechanical-biological pre-treatment plants and are subsequently utilized as RDF in industrial plants, thereby substituting conventional fuels. According to the Association of Austrian Cement Industry, the share of refuse-derived fuels in the European cement industry reached a level of 34% by 2012 [2]. In Austria in 2014 already 75.5% of the energy required in cement works stem from secondary fuels [2]. These fuels are, on the one hand, associated with several benefits for the operators: they are usually cheaper, domestically available, and usually less CO_2 intensive than conventional fuels (e.g. coal) [3,4]. However, their utilization goes along with various challenges. Probably the biggest challenge for producers and operators is the heterogeneity of the fuel, which requires reliable, practical and cost effective methods to characterize their quality and thus the environmental aspects associated with their thermal utilization. Besides the compulsory parameters according to EN 15359:2011 [5] (calorific value, content of chlorine and heavy metals), other specifications like, phosphorous content or the biomass content are becoming of increasing importance with respect to the quality and economic value of solid recovered fuels (SRF, which are RDFs produced in accordance with European Standards). The European Recovered Fuel Organization, for example, addresses the significance of determining

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Abbreviations: A, ash content; aBM, adapted Balance Method; CV, coefficient of variation (related to the mean); HD-PE, high-density polyethylene; MS, mean sum of squares; n, number of analyses; N, number of analysis samples; PET, polyethylene terephthalate; PS, polystyrene foam; RDF, refuse-derived fuel; RSD, relative standard deviation (related to the mean); SD, standard deviation; SRF, solid recovered fuel; SS, sum of squares; TIX_{wf}, total inorganic content of the respective element in the water-free ignition residue; TOC, total organic carbon; TOH, total organic hydrogen; TON, total organic nitrogen; TOO, total organic oxygen; TOS, total organic sulfur; TOCl, total organic sulfur; TOX_{waf}, total organic content of the respective element in the water-and-ash-free sample; TX_{wf}, total content of the respective element in the water-free sample; UCM, ultra-centrifugal mill; VCA, variance component analysis; waf, water-and-ash-free; wf, water-free; wt%, percentage by weight; x_B, biogenic matter; $x_{B,aBM}$, biogenic mass fraction determined by the adapted Balance Method; $x_{B,Theory}$, theoretical biogenic mass fraction; x_F, fossil matter; σ^2rel., relative variance component (related to the overall variance); σ^2, variance component.

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the biomass content in SRF for the sake of reducing greenhouse gas emissions through the substitution of fossil fuels [6].

Both producers and users of RDF are interested in reliable and cost-effective methods for characterizing the fuel in terms of greenhouse gas-relevance. Until now, three methods to determine the biomass content in SRF have been described in the standard EN 15440:2011 [7], namely the manual sorting method, the selective dissolution method, and the radiocarbon method. All three methods are commonly applied (for example [8–12]). In addition to the standardized methods, the Balance Method has been developed and implemented in various waste-to-energy plants in recent years and is currently in the last stage of standardization [13–16]. This method combines standard data on the chemical composition of biogenic and fossil organic matter with routinely measured operating data from waste-to-energy plants and has been demonstrated as a reliable method with very low costs in comparison to alternative methods [16,17]. However, the Balance Method does not allow a characterization of the fuel before its utilization as it employs post-combustion data. Hence, the authors have developed a laboratory-based analysis method – the so-called adapted Balance Method (aBM) – which shows promising results [18,19]. Analyses of defined mixtures of biogenic (like cardboard and wood) and fossil materials (like polyethylene and polystyrene) revealed deviations from the theoretical value of below 1% when the materials were mixed after milling [20]. When materials were mixed prior to the sample preparation, results of the aBM differ by <5% (relative) from the known composition of a two-component mixture consisting of paper and polyethylene [19].

However, waste materials are typically strongly heterogeneous with respect to their physical properties and texture and thus, different steps during sampling, sample processing, and analysis can be critical factors for a reliable analysis result [21]. Due to different material characteristics, the components of the mixture may behave differently when it comes to comminution or sample size reduction. Hence, besides sampling, the sample preparation needs careful attention in order to ensure correct and reproducible analysis results. This is particularly valid when only very small test specimens are required for the analysis. For example, the adapted Balance Method (which relies on the elemental analysis) or the radiocarbon method depends on the analysis of only a few milligrams or centigrams per measurement.

Hence, the aim of the investigations presented in this paper is to elaborate an appropriate sample preparation procedure in order for the adapted Balance Method (aBM) to achieve highly reproducible results. In particular, the following aspects are addressed:

- Determination of the reliability of the aBM in terms of accuracy and precision (by means of predefined RDF model mixtures)
- Evaluation of the influence of different sample preparation steps on the final result of the aBM (hierarchical experimental set-up)
- Identification at which layer of the analysis procedure (different sample conditioning steps and chemical analysis) most of the efforts should be concentrated in order to avoid/minimize potential errors
- Identification of approaches for optimizing the conditioning procedure (comparison of different milling strategies).

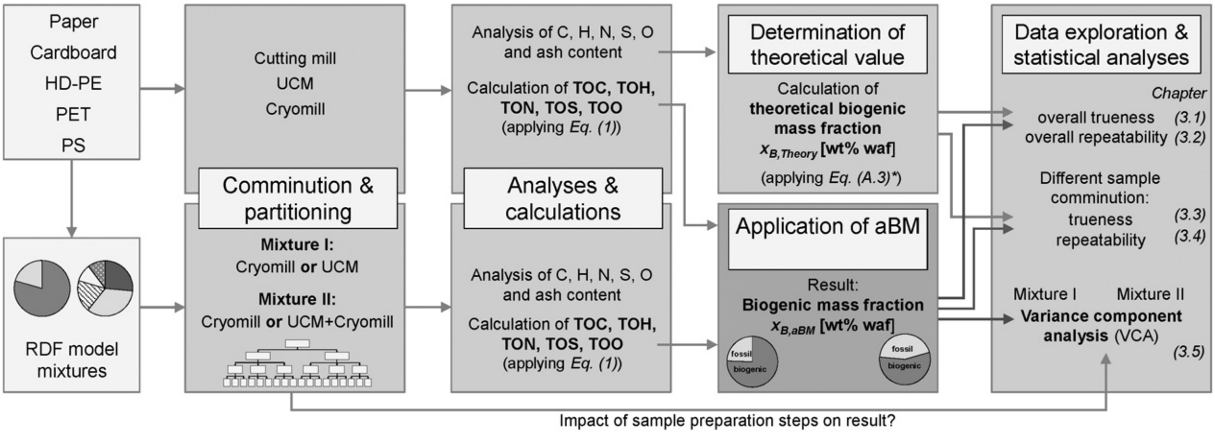
2. Materials and methods

Within the framework of the present study the biomass content of two predefined material mixtures with different composition and different heterogeneity is determined using the adapted Balance Method (aBM) (Fig. 1). Mixture I consists of paper and polyethylene, whereas mixture II is made out of paper, cardboard, polyethylene, polyethylene terephthalate and polystyrene. A special focus is given to the effects of the sample preparation on the final analysis results, different comminution steps are applied and evaluated using various statistical methods, such as the variance component analysis (VCA). For the latter in particular, a hierarchical experimental set-up is chosen, meaning that after each conditioning step replicate samples are produced.

2.1. Determination of the biomass content using the adapted Balance Method

The adapted Balance Method (aBM) relies on the distinctly different chemical composition of water-and-ash-free biogenic and fossil organic matter, where fossil in this context is understood as materials produced out of crude oil, natural gas or coal.

The necessary input data for the calculation are derived from elemental analyses (CHNSO). Additional data on the chemical composition of the water-and-ash-free biogenic and fossil matter are required, which can be derived from literature or from separate analyses of pure biogenic and fossil organic matter present in the fuel (see [18]). Mass balance equations are set up for carbon, hydrogen, nitrogen, sulfur and oxygen. Each balance equation contains the two unknown mass fractions of fossil and biogenic matter (x_B and x_F). As an example, the two pie charts on the left in Fig. 2 show the elemental composition of water-and-ash-free biogenic and fossil matter present in municipal solid waste (total organic carbon TOC, total organic hydrogen TOH, total organic nitrogen TON, total organic sulfur TOS, total organic oxygen TOO and total organic sulfur TOCl) (data as given in [17]). By multiplying these compositional data by the respective mass fractions of waf biogenic organic matter (x_B) and fossil organic matter (x_F), the composition of the material mixture (or RDF) is obtained (pie chart on the



* *Eq. (A.3) can be found in the supplementary information*

Fig. 1. Schematic illustration of the procedure chosen for the investigations conducted: application of the adapted Balance Method (aBM) to two different predefined RDF model mixtures and evaluation of the impact of different comminution steps on the final results.