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SAMPLE PREPARATION OF REFUSED DERIVED FUELS – (IR)RELEVANT FOR DETERMINING THEIR CLIMATE IMPACT?

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SUMMARY: The paper presents investigations on the effect of sample preparation on the result of the adapted balance method (aBM). The aBM is deployed to determine the biomass content in defined waste mixtures. “Waste” mixtures are generated out of defined mass fractions of biogenic (paper, cardboard) and fossil (plastics) materials. Different mills are used to comminute the mixtures down to a grain size of < 200 µm. Finally the mixtures are analyzed using a combustion elemental analyzer (CHNSO). The water-and-ash-free composition is derived which serves as input for the aBM. The results of the aBM demonstrate a good agreement between calculated mass fractions (biogenic, fossil) and theoretical data of the defined mixtures (deviation of below 3 %rel). However, a significant effect of the sample preparation on the result is observed comparing samples comminuted with different mills (ultracentrifugal mill, cryogenic mixer mill). Combining both mills reveals smaller variances. We conclude that plastics as well as cellulose fibers are crushed sufficiently when both mills are applied at the final milling step.

1. INTRODUCTION

In recent years energy recovery from mixed wastes and refused derived fuels (RDF) has become of increasing importance for energy-intensive industry branches such as cement manufacture or steel production. It is a means to reduce costs for primary energy carriers and to lower emissions of fossil carbon dioxide (CO₂). Hence, information on the biogenic content of the secondary fuel product before the utilization is required. Several methods are available to derive the ratio between biogenic and fossil CO₂-emissions from waste combustion. All of them rely on representative sampling, and thus on the production of reliable samples for analysis and on the appropriate selection of the analytical method itself. The typically highly varying composition and strongly heterogeneous character of fuels from mixed waste require special attention to sampling and sample preparation.

The objective of the present investigations is to elaborate an appropriate sample preparation procedure for the adapted balance method (aBM). The aBM is based on elemental analyses and was developed to determine the biomass content in mixed wastes and refuse derived fuels with lower costs and less time effort compared to established methods, such as sorting analysis, selective dissolution method or radiocarbon method (Fellner et al., 2011 and Staber et al., 2008). The originally developed balance method (BM), described in detail in Feller et al, 2007, is based on

standard operation data derived routinely from incinerators. Unlike the BM, the aBM allows to assess the amount of biomass in the mixture **prior to** combustion.

2. MATERIAL AND METHODS

2.1 Determination of the biomass content

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

The necessary input data for the aBM are derived from elemental analyses (CHNSO). Additionally data on the chemical composition of the water-and-ash-free biogenic and fossil matter are required, which can be collected from literature or from additional analyses. 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. As an example, the two left pie charts in Figure 1 show the elemental composition of biogenic and fossil matter used for current calculations given in total organic carbon (TOC), total organic hydrogen (TOH), total organic nitrogen (TON), total organic sulphur (TOS), and total organic oxygen (TOO) given as relative contents. Inserting the mass fractions for biogenic matter (m_B) and the fossil matter (m_F) in the symbolic equation, the composition of the mixture can be obtained (right side in Figure 1). The set of five balance equations is overdetermined (more equations than unknowns), thus a data reconciliation algorithm, based on non-linear optimization can be applied to reveal the quantity of the unknown mass fractions (biogenic m_B , fossil m_F). Further details of the adapted balance method can be found in Fellner et al. 2011.

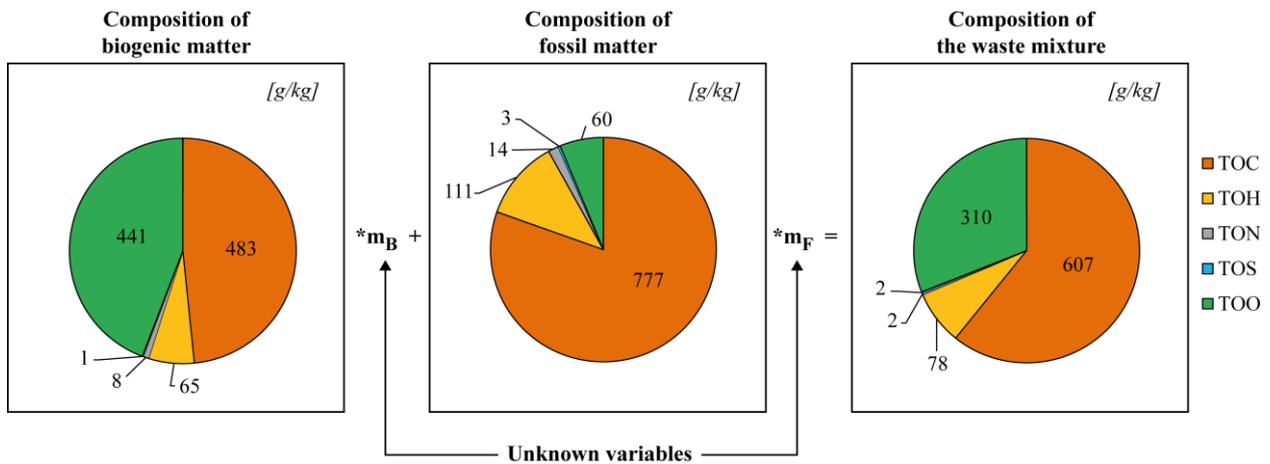


Figure 1. Schematic illustration of the adapted balance method, showing the relation between the chemical composition of biogenic and fossil matter and the waste mixture.

2.2 Preparation of defined mixtures of waste

For the preparation of the predefined material mixtures the following biogenic and fossil materials are used:

Biogenic:

- Cardboard: packaging, double walled
- Paper: A4, 80g/cm², Antalis Austria GmbH

Fossil:

- High-density polyethylene (HD-PE): laboratory grade HD-PE bottles, 250 ml, SciLabware
- Polyethylenterephthalat (PET): cleaned PET-bottles, 237 ml, SPAR Enjoy Smoothie, SPAR Österreichische Warenhandels-AG
- Extruded polystyrene foam (PS): insulation boards, Austrotherm GmbH

Before being mixed, all materials are shredded down to a grain size of below 4 mm by a cutting mill (Retsch SM 2000). Paper and cardboard are considered as biogenic matter, whereas HD-PE, PET and PS are considered as fossil materials (produced out of crude oil). Two material mixtures of different composition with regards to biomass content (79.4 m% and 60.6 m% of water free biogenic material) are prepared (see Table 1). The theoretical biomass content of the mixture is determined by considering the mass fractions on a water and ash free reference base (calculated according to Formula (1)).

Table 1. Composition of the material mixtures.

	<i>Biogenic</i>		<i>Fossil</i>			<i>Theoretical biogenic fraction in mixture</i>	
	Paper wf [m%]	Cardboard wf [m%]	HD-PE wf [m%]	PET wf [m%]	PS wf [m%]	Biogenic mass fraction wf [m%]	Biogenic mass fraction waf [m%]
Mixture I (initial amount: 600g)	79.4	-	20.6	-	-	79.4	75.5
Mixture II (initial amount: 1200g)	26.4	34.3	18.8	10.3	10.2	60.6	55.9

wf water free

waf water- and ash-free

m% percentage by mass (ratio of mass to total mass)

2.3 Sample comminution and partitioning

For the CHNSO elemental analysis (necessary to characterize the chemical composition of the material mixture) a final sample size of only a few hundred milligrams is required. Thus an elaborated sample preparation procedure (comminution, reduction) is necessary to ensure reliable analytical results. The sample preparation is carried out in agreement with the Norm DIN EN 15413:2011 (EN, 2011c).

In order to prepare the defined material mixtures the respective amounts of the materials (with a grain size of 4 mm) are filled into a 60 L container and are thoroughly mixed by shaking the container in circular motions for 10 minutes. Subsequently the material mixture undergoes the sample comminution and segregation steps as outlined in Figure 2. At each level of conditioning replicate samples are produced. The first splitting of the mixture takes place at a grain size of 4 mm by using a riffle divider (Rational Kornservice 5 liter with 18 splits á 19.1 mm) resulting in two divided parts with each around 350 g. Afterwards the grain size is reduced to below 1 mm using a cutting mill (Retsch SM 2000). The thereby observed sample loss is below 7 g (~ 1.8 m% of initial mass). After each preparation step the sample is split, leaving two or three randomly divided parts

which are further treated before being divided again.

For mixture I the fraction with a grain size of 1 mm is milled down to $< 200 \mu\text{m}$ using either a high speed rotor mill (ultra-centrifugal mill, Retsch ZM 200) or a cryogenic mixer mill (Cryomill, Retsch). As seen in Figure 2, level 4, parts (one half) of the five-component mixture (mixture II) are also grinded using only the Cryomill as a final milling step. The other parts (second half) are milled by the ultra-centrifugal mill (UCM) before being crushed into fine powder by the Cryomill in a further step. Thus, two different milling strategies for each mixture are applied, while at the same time two different material mixtures can be compared after being treated the same way. The material losses from UCM-milling amount to 5.3 m% in average (1.4 to 3.0 g per sample), whereas the Cryomill in this case causes an average sample loss of 1.1 m% (0.4 to 2 g).

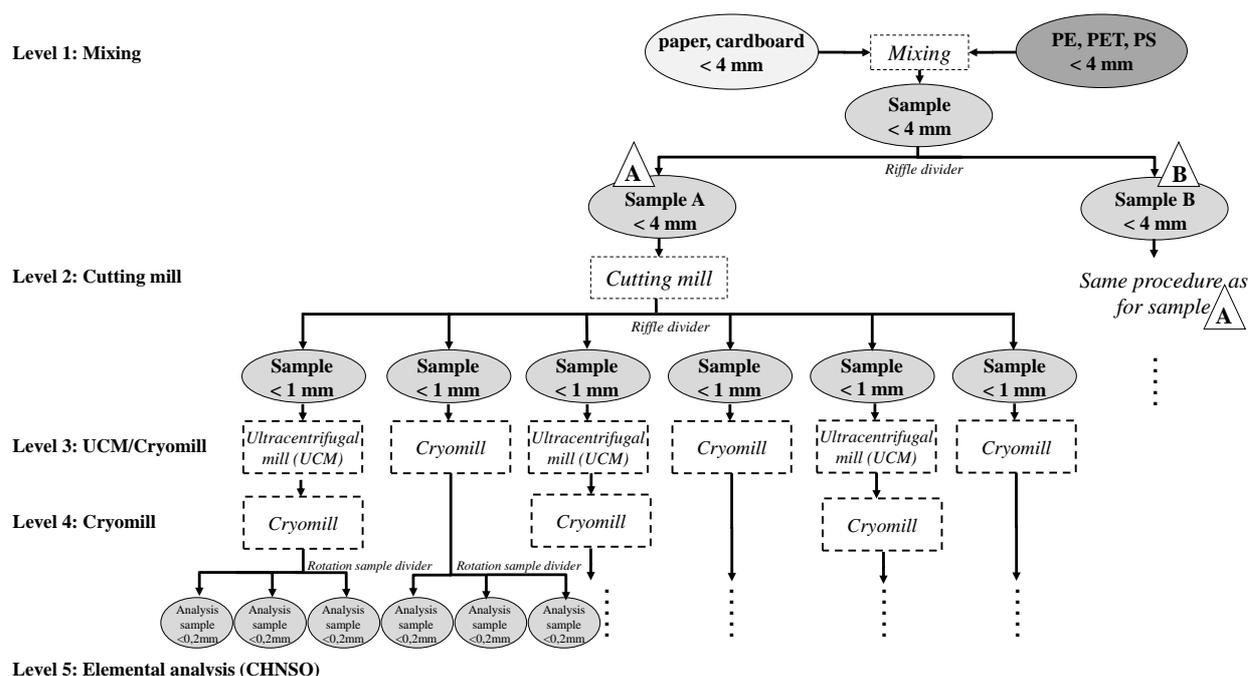


Figure 2. Scheme of comminution and partitioning steps (for material mixture II; for mixture I only Ultracentrifugal mill OR Cryomill is used as last comminution step).

2.4 Analyses

2.4.1 Water content and ash content

The herein applied method for assessing the biomass content of the material mixtures requires a determination of their elemental composition on a moisture- and ash-free basis. Thus, for each analysis sample the water content and ash content is analyzed in duplicate and in agreement with EN 15414-3:2011 (EN, 2011a) and EN 15403:2011 (EN, 2011b). Three to 4 g of material from each sample are dried at $105 \text{ }^\circ\text{C}$ for 24 hours before being combusted at $350 \text{ }^\circ\text{C}$ in a muffle furnace for one hour and at $550 \text{ }^\circ\text{C}$ for four hours under air injection in order to determine the ignition loss and ash content.

2.4.2 Elemental analysis

The water free (dried at $105 \text{ }^\circ\text{C}$ for 24 hours) samples undergo a CHNSO elemental analysis using an Elementar Macro instrument (Elementar Analysensysteme GmbH, Hanau, Germany). At a

combustion temperature of 1,150 °C, the total carbon (TC), total hydrogen (TH), total nitrogen (TN), and total sulphur (TS) content is determined according to DIN 51732:2007 (DIN, 2007). Additionally the ignition residue of each test sample is analysed for its elemental composition to appraise the total inorganic content of carbon, hydrogen, nitrogen, sulphur and oxygen. Five measurements per sample, each of them comprising 40 mg of sample material, are carried out.

The total oxygen content (TO) and total inorganic oxygen content are determined using an Elementar Vario EL instrument (Elementar Analysensysteme GmbH, Hanau, Germany). The analysis is based on the pyrolysis of the sample at 1150°C and the conversion of all oxygen into CO. Compared to the CHNS-analysis, for each measurement only 4 mg of sample mass can be analyzed (due to limitations of the analyzer of maximum 2 mg oxygen absolute). Seven measurements per sample are carried out.

The measured values are converted according to Formula (1) in order to receive the elemental composition on a water and ash free reference base.

$$TOC_{waf} = \frac{TX_{wf} - TIX_{wf} * A}{(1 - A)} \quad (1)$$

whereby TOX_{waf} [g/kg] represents the total organic fraction of the respective compound (C, H, N, S, O) in the water and ash free sample, TX_{wf} [g/kg] the total fraction of the respective compound in the water free sample as measured, TIX_{wf} [g/kg] the total inorganic fraction of the respective compound in the water free ignition residue as measured, and A [kg/kg] the ash content (see also Schnöller et al., 2014). The received values for total organic carbon (TOC), total organic hydrogen (TOH), total organic nitrogen (TON), total organic sulphur (TOS), and total organic oxygen (TOO) represent the input parameter required for the adapted balance method.

4. RESULTS AND DISCUSSION

4.1 Determination of the biomass content

The biomass contents (determined by the adapted balance method) of mixture I and mixture II are presented in Figure 3. The calculated values are in good agreement with the theoretical values (see Table 1). When comparing the biogenic mass fraction of all samples analysed (52 in total), the deviation from the theoretical values amounts to less than 1.5 %abs (at a confidence level of 95 %). This corresponds to a relative deviation of less than 3 %rel.

Based on these results the precision of the values for the biogenic fraction is estimated to 1.2 %abs (at a confidence level of 95 %), which means that the values are scattered ± 1.6 %rel.

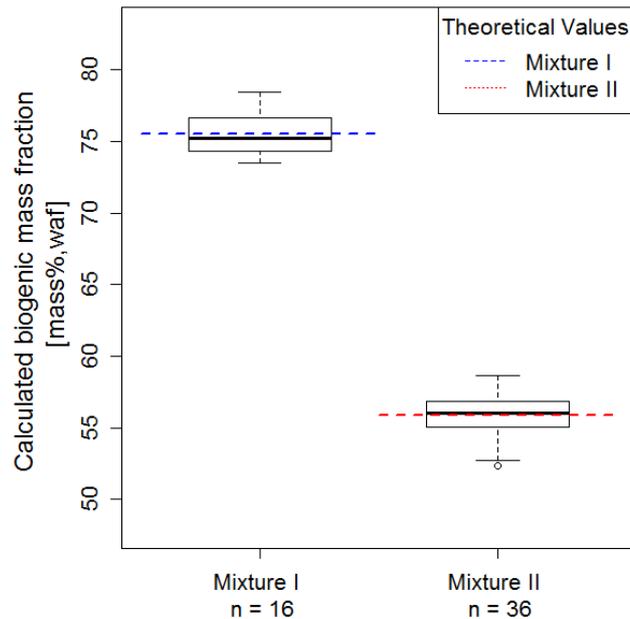


Figure 3. Biogenic mass fraction of all samples (n...number of samples) analyzed on water and ash free (waf) basis (for mixture I and mixture II).

4.2 Sample splitting

Non-parametric analysis of variance revealed that the differences between the two data sets after the first splitting (part A and B) of mixture II are significant (unlike for mixture I), and thus samples of A and B subsequently analyzed are not from the same population. Figure 4 shows analysis results of each sample divided into measurements of part A (upper graphs) and part B (lower graphs). The average contents of total organic carbon (TOC) and total organic hydrogen (TOH) for samples originating from part A are higher than those obtained for samples from part B, thus revealing also different results when finally calculating the biogenic mass fraction (points in upper graphs in Figure 4 are brighter by trend than the points in lower graphs). Thus it is assumed that the first splitting step (at a grain size of around 4 mm) is crucial especially for more complex mixtures and a further reduction of particle size should be conducted before being split in order to ensure representative samples. However it has to be noted that no published data are currently available to confirm this assumption. As a consequence for the current investigations the two data sets (part A and part B) are treated separately from mixture II during the further evaluation of results.

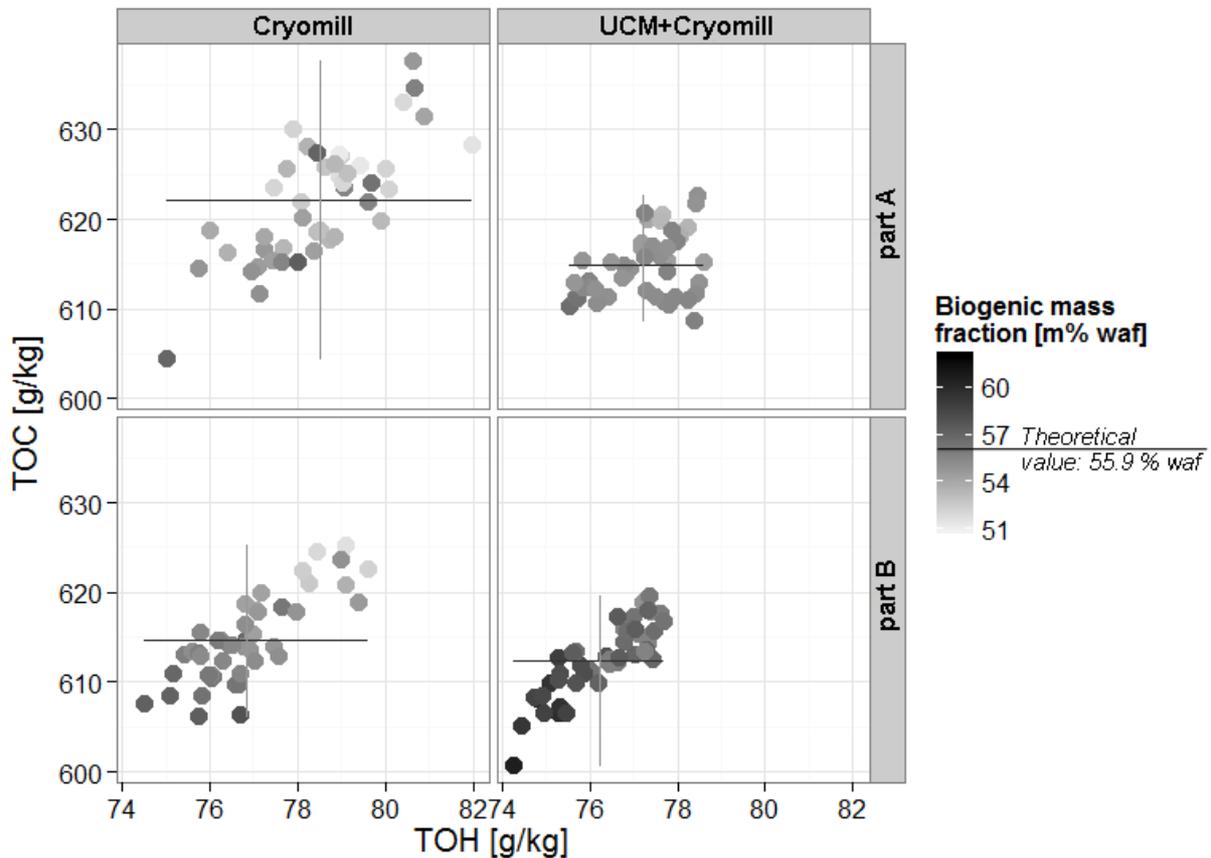


Figure 4. Contents of total organic carbon (TOC) and total organic hydrogen (TOH) for samples of mixture II, divided according to the final milling process (Cryomill or UCM plus Cryomill) and including the corresponding biogenic mass fraction (determined by the adapted balance method) - the brighter the colour the lower the biogenic mass fraction. (waf...water and ash free).

4.3 Comparison of results when deploying different mills

The calculated biogenic mass fractions for samples comminuted with different mills are summarized in Table 2 and are expressed as mass percent based on water and ash free material (waf).

A non-parametric analysis of variance gives strong evidence that the medians between groups with different final sample preparation originate from different populations. This difference between UCM- and Cryomill-finished samples is found for all observed parameters (TOC, TOH, TOO, ash content, biogenic fraction) and is reflected in the ascertained mean biogenic fraction for the different data sets (see also Figure 4 for results of mixture II). While for samples prepared by UCM the biogenic fraction is overestimated by trend (on average 1.2 %rel for mixture I and up to 3.7 %rel for mixture II), the solely Cryomill-finished samples show on average lower biomass content compared to the theoretical values (1.1 to 3.2 %rel). As the biogenic mass fraction determined by the balance method is strongly dependent on the analytical results of the organic contents of C, H and O, the overestimation (or underestimation) of the biogenic mass fraction is a consequence of low (or high) TOC and TOH and high (or low) TOO contents. It is assumed that the sample preparation, particularly the high thermal and mechanical stress during the milling processes, may have changed the composition of the material mixtures.

Table 2. Biogenic mass fractions calculated by the adapted balance method for both mixtures given as mean value of all samples analyzed \pm standard deviation.

	<i>Mixture I</i> <i>Paper:PE</i> (79.4 m% : 20.6 m%, wf)		<i>Mixture II</i> <i>Paper:Cardboard:PE:PET:PS</i> (26.4 m% : 34.3 m% : 18.8 m% : 10.3 m% : 10.2 m%, wf)			
	<i>UCM- finished samples</i>	<i>Cryomill- finished samples</i>	<i>UCM+Cryo mill-finished samples A</i>	<i>UCM+Cryo mill-finished samples B</i>	<i>Cryomill- finished samples A</i>	<i>Cryomill- finished samples B</i>
	<i>n = 8</i>	<i>n = 8</i>	<i>n = 9</i>	<i>n = 9</i>	<i>n = 9</i>	<i>n = 9</i>
Calculated mass fraction biogenic $X_{B;aBM}$ [m% waf]	76.4 \pm 1.7	74.7 \pm 0.7	56.0 \pm 0.8	58.0 \pm 0.9	54.1 \pm 1.3	55.7 \pm 1.2
Deviation from theoretical biogenic mass fraction [%rel]	+1,2 %	- 1.1 %	+ 0.2 %	+ 3.7 %	- 3.2 %	- 0.4 %
Theoretical mass fraction biogenic $X_{B;Theory}$ [m% waf]	75.5 \pm 0.3		55.9 \pm 0.4			

wf water-free

waf..... water- and ash-free

m% percentage by mass (ratio of mass to total mass)

n number of samples

 $X_{B;aBM}$... biogenic mass fraction on water- and ash-free basis, determined by applying the adapted balance method $X_{B;Theory}$. Theoretical biogenic mass fraction on water- and ash-free basis, defined by the preset composition of each mixture (Table)

Furthermore, differences in the variance of the results are observable for samples processed with different mills (Figure 4 shows the scatterplots for mixture II for the two different milling treatments). The differences in variance are most apparent when the two mills are applied solely without following a further processing step (as for mixture I). The coefficients of variation are outlined in Figure 5. For mixture I the coefficient of variation (CV) based on the mean values range from 1.0 m% for Cryomill-finished samples to 2.3 m% for UCM-finished samples. When mixture II is regarded, this difference in CV is slightly reduced to 1.4 to 1.6 m% for samples with UCM plus Cryomill conditioning and to 2.2 to 2.5 m% for solely Cryomill-finished samples. The difference in variance between the two conditioning strategies is however still apparent. In Figure 5 it can be seen that the results are scattered stronger when UCM samples are compared to Cryomill samples, but also when Cryomill samples are compared to samples for which both mills are deployed.

These inhomogeneous variances for samples of different final preparation are attributed to unequal grain size distributions within the analytical samples. When applying the UCM, cellulose fibers of paper and cardboard material in the mixtures are not completely destroyed and tend to agglomerate to particles larger than the desired 200 μ m (visual observation and confirmed by sieve analysis conducted). The Cryomill has the ability to crush fibers to a large extent, but does not allow generating samples of defined particle sizes. The grinding jar of the Cryomill is cooled with liquid nitrogen (-196°C) from the outside to embrittle materials so that also elastic particles may be

crushed rather than just plated. Nevertheless plastics tend to accumulate in the larger grained fraction of the sample, as demonstrated by sieve analyses conducted (results of tests are not shown here). To facilitate an entire grinding of plastics and cellulose fibers to a grain size below 200 μm , a combination of both types of milling processes (high speed rotor mill, mixer mill) is proposed.

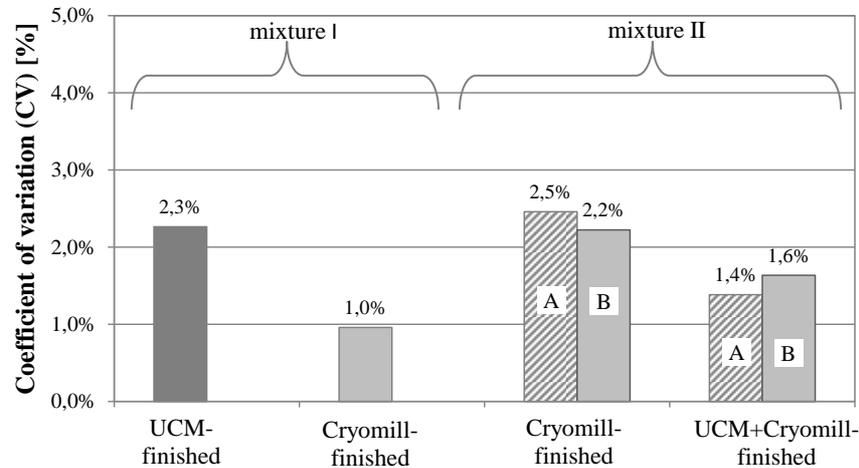


Figure 5. Calculated coefficients of variation for the biomass content of samples finished with different milling steps.

4.4 Influence of type of material mixture

The two mixtures are prepared by alike strategies. In order to evaluate the influence of the material mixture on the precision of the result of the adapted balance method, the results for the different material mixtures are compared. As seen in Figure 5 higher variances of the results for mixture II, which is characterized by a higher plastic content (44.1 m% compared to 24.5 m% for mixture I) and more components (5 different materials compared to 2 materials for mixture I), can be observed. This indicates that the precision of the final results of the adapted balance method depends not only on the sample preparation but also on the complexity and composition of the material mixture. A consecutive usage of both mills reduces the variance of final results for mixture II almost to the level of the more simple material mixture I.

5. CONCLUSIONS

The investigations confirm the feasibility of the adapted balance method for determining the biogenic mass fraction in the two pre-defined mixtures (2-component and 5-component mixture with 75.5 and 55.9 m% biogenic content respectively). The determined biogenic shares are in good agreement with the theoretical value, revealing a deviation of less than 1.5 %abs (less than 3 %rel) at a confidence level of 95 %. A precision of 1.6 rel% (at a confidence level of 95 %) is observed when applying the proposed sample preparation procedure to both mixtures (cutting mill down to < 1mm grain size with subsequent milling down to 200 μm by means of UCM or/and Cryomill). The overall performance of the analytical results is better than reported by Schnöller et al. (2014) who conducted similar investigations with a paper/HD-PE mixture. They however used only 20 mg (instead of 40 mg) for elemental analysis and oxygen measurements were not considered.

A small but nonetheless significant effect of the sample preparation method on the final result is observed. The ratio of biogenic matter in the sample tends to be slightly overestimated (< 4 %rel)

when an UCM is applied and underestimated (< 4 %rel) when a Cryomill is deployed. The best performance regarding accuracy of the mean and precision (0.2 %rel accuracy; 1.4 %rel precision) is obtained when an UCM followed by a grinding via Cryomill is applied for the final sample preparation. This procedure ensures a low systematic variation of results, as potential errors due to milling and subsampling for final analysis are minimized.

The observed difference in the variance of final results for different material mixtures (75.5 m% and 55.9 m% biogenic content), which have been prepared alike (with Cryomill as the final conditioning step) suggests that the results and thus the performance of the adapted balance method might also be dependent on the composition of the material mixture.

Summarizing, the following main factors are likely to influence the obtained accuracy of the mean and precision (1) Method of sample splitting (and particles sizes at the splitting step), (2) Composition and complexity of the mixture, (3) Choice of milling processes with regard to thermal and mechanical stress, (4) Choice of milling process with regard to grain size distribution (including particle and fiber destruction performance of the chosen mill), (5) Method of subsampling for analysis (including proper homogenization).

Future experiments will focus on real samples of refused derived fuels and waste fractions in order to substantiate the described findings and to investigate if preparation or analysis effort might be reduced without impairing the accuracy of the final results. Furthermore, the performance of the adapted balance method together with the proposed sample preparation will be compared to standardized methods such as the selective dissolution method and the ¹⁴C-method.

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