

An alternative approach for the estimation of biochar yields

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Abstract: In this study, a novel approach for the determination of the solid mass yield from slow pyrolysis based on a comparison of the volatile matter contents of feedstock and char is presented. The approach was tested with experimental data from literature and own measurements. For these experiments, gravimetric data is available to determine the mass yield. The proposed method was compared with conventional ash-based calculations and the gravimetric determination of the yield. It was shown that the new approach does not only perform significantly better than ash-based methods, it also approximates the real mass yield of slow pyrolysis under atmospheric pressure quite accurately. These findings may indicate that secondary char formation does not contribute significantly to the mass yield of biomass pyrolysis under conditions found in practical production processes (low heating rates, atmospheric pressure and medium temperatures).

Keywords: *Biomass, Slow pyrolysis, Biochar, Devolatilization, Mass yield, Ash-tracer, Secondary char formation*

1. Introduction

Pyrolysis is a common process to convert biomass into a secondary fuel or feedstock for other processes. Biomass is heated without the addition of an oxidizing agent, decomposing the original structure and forming permanent gases, liquids (usually an aqueous and at least one oil phase) and a solid char. During primary pyrolysis, the feedstock releases water and volatile matter. The latter being composed of permanent and condensable gases. During secondary pyrolysis, these primary products may react further, altering the product composition. Especially condensable hydrocarbon gases may be cracked, yielding more permanent gas. It is believed that gas components can re-polymerize, forming secondary char and that carbon from the solid structure can oxidize with reactive gases [1–6].

Slow pyrolysis at heating rates of approximately 5-20 K/min aims to produce a carbonaceous solid with a porous structure. Slow heating rates and long residence times ensure that the overall biomass structure remains largely intact. With increasing degree of carbonization, the structure undergoes a change from the

original fibrous structure of biomass to a brittle and crystalline nature in the char. The appearance however resembles that of the original wood. This can easily be seen when comparing barbecuing charcoal with wood.

Additional information can be gained from the product distribution of primary pyrolysis, i.e. the amount of gaseous to liquid and solid products formed during devolatilization. Ideally, the yield of these is determined gravimetrically during the experiment by measuring the weight difference between the raw biomass and the product. The mass yield y_{mass} is therefore the ratio of char mass (m_{char}) to feedstock mass ($m_{feedstock}$):

$$y_{mass} = \frac{m_{char}}{m_{feedstock}} \cdot 100 \quad [\%] \quad (1)$$

This can easily be carried out for batch type reactors, however it may be more difficult in continuously operated reactors. In such cases, the solid yield may be calculated based on the mass concentration of one specific component in the raw biomass and the char. This requires the assumption that the considered component (the so-called tracer) is stable during thermal conversion and its absolute mass does not change. Hence, its relative increase in the char may serve as an indicator of how much solid mass has been converted during pyrolysis. In coal conversion, the ash content is typically used as a tracer. Noteworthy volatilization of coal ash occurs only at temperatures above ca. 1500 °C [7] and hence the ash may be considered inert at temperatures below that. Some inorganics may be released at lower temperatures [7]. However, as these release temperatures are below the determination temperature of the ash content (around 800 to 900 °C, depending on the standard) it is assumed that they do not influence the validity of the ash-tracer method, because the release of these species occurs equally during ash determination of feedstock and char [8,9].

The simplest way for calculating the solid product yield from the ash content of the feedstock ($ash_{feedstock}$) and char (ash_{char}) is by using the ratio thereof:

$$y_{mass} = \frac{ash_{feedstock}}{ash_{char}} \cdot 100 \quad [\%] \quad (2)$$

Similar to the gravimetric determination of the yield, the calculation according to equation (2) considers the entire solid mass as part of the yield. An alternative approach is to base the yield calculation on the ash-free part of the biomass, equation (3). This method is known as the ash-tracer method [7,8,10]:

$$y_{mass} = \left(1 - \frac{ash_{char}}{1 - ash_{feedstock}}\right) \cdot 100 \quad [\%] \quad (3)$$

The ash-tracer method has also been used for biomass pyrolysis [11–18], assuming that all ash is retained in the char. However, this assumption is questionable due to the high content of alkali and alkaline earth metals in biomass ash [19,20], which are known to be partly released into the gas phase during thermochemical conversion [19,21–28]. Herbaceous biomass such as straw may also contain noteworthy amounts of chlorine, which is also (partly) released into the gas phase [29]. The release of inorganics during pyrolysis leads to an overestimation of the mass yield according to equations (2) and (3). In addition, the low ash content in many biomasses can cause high measurement uncertainties. As a result, even small errors during analysis or minor contaminations of the sample may have a large influence on the measured ash content and on the mass yield calculated therefrom [30]. Septien et al. [17] have estimated that the overall error of the ash-tracer method for biomass fast pyrolysis can be up to 25 %.

As an alternative, other tracers have been used to evaluate the biomass conversion, for example stable ash components [31–33] or inert minerals that were mixed with the biomass before the experiment [34].

The goal of this study is to provide an alternative method for the calculation of the solid mass yield from biomass pyrolysis. This approach is based on the volatile matter contents of biomass and char. The method was validated for slow pyrolysis, using both literature data as well as own slow pyrolysis experiments in a fixed bed reactor.

2. Materials and methods

2.1 Volatile based determination of the mass yield

In response to the challenges related to the commonly used ash-based calculation methods described above that seemed unreliable for the determination of the mass yield, an alternative and novel approach, based on the volatile matter content, is proposed:

$$y_{mass} = \frac{1 - VM_{biomass}}{1 - VM_{char}} \cdot 100 \quad [\%] \quad , \quad (4)$$

where y_{mass} is the mass yield of the solid product, $VM_{biomass}$ and VM_{char} are the volatile matter contents (as fraction of one, on dry basis) of the biomass and the char, respectively. As the proximate composition (on dry basis) defines a fuel to be composed of volatiles, ash and fixed carbon, equation (4) can be re-written as the ratio between the sum of ash and fixed carbon contents of the biomass (enumerator) and the char (denominator). The underlying assumption of this approach is that both the fixed carbon content and the ash content remain unchanged during pyrolysis, i.e. that gaseous and tarry products stem only from the volatiles and the char only from fixed carbon and ash. As in the purely ash-based calculations, the uncertainties associated with the ash determination as well as the release of inorganics into the gas phase during conversion are causes of errors. However, since the fixed carbon is considered in addition, the influence of an error in the ash determination on the overall result is much smaller as it is in a purely ash-based calculation. Due to the low ash content in biomass, the contribution of released inorganics to the total volatile release is small, another factor limiting the error for this mass yield determination.

At a first glance, this approach does not seem to be suitable for calculating the mass yield of slow pyrolysis as it contradicts the concept of secondary char formation from the gas phase. However, it has been pointed out by Antal et al. [35] that these secondary reactions might require pressurized conditions, making the proposed method a valid approximation for the mass yield obtained under atmospheric conditions. In order to validate the method, slow pyrolysis experiments in a fixed bed reactor were performed and the gravimetric solid yield was compared to the calculated yields from the purely ash-based approaches (equations (2) and (3)) and the novel method proposed here (equation (4)). For further verification of the new approach, this comparison was also done for several slow pyrolysis experiments presented in literature, with the results shown in Section 3.

2.2 Biomass feedstock

Three different types of biomass were used for the pyrolysis experiments: mixed Norwegian forest residues, bark and walnut shells. The residues stem from birch wood and consist of a mixture of stem wood, small

branches and bark. These types of residues represent a noteworthy amount of biomass in Norway [36,37].

The pure bark fraction was separated from the mixed wood and used as an additional feedstock.

Walnut shells are residuals from the walnut processing. Instead of disposal, walnut shells are commonly used as a gentle alternative for sandblasting applications. The walnut shells used in the present study stem from the processing industry in France.

The samples mixed birch forest residue and bark were visibly free from contaminations such as sand, soil, leaves or needles. They were ground, sieved to a particle size between 50 and 200 μm and pre-dried before the experiment. Walnut shells were bought in sandblasting quality (below 200 μm), sieved to particle sizes between 90 and 106 μm and also pre-dried before the experiment. A small particle size was chosen in order to minimize intra-particle gradients, avoid an additional comminution step for the determination of the volatile matter content and achieve a homogeneous product. In practical biochar production, larger particles are common. These will devolatilize slower, possibly rendering a larger residual volatile matter content in the char or requiring longer residence times for sufficient devolatilization.

A characterization of the mixed birch forest residue (referred to as BFR), the bark and the walnut shells is given in Table 1. All methods for processing and analysis are listed in section 2.4.

The bark contains more carbon than the BFR and the walnut shells and has an accordingly higher heating value (dry and ash free (daf)). The ash content of the woody feedstocks is higher than that of the walnut shells. The differences in the ash composition should be noted: as generally the case for bark [38], it contains significantly more alkali and alkaline earth metals than BFR, e.g. more than three and a half times the calcium, about 50 % more potassium and 70 % more magnesium. The walnut shells show a noteworthy amount of potassium. The total ash content of the different types of biomass was determined at different temperatures in order to evaluate the influence on the amount of ash measured (more details on the ash determination are found in Section 2.4). For BFR and bark, the differences are small. This indicates that (under the conditions used during proximate analysis) a possible release of significant amounts of inorganics into the gas phase occurs mainly either below 750 or above 950 $^{\circ}\text{C}$. The ash content of walnut shells is much lower, less than 0.6 % (for the temperatures considered). For this biomass, the determination temperature seems to influence the relative ash content much more, likely also due to the large amount of potassium. Combined with the relatively low amount of total inorganics, this may pose a significant cause of error.

Table 1 Characterization of birch forest residues, birch bark and walnut shells (daf = dry and ash free). Standard deviations are given in brackets.

	Forest residue (BFR)	Bark	Walnut shells
HHV [kJ/kg] daf	20 254 (32)	22 376 (73)	20 238 (64)
<i>Proximate composition [wt%], as received</i>			
Water	5.17 (0.11)	4.66 (0.62)	2.01 (0.07)
Volatile matter	74.51 (0.65)	70.78 (0.37)	75.57 (0.24)
Ash (750 °C)*	2.16 (0.03)	2.73 (0.11)	0.60 (0.01)
Ash (815 °C)*	2.12 (0.02)	2.69 (0.11)	0.44 (0.02)
Ash (950 °C)*	2.00 (0.04)	2.56 (0.10)	0.26 (0.05)
C _{fix} ** (by difference)	18.32 (0.50)	22.00 (0.15)	22.16 (0.12)
<i>Ultimate composition [wt%], daf</i>			
C	51.09 (0.40)	56.02 (0.29)	50.52 (0.01)
H	5.72 (0.13)	6.03 (0.09)	5.40 (0.03)
N	0.80 (0.06)	1.06 (0.03)	0.59 (0.02)
O (by difference)	42.39 (0.39)	36.89 (0.39)	43.49 (0.04)
<i>Inorganics [mg/kg]</i>			
Ca	2620	9420	830
K	952	1440	2060
Ma	497	865	128
Fe	410	182	29.5
Si	400	470	63.1
Mn	381	575	34.5
P	377	543	125
S	326	424	82.8
Na	222	348	27.9
Al	196	209	18.6
Zn	116	230	< 10
W	37.5	50.7	< 10
Cu	36.6	19.5	21.1
Ba	33.5	86.9	< 10
Ti	26.8	24.0	< 10
B	< 10	16.2	< 10
Sr	< 10	23.2	< 10
Ag, Be, Bi, Cr, Ld, Ga, In, Li, Ni, Nb, Sb, Sn, Ta, V, Zr	< 10	< 10	< 10
As, Co, Mo, Se, Te,	< 1	< 1	< 1
Cd, Tl	< 0.1	< 0.1	< 0.1

* The ash content was determined at different temperatures, identified in the brackets in the first column. Details on the determination of the ash content are given in Section 2.4.

** The fixed carbon content was determined by difference, using the ash content measured at 950 °C

2.3 Experimental setup of slow pyrolysis

The slow pyrolysis experiments were carried out in a batch-type micro fixed bed reactor (MFBR). The test rig consists of a quartz glass reactor tube with a diameter of 10 mm, which is electrically heated from the outside. A mass flow controller ensures a steady inflow of nitrogen (non pre-heated, purity 99.9992 %) at a flow rate of 0.2 l/min (standard temperature and pressure STP) into the reactor. Biomass (pre-dried at 105 °C, sample mass about 0.1-1 g, depending on the bulk density) is filled into a quartz glass crucible, which is then placed onto a frit inside the glass tube. Gas is leaving the reactor through a cooled tar trap. Type K thermocouples are used to measure the temperature of the bed and the gas outlet. The reactor tube is mounted into the heating element, which is equipped with a temperature controller including ramp function. The heating rate in each experiment was 5 K/min up to 600 °C (referring to the bed temperature) with a holding time of 60 min. After this time, the tar trap was disconnected and the reactor was removed from the heating element to quench the char sample. The mass yield was determined gravimetrically by weighing the raw biomass and char samples.

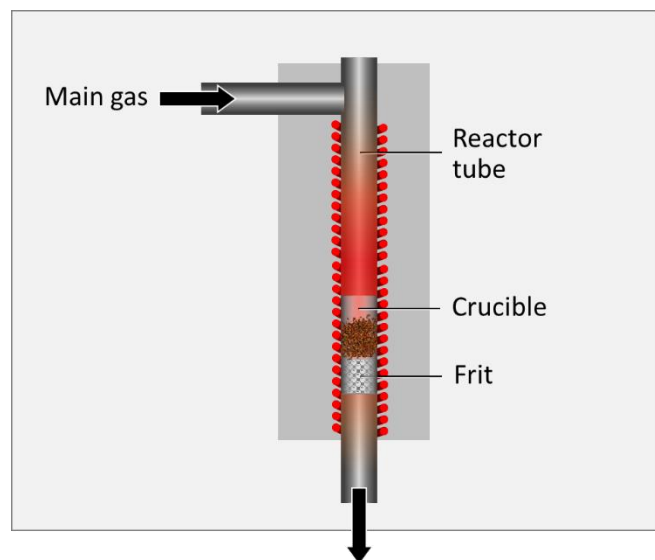


Figure 1 Sketch of the fixed bed reactor for slow pyrolysis experiments

2.4 Processing and analytical methods

Comminution of BFR and bark was performed in a cutting mill (Retsch SM-1) and a cryogenic mill (Retsch MM-400 incl. cryo kit). The desired particle size fraction of 50 to 200 μm was obtained by sieving. The comminuted biomass was used for the analyses described below.

The proximate analyses of all samples, both raw biomasses as well as chars, were carried out in a thermogravimetric analyzer (TGA), Mettler Toledo SDTA851e. This was mainly due to the small amount of collected char samples, which made a double determination in a muffle furnace using a common standard (e.g. 300 g for moisture determination according to EN ISO 18134-1) impossible. For all samples, at least a double determination in the TGA was performed, using a minimum amount of 20 mg each. The heating profile was partly based on the procedure presented in [39]: after an initial settling period of 5 minutes at 30 $^{\circ}\text{C}$ in N_2 -atmosphere, the temperature was raised to 105 $^{\circ}\text{C}$ and held for 10 minutes to determine the water content. Heating to 900 $^{\circ}\text{C}$ with a holding time of 10 minutes thereat was done to measure the amount of volatile matter. After cooling to 750 $^{\circ}\text{C}$, the gas atmosphere was switched from pure N_2 to an additional 21 vol.-% of oxygen. The ash content was then determined at three different temperatures, 750, 815 and 950 $^{\circ}\text{C}$, each with a holding time of 20 minutes. All heating and cooling was done at a rate of 25 K/min. The different temperatures were used in order to gain a better understanding of the influence of the analytical procedure on the ash determination and are based on common temperatures used in different standards for solid fossil fuels [40,41]. Deviating from the typical ashing temperatures for solid biofuels of 550 $^{\circ}\text{C}$ (e.g. in ISO 18122:2015) is not uncommon for biochar and has been suggested in [39] or [42]. For a valid comparison, the raw biomass was treated under the same conditions. The values given in Table 1 and Table 3 are the average values (also for the other parameters given in the tables).

The elemental analysis was performed in a LECO TruSpec CHN Micro, using a sample mass of 2 mg. Due to this small size combined with the inhomogeneity of the fuel, a triple determination was done for all chars and a quadruple or quintuple determination for untreated biomass.

An isoperibol calorimeter (IKA C200) was used to determine the heating values of the biomass.

The ash composition was determined in an external laboratory, using inductively coupled plasma (ICP) according to DIN EN ISO 11885.

2.5 Literature-based validation of the novel approach

In addition to the slow pyrolysis experiments, the novel approach was also used to calculate the solid mass yield from experiments presented in the literature. An overview of these experiments and their conditions is given in Table 2 (whenever an information was not clearly given in the publication, this is indicated with n.a., not available, in the table).

Table 2 Slow pyrolysis cases from literature used for validation

Authors	Biomass	Reactor	Heating rate	Maximum temperature [°C]	Residence time	Sample mass or volume
Bourgois & Guyonnet [43]	Pine sawdust	n.a.	Preheated reactor	260	15-240 min	n.a.
Karaosmanoglu et al. [44]	Rapeseed straw-stalk	Tubular fixed bed	5 K/min	400-800	30 min	30 g
Keiluweit et al. [45]	Pine shavings, Straw	Fixed bed (muffle furnace)	n.a.	100-700	60 min	n.a.
Lee et al. [46]	Bagasse, cocopeat, palm kernel shells, straw, stem wood and bark	Fixed bed	10 K/min	500	60 min	100-400 g
Park et al. [47]	Rice straw	Fixed bed	10-12 K/min	300-700	60 min	100-110 g
Quicker et al. [48]	Rape straw, forest residues, waste wood, coconut, bark	Rotary kiln	Preheated reactor	700	n.a.	1 kg/h
	Waste wood, bark, hazelnut shells, palm kernel shells, rape straw, wheat straw, rye straw, grass clippings, coconut, digestate	Fixed bed (retort)	8.5 K/min	780	ca. 60 min	500 ml

A total of 54 single samples from the publications listed in Table 2 were considered. For each of these, the mass yield was calculated according to the proposed method based on the volatile matter (cf. equation (4)) as well as the two ash-based calculation methods (cf. equations (2) and (3)) and the results compared with the gravimetric yield (cf. equation (1)) given in the publication. The feedstocks to the experiments listed in the table were typically pre-processed, i.e. ground to a small particle size (less than 1 mm to 40 mm). It should be noted that the experiments considered include setups with and also without induced gas flow through the reactor, i.e. in [43], it is reported that product gases were circulated through the apparatus and in the rotary kiln experiments in [48], no additional gas was added to the reactor. The temperature range considered in these publications (maximum temperature of 800 °C) is representative for temperatures used in practical production facilities [49].

3. Results

The slow pyrolysis of BFR, bark and walnut shells resulted in chars with the volatile matter, ash content and mass yield (gravimetric determination) shown in Table 3.

Table 3 Properties of biochars obtained from slow pyrolysis. Standard deviations are given in brackets.

Fuel	Forest residue (BFR)	Bark	Walnut shells
Mass yield [wt%]	29.5	31.0	27.6
<i>Proximate composition [wt%], dry basis</i>			
Volatile matter	15.73 (1.85)	12.92 (1.83)	10.40 (0.04)
Ash (950 °C)	6.88 (0.16)	4.69 (0.04)	1.22 (0.03)

The mass yields from the experiments can be compared with the mass yields calculated from equations (1), (2) and (3). A comparison of the results is shown in Figure 2. The mass yield of BFR is quite accurately calculated by both the ash method (30.6 %) and the ash-tracer method (29.0 %). Both approaches seem to be suitable for the calculation in this case. The method using the volatile matter slightly underpredicts the mass yield, at 25.4 %. The problems associated with the use of ash as a tracer become clearer when the mass yield of bark is considered. Whereas the yield is well estimated using the method based on the volatile matter (29.6 %), both ash-based calculations highly overpredict the mass yield (56 and 57 %). Because the bark contains significantly more alkali and alkaline earth metals (Table 1), the release of volatile alkaline ash components causes large deviations of the ash-based calculations from the real mass yield. The mass

yield of walnut shell pyrolysis is very well predicted using the volatile matter content (27.3 %), whereas both ash-based calculation methods underpredict the amount of solid residues. Here, it should be noted again that the ash content of this biomass has shown to be very sensible to the determination temperature and that the total amount is rather low. These may be two reasons rendering the ash-based methods less accurate for calculating the mass yield.

Considering all cases, the slow pyrolysis of mixed forest residue, bark and walnut shells, the volatile matter method seems to give more reliable results, which are hardly influenced by volatile ash components or uncertainties in the determination of the ash content.

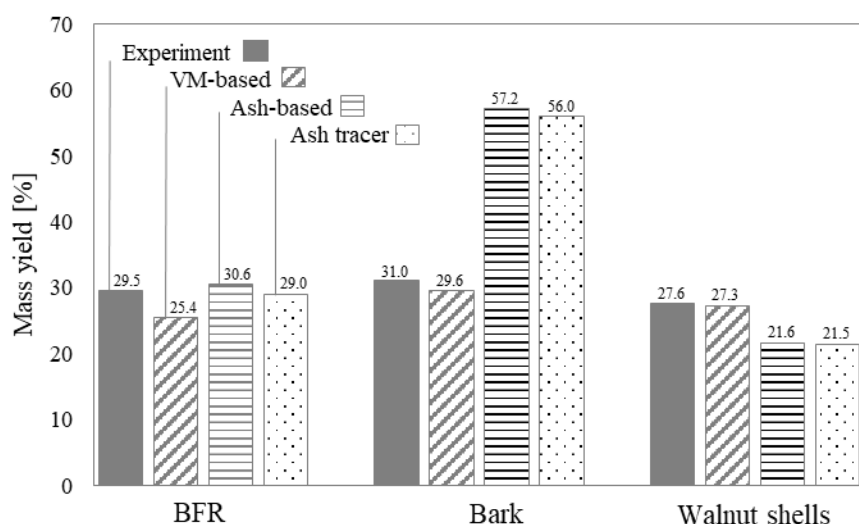


Figure 2 Comparison of the gravimetric mass yield (experiment) with the calculated mass yields from different methods for forest residues, bark and walnut shells, pyrolyzed in slow heating rate conditions

Literature data for slow pyrolysis was collected to make an additional, more substantial comparison of the mass yield calculation methods (see Section 2.5).

A comparison of the gravimetric mass yield with the ash-based calculation methods can be found in Figure 3 (ash method according to equation (2)) and Figure 4 (ash-tracer method according to equation (3)). The results of the calculations based on the volatile matter content (equation (4)) are shown in Figure 5. In each figure, the dashed line indicates the trendline for the complete dataset. The solid line, the angle bisector, represents the ideal case, in which the calculated yield corresponds to the gravimetrically determined yield. For both cases, the trend and the ideal case, the R^2 -values (coefficients of determination) are given in the figures. The grey shaded area marks the range of 20 % deviation from the bisector. The results from the

three experiments described in Section 2.3 are also included in this evaluation (marked by red circles). The data is grouped into two categories, woody feedstocks (including nut shells) are shown in green squares, non-woody feedstocks (e.g. grass, straw, digestate) are shown as orange triangles. The R^2 -values do not distinguish between the feedstocks but are given for the entire dataset.

It can clearly be seen from the distribution of the values and the R^2 -values that the purely ash-based calculations hardly offer a reliable method in determination of the mass yield. The proposed volatile-matter-method however gives significantly better results with much less variation and the trendline nearly overlapping the bisector. It may be suggested that the mass yield of non-woody biomass may be more accurately predicted than that of woody biomass by using the ash content. This may be caused by the fact that non-woody biomass often contains significantly more ash than woody biomass, and is therefore less influenced by errors in the ash determination. However, given the inhomogeneous nature of the feedstocks as well as the fact that there is no information about the ash composition available, no definitive conclusion shall be given here.

The cases considered as a basis for the evaluation are slow pyrolysis experiments. These often maximize the residence and contact time between volatilized gases and solid. Therefore, it is surprising that in most cases, the mass yield can be predicted quite accurately with the volatile matter content alone. This implies that the contribution of repolymerization of the volatilized gases to the produced solid is insignificant or compensated in weight by the volatilization of inorganic components.

Figure 6 shows an error distribution of the three calculation methods (presented as a box plot diagram). In more than half of the 57 cases considered, the ash-based calculations deviated more than 20 % from the gravimetric yield. For both methods, the error may actually be as high as 200 %. The median error of the two methods are comparable, about 23 %. On the other hand, for the approach based on the volatile matter content, there were only seven samples for which the mass yield calculation deviated more than 20 % from the experimentally determined yield, with the maximum error of 37 %. From the data available, no obvious correlation between the experiments or samples with the highest deviations could be found. More than half of the samples (29) could be calculated with an error of less than 10 %. In fact, for 15 samples, the deviation from the gravimetric result was not more than 5 %. The median error of this method is found to be 9 % in this case.

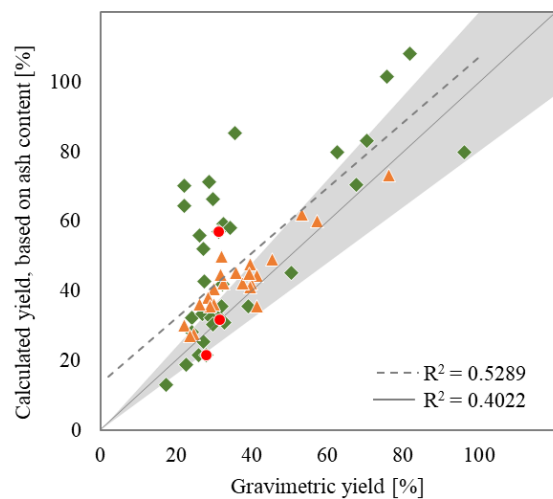


Figure 3 Comparison of the gravimetric mass yield and the mass yield obtained from the ash content. Woody feedstocks are indicated with green squares, non-woody feedstocks with orange triangles. Own measurements are marked with red circles.

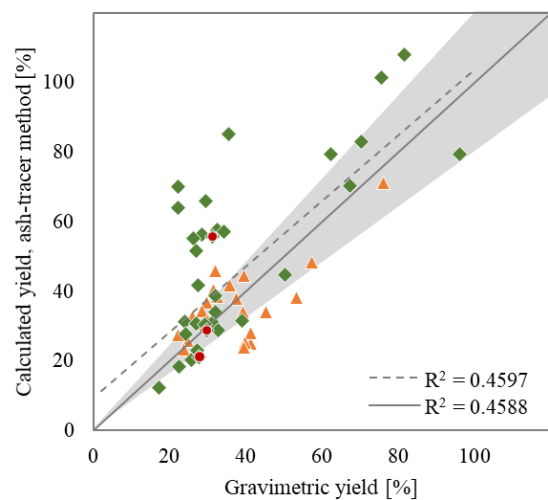


Figure 4 Comparison of the gravimetric mass yield and the mass yield obtained from the ash-tracer method. Woody feedstocks are indicated with green squares, non-woody feedstocks with orange triangles. Own measurements are marked with red circles.

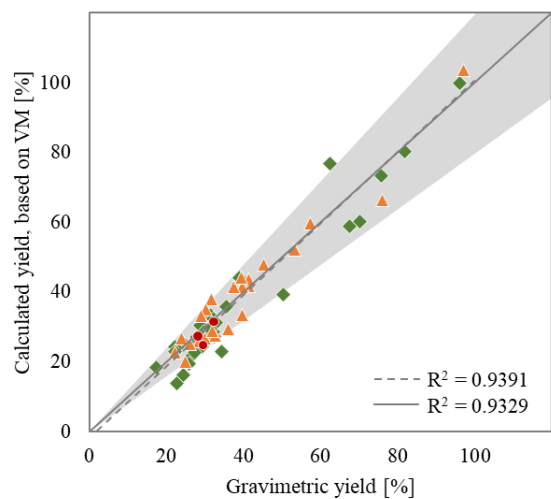


Figure 5 Comparison of the gravimetric mass yield and the mass yield obtained from the volatile matter content Woody feedstocks are indicated with green squares, non-woody feedstocks with orange triangles. Own measurements are marked with red circles.

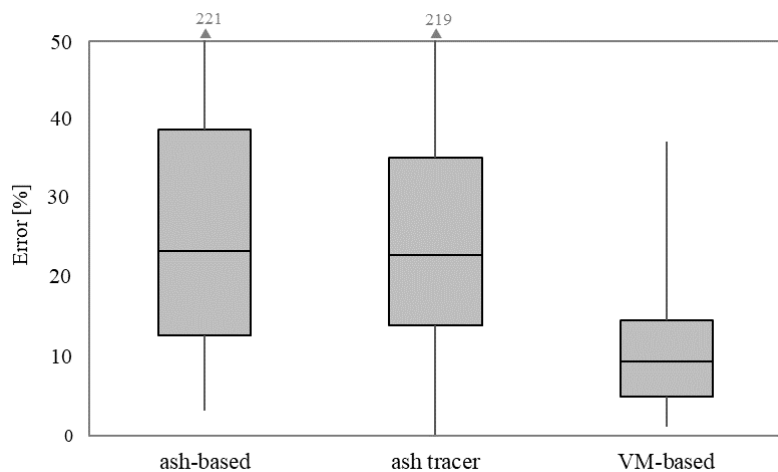


Figure 6 Error distribution of the mass yield calculation methods. Numbers above the chart indicate the maximum error values of ash-based and ash-tracer methods.

4. Summary and Conclusion

In the present study, a novel approach for the calculation of the solid mass yield from biomass slow pyrolysis is presented. The approach is based on the assumption that both the ash and the fixed carbon remain unchanged during pyrolysis. The solid mass yield is calculated from the volatile matter content of the raw biomass and the char. However, release of volatile ash components is a known phenomenon during pyrolysis and leads to unreliable results of the mass yield using common calculation approaches based on the ash content alone (e.g. ash-tracer method). Accordingly, this is also a source of error in the proposed volatile matter-based method, but since the ash content is small (and hence also the amount of inorganic volatiles released from the ash) compared to the sum of ash and fixed carbon, the resulting error is very small. The proposed volatile-matter method was validated for slow pyrolysis at atmospheric pressure and production temperatures up to 800 °C by comparison with the gravimetric yield and two ash-based methods. Data was taken from literature as well as from own experiments. The validation clearly showed that both ash-based methods give unreliable results and are in many cases not suitable to calculate the solid mass yield of biomass pyrolysis. The proposed volatile matter method does not only give significantly better results than the purely ash-based methods, the calculation of the actual mass yield is possible with good accuracy. Secondary char formation does not appear to make a significant contribution to the formation of char under atmospheric pressure and typical production temperatures of practical applications.

The methods seems to be applicable to the conditions presented in this study (slow pyrolysis at atmospheric pressure and temperatures up to 800 °C). Whether or not the proposed method can also be used for other pyrolysis conditions (e.g. very high production temperatures, fast heating rates) remains to be determined in future studies.

5. Practical Implications

In summary it can be stated that whenever possible, a gravimetric determination of the mass yield should be conducted. However, the proposed method offers an attractive alternative if the experimental setup or production conditions do not enable a complete collection of the material. The analytical efforts required are small, considering that the determination of volatile matter is performed with comparable ease to the ash content. In addition, ash release does not lead to a yield of more than 100 %, which could be the case for ash-based approaches. Methods for mass calculation based on other tracers (i.e. a single thermally stable

ash component) require an additional analytical step to determine the inorganics. This step is obsolete for the method proposed.

The fact that the solid mass yield of slow biomass pyrolysis can be calculated with the volatile matter content, has several implications. The attainable amount of biochar (excluding volatile matter) can be estimated from the fixed carbon content of the raw biomass. Therefore, in practical reactor design, increasing the gas residence time in the reactor does not necessarily lead to the production of more char.

6. Acknowledgement

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