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Determination of Biomass Fraction for Partly Renewable Solid Fuels

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Abstract

Biomass-based waste fuels are used in many industrial applications since combustion of biomass gives no net emissions of carbon dioxide. Some waste fuels, e.g. refuse derived fuels (RDF), contain not only biomass, but also some fossil material, hence can be classified as partially CO_2 neutral fuels. The biomass fraction of a mixed solid fuel is an essential parameter for the determination of net CO_2 emissions. It is also important to know the accuracy of the different biomass fraction determination methods. In the present study, the biomass fraction of artificially made RDF was determined by means of the selective dissolution method (SDM) in total carbon basis and also by the ^{14}C method in total carbon, weight and calorific value bases. Then the relative accuracy was compared using findings from a previous study. SDM shows very high accuracy in weight and calorific value basis. The ^{14}C method gives comparable results in most cases, but shows considerable deviations for some samples. The SDM results in total carbon basis show less accuracy compared to the other bases. When performing the SDM analysis in total carbon basis, one should correct for ash forming matter in order to increase the accuracy of the biomass fraction determination.

Key words: Biomass fraction; Refuse derived fuel; Selective Dissolution Method; ^{14}C method; Accuracy; Ash forming matter

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Nomenclature

$A_{residue}^{total}$	Ash content of residue out of total original sample in dry basis (wt%)
A_{SRF}	Ash content of solid recovered fuel sample in dry basis (wt%)
$C_{bio,SRF}$	Biogenic carbon content of solid recovered fuel in dry basis (wt%)
$C_{plast-mix}$	Total carbon content of dried plastic mix sample (wt%)
$C_{residue}$	Total carbon of dissolution residue out of residue in dry basis (wt%)
$C_{residue-ash}$	Total carbon content of residue ash in dry basis (wt%)
C_{SRF}	Total carbon content of solid recovered fuel in dry basis (wt%)
$C_{Theo,SRF}$	Theoretical total carbon content of dried solid recovered fuel sample in dry basis (wt%)
C_{wp-mix}	Total carbon content of dried wood-paper mix sample (wt%)
$m_{residue-ash}$	Weight of residue ash in dry basis (kg)
m_{SRF}	Weight of total original sample in dry basis (kg)
q_{SRF}	Calorific value of the solid recovered fuel sample in dry basis (kJ/kg)
q_{wp-mix}	Calorific value of the wood-paper mix sample in dry basis (kJ/kg)
$W_{wp.plast}$	Wood-paper mix: plastic mix ratio in solid recovered fuels in dry basis (kg/kg)
x_B^{cal}	Biomass fraction, expressed as a percentage by calorific value (%)
x_B^{TC}	Biomass content in dry basis by total carbon (wt%)
$x_{B,Theo}^{TC}$	Theoretical biomass content in dry basis by total carbon (wt%)
x_B^{wt}	Biomass content in dry basis by weight (wt%)
$x_{B,Com}^{wt}$	Combustible biomass content in dry basis by weight (wt%)
x_{NB}^{cal}	Non-biomass fraction, expressed as a percentage by calorific value (%)
$x_{residue}$	Dissolution residue out of total original sample in dry basis (wt%)
$^{14}C_{REF}$	^{14}C content of reference (100% biogenic carbon) in dry basis (pMC)
$^{14}C_{SRF}$	^{14}C content of solid recovered fuel in dry basis (pMC)

1. Introduction

The world economy is strongly dependent on fossil fuels. Rising fuel prices and the Kyoto Protocol are driving a shift towards renewable energy sources to reduce CO_2 emissions. In that sense, energy from waste play an important role in tackling climate change, by displacing the use of fossil fuels and by providing a more environmentally sustainable method for waste management. Since wastes or solid recovered fuels (SRF) are generally composed of fossil and biogenic materials, only part of the CO_2 emissions is accounted for in greenhouse gas

inventories or emission trading schemes. However, quantifying accurately the biomass fraction is not straight-forward. Hence, development of proper methodologies for the measurement of the biogenic fraction in mixed waste fuels is necessary to be in compliance with the reporting requirements.

Refuse derived fuel (RDF), also called solid recovered fuel (SRF), is typically produced by shredding, classifying and drying municipal and industrial solid wastes, and is a very heterogeneous fuel [1]-[3] . It contains several materials, such as paper, plastics, wood, organic waste, fabrics, rubber and metals in very different compositions, depending on the origin of the waste [1], [4]. Table 1 shows compositions of some different RDF materials found in the literature. However, column 2 in the table refers to RDF samples manually sorted by authors. This RDF sample was collected from a cement plant where RDF is used as an alternative fuel in the precalciner unit. The facts that RDF contains a considerable amount of biomass and is also a less expensive fuel, explains the increasing usage of RDF as an alternative energy source in industrial applications [1], [5]-[6]. Cement industry [7]-[9] and power plants ([2], [4], [10]) are few potential examples where RDF is used as fossil fuel replacements.

Table 1. Composition (wt%) of some RDF samples

Type	Our analysis	[11]	[3]	[10]	
				Flemish region	Italy
Plastics	13.4	25.0	29.2	31.0	23.0
Paper/cardboard	15.6	19.0	8.1	13.0	44.0
Wood	10.0	8.0	4.6	12.0	4.5
Tissue/sanitary products		12.0			
Fabrics/textile	4.3	14.0	7.4	14.0	12.0
Leather/rubber	0.1	3.0	1.1		
Carpets/mats		3.0			
Liquid packaging board		3.0			
Food/Biological waste	2.2		0.0		14.0
Glass	0.6		0.0		2.5
Metal	0.3		1.1		
Ceramic	0.9		0.0		
Fines	52.6	13.0	48.5		
Other				30.0	

In Norway, plants with significant CO_2 emissions have to comply with the national emissions trading regulations [12]-[13], which are based on the EU Emissions Trading Directive [14]. When reporting net CO_2 emissions, the biomass content (or conversely the fossil fraction) of RDF is a key parameter. It can be represented by weight, calorific value or carbon content.

Four methods for the determination of biomass content and hence fossil fraction in solid recovered fuels are published in technical specification CEN/TS 15440:2006 [15], the subsequent European pre-standard Draft prEN 15440 [16] and later in NS-EN 15440:2011 [17]. These are; the selective dissolution method (SDM), the ^{14}C method, the manual sorting method and the informative reductionistic method.

Investigations related to this research field have been carried out by several authors. Accelerator mass spectrometry (AMS) radiocarbon analyses have been applied on carbon dioxide sampled at the stack of three power plants burning natural gas, landfill biogas and solid recovered fuel derived from municipal solid waste [18]. The same procedure has been used for waste incinerators [19]. [14]C analysis for flue gas is recommended by some more authors [20]-[22], and some of them [20]-[21] have proved the reliability of the method by comparison with those based on carbon mass input and output and an energy balance data of the relevant plants. The bio-based content of manufactured products has been found by some researchers using radiocarbon dating procedures [23]. Further information can be found for ^{14}C contents of different biogenic waste as well as mixtures of different wastes and solid recovered fuels [24]. The repeatability and accuracy of SDM have previously been investigated by the current authors, and a simplified method has been developed [25]-[26]. An alternative method called the balance method has been developed to determine fossil and biogenic CO_2 emissions from waste-to-energy plants [27]. Similarly, a method to determine the mass, energy and carbon content of biogenic and fossil matter in RDF is described by combining standard chemical information about biogenic and fossil material with data from a chemical analysis of the RDF [28]. In another paper [29], the balance method, SDM and the ^{14}C method are explained in detail. In still another study, a method to evaluate the renewable and non-renewable energy fractions released during combustion of biofuels and bioliquids that could be produced through chemical processes is presented [30]. A comparison of the manual sorting method and SDM for a range of process streams from a mechanical–biological treatment plant has also been presented [31]. Further, one may find comparison between manual sorting, SDM and reductionistic method results in references [11] and [32]. Similarly, some authors have used the ^{14}C method, sorting analyses and the balance method in order to determine the fossil fraction in municipal solid waste (waste and flue gas) in Sweden [33].

In the present study, different artificial RDF mixtures are analysed by SDM in total carbon basis and ^{14}C method in weight basis, calorific value basis and total carbon basis. These results are compared with previous findings of SDM for weight basis and calorific value basis [25] in order to compare the accuracy of the SDM method and the ^{14}C method. Furthermore, the effect of biomass ash forming matter on the SDM result in total carbon basis is analysed, and possible corrections are proposed.

2. Materials

Spruce wood (50 wt%, dry and ash free; DAF) and copy paper (50 wt%, DAF) were mixed to mimic the biomass content in RDF, whereas polyethylene (PE, 74 wt%), polyvinyl chloride (PVC, 20 wt%) and polyethylene terephthalate (PET, 6 wt%) were mixed to mimic the fossil

fraction of RDF (all weight fractions in dry and ash free basis). Prior to mixing, the pure materials were separately ground into <1 mm particles and then dried in an oven to remove the moisture. For the grinding, a Retsch SM 2000 grinding apparatus was used. The PE: PVC: PET proportion in the plastic mix was according to data on plastic manufacturing and recycling rates in Western Europe [34]. Table 1 shows that the wood:paper ratio varies a lot, and according to "our analysis" in that table, the paper:wood ratio is 1.56. However, the plant where that RDF sample was collected had a plan to increase the wood percentage of RDF by mixing it with impregnated wood, so an approximate value of 50:50 (DAF %) was selected for the wood-paper mix.

The two mixtures were mixed with each other in different proportions. Altogether seven artificial RDF samples with different higher heating values (HHVs; gross calorific values) were made. One can observe from Table 1, that the compositions can vary within a wide range. Therefore, the higher heating values of the artificial mixtures were specified so as to obtain evenly distributed values covering a relatively broad range, from about 20 MJ/kg to about 40 MJ/kg in DAF basis (Table 3). Table 2 summarizes the compositions of the artificial mixtures made.

Table 2. Corresponding compositions of artificial mixtures.

Mixture	Composition (wt% dry)	
	Wood-paper mix	Plastic mix
AM 1	93	7
AM 2	82	18
AM 3	68	32
AM 4	57	43
AM 5	45	55
AM 6	24	76
AM 7	0	100

3. Theory

3.1. The selective dissolution method

The basic theory behind the dissolution test calculation is that the biomass in RDF selectively dissolves and oxidizes in H_2SO_4/H_2O_2, while the non-biomass (fossil material) and the inert material remain in the residue[1]. Cellulose, which is the major constituent of the biomass fraction is first degraded by acid hydrolysis and gives glucose base units. The reaction is strongly pH-dependent and continues at a very strong rate at low pH and temperature well under 100 °C. Secondly, the oxidizing reagent deteriorates the physical properties of fibrous cellulose rapidly under hydrolytic conditions [35]-[36].

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[1] Residue is the remaining filter cake after the sample dissolving, filtering and drying.

However, it should be noted that some of the ash forming matter from both biomass and non-biomass can be dissolved in the H_2SO_4/H_2O_2 solution and then penetrate through the filter, while the rest remains in the residue. Moreover, some of the ash forming matter will remain on the surface of the filter paper along with the residue while some will penetrate into the pores of the filter paper. The latter phenomenon has to be compensated in some cases when calculating the biomass and non-biomass fractions of RDF in calorific value basis [25]. The effect of ash forming matter on calculation procedure in total carbon basis is discussed in more detail in sub section 6.4.

3.2. The ^{14}C method

[14]C develops in the atmosphere by an interaction of cosmic radiation and the existing nitrogen. The radioactive ^{14}C atoms are quickly oxidized to CO_2 in the terrestrial atmosphere. The CO_2 is absorbed by plant tissues and moves up the food chain until the ^{14}C/^{12}C ratio in all living matter is essentially the same as that in the atmosphere. After life ends, the amount of ^{14}C diminishes with time because carbon uptake has stopped while the ^{14}C continues to undergo radioactive decay according to the half-life period of 5730 years with the emission of β radiation. Consequently, the ^{14}C/^{12}C ratio declines with time since the amount of [12]C (which is stable) remains constant [23].

The ^{14}C method uses this principle for the determination of biogenic content in wastes. After about 18 half-life periods (<100 000 years) the ^{14}C content is about 0.0004%, which is negligibly small and not determinable. Fossil energy carriers, such as coal or oil, as a rule are much older than 100 000 years, whereas renewable energy carriers, such as wood, last for several hundred years and should have a measurable ^{14}C content (modern carbon) [29]. The relation between the fraction of biomass and its ^{14}C value is considered as linear [21]. However, due to nuclear weapons tests in the past century, the radiocarbon content in the atmosphere has not been constant, which has resulted in a varying ^{14}C content of biogenic matter, depending on the period of growth ([19], [24], [29]).

4. Method

The experimental plan and procedures are explained in sub sections 4.1 and 4.2. One may also refer to Fig. 1, to get an overview of the experimental plan. In Fig. 1, the samples analysed, the analyses carried out and the reason for analyses are indicated by thick margined blocks, normal margined blocks and grey blocks, respectively. Most of the analyses were carried out in three parallels, and averages of the parallels are used when comparing values.

4.1. The selective dissolution method

The experimental procedure mentioned in Annex E of CEN/TS 15440:2006 [15] was followed, and this procedure is also described in [16] and [17]. Three dried representative samples were taken from each artificial mixture (Table 2) and one of those was analysed for ash according to [37] and this result of ash analysis was also taken for the ^{14}C calculations whenever required. Selective dissolution was carried out for the second sample, and the residue was collected for total carbon analysis. This residue and the third artificial mixture sample were sent to an external

laboratory for total carbon analyses [38]-[40]. This procedure was carried out for all seven artificial mixtures, and the total carbon content of the wood-paper mix was also determined as that result is required for comparison. However, the total carbon of the mixture ashes were not determined since the ash contents of artificial mixtures were below 10 wt% [15].

For SDM, the used volumes of chemical solutions were proportioned in accordance with the sample weights. The materials were dried at 105 °C until a constant weight was achieved, using an electric oven. The ash analyses were carried out in a muffle furnace, in accordance with CEN/TS 15403:2006 [37]. An electronic balance with a lower measuring limit of 0.1 mg was used for weighing purposes.

4.2. The ^{14}C method

Samples of 1g from each of the seven artificial mixtures (Table 2) and the pure wood-paper mix were given to an external laboratory for ^{14}C analysis, as the authors did not have access to the required laboratory equipment for that type of analysis.

At the laboratory, the sample was prepared by first removing contamination, then combusting the carbon and finally reducing the CO_2 into graphite. Then the graphite was analysed using the accelerated mass spectrometry method. A NEC 15SDH-2 Pelletron instrument was used for the AMS analysis. Pretreatment typically takes some days whilst combustion and conversion into graphite takes around 24 hours. The time for AMS measurement depends on ^{14}C content of the sample, however typically it is 30 minutes/sample. The results from the laboratory were given as percent modern carbon (pMC), which corresponds to the content of biomass.

The calorific values of each artificial mixture and wood-paper mix were determined by the authors. For the determination of higher heating value, a Leco AC-350 automatic calorimeter was used. The sample weights after drying were in the range 0.6-1.4 g. The range of the calorimeter is 14-35 MJ/kg for a 1 g sample, the precision is ≤ 0.05 % RSD and the resolution is 1 kJ/kg.

5. Calculations

5.1. SDM in total carbon basis

The calculations related to theoretical carbon content, experimental biomass fraction and theoretical biomass fraction are presented here. The experimental carbon content in dry basis is directly given by the elemental analysis.

5.1.1. Theoretical carbon content

The theoretical carbon content of the artificial mixtures are based on the measured total carbon content of wood-paper mix and chemical formulas of PE, PVC and PET. The calculated carbon content of plastic mix is 75 wt%. The theoretical carbon percentage in dry basis of each artificial mixture is calculated using equation (1).

For the calculation of theoretical carbon contents of SDM residues, it is assumed that only the plastic mix is retained as the residue i.e. no ash forming matter from biomass and non-biomass. Therefore, the carbon content of the residue should theoretically be equal to that of plastic mix (AM 7).

$$C_{theo,SRF} = (C_{wp-mix} W_{wp.plast} + C_{plast-mix})/(W_{wp.plast} + 1) \tag{1}$$

5.1.2. Experimental biomass fraction

As mentioned in CEN/TS 15440:2006 [15], equation (2) is used to calculate the biomass fraction in total carbon basis since the ash content of the original mixtures is less than 10%. Here it is assumed that there is no inorganic carbon in the biomass fraction, and also no inorganic carbon in the dissolution residue [15]; i.e. $x_{residue}$ is based on the plastic mix only. However, when collecting the residue for total carbon analysis, care should be taken in order to correct the result for fractions of ash forming matter. This is discussed in sub section 6.4.

$$x_B^{TC} = 100\% - (x_{residue} \ C_{residue} / C_{SRF}) \tag{2}$$

5.1.3. Theoretical biomass fraction

Since the total carbon content of the ash in the sample was not measured, the theoretical calculation of biomass fraction was based on total carbon of biomass fraction including ash forming matter of biomass. Equation (3) is used to calculate the theoretical biomass fraction in total carbon basis for the dry sample.

$$x_{B,Theo}^{TC} = \frac{(C_{wp-mix} W_{wp:plast}) \, 100\,\%}{(C_{wp-mix} W_{wp:plast} + C_{plast-mix})} \tag{3}$$

5.2. Calculations for ¹⁴C analyses

The biomass content from ¹⁴C analyses are calculated according to Annex C in Draft prEN 15440 [16]. The same calculation procedure can be found in [17]. First the biogenic carbon content in dry basis is calculated by equation (4).

$$C_{bio,SRF} = (C_{SRF} \, ^{14}C_{SRF})/^{14}C_{REF} \tag{4}$$

Here, the reference $^{14}C_{REF}$ value is taken as 115.02 pMC which is corresponding to the value of the pure biogenic wood-paper mix. Then the biomass fraction of the dried sample in weight basis is calculated by equation (5).

$$x_B^{wt} = C_{bio,SRF} \, 100\,\% \, / \, C_{wp-mix} \tag{5}$$

For comparison with SDM, the combustible biomass can be calculated according to equation (6), since there are no ash and ash forming matter other than in biomass here.

$$x^{wt}_{B,Com} = x^{wt}_{B} - A_{SRF} \qquad (6)$$

The biomass fraction of the dried sample in total carbon basis and calorific value basis are calculated by equation (7) and equation (8), respectively.

$$x^{TC}_{B} = C_{bio,SRF} \, 100\,\% \, / \, C_{SRF} \qquad (7)$$

$$x^{cal}_{B} = C_{bio,SRF} \, q_{wp-mix} \, 100\% \, / \, C_{wp-mix} \, q_{SRF} \qquad (8)$$

Equation (9) is used, when the calorific value basis results are presented as fossil fraction instead of biomass fraction.

$$x^{cal}_{NB} = 100\% - x^{cal}_{B} \qquad (9)$$

6. Results and discussion

The results are discussed in the subsections below. First in 6.1, the results of ash and higher heating value analyses of wood-paper mix and the artificial RDF mixtures are discussed. Next in 6.2 and 6.3, the total carbon analysis results along with theoretical manipulations followed by ^{14}C results are presented. Finally in 6.4, the main results, the biomass fractions in three bases are presented and discussed.

6.1. Ash and HHV analyses

The average ash and HHV analyses of the wood-paper mix and artificial mixtures are presented in Table 3. While the second and third columns are direct experimental measurements, the values in the fourth column are calculated based on the two former columns. The ash contents are required when the combustible part of the biomass content is calculated in weight basis. The higher heating values of the wood-paper mix and the artificial mixtures (Table 3) are used in equation (8). It can be observed that the ash contents of all artificial mixtures are below 10%, therefore a correction for carbonate present in the ashes is not made, in accordance with the recommendation [15].

Table 3. Average ash contents and higher heating values of wood-paper mix and artificial mixtures (relative standard deviations given in parentheses) [25]

Material	Ash content in dry basis (wt%)	Higher heating value in dry basis (kJ/kg)	Higher heating value in DAF basis (kJ/kg)
Wood-paper mix	10.4 (0.2%)	16 696 (0.1%)	18 634
AM 1	9.7 (0.5 %)	18 088 (0.1 %)	20 028
AM 2	7.8 (0.6 %)	20 857 (1.0 %)	22 632
AM 3	7.3 (1.2 %)	23 779 (0.2 %)	25 658
AM 4	6.0 (1.3 %)	26 391 (0.7 %)	28 089
AM 5	5.8 (1.5 %)	28 748 (0.1 %)	30 526

AM 6	3.1 (2.3 %)	33 538 (0.1 %)	34 627
AM 7	0.0 (NA)	39 395 (0.6 %)	39 395

6.2. Total carbon content

The total carbon contents of the artificial mixtures and the wood-paper mix are presented in Fig. 2. The maximum error within the measurement is around 8%. The errors are likely due to sample preparation and analysis errors. Basically, total carbon determination necessitates very small amounts of test material (in order of mg), which demands very representative samples to obtain a high accuracy [11].

It has been assumed that only plastic mix was left on the filter paper as residue, hence the total carbon content of the residue should be equal to that of the plastic mix. This is an assumption proposed in [15]. Generally, the deviations do not show any systematic error (Fig. 3). However, the deviations can be due to; 1) the assumption made that the residue is only composed by plastic material (this is more explained in sub section 6.4); 2) the residue after SDM is often more heterogeneous than the initial sample [32] and analysis necessitates very small samples as described above.

6.3. ^{14}C analyses

The measured ^{14}C values and the calculated biogenic carbon content values are presented in Table 4.

Table 4. Measured ^{14}C values and calculated biogenic carbon contents for the mixtures

Material	^{14}C in dry basis (pMC)	Biogenic carbon content (wt% dry)
Wood-paper mix	115.02	48.40
AM 1	90.57	36.93
AM 2	95.50	40.68
AM 3	76.62	35.11
AM 4	38.26	19.93
AM 5	47.56	23.94
AM 6	27.61	16.44
AM 7	0.23	0.14

According to [16], for the calculation of the biogenic carbon, a ^{14}C content of 105.26 pMC is regarded as a 100% biogenic carbon content for biomass. However, it can be seen that the wood-paper mix, which is a pure biogenic mix, has ^{14}C value of 115.02 pMC, which is higher than the normal value (Table 4). This is due to varying radiocarbon content in the atmosphere in different years as described in sub section 3.2. It can be concluded that the wood-paper mix has been derived from young biomass materials. However, for the calculation of biogenic carbon content, 115.02 pMC was taken as reference value since that is the actual value measured for the wood-paper mix, and the other artificial mixtures are derived from this wood-paper mix and a plastic mix. The analyses showed that the maximum and minimum errors for the ^{14}C measurement in pMC are around 0.56% and 0.09% for wood-paper mix and plastic mix, respectively.

6.4. Biomass fraction

In this section, the results from the ^{14}C method and from SDM are compared for all three bases; weight, total carbon and HHV. The theoretical and SDM results in weight basis and HHV basis from a previous study done by current authors [25] are used for comparison. In [25], an accuracy improvement procedure for HHV based results of SDM has also been suggested and used. (Since SDM is not recommended for fuel mixtures with biomass content higher than 95%, SDM results are not available for the pure wood-paper mix.)

SDM gives very good agreement with theoretical values, both in weight basis (Fig. 4) and in HHV basis (Fig. 5) [25]. The error is on average less than 2% in weight basis, and around 4% in HHV basis (Fig. 7). These results are qualitatively comparable with SDM results for reassembled SRF samples derived from municipal solid waste as discussed in [11] and [32]. Even though the suggested correction procedure [25] is followed to improve the HHV based result, it can give larger errors than the weight based results, because the errors introduced during the HHV analysis can increase the total error [32].

For the ^{14}C method (Fig. 4) in weight basis, five out of eight samples show quite good agreement between experimental and calculated results (average 5 % error). For the remaining three samples (AM 1, AM 4 and AM 6), the error is however quite large (20-45%), so the average error based on all eight samples is around 16% (Fig. 7).

The ^{14}C method in calorific value basis has an average error of 22% (Fig. 7). Two samples (AM 1 and AM 4) contribute with more than 15% error, while the others have around 3% error (Fig. 5).

The errors encountered with ^{14}C do not follow any trend, which indicates that the basic errors are random errors. Since several instruments were used in the ^{14}C method, the accumulated instrument error may be quite high. The calculation of biomass fractions in all three bases also requires a total carbon measurement of all samples, which may introduce additional uncertainties as described in sub section 6.2. The cleanliness of the original sample and process contamination are also important parameters with regard to accuracy in the ^{14}C method.

In total carbon basis, neither SDM nor the ^{14}C method show good agreement with the theoretical values (Fig. 6 and Fig. 7). The SDM error is on average about 18%, mainly due to the 71% error of sample AM 6. For the ^{14}C method, the average error is about 20%; two samples (AM 4 and AM 6) have a relatively high error (on average 35%).

Generally, compared to the other bases, the total carbon basis gives a much larger error for SDM. Also in [32] it was reported that the total carbon basis gives the largest errors. For the ^{14}C method, the three bases give comparable errors (Fig. 7).

Many researchers recommend ^{14}C analysis of flue gas samples ([18]-[22], [29], [33]), but few have discussed SRF itself for the determination of fossil fractions ([22], [29], [33]). Some

discuss uncertainties associated with representative sampling and ^{14}C concentration in the atmosphere.

In Fig. 6, it is observed that around 50% of the experimental values from SDM are almost similar to the theoretical values, whereas the other values have some deviation. Since the measured total carbon content of all mixtures is in a quite good agreement with theoretical numbers (Fig. 2), the weight percentage and the total carbon content of the dissolution residue are the decisive factors when calculating biomass content in total carbon basis. (The discrepancy of total carbon in the residue is shown in Fig. 3.) When doing the theoretical analyses, it has been assumed that only the plastic mix leaves as residue, and that value is an input to the total carbon analysis. However, there may be some inorganic carbon (in addition to the plastic mix) left in the residue, which gives somewhat higher values for $x_{residue}$ but lower for $C_{residue}$ in equation (2). The deviation of biomass fraction is the combined result of these. Some samples have very little deviation, though, indicating that the residue of those mixtures contains only plastic mix and only negligible amounts of ash forming matter. Hence, care should be taken to correct for the ash forming matter content in order to improve the accuracy of the biomass fraction results. The authors propose a correction procedure as described below.

A dried RDF sample which has been subjected to the SDM can be represented by several fractions as shown in Fig. 8. Basically, this is composed of combustible biomass (a), combustible non-biomass (e), inert (g) and different ash forming matter. Some portion of the biomass ash forming matter can dissolve (b), some can penetrate into filter paper pores (c), and some can be retained on top of the filter as part of the collected residue (d) in SDM. Since the ash forming matter from the non-biomass fraction (f) is usually negligible in a real RDF sample, it is assumed to be zero.

The residue used in a total carbon analysis consists of d, e, f and g. Therefore, these parts are considered when determining $x_{residue}$ and $C_{residue}$ in equation (2). When inspecting equation (2), it is observed that the ash forming matter of biomass retained on the filter paper (d) is not included in the biomass fraction. Since this is also part of the biomass, it should be accounted for. Otherwise, errors may be introduced, depending on the mass and the total carbon of the ash forming matter of biomass retained on the filter paper and collected as residue. The ash forming matter may contain some carbon as carbonate, and in such cases it must be corrected for [15]. If one uses ash corrections according to formula (E.1) mentioned in Annex E of CEN/TS 15440:2006 [15], still ash forming matter which is penetrated through filter paper and ash forming matter penetrated into filter paper pores are not counted into the biomass fraction.

For the correction, the authors propose to carry out SDM for an additional sample. The residue from this sample after SDM should be scraped and analysed for ash [37], and then the ash percentage of the residue (out of total mass of the sample) should be calculated according to equation (10). Further, this ash should be analysed for total carbon, and this value should be given as the total carbon content of the residue. This residue ash contains the fractions d and g according to Fig. 8. To calculate total biomass fraction in total carbon basis, equation (11) is used.

$$A_{residue}^{total} = m_{residue-ash} 100\% / m_{SRF} \qquad (10)$$

$$x_B^{TC} = 100\% - ((x_{residue} C_{residue} - A_{residue}^{Total} C_{residue-ash}) / C_{SRF}) \qquad (11)$$

For accurate results, authors recommend equation (11), both when the residue is scraped off from the filter paper and when residue is taken along with crushed filter paper as well.

However, appropriate repeated determinations or higher amount of test material for total carbon analyses are also recommended [11] in addition to above corrective procedure in order to avoid the errors introduced by non-representative analyses of heterogeneous materials.

7. Conclusion

Substitute fuels for thermal utilization in waste-to-energy systems are quite popular, and fuels such as RDF are already being used in the cement industry and in power plants. One of the quality characteristics of partly CO_2-neutral fuels is the biomass content since this value is one of the key inputs to calculations of net CO_2 emissions when reporting under the international emissions trading system for greenhouse gases. Hence, for the plants utilizing alternative fuels, it is important to have access to easy, reliable and accurate methods for the determination of biomass content in such fuels. The present study puts effort to compare two determination methods with regard to accuracy.

The Selective Dissolution Method (SDM) and the ^{14}C method were used for the determination of biomass fraction in seven artificial waste mixtures mimicking RDF. SDM gives the most accurate results for weight and calorific value bases. The ^{14}C method gives comparable results, but has larger errors for some samples. The SDM results in total carbon basis show less accuracy compared to weight and calorific value bases.

The higher accuracy and lower time consumption of SDM compared to the ^{14}C method, which also requires laboratories that are specialized in this technique, suggests that SDM is more suitable for regular determinations of biomass fractions in industry.

Corrections for the ash forming matter of biomass should be taken into account when SDM is used. The present study proposes such an ash correction procedure for determination of biomass content in total carbon basis.

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Figure captions:

Fig. 1 Flow chart for the whole methodology
Fig. 2 Total carbon content of mixtures in dry basis
Fig. 3 Total carbon content of dissolution residues in dry basis
Fig. 4 Comparison of results from ^{14}C and SDM for combustible biomass fraction in weight basis
Fig. 5 Comparison of results from ^{14}C and SDM for fossil fraction in higher heating value basis
Fig. 6 Comparison of results from ^{14}C and SDM for biomass fraction in total carbon basis
Fig. 7 Comparison of average errors for two methods in three bases
Fig. 8 Representation of a dried refuse derived sample subjected to SDM

Note: Each figure fits with single column.
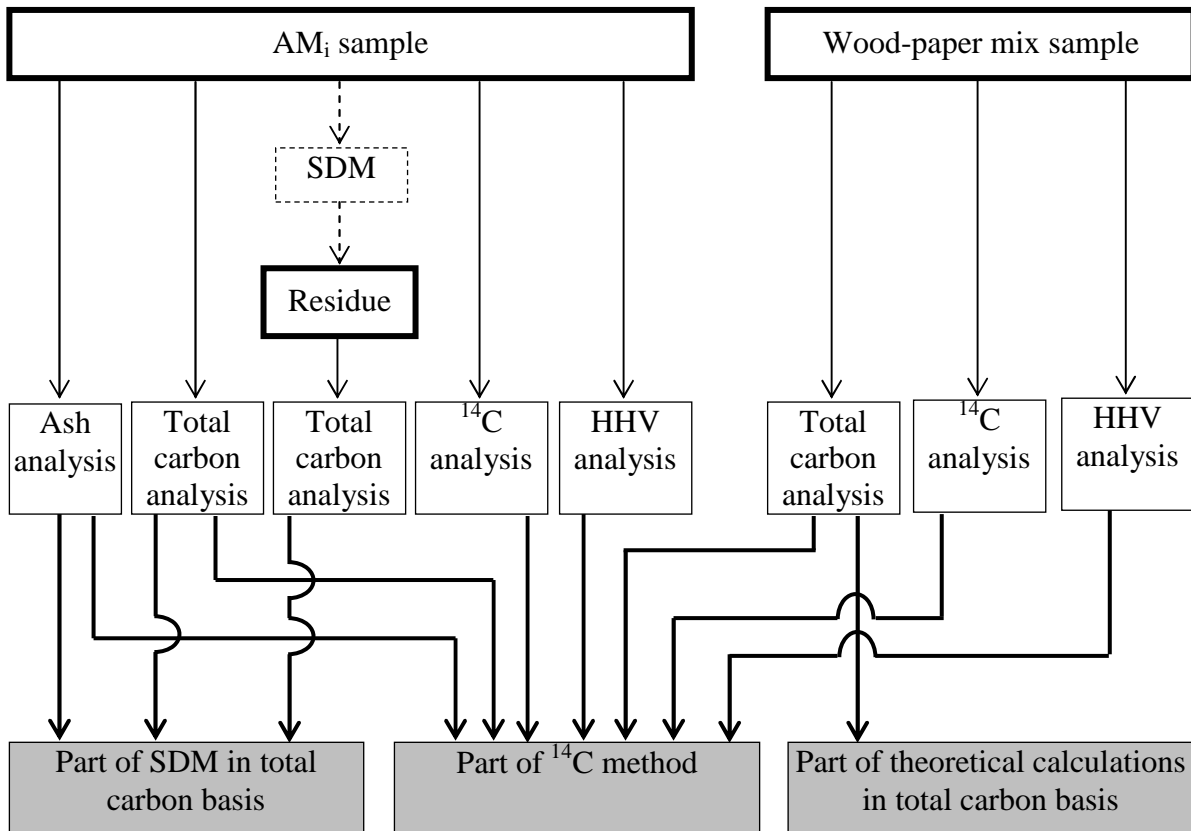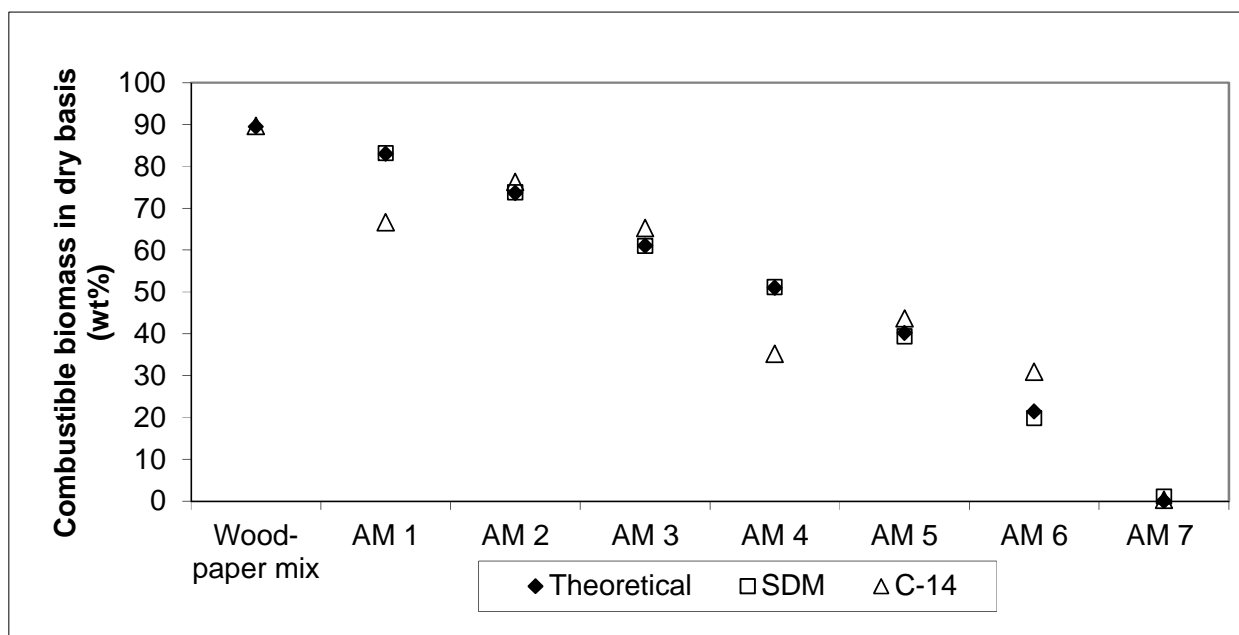
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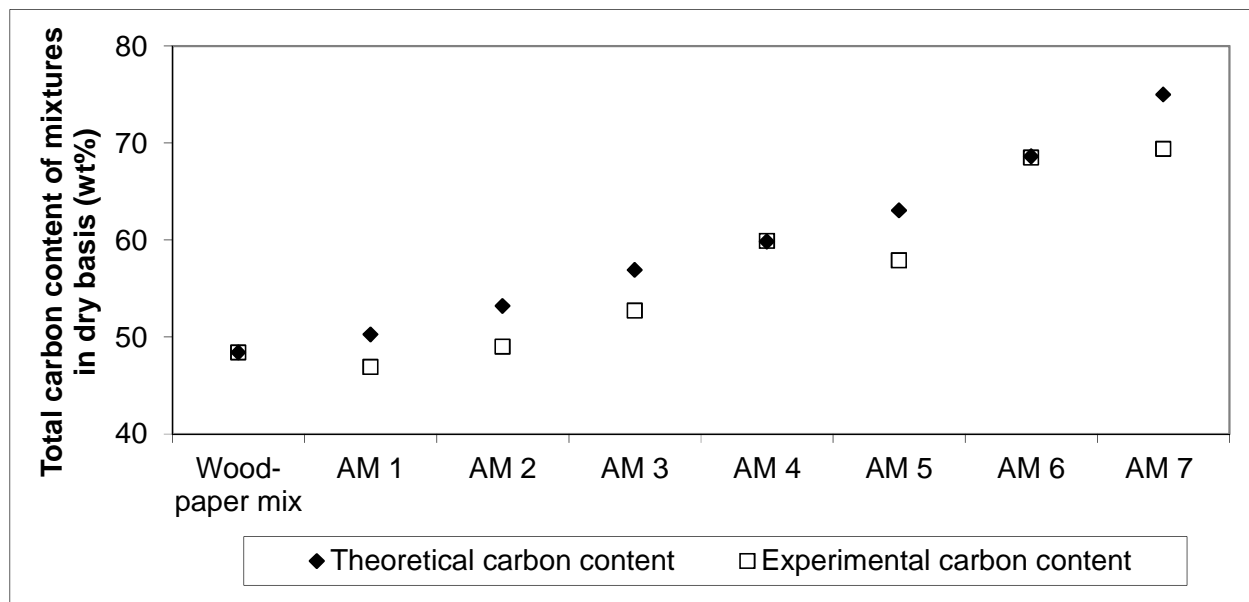
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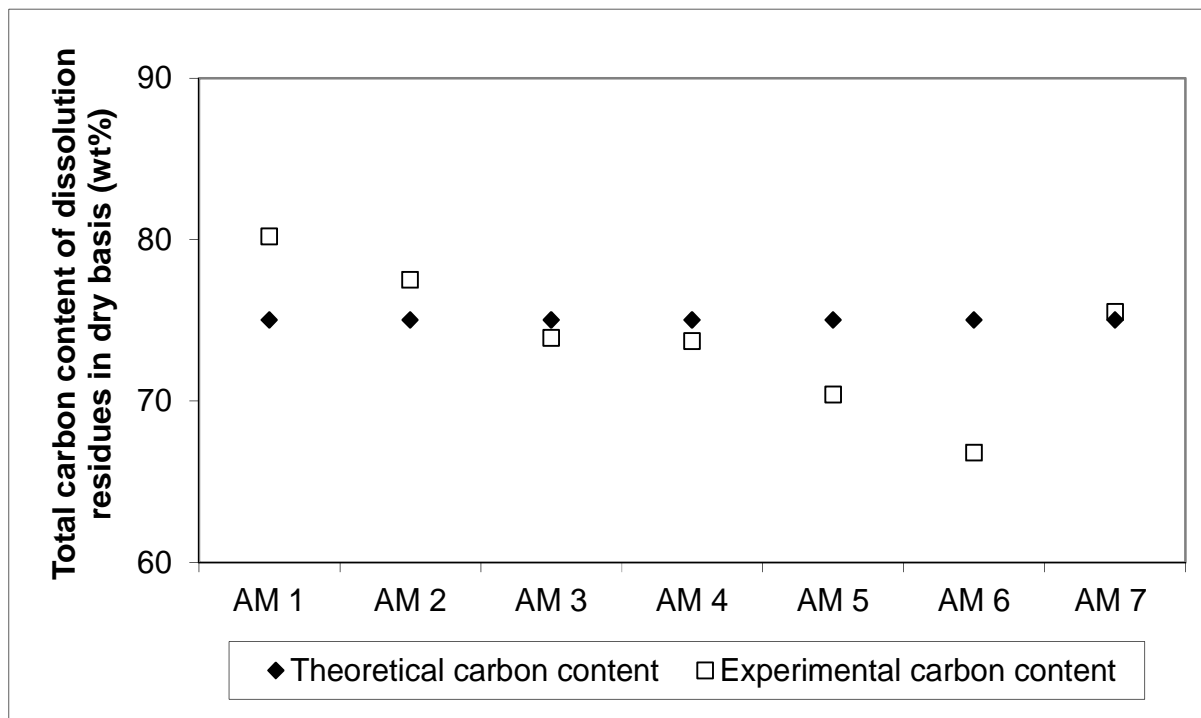
Fig. 3

Fig. 4
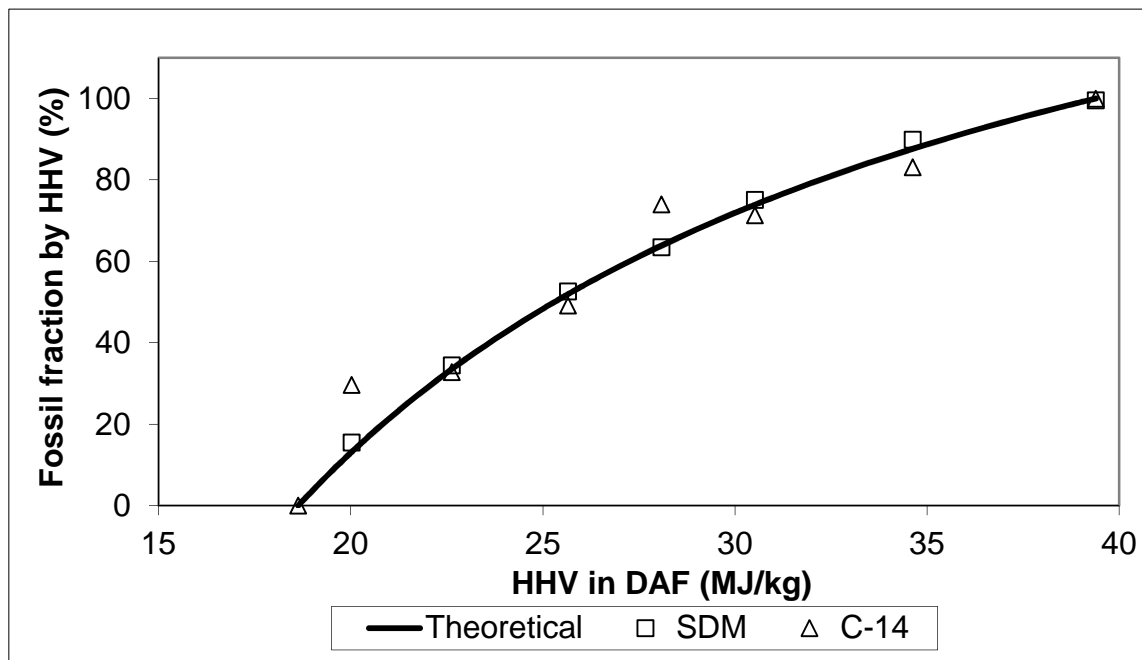
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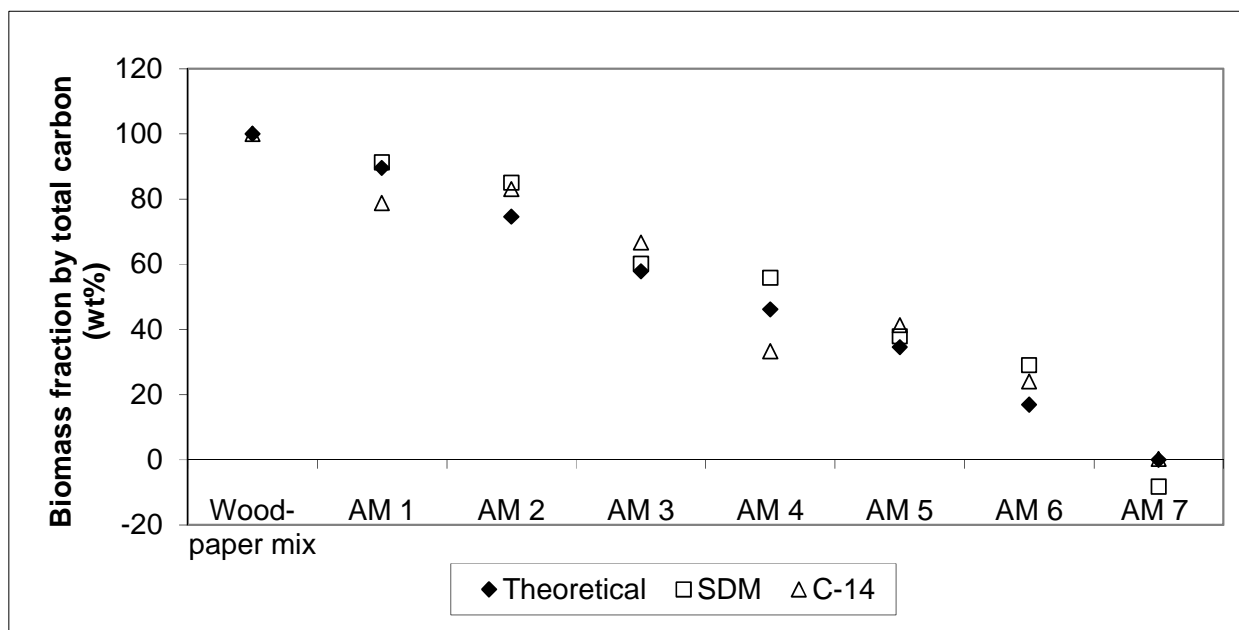
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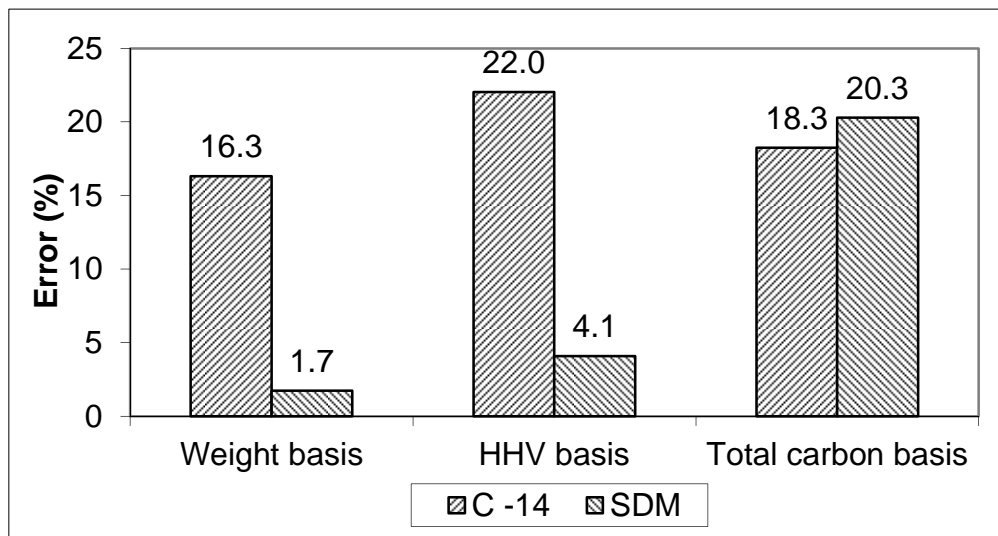
Fig. 7

Biomass: combustible (a)	Non-biomass: combustible (e)	Inert (g)
Biomass: ash forming matter dissolved (b)		
Biomass: ash forming matter penetrated into filter (c)	Non-biomass: ash forming matter (f)	
Biomass: ash forming matter retained on the filter (d)		

Fig. 8