Determining the biomass fraction of mixed waste fuels: a comparison of existing industry and ^{14}C -based methodologies

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ABSTRACT

^{14}C analysis of flue gas by accelerator mass spectrometry (AMS) and liquid scintillation counting (LSC) were used to determine the biomass fraction of mixed waste at an operational energy-from-waste (EfW) plant. Results were converted to bioenergy (% total) using mathematical algorithms and assessed against existing industry methodologies which involve manual sorting and selective dissolution (SD) of feedstock. Simultaneous determinations using flue gas showed excellent agreement: $44.8 \pm 2.7\%$ for AMS and $44.6 \pm 12.3\%$ for LSC. Comparable bioenergy results were obtained using a feedstock manual sort procedure (41.4%), whilst a procedure based on selective dissolution of representative waste material is reported as 75.5% (no errors quoted). ^{14}C techniques present significant advantages in data acquisition, precision and reliability for both electricity generator and industry regulator.

Keywords: ^{14}C (AMS/LSC) methods, energy-from-waste (EfW) plant, selective dissolution, manual sort, bioenergy.

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1. Introduction

1.1 Context

In order to meet its commitments on renewable energy generation and greenhouse gas reductions (e.g. Climate Change Act 2008; Directive 2009/28/EC (European Parliament)), the UK government implemented a number of mechanisms offering financial incentives for the generation and supply of renewable power and heat (RO, 2009). The technologies supported under these mechanisms are thermal treatment technologies, which aim to recover energy from waste feedstock (e.g. municipal solid waste - MSW) in the form of heat and/or power. These technologies encompass standard incineration, advanced conversion techniques (pyrolysis and gasification), and anaerobic digestion. Recycling energy from waste has been implemented in the UK and other European countries, providing a valuable energy resource. However, distinguishing between the proportions of biomass and fossil-derived energy is not simple and presents significant technical and administrative challenges, since only biomass-derived energy is eligible for incentive reward. Any energy which is simultaneously recovered from fossil-derived components must be discounted. The financial implications of erroneous estimates of the fossil-derived energy fraction are not insignificant for both generator and regulator. In the present context, fossil substances include both 'native' fossil fuels (coal, petroleum and natural gas) as well as fossil-derived materials such as plastics. Biomass, on the other hand, comprises recently living material: plant matter, animal matter, fungi and algae. Consequently, the energy origins of waste may be considered as either ancient (millions of years old) or modern, typically no more than tens of years old.

1.2 Determination of biobased energy fraction – current industry methods

Current methods for determining the energy origins of waste involve collecting feedstock samples and undertaking either manual or chemical ‘selective dissolution’ analysis (*e.g.* EN 15440: 2011) or a mass and energy balance method. The manual procedure involves sorting a representative waste sample into primary categories (paper, card, textiles, plastics etc.). Standard factors representing gross calorific value (GCV) and biodegradable fraction, obtained from an industry standard data source are assigned to each category enabling the biomass energy content to be determined (DoE report, CWM 087/94). Subsequently, the energy origins of the whole sample can be determined, and applied to the EfW plant’s entire waste feedstock with determinations made for each reporting period as required. The mass balance method developed by Fellner *et al.* (2007) can also be used to determine the proportion of energy derived from biomass and fossil emissions, and has been implemented in a number of comparative studies *e.g.* Mohn *et al.* (2008) and Larsen *et al.* (2013). This method requires input data derived from power station operations in conjunction with data on the chemical composition of fossil and biomass to solve theoretical mass balance equations and hence resolve energy production from renewable and fossil sources.

These approaches are accepted, under certain strict conditions, by the energy industry regulator Ofgem (Office of the Gas and Electricity Markets) who administer incentive schemes for the UK government, however, in this study only the two most commonly used methods in the UK (SD and manual sorting) were examined.

Mixed waste is a highly heterogeneous material; consequently, any method characterising large quantities of waste material based on manually collected samples must address issues of representativeness. Similarly, the chosen analytical method must

be equally transparent, reliable and accurate. Concerns about the reliability of results obtained using ‘approved’ techniques remain: however, to date no attempt has been made to systematically characterise these alongside ^{14}C methods.

1.3 Radiocarbon (^{14}C) in biobased and fossil fuel fractions

Since 2011, analysis of the radioactive isotope of carbon (^{14}C) in post-combustion flue gases has been accepted by Ofgem as an alternative method for determining the fossil fuel and biobased energy fractions of waste and is as follows.

Modern atmospheric CO_2 is overwhelmingly comprised of the stable isotopes ^{12}C and ^{13}C . The radioactive isotope ^{14}C is also present and is produced at an approximately constant rate by the interaction of nitrogen with thermalised neutrons in the upper atmosphere, resulting in concentrations of around 1 atom of ^{14}C for every 10^{12} atoms of ^{12}C . ^{14}C is unstable and undergoes radioactive decay with a half-life of 5,730 years. Consequently, and because of their great age, fossil fuels and their derivatives contain no ^{14}C whilst living and recently alive organisms (*i.e.* biomass) contain levels of ^{14}C that closely reflect contemporary atmospheric abundances.

The carbon isotope ratios within the biomass and fossil components of mixed wastes can be considered a binary mixture representative of either modern carbon (MC) or fossil carbon (devoid of ^{14}C).

1.4 Measuring the abundance of the ^{14}C isotope

Accurate measurement of the abundances of total C and the $^{13}\text{C}/^{12}\text{C}$ isotope ratio in environmental samples is analytically routine. However, accurate measurement of the

^{14}C isotope is more challenging due to the very low abundance encountered. Two approaches are available.

1. Radiometric analysis: This is most frequently carried out by liquid scintillation counting (LSC). Radiometric analysis relies on ‘counting’ the beta particles produced during radioactive decay of ^{14}C atoms where the number of counts per unit time is a measure of ‘activity’. The primary limitation of this technique is the relatively low specific activity of ^{14}C in waste samples, therefore, large samples (*e.g.* several g of carbon) and lengthy counting times (>15 hours) are required if acceptable levels of analytical precision are to be achieved.

2. Direct atom counting by accelerator mass spectrometry (AMS): This technique is used to measure the ratio of ^{14}C atoms in a sample of purified carbon relative to either the ^{12}C or ^{13}C atoms. It does not rely on counting decaying ^{14}C atoms. Since 1 g of modern carbon contains 6×10^{10} atoms of ^{14}C , and a typical AMS system can measure around 100 atoms per second, sample size and counting times are significantly reduced (Fifield, 1999). A typical AMS sample size is in the range of 1-2 mg C and the counting time is in the order of minutes rather than hours.

1.5 Development of ^{14}C procedures

The techniques developed here involve sampling and pre-concentration of CO_2 from post-combustion flue gases for analysis. Carbon in post-combustion flue gas can be considered as isotopically representative of the fuel from which it was formed but with significantly increased spatial homogeneity. Therefore, results based on the analysis of flue gas samples should be more representative of the waste stream as a whole than those based on physical or chemical analysis of ‘snapshot’ samples taken

from the feedstock stream, leading to improvements in precision and accuracy. Consequently, a key objective was to test LSC performance against both AMS and established industry methodologies. An additional benefit of developing a technique based on LSC flue gas sampling is that experimental precision can be increased by sampling a larger volume of gas or by increasing the LSC counting period, which is relatively straightforward when compared with alternative approaches for which it would be necessary to sample a larger quantity of waste.

The experimental technique is based on the established standard US technique (ASTM, 2010) (method ‘A’ – CO₂ absorption and LSC measurement), coupled with algorithms developed by consultant engineers Fichtner. Fichtner’s algorithms (Fichtner, 2007) describe how the mean ratio of gross calorific values GCV to carbon content differs between the biomass and fossil components typically found in MSW. Essentially, fossil materials have an energy density that is on average 21% higher than the biomass components of MSW. This is a commercially important detail because incentives are awarded for the biomass energy fraction of waste, and not the mass fraction. Consequently, Fichtner’s algorithms, enable the conversion from mass fraction to energy fraction with a ca. $\pm 5.5\%$ relative uncertainty, and are used to convert all LSC/AMS determinations of ¹⁴C abundance in this study.

1.6 Notation and conventions

By convention, 100 percent modern carbon (100 pMC) is defined as 0.7459 x ¹⁴C activity of the internationally recognised Oxalic acid II standard SRM-4990C (134.07 pMC), normalised to -25‰ with respect to ¹³C. In addition, the ¹⁴C content of a material is expressed relative to its stable carbon isotope content. For materials which

contain both biomass and fossil carbon, the overall pMC value is dependent on the pMC and mass fraction of both components. For the fossil carbon fraction, it is reasonable to assume that the ^{14}C content is zero pMC. However, the pMC value for biomass depends on when its carbon was photosynthetically fixed from atmospheric CO_2 .

Whilst the atmospheric concentration of ^{14}C remained relatively constant over millennia, atomic weapons testing during the 1950s and early 1960s resulted in significantly increased levels of atmospheric ^{14}C such that by 1963 the activity in the northern hemisphere was approximately 200 pMC. Levels have since declined to an abundance of ca. 104 pMC in 2011 due to excess ^{14}C entering the oceans and biota, and dilution by emissions of ^{14}C -dead CO_2 from fossil fuel burning. Nevertheless, the ^{14}C content of modern biomass is a cumulative reflection of a dynamic process. For example, a seventy year old tree felled in the year 2010 will have grown over periods when ^{14}C was ‘diluted’ as a result of fossil fuel burning (pre-1950s; ca. 97 pMC), to an atmospheric maxima in 1963 (approx. 200 pMC), and a further growth period in which ^{14}C concentrations exponentially decreased to ca. 104 pMC (2011). Therefore, its mean ^{14}C content and that of any product subsequently derived from it will lie somewhere between these limits and will be strongly influenced by atmospheric concentrations during periods of greatest net photosynthesis. By contrast, ‘recent’ materials such as garden and food waste will have a mean ^{14}C content that closely reflects present-day levels of atmospheric ^{14}C , since they contain recently fixed carbon. The average ^{14}C content of biomass in mixed wastes will reflect both recent and less recently fixed components.

Faced with this uncertainty, ASTM (2010) suggest that all pMC values must be multiplied by 0.95 (equivalent to dividing by 105.3 pMC) to ‘better reflect’ the true bio-

based content of the sample. However, and as outlined above, this is only accurate for new biomass, and is less effective for older biomass and mixed biomass where multiplying by 0.95 could lead to a systematic over-estimation of the biomass fraction. Mohn *et al.* (2008) carried out a detailed analysis of the ^{14}C content of the biogenic fractions of typical municipal mixed wastes. In their study they paid close attention to the age-distributions within the paper/cardboard, fresh biomass and wood fractions. They found that for 2008 waste, the average ^{14}C content was 113.0 pMC. By extrapolating their findings, a 2011 average pMC value of 110.5 (± 3.5 , 1σ) can be determined. Therefore, all ^{14}C results obtained from the EfW plant in this study, which was undertaken in 2011, are divided by 110.5 pMC. Fellner and Rechberger (2009) noted that solid recovered fuels (SRF) contained higher pMC values due to the nature of the mechanical sorting processes which contain higher ‘older’ material such as paper and wood. In this instance, the ^{14}C reference value attributed to SRF was extrapolated from the data of Fellner as 116.0 pMC (± 3.8 , 1σ) for 2011.

This paper describes the development and deployment of radiocarbon (^{14}C) based techniques (AMS and LSC) for determining the origins of energy recovered from waste. Both techniques rely on the measurement of ^{14}C , present as carbon dioxide molecules (CO_2) in flue gas. Trials were undertaken on samples collected from an operational EfW plant using AMS/LSC ^{14}C techniques and assessed against existing SD and manual sorting methods for bioenergy determination. The relative performance and reliability of each method is discussed.

2. Methods

2.1 Overview

A programme of work was undertaken in three stages.

1. Apparatus for combusting waste samples and isolating pure CO₂ from resultant combustion gases was developed and coupled to a LSC-based analytical system for determining ¹⁴C abundance. The system was calibrated using six internationally recognised ¹⁴C standards (0 to 134 pMC: Table 1) which were oxidised and introduced by a variety of means. Three size fractions of solid recovered fuel (SRF) were obtained (fine <6mm; medium 6-16mm; coarse >16mm), homogenised and introduced to the system. The SRF samples were combusted and the resultant CO₂ isolated. Parallel determinations of ¹⁴C abundance within the CO₂ were made using LSC and AMS. The latter more precise technique was used to validate the LSC technique.

2. Representative samples of the same SRF materials analysed in Stage 1 were sent to two independent laboratories (Laboratories X and Y) for analysis using the SD technique (CEN/TS 15440: 2006, since revised as EN 15440:2011). The purpose of this exercise was to assess the relative strengths, or otherwise, of the two isotopic determination techniques (LSC and AMS) and the SD technique.

3. The bioenergy fraction of waste feedstock at an operational EfW plant was determined by: (i) LSC analysis of flue gas samples (ca. 20l each) collected in foil gas sampling bags. These samples were analysed in the laboratories at SUERC (Scottish Universities Environmental Research Centre); (ii) AMS analysis (also at SUERC) of sub-samples of the flue gases collected for LSC analysis; (iii) a manual sort of a sample of plant's waste feedstock, using the methodology outlined by Ofgem (2013b) and (iv) the SD technique (CEN/TS 15440: 2006), carried out by Lab X only.

A summarised programme of work is presented in Figure 1.

2.2 Development of laboratory apparatus

Apparatus which enabled CO₂ to be purified and quantitatively isolated under vacuum was developed. The vacuum system was designed to accommodate apparatus for combusting waste samples or chemically liberating CO₂ from inert standards and is similar to that described by ASTM (2010) (method 'A' – CO₂ absorption and LSC measurement) and Noakes *et al.* (2006). The system terminates with a sonic-bath which houses a scintillation vial where CO₂ is trapped in an amine trapping solution (Carbosorb E: 2-methoxy ethylamine). Once trapped, a scintillation 'cocktail' (Permafluor E) is added to the mixture, and measurements of ¹⁴C undertaken using standard LSC analytical procedures.

Successful development of this stage was measured in two ways. First, through the construction of a linear calibration curve (Fig. 2) using standards prepared using the vacuum system with subsequent LSC analysis. Second, through the ability to reliably determine the bioenergy content of the SRF samples prepared using the same analytical regime. Analyses were verified using AMS analysis. Results presented in Fig. 2 show that initial measurements of standards were in good agreement with consensus values. All standards were within ca. $\pm 10\%$ of mean values which was deemed an acceptable level of precision for the LSC CO₂ absorption technique.

2.3 Solid recovered fuel (SRF) samples

SRF samples were used to assess the existing SD method for determining the biobased energy content of waste and to compare this with LSC and AMS analysis of the same material. EfW plants tend to thermally treat either the residual component of MSW (*i.e.* municipal waste which has had the recyclable components removed) or refuse derived fuel (RDF)/SRF. RDF is a product typically made by shredding and

dehydrating (MSW) and is considerably more homogenous than unprocessed residual waste; SRF can be considered as RDF which has been produced to a particular standard, *e.g.* CEN/TS 15359: 2006. The SRF used here was obtained from a single anonymous supplier. Each size fraction was homogenised to a fine consistency and divided into three roughly-equal masses (ca. 2kg).. A sample from each size fraction was sent to laboratories X and Y for SD. The remaining sample material from each size fraction was retained at SUERC for LSC/AMS analyses. SRF samples were stored at $<3^{\circ}\text{C}$ prior to analysis to minimise bacterial action. LSC, AMS and SD techniques used to analyse SRF samples are discussed here.

2.3.1 SRF - LSC analysis

Sub-samples of each SRF fraction were dried prior to analysis. Approximately 3-4 g from each of the 3 grades of SRF were weighed and introduced to a 6000 cc combustion vessel. The vessel was evacuated to 10^{-3} mbar and then pressurised with pure oxygen. Each sample was electronically ignited and sample material combusted to extinction. Combustion gas was introduced into the vacuum line, where CO_2 was isolated and cryogenically purified using liquid nitrogen according to ASTM (2010) (method A) and Noakes *et al.* (2006). Three separate combustions (A, B and C) were undertaken for each SRF size fraction producing sufficient CO_2 for duplicate analyses. Bioenergy content was determined using the method outlined in section 2.3.3.

2.3.2 SRF – AMS analysis

The validation technique is a derivative of another standard US technique: ASTM (2010) (method B). AMS methods are routinely undertaken at SUERC so no

method development was required. Approximately 10–15 ml of CO₂ was sub-sampled from SRF combustions (A and B only), transferred under vacuum and converted to graphite according to Slota *et al.* (1987) prior to analysis by AMS. Sample targets were measured on a 250kV single-stage AMS (SSAMS; Freeman *et al.*, 2008, 2010) with quality assurance data (Naysmith *et al.*, 2010) and ¹⁴C content calculated relative to the International Standard Oxalic acid II. Bioenergy content was determined according to section 2.3.3.

2.3.3 Determination of *pMC*, biobased fraction (f_{bio}) and bioenergy (% bioenergy) of sample CO₂

Percent modern carbon (*pMC*) was calculated for each sample according to the convention outlined by Stuiver and Polach (1977) and corrected for isotopic fractionation by measuring the ¹³C/¹²C ratio ($\delta^{13}\text{C}$) using a VG SIRA 10 isotope ratio mass spectrometer, comparing sample values with those of a working standard reference gas of known isotopic composition. The internal reference gas was pre-calibrated using sample gases of known isotopic composition produced from International Reference Materials such as NBS 19 and IAEA-CO-1. The measurement results were expressed using the δ notation (Craig, 1957) as per mil deviations from the VPDB standard, and a fractionation correction applied to normalise to a $\delta^{13}\text{C}$ value of -25‰. The *pMC* is calculated using Equation 1.

$$pMC = \{ (^{14}\text{C}/^{13}\text{C})_{\text{sample}} / (^{14}\text{C}/^{13}\text{C})_{\text{standard, 1950}} \} * 100 \quad (1)$$

where $(^{14}\text{C}/^{13}\text{C})_{\text{sample}}$ is the fractionation corrected ratio in the sample and $(^{14}\text{C}/^{13}\text{C})_{\text{standard, 1950}}$ is the fractionation and activity corrected ratio of the primary standard Oxalic acid II in the year 1950 where $pMC = 100$.

Determination of the biobased fraction (f_{bio}) of sample CO_2 is described by Mohn *et al.* (2008), and by Palstra and Meijer (2010) who incorporate additional mathematical terms to account for sources of CO_2 other than those derived purely from the combustion of municipal waste. The ^{14}C content of a sample (pMC_{sample}) is distinguished by the ^{14}C content and mass fraction (f) of each CO_2 source in the sample: biobased (f_{bio}), fossil (f_{fossil}) and non-fuel derived CO_2 sources (f_x) *e.g.* atmospheric CO_2 , according to Equation 2.

$$pMC_{\text{sample}} = pMC_{\text{bio}} * f_{\text{bio}} + pMC_{\text{fossil}} * f_{\text{fossil}} + pMC_x * f_x \quad (2)$$

Since pMC_{sample} is the measured value and ^{14}C has completely decayed in fossil fuel (*i.e.* $pMC_{\text{fossil}} = 0$) the fraction of biobased CO_2 (f_{bio}) in a binary sample of biobased and fossil CO_2 , with no other significant CO_2 inputs (*i.e.* $f_x = 0$), is directly proportional to the ^{14}C content of the sample, then f_{bio} is determined by Equation 3:

$$f_{\text{bio}} = pMC_{\text{sample}} / pMC_{\text{bio}} \quad (3)$$

The pMC of a sample is provided by direct AMS/LSC measurement, whereas the pMC_{bio} is dependent upon the mean ^{14}C content of pure biobased material being measured and is dependent on when the biomass component was fixed from

atmospheric CO₂. In this study we extrapolated the detailed findings of Mohn *et al.* (2008) *i.e.* by dividing the pMC_{sample} by 110.5 pMC.

Fraction biobased carbon (f_{bio}) was converted to percentage biobased energy (% *bioenergy*) using the algorithms of Fichtner (2007) where f_{bio} is the fraction biobased carbon in mixed fuel determined from ¹⁴C analysis. Fichtner's mean GCV (MJ/kg) to carbon content ratio for the biomass component of waste is 0.390 MJ/kg (± 0.008 , 1 σ). For fossil fuels it is 0.47 MJ/kg (± 0.034 , 1 σ). Using these values, % *bioenergy* is given as Equation 4:

$$\% \text{ bioenergy} = \{0.39 * f_{bio} / (0.39 * f_{bio} + 0.47(1 - f_{bio}))\} * 100 \quad (4)$$

All associated uncertainties were calculated using standard statistical rules.

Fichtner's energy conversion is approved by Ofgem, provided certain criteria are met, but is based upon the net 'dry' calorific content or lower heating value (LHV) of MSW and consequently does not account for energy loss during water vapourisation when applied to 'wet' MSW. This will introduce an additional element of uncertainty. However, Fichtner's data was derived from the UK's most definitive MSW chemistry data set (DoE report CWM 087/94), and was considered as the 'best available' UK-based energy conversion for this work.

2.3.4 SRF – Selective dissolution analysis

Representative shredded samples (ca. 2 kg each) were taken from bulk SRF material. The samples were bagged, labelled and sent to two anonymous UK

Accreditation Service (UKAS) approved laboratories (X and Y) for analysis. The two laboratories determined the gross calorific value (GCV) and gross-biobased energy content of the samples according to procedure CEN/TS 15440: 2006. Other than during transportation (ca. 24h) samples were stored below 3°C. Each laboratory undertook sample pre-treatment according to its own specifications.

2.4 Determination of biobased content of waste at an operational EfW plant

2.4.1 Site Description

In order to trial and assess ^{14}C methods against manual sorting and SD methods, measurements of flue gases and waste-feedstock were made at a mass-burn EfW plant. The plant is of the moving-grate design and thermally treats MSW with an average throughput of ca. 12.5 tonnes per hour. The bioenergy content of the MSW feedstock is currently not routinely determined since the plant does not meet incentive eligibility criteria. Information obtained from the plant's Continuous Emission Monitoring System (CEMS) revealed that mean flue gas temperature was ca. 120°C, water vapour ca. 8% by volume and CO_2 concentration ca. 8% by volume. The contribution of ambient air to flue gas CO_2 was determined $<0.5\%$. Three consecutive samples were collected over hourly intervals to investigate whether the biomass derived energy component of the waste feedstock varied temporally. Onsite sampling of flue gas CO_2 was undertaken during July 2011.

2.4.2 Flue gas sampling and analysis

The aim here was to test *experimental* precision and accuracy, which includes both sampling and analysis since *analytical* precision was determined in the laboratory.

Post-combustion flue gas was extracted from the stack manifold inspection port (post flue gas clean-up) located close to the plant's CEMS *via* a 1m long stainless-steel gas sampling probe. The port was sealed around the probe to prevent atmospheric CO₂ entering the stack whilst taking samples. Samples were extracted under vacuum and moisture removed with traps surrounded with solid CO₂ and ethanol (-78°C) into Tedlar foil gas bags. Three (20l) samples were collected in total and returned to SUERC for subsequent processing within 24 hours of collection. In the laboratory, flue gas samples were released into the vacuum system and CO₂ isolated, purified and processed according to the methods described in ASTM (2010) and Noakes *et al.* (2006). Sub-samples from each flue gas sample were taken for AMS analysis.

2.4.3 Municipal solid waste (MSW)

In addition to flue gas samples, three 'grab' samples (ca. 5 kg each) of MSW were taken and manually sorted according to the methodology described by Ofgem (2013a, 2013b). Samples were randomly collected from feedstock in the plant's waste reception hall immediately prior to incineration and flue gas sample collection. It should be noted that the plant takes black-bag waste, some of which is 'unsorted' and some of which is 'post-sort residual'. Once the categories had been weighed, each sample was homogenised and shredded to ca. <30mm. GCV was assigned to each weighed category based on the findings of the waste data stream analysis (DoE report, CWM 087/94) to enable determination of the biomass energy fraction of the waste stream. The categories from each grab were re-combined and three subsamples (ca. 2.0 kg) were taken from each grab sample and sent to Laboratory X (chosen arbitrarily) for biomass energy calculation using SD (CEN/TS 15440: 2006).

3. Results and Discussion

3.1 SRF Results

Initial experiments were carried out using the three size fractions of SRF as a homogenous surrogate for mixed waste. These experiments aimed to optimise the LSC based technique and to compare its reliability for bioenergy determination with the more precise AMS technique, and with the technique most commonly used by industry - SD (laboratories X and Y). Results are presented in Table 2.

3.2.1 SRF pMC/ Bioenergy determination by LSC and AMS techniques

Three (paired) combustions of each grade of SRF were undertaken producing samples (A, B and C) and measured by LSC. Sub-samples of combustion gases A and B were taken and analysed by AMS to cross-check LSC results. Results were converted from pMC to bioenergy (% total energy) according to section 2.3.3. Mean measured analytical uncertainty for LSC and AMS was ± 10.0 and ± 0.3 (pMC, 1σ), respectively. Conversion from pMC to bioenergy introduced further uncertainty based upon Fichtner's reported values of 0.390 MJ/kg (± 0.008 , 1σ) for biomass and 0.47 MJ/kg (± 0.034 , 1σ) for fossil fuels. Error propagation incorporating these values produced total mean measured bioenergy (%) uncertainties of ± 12.1 and ± 3.9 for LSC and AMS, respectively. Greater uncertainties associated with LSC combustion C are attributable to shorter count times for these samples (<700 mins) due to project time constraints. Sample C (fine fraction) has no weighted value as its paired counterpart failed during analysis. SRF LSC results compared favourably to those obtained by AMS and confirmed that LSC can be used to determine the bioenergy content of SRF with

acceptable levels of uncertainty. The largest bioenergy disparity between LSC and AMS was for the medium size fraction (4.5%). Bioenergy was significantly higher in the fine SRF fraction when compared with coarser SRF fractions (ca. 18%). On enquiry, the SRF manufacturer revealed that the fine fraction is *typically* composed of a higher biobased fraction than coarser SRF grades. No definitive information was available on absolute biobased values of SRF material.

3.2.2 Inter-Laboratory comparison of SRF - Selective Dissolution

The chemical analysis procedure typically involves homogenising a sample before undertaking a ‘selective dissolution’ determination of biomass energy fraction (*e.g.* EN 15440: 2011). The procedure is based on the principal that the biomass components of waste are soluble in acid whilst the fossil fuel components are not.

Significant differences in bioenergy determinations were found between the two contract laboratories. Laboratory X’s findings exceeded Laboratory Y’s bioenergy (%) values by 9.3, 26.9 and 26.1 for fine, medium and coarse fractions respectively. It is impossible to state with any certainty whether this discrepancy is due to the laboratories’ sub-sampling or analytical procedures, or indeed which laboratory is more accurate. However, the fact that (relative) GCV determinations by the same laboratories varied by a mean value of less than 11% (data not presented) suggesting that sampling error can be largely discounted, *i.e.* the disagreement in bioenergy determination between the two laboratories is likely to have arisen as a result of analytical error associated with the SD technique rather than sampling inconsistencies as the material provided was fully homogenised.

Neither laboratory (X or Y) presented results comparable to those obtained by the LSC/AMS ^{14}C analyses raising the question as to which, if any, laboratory is correct? ^{14}C derived results were substantiated by method development on known-age standards (certifying analytical procedure) and data from SRF samples verified by AMS analysis. However, this does not preclude potential bias in results due to differences in algorithms used to define bioenergy content. These results demonstrate that determining the bioenergy content of waste using SD is highly unsatisfactory, with inter-laboratory bioenergy (%) differences of up to 26.9 for analysis of identical bulk samples of SRF potentially resulting in significant under or over reward of financial incentives.

3.3 Bioenergy determination at an operational EfW facility

Heat and electricity recovered from incineration of MSW is derived from both fossil and biobased sources. The renewable biobased energy component is eligible for reward under UK incentive schemes *e.g.* the Renewables Obligation (RO, 2009), the Renewable Heat Incentive (Ofgem, 2013a) and the forthcoming Contracts for Differences (DECC, 2013) whilst the fossil-derived energy component is not.

3.3.1 Determination of the biobased energy content of flue gas

LSC analysis of flue gas samples, collected consecutively from the EfW plant produced a mean measured bioenergy content for the plant's feedstock of $44.6 \pm 12.3\%$ (1σ) (Table 3). This was in excellent agreement with AMS bioenergy results of $44.8 \pm 2.7\%$ (1σ). Overall uncertainties associated with LSC flue gas samples (± 12.3 , 1σ) were comparable with those reported for LSC SRF samples (± 12.1 , 1σ), and slightly smaller for AMS analysis of flue gas (± 2.7 , 1σ) compared to SRF samples (± 3.9 , 1σ). This can

be attributed to the homogenous nature of flue gas minimising sample variance and offsetting potential experimental or sampling errors. The small associated uncertainties of AMS samples underline the applicability of this technique to flue gas bioenergy analysis.

Temporal variation was observed in the bioenergy component of the plant's feedstock over the sample collection period (hourly intervals for 3 samples; ca. 10 min collection per sample) where sample 2 showed a measured decrease of ca. 3.5% in total bioenergy. AMS analysis was the only technique sensitive enough to identify effects of this order. Nevertheless, LSC, although lacking AMS measurement precision, could provide useful data on temporal trends in feedstock bioenergy composition of greater magnitude.

As noted, Fichtner's bioenergy conversion does not account for energy losses during the vapourisation of water, inclusion of this factor would reduce total (%) bioenergy. However, quantification of this energy loss was beyond the scope of this study.

The results illustrate that ^{14}C AMS and LSC analytical methods have the potential to provide robust results for the determination of the biomass content of flue gas but the values used for conversion to bioenergy would need to be re-examined. AMS measurements demonstrate the superior precision of the technique (over LSC) and its ability to resolve small temporal changes in flue gas CO_2 composition.

3.3.2 Determination of the bioenergy of MSW using a manual sorting method

Table 4 presents bioenergy content of each of the three 'grab' samples taken. The mean bioenergy content of mixed waste was calculated to be 41.4%, which is in relatively close agreement with ^{14}C analysis. Manual sorting, however, has a number of

significant limitations (Fichtner, 2007) where: (the technique) cannot handle composite samples of fossil/biomass material found in residual MSW; particles must be discrete and >1cm in size; the technique is highly labour intensive and requires very large sample sizes to be truly representative; the method is not suitable for fuels derived from mixed waste. Additionally and crucially, the method is subject to human error and is open to abuse, especially where substantial financial reward is at stake.

3.3.3 Determination of the biobased energy of MSW using selective dissolution

Summary results from manual sorting, SD and ^{14}C techniques are presented in Table 5. Chemical analysis using SD (CEN/TS 15440: 2006) of the mixed components of MSW gave an average of 76% total bioenergy. This represents an over-estimation (mean 30–35%) when compared with the other three techniques. Furthermore, this degree of disparity would be increased once inclusion of energy losses from water vapourisation was included in the (^{14}C) biomass to bioenergy conversion stage. Clearly, this has significant implications for UK incentive schemes which rely on bioenergy determination made using the manual sort technique. Data from LSC/AMS analysis of flue gas are not *strictly* comparable with data from SD and manual sort techniques, since they do not measure the same sample of waste; however, they are useful comparators. Fichtner (2007) reported the limitations of the SD technique with some notable examples *e.g.* some biodegradable plastics of 100% biomass are returned as 0% biomass by SD; coal is shown to be 43.5% biomass by SD; nylon and polyurethane (neither biomass derived) are 95% biomass by SD. Staber *et al* (2008), state the associated problems in representative sampling of heterogeneous material for SD. Séverin *et al* (2010) further report on statistical differences in biogenic content of SRF

analysed by manual sort and SD techniques. With these inaccuracies in mind, SD data from this study emphasise the limitations this technique has in producing robust and reliable measurements for determining the bioenergy content of mixed wastes.

4. Conclusions

This study provides convincing evidence of the need for a new approach to the determination of the bioenergy fraction of waste in the UK and is equally applicable to other countries with issues of bio-compliance and energy production. It provides a benchmark for the precision, accuracy and uncertainty of existing analytical techniques. Experiments revealed that current industry approaches to biomass/bioenergy determination are unreliable, with financial implications for incentive claims. ^{14}C techniques, particularly AMS, present significant advantages over current industry techniques in terms of feedstock representation, data acquisition, precision/sensitivity and reliability in bioenergy determination for both electricity generator and industry regulator.

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Captions

Table 1: Details of six ¹⁴C standards used for technique validation. ‘Treatment’ refers to the method by which CO₂ was liberated from the sample.

Table 2. Percent modern carbon (pMC, 1σ) and bioenergy conversion (% total energy) results for three size fractions of (dry) SRF analysed by LSC and AMS. AMS analyses were undertaken on sub-samples A and B only. SUERC bioenergy results were calculated on combined data using weighted means. Bioenergy determination of the same size fractions of SRF by SD (laboratories X and Y) is given. Mean and standard deviation (Stdev.) is based on combined data for laboratories X and Y.

Table 3. SUERC analysis of three flue gas samples collected at an operational EfW plant. Percent modern carbon (pMC) results are given for ^{14}C analysis of flue gas using LSC and AMS techniques. Conversion values to bioenergy (% total energy) are given for each method. AMS analyses were undertaken on subsamples of collected flue gas. Uncertainties are propagated combining ^{14}C measurement uncertainties (1σ) with the algorithms of Fichtner (2007) using standard statistical methods.

Table 4. The bioenergy fraction of waste feedstock at an operational EfW plant determined by manual sorting of municipal solid waste (MSW). MSW was sorted according to Ofgem's fuel measurement sampling guidelines (Ofgem, 2013a, 2013b). Gross Calorific Values (GCV - wet) were assigned to each weighted category ('as received' (AR)) based on the finding of the 1992 and 1993 Waste Data Stream Analysis (DoE report, CWM 087/94).

Table 5. Summary of data produced for the determination of the bioenergy (% total energy) content of waste at an operational EfW facility by a manual sort method,

selective dissolution technique (laboratory X only) and LSC/AMS ^{14}C analysis of flue gas.

Figure 1: Summary of programme of work: MSW – municipal solid waste. SRF – solid recovered fuel

Figure 2: Calibration curve for vacuum line/LSC determination of six internationally recognised ^{14}C standards. Error bars represent experimentally determined precision based on multiple analyses of each standard. ^{14}C decays were counted by LSC for > 1,000 minutes. The calibration was normalised to ‘doublespar’ and ‘Oxalic acid II’ standards (0.018 and 134.07 pMC respectively).

Table 1

Standard	Activity (pMC)	Source	Treatment
Doublespar carbonate	0.18 ± 0.006	Third International Radiocarbon Intercomparison (TIRI)	Acid hydrolysis
C2 Travertine	41.14 ± 0.03	International Atomic Energy Agency	Acid hydrolysis
C7 Oxalic Acid	49.53 ± 0.12	International Atomic Energy Agency	Wet oxidation ($\text{KMnO}_4 + \text{H}_2\text{SO}_4$)
Humic Acid	65.82 ± 0.033	Fifth International Radiocarbon Intercomparison (FIRI)	Combustion
Barley Mash	116.35 ± 0.008	Third International Radiocarbon Intercomparison (TIRI)	Combustion
Oxalic Acid II (SRM-4990C)	134.07	US National Institute of Standards and Technology	Wet oxidation ($\text{KMnO}_4 + \text{H}_2\text{SO}_4$)

Table 2

Method	Sample name	percent modern carbon (pMC)						Bioenergy (% total energy)					
		SRF size fraction						SRF size fraction					
		Fine	$\pm 1\sigma$	Medium	$\pm 1\sigma$	Coarse	$\pm 1\sigma$	Fine	$\pm 1\sigma$	Medium	$\pm 1\sigma$	Coarse	$\pm 1\sigma$
LSC/SRF (Paired data)	A	86.5	9.1	78.8	8.6	83.3	8.7	70.9	11.9	63.7	10.5	67.9	11.1
	B	88.4	9.4	62.3	8.9	70.0	8.0	72.7	12.5	49.1	9.3	55.8	9.1
	C	100.2*	14.2	64.1	10.6	69.6	12.5	84.0	20.4	50.6	11.1	55.5	13.6
	mean	91.7	10.9	68.4	9.3	74.3	9.7	75.9	14.9	54.5	10.3	59.7	11.3
	Stdev.	7.4		9.0		7.8		7.1		8.0		7.1	
AMS/SRF	sub sample A	94.6	0.3	79.0	0.3	81.0	0.3	78.6	4.7	63.9	3.7	65.7	3.9
	sub sample B	92.6	0.3	67.9	0.2	73.6	0.3	76.7	4.6	54.0	3.2	59.0	3.5
	mean	93.6	0.3	73.5	0.2	77.3	0.3	77.6	4.7	58.9	3.5	62.4	3.7
	Stdev.	1.4		7.8		5.2		1.4		7.0		4.7	
SD/SRF**	Laboratory X							74.8	-	84.7	-	69.9	-
	Laboratory Y							65.5	-	57.8	-	43.8	-
	mean							70.2		71.3		56.9	
	Stdev.							6.6	-	19.0	-	18.5	-

* No duplicate measurement was available for this sample as it failed during processing

** No uncertainties provided

Table 3

Flue Gas sample (¹⁴C technique)	pMC	± 1σ	Bioenergy (% total energy)	± 1σ
sample 1 (LSC)	57.3	11.7	47.2	12.3
sample 2 (LSC)	52.0	14.1	42.5	14.1
sample 3 (LSC)	53.8	10.2	44.0	10.5
mean	54.4	12.0	44.6	12.3
Stdev.	2.7		2.4	
subsample 1 (AMS)	56.2	0.2	46.2	2.8
subsample 2 (AMS)	52.0	0.2	42.5	2.6
subsample 3 (AMS)	55.8	0.2	45.9	2.7
mean	54.7	0.2	44.8	2.7
Stdev.	2.3		2.3	

Table 4

	Weight (g)	GCV (AR) 1992	GCV (AR) 1993	Mean GCV (AR)	Weight x GCV	% by GCV	Bio- degradable content	Qualifying %
Sample 1								
Food	1542.0	5.7	5.0	5.3	8242.0	13.5	1.0	13.5
Garden/Other Putrescible	0.0	6.9	6.1	6.5	0.0	0.0	1.0	0.0
Paper/Card/Sanitary	1200.0	12.8	12.1	12.4	14884.3	24.3	1.0	24.3
Textiles	216.0	16.3	15.6	15.9	3443.0	5.6	0.5	2.8
Wood	0.0	20.1	20.1	20.1	0.0	0.0	1.0	0.0
Plastics	1278.0	26.0	24.2	25.1	32043.1	52.4	0.0	0.0
Fines (<20 mm)	522.0	5.0	4.6	4.8	2521.3	4.1	0.5	2.1
Total	4758.0				61133.7			42.7
Sample 2								
Food	1108.0	5.7	5.0	5.3	5922.3	8.1	1.0	8.1
Garden/Other Putrescible	0.0	6.9	6.1	6.5	0.0	0.0	1.0	0.0
Paper/Card/Sanitary	1756.0	12.8	12.1	12.4	21780.7	29.6	1.0	29.6
Textiles	0.0	16.3	15.6	15.9	0.0	0.0	0.5	0.0
Wood	224.0	20.1	20.1	20.1	4506.9	6.1	1.0	6.1
Plastics	1623.0	26.0	24.2	25.1	40693.2	55.3	0.0	0.0
Fines (<20 mm)	135.0	5.0	4.6	4.8	652.1	0.9	0.5	0.4
Total	4846.0				73555.1			44.2
Sample 3								
Food	1944.0	5.7	5.0	5.3	10390.7	11.9	1.0	11.9
Garden/Other Putrescible	258.0	6.9	6.1	6.5	1677.0	1.9	1.0	1.9
Paper/Card/Sanitary	1304.0	12.8	12.1	12.4	16174.3	18.5	1.0	18.5
Textiles	450.0	16.3	15.6	15.9	7173.0	8.2	0.5	4.1
Wood	0.0	20.1	20.1	20.1	0.0	0.0	1.0	0.0
Plastics	2020.0	26.0	24.2	25.1	50647.2	57.9	0.0	0.0
Fines (<20 mm)	300.0	5.0	4.6	4.8	1449.0	1.7	0.5	0.8
Total	6276.0				87511.1			37.2
Mean (Samples 1-3)								
Stdev.								
								41.4
								3.7

Table 5

Sample	Bioenergy (% total energy)			
	manual sort	selective dissolution	LSC analysis (flue gas)	AMS analysis (flue gas)
1	42.7	76.6	47.2	46.2
2	44.2	80.7	42.5	42.5
3	37.2	69.1	44.0	45.9
Mean	41.4	75.5	44.6	44.8

Figure 1

Figure 2