RENEWABLE ENERGY ASSOCIATION

C14 DETERMINATION OF BIOMASS ENERGY CONTENT OF FUELS

DESCRIPTION OF METHOD

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MANAGEMENT SUMMARY

It is possible for electricity generated from mixed wastes and from biomass to qualify for support under the Renewables Obligation. In order to obtain this support, the operator of the energy-from-waste plant is required to determine the fraction of the energy content of the fuel which is derived from biomass (i.e. non-fossil fuels).

The standard method of determining the biomass energy content of a mixed fuel is to sample the fuel prior to thermal treatment for composition and energy content analysis. This method is favoured by the regulator, OFGEM, and is used for dedicated biomass plants. However, the fuels used by these plants are relatively homogenous and contain low levels of contamination with fossil fuels. For heterogeneous fuels, such as mixed municipal solid waste or refused derived fuels, this method can be extremely difficult, costly and inaccurate due to the difficulty of obtaining representative samples for analysis. For smaller plants, the cost of sampling and analysis would be higher than the value obtainable from ROCs.

This report describes an alternative method of determining the biomass energy content of a mixed fuel, based on radiocarbon analysis of the combustion gases (known as C14 analysis). The method involves the following steps:

1) Take a representative composite sample of the flue gases from the combustion plant over a period of one month.
2) Use radiocarbon analysis of the sample gases to calculate the fraction of the carbon in the flue gases which was derived from non-fossil fuel sources.
3) Combine this information with knowledge of the relationship between energy content and carbon content for biomass and non-biomass fuels to determine the fraction of the energy content of the original fuel which was derived from non-fossil fuel sources.

The main advantages of this method are that the combustion gases would be much more homogenous than the original waste and that it would be much easier to take a representative sample from a gas stream than from a solid fuel.

We estimate that this method could determine the fraction of the biomass energy content of the waste from which the combustion gases were derived with an uncertainty of ±5.5%. There would also be a sampling error associated with obtaining a representative sample of combustion gases and the magnitude of this error has not been determined in this report. However, the sampling error is likely to be significantly smaller than for the alternative sampling methods which are all based on sampling of solid fuels.

There is no quantitative information available on the accuracy of the alternative methods of determining the biomass content of heterogeneous fuels. Based on a qualitative assessment, we consider that it is likely the proposed method will be more accurate for mixed municipal waste than the alternative methods involving sampling of the solid fuel for analysis by selective dissolution, manual sorting or C14 analysis.

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1 INTRODUCTION

1.1 Background

Under the Renewables Obligation Order 2006, electricity generated from renewable energy sources such as biomass will qualify for Renewables Obligation Certificates (ROCs) which have considerable value. Electricity generated from fossil fuel derived energy sources does not qualify for ROCs.

Fuels containing mixtures of biomass and fossil fuels can qualify for ROCs provided that one of a number of specific conditions is met. These conditions include:

1) Advanced thermal conversion of the solid fuel into gaseous or liquid form prior to combustion for power generation.
2) Combined heat and power scheme meeting specified quality criteria.
3) Co-firing of fossil fuels and biomass meeting specified criteria.
4) Where the input fuel mix contains 90% or more biomass by energy content.

Where mixed fuels are used, only the power generated using the biomass portion of the fuel will qualify for ROCs. It is therefore necessary to determine the proportion of energy content in the mixed fuel input that is attributable to biomass.

One method of determining the biomass energy content of a mixed fuel is to sample the fuel prior to thermal treatment for composition and energy content analysis. The difficulty with this method is that it can be extremely difficult and costly to obtain representative samples for analysis from heterogeneous fuels, such as municipal solid waste. For smaller plants, the cost of sampling and analysis would be higher than the value obtainable from ROCs.

This report considers an alternative method for determining the biomass energy content of a mixed fuel that has been used for generating electricity that does not require sampling of solid fuel input. This method consists of three main steps:

1) Sampling of combustion exhaust gases
2) Carbon 14 analysis of the sampled gases, using a similar technique to that used for carbon dating to determine the ratio of biomass carbon to fossil fuel carbon
3) Using the ratio determined in step 2 to determine the ratio of biomass energy to fossil fuel energy in the mixed fuel input and hence the proportion of electricity generated that should qualify for ROCs.

This report addresses steps 2 and 3. Step 1 is the subject of a separate study.

1.2 Objectives

The main objectives of this assessment are:

1) To assess whether carbon 14 analysis can reliably determine the ratio of biomass carbon relative to fossil fuel carbon in a mixed fuel.
2) To assess whether the ratio determined in 1) above can be used to reliably determine the ratio of biomass energy to fossil fuel energy in the mixed fuel input.
3) To qualitatively determine whether the proposed method is likely to be at least as accurate as the alternative methods.

2 CONCLUSIONS

1) A study by Columbia University indicated that carbon 14 analysis can determine the ratio of biomass carbon relative to fossil fuel carbon in a mixed fuel to a reasonable degree of accuracy. For all of the samples, the measured value was within 1.1 percentage points of the calculated value.
2) A study by Iowa University indicated that the uncertainty of the radiocarbon dating analysis was around ±3%.
3) Analysis of different fractions of waste demonstrates that the ratio of biomass carbon relative to fossil fuel carbon is not the same as the ratio of biomass energy to fossil fuel energy. Therefore, a method is presented in this report by which the percentage of biomass carbon in the mixed fuel could be used to determine the ratio of biomass energy to fossil fuel energy in the waste.
4) This method is estimated to have an uncertainty of around 5%, excluding sampling error associated with obtaining a representative sample of combustion gases.
5) For waste fuels derived from mixed wastes, this method is likely to be more accurate than the alternatives including:
   a) Solid fuel sampling for analysis by selective dissolution;
   b) Solid fuel sampling for manual sorting;
   c) Solid fuel sampling followed by C14 analysis.

   The main reason for this conclusion is that gases mix far more readily than heterogeneous solid waste so that gas samples will be significantly more representative compared to solid fuel samples.
6) The proposed method for determining biomass content of fuels appears to meet the requirements of the legislation.

3 CARBON 14 ANALYSIS OF COMBUSTION GASES

3.1 Principles of the Method

This method uses radiocarbon dating, which is more conventionally used to assess the dates of archaeological discoveries, to assess the percentage of the carbon derived from fossil fuels within a mixed sample. The method has been developed by Beta Analytic Inc., an American company with 25 years of experience in conventional radiocarbon dating.

Carbon-14 (^{14}C) is a radioactive isotope of carbon with a half life of 5,730 years once it is no longer part of a living organism. This means that, in practical terms, all of the ^{14}C in fossil fuels has decayed, but "modern carbon" which was recently part of a living organism still contains a proportion of ^{14}C. In the context of municipal waste, it can be assumed that all of the carbon is either fossil carbon or modern carbon.

Radiocarbon dating, using method ASTM D6866-04a, can be used to determine the ratio between ^{14}C and ^{13}C in a sample, where ^{13}C or carbon-13 is a stable carbon isotope with a relative molecular mass of 13 compared to only 12 for normal carbon atoms or 14 for carbon 14 atoms. This ratio is then compared with the standard ratio in oxalic acid to give a value for "percent modern carbon" (pMC), and pMC is divided by 1.075, which is a factor to take account of the additional radiation in the atmosphere as a result of nuclear bombs and nuclear testing in the twentieth century. The resultant figure varies between 0 and 1, with a value of 0 indicating that all of the carbon is derived from fossil fuels and a value of 1 indicating that all of the carbon is derived from biomass.

3.2 Statistics

Much of the remainder of this section considers the accuracy and precision of the C14 method. These are two different concepts.

- "Accuracy" refers to the agreement between the measured value and the true value and the difference between the two is the "error".
- By contrast, "precision" refers to the repeatability of measurement, with a more precise measurement technique giving a lower spread of results, and the "uncertainty" of a measured value gives an indication of its precision.

In order to have confidence in a measurement technique, it is important that it is precise (i.e. that the measurement is repeatable) and that it is accurate (i.e. that the measured value is close to the true value).

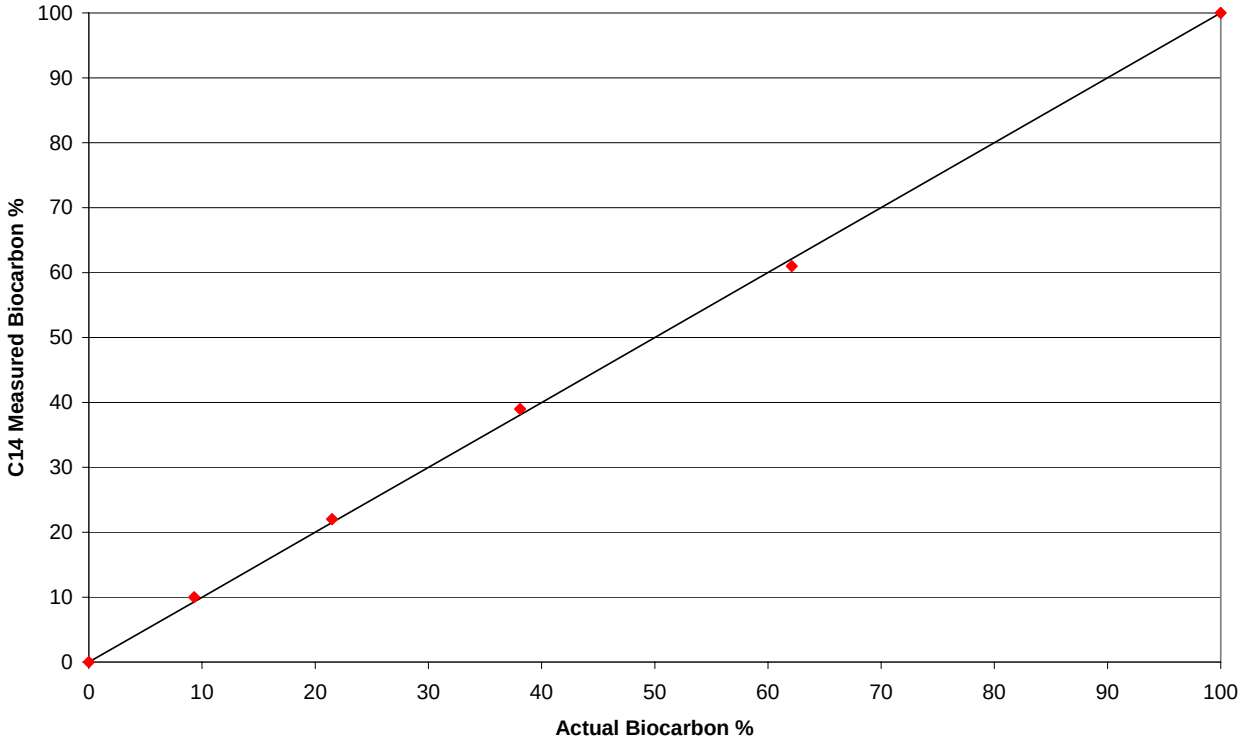
3.3 The Columbia University Study

This study is attached in Appendix A. The objective of this study was to assess the ability of the C14 method to determine the biomass fraction in a mixture of combustible materials. The study consisted of the following steps.

1) Six samples were prepared by mixing known quantities of a biogenic material (dry paper) with a non-biogenic material (polyethylene).
2) Each sample was combusted with oxygen in a Parr Bomb Calorimeter. Samples of the combustion gas were sent to Beta Analytic who carried out C14 analysis to determine the fraction of biogenic carbon in the gases.

3) The fraction of biogenic carbon in the sample was calculated by reference to the assumed chemical composition of the paper and polyethylene. The chemical composition of the paper used was provided by the paper manufacturer but it would have been preferable for the paper to have been analysed to determine the carbon content.

4) The Beta Analytic result was compared with the calculated result and "excellent agreement was obtained". The percentage error varied between 1.8% and 7.5%, but the only measurement with an percentage error greater than 2.5% was for the sample with a very low percentage of biocarbon. The results are illustrated graphically below.



The study shows that the C14 method can be used to determine the biocarbon percentage in a solid sample by analysing the combustion gases from that sample and that the accuracy is reasonable, on the assumption that the chemical composition of the paper was correct. The study does not explain how this method could be applied to a more complex mixture of solid fractions, such as municipal solid waste or even RDF. This is discussed in section 4 of this report.

3.4 Quality Assurance

It is obviously crucial that the sample to be tested is not contaminated at any stage in the process. To avoid this, the following methods were used during the Columbia University study to process gas samples for analysis:

1) Samples of gas are kept in sealed bags until required for testing.

2) The gas is extracted from the bag into a closed catalyst chamber. All elements of chamber and extraction line are purged with argon and water vapour before the gas is extracted.

3) Pure hydrogen is introduced into the catalyst chamber, which contains a cobalt catalyst. The chamber is then heated externally to 600°C for sufficient time for the carbon dioxide to be "cracked" with hydrogen to form a graphite carbon layer on the catalyst and water vapour.

4) The water vapour is removed using a cryogenic pump and the graphite is removed and sent to be analysed using Accelerator Mass Spectrometry (AMS).

We are confident that these methods are sufficient to avoid contamination.

The paper contained in Appendix A from Columbia University describes the use of radiocarbon dating to determine the percentage of modern carbon in the gases resulting from the combustion of mixed biogenic and petrochemical wastes. This includes the controlled combustion of that waste, which is carried out as follows:

1) The solid wastes (plastic and paper in this case) are put into a Parr Bomb Calorimeter. This is fully enclosed. Air is extracted and replaced with pure oxygen.
2) The mixture is ignited using a resistance wire (to avoid introducing air) and fully combusted.
3) A sample of the combustion gases is extracted and sent for analysis.

Again, we are confident that this operating method will avoid contamination of the sample.

3.5 Precision

In 2004, Iowa State University commissioned a sequence of analyses of over 100 manufactured products containing a proportion of biomass carbon. The analyses were carried out by a number of laboratories using the three methods of radiocarbon dating specified in the ASTM standard (CO2 absorption, AMS and Benzene Synthesis). It was concluded that:

- The CO2 absorption method was less accurate and less precise than the other two methods; and
- The precision of the AMS and Benzene Synthesis methods was similar, giving an uncertainty of ±3%.

4 DETERMINATION OF BIOMASS ENERGY CONTENT IN A MIXED FUEL

4.1 Biomass Fuels - Ratio of GCV to Carbon Content

As part of the National Household Waste Analysis Project[1] (NHWAP), household waste was collected, sorted into different fractions and analysed to determine their chemical composition and calorific values. This study was used because it is believed to be the most comprehensive study available on UK household waste. The following table presents data for the waste fractions that can be readily classified as 100% biomass. The data presented is average data collected in 1992 and 1993.

Table 4.1 CV and Carbon Data for Biomass in MSW

Waste Fraction	Gross CV – Dry	Carbon - Dry	GCV/Carbon
	MJ/kg	Wt%	MJ/kg
Newspaper	18.41	46.67	0.394
Magazines	12.60	33.02	0.382
Other Paper	15.60	39.58	0.394
Card Packaging	17.54	44.32	0.396
Other Card	17.52	43.78	0.400
Garden Putrescibles	15.47	40.85	0.378
Other Putrescibles	14.39	36.18	0.397
Mean Average			**0.390**
Standard Deviation			**0.008**

The data shows that the ratio of GCV to carbon content for biomass fuels typically found in MSW is approximately 0.39 ± 0.01 MJ/kg and that this ratio is relatively consistent.

For context and comparison, data for other biomass which is not normally expected to be present in MSW in significant quantities is presented in the following table. The data was derived from the Phyllis database for biomass and waste[2] provided by the Energy Research Centre of the Netherlands. This data shows that the ratio of GCV to carbon content is very similar for different biomass fuels including those not normally found in significant quantities in MSW.

[1] National Household Waste Project, Phase 2, Volume 3, Chemical Analysis Data – Report No. CWM/087/94

[2] www.ecn.nl.phyllis – accessed 11th May 2007.

Table 4.2 CV and Carbon Data for Non MSW Biomass	
	GCV/Carbon
	MJ/kg
Untreated wood	0.397
Straw	0.398
Manure	0.436
Mean Average	**0.411**

4.2 Fossil Fuels - Ratio of GCV to Carbon Content

A similar table is presented below, derived from the NHWAP, for waste fractions that can be readily classified as 100% fossil fuel derived. The data shows that the ratio of GCV to carbon content for waste fossil derived fuels typically found in MSW is approximately 0.47 ± 0.03 MJ/kg.

Table 4.3 CV and Carbon Data for Fossil Fuel Derived Fractions in MSW			
Waste Fraction	**Gross CV – Dry**	**Carbon - Dry**	**GCV/Carbon**
	MJ/kg	**Wt%**	**MJ/kg**
Refuse Sacks	30.96	66.30	0.467
Other Plastic Film	33.62	67.21	0.503
Clear Plastic Beverage Bottles	22.50	52.67	0.433
Coloured Plastic Beverage Bottles	24.64	56.45	0.440
Other Plastic Bottles	35.66	69.28	0.513
Other Dense Plastic	29.70	59.65	0.498
Mean Average			**0.470**
Standard Deviation			**0.034**

A similar set of data is derived from the Phyllis database for different grades of plastics and also for rubber. The ratio of GCV to carbon is very similar to those for waste plastics.

Table 4.4 CV and Carbon Data for Non MSW Fossil Fuels	
	GCV/Carbon
	MJ/kg
HDPE (dry)	0.539
LDPE (dry	0.544
PMMA (dry)	0.430
PVC (dry)	0.505
Rubber (dry)	0.419
Polypropylene (dry)	0.505
Average	**0.480**

4.3 Converting C14 Analysis Results to Energy Content

It can be seen from the figures in sections 4.1 and 4.2 that the biomass carbon percentage in the fuel is not the same as the percentage of biomass energy in the fuel. This is because the biomass and fossil fuel carbon are contained within different chemical compounds and the heat released from the combustion of the different compounds varies. However, it can also be seen that the ratio of gross calorific value to carbon content for biomass is consistent across a number of different types of biomass and that this is also true for materials derived from fossil fuels which are normally found in MSW.

It is possible to combine the calculations above with the C14 measurement of the biomass carbon percentage in the fuel to determine the biomass energy in the mixed fuel. The principles and precision of this method are set out below.

4.3.1 Calculation Method

This calculation uses the following definitions:

BGCV	=	Ratio of GCV to carbon content for biomass	=	0.39 MJ/kg
FGCV	=	Ratio of GCV to carbon for fossil fuels	=	0.47 MJ/kg
BCAR	=	Fraction of biomass carbon in mixed fuel determined using carbon 14 analysis		
FCAR	=	Fraction of fossil carbon in mixed fuel determined using carbon 14 analysis		
	=	1 - BCAR		
BEN	=	Biomass energy in mixed fuel	=	BCAR x BGCV
FEN	=	Fossil energy in mixed fuel	=	(1 - BCAR) x FGCV

From these definitions, it is possible to determine the percentage of biomass energy in mixed fuel (PBE), which is the quantity required.

$$PBE = \frac{BEN}{BEN + FEN}$$

$$PBE = \frac{BGCV \times BCAR}{BGCV \times BCAR + (1 - BCAR) \times FGCV}$$

$$PBE = \frac{BGCV \times BCAR}{FGCV + BCAR \times (BGCV - FGCV)}$$

Inserting the values for BGCV and FGCV, we get the following answer:

$$PBE = \frac{0.39 \times BCAR}{0.47 + BCAR \times (0.39 - 0.47)}$$

$$PBE = \frac{0.39 \times BCAR}{0.47 - 0.08 \times BCAR}$$

Hence, percentage of biomass energy in mixed fuel can be determined from the measured value for biocarbon in waste.

4.3.2 Uncertainty Calculations

The uncertainty in a calculated value can be derived from the uncertainty in the individual terms using the following standard statistical rules, where V, A and B are values and E_V, E_A and E_B are the uncertainties (one standard deviation) associated with these values

If	V	=	A	±	B
Then	E_V^2	=	E_A^2	+	E_B^2

If	V	=	AB	or	A/B
Then	$(E_V/V)^2$	=	$(E_A/A)^2$	+	$(E_B/B)^2$

The size of the uncertainty in the final result will depend on a number of parameters but some example calculations in the following section will serve to illustrate the potential size of uncertainty involved.

4.3.3 Estimation of Uncertainty

The equations in section 4.3.1 illustrated that only three quantities are required to calculate the percentage of biomass energy in mixed waste. We can assign uncertainties to each of these items:

- BGCV has a value of 0.39 MJ/kg and an uncertainty of 0.008 MJ/kg, or 2.1%
- FGCV has a value of 0.47 MJ/kg and an uncertainty of 0.034 MJ/kg, or 7.2%
- BCAR is determined by the carbon-14 analysis. For the purpose of this example, it is assumed that BCAR has a value of 0.68. The uncertainty is taken as 3%, or 0.0204, based on the Iowa State University study.
- The absolute uncertainty of (1-BCAR) is the same as the uncertainty for BCAR, but the percentage uncertainty is different. This is calculated to be 6.4%.

Given these values, it is possible to determine the percentage of biomass energy in mixed waste and the uncertainty on that figure.

Quantity	Derivation	Value	Uncertainty
BEN	=BCAR x BGCV	=0.68 x 0.39 =0.2652	$=\sqrt{0.021^2+0.03^2}=3.63\%$ or ±0.0096
FEN	=(1-BCAR) x FGCV	=(1-0.68) x 0.47 = 0.1504	$=\sqrt{0.072^2+0.064^2}=9.64\%$ or ±0.0145
BEN+FEN		=0.2652 + 0.1504 = 0.4156	$=\sqrt{0.0096^2+0.0145^2}=0.0174$ or ±4.19%
PBE	=BEN / (BEN+FEN)	= 0.24652/0.4156 =0.638	$=\sqrt{0.0363^2+0.0419^2}=5.55\%$ or ±0.0354

Therefore, the percentage of biomass energy in the fuel can be calculated to be 0.638 with an uncertainty of ±5.5%.

It is important to note that this calculation does not take account of sampling error. The intention is to use the Carbon-14 method on samples of combustion gas collected from a combustion plant. The method for collecting a composite gas sample for the month is being developed to give minimum sampling error. Details of this methodology are the subject of a separate report.

4.3.4 Customisation of the Calculation Method

The preceding sections describe the basic method for calculating biomass energy content from sample results. Some customisation of the calculations may be appropriate depending on specific circumstances for an individual plant. The most likely customisations include:

1) Corrections for supplementary fuel firing (e.g. support fuel). The quantity of supplementary fuel used can be measured and appropriate corrections applied. It should be noted that there is no need to correct for start up or shutdown fuel used unless it contributes to power generation.

2) The preceding calculations use an assumed composite ratio of calorific value to carbon content for the biomass and fossil fuel components. These assumptions are necessary for fuels, such as those derived from residual MSW, which contain a mixture of many components. For fuels that have only a small number of well defined components, such as wood chips contaminated with only small quantities of plastics, more accurate ratios of calorific value to carbon content can be used. For these fuels, the accuracy of the method is likely to be better than estimated above.

5 COMPARISON OF PROPOSED METHOD AGAINST ALTERNATIVES

5.1 Alternative Methods for Determination of Biomass Energy Content of Heterogeneous Fuels

The alternative methods for determination of biomass energy content of heterogenous fuels, as described in the European Standard CEN/TC 343, are all based on sampling of the solid fuel followed by determination of the biomass energy content by different means as follows:

1) Selective dissolution of the solid samples in sulphuric acid and hydrogen peroxide. This method relies on the assumption that biomass fuel components will dissolve but fossil fuel components will not; or
2) Manual sorting. This method relies on each fuel particle being readily identifiable as biomass or fossil so that they can be sorted manually; or
3) Carbon 14 analysis. This method of analysis is similar to the C14 method proposed in this report but with the key difference being that this method is based on sampling the solid fuel then burning it to produce a gas sample for analysis rather than sampling of the combustion exhaust gases from the operating plant as proposed in this report.

5.2 Accuracy of Alternative Methods

The overall accuracy and precision of any method depend on the accuracy and precision of the sampling techniques and the accuracy and precision of analysis. The sub standards under CEN/TC 343 that describe the different methods do not currently quantify the accuracy or uncertainty associated with each method and state that accuracy has not yet been determined.

Fichtner has therefore made the following qualitative assessment of accuracy and precision associated with each method.

5.2.1 Sampling Accuracy

The C14 method proposed in this report is based on sampling of the combustion exhaust gases. The accuracy of the sampling regime will be demonstrated as part of the sampling trials to be undertaken but some comments can be made at this stage:

1) Samples are taken of the actual combustion exhaust gases from the plant in normal operation;
2) Samples can be taken from locations where the gases have been uniformly mixed so that the sample size can be relatively small and still be representative;
3) Samples can be taken automatically and continuously or frequently for each month of operation. Short and long term variations in fuel composition will be readily captured.

It is important to note that continuous sampling of combustion exhaust gases for analysis is widespread in the process industry and deemed to be sufficiently accurate for regulatory purposes. For example, the means of demonstrating compliance with emissions limits under the Waste Incineration Directive to the satisfaction of the Environment Agency is through a combination of long term continuous and short term (continuous sampling over periods of a few hours) sampling and analysis of flue gases.

By contrast, the alternative method of sampling the solid fuel suffers from a number of problems:

1) The composition of many solid fuels, particularly those derived from mixed wastes, can vary considerably so that obtaining representative samples can be extremely difficult if not completely impossible. In particular, it would be extremely difficult to obtain representative samples from residual MSW as this is very heterogeneous.
2) Mixing of solid fuels is extremely difficult compared to mixing of combustion gases.
3) With the exception of fine (small particle size) wastes, continuous automatic sampling of solid fuels is either difficult or in some cases impossible. It is therefore difficult to capture all short and long term variations in fuel composition.

Based on the above qualitative analysis it is clear that the proposed exhaust gas sampling method will be at least as accurate and representative as any solid sampling method. In the case of heterogeneous wastes, we would expect the gas sampling to be far more accurate, representative and less costly than solid sampling.

5.2.2 Analysis Accuracy

The possible analysis methods are:

1) Selective dissolution (SD). This method assumes that biomass fuel components will dissolve and fossil fuel components will not dissolve. The potential inaccuracies introduced by this method depends on the fuel being analysed but some observations can be made as follows:
   a) Natural rubber is 100% biomass but the SD method would show that it is only 84% biomass;
   b) Frying fat is 100% biomass but the SD method would show that it is only 41% biomass;
   c) Wool is 100% biomass but the SD method would show that it is only 82% biomass;
   d) ECOPLA (a biodegradable plastic produced from corn) is 100% biomass but the SD method would show that it is 0% biomass;
   e) Nylon and polyurethane are not biomass but the SD method would show that they are over 95% biomass;
   f) Coal is not biomass but the SD method would show that hard coal is 43.5% biomass and lignite 93% biomass.

   The impact of the above has not been assessed in the standard and will depend on the composition of the waste. However, it is worth noting that the substances listed above are not likely to be significant components of municipal waste. It is likely that the accuracy of the C14 analysis method proposed in this report is at least comparable to the SD method.
2) Manual sorting. It is necessary to visually determine whether a fuel particle is biomass or fossil fuel.
   a) This method relies on the fuel comprising of discrete particles. The sub standard CEN/TS 15440:2006 recommends that this method should only be used if the minimum particle size is over 1cm. In practice, the fuel will have a range of particle size with at least some smaller than 1cm;
   b) Sample sorting will be extremely labour intensive for samples of any significant size (and sample size will need to be very large to be representative);
   c) This technique cannot handle composite particles containing biomass and fossil fuel portions. This issue will be particularly relevant for fuels derived from residual MSW;

d) Sorting will be subject to human errors of judgement.

The applicability of this method is limited to fuels that are made up of discrete particles and where biomass components can be readily identified and sorted from fossil fuel components. This method is not suitable for fuels derived from mixed wastes.

3) Carbon 14 analysis. The accuracy of C14 analysis will be the same as that proposed in this report.

5.2.3 Overall Accuracy

The following table provides a qualitative assessment of the relative accuracy of the different methods available for determination of the biomass content of fuels derived from mixed wastes.

Method	Sampling Method	Analysis Method	Comments
A	Exhaust gas sampling	C14	Proposed method
B	Solid fuel sampling	Selective Dissolution	Sampling significantly less accurate and precise than method A. Analysis likely to be comparable to method A. **Overall accuracy likely to be lower than method A for mixed waste fuels.**
C	Solid fuel sampling	Manual Sorting	Sampling significantly less accurate and precise than method A. Analysis method likely to be unsuitable or less accurate compared to method A. **Overall accuracy likely to be significantly lower than method A for mixed waste fuels.**
D	Solid fuel sampling	C14	Sampling significantly less accurate and precise than method A. Analysis accuracy same as method A. **Overall accuracy likely to be significantly lower than method A for any fuels.**

From the above assessment, it is clear that the proposed method of flue gas sampling for C14 analysis is likely to be the most accurate method compared to the available solid fuel sampling alternatives for fuels derived from mixed wastes. The main reason for this conclusion is that it is hard to obtain representative samples of heterogeneous solid fuels.

This means that the proposed method would also have advantages for other fuels where it is difficult to measure the biomass content by taking samples of the solid fuel. One example of this is contaminated wood where the contamination, such as paint, surface treatments and some plastics, is contained within the wood.

6 LEGALITY OF PROPOSED C14 METHOD

We understand that OFGEM is considering the legal position for use of the proposed C14 method since it does not directly measure the GCV of the fuel as stipulated in their guidance note.

Some comments which may assist OFGEM in reaching a decision on this issue follow:

1) The energy content is defined as the GCV multiplied by the weight or volume of that fuel. (article 2(1) in the Renewables Obligation Order 2006 ("The Order"))
2) For biomass power plants, there is then a requirement for the energy content to be measured (also article 2(1) in the Order).
3) For waste combustion plants, the renewable output has to be determined with reference to the energy content (article 9(4) of the Order), although there is no actual requirement to measure the energy content in this case.
4) For CHP plants, the renewable output is determined by subtracting the electricity generated from fossil fuels from the gross electrical output, with no reference to energy content (article 9(6) of the Order).

From a technical perspective, there is no reason why the only way to measure energy content is to measure the GCV and the weight or volume separately and then multiply them. The "energy content" is a physical quantity in its own right which can be measured in its own right and there is no specific requirement in the Renewables Obligation to measure the GCV or the weight or volume of the fuel. In fact, the method used to determine the GCV is actually to determine the energy content of a sample and then divide it by the weight of material - the GCV is not a separately measured quantity in the analysis.

The fundamental question is whether the definition of energy content is merely:

a) a definition to emphasise that gross calorific value is being used, or

b) a prescriptive statement as to the only acceptable way to measure the energy content.

We consider that interpretation a) should be the intention and that there is no technical or practical justification for interpretation b).

Whilst the proposed C14 method may not necessarily comply with the fuel sampling guidance which is an interpretation of the requirements of the Renewables Obligation Order, we consider that it is likely to be more accurate than the alternative methods that can comply with the fuel sampling guidance.

Appendix A Columbia University Report on C14 Analysis

COLUMBIA UNIVERSITY

EARTH ENGINEERING CENTER

WASTE-TO-ENERGY RESEARCH AND TECHNOLOGY COUNCIL

CONFIDENTIAL REPORT

Testing of Beta Analytic Method for measuring % biocarbon in the CO2 in combustion gases from combustion of mixed biogenic and petrochemical wastes

and

Preliminary Correlation of % Biocarbon in Combustion Gases to

1) % Biomass Fraction in Combustibles

2) Lower Heating Value Per kilogram of MSW Containing 30% Moisture and 20% Inerts

1. Measured amounts of a biogenic material (dry paper of known inorganic content) and a petrochemical (polyethylene) were mixed in various proportions and combusted with oxygen in a Parr Bomb Calorimeter. Samples of the combustion gases were sent to Beta Analytic in Florida who analyzed the CO2 in the gas sample for Carbon 14. The results of BA are compared to the known mixtures in Table 1 below. It can be seen that excellent agreement was obtained.

2. In prior studies of the composition of municipal solid wastes at Columbia University, the ultimate (atomic) analysis of various types of wastes and the atomic weights of the respective elements were used to derive the composite molecular formula corresponding to mixed food wastes and paper:

Mixed food and green wastes: $C_6H_{9.6}O_{3.5}N_{0.28}S_{0.2}$

Mixed paper: $C_6H_{9.6}O_{4.6}N_{0.036}S_{0.01}$

It can be seen that sulfur and nitrogen are relatively minor components and occur principally in mixed and green food wastes. Also, if one excludes nitrogen and sulfur, the molecular structure of mixed paper is very close to cellulose, $(C_6H_{10}O_5)_x$. Excluding the minor elements and the inorganic materials in MSW, the average molecular structure of the biomass in MSW can be approximated by the molecular composition $C_6H_{10}O_4$ (Themelis 2002). It is interesting to note that this composition corresponds to the structural formula of at least ten organic compounds, such as ethyl butanedioic acid, succinic acid, adipic acid, ethylene glycol diacetate, and several others (HSC Chemistry, 2006). The heat of formation of these compounds is nearly the same and can be used to derive the thermochemical energy released in the combustion of this compound with oxygen to form water and carbon dioxide.

The biomass fraction in a combustible mixture of biogenic and fossil-based materials can be correlated to the biocarbon fraction in the combustion gas by taking into account the respective formulae and carbon concentrations of these two types of materials.

The Lower Heating Value of a combustible mixture is then computed from the

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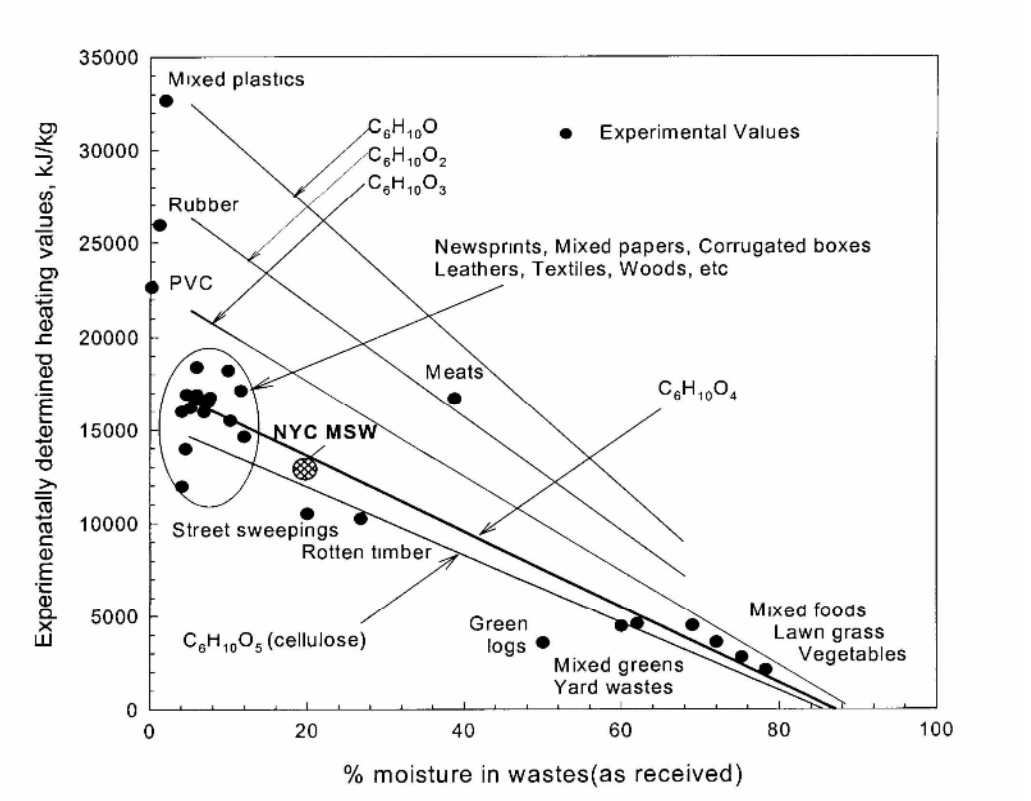
respective fractions and Lower Heating Values of the two materials. This was done in Table 2 below. The LHV of the combustible mixture is then corrected for a) the estimated % moisture content of the MSW and b) the estimated concentration of inert materials (e.g., glass, metals, etc.) in the MSW. The resulting calculations for various % biocarbon fractions and for an assumed 30% moisture and 20% inert materials in the MSW are shown in Table 2 below.

Table 1. Testing of accuracy of Beta Analytic Method for % biocarbon in CO_2 mixtures

Composition of biomass used (material dried fully before use)				
	$C_6H_{10}O_5$	% in paper	% of total	
Carbon	72	44.4%	35.1%	
Hydrogen	10	6.2%	4.9%	
Oxygen	80	49.4%	39.0%	
Molecular weight	162	100.0%	79.0%	
Inorganics content, provided by manufacturer			21.0%	
Polyethylelene n(C_2H_4) (dry)		% in polyethylene		
Carbon	24	85.7%	85.7%	
Hydrogen	4	14.3%	14.3%	
Total	28	100.0%		
Mixtures		WTERT calculation of	BetaLab	
%Poly	% paper	% biocarbon	%biocarbon	
100	0	0.0%	0	
80	20	9.3%	10	
60	40	21.5%	22	
40	60	38.1%	39	
20	80	62.1%	61	
0	100	100.0%	100	

Calculation of Lower Heating Values:			
Lower Heating Value of n(C_2H_4)	1322	kJ/mol	
Molecular weight:	28	g/kmol	
LHV of n(C_2H_4)	47.2	kJ/g	
LHV of n(C_2H_4)	47.2	MJ/kg	
LHV of mixed plastics (Themelis, Waste Management & Research (see Figure 1)	33	MJ/kg	
Lower Heating value of mixed biomass ($C_6H_{10}O_4$) (see below)	-17.9	MJ/kg	
% C in biomass ($C_6H_{10}O_4$)	44.4	%	

Table 2. Correlation of % biocarbon in combustion gases to Lower Heating Value of MSW						
% bio C in CO2 of process gas	% biomass in combust-ibles.	LHV of biomass fraction, MJ/kg	LHV of fossil fraction, MJ/kg	LHV,total of combustibles. MJ/kg	LHV, tot at 30% H2O MJ/kg	LHV, total at 30% H2O and 20% inerts
0	0.0%	0.0	33.0	33.0	22.85	18.28
10	14.2%	2.5	28.3	30.9	21.35	17.08
20	27.2%	4.9	24.0	28.9	19.98	15.98
30	39.0%	7.0	20.1	27.1	18.73	14.98
40	49.8%	8.9	16.6	25.5	17.58	14.06
50	59.9%	10.7	13.2	24.0	16.52	13.22
60	69.1%	12.4	10.2	22.6	15.54	12.44
70	77.7%	13.9	7.4	21.3	14.64	11.71
80	85.6%	15.3	4.7	20.1	13.80	11.04
90	93.1%	16.7	2.3	18.9	13.01	10.41
100	100.0%	17.9	0.0	17.9	12.28	9.82



Effect of constituents and moisture on heating value of MSW
(Themelis, Kim, Brady Waste Management and Research, 2002

Appendix 1. Calculation of Lower Heating Value of biomass

C6H10O4(22Dl) + 6.5O2(g) = 6CO2(g) + 5H2O(g)

T C	deltaH kJ	deltaS J/K	deltaG kJ	K	Log(K)
0.000	-2596.177	637.732	-2770.374	1.000E+308	308.000
100.000	-2603.125	615.854	-2832.931	1.000E+308	308.000
200.000	-2607.893	604.445	-2893.886	1.000E+308	308.000
300.000	-2610.938	598.559	-2954.002	1.732E+269	269.239
400.000	-2612.494	596.026	-3013.709	7.503E+233	233.875
500.000	-2612.706	595.711	-3073.280	4.473E+207	207.651
600.000	-2611.672	596.954	-3132.903	2.729E+187	187.436
700.000	-2609.471	599.329	-3192.709	2.430E+171	171.386
800.000	-2606.167	602.553	-3252.797	2.189E+158	158.340
900.000	-2601.847	606.395	-3313.240	3.425E+147	147.535
1000.000	-2596.595	610.687	-3374.091	2.775E+138	138.443

LHV of biomass: -2610 kJ/mol = -2610/148.1 = -17.86 kJ/g = -17.86 MJ/kg

Appendix 2. Composition of biomass in U.S. MSW

Table 3 is based on the characterization of U.S. MSW [7]. Biomass materials, i.e. paper, food and yard wastes, wood, leather, cotton and wool, constitute 69.5% of the MSW and petrochemicals another 15%. The rest are inorganic materials such as metals, glass, gypsum, and other minerals.

Table 3. Characterization of U.S. MSW by USEPA [7]

Biomass components	%	**Petrochemical components**	%
Paper/board	36.2	Plastics	11.3
Wood	5.8	Rubber, nylon, other textiles.*	3.7
Yard trimmings	12.1		
Food scraps	11.7		
Textiles (cotton, wool, leather)*	3.7		
Total biomass	69.5%	Total fossil-based	15.0%

**Rubber, leather and textiles category of USEPA 7.4%) were assumed to be divided equally between natural and man-made products*

Appendix 4. Combustion tests to obtain gas samples for C12/C14 ratio analysis (by Werner Sunk)

White paper (Corporate Express Earthsaver Recycled Paper, 75g/m^2, 92 Brightness , 4.5% moisture, 20-22% mineral content, 73-75% wood fiber) and High Density Polyethylene (HDPE, Aldrich, Product No.: 427985) were combusted with oxygen (research grade, [CO_2]<0.01ppm) in changing paper/HDPE ratios.

Both the paper and HDPE were ground (easier processing and better combustion) and dried in a furnace at 105-110 degree C. Samples with a total weight of 1g (±3%) in 0% paper, 20%, 40%, 60%, 80%, 100% HDPE ratios were prepared and pressed into pellets. The combustion bomb (V=0.35 liter) of a calorimeter was used to combust the 1g-samples under pressure with approx. 50% excess oxygen and to collect the combustion gas. Only a fraction of the produced off-gas was collected to avoid overloading of the gas sample bags.

Paper/HDPE ratio distribution:

Gas sample No.	Mixtures (total weight 1g)	Weight Ratios [g] Paper	HDPE	Collection date
1	0% paper/100% HDPE	0.00	1.00	03/12/07
2	20% paper/80% HDPE	0.20	0.80	03/12/07
3	40% paper/60% HDPE	0.40	0.60	03/13/07
4	60% paper/40% HDPE	0.60	0.40	03/13/07
5	80% Paper/20% HDPE	0.80	0.20	03/13/07
6	100% paper/0% HDPE	1.00	0.00	03/12/07

Nickolas J. Themelis, April 16, 2007