Measurement method for determination of the ratio of biogenic and fossil-derived CO_2 in stack gas

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ABSTRACT

In this paper, we present a measurement method for sampling and analysis of the ratio of biogenic and fossil-derived CO_2 in stack gases from the combustion of mixed fossil and biogenic fuels. The measurement method was developed as a part of a project performed for Energinet.dk and the association of waste incineration and treatment plants in Denmark.

The methodology for sampling and analysis is described, and preliminary measurement results from a field test at a Danish waste incineration plant are presented. The method follows the guidelines of the prEN ISO 13833 standard that is currently being developed.

After a number of laboratory and full scale tests, the measurement method was used in a field test at a Danish waste incineration plant, where the composition of waste was varied in 5 full scale experiments. The ratio of biogenic and fossil carbon in the waste was varied as much as possible through mixing known amounts of commercial and industrial waste, biomass and plastics with household waste. Preliminary results showed that during the field test, diurnal emissions of biogenic CO_2 varied between 53% and 67% out of the total CO_2 emission from the waste incineration plant.

Based on the preliminary field test results, it is concluded that the reproducibility of the measurement method is 1%-6% RSD, including uncertainties from both sampling and analysis. Compared to the uncertainties generally deriving from similar measurements of gases in stack emissions, this is found to be fully acceptable.

INTRODUCTION

In several countries, an increasing share of renewable energy comes from waste incineration. However, the current data for contents of biogenic and fossil carbon in combustible waste is often uncertain. To provide accurate accounts of national CO_2 emissions, better data on emissions from fossil-derived carbon in mixed fuels has to be provided.

Different approaches have been used to quantify the biogenic carbon contents of solid fuels (Staber et al. /1/, DS/CEN/TS 15440:2011 /2/). Another approach is the determination of biogenic carbon through mass balance calculations, as suggested by e.g. Fellner and Rechberger /3/. Mass balance calculations include a complex system of equations e.g. for mass, ash, energy, carbon, and oxygen based on plant operating data in order to predict the content of fossil and biogenic carbon in the fuel. A third approach is to sample flue gas directly from combustion plants and then analyze the sampled CO_2 through radiocarbon dating. This direct measurement method is advantageous to use on inhomogeneous waste materials with unknown and varying composition. The validity of the direct measurement method has recently been demonstrated at waste incineration plants in e.g. Switzerland (Mohn et al. /4/) and Holland (Palstra and Meijer /5/). The direct measurement method has been introduced as an ASTM standard in the US /6/ and is currently being developed as an EN/ISO standard /7/.

As a part of the project "Biogenic Carbon in Danish Combustible Waste" supported by Energinet.dk and the Association of waste Incineration and Treatment Plants in Denmark, the direct measurement method was used. The objective of the measurements was to obtain valid data on the emission of fossil and biogenic CO_2 from Danish waste incineration plants in order to improve emission factors used for the National GHG emission inventories. As part of the project, procedures for sampling and analysis were developed.

The project "Biogenic Carbon in Danish Combustible Waste" has included:
- The development of the test method, including laboratory and full scale tests.
- A first field test experiment, where measurements were performed in stack gas from the full scale combustion of different waste composition under controlled conditions.
- Monitoring of day-to-day, week-to-week and month-to-month variations at selected Danish waste incineration plants.

In this paper, the method developed for sampling and analysis will be described, and preliminary results of the first field test will be presented.

All measurements and analyses were performed by FORCE Technology in collaboration with the Technical University of Denmark.

METHODOLOGY

The use of ^{14}C analysis for determination of the share of biogenic and fossil-derived CO_2 is based on the fact that the share of ^{14}C in fossil-derived carbon is negligible. As all ^{14}C in a sample containing absorbed CO_2 from stack gas will derive from biogenic carbon, the content of ^{14}C in the sample will be proportional to the ratio of biogenic carbon in the fuel used in the sampling period. The ratio of biogenic carbon (or biogenic CO_2) is calculated from the expected content of ^{14}C in a reference sample of 100% biogenic carbon. Guidelines for measurement of biogenic and fossil-derived CO_2 are being developed in a draft prEN ISO 13833 standard /7/. This EN/ISO standard will describe the applicable types of sampling (grab sampling and different types of absorption media) and different methods applicable for analysis of ^{14}C in the samples: Accelerator Mass Spectrometry, Beta Ionization and Liquid Scintillation Counting (LSC).

The method developed for this project was based on the collection of CO_2 from the stack gas through liquid absorption in alkaline solution. The content of ^{14}C in the carbonate was analyzed through LSC in the laboratory.

Sampling
CO_2 was collected as carbonate through absorption in an aqueous solution of 4M KOH as used by Mohn et al. /4/ for short-term sampling of CO_2.

The sampling method was designed for both short and long-term sampling. Long-term sampling should be possible over 24 hours, a week or even a month. The high capacity of KOH for CO_2 absorption enables sampling periods of several weeks with a sampling flow that is high enough to be maintained through a commercial mass flow controller. If strong fluctuations in the content of biogenic CO_2 occur, improved representativity may be obtained from long-term sampling, using flow proportional sampling.

Figure 1 shows the equipment used for sampling during the field test in the first field test experiment.

The sampling flow was determined from the expected CO_2 concentration, and so that a total amount of minimum 4 g of carbon (15 g of CO_2) was absorbed in the sample after the sampling time in question. This will give sufficient ^{14}C signal for determination through analysis by LSC. The flow must at the same time be low enough to ensure that the capacity of the KOH solution is not exceeded during the sampling period.

The stack gas flow was measured continuously by means of an S-pitot tube and a transducer for registration of the differential pressure. The temperature in the stack gas was measured by means of a NiCrNi element.

Figure 1. Sampling setup.
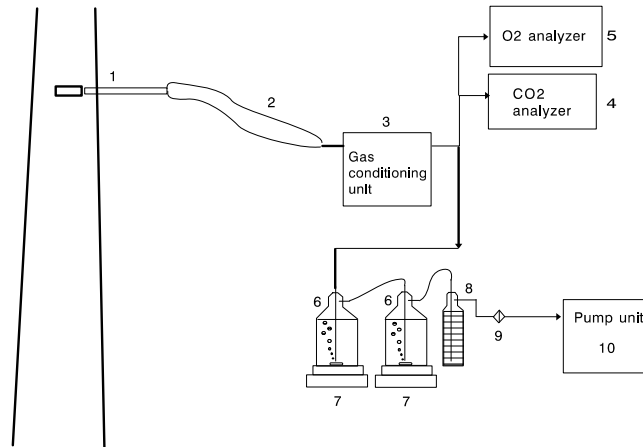
1. Probe with particle filter
2. Heated sample line.
3. Conditioning unit, reducing the dew point for water to 4 °C. Contains a pump that ensures sufficient excess flow to supply the CO_2 and O_2 analyzers.
4. CO_2 analyzer (BINOS 100, NDIR) with internal pump
5. O2 analyzer (Brühler BA-4000, paramagnetic)
6. Absorption flask containing 4 M KOH.
7. Magnetic stirrer.
8. Drying unit containing silicagel.
9. Particle filter.
10. Pump unit containing a flow regulator, pump, rotameter and a gas meter.

With an expected concentration of CO_2 in the stack gas of about 10% v/v, the sampling flow was adjusted to 1000 mL/min during 6 hrs sampling periods, and to 600 mL/min during the 18 hrs sampling periods.

Two sampling equipments were used in parallel during the first field test in order to describe the reproducibility of the method. Figure 2 shows the sampling equipment during the field test.

Figure 2. Sampling of biogenic CO_2 at the waste incineration plant (Næstved Waste Incineration Plant) during the field test.

Analysis

CO_2 is released from an aliquot of the exposed absorption liquid by the gradual addition of dilute H_2SO_4. The pH of the liquid is carefully controlled in order to prevent the liberation of volatile acids (e.g. HNO_2) that may be present as the absorption liquid may contain minor amounts of sulphate, sulphite, nitrate and nitrite ions, as well as some organic acid residues. The CO_2 produced is absorbed in CarboSorb E directly in a scintillation vial. The amount of absorbed CO_2 is determined by weighing the vial before and after absorption, with correction for losses for Carbosorb sticking to used utensils. After absorption of CO_2, a scintillator reagent (PermaFluor) is added to the vial. Each β particle emitted from the ^{14}C atoms present in the scintillation vial will induce a light pulse due to fluorescence of the scintillation reagent. Through counting of the emitted light pulses, the emitted β particles are counted in the LSC apparatus over a period of 24-48 hours. A sensitive LSC apparatus (1220 Quantulus) is used.

After counting, traceable internal ^{14}C capsules are added to the vials, which are then counted again. The use of internal standards for all samples is mandated by the counting efficiency being strongly affected by the degree of CO_2-loading of the scintillation cocktail.

For the stack gas samples, the lower detection limit of the method is estimated to be <1 pmC. The upper detection limit is estimated to be 100 pmC.

The ratio of biogenic CO_2 to total CO_2 in the stack gas (equaling the ratio of biogenic carbon to the total mass of carbon in the fuel) is calculated according to equation (I):

$$(I) \qquad \mathrm{pmC}_{sample}[\%] = \frac{\left(\mathrm{DPM}_{sample} - \mathrm{DPM}_{background}\right)}{\varepsilon \cdot \mathrm{M}_{C.sample}[\mathrm{g}] \cdot C\left[\frac{dpm}{g}\right]} \cdot \frac{100}{\mathrm{pmC}_{ref}} \cdot 100[\%]$$

Where:

pmC$_{sample}$	=	the percentage of biogenic carbon in the sample, relative to the total mass of carbon in the sample
DPM$_{sample}$	=	the number of disintegrations per minute measured during LSC for the sample [min^{-1}]
DPM$_{background}$	=	the number of disintegrations per minute measured during LSC for a sample 100% fossil carbon (without biogenic carbon)[min^{-1}]
ε	=	the total counting efficiency of the LSC detection, measured by spiking the sample with a reference sample of known ^{14}C abundance (including all quenching and geometry effects)
M$_{C, sample}$	=	the mass of carbon collected in the sample [g]
C	=	a constant representing the number of disintegrations per gram of biogenic carbon = 13.65 [min^{-1}·g^{-1}] (ref.: /8/)
pmC$_{ref}$	=	a reference value representing the level of ^{14}C in the biomass used, given as an index value relative to the ^{14}C content in the atmosphere before 1950.

As shown in equation (I), the final result for pmC is corrected with the reference value pmC$_{ref}$ in order to correct for the level of radioactivity in the ^{14}C in the biomass used. The definition of pmC$_{ref}$ is therefore very important. pmC$_{ref}$ can be considered to be constant for biomass that was harvested before 1955, but due to the above-ground nuclear tests that occurred between 1955 and 1963 in several countries, the amount of ^{14}C in the atmosphere increased dramatically until 1963. Since 1963, the content of ^{14}C in the atmosphere has decayed, and this decay has been accelerated in recent years due to the increasing emission of fossil-fuel derived CO_2 to the atmosphere. Due to the ongoing reduction of the ^{14}C content in the atmosphere over time, the level of ^{14}C in fresh biomass is also reduced over time. Since 1963, the "true" reference value pmC$_{ref}$ has therefore decayed over time. In waste incineration plants, mixtures of biomass of different age are typically combusted. The "true" pmC$_{ref}$ for a given mixture of biomass fed into the incinerator will depend on the composition of e.g. wood and paper, and their time of felling and harvesting. As the composition/age of biomass fed to municipal waste incinerators is rarely known, it is neither practical nor possible to use a site or time

dependent pmC_{ref} value. For routine measurements, a default value must be defined. This default value may be defined for a given region and for a given period of time.

In the US standard ASTM D 6866-11, the reference value pmC_{ref} is defined as 105, representing a default ^{14}C content in biomass that was produced and harvested in 2010 /9/. However, this default value does not necessarily apply to biomass combusted in a waste incineration plant.

Based on a study performed in 2006-2007 on three municipal waste incinerators in Switzerland, Mohn et al. /4/ found that a pmC_{ref} value of 113 was applicable for biomass combusted in Swiss waste incinerators. This value was found to be appropriate for Danish municipal waste incinerators, and a pmC_{ref} = 113 has been used in this study.

FIELD TEST PROGRAMME

The composition of waste was varied in 5 waste composition experiments during the first field test. Commercial and industrial waste, household waste, biomass (e.g. garden waste), and plastics were collected and stored by Næstved Waste Incineration Plant over a period of time before the first field test. The actual content of biogenic and fossil carbon in the different types of waste is not known and will depend on the composition of the incoming waste at the time of collection. The compositions of the five waste mixtures are shown in figure 3.

Each experiment lasted 36 hours. The measurements were started after about 12 hours of incineration of the above mixtures in order to ensure that the waste in the incinerator consisted of these mixtures only. The measurement programme for each experiment included (1) a 6 hour sampling period and (2) an 18 hour sampling period. Two identical sampling units were used, each with a setup as shown in figure 1. As the variations in stack gas flow during the field test were low, constant flow sampling were used in both units.


PRELIMINARY RESULTS

Preliminary results from the first field test are shown in figure 3. The graph shows the calculated diurnal, time weighted averages obtained by means of the two parallel sampling units. The diurnal averages reflect the average ratio of biogenic CO_2 out of the total emitted CO_2 during each experiment in the field test.

The contribution from biogenic CO_2 in ambient air, added to the stack gas through the combustion air, is included in the results for biogenic CO_2 shown in figure 3. This contribution of biogenic CO_2 from ambient air during the experiments was estimated to be 0.4 % of the total CO_2 emitted through the stack gas.

Based on standard deviations between results obtained through parallel measurements with identical sampling units, the reproducibility of the measurement method during the test (including sampling and analysis) was 0.5 pmC - 3.7 pmC, corresponding to a relative uncertainty of 1%-6% RSD.

Figure 3. Averaged ratio of biogenic CO_2 (top graph) and composition of waste (bottom graph) during experiment 1-5 in the field test. Error bars show the calculated standard deviation, reflecting both the measurement error and the actual fluctuation in biogenic CO_2 in the stack gas from morning (6 hr sampling) to afternoon/evening (18 hr sampling). The results shown here are preliminary.
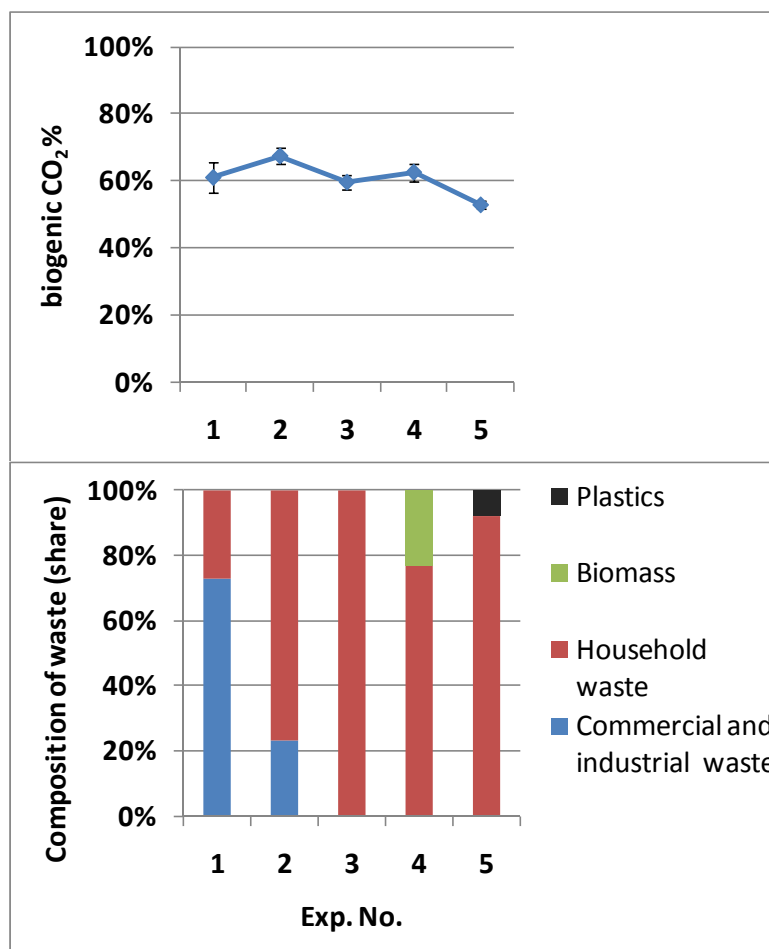
DISCUSSION AND CONCLUSION

The described measurement method performed well during the field tests. From parallel measurements with identical sampling units, the reproducibility of the measurement method during the test was found to be 0.5 pmC - 3.7 pmC, corresponding to a relative uncertainty of 1%-6% RSD. Compared to the uncertainty involved in measurement of gases in stack emissions in general, a reproducibility of 1%-6% RSD including sampling and analysis is found to be satisfactory and fully acceptable.

Figure 3 illustrates the share of biogenic CO_2 emitted during the 5 different waste composition experiments represented in the field test. Out of the total diurnal emission of CO_2 during the 5 experiments, the share of biogenic CO_2 varied between 53% and 67%. The highest emission of biogenic CO_2 was found during experiment 2, where a mix of 77% household waste and 23% commercial and industrial waste was combusted. It is rather surprising that this waste composition shows a higher ratio of biogenic CO_2 than during experiment 4, where the waste composition was 77% household waste and 23% biomass. One explanation may be that the content of biogenic carbon in industrial waste can vary strongly, depending on e.g. the contribution of wood from demolition. A high content of wood in the industrial waste during experiment 2 may explain why the biogenic CO_2 emission was slightly higher than during experiment 4. The contribution of fossil carbon from plastics in experiment 5 explains why this experiment resulted in the lowest measured ratio of biogenic CO_2.

Due to the character of the field experiments, the measurements described here were all based on relatively short sampling periods (6 hrs – 18 hrs). During normal operational conditions at municipal waste incineration plants, the ratio of biogenic CO_2 in the stack gas may fluctuate as the waste composition will vary over time. As long-term sampling will account for such fluctuations, representative results may be obtained from a limited number of long-term samples on waste incineration plants. In order to describe the variation in biogenic CO_2 emissions from plant to plant and from month to month, long-term sampling (flow proportional sampling over 1-4 weeks per sample) has been performed on 5 different Danish Incineration plants over a period of one year (2010-2011) as part of this project. The results of the long-term samples are presently being analysed and will be presented at a later stage.

ACKNOWLEDGEMENT

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