

CALIBRATION OF THE METHOD FOR MEASURING ^{14}C IN COMBUSTION GASES

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ABSTRACT. Much recent effort has been focused on the development of monitoring methods to calculate the percentage of biomass in the fuel used for energy generation in power plants. One possible method is based on measurements of radiocarbon concentration in combustion gases by liquid scintillation (LS) spectrometry. Fossil fuels contain no ^{14}C due to their age. Therefore, after the combustion of such fuels, the resulting CO_2 contains no ^{14}C as well. The only source of ^{14}C comes from the admixture of biomass containing modern carbon. ^{14}C is a beta-emitting radionuclide with a maximum beta energy of 156 keV. There is no emission of gamma rays during decay; therefore, no possibility of gamma spectrometry exists. A difficult task thus is to validate the method and to calibrate it in agreement with the known amount of biomass in the fuel. For this purpose, a set of samples was prepared that were mixtures of hard coal and biomass with a known percentage of carbon. The oxycombustion method was applied for sample preparation in which the combustion of the fuel is done in pure oxygen; therefore, the combustion gas contains mostly CO_2 and steam. The CO_2 from the gas sample is then adsorbed by 3-methoxypropylamine. A known amount of this adsorbent was mixed with a scintillation cocktail and measured in the LS spectrometer. In this way, a calibration curve has been obtained, allowing quantitative measurements of biomass content in the fuel.

INTRODUCTION

The application of biomass for power generation is one of the methods for reducing carbon dioxide emission due to the use of fossil fuels (EU Directive 2009/28/EC). The difficulty for power plants is to prove the percentage of used biomass, which is also very important for economic reasons. The European Committee for Standardization (CEN) has developed a new classification system for fuels made of the waste materials. Technical requirements for that system have also been given. The CEN proposed the term solid recovered fuels (SRF) for fuels produced from biomass and other waste materials. The estimation of biomass percentage in the fuel mixtures (SRF) is very important to assess the percentage of an energy produced from renewable sources. In 2011, the European standard EN 15440:2011 (CEN 2011) was issued, which employs a method based on estimation of ^{14}C content in combustion gases as an alternative for analytical and gravimetric methods. Importantly, the standard states that because the method was not yet sufficiently validated, it must be carefully applied, taking into account local conditions and capabilities of the radiometric laboratories. Therefore, our goal was to develop a method of ^{14}C estimation in combustion gases produced during co-combustion of fossil fuels and biomass, using liquid scintillation counting (LSC).

The experiments included preparation of mixtures of hard coal (fossil fuel) with a chosen biomass, analysis of important parameters of fuel mixtures, combustion of fuel samples in oxygen atmosphere and collection of combustion gases, preparation of samples for LSC and measurements, and the analysis of the results. Samples were prepared with increasing amounts of biomass (5, 10, 15, 25, and 35% of biomass) with hard coal (see Table 3). Both materials were analyzed to estimate the carbon content and other parameters (Tables 1 and 2). Combustion of these samples was done in an oxygen atmosphere (oxycombustion, described later), and the combustion gases were collected for further analyses. A special adsorbent was then applied to react with CO_2 from the collected gas samples to obtain liquid samples to be mixed with the liquid scintillation cocktail. The final samples have been measured in a low-level liquid scintillation spectrometer, as described below.

MATERIALS AND METHODS

Sample Preparation

Mixtures of hard coal and biomass were prepared using the hard coal of a mine located in the Upper Silesian coal basin of Poland (Table 1). The parameters of the biomass, obtained from the ELCHO power station, are given in Table 2.

Table 1 Basic physical and chemical parameters (in analytical state) of studied hard coal.

Coal mine	Hard coal type	Total moisture W (%)	Ash A (%)	Heat of combustion Q_s (kJ/kg)	Total sulfur S_t (%)	Carbon C_t (%)	Nitrogen N (%)
Murcki-Staszic		32.2	3.93	31,686	0.43	80.91	1.29

Table 2 Basic physical and chemical parameters (in analytical state) of studied biomass.

Sample	Total moisture W (%)	Ash A (%)	Volatile V (%)	Heat of combustion Q_s (kJ/kg)	Calorific value Q_i (kJ/kg)	Percentage of total sample mass			
						S_t (%)	C_t (%)	H_t (%)	N (%)
Distillery biowaste	8.66	1.66	75.4	16724	15,318	0.15	39.39	5.47	2.31

The fuel samples (hard coal and biomass mixtures) prepared for the experiment are described below. Analyses of the biomass and hard coal used (see Tables 1 and 2) were performed in the accredited laboratory of the Department of Solid Fuel Quality Assessment of the Central Mining Institute according to the following relevant Polish standards (PB, PN-G) and testing procedures:

- Analytical moisture content: PN-G-04560:1998 and PB-4, ed. 11,
- Ash content: PN-G-04560:1998 and PB5, ed. 11,
- Heat of combustion and calorific value: PN-G-04513:1981 and PB-7, ed. 11,
- Total sulfur content: PN-G-04584:2001 and PB-15, ed. 11,
- Carbon, hydrogen, and nitrogen contents: PN-G-04571:1998 and PB-19, ed. 11.

The hard coal and biomass have been mixed using different weight ratios (see Table 3) to obtain mixtures with different contents of biomass and ^{14}C concentration.

Table 3 Composition of artificial fuel samples.

Biomass percentage in fuel (%)	Hard coal percentage in fuel (%)	Biomass weight (g)	Coal weight (g)	Percentage of biomass carbon in total carbon of fuel sample (%)
5	95	2.5	47.5	2.6
10	90	5	45	5.2
15	85	7.5	42.5	7.8
25	75	12.5	37.5	13.0
35	65	17.5	32.5	18.2

The purpose of this procedure was to validate and calibrate the method for the analysis of biomass content in fuel samples by means of liquid scintillation spectrometry.

Combustion of Fuel Samples: Experimental Setup

The experimental study on biowaste combustion was performed in the laboratory-scale fixed-bed reactor installation using a thermogravimetric analyzer SDT Q600 (TA Instruments) of the Laboratory of Advanced Energy Technologies (see Figure 1). The fixed-bed reactor consists of gas inlets (valves, flow regulators), the fixed-bed reactor (~ 0.8 L in volume), a resistance furnace, process gas treatment, and measurement system (Smoliński 2011). The composition of dry and cooled gas samples collected in gas bags was analyzed via a two-channel gas chromatograph (Agilent 3000A). In the first channel, the column PLOT U ($8\text{ m} \times 0.32\text{ mm}$) was derived with a thermoconductivity detector (TCD) (for separation of CO_2 and $\text{C}_1\text{-C}_5$). In the second channel, a backflush injector module with a precolumn PLOT U ($3\text{ m} \times 0.32\text{ mm}$) and an analytical column MS5A PLOT ($10\text{ m} \times 0.32\text{ mm}$) were applied with a TCD detector (for separation of H_2 , N_2 , CO , CH_4). Helium and argon were used as carrier gases in the PLOT U and MS5A PLOT columns, respectively. The temperature of the inlet, injector, and the columns was 60°C , and the injection time was $50 \times 10^{-3}\text{ s}$ for both columns. The run time and post-run time were 150 and 10 s for PLOT U and MS5A PLOT, respectively, whereas the backflush time for column PLOT U was 12 s.

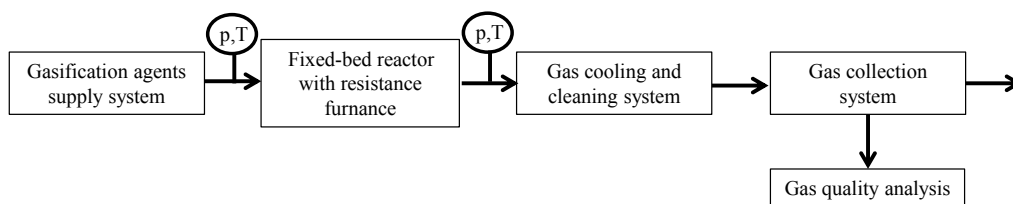


Figure 1 Scheme of the laboratory-scale fixed-bed reactor installation for biowaste combustion tests

Two series of experiments were performed. The first was focused on biowaste combustion in a fixed-bed reactor. The biowaste samples (10 g mass, grain size <0.2 mm) were placed inside the reactor and heated in the oxygen atmosphere to 700°C at the heating rate of $80^\circ\text{C}/\text{min}$. The product gas was cooled and dried in the gas cleaning system and collected in gas bags. In the second series of experiments, the combustion of biowaste was tested using a thermogravimetric analyzer. The heating rate was set to $10^\circ\text{C}/\text{min}$ up to 700°C under air atmosphere. The thermogravimetric analyzer was then used to determine the thermal degradation of the fuel mixtures in the combustion process.

Sampling and Measurement of ^{14}C

^{14}C is beta-emitting radionuclide; therefore, liquid scintillation counting (LSC) is applicable for its measurement. The most difficult task was to develop a sampling technique for the gas and sample preparation that could be suitable for further LSC measurements.

The reagent most commonly used for the adsorption of CO_2 from the air is an organic chemical, 3-methoxypropylamine, known under the commercial brands CarboSorb (PerkinElmer) or Carbon-Trap (Meridian). This substance is able to adsorb 48 mmol of CO_2 per 10 mL of its volume (Edler 2009). After reaction with CO_2 , the adsorbent can be mixed with a suitable scintillation cocktail to obtain a final sample, ready for measurement. For this purpose, the following cocktails can be used: Permafluor E+ (PerkinElmer) or CarbonCount (Meridian) (Molnár et al. 2005; Varti 2009). In our experiments, 10 mL of 3-methoxypropylamine was mixed with 10 mL of Permafluor E+ to create a final sample for LSC. The stages of sample preparation are as follows:

1. Fill a bubbler with 15 mL of 3-methoxypropylamine;

2. Put the bubbler into a cooling bath (water with ice);
3. Bubble the gas from the gas bag(s) through the adsorbent;
4. Transfer 10 mL of adsorbent from the bubbler into a scintillation vial (Teflon™ or PTFE type);
5. Add 10 mL of LS cocktail; and
6. Leave the sample in the cooler for at least 8 hr and conduct the measurement.

RESULTS

Results of Sample Combustion

During preliminary experiments, several samples were prepared (combusted) at the Silesian Technical University in Gliwice, Poland. However, due to significant problems with the measurement of these samples, further experiments were performed in the Central Mining Institute (GIG). In the first series of experiments in GIG, artificial fuel mixtures were combusted in the fixed-bed reactor. In the combustion phase, the fuel sample was heated to 700°C in an oxygen atmosphere. The percentage composition of a gaseous product mixture as well as the total amount of produced gas are presented in Table 4. The product gas was composed mainly of CO₂ (94.39% vol.).

Table 4 Composition of the product gas in the oxygen combustion process of fuel mixtures.

Compounds	Average concentration (% vol.)
CO ₂	94.39
CO	4.54
H ₂	1.07

Example diagrams representing the derivative weight loss (% w/w/°C) and mass loss (% w/w) are presented in Figure 2. Thermal gravimetric analysis (TGA) tests confirmed the good repeatability of biowaste combustion. As mentioned earlier, two series of combustion experiments were performed. The first was conducted in a fixed-bed reactor, where all produced gases were collected in the bag and there was no possibility to study the variation in the combustion products nor the mechanism of the combustion process. This was the reason why the second series of experiments was proposed. TGA tests were repeated three times and these tests confirmed the good repeatability of the biowaste combustion mechanism. An example thermogram of the derivative weight loss and mass loss is presented in Figure 2, where three thermal events can be observed. The first one, between the temperature of 30 and 100°C, is related to moisture evaporation (8.701% w/w). The major thermal events were observed approximately between 150 and 375°C and between 375 and 650°C, respectively. The proceeding peak in the temperature range of 150–375°C represented the greatest weight loss, of 59.67% w/w. It was followed by a smaller peak between 400 and 650°C. These two peaks show different mechanisms of thermal decomposition of the fuel mixtures during combustion at 150–375 and 375–650°C, respectively.

Results of ¹⁴C Measurements

After combusting the fuel samples, the combustion gases were collected in special bags made of material impermeable for gas (special plastic bags with or without an aluminum cover). Initially, the volume of gas was up to 15 L as the combustion at the Technical University had been done in air, not in pure oxygen.

Unfortunately, the preliminary results were difficult to analyze and interpret. No linear relationship between the biomass content and ^{14}C concentration in the gas samples was found. We realized that probably the main reason of that effect was the fact that the sample was not cooled during bubbling of CO_2 through the 3-methoxypropylamine. The exothermic reaction caused significant changes of the absorber's parameters, especially viscosity. Therefore, it was difficult to recover 10 mL of the sample; moreover, in most of the samples a paraffin-like deposit was found. Due to the presence of such deposits, the counting efficiency decreased and no linearity was found for the set of samples as well as no correlation with biomass content.

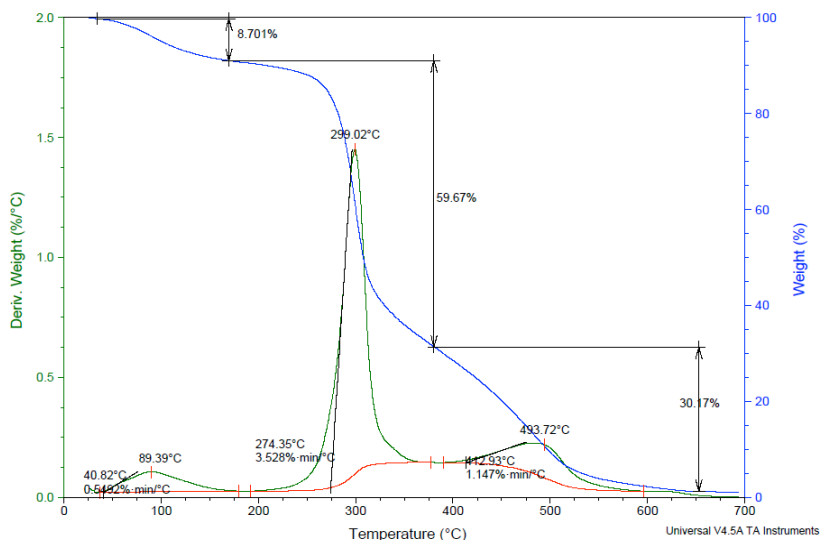


Figure 2 Derivative weight loss versus temperature in combustion process of fuel mixtures

A significant drawback of this sample preparation technique is the inability to check the saturation of the 3-methoxypropylamine with CO_2 in the preliminary stage of the experiments. When CO_2 is not fully loaded to the adsorbent, the measurement would show an increased content of nonbiological CO_2 in the sample. Therefore, it was important to know the surplus of the CO_2 transferred into the 3-methoxypropylamine. If we take into account such an assumption, it leads to the conclusion that sample volume should be at least 5 L of gas (if the content of CO_2 is $\sim 20\%$). On the other hand, even if a much lower volume of CO_2 is used, it would still be possible to assess the presence of ^{14}C in the sample. It was thus decided to weigh containers with the adsorbent to estimate the amount of CO_2 that reacted with 3-methoxypropylamine.

Other aliquots of fuel mixtures were combusted, but in an atmosphere of pure oxygen (oxycombustion). Gas samples were collected and the procedure with absorption was repeated. Due to the experience from previous experiments, some modifications in the procedure have been applied. The most important were the following:

- The bubbler with absorber was kept in the cooling bath at $0\text{--}2^\circ\text{C}$;
- The amount of gas transferred through the bubbler was reduced to a maximum of 5 L;
- The sample was weighed before and after bubbling to estimate the amount of absorbed CO_2 .

The final samples (mixture of absorber and scintillation cocktail) were measured in a Quantulus

low-background liquid scintillation spectrometer. The counting time was at least 6 hr for a single sample, and in special cases even longer, up to 24 hr.

Validation of the LSC method was performed prior to the experiments. Measurements of the blank samples and standards were done first, to adjust chosen window settings and to assess the background values for chosen vials. We found that in the narrow counting window (channels 150–400), the background count rate for Teflon vials was 1.30–1.40 counts per minute (cpm). On this basis, we were able to estimate the suitable counting time as well as the decision threshold and detection limit for ^{14}C . It was determined that the counting time should be at least 6 hr. Calculations of the decision threshold and detection limit were performed for the counting time of samples, blanks, and standards equal to 5 hr (18,000 s). Counting efficiency (yield, y) has been established on the basis of measurements of standard samples. Standard samples have been prepared using ^{14}C standards with known activity, received from the company Wallac. The capsule containing ^{14}C was immersed into the mixture of adsorbent and scintillator and measured. For calibration, standards with activity 45,600 disintegrations per minute (dpm) were taken and the average count rate was 25,800 cpm, so the calculated value of counting efficiency was $y = 0.56$.

The decision threshold (L_c) and detection limit (L_d) were estimated according to the International Organization of Standardization (ISO 2005):

$$L_c = \frac{1}{w} \cdot k \cdot \sqrt{\frac{R_0}{t_{M,S}} + \frac{R_0}{t_{M,0}}} \quad L_d = \frac{2 \cdot L_c + \frac{1}{t_{M,S}} k^2 \cdot w}{1 - k^2 \cdot s^2(w)}$$

where k = quantile of the standardized normal distribution (1,645); R_0 = background count rate; $t_{M,S}$ = counting time of the sample; $t_{M,0}$ = counting time of the blank sample; $w = \varepsilon \cdot y$, overall efficiency; $s(w)$ = standard deviation of the overall efficiency; ε = counting efficiency; and y = chemical yield.

According to previous research (Walanus and Goslar 2009), the ^{14}C content in “modern carbon” is 0.225 Bq/g. It can thus be estimated that the ^{14}C activity in the sample coming only from the biological CO_2 is 0.13 Bq. The detection limit (L_d) of the method is 0.0041 Bq; therefore, it is possible to detect 5% of biological CO_2 in the presence of 95% nonbiological CO_2 . The most common way to report the content of ^{14}C in the total carbon is to express it as a percent of modern carbon (pMC).

Calibration of LSC Method Using Reference Sample with Known ^{14}C Activity

The problem with the calibration of the method was that the ^{14}C from the gas combustion is uniformly distributed within the final sample, while ^{14}C standards can be treated as a source with activity cumulated in one point. Therefore, we conducted a calibration using sample(s) with a known pMC value. From the University of Georgia (USA), we received ANU sucrose (IAEA C-6) with known pMC (150.6%) as the reference standard. Two subsamples of the sucrose were combusted and prepared for LSC analysis. Our average result for these samples is 147.2 pMC, which is in very good agreement with the reference value. This result confirms that the applied calibration procedure is accurate.

Many samples were prepared as replicates to increase the accuracy and precision of measurements. After combustion, a gas sample was divided into two subsamples and transferred through the absorber twice. Also, a significant improvement in the method was due to the gravimetric estimation of adsorbed CO_2 in each sample. The results confirm that this approach leads to accurate results.

RESULTS

Results of the measurements are given in Table 4 and shown in Figure 3.

Table 4 Results of measurements of ^{14}C in fuel mixtures.

Type of fuel mixture	Amount of gas produced during combustion (L)	Assessment of biomass content using ^{14}C (%)	Corrected value due to the percentage (50%) of carbon in biomass (%)
5% of biomass + 95% of hard coal	2×5	6.5	7.1
10% of biomass + 90% of hard coal	$5 + 3$	7.3	11.6
15% of biomass + 85% of hard coal	2×5	11.9	19.0
25% of biomass + 25% of hard coal	2×5	17.0	27.2
35% of biomass + 75% of hard coal	2×5	23.6	37.8

When calculating the biomass content in the fuel mixtures made of hard coal and biomass, it is necessary to take into account the abundance of carbon in both components of the mixture. In the literature, the carbon content in biomass is reported as roughly 50%. Therefore, the estimate based on ^{14}C measurements of the percentage of biomass in the fuel should be multiplied by a factor of 2 to correct for this effect. Yet another important factor is the percentage of carbon in the fossil fuel (e.g. hard coal). In our experiments, the abundance of carbon in hard coal was 80% only, not 100%. Thus, the correction factor should be smaller, only 1.6 instead of 2.0. Taking into account the lower abundance of carbon in the biomass sample (40%), this factor must be corrected again. Taking the content of carbon in biomass as $a\%$ and the content of carbon in fossil fuel as $b\%$, then the correction factor (cf) should be calculated as $cf = b/a$. For the data above, ($a = 39.39\%$, $b = 80.91\%$), $cf = 2.05$.

LSC measurements of ^{14}C activity were used to estimate the biomass content in the artificial fuel mixtures. The linearity (correlation) between the reference values and values, estimated on the basis

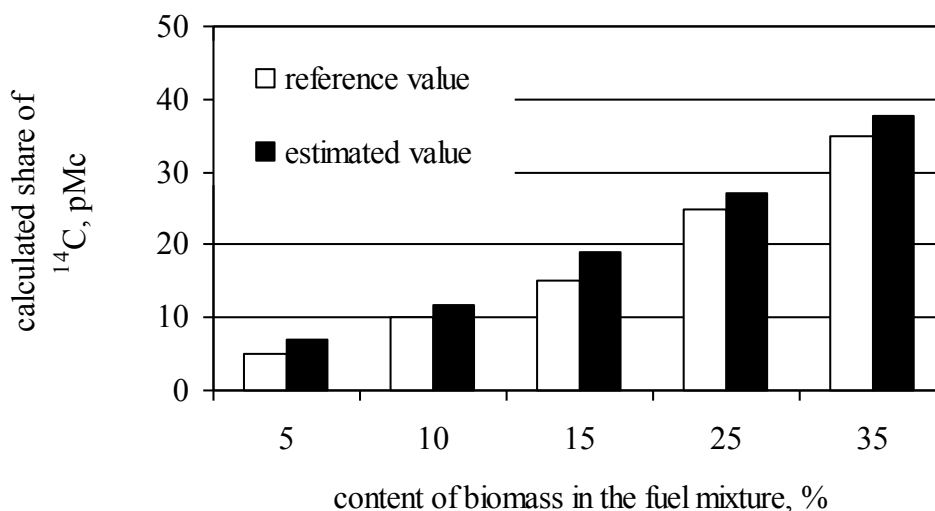


Figure 3 Measurement results of fuel mixtures and comparison with reference values. Reference values were calculated on the basis of chemical analyses of carbon content in biomass and hard coal, with an assumption that there was no ^{14}C in hard coal and the pMC value for biomass was 100%. Estimated values are based on measurements of combusted samples with standardization employing ANU sucrose.

of ^{14}C measurements, is good and confirms the method. Unfortunately, we found disadvantages of the LSC method as well. The counting time of a single sample must be very long, up to 24 hr, to achieve the proper detection limit and diminish the uncertainty. Even for such long counting times, the uncertainty is at least 25–30% of the result for a 10% biomass content level in the fuel mixture. Thus, this method is best employed as an indicative one, and not necessarily a quantitative method.

CONCLUSIONS

The demand of the legal system in Poland (EU) is to add a certain amount of biomass to fossil fuels prior to being combusted in power plants. The industry is thus interested in implementing a reliable and precise method of analysis, to prove the use of biomass in the percentage (mass) exceeding the threshold level. One such method involves LSC based on measurements of ^{14}C concentration in combustion gases. This nuclide is present in the biomass only, not in the fossil fuels.

The simple and inexpensive LSC method consists of collection of combustion gas and further absorption of carbon dioxide (with ^{14}C) on a special chemical, 3-methoxypropylamine. This approach reduces significantly the need for chemical procedures during sample preparation.

The validation and calibration of the method were performed using the specially prepared artificial fuel mixtures made of hard coal and biomass. Results show that the precision of the method is not sufficient for exact biomass percentage estimation since the uncertainty of the results is high; thus, the method can be treated as only qualitative and not quantitative.

ACKNOWLEDGMENTS

The authors are grateful to the authority of ELCHO Power Station for providing samples of biomass, Dr Leokadia Róg for providing coal analyses, Dr Jacek Pawlyta for the assistance in the first stage of investigations, and Dr Randy Culp for the reference sample.

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