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Determination of biomass-coal blending ratio by ^{14}C measurement in co-firing flue gas*

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Abstract: To verify the feasibility of using radiocarbon detection for the measurement of the biomass-coal blending ratio in co-firing heat and power plants, ^{14}C activity detection technology that uses benzene synthesis as the sample preparation method and a liquid scintillation counter as the detection instrument was studied. A benzene synthesis system was built to enrich carbon in the combustion flue gas in the form of benzene. The benzene sample was mixed with scintillator (butyl-PBD) and ^{14}C activity was measured using a liquid scintillation counter (Quantulus 1220). Three kinds of coal and six kinds of biomass were tested repeatedly. The measured ^{14}C activity was 0.3365 DPM/gC in Zhundong lignite, 0.2701 DPM/gC in Shenmu bitumite, and 0.3060 DPM/gC in Changzhi anthracite. These values were much higher than the instrument background activity. For the co-fired experiment, we used groups with biomass ratios (based on the carbon) of 6.51%, 12.95%, and 20.75%. A modified empirical expression to determine the biomass, coal blending ratio based on the ^{14}C activity measured in the co-firing flue gas, was proposed by analyzing and verifying measurement accuracy. From the ^{14}C measurements of the co-fired samples, the corresponding estimated biomass ratios were (5.54±0.48)%, (12.31±0.67)%, and (19.49±0.90)%. The absolute measurement error was around 1% for a typical biomass-coal co-firing application.

Key words: Biomass co-firing; Blending ratio determination; Radiocarbon; Benzene synthesis
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1 Introduction

Biomass-coal co-firing is an attractive technology for reducing carbon dioxide emissions from coal power plants (Lazaroiu et al., 2009; García-Galindo et al., 2010; Agbor et al., 2014; Contreras et al., 2018; Wolf et al., 2018). However, it cannot be broadly applied in China primarily because of the lack of an effective and reliable means to measure the biomass-coal blending ratio of the feedstock fed into the combustor. Thus, government economic subsidies for emission reduction are difficult to implement fairly and reasonably.

^{14}C detection is a mature technique used to identify biogenic and fossil carbons (Palstra and Meijer, 2014; Lu et al., 2018). It has been widely used for the detection of ^{14}C activity in the atmospheric environment which could show the impact of fossil energy on the atmosphere and plants (Zhou et al.,

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2014; Wu, 2017; Niu et al., 2018). The ^{14}C activity of aerosol particles can reveal the extent of emissions from fossil fuel or biomass combustion (Lewis et al., 2004; Hanke et al., 2017; Salma et al., 2017). The use of biogenic industrial products (e.g. bio-based plastics or tyres) has been praised for reducing the application of fossil fuels (Quarta et al., 2015; Rodríguez et al., 2017). This outcome can be verified by ^{14}C detection. ^{14}C measurement is also a commercial method used in waste incineration power plants to determine accurately the proportion of biofuels in burned wastes (Mohn et al., 2012; Fuglsang, 2014; Stachów, 2016). The main principle underlying ^{14}C measurement is shown in Fig. 1.

^{14}C is a carbon isotope with a half-life of 5730 years, and is created from the collision of ^{14}N with a thermal neutron produced by cosmic radiation (Hua et al., 2013; Nikolov et al., 2018). Because of the role of carbon exchange, biomass materials are consistent with the ^{14}C activity level of the atmosphere during an organism's lifetime, and gradually decline after death. However, radiocarbon in fossil fuels decays to almost zero during transformation over millions of years. If the ^{14}C activity in the flue gas of a biomass-coal co-firing power plant can be obtained, the blending ratio of biomass fuel can be calculated.

However, it is difficult to ascertain the average ^{14}C content of biogenic materials directly using ^{14}C detection, especially for waste incineration, because of the complexity of fuel derived from various resources. Researchers have made considerable efforts to ascertain the average ^{14}C content of biogenic matter in waste fuels. The recommended biomass standard value of ASTM (2016) was 100.5 pMC (percent modern carbon) in 2018. Mohn et al. (2008) estimated the average value of ^{14}C of biomass materials in garbage at (107.2±3.8) pMC in 2018 through a literature research and field investigation. Based on that study, Fellner and Rechberger (2009) used a similar method and achieved the result of (113.4±3.6) pMC in 2018. They concluded that the error in the measurement of the biomass fraction could be reduced if the fraction and ^{14}C activity of each biogenic component in the fuels could be determined more accurately.

Unlike in waste power plants, every individual biofuel fraction in the feedstock of biomass-coal co-firing power plants can be predetermined to regulate the measurement of ^{14}C activity of carbon elements in the flue gas. Using the known fraction and ^{14}C activity of each biofuel, the biofuel blending ratio can be calculated more accurately by testing the ^{14}C

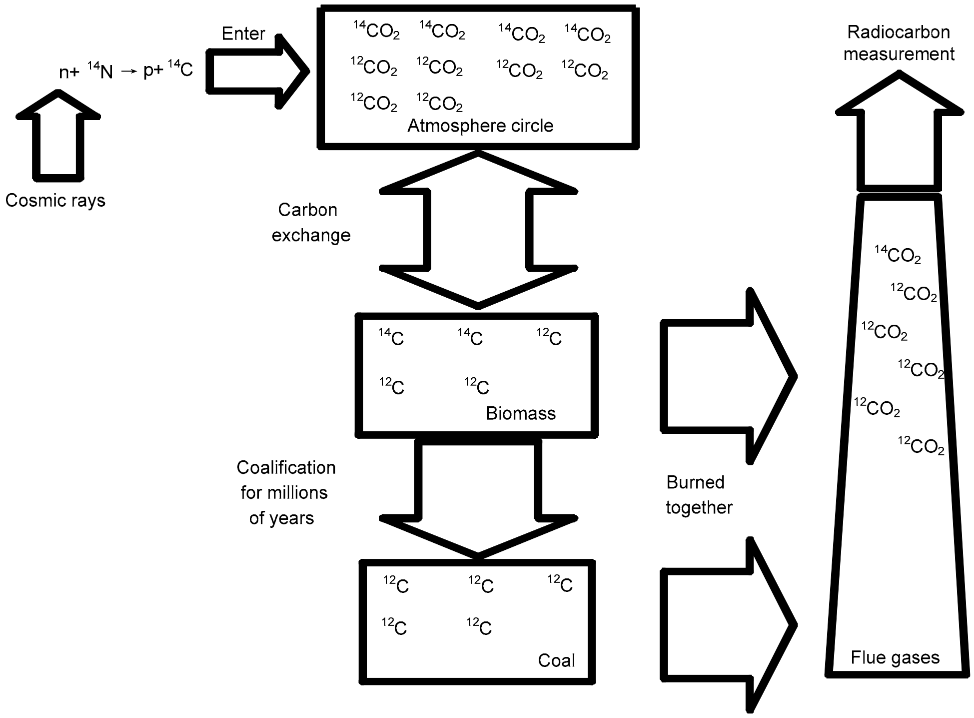

Fig. 1 Principle of ^{14}C measurement for biomass-coal co-combustion

activity of carbon elements in the flue gas from biomass-coal co-combustion. Palstra and Meijer (2010) compared the ^{14}C application in waste incinerators and co-firing power plants. They highlighted that the effects of carbon sources in atmospheric air during combustion should be considered for the relatively low biofuel ratios used in typical biomass-coal co-firing applications. However, Lowe (1989) reported that the activity of microbes and fungi led to an increase of ^{14}C content in coal samples, which may make it unreasonable to ignore the ^{14}C activity of coal when measuring the biomass-coal ratio in co-firing power plants.

In this study, a ^{14}C analysis and calculation method to ascertain the biomass blending ratio was developed. The ^{14}C measurement values of different coal samples, typical biomass samples, and biomass-coal mixture samples were analyzed. On that basis, an empirical expression to calculate the biomass-coal blending ratio based on ^{14}C measurement in the flue gas was proposed, and the usability and accuracy of this method were verified.

2 Materials and methods

2.1 Methods and equipment

Theoretically, fossil fuels have zero radiocarbons, whereas biogenic materials are enriched in ^{14}C from abundant atmospheric $^{14}CO_2$. ASTM (2016) recommends three methods for sample preparation and measurement of ^{14}C activity: accelerator mass spectrometry (AMS), CO_2 absorption amine, and benzene synthesis. AMS technology, the most accurate and expensive method, generally tests the graphite converted from the sample and obtains the absolute amounts of ^{14}C (Quarta et al., 2018). The benzene synthesis method can achieve accuracy close to that of AMS and liquid scintillation counter (LSC) is more cost-effective for the measurement of samples. The CO_2 absorption amine method is simple. Staber et al. (2008) used Carbosorb-E to verify the reliability of the ^{14}C method in lab, but the carbon concentration in the samples was too low, resulting in much lower measurement accuracy.

Considering the accuracy and test cost, in this study benzene synthesis was selected to enrich the carbon elements. To analyze the carbon-containing raw materials, the first step is to convert the fuel samples to $SrCO_3$. Fuel samples were combusted in pure oxygen supplemented by Pt catalyst. Subsequently, the flue gas was absorbed by 20% excess KOH solution after the removal of impurity gas with $AgNO_3$ and KMO_4-H_2SO_4 solutions. The NH_4Cl solution was dripped into the CO_2-absorbed solution to adjust the pH to about 10. Next, a slightly excessive $SrCl_2$ solution, preheated to 75 °C, was added to the CO_2-absorbed solution. The precipitated $SrCO_3$ was then filtered and dried at 105 °C for 10 h. Before benzene synthesis, the $SrCO_3$ was ground into a fine powder and then mixed evenly with Mg powder. The chemical process of the $SrCO_3$-Mg method is long, but can be split into segments, operated in parallel and arranged flexibly.

The benzene synthesis system is shown in Fig. 2. The mixture of $SrCO_3$ and Mg powder was heated to 800 °C for 1 h in the reaction vessel A under a high vacuum so that the $SrCO_3$ was reduced to SrC_2. Subsequently, the reactor was heated to 900 °C for 40 min to increase the conversion rate of SrC_2. When the temperature of the reactor dropped to ambient temperature, the C_2H_2 gas was released by slowly dripping 0.25 mol/L dilute HCl solution from the separating funnel B. The C_2H_2 gas was trapped by H_3PO_3, KOH, and −80 °C ethanol traps to remove the impurities, and was then fixed by liquid nitrogen traps. During this period, the vacuum pump remained in the suction state to remove Rn from C_2H_2. The CrO_3-SiO_2-Al_2O_3 catalyst was placed in a water bath M at 75 °C, and then the C_2H_2 gas was slowly injected into the catalytic bed. The temperature of the catalytic bed was strictly controlled at less than 120 °C. The benzene was finally condensed in a collection bottle N with a −80 °C ethanol trap. Then 4 mL of prepared sample benzene solution was put into a 20 mL Teflon bottle mixed with a 75 mg butyl-PBD scintillator, and 7 mL commercial spectrum grade benzene solution was added to reduce the optical effects of the solution volume. Different volumes of commercial spectrum grade benzene were tested in 20 mL scintillation bottles. The results are shown in Fig. 3. Increasing the benzene enhanced the counting rate, while the counting rate of benzene per unit volume declined. When the benzene amount exceeded half the volume of the scintillation bottle, the increase in the unit volume counting rate due to optical effects was insignificant. Taking into account the limited benzene samples and the need to reduce the background, 11 mL of benzene was finally selected as the test standard in this study. The prepared samples should be kept in the dark for more than 72 h before ^{14}C activity is tested (Pawlyta et al., 1997; Horvatinčić et al., 2004).

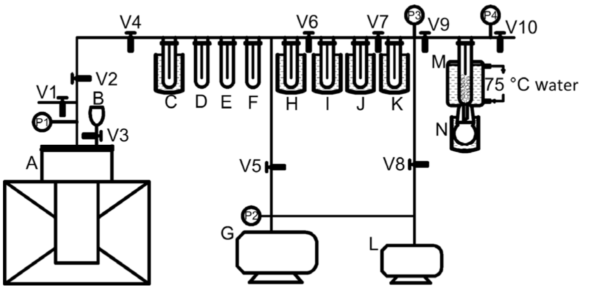

Fig. 2 Benzene synthesis system

A: reaction vessel and furnace; B: separating funnel; C and H: water traps cooled with ethanol at −80 °C; D and F: traps with H_3PO_3; E: trap with KOH; G: mechanical pump; I, J, and K: C_2H_2 traps cooled with liquid nitrogen; L: diffusion pump; M: CrO_3-SiO_2-AlO_3 catalyzer heated in a water bath at 75 °C; N: benzene trap cooled with ethanol at −80 °C, and a collection bottle; V1–V10: valves; P1–P4: vacuum pressure gauges

The measurement of ^{14}C by a liquid scintillation counter is an indirect method (Noakes et al., 2005). The beta particles emitted by ^{14}C atoms in a benzene sample during decay excite the scintillator to emit photons. The flash produced during decay is captured and amplified by the photomultiplier tube, forming a count. Based on the principle of nuclear decay, the theoretical standard deviation of the counting rate is associated with the size of the counting rate and the counting time:

$$\delta_C=\sqrt{C/t}, \tag{1}$$

where δ_C denotes the standard deviation of the sample counting rate (CPM, counted scintillation times per min); C is the counting rate of the sample (CPM); t is the counting time of the sample (min).

Here, the sample ^{14}C activity was calculated using Eq. (2). The standard deviation of the sample activity (δ_D) was calculated by the laws of error propagation.

$$D_{\text{sample}}=\frac{C_{\text{sample}}-C_{\text{instrument background}}}{(m_{\text{sample benzene}}\times 0.9225)\varepsilon}, \tag{2}$$

where D_{sample} denotes the decay times per g of carbon per min of the sample benzene (DPM/gC), representing the ^{14}C activity of the sample; C_{sample} is the counted scintillation times per min of the sample benzene (CPM); $C_{\text{instrument background}}$ is the counted scintillation times per min of commercial spectrum grade benzene (CPM); $m_{\text{sample benzene}}$ is the quality of the sample benzene (g); ε is the counting efficiency (%).

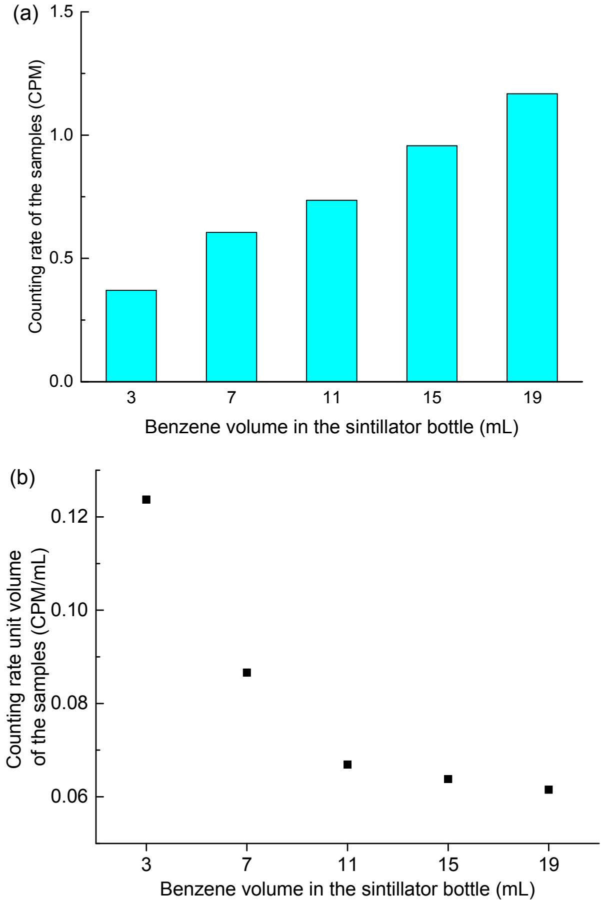

Fig. 3 Effects of the amount of benzene on the counting rate of the samples (a) and the counting rate unit volume of the samples (b)

The original purpose of isotope fractionation correction (Craig, 1954; Mook and van der Plicht, 1999) was to verify the effects of differences in the ^{13}C content of different substances on their ^{14}C activity. In general, the $\delta^{13}C$ (^{13}C deviation to reference substances) was revised to −19‰ according to standard substances or −25‰ considering most trees, which enables the comparison of results between different laboratories (Calcagnile et al., 2011; Quarta et al., 2015). The average ^{14}C content of the biogenic materials used here was the weighted average of the test ^{14}C activity of biomass for co-firing. It was unnecessary to make comparisons with the modern carbon standard or for revision by isotope fractionation correction. Thus, the ^{13}C content was not amended in the calculation, and the pMC was not used as the calibration unit.

The testing and analysis of the ^{14}C activity of samples are routine. All samples here were measured on the Quantulus 1220 Ultra-low background liquid scintillation analyzer (Perkin Elmer, USA) at the Zhejiang Radiation Station, China. The counting time was 300 min for pure biomass samples, and 1800 min for the other samples.

2.2 Materials and experiment

The fuels used here were coal and raw biomass residues (Table 1). Three coal samples with different degrees of coalification, Zhundong (ZD) lignite, Shenmu (SM) bitumite, and Changzhi (CZ) anthracite, were tested to analyze and verify whether the degree of coalification affects the ^{14}C activity of coal. Given the effects of growth years and species of biomass on the ^{14}C activity in organic matter, different types of biomass, e.g. peanut shell (PS), wheat straw (WS), and corn straw (CS) biochar, were selected for the test. Furthermore, CS2 from a different source from CS1 was tested. The deviation of ^{14}C activity in different parts of plants (CS2 stalk and CS2 leaf) was also studied. The different fuel characteristics introduced some little obstructs in the burnout of the fuels for the combustion instrument. The biomass had lots of volatile matter which released too fast to burnout completely before escaping from the furnace. Pure oxygen combustion and a second furnace with Pt catalyst were used in this study to guarantee that carbon recovery reached 98%.

The raw materials selected to study the measurement of the biomass blending ratio were CZ anthracite and CS2. During biomass-coal co-firing applications of commercial scale, a small fraction of biomass is usually added in large coal heat and power plants. Thus, the designed biomass-coal blending ratio used in this study was relatively low. The mixing sample experiments were divided into five groups. The biomass mixing ratio on a mass basis (% in weight) and the corresponding calculated carbon ratio of CS2 (% in weight) of each group are shown in Table 2.

The carbon base blending ratio of biomass in the biomass-coal mixture can be expressed by the following biomass blending ratio:

$$f_{\text{biomass}}^{\text{cb}}=\frac{f_{\text{biomass}}^{\text{mb}}\times C_{\text{ad,biomass}}}{f_{\text{coal}}^{\text{mb}}\times C_{\text{ad,coal}}+f_{\text{biomass}}^{\text{mb}}\times C_{\text{ad,biomass}}}\times 100\%, \quad (3)$$

Table 2 Characteristics of the experimental mixed samples

Group	Blending ratio of CS2 on mass basis (%)	Blending ratio of CS2 based on carbon ratio (%)
1	0	0
2	9.7	6.51
3	18.66	12.95
4	28.76	20.75
5	100	100

Table 1 Proximate analysis and ultimate analysis (in weight, on a dry basis)

Sample	Proximate analysis				Ultimate analysis					HHV (MJ/kg)
	M (%)	A (%)	V (%)	F (%)	C (%)	H (%)	N (%)	S (%)	O (%)	
SM bitumite	3.43	38.20	22.17	36.20	44.84	2.44	0.72	0.34	10.03	16.695
ZD lignite	8.63	8.92	29.11	53.34	63.07	2.43	0.57	0.35	16.03	23.468
CZ anthracite	1.56	22.51	10.96	64.97	67.90	2.67	1.18	0.31	3.87	26.817
Pine sawdust (PS)	8.01	1.22	77.33	13.44	49.69	3.74	0.12	0.42	36.80	18.688
Wheat straw (WS)	8.65	7.28	66.44	17.63	43.68	3.36	0.71	0.24	36.08	16.604
Corn straw 1 (CS1)	8.89	6.53	66.67	17.91	43.60	3.46	1.20	0.30	36.02	16.376
Corn straw 2 (CS2)	7.12	8.04	70.66	14.18	44.03	3.70	0.60	0.19	36.32	16.494
CS2 leaf	7.65	7.28	70.75	14.32	43.43	3.55	0.59	0.14	37.36	16.309
CS2 stalk	6.79	4.14	72.44	16.63	46.31	3.76	0.38	0.21	38.41	17.324

M indicates moisture; A indicates ash; V indicates volatile; F indicates fixed carbon; HHV indicates high heat value where $f_{\text{biomass}}^{\text{cb}}$ denotes the biomass blending ratio with carbon base (%), $f_{\text{biomass}}^{\text{mb}}$ is the biomass blending ratio with mass base (%), $f_{\text{coal}}^{\text{mb}}$ is the coal blending ratio with mass base (%), $C_{\text{ad,biomass}}$ is the organic carbon content in the biomass with air dry basis (%), and $C_{\text{ad,coal}}$ is the organic carbon content in coal with air dry basis (%).

3 Results and discussion

3.1 Instrument background activity and testing efficiency

The testing background activity was considered to be composed of three parts, based on Vogel et al. (1987) and Lowe (1989):

1. The instrument background activity during a blank sample test;

2. The contamination induced during the sampling process and preparation;

3. The original contamination in the sample.

To investigate the instrument background activity of the LSC when measuring benzene and the effects of the benzene synthesis process on the background value, the ^{14}C test value of commercial spectrum grade benzene, a benzene sample made from commercial C_2H_2, and a benzene sample made from commercial $SrCO_3$ were measured (Fig. 4).

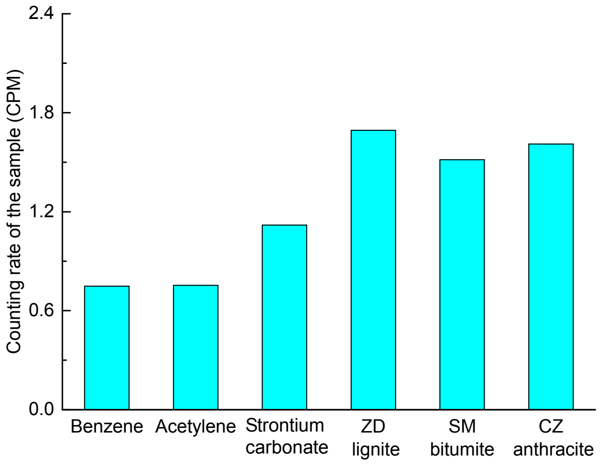

Fig. 4 Comparison of the possible background activity (C_2H_2 and $SrCO_3$ were selected as the chemical intermediates of the benzene synthesis process to study the background changes)

These commercial agents for background research are produced from fossil fuels. As shown in the figure, the increase in sample background activity caused by the benzene synthesis process was primarily caused by the reduction of $SrCO_3$. McCormac et al. (1992) found that the ^{14}C test value of commercial spectrum grade benzene increased after being re-made by the benzene synthesis system. They noted that modern carbon impurities in the metal used as the reducing agent was the main reason for the increase in the background value. Improving the purity of Mg metal can reduce the contamination from sample preparation, but will increase the cost. However, the ^{14}C test value of benzene samples converted from coal was significantly higher than that of the commercial agents mentioned above.

The above results suggest that it is unreasonable to generally regard the ^{14}C test value of a coal sample as the test background when using the benzene method to measure ^{14}C. Coal may contain traces of ^{14}C (Lowe, 1989). It should be treated more carefully, particularly when ^{14}C determination technology is used for measuring the biofuel proportion in a co-firing power plant. The ^{14}C test value of spectrum grade benzene is the instrument background, affecting all benzene samples, which should be reduced directly. The ^{14}C test value of a benzene sample made from commercial $SrCO_3$ reveals the effects of contamination induced by the sample preparation process, which should be revised in accordance with the specific sample. The ^{14}C test value of coal sample reveals there are original contaminants in coal and air to be processed in an industrial furnace.

The counting value of the LSC and the actual decay number of samples were converted by counting efficiency. To obtain the counting efficiency of the instrument when the LSC was used to test benzene solution, the ^{14}C standard solution ((2.024±0.018) kBq/g Na_2CO_3 solution) from the National Physical Laboratory, UK was purchased and diluted to the same order of magnitude as the biomass ^{14}C activity in the laboratory, which was finally converted to benzene. The test counting value calibrated by instrument background was (25.7741±0.1531) CPM/gC, and the calculated ^{14}C activity of the standard sample was (31.529±0.280) DPM/gC. Thus, the counting efficiency of the Quantulus 1220 LSC in the benzene solution test was (81.75±0.87)%. The real decay times per g of carbon per min of all possible background matter could be calculated by Eq. (2). The results are shown in Fig. 5, which shows the same trend as Fig. 4. The ^{14}C activity of C_2H_2 was almost zero (equivalent to background). The disparity between C_2H_2 and $SrCO_3$ further proved that it was the reduction process that caused the background to increase, which we attribute to the effect of modern carbon impurities in the Mg powder in this study. Compared to these two chemical intermediates, the variable degrees of enhancement of ^{14}C activity in the different coal samples show that some modern carbons were induced in these unpretreated coals.

3.2 Stability and accuracy

The repeatability and stability of ^{14}C activity detection by the benzene synthesis method are of huge importance. In (ASTM, 2016), the measurement error of the benzene synthesis method is 2%–3%. Norton and Devlin (2006) reported that a relatively reasonable measurement error of the benzene synthesis method is nearly 3%.

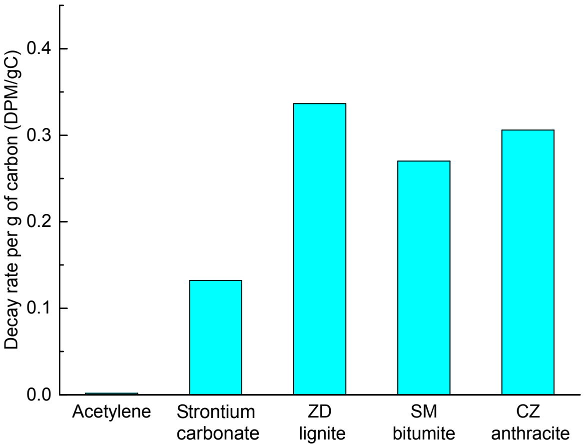

Fig. 5 Real decay times per g of carbon per min of all possible background materials

The biomass and coal fuels used in the test were converted into benzene samples through the same sample preparation process and tested with the same instrument. The average and standard error values of ^{14}C activity calculated by the laws of error propagation of samples are listed in Table 3.

The measurement error of biomass under the test method here was consistent with the conclusions of previous studies. The relative standard deviation of coal samples with low ^{14}C activity remained higher than that of biomass samples even after the increase in the counting time to six times. This is the result of the statistic error rule of radioactivity measurement. Though the test error can be reduced by further extending the counting time, the measurement accuracy is sufficient to satisfy the practical requirement of identifying the biomass proportion in biomass-coal co-firing applications. Thus, the counting time was not increased.

Each biomass sample selected underwent three separate benzene synthesis and testing processes. The results are shown in Fig. 6. The measurement points of each biomass sample fell within the error range given in Table 3, suggesting that the ^{14}C measurement method built in our laboratory is reliable and accurate.

Under the Suess effect (Levin and Kromer, 2004), the ^{14}C activity level in the atmosphere decreases year by year due to the application of fossil fuels. Accordingly, the ^{14}C activity of PS as perennial wood waste is significantly higher than that of WS

Table 3 Averages and standard deviations of sample ^{14}C activity

Sample	Average D_{sample} (DPM/gC)	Standard uncertainty (absolute, 2δ)	Relative uncertainty (95% confidence interval)
ZD lignite	0.3365	0.0272	8.09%
SM bitumite	0.2701	0.0257	9.51%
CZ anthracite	0.3060	0.0266	8.68%
PS	14.5946	0.4109	2.82%
WS	13.2966	0.3838	2.89%
CS1	13.3625	0.3863	2.89%
CS2	13.9148	0.3979	2.86%
CS2 leaf	13.8568	0.3973	2.87%
CS2 stalk	13.8132	0.3974	2.86%

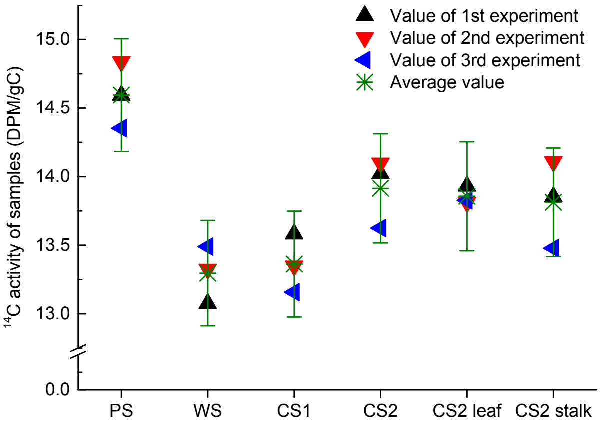

Fig. 6 Three experimental measurements of the ^{14}C activity of biomass (average values with 2δ are also shown to present the experimental stability intuitively)

and CS as herbage waste. For the same plant growing in different areas, e.g. CS1 and CS2, the ^{14}C content in the plants may be different, requiring more effort to determine the average ^{14}C content of biofuels in practice. Zhou et al. (2014) have sampled green foxtails and air samples from different depositions in Xi'an, China. They found a significant difference of ^{14}C content between the samples from a road side in the downtown area and a public park. For the different parts of corn straw, no difference was found in ^{14}C activity, suggesting that the effects of different parts of the same batch of a plant need not be considered when ascertaining the average ^{14}C content of biofuels in a practical biomass-coal co-firing power plant.

Besides the ^{14}C activity of the biofuels, it is also vital to determine the ^{14}C activity of the coal used in co-firing. The ^{14}C test values of the three coals were slightly different, but there was no obvious correlation between the ^{14}C test values and the degree of coalification. This is because even lignite has experienced millions of years of coalification, during which the 'old' ^{14}C has already decayed. Lowe (1989) highlighted microbial and fungal of coal as the main cause of ^{14}C activity in coal sample, especially in young lignite. However, the air ^{14}C contaminant caused by different sampling methods and operators could not be eliminated completely.

3.3 Determination of the blending ratio

The key to applying ^{14}C detection technology to the measurement of the biomass blending ratio in a co-firing power plant is to calculate the biomass-coal ratio using the test data of ^{14}C activity in the co-firing flue gas. Eq. (4) was used to calculate the biomass blending ratio (carbon base) based on the ^{14}C test value (Mohn et al., 2008; Palstra and Meijer, 2010; Fuglsang et al., 2014).

$$f_{\text{biomass}}^{\text{cb}} = \frac{D_{\text{mix}} - D_{\text{coal}} \times f_{\text{coal}}^{\text{cb}} - \sum_{i=1}^{n}(D_{\text{x}\_i} \times f_{\text{x}\_i}) \times f_{\text{x}}^{\text{cb}}}{\sum_{i=1}^{n}(D_{\text{biomass}\_i} \times f_{\text{biomass}\_i})} \times 100\%, \tag{4}$$

$$f_{\text{biomass}}^{\text{cb}} + f_{\text{coal}}^{\text{cb}} + f_{\text{x}}^{\text{cb}} = 1, \tag{5}$$

where D_{mix}, D_{coal}, and D_{biomass} denote the decay times per g of carbon per min of the co-firing sample, pure coal, and pure biomass benzene, respectively (DPM/gC); D_{x} is the ^{14}C activity of atmospheric air CO$_2$ induced during the combustion and sampling process (DPM/gC); $f_{\text{coal}}^{\text{cb}}$ is the coal blending ratio with carbon base (%); f_{x}^{cb} means the fraction of atmospheric air CO$_2$ in the flue gas, which generally is 3‰; f_{biomass_i} and f_{x_i} are the carbon fractions of the biomass and atmospheric air CO$_2$ source i within the total of all biomass and atmospheric air CO$_2$ carbon, respectively.

In this study, a single biofuel CS2 was used in the co-firing experiment. Since pure oxygen combustion was used here, $f_{\text{x}}^{\text{cb}}=0$. If $D_{\text{coal}}=0$ (Mohn et al., 2008; Palstra and Meijer, 2010; Fuglsang et al., 2014), Eq. (4) can be re-written as

$$f_{\text{biomass}}^{\text{cb}} = \frac{D_{\text{mix}}}{D_{\text{biomass}}} \times 100\%. \tag{6}$$

However, previous experiments using different coals have revealed that coals may have variable ^{14}C content. Thus, ignoring the coal ^{14}C activity when using benzene synthesis may increase the calculated results:

$$f_{\text{biomass}}^{\text{cb}} = \frac{D_{\text{mix}} - D_{\text{coal}}}{D_{\text{biomass}} - D_{\text{coal}}} \times 100\%. \tag{7}$$

In addition, Eq. (7) may underestimate the biomass blending ratio when the data of the measured

^{14}C activity are put into the equation. This is because the ^{14}C activity of the tested samples can increase when they are polluted by modern carbon sources in metal Mg during the synthesis of benzene. Coal and the low biomass blending ratio samples were polluted to a relatively high extent, while pure biomass was basically unaffected. Based on the characteristics of the effects of pollution on the ^{14}C activity test, the following assumptions were made:

1. The ^{14}C activity of introduced modern carbon was consistent with the average ^{14}C activity of the biofuel applied in co-firing;
2. The introduced modern carbon quality per g of carbon was the same for every sample;
3. The effects of introduced modern carbon on the ^{14}C test values of blank samples could be obtained from the commercial $SrCO_3$ test.

The revised equation is written as

$$D'_{\text{sample}} = \frac{D_{\text{sample}} \times m_{\text{sample benzene}} - D_{\text{contamination}} \times m_{\text{contamination benzene}}}{m_{\text{sample benzene}} - m_{\text{contamination benzene}}}, \tag{8}$$

where

$$D_{\text{contamination}} = D_{\text{biomass}},$$

$$m_{\text{contamination benzene}} = \frac{m_{\text{sample benzene}} \times D_{\text{SrCO}_3}}{D_{\text{contamination}}},$$

and then,

$$D'_{\text{sample}} = \frac{D_{\text{sample}} - D_{\text{SrCO}_3}}{D_{\text{biomass}} - D_{\text{SrCO}_3}} \times D_{\text{biomass}},$$

where $D_{\text{contamination}}$ denotes the decay times per g of carbon per min of the introduced modern carbon sample benzene (DPM/gC); D_{SrCO_3} refers to the decay times per g of carbon per min of the commercial $SrCO_3$ sample benzene (DPM/gC); $m_{\text{contamination benzene}}$ is the quality of the introduced modern carbon sample benzene (g); symbol ′ denotes the revised value of the introduced modern carbon contaminant.

Finally, the equation for calculating the carbon ratio from biofuel in the co-firing flue gas is written as

$$f^{\text{cb}}_{\text{biomass}} = \frac{D'_{\text{mix}} - D'_{\text{coal}}}{D'_{\text{biomass}} - D'_{\text{coal}}} \times 100\%. \tag{9}$$

The given blending ratio of the mixed biomass and coal, and the blending ratio calculated from Eq. (9), are shown in Fig. 7 and Table 4.

The calculated values of the biomass-coal blending ratio obtained from the flue gas ^{14}C activity test are consistent with the given values. The absolute error between the actual ratio and the calculated value is around 1%, which is acceptable for engineering applications.

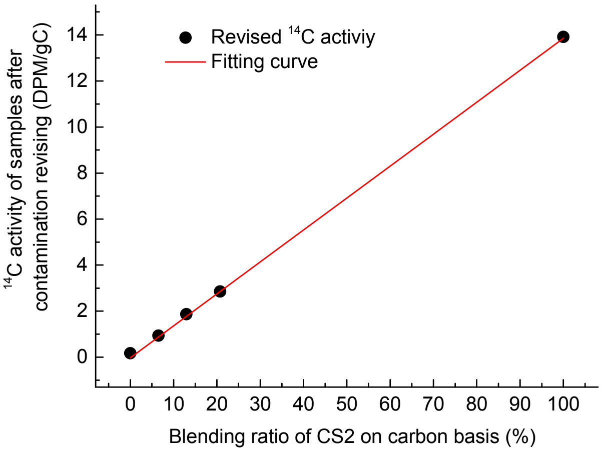

Fig. 7 **^{14}C activity of the co-firing experiments after contamination revision**

Table 4 **^{14}C activity of the co-firing experiments**

Group	Blending ratio of CS2 on carbon ratio (%)	Calculated carbon ratio of CS2 (%)	Standard uncertainty (absolute, 2δ)	Relative uncertainty (95% confidence interval)
1	0	0	–	–
2	6.51	5.54	0.48	8.69%
3	12.95	12.31	0.67	5.44%
4	20.75	19.49	0.90	4.62%
5	100	100	–	–

The measurement accuracy of the benzene method is limited by the principle of nuclide decay and the upper limit of LSC measurement, causing a part of the error shown in Table 4 in the whole detection experiment. The relative uncertainty increased as the blending ratio decreased. In a real industrial boiler, the biofuel co-fired ratio may be less than that designed in this study, which means higher relative uncertainty. The major error source is the system error brought by the experimental device when the biomass blending ratio is relatively low. However, the absolute uncertainty, which matters most to regulators, reduced as the biomass mixing ratio decreased. This means that the ^{14}C measuring method could be used to determine the biomass blending ratio in a co-fired power station. For higher accuracy, the systematic error caused by the combustion device appears to be not negligible and needs further study.

In similar studies, researchers often collected the flue gas in a power plant boiler directly and then prepared it for the test. They obtained estimates of the blending ratio, but it was difficult to obtain accurate real values of the biofuel or fossil fuel contents for calibrating the determination. In this study, the mixture of biomass and coal with a designed blending ratio was burned in the laboratory, so the absolute deviation between the calculated biomass blending ratio and the designed ratio could be more readily obtained. The availability and accuracy of the ^{14}C technology when used to monitor the co-firing power plant were examined intuitively. The revision of the ^{14}C activity of the coal samples worked well in this study. However, the original contamination in the coal was not completely established, and further studies with the help of AMS are necessary.

4 Conclusions

The benzene synthesis test platform built by our laboratory ran well. In this study, the availability and accuracy of ^{14}C technology were examined intuitively.

1. Multiple commercial agents and coals were analyzed and compared to investigate background constituents. The ^{14}C value of spectrum grade benzene revealed the instrument background activity, and $SrCO_3$ revealed the contamination in the preparation process. The test ^{14}C activity of coal sample was not negligible when using the benzene method.

2. The independent repetitive experimental results of six biomass samples all fell within the standard deviation range, which proves the stability of the benzene synthesis and measurement system designed in this study. The differences in ^{14}C activity between plant types and between plants of the same type from different areas were significant, and would require more work in particular applications.

3. A modified empirical expression based on ^{14}C activity measurement in the co-firing flue gas was proposed, considering the effects of coal ^{14}C activity. The absolute measurement error was about 1% for a typical biomass-coal co-firing application.

However, for commercial applications, the relatively complex conditions of fuels and the varying combustion conditions in the furnace might affect measurement accuracy and need further study.

Contributors

Yu-xing TANG wrote the first draft of the manuscript. Chun-jiang YU and Wen-nan ZHANG revised and edited the final version. Zhong-yang LUO managed the execution of research activity. Jian-meng CEN and Qian-yuan CHEN assisted in the experiments.

Conflict of interest

Yu-xing TANG, Zhong-yang LUO, Chun-jiang YU, Jian-meng CEN, Qian-yuan CHEN, and Wen-nan ZHANG declare that they have no conflict of interest.

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中文概要

题　目： **以 ^{14}C 法为基础的共燃烟气中生物质与煤的掺混比例测定方法**

目　的： 准确且可靠的生物质燃料掺混比例数据的缺失，阻碍了生物质/煤混燃发电技术在中国的发展。本文旨在建立以 ^{14}C 法为基础的生物质掺混比例检测系统，并研究煤作为化石燃料的测试本底、不同生物质之间 ^{14}C 含量的差异以及苯合成工艺中引入的现代碳污染对测试精度的影响，以验证该方法在混燃电站中实际应用的可行性。

创新点： 1. 建立并使用适用于在工业混燃电站中应用的计算方法；2. 通过实验测试，获得了 3 种由制样过程污染产生的煤中 ^{14}C 含量；3. 通过对实际过程的经验拟合，提出更为合理的污染修正公式。

方　法： 1. 自主搭建苯合成系统（图 2），并以液体闪光计数技术为核心形成样品 ^{14}C 值测试体系；2. 通过实验测试，获得 6 种生物质与 3 种煤的 ^{14}C 测试值（图 3 和 4），并验证混燃测试的可行性（图 5）；3. 通过公式推导，在考虑煤中 ^{14}C 含量后，更为合理地修正苯合成过程中引入的污染，以减小混燃测试的绝对误差（公式（9））。

结　论： 1. 光谱级纯苯的测试值为仪器的测试本底，而商用 $SrCO_3$ 制苯的测试值则反应了苯合成过程中引入的污染本底。2. 对不同生物质的重复实验的测试值落点均在理论计算误差范围内，证明了实验中苯合成系统的可靠性。3. 运用研究中建立的计算方法，获得了生物质混燃比例的测试值；^{14}C 法应用于生物质/煤混燃电站的绝对测试误差在 1%左右。

关键词： 生物质混燃烧；掺混比例测量；放射性碳；苯合成