Using chemometric analysis to classify and confirm the origin of bio-char

Marcin Sajdak*, Sławomir Stelmach

Institute for Chemical Processing of Coal, 1 Zamkowa St, 41-803 Zabrze, Poland

A R T I C L E   I N F O

A B S T R A C T

In this article, we present a method for detecting the amount of polymer added in the biomass pyrolysis process to obtain fuel for energy generation. The main aim of these research was to develop a new methodology to determine the amount of polypropylene added in the pyrolysis process, which was used as a case study of the type of impurities that can contaminate biomass. In our best knowledge these methods, based on chemometric methods combined with spectral data from Fourier transform infrared spectroscopy (FTIR) applied to bio-char analysis are new one and could allow a more accurate control of bio-char than existing methods such as selective dissolution analysis of the ^{14}C content. As a chemomteric methods in this studies the classification analysis (CA) and principal component analysis (PCA) were applied. Thereby we could describe relation between the third principal component (calculated from FTIR spectra) and amount of polypropylene additive depending on the pyrolysis temperature.

To the best of our knowledge, there have been no reports in the literature on determining the amount of polymer added in using a bio-char control instead of raw biomass for co-firing.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The global primary energy demand in 2013 increased by 2.3% over the previous year. Market analysts predict that the global energy demand will increase by 41% by 2035. Rising fossil fuel prices have led to the expectation that by 2035, renewable energy sources will become the second largest source of electricity generation globally [1–3]. The increasing use of biomass for the production of primary energy has resulted in more frequent problems that are related to the physicochemical properties of biomass. These problems may be eliminated (or at least limited) by pre-processing the biomass into fuels with greater stability, as characterized by enhanced physicochemical properties (e.g., the calorific value). There are well known methods for thermal biomass upgrading (such as torrefaction or pyrolysis). These processes can be used to obtain fuels with quality parameters that are comparable to those of hard coal. These parameters depend on the process conditions and the properties of the material used. The key to the wide application of bio-chars as alternative renewable fuels for energy generation is the type of material used in thermal pre-processing. Bio-char must be completely produced from biomass

to be considered as a renewable fuel. Unfortunately, the bio-char or torrefied biomass entering the market may be knowingly contaminated by chars obtained from coals or plastics pyrolysis. Therefore, an appropriate (and relatively cheap) method of analysis must be developed to accurately classify the bio-material used for energy production.

The first mention about biomass origin analysis in which the statistical and chemometric methods were applied have been presented in the work on the biomass properties [4,5]. Unfortunately authors used chemometric methods only to data visualization, do not builded a specific algorithm for classification, which would determine the type of biomass on the basis of chemical analysis of samples. In other manuscripts can be found some information about spectrometry method coupled with chemometric analysis which were used to quality analysis of biomass [6–9]. Nowadays the analytical laboratories that perform analysis of biomass and biodegradable materials derived from biomass have the ability to mark the biodegradability, which is determined according to the European standard: EN 15440 Testing for Solid Recovered Fuels (Selective Dissolution Method (SDM) and Carbon-14 Method). According to the standard, this method is not appropriate if the SRF sample has biomass components that are insoluble in sulfuric acid or fossil-based components that are soluble in the acid. The second method – the Carbon-14 Method – measures the radiocarbon content of the mixed wastes and is applicable to all materials [10].

* Corresponding author. Tel.: +48 322710041.
E-mail address: msajdak@ichpw.zabrze.pl (M. Sajdak).

Table 1
Experimental matrix (central composite rotatable design $2^2 + 2 \times 2 + 3$) for biomass and biomass-PP blends.

	No.	Coding – classical experimental design	
		Temp. [°C]	PP [%]
	1	500	10
	2	500	50
	3	700	10
Regular experiment	4	700	50
	9	458	30
	6	740	30
	7	600	0
	8	600	58
	9	600	30
Central	10	600	30
	11	600	30
	12	500	0
Blank	13	600	0
	14	700	0
	15	458	0

Table 2
Principal component analysis results. Significant values of the principal components (above 0.7) are marked in bold.

No	PC 1	PC 2	PC 3	Temp. [°C]	PP [%]
1	**0.984**	0.141	−0.079	500.00	10.00
2	**0.920**	0.374	0.086	500.00	50.00
3	**0.933**	0.262	−0.035	458.00	30.00
4	**0.978**	0.164	−0.106	458.00	0.00
5	**0.989**	0.090	−0.114	500.00	0.00
6	0.613	**0.746**	0.183	700.00	0.00
7	0.453	**0.853**	0.242	600.00	30.00
8	−0.111	**0.744**	0.588	700.00	10.00
9	−0.020	**0.964**	0.225	600.00	58.00
10	0.501	**0.836**	0.199	600.00	30.00
11	0.496	**0.850**	0.141	600.00	0.00
12	−0.050	0.233	**0.962**	740.00	30.00
13	−0.078	0.264	**0.959**	740.00	30.00

The analysis methods that were initially used were based on chemometric analysis, and the pre-classification of the biomass and the origin of the bio-char were performed using proximate and ultimate analysis and spectroscopy [11–14].

In this paper, we present current results from using chemometric analysis to classify and verify the origin of bio-char: a FT-IR DRIFT analysis was conducted in combination with a few chemometric methods.

2. Experimental

2.1. Materials and analytical methods

In this study on the pyrolysis process, the materials used consisted of pine wood biomass and polypropylene without any filler, in the form of 4 mm radius granules and colored with charcoal (Daplen provided by Borealis). The biomass investigated was prepared for chemical analysis and the thermal conversion process. A detailed description of the methods used in the raw material preparation has been previously presented [15].

The prepared samples were pyrolyzed under different thermal conditions ranging from 458 °C to 740 °C and with different amounts of added polypropylene, following a central composite design in the design of experiment method (DOE, see Table 1). In the thermal conversion process (co-pyrolysis), 150-g samples were pyrolyzed under a nitrogen atmosphere. A detailed description of the pyrolysis process, a schematic of the laboratory-scale apparatus and the thermogravimetric analysis of the applied polypropylene has been given in a previous paper [16]. Table 2 summarize the primary parameters used in the design and the subsequent performance of the experiments.

A similar research study on biomass pyrolysis under various thermal conditions has already been published [17–19]. However, only pure biomass without the addition of any other materials was investigated in the aforementioned study. All of the samples of carbonized biomass were investigated by FT-IR analysis using the DRIFT method.

2.2. Analytical method for bio-char investigation

A sample (0.6 mg) was mixed with KBr (300 mg), finely ground and placed in a sample cup. The sample cup was overfilled with the sample, and the sample surface was flattened with a spatula.

The sample was then placed into a diffuse reflectance accessory to generate the spectrum using potassium bromide as a reference material. The relationship between the concentration and the spectral response was linearized by applying the Kubelka–Munk function to the spectral data. Fig. 1 presents a representative spectrogram that was used to analyze the carbonized biomass containing PP (500 °C – 0% PP, 10% PP, and 50% PP).

2.3. Chemometric and compositional data analysis of bio-char

First, all of the FT-IR spectral data were normalized using Eq. (1), which was essential for the subsequent chemometric analysis and to properly interpret the results [20]. This procedure was used to unify examined variable values and determine the variance in the data set considered.

$$x_{ij} = \frac{a_{ij} - b_j}{s_j} \tag{1}$$

The terms in the equation above are defined below:

- x_{ij} – standardized parameter value,
- a_{ij} – initial value of parameter,
- b_j – average value of parameter, and
- s_j – standard deviation of j-th parameter.

Fig. 2 shows the results of the spectral data normalization that was performed using Eq. (1). Fig. 2a shows the raw spectral data (before normalization) for the tested samples, and Fig. 2b shows the spectral data that were obtained after the normalization process and were then subjected to cluster analysis and principal component analysis. The normalization procedure enabled the tested materials to be analyzed comparatively using the raw spectra from the FT-IR analysis.

After pre-preparation, the data set was subjected to cluster analysis (CA) followed by principal component analysis (PCA).

Cluster analysis is one of several exploratory multivariate methods that can be used to determine the relationships among variables. A data set must be normalized to examine the similarity between variables. In hierarchical clustering analysis (HCA), Ward's method is used to obtain a cleaner plot of clusters. This method differs from other methods in that an analysis-of-variance is used to evaluate the distance between clusters. In this method, the sum of squares (SS) of any two clusters that can be formed at each step is minimized. This method is considered to be very efficient. The Euclidean distance given by Eq. (2) was used in the analysis:

$$d_{ij} = \sqrt{\sum_{k=1}^{m} (x_{ik} - x_{jk})^2}, \tag{2}$$