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# Application of chemometric methods to evaluate the origin of solid fuels subjected to thermal conversion

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ABSTRACT

Biomass is the oldest and currently the most often used renewable source of energy. Increasingly, biomass is used in thermal conversion processes. The presented studies focused on the quality control of solid products (char) from the thermal conversion process of biomass in terms of their contamination with polymeric material. To perform these studies, spectral techniques (FT-IR) were coupled with chemometric methods. The aim of the studies was to determine the relationship between the addition of polypropylene and the changes in the chemical properties of char obtained at different temperatures. Pyrolysis processes were conducted in a fixed bed with a continuous flow of nitrogen. Two types of biomass (alder and pine) and plastic waste material such as polypropylene (PP), polyethylene terephthalate (PET), acrylonitrile butadiene styrene (ABS) and styrene-butadiene rubber (SBR) from tire waste were used as examples of materials that may undergo pyrolysis alongside biomass. The FT-IR spectra of the tested materials (bio-char) in primary form and in its first derivative were used. The chemometric methods made it possible to show the differences in the pyrolysis solid products depending on the pyrolysis of polypropylene as an additive. Principal component analysis was applied to help identify the absorption bands, allowing a quantitative estimate of the additive polymer material and types in the case of SBR and PET.



## 1. Introduction

Bio-char is a prospective solid fuel for co-firing in power plants with conventional fuels for power generation. Unfortunately char is obtained under a thermal conversion process and characterized by a high degree of processing. Thus, above 450–500 °C, it is very difficult to check that biochar–biomass-derived fuel applied to combustion in power boiler is not contaminated with polymer-derived materials. In our best knowledge this subject is quite new and in this time in literature is not enough information about problem in identification of biochar origin (obtained from 100% biomass under thermal conversion process). The first information about biomass origin analysis used to the chemometric method was presented in two manuscripts described biomass properties [1,2]. In the literature can be found also some information about quality analysis of biomass in which were used spectrometry method coupled with chemometric analysis [3–6]. Analysis of classification and origin, before problems with biochar analysis, was studied in the case of coal also applied chemometric methods [7–9]. Some information about biochar analysis obtained from biomass thermal conversion process can be found in previous works [10–12] and in Ph.D. thesis [13].

Analytical laboratories that are researching biomass materials 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). The first method is based on the reaction of biomass in a mixture of sulfuric acid and hydrogen peroxide. 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 [14].

Unfortunately, the comparative results tests using both methods are not appropriate if the biomass sample was obtained under a thermal conversion process with plastic waste additions (unpublished research) due to problems in identifying the amount and type of polymer material added during the pyrolysis process. These problems are being studied to examine the possibility of using existing analytical techniques to resolve this issue.

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## 2. Experimental

### 2.1. Materials and analytical methods

This research on the pyrolysis process used alder wood biomass and plastic waste such as polypropylene (PP), polyethylene terephthalate (PET), acrylonitrile butadiene styrene (ABS) and styrene-butadiene rubber (SBR) from tire waste. The main goal of this research was to find a suitable pre-treatment method using spectral data from the FT-IR analysis of char obtained in a co-pyrolysis process involving both biomass and plastics. In previous studies, standard variate normalization (SNV) was applied as a spectral data pre-preparation method. In addition, the impact of the application of the first derivative for normalized spectral data was tested. STATISTICA 10 [15] was applied for chemometric analysis.

The tested biomass (alder wood samples) was prepared for chemical analysis and for the thermal conversion process. The raw material preparation methods were detailed in previous publications [16,17]. The prepared samples were pyrolized in different thermal conditions ranging from 458 °C to 740 °C and with different amounts of polypropylene added.

The thermal conversion process (co-pyrolysis) used 150 g of samples that had been pyrolized in a nitrogen atmosphere. The pyrolysis process and the schema of the laboratory-scale set-up were detailed in previous publications [18,19].

### 2.2. Analytical method for bio-char study

The transmittance spectra of the investigated samples were measured using a Tensor 27 FTIR spectrometer (Bruker Co.) The instrument is internally calibrated using a He–Ne laser so that the frequency scale is accurate to 0.2 $cm^{-1}$. Samples for analysis were prepared using the KBr pellet technique. A sample (0.6 mg) was mixed with KBr (300 mg), finely ground in an agate mortar and then pressed in a 13-mm die under a 9-t load for 2 min under vacuum. Infrared spectra were obtained using a Fourier transform spectrometer, in which direct infrared analysis was performed with the KBr disc in a disc holder. During measurement, the experimental chamber was purged continuously with dry boil-off nitrogen. Infrared spectra were recorded at resolution 2 $cm^{-1}$ over the range of 4000–500 $cm^{-1}$, and 128 scans were coadded prior to the Fourier transformation. Software facilities were used for baseline corrections of the spectra. Table 1 describes the chemical groups (adsorption band) observed in the tested material.

**Table 1**
The adsorption band – chemical groups observed in the tested material.

| IR frequency, $cm^{-1}$ (±10) | Assignment |
|---|---|
| 3417 | O—H ethers |
| 3050 | C—H in aromatic compounds |
| 2840, 2891, 2923, 2957 | $CH_3$, $CH_2$ symmetric and asymmetric stretch |
| 1700 | C=O stretch, aldehyde, ketone, carboxylic acids |
| 1581, 1510 | Aromatic, stretch |
| 1423 | Combination $CH_2$ scissors and asymmetric $CH_3$ |
| 1284 | C—O—C asymmetric |
| 1247 | $CH_3$ bending |
| 1156 | Skeletal vibration involving $CH_3$ branch of propylene |
| 1137, 1126, 1113 | C—O—C ethers |
| 1019 | Ring vibrations |
| 947 | C—H bending (*trans*) |
| 874 | Isolated hydrogen |
| 812 | 2 adjacent hydrogen |
| 783 | 3 adjacent hydrogen |
| 751 | 5 adjacent hydrogen |
| 734 | Ring vibrations |

Fig. 1 presents example spectrograms of the analyzed carbonized biomass with PP, PET, SBR and ABS.

Fig. 1 shows spectra taken in the range of 4000–500 $cm^{-1}$ for char obtained in pyrolysis wood biomass in the temperature range 458–600 °C with different amounts of waste polymer materials. In Fig. 1, the type of biomass marked as "O" (alder) is then specified temperature at which the process was performed, the percentage of polymer additive and the type of polymer used (PP – polypropylene, ABS – acrylonitrile-butadiene-styrene, PET – polyethylene terephthalate, SBR – styrene-butadiene rubber).

From the FT-IR spectra, we can obtain qualitative information about the functional groups present in the studied materials, which, because of the process in which they were obtained, are characterized by a high similarity that makes direct interpretation difficult in the case of added polymeric materials.

Therefore, to obtain (extraction) information about the amount and type of polymeric material added to the biomass during pyrolysis, several studies have been performed using chemometric methods to allow the simultaneous analysis of multi-dimensional data set. In this research, the studied data were a 35 × 1866 matrix.

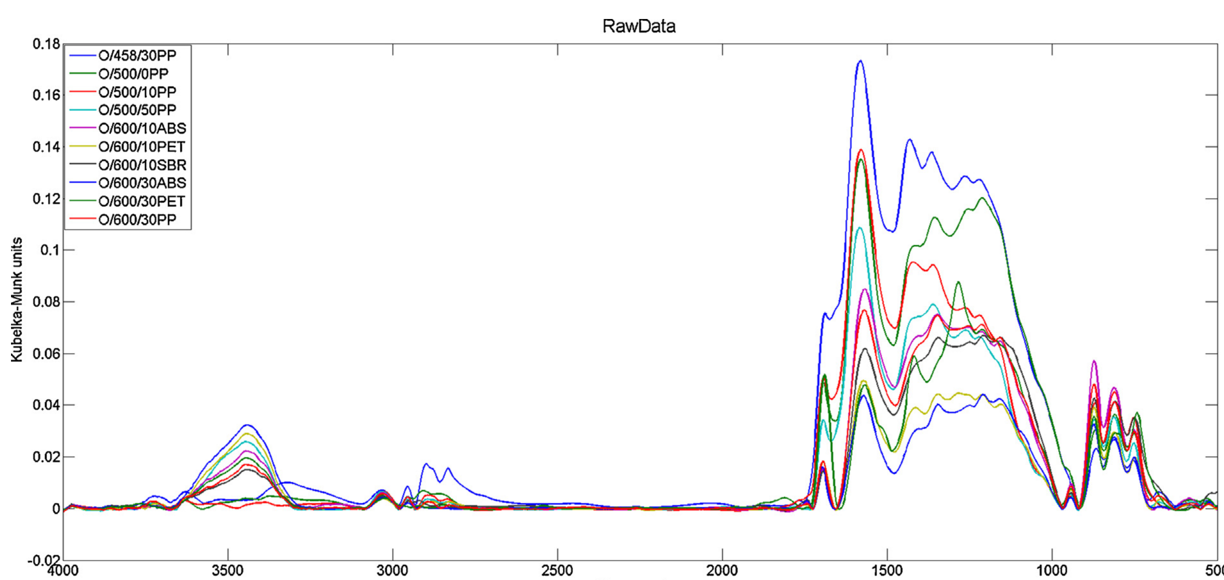


**Fig. 1.** Example spectrogram of analyzed char from biomass and plastic additions.

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