ANALYTICAL PYROLYSIS COUPLED WITH CHEMOMETRIC METHODS

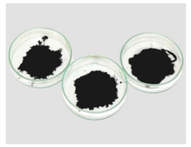
In solid biofuels control and detection of illegal waste combustion in domestic boilers

Marcin Sajdak, Roksana Muzyka, Maciej Chrubasik
Institute for Chemical Processing of Coal, Zamkowa 1, 41-803 Zabrze, Poland

Aim

The main objectives of the research were to determine the possibility of applying the analytical pyrolysis coupled with chemometric methods such as clustering analysis (CA), principal component analysis (PCA), and classification and regression trees (C&RT) to quality control of solid biofuels such as biomass pellets, torrefied biomass, biochar and detection of illegal waste combustion in domestic boilers.

The material used in the study



1. Mix of biochar and kraft lignin, peat and lignite

2. Contaminated biomass pellet

3. Ash sample from domestic boilers

Analytical pyrolysis (Py-GC-TOFMS)

Pyrolysis-gas chromatography-mass spectrometry (Py-GC-TOFMS) has used to determine the pyrolysis behaviours of different three type of studied materials:

4. LECO Pegasus 4D

- biochars mixed with fresh low-rank fuels,
- contaminated biomass pellet,
- ash sample obtained by combustion of coal and plastics waste

Py-GC-TOFMS experiments were performed using a PEGASUS® 4D (LECO) equipped with a thermo-desorption unit (TDU, Gerstel), pyrolysis module (Pyro, Gerstel) and cooled injection system (CIS-4, Gerstel). *Pegasus* 4D is a comprehensive two-dimensional GC-TOFMS system. For this study, the instrument was switched to one-dimensional mode.

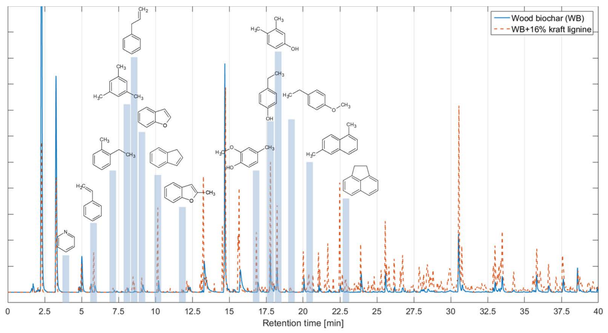
MATLAB in Py-GC-MS data processing

Raw Py-GC-MS data was processed using the MATLAB software. In the first step, chromatographic data have been subjected to the bases line correction by applying MATLAB baseline script. The next step in pre-processing raw chromatographic data was retention time correction (by icoshift MATLAB script).

Chemical markers indicating the contamination by external fuels of biochar

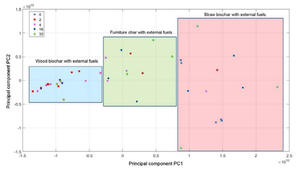
Chemical Component	External Fuel Additives		
	Kraft lignine	Peat	Lignite
Pyridine		+	
Styrene	+	+	+
Benzene, 1-ethyl-2-methyl-	+	+	+
Mesitylene	+		+
Benzene, 2-propenyl-	+		+
Benzofuran	+		+
Indene	+	+	+
Benzofuran, 2-methyl-	+		+
Creosol	+		+
Phenol, 4-ethyl-	+		
Phenol, 3,4-dimethyl-	+		
Benzene, 1-ethyl-4-methoxy-	+		
Naphthalene, 1,6-dimethyl-			+
Acenaphrhene			+

5. Chemical markers from different biochar contaminates

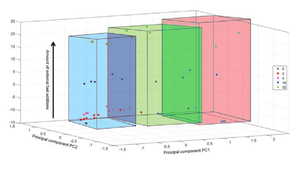


6. Chromatographic comparison of pure biochar and after contamination by kraft lignin

Principal component analysis (PCA) in a quick method of contamination detection in biochar



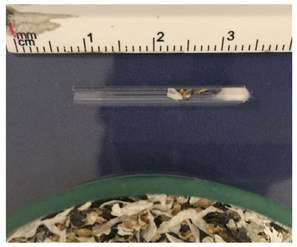
7. PCA plot for different biochars contaminated by external fuels



8. PCA plot for different biochars contaminated by the various amount of external fuels

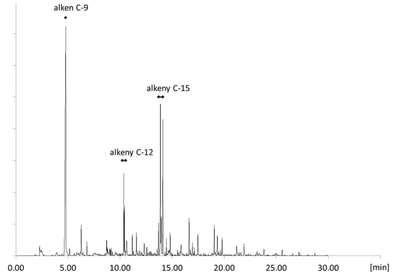
Combined the Py-GC-MS as an analytical method with PCA as an exploration data method, it is possible to determine what kind of biomass was applied to pyrolysis process and determine what it was contaminated with and in what amount.

Plastics residue analysis in biomass pellets



9. The separated fraction of contaminants from the tested biomass pellet sample

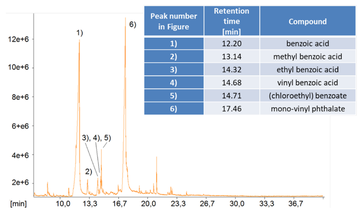
In this application, a 5 mg sample of ash was placed in a quartz tube reactor, inserted into the pyrolysis module. The sample was heated to 700°C at a rate of 5°C/sec and kept at that temperature for 10 min. All vapours were transferred to the CIS-4 (Gerstel) and held at -150°C (cooled with liquid nitrogen).



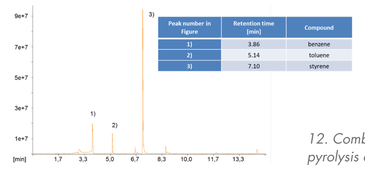
10. Chromatogram of contamination from tested biomass pellet

The analysis of Py-GC-MS confirmed the preliminary observation that the commercially available biomass pellets contained some polymeric parts. According to Polish law, such material no longer constitutes fuel and cannot be offered and sold on the market.

Detection of illegal waste combustion in domestic boilers

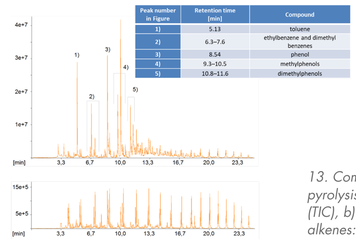


11. Combustion of PET with coal: analytical pyrolysis of an ash sample [1].



12. Combustion of PS with coal: analytical pyrolysis of an ash sample [1].

In this application, the same pyrolysis process conditions as described above for plastics residue analysis in biomass pellets were applied



13. Combustion of LDPE with coal: analytical pyrolysis of an ash sample, a) total ion current (TIC), b) ions characteristic of alkanes and alkenes: 55, 57, 69 and 71 Da [1]

In this approach, we presented an analytical technique for determining illegal waste combustion in heating devices. This method can detect the combustion of plastic wastes and provides some information about the type of plastic that was burned.

Conclusions

Our study presented several analytical approaches for determining the origin of contamination in the solid biofuels such as biomass pellets and biochars and illegal waste combustion in heating devices. This method is based on analytical pyrolysis and requires a GC coupled with an analytical pyrolyser. This method can detect the combustion of plastic wastes and provide some information about the type of plastic burned.

Utilising multivariate chemometric analysis in this application could develop a quantitative regression model to predict biochar polluted level. While our studies were identified, markers (chemical components) indicate the specific pollution of external fossil fuels. Except for this one, the Py-GC-MS analysis combined with Principal Component analysis is also very useful to determine the test biochar type.

Acknowledgements

This research was conducted in the Institute for Chemical Processing of Coal in Poland and funded by the Ministry of Science and Higher Education under the Iuventus Plus Program (project No. IP2014 041073) and Statutory R&D Project IChPW no. 11.17.003 and 11.19.001.

[1] Muzyka, R., Chrubasik, M., Pogoda, M. et al. Py–GC–MS and PCA Analysis Approach for the Detection of Illegal Waste Combustion Processes In Central Heating Furnaces. Chromatographia 82, 1101–1109 (2019). https://doi.org/10.1007/s10337-019-03747-4