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Sebastian WERLE[1], Łukasz ZIÓŁKOWSKI[1], Cristina TOMESCU[2], Valentin RUSU[2] Adriana MILANDRU[2] and Marta POGRZEBA[3]

USE OF THE FTIR-ATR TECHNIQUE FOR TESTING HEAVY METAL CONTAMINATED ENERGY CROPS

WYKORZYSTANIE TECHNIKI FTIR-ATR DO BADANIA ROŚLIN ENERGETYCZNYCH ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI

Abstract: Spectroscopic methods are one of the most popular tools for identifying and analysing the organic compound structure. They are characterized by high speed of measurement and a small amount of material necessary for testing. Attenuated Total Reflectance (ATR) is a relatively new technique for infrared spectroscopy. In contrast to classical transmission measurement, the ATR technique is a reflexive method. Its advantage is the lack of sample preparation and the possibility of testing various materials containing organic carbon such as biomass. In the paper, the FTIR (Fourier-transform infrared spectroscopy) analyses of two energy crop feedstock were carried out: (1) grass *Miscanthus* x *giganteus*, *MG* - representative of the monocotyledonous plant, and (2) perennial plant *Sida hermaphrodita*, *SH* - representative of the diocotyledonous plant. Spectra were recorded using the Spectrum GX spectrometer with the ATR supplement from a Perkin Elmer company with the 32 scans and a 4 cm^{-1} resolution. Analysis of the spectra of both biomass samples indicates the presence of the groups -OH (3415 cm^{-1} for *MG* and 3412 cm^{-1} for *SH*). In addition, C = O (1733 cm^{-1} for *MG* and 1735 cm^{-1} for *SH*) are also present in ketones and quinones, C-C-O, C-H from aromatic rings and CH_2 from saturated compounds. In addition, the spectra of both biomass samples were compared with library spectral masses of the coarse cardboard and cellulose with lignin. The similarity coefficient for *MG* is 87% for coarse cardboard and 85% for lignin and cellulose, and for *SH* - 86% for coarse cardboard and 81% for lignin and cellulose.

Keywords: FTIR-ATR, energy crops, *Miscanthus* x *giganteus, Sida hermaphrodita*

Introduction

Biomass considered as one of the most promising and important renewable energy source in future for Poland. In fact, the largest resources come from forestry and agricultural residues or forestry fuel wood [1-3]. The woody biomass, followed by waste and agricultural biomass, were considered as a main source for bio-energy also all over Europe [4-7]. Most of these resources are generally used for heat and in cogeneration. Among the European Union (EU) countries the main producers are those with large forestry resources - for instance France, Finland, Sweden, Germany and Poland. Nowadays and in the future the biomass will be more and more important source of energy in the EU market, taking into consideration the obligation of the 20% target for using renewable energy sources till the year 2020 and also reduction of CO_2 emission in Europe [8]. More common using of biomass tend towards diversification of energy supply so it has good influence on energy safety as well.

Biomass absorb the energy from the sun in a process of photosynthesis and then stores it. Next, during the thermal processing, the chemical energy from the biomass is converted

[1] Institute of Thermal Technology, Silesian University of Technology, ul. S. Konarskiego 22, 44-100 Gliwice, Poland

[2] Institutul de Studii si Proiectări Energetice, Lacul Tei 1-3, 020371 Bucharest, Romania

[3] Institute for Ecology of Industrial Areas, ul. L. Kossutha 6, 40-844 Katowice, Poland

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and released as a heat [9-11]. There are a few common types of biomass conversion, such as direct combustion, gasification, pyrolysis, carbonization or production of liquid biofuels and biogas [12, 13]. In fact, appliance of biomass for heat production in processes of direct burning in economically the least profitable way of converting the chemical energy into usable energy. In many cases pyrolysis and gasification tends to be a more effective manner of conversion, because as a result are obtained different products for direct usage as a fuel (e.g. bio-oil, charcoal) or it can serve as component for fuel production (e.g. synthesis gas) [14-16].

Nowadays, there can be observed the growing interest in the cultivation of lignocellulosic plants for energy production, known as energy crops. In the case of tree plants, the trunk and leaves form the largest group of available woody biomass. Such plant usually has a short growing period and high yields and require little or even no fertilizer at all so it provides quick return of the investment costs. In the case of energy production, wooden crops, e.g. Miscanthus, Willow, Switchgrass and Poplar are densely planted and often used. Moreover, these plants have high-energy yield per unit of land area and require much less energy for maintenance [17-20]. What is more, energy crops can be used for soil remediation purposes.

Phytoremediation phenomenon consists of removing, transfer or immobilizing contaminants in soil and groundwater. It can be distinguished several types of phytoremediation, one of these is phytoextraction also known as phytoaccumulation. During phytoextraction process plants are able to absorb contaminants with other nutrients and water to the roots and also keep them in the leaves or tissues of the stem. Although the contaminants are not destroyed, they are removed from soil and concentrated in the mass of the plant, so it is easier to get rid of them from the natural environment and also reduces the costs of further deactivation. This method is usable to extract metals from the ground and what is more, in some cases to recover them later for reuse by applying more and more popular process of phytomining. Promptness of heavy metal phytoextraction from the soil depends on the form the occurrence of the metal. For instance, metal forms soluble in the water are taken as the first ones. The phenomenon of phytoextraction can be applied as the continuation or assisted process. Continuous phytoextraction is the technique based on physiological processes that enables the plants to accumulate the metal ions during the whole vegetation period and there are used mostly hyperaccumulators. However, assisted phytoextraction is the method of adding the natural or synthetic substances to the soil in order to improve a collection of contaminants and also to facilitate their transport from the roots to the higher parts of the plant. Generally, phytoremediation is extremely necessary because nonbiodegradable heavy metals can accumulate in the ground and then get through the food chain. It is also eco friendly, efficient and cost-effective method. Basically, in the phytoremediation there have used the plants with ability to big accumulation that can be cultivated in the unfavourable environment and despite the high concentration of pollutants in the soil, plants take a big quantity of harmful substances and collect them inside. Phytoremediation is dedicated for places with lower concentration of the contamination, but also in more serious cases - where there can be used the trees that can take up the contaminants from deeper sites in the ground thanks to well-developed root system. Besides accumulation, there is also known the phenomenon of hyperaccumulation which is internal, physiological mechanism of adaptation to extremely unfavourable living conditions. Even if there is the very high concentration of the heavy metals in the soil, that is considered to be a very toxic for plants. Usually, in this case the only disadvantage of hyperaccumulation is slower growth of plants. More effective accumulation takes place when all the contaminants collect on the leaves and stems, and not in the roots because it is not practical to remove the underground parts and plant again the new crops. The important problem of phytoremediation is the necessity of development the contaminated crop utilization method. In this case the available method can be the thermal processes like gasification, pyrolysis or combustion [21-26]. Nevertheless, before the thermal utilization, the chemical composition of the contaminated samples should be determined and compared with the samples not contaminated. Spectroscopic methods are one of the most popular tools for identifying and analysing the organic compound structure.

The aim the paper the FTIR (Fourier-transform infrared spectroscopy) analyses results of *Miscanthus* x *giganteus* and *Sida hermaphrodita* were carried out. Moreover, the spectra of both biomass samples were compared with library spectral masses of the coarse cardboard and cellulose with lignin.

Materials and methods

Site description

The biomass were collected from former sewage sludge dewatering site in Leipzig, Germany (51°25'23.7"N 12°21'56.2"E). The site is a former sewage sludge dewatering site, which was in operation from 1952 to 1990. Following its closure, approximately 0.65 Tg (650,000 t) of sewage sludge remained in several basins. The picture of the site is presented in Figure 1.

Fig. 1. Site view

The soil has content of Pb, Cd and Zn that exceed the limits set by national law for arable lands which excludes such areas from food production. The soil characteristic is presented in Table 1.

Table 1

Soil characteristic

Parameter	Value
pH (1:2.5 soil/KCl ratio)	6.374 ± 0.010
Electrical conductivity [μS/cm]	797.45 ± 0.04
Organic matter content [%]	33 ± 13
Sand (1-0.05 mm) [%]	58
Silt (0.05-0.002 mm) [%]	19
Clay (< 0.002 mm) [%]	23
Total heavy metal concentration (extraction with aqua regia)	
Pb [mg kg^{-1}]	575 ± 25
Cd [mg kg^{-1}]	31.2 ± 2.0
Zn [mg kg^{-1}]	3592 ± 146
$CaCl_2$ extractable metal fraction [a]	
Pb [mg kg^{-1}]	BDL
Cd [mg kg^{-1}]	0.28 ± 0.05(0.89) [b]
Zn [mg kg^{-1}]	16.24 ± 1.01(0.45) [b]

BDL - below detection limit, Values represent the mean of three replicate samples ± SE: [a] - extraction with 0.01 M $CaCl_2$, [b] - in parentheses percentages of total metal concentrations are presented

Feedstock description

Ultimate and proximate analysis of all analysed samples is presented in Table 1. The main components in the analysed energy crops were determined using PO-ATI-16 Method with Perkin-Elmer 2400 analyser. The moisture, volatile and ash content was obtained according to European standards (EN ISO 18134-3:2015, PN-EN 15402:2011, PN-EN 15403:2011 [27-29]). Results show that *Sida hermaphrodita* is characterized by higher content of volatile and moisture in comparison to *Miscanthus* x *giganteus*. The percentage of carbon, hydrogen, nitrogen, chloride and sulphur is higher for *MG* samples in comparison to *SH*.

Table 2

Ultimate and proximate analysis of the analysed feedstock

[% mass]	***MG***	***SH***
C	43.08	42.38
H	6.06	5.98
N	0.99	0.80
O	49.64	50.66
Cl	0.09	0.08
S	0.14	0.10
Moisture	6.8	7.8
Volatiles	77.93	83.14
Ash	5	5
Pb [mg kg^{-1}]	2.53	2.65
Cd [mg kg^{-1}]	1.608	0.712
Zn [mg kg^{-1}]	342.569	94.299

FTIR analysis

FTIR is a technique, which can be used for qualitative identification of a number of organic and inorganic compounds by selective absorption of radiation in the infrared range. It uses a chemical's particle's ability to absorb infrared radiation energy quantum.

As a result the radiation energy oscillating-rotating molecules is increasing, which is reflected by an increase in the amplitude of the vibration. The result of absorbance and transmittance of the sample is the molecular fingerprint of the sample. FTIR analysis made it possible to identify the presence of the individual major functional groups such as O-H, C=O, alkanes and species like CH_4, CO_2, CO. On the above mentioned graph the fingerprint region is also mentioned. It is the region where it is very difficult to pick the individual bond and every compound has a different pattern of troughs in this part of the spectrum [30-33].

Spectroscopic methods are one of the most popular tools for identifying and analysing the organic compound structure. They are characterized by high speed of measurement and a small amount of material necessary for testing. Attenuated Total Reflectance (ATR) is a relatively new technique for infrared spectroscopy. In contrast to classical transmission measurement, the ATR technique is a reflexive method. Its advantage is the lack of sample preparation and the possibility of testing various materials containing organic carbon such as biomass. In the present study, spectra were recorded using the Spectrum GX spectrometer with the ATR supplement from a Perkin Elmer company with the 32 scans and a 4 cm^{-1} resolution.

Results

For both analysed biomass samples the FTIR spectrum were recorded and were identified characteristic absorption bands presented in Tables 3 and 4. The results was also presented on the Figures 2 and 4.

Table 3

Characteristic absorption bands of *Miscanthus* x *giganteus* sample

Plant	***Miscanthus* x *giganteus***
OH [cm^{-1}]	3415; 670
CH_2 from saturated compound [cm^{-1}]	2917; 2850; 1459; 1425; 1374; 1320; 1248; 613
C=O [cm^{-1}]	1733
aromatic ring [cm^{-1}]	1646; 1516; 899
C-C-O- [cm^{-1}]	1162; 1054
C-H from aromatic ring [cm^{-1}]	861; 835; 823; 771

Table 4

Characteristic absorption bands of *Sida hermaphrodita* sample

Plant	***Sida hermaphrodita***
OH [cm^{-1}]	3412; 667
CH_2 from saturated compound [cm^{-1}]	2918; 2850; 1459; 1426; 1375; 1319; 1249; 615
C=O [cm^{-1}]	1735
aromatic ring [cm^{-1}]	1627; 1509; 896;
C-C-O- [cm^{-1}]	1159; 1055
C-H from aromatic ring [cm^{-1}]	850; 835; 826; 780

Analysis of the spectra of both biomass samples indicates the presence of the groups -OH (3415 cm^{-1} for *MG* and 3412 cm^{-1} for *SH*). In addition, C = O (1733 cm^{-1} for *MG* and 1735 cm^{-1} for *SH*) are also present in ketones and quinones, C-C-O, C-H from aromatic rings and CH_2 from saturated compounds. In addition, the spectra of both biomass samples were compared with library spectral masses of the coarse cardboard and cellulose with lignin - Figures 3 and 5.

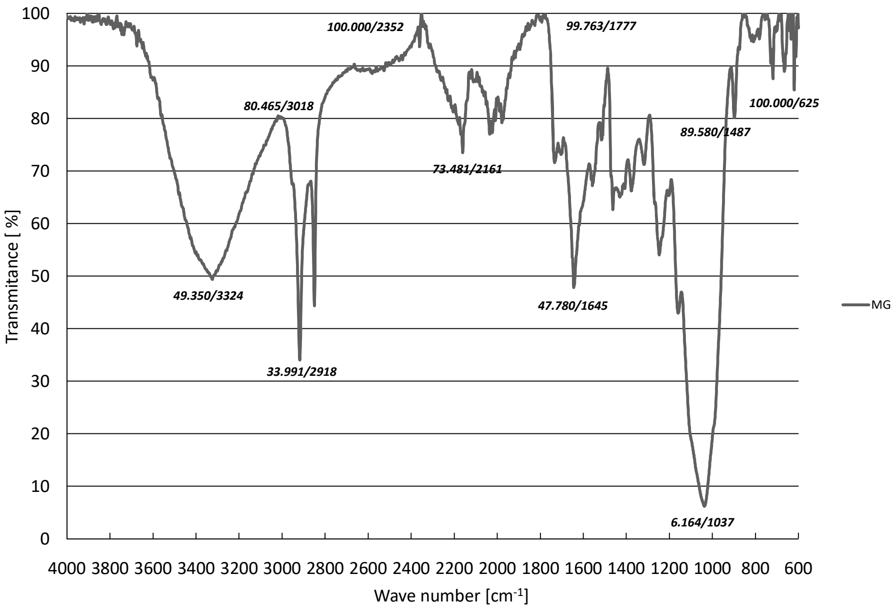

Fig. 2. FTIR spectrum of *Miscanthus* x *giganteus* sample

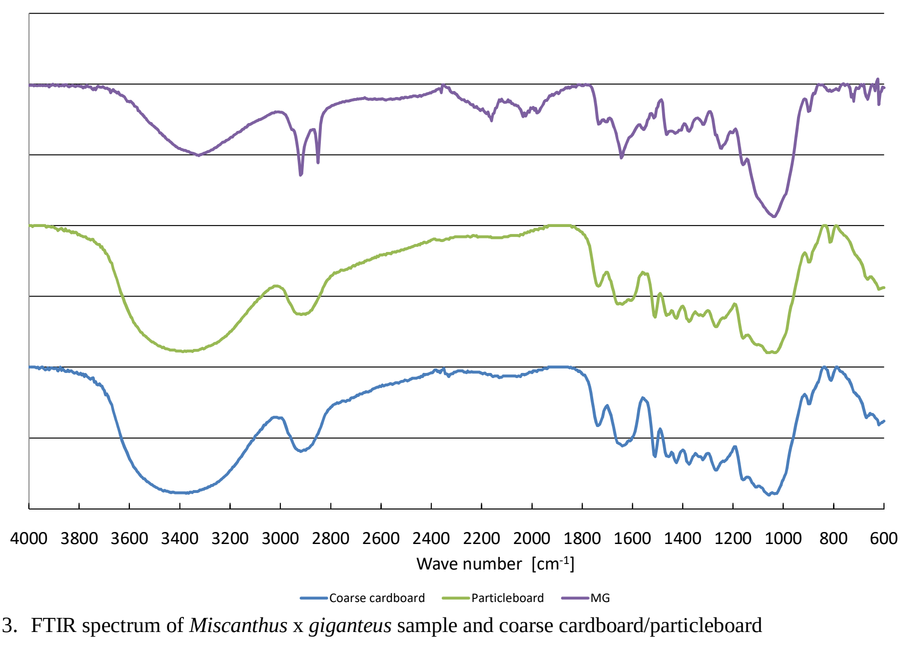

Fig. 3. FTIR spectrum of *Miscanthus* x *giganteus* sample and coarse cardboard/particleboard

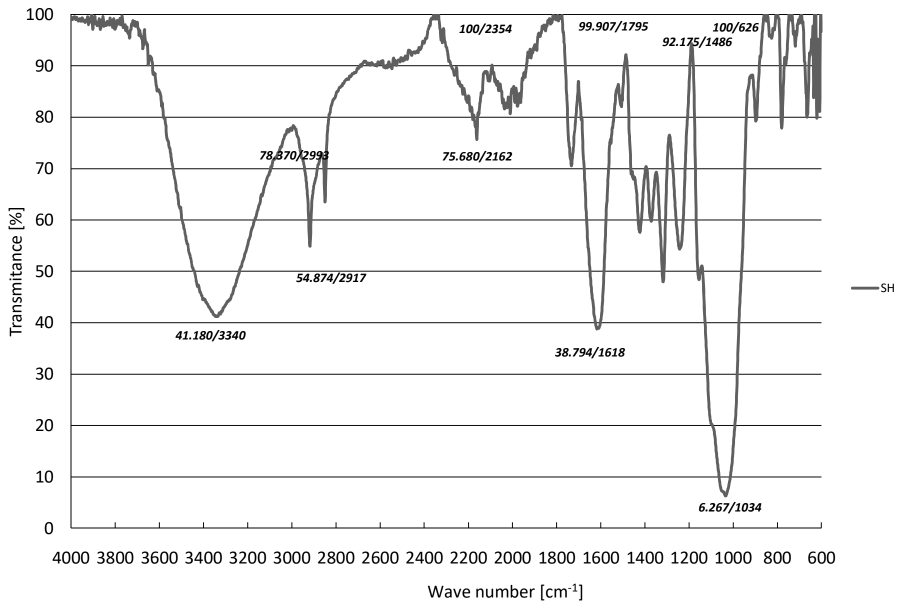

Fig. 4. FTIR spectrum of *Sida hermaphrodita* sample

Fig. 5. FTIR spectrum of *Sida hermaphrodita* sample and coarse cardboard/particleboard

By comparing the sample spectrum of *Miscanthus* x *giganteus* sample with FTIR standard library spectra, it has been identified as a coarse cardboard or a particle board, composed by cellulose and lignin with a fitting degree of 87%, respectively 85%.

In case of *Sida hermaphrodita*, by comparing the sample spectrum biomass with FTIR standard library spectra, it has been identified the sample as a coarse cardboard or a particle board, composed of cellulose and lignin, with a fitting degree of 86%, respectively 81%.

All the biomass samples contain clusters of wooden structure, with approximately equal amounts of cellulose, with the largest amount of lignin in the samples of *Miscanthus* x *giganteus*, which gives a greater mechanical strength but also a higher chemical reactivity of this sample.

Conclusions

Phytoremediation is one of the techniques used for remediation of contaminated areas. The group of energy crops has taken into consideration include native and foreign species such as perennial dicotyledonous plants and perennial grass species. A Fourier-Transform--Infrared (FTIR) spectroscopy, is an excellent and easy solution for characterization quality of the biomass to thermal treatment purposes. All the analysed biomass samples contain clusters of wooden structure, with approximately equal amounts of cellulose. The largest amount of lignin was found in the samples of *Miscanthus* x *giganteus*. This feature is very attractive taking into consideration quality (e.g. gas composition) of the products after thermal decomposition of heavy metal contaminated biomass. This can be explained by the fact that CO is mainly formed by the degradation of lignin during pyrolysis.

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WYKORZYSTANIE TECHNIKI FTIR-ATR DO BADANIA ROŚLIN ENERGETYCZNYCH ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI

[1] Instytut Techniki Cieplnej, Politechnika Śląska, Gliwice, Polska
[2] Instytut Badań Energetyki, Bukareszt, Rumunia

Abstrakt: Metody spektroskopowe są jednym z najpopularniejszych narzędzi do identyfikacji oraz badania budowy związków organicznych. Cechują się dużą szybkością wykonania pomiaru oraz niewielką ilością materiału niezbędnego do badania. Stosunkowo nową techniką spektroskopii w podczerwieni jest spektroskopia osłabionego całkowitego odbicia (ang. Attenuated Total Reflectance - ATR). W przeciwieństwie do klasycznego pomiaru metodą transmisyjną technika ATR należy do metod refleksyjnych. Jej zaletą jest brak konieczności przygotowania próbki oraz możliwość badania różnych materiałów zawierających węgiel organiczny, jak np. biomasa. W pracy wykonano analizy FTIR dwóch gatunków roślin energetycznych: (1) trawy z gatunku Miskant olbrzymi (łac. *Miscanthus* x *giganteus, MG*), przedstawiciela klasy jednoliściennych, oraz (2) byliny z gatunku Ślazowiec pensylwański (łac. *Sida hermaphrodita, SH*), przedstawiciela klasy dwuliściennych. Widma zarejestrowane zostały za pomocą spektrometru Spectrum GX z dostawką ATR firmy Perkin Elmer. Widma były rejestrowane w 32 powtórzeniach z rozdzielczością 4 cm^{-1}. Analiza widm obu próbek biomasy wskazuje na obecność grup -OH (3415 cm^{-1} dla *MG* oraz 3412 cm^{-1} dla *SH*). Ponadto obecne są grupy C=O (1733 cm^{-1} dla *MG* oraz 1735 cm^{-1} dla *SH*), prawdopodobnie w ketonach i chinonach, C-C-O, C-H z pierścieni aromatycznych oraz CH_2 ze związków nasyconych. Dodatkowo widma obu próbek biomasy zestawiono z widmami mas biblioteki wzorców kartonu oraz celulozy z ligniną. Współczynnik podobieństwa w przypadku *MG* wynosi 87% dla kartonu i 85% dla ligniny i celulozy, a w przypadku *SH* - 86% dla kartonu i 81% dla ligniny i celulozy

Słowa kluczowe: FTIR-ATR, rośliny energetyczne, *Miscanthus* x *giganteus*, *Sida hermaphrodita*