# Thermogravimetric analysis of the heavy metal contaminated energy crops in $CO_2$/$N_2$ atmosphere. Influence of the fertilizer and inoculum application to soil on the feedstock thermal decomposition

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## ABSTRACT

Energy crops can be used in the phytoremediation process. It is very popular and effective process for remediation of contaminated areas and could be applied both to organic and inorganic elements. After harvesting, such energy crops are characterized by high levels of contamination. The utilization of these biomass can be effective made by thermal conversion. TG analysis is extremely useful technique in the characterization of the decomposition of these fuels.

In the work TG analysis of the heavy metal contaminated (HMC) samples of *Miscanthu*s x *giganteus, Sida hermaphrodita* and *Spartina pectinata.* The experimental plots were established on heavy metal contaminated arable land located in Bytom (southern part of Poland, Silesian Voivodship). The experimental field (0.25ha) was divided into subplots with buffer zone 6m. Three series of land experiments were performed: (1) control plots without additives, (2) plots with N and P fertilizer addition and (3) plots with microbial inoculum to stimulate successful and sustainable biomass growth on heavy metal contaminated sites and minimize the negative effect of pathogens. The TGA experiment was carried out using Netzsch STA 409 Thermogravimeter. Approximately 15 mg of sample was heated from ambient temperature to 800 °C at a constant rate of 10°C/min in a $CO_2$/$N_2$ (80/20 %vol.) mixture. The TG and DTG curves for each of the samples were obtained. The ordinate on the TG curves was the percentage ratio of the instantaneous weight of the sample to the initial weight. The DTG curves are the result of mathematical transformation (dm/dT=f (T)).

Results show that in the case of the all control samples the maximum weight loss rates (DTG curves) occur in quite similar temperature ranges – 320-340 °C. The highest inoculum effect addition is visible for *Sida hermaphrodita* samples. In that case the DTG peak is the highest. There is no strong effect of the N and P fertilizer addition.

**KEYWORDS:** TG Analysis, energy crops, heavy metals, fertilizer application, inoculum application

## INTRODUCTION

Polluted soil is a serious environmental problem. According to the European Environmental Agency [1], the 32 European countries have reported occurrences of 250 000 polluted sites. It mostly polluted with heavy metals. Additionally, more than three million sites are presumably polluted, based on knowledge about potentially polluting activities on the site.

Remediation of soils polluted by organic compounds (OC) is very popular. Several techniques are available for it. Unfortunately, only a few methods exist for remediation of heavy metal (HM) contaminated soils. Moreover, these methods are poorly developed yet. HM are non-degradable and generally strongly retained in the soil. Due to this,phytoremediation appears to be an economically attractive in situ technique [2, 3]. Over the years several studies have been made to optimize the method and to find the most suitable plants. Examples of commonly used plants are *Salix L.*, *Miscanthus* x *giganteus*, *Spartina pectinata*, *Panicum virgatum*, *Sida hermaphrodita*, *Rosa multiflora* [4].
The knowledge about the suitability of *Salix L.* to remove heavy metal ions under field conditions is much more limited, in particular when it comes to calcareous soils with strong retention of cationic heavy metals [5]. Besides that, studies such as that of [6] have shown that the determination of metal bioavailability based on laboratory test of sampled soils is not representative of field soils and in situ conditions.
Based on the seven-year field tests carried out by Institute for Ecology of Industrial Areas (IETU) it was recognized that some conventional energy crops such as *Miscanthus* x *giganteus, Sida hermaphrodita, Spartina pectinata, Panicum virgatum* are characterized by the huge potential of the heavy-metal uptake capacity and – simultaneously - potential for biomass production for energy purposes. Additionally, in previous works [7-10] it was concluded that the analysed energy crops are characterized by the yield equal to: 11.7 Mg/ha in the case of *Sida hermaphrodita*, 9.5 Mg/ha in the case of *Spartina pectinata*, 15.0 Mg/ha in the case of *Miscanthus* x *giganteus* and 13.3 Mg/ha in the case of *Panicum virgatum*. Phytoremediation results show [11] that *Miscanthus* x *giganteus* is a more tolerant species to the total contaminated soil with Zn and Pb to *Sida hermaphrodita.* Additionally, it was proven in [12] that *Spartina pectinata* and *Panicum virgatum* are also very suitable for heavy metals phytostabilization.
Recently, the investigation of the phytoremediation process is focused on the development a microbiological method stimulating the biomass yield and phytoremediation effect of heavy metal contaminated sites and the finding an environmentally safe way of converting the heavy metal contaminated biomass into energy.
TG technique can advantageously use in the study of the selected physical properties of the substance under the influence of temperature or atmosphere. TGA method is a simple, accurate and proven method and has been used by many authors [13-20] to determine reactivity of various fuels, mostly laboratory prepared. It was chosen for this preliminary study to minimize transport effects and isolate the influence of fuel chemistry and microstructure. Thermogravimetric analyzers are important instruments for thermal analysis of gas–solid reactions in general and hence, they are also broadly used for laboratory investigation of solid fuel conversion as a function of process parameters like temperature, pressure or reaction atmosphere. Time-dependent weight change curves of fuel samples, either under heating or isothermal conditions are the basis for the characterization of devolatilization processes, quantification of release rates and determination of reaction kinetics.
The general objective of this work was to identify general trends in the decomposition behavior of HMC biomass. The detailed goal of the task is to determine the influence of used both fertilization and inoculation on thermal decomposition of the analysed HMC energy crops.

## MATERIALS AND METHODS

In order to study the three plants were selected: Miscanthus (*Miscanthus* x *giganteus*), Virginia mallow (*Sida hermaphrodita*) and Cordgrass (*Spartina pectinata*). The field experimental options include:

- 3 control plots (no additives),
- 3 plots with standard NPK fertilization, specific for each of the species - two weeks before planting ammonium sulphate and Polifoska (Grupa Azoty Zakłady Chemiczne "Police" S.A., Poland) were applied
- 3 plots with commercially available microbial inoculum solution (EmFarma Plus, ProBiotics Magdalena Górska, Poland) – inoculum was applied on rhizomes before planting and on the leaves as aerosol in the middle of each month of the growing season

The test site is located in Poland in the Upper Silesian Industrial Region, on the outskirts of Bytom - an industrial city about 15 km from Katowice, in the proximity of a shut down large lead/zinc/cadmium works consisting of the ore mining, enriching and smelting facilities. This metallurgical complex was in operation for more than 100 years and contributed significantly to the contamination of the local soils. During the last 30 years the area was used for agricultural purposes. Recently the land has been used for grain crop farming, especially for wheat production. Soil contamination with lead, cadmium and zinc in this area exceeds permissible limits for agricultural soil in Poland. Analyzing Figure 1, it can be noted that this area is characterized by very strong soil contamination level.

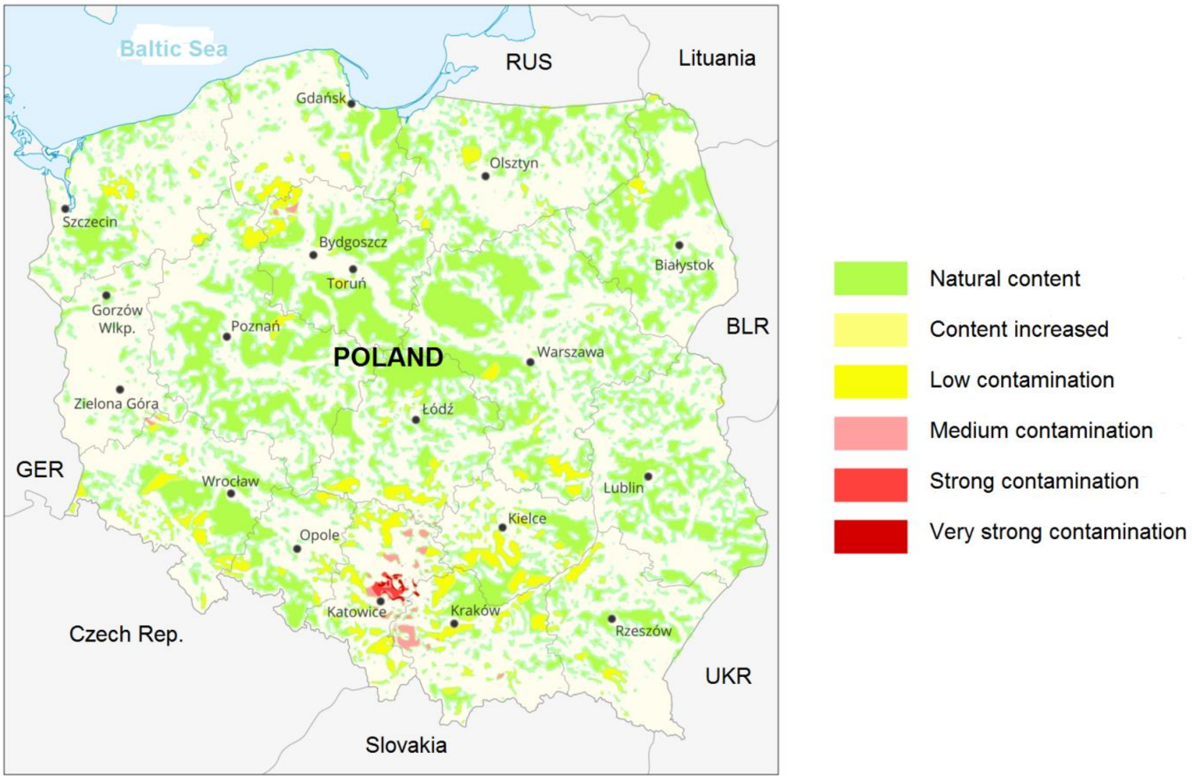


Figure 1. Level of the soil contamination in Poland

Ultimate and proximate analysis of all analysed samples is presented in Table 1. The main components in the analyzed energy crops were determined using PO-ATI-16 Method with Perkin-Elmer 2400 analyzer. Total organic carbon determination (TOC) is done according to EN 1484:2006 [21]. The moisture was obtained following standard PN-EN 14774-3:2010

[22]. The volatile content was determined according to standard PN-EN 15402:2011 [23]. The ash content was obtained using standard PN-EN 15403:2011 [24].

Table 1.

Ultimate and proximate analysis of the analysed feedstock

| | MG | $MG_{NPK}$ | $MG_{EFP}$ | SH | $SH_{NPK}$ | $SH_{EFP}$ | SP | $SP_{NPK}$ | $SP_{EFP}$ |
|---|---|---|---|---|---|---|---|---|---|
| C, %mass | 46.90 | 45.50 | 46.50 | 46.20 | 46.40 | 47.00 | 46.70 | 46.30 | 47.00 |
| H, %mass | 7.32 | 6.88 | 7.13 | 6.69 | 7.22 | 7.06 | 6.33 | 6.77 | 7.07 |
| N, % mass | 1.38 | 1.13 | 1.49 | 0.43 | 0.38 | 0.30 | 0.32 | 0.38 | 0.59 |
| S, % mass | <0.20 | <0.20 | <0.20 | <0.20 | <0.20 | <0.20 | <0.20 | <0.20 | <0.20 |
| O, % mass | 44.20 | 46.29 | 44.68 | 46.48 | 45.80 | 45.44 | 46.45 | 46.35 | 45.14 |
| Moisture, % mass | 8.60 | 8.30 | 8.20 | 9.80 | 9.10 | 9.40 | 8.30 | 8.40 | 9.50 |
| Volatiles, % mass | 74.90 | 76.50 | 75.30 | 75.80 | 76.90 | 76.60 | 77.90 | 77.50 | 75.70 |
| TOC, mg/kg | 21218.00 | 24442.00 | 24002.00 | 19050.00 | 17537.00 | 15151.00 | 22534.00 | 21175.00 | 20521.00 |
| Ash, % mass | 5.50 | 4.20 | 4.90 | 2.70 | 2.40 | 4.80 | 3.70 | 3.40 | 3.40 |

Legend:
MG - *Miscanthus* x *giganteus* –control
$MG_{NPK}$ - *Miscanthus* x *giganteus* -nutrients NPK
$MG_{EFP}$ - *Miscanthus* x *giganteus* – Em Farma Plus
SH - *Sida hermaphrodita*- control
$SH_{NPK}$ - *Sida hermaphrodita* - nutrients NPK
$SH_{EFP}$ - *Sida hermaphrodita* - – Em Farma Plus
SP - *Spartina pectinata* - control
$SP_{NPK}$ - *Spartina pectinata* - nutrients NPK
$SP_{EFP}$ - *Spartina pectinata* - Em Farma Plus

The value obtained during the biomass experimental tests and presented above represents the average of two determinations. As it can be seen from the ultimate analysis results, the largest share in all the biomass samples is for oxygen and carbon, while nitrogen and sulphur has the smallest share. The percentage of carbon, hydrogen and oxygen are quite similar for all biomass types. The highest nitrogen content was found in samples of *Miscanthus* x *giganteus* biomass grown on a plot with EmFarma application and NPK treatment. There are no strong differences between feedstock elemental composition so at this stage it can be concluded that treatment applied does not affect on the biomass quality. Analyzing the TOC parameter, it can be concluded that in the case of *Miscanthus* x *giganteus* treatment applied causes that organic component concentration is increasing. Taking into consideration the *Sida hermaphrodita* ash content, treatment applied causes the increment of this value.

The experiment (see Figure 2) was carried out using Netzsch STA 409 Thermogravimeter (TG) (Erich NETZSCH GmbH & Co. Holding KG, Selb, Germany). The equipment consists of (i) the high sensitivity weight, (ii) furnace which allows the sample heating up ($10^{o}C/min$) to a temperature equal to 1500°C and (iii) a gas dispensing system. TG measurement is carried out in an inert gas atmosphere ($CO_2/N_2$ (80/20 %vol.)). The gas volumetric flow rate was equal to 80 ml/min. The initial sample mass with fraction less than 1 mm was equal to 10mg (see Figure 3). The biomass sample is weighted on the outer weight model Radwag WAS 220/C/2 (Radwag, Radom, Poland) with an accuracy of 0.1 mg.

Simultaneously with TG measurements, differential thermal analysis (DTG) can be determined. DTG method can be used to test substances which are susceptible to various exothermic or endothermic transitions. It allows the effects of thermal characteristic of a given substance to its identification and determination of its content.

Figure 2. TGA equipment


Figure 3. Feedstock samples for TG analyses

## RESULTS AND DISCUSSION

Figure 4 depicts the TG/DTG curves of analysed samples: *Sida hermaphrodita*, *Miscanthu*s x *giganteus* and *Spartina pectinata* cultivated without additives (SH, MG, SP), *Sida hermaphrodita*, *Miscanthu*s x *giganteus* and *Spartina pectinata* cultivated with N, P, K fertilizer application ($SH_{NPK}$, $MG_{NPK}$, $SP_{NPK}$) and *Sida hermaphrodita*, *Miscanthu*s x *giganteus* and *Spartina pectinata* cultivated with microbial inoculum addition ($SH_{EFP}$, $MG_{EFP}$, $SP_{EFP}$) for the heating rate of 10°C/min in a $CO_2/N_2$ (80/20 %vol.) mixture.
During the biomass degradation (DTG=f(T) and TG=f(T)), there are visible characteristic peaks of temperature associated with the decomposition of the biomass components: cellulose, hemicellulose and lignin. The first region is the temperature interval between the starting temperature of the TG analysis and appx. 200°C and it can be assumed that it corresponds to the loss of the water and light volatile compounds in the biomass samples. The second region is between 200°C and appx. 480°C and is connected with active processes of the pyrolysis and gasification take place and corresponds with the decomposition of cellulose and hemicellulose and partial loss of lignin in the biomass samples.
Influence of the fertilizer and inoculum addition during the cultivation process on thermal decomposition is presented in Figures 5-9.

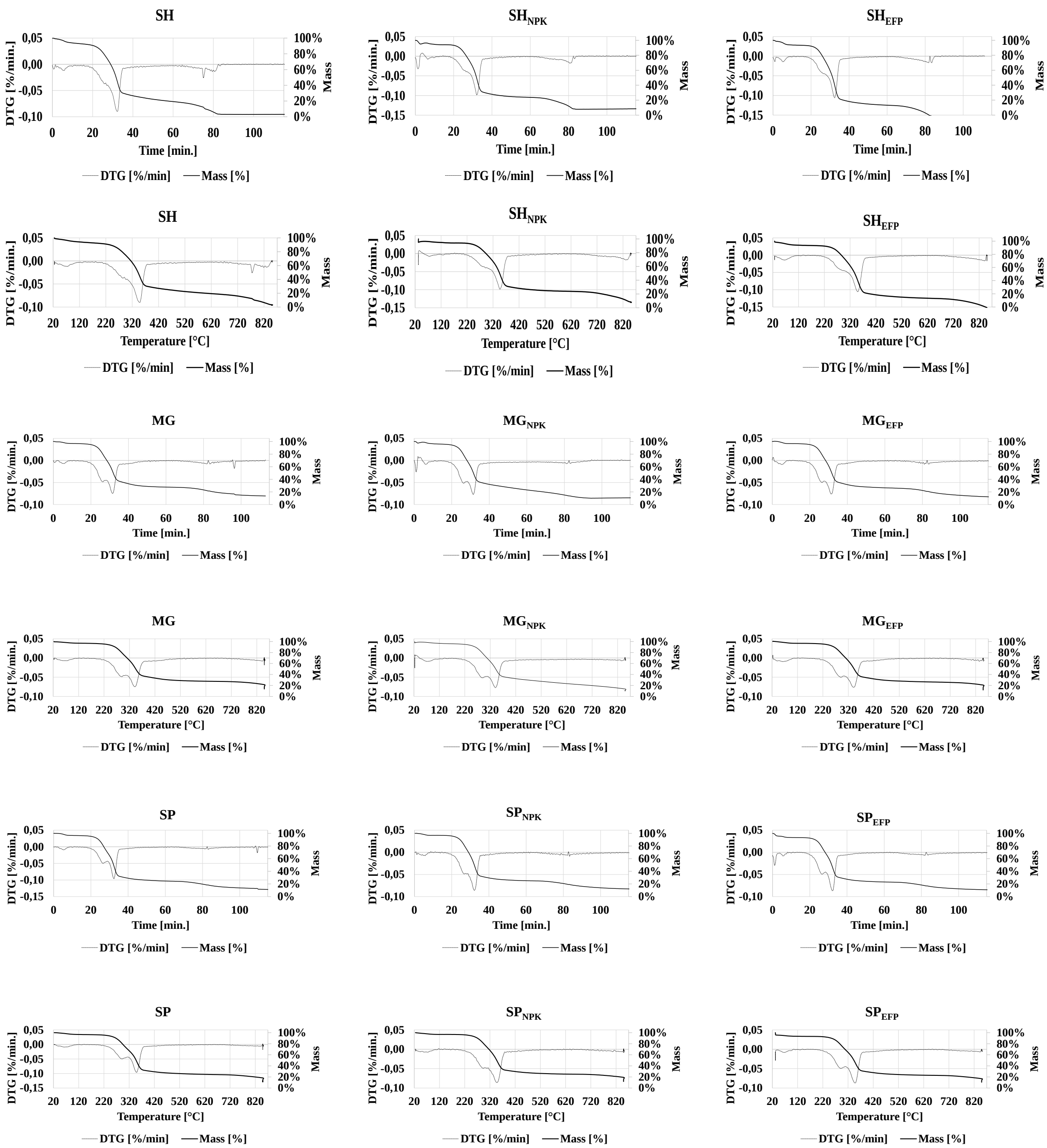


Figure 4. TG and DTG curves of all analysed samples

As seen in Figure 5, three sequent stages can be observed in TGA, as the temperature of the furnace was increased. During the biomass degradation, the temperature range of distinct stages was associated with the decomposition of the biomass components. Within the range of the temperatures 220-440°C (during the decomposition of hemicellulose and cellulose), the DTG profile of all SH samples exhibited only one peak temperature. The minimum of DTG is for $SH_{EFP}$ samples. At temperatures over 440°C, the mass loss was mainly caused by the decomposition of remaining lignin, accompanied by its conversion into char, and further oxidation of the char.

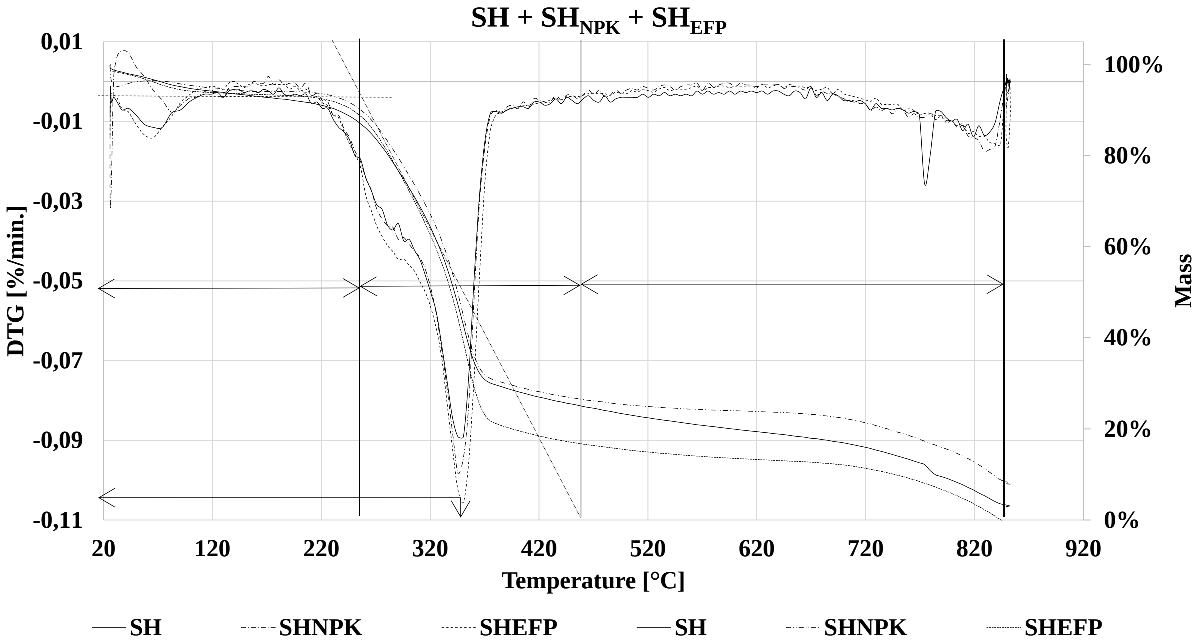


Figure 5. TG and DTG curves for the SH sample – influence of the additives on thermal decomposition

Analyzing Figure 6, it can be seen that during the MG samples within temperatures of 220-440°C (during the decomposition of hemicellulose and cellulose), the DTG profile exhibited two temperature peaks. It means that some amount of lignin was decomposed as well. The minimum of DTG is for $MG_{NPK}$ samples.

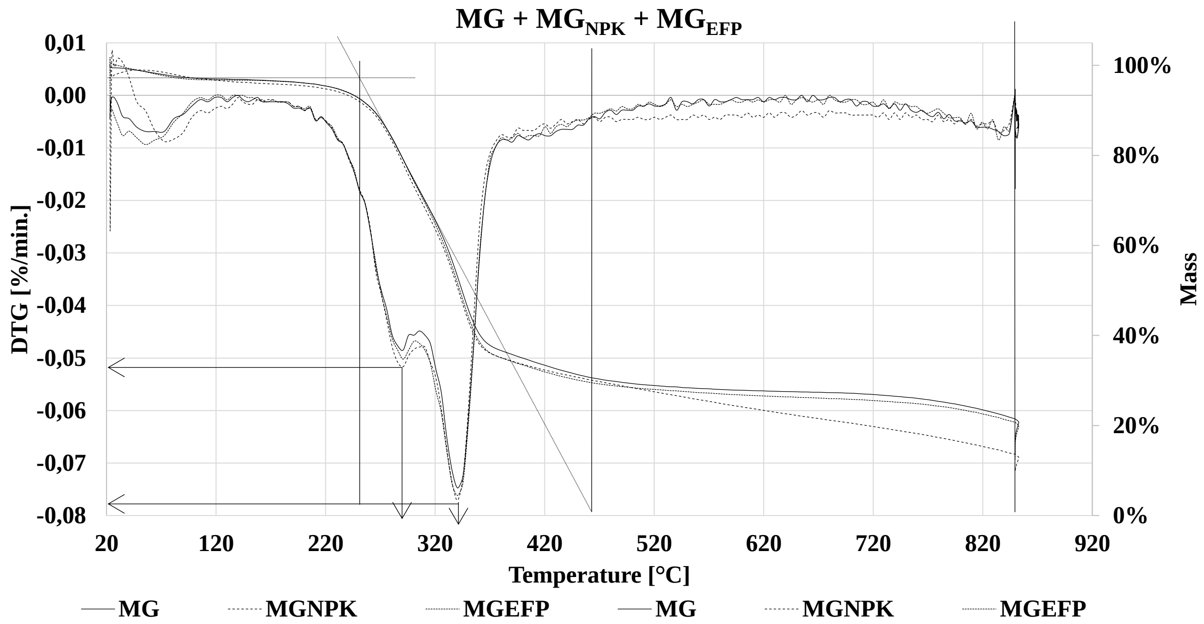


Figure 6. TG and DTG curves for the MG sample – influence of the additives on thermal decomposition

Similar features are visible for SP samples (see Fig. 7). Nevertheless, the minimum of DTG is for SP samples (without addition during cultivation).

These two peaks also document that *Spartina pectinata* and *Miscanthus* x *giganteus* are characterized by the large amount of lignin. This feature is very attractive taking into consideration quality (eg. 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.

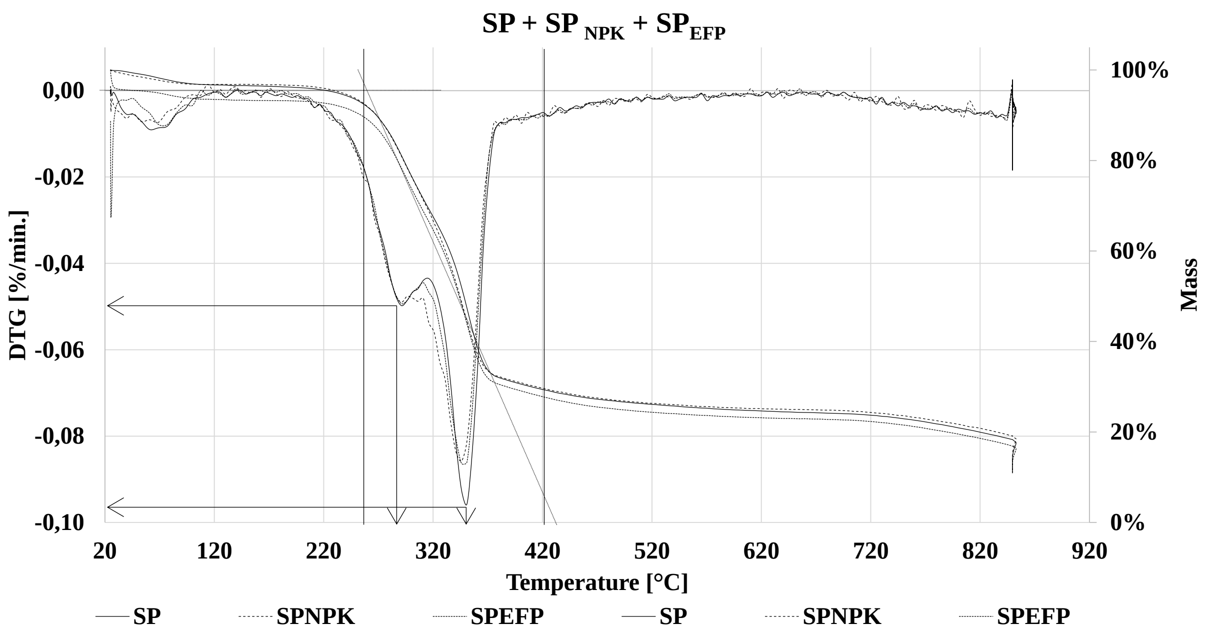


Figure 7. TG and DTG curves for the SP sample – influence of the additives on thermal decomposition

Based on the combined analysis of TG and DTG curves for samples treated by the NPK fertilizer during cultivation (Fig. 8), it can be concluded that *Sida hermaphrodita* had the highest reactivity – DTG minimum is equal to 0.10%/min.

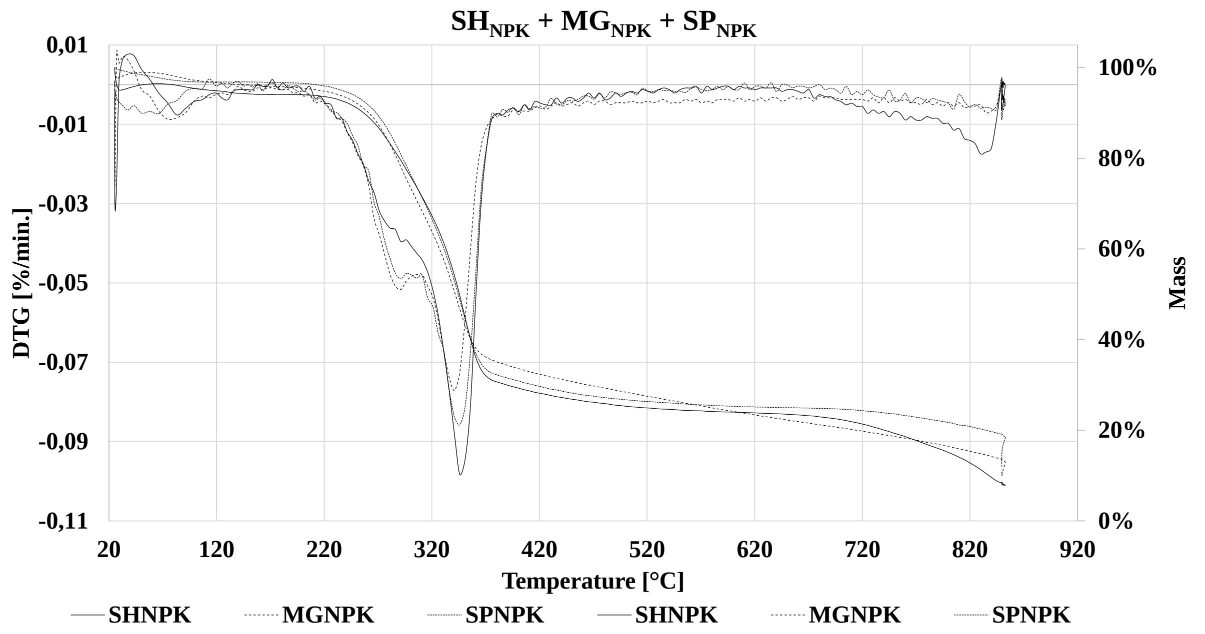


Figure 8. TG and DTG curves for the SP sample – influence of the NPK addition on thermal decomposition

Analyzing data presented in Figure 9, it can be concluded that also in case of the inoculum application, the *Sida hermaphrodita,* is characterized by the highest reactivity. The DTG minimum for it is 0.106%/min.

*Sida hermaphrodita* is an example of perennial dicotyledonous plants so it can be postulated that the NPK and inoculum addition during cultivation positively influence on the thermal decomposition of it.

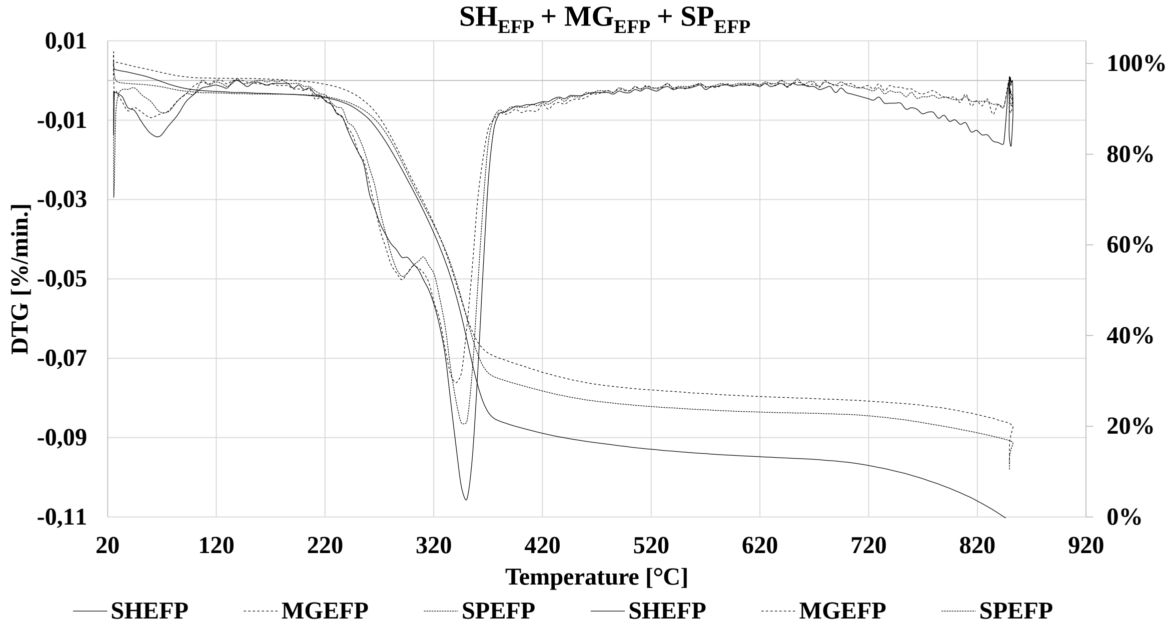


Figure 9. TG and DTG curves for the SP sample – influence of the inoculum application of thermal decomposition

## CONCLUSION

Based on the investigation following general conclusion can be drawn:

- 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 (*Sida hermaphrodita)* and perennial grass species (*Miscanthu*s x *giganteus,* and *Spartina pectinata)*
- The NPK fertilizer and microbial inoculum addition can positively impact on remediation effectiveness and also on the thermal decomposition of such biomass
- It can be postulated that NPK fertilizer or microbial inoculum used during cultivation of perennial dicotyledonous plants can positively influence of such treated feedstock
- Taking into consideration chemical structure of the energy crops, *Miscanthu*s x *giganteus,* and *Spartina pectinata* are characterized by higher content of lignin (two characteristic peaks during thermal treatment); this feature is very attractive taking into consideration quality (eg. 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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