WP3 – TG Analysis

PHYTO2ENERGY

Phytoremediation driven energy crops production on heavy metal degraded areas as local energy carrier

The research leading to these results has received funding from European Community´s Seventh Framework Programme (FP7/2007-2013) under Grant agreement 610797.

Contents

1. Overview
2. Methodology
3. TGA results
4. Conclusions

TGA - Overview

- TGA - technique which measures the change in the mass of a sample over a range of temperatures.

- TGA - technique can be used in the study of the selected physical properties of the substance under the influence of temperature or atmosphere.

- The basic principle of TGA is that as a sample is heated, its mass changes. This change can be used to determine the composition of a material or its thermal stability.

- Usually, a sample loses weight as it is heated up due to decomposition, reduction, or evaporation. A sample could also gain weight due to oxidation or absorption.

- While in use, the TGA machine tracks the change in weight of the sample via a microgram balance. Temperature is monitored via a thermocouple.

- The TGA can also track changes in weight as a function of time.

TGA - Experiment conditions

The experiment was carried out using:

- TGA equipment Netzsch STA 409 Thermogravimeter
- The biomass sample is weighted on the analytical balance model Radwag AS 220/C/2 with an accuracy of 0.1 mg

Experimental conditions in TGA measurements:

- Gas composition: N_2/CO_2 (80/20)
- Gas volumetric flow rate 80 ml/min
- Is carried out in an inert gas atmosphere
- Final sample temperature 850 °C
- Sample heating rate: 10 K/min
- Initial sample mass: 10 mg

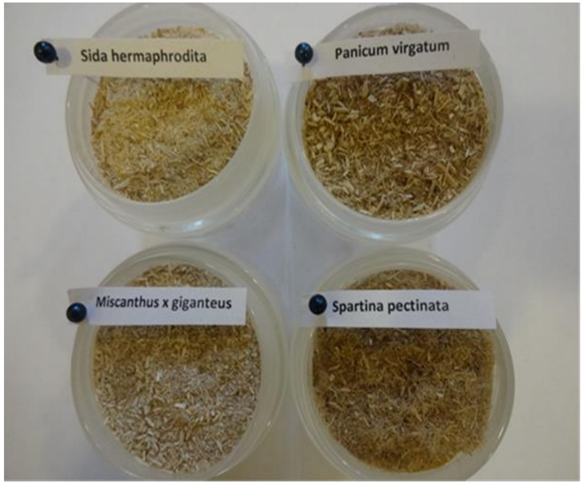
A typical TGA system

Samples preparation

The experimental plots were established on heavy metals contaminated arable land located in Bytom (southern part of Poland, Silesian Voivodeship) and a heavy metals contaminated postindustrial site in Leipzig (Germany)

Type of biomass used for TGA:

- *Miscanthus* x *giganteus*
- *Sida hermaphrodita*
- *Spartina pectinata*
- *Panicum virgatum*



Experimental options for each plant included:

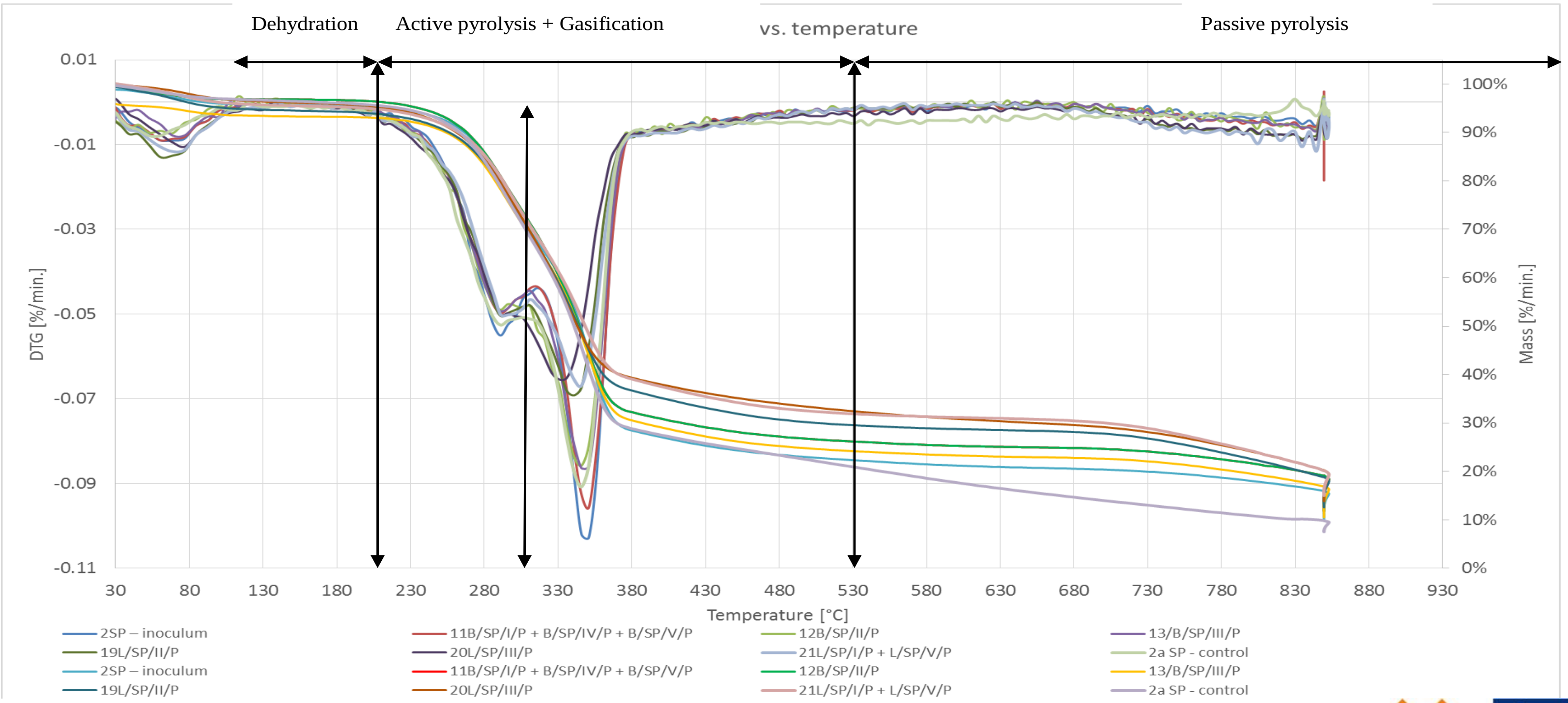
- I - control without additives
- II - with NPK fertilizer additions
- III - with addition of commercial available inoculum

For the TG analysis of the biomass, *Miscanthus* x *giganteus, Sida hermaphrodita, Panicum virgatum, Spartina pectinata* samples were prepared according to the methodology and the specification of the instrumentation.

TG analysis

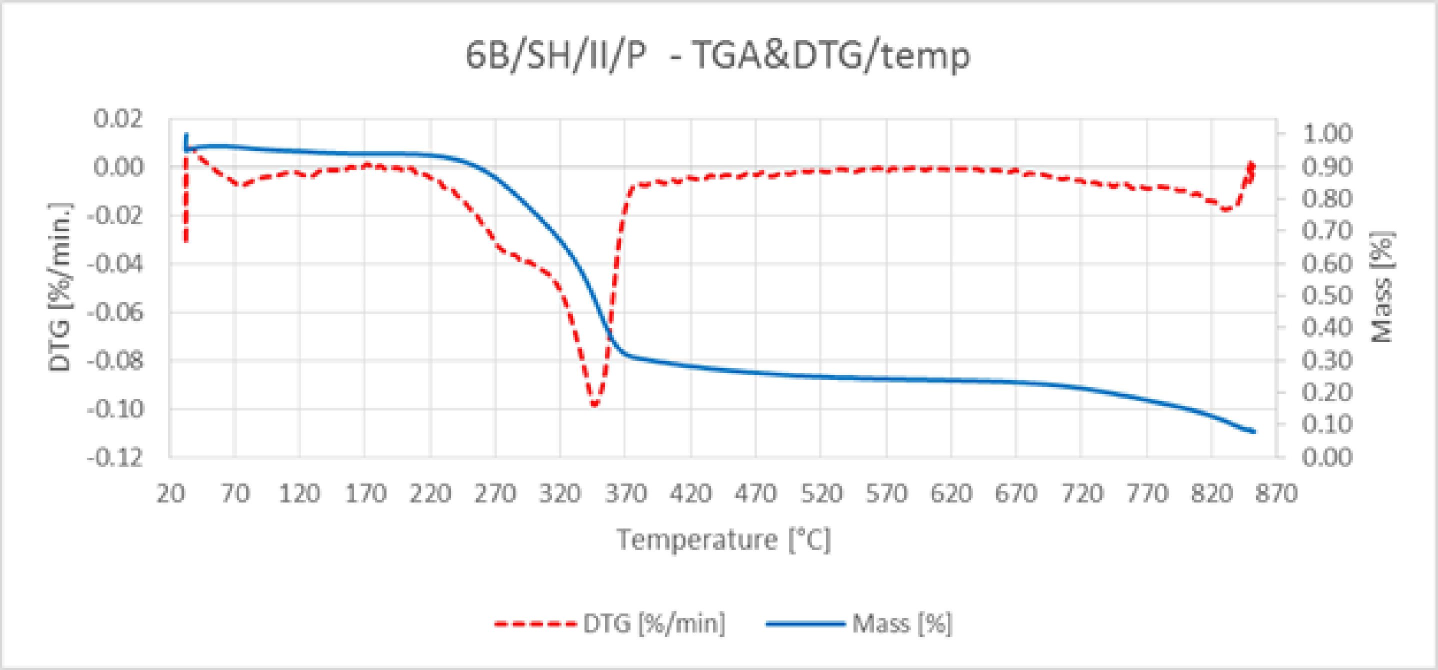
- TGA continuously measures mass loss while the temperature of a sample is changed over time. Mass, temperature, and time in thermogravimetric analysis are considered base measurements
- Simultaneously with TG measurements, differential thermal analysis (DTG) can be determined. TG and DTG curves for 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)).
- TGA measures changes in weight in relation to changes in temperature. The measured weight loss curve gives information on:
    - changes in sample composition
    - thermal stability
    - kinetic parameters for chemical reactions in the sample
- A derivative weight loss curve can be used to tell the point at which weight loss is most apparent.
- After the TGA experiment for each biomass sample was carried out, the results were exported to a .txt file and after that were processed with the help of the Microsoft Excel program in order to obtain the TGA and DTG graphs. For all the biomass samples were presented graphs for temperature and mass versus time and TGA and DTG versus time and temperature.
- Over 200 different graphs were made in order to determine the highest reactivity of the samples.

TG analysis results



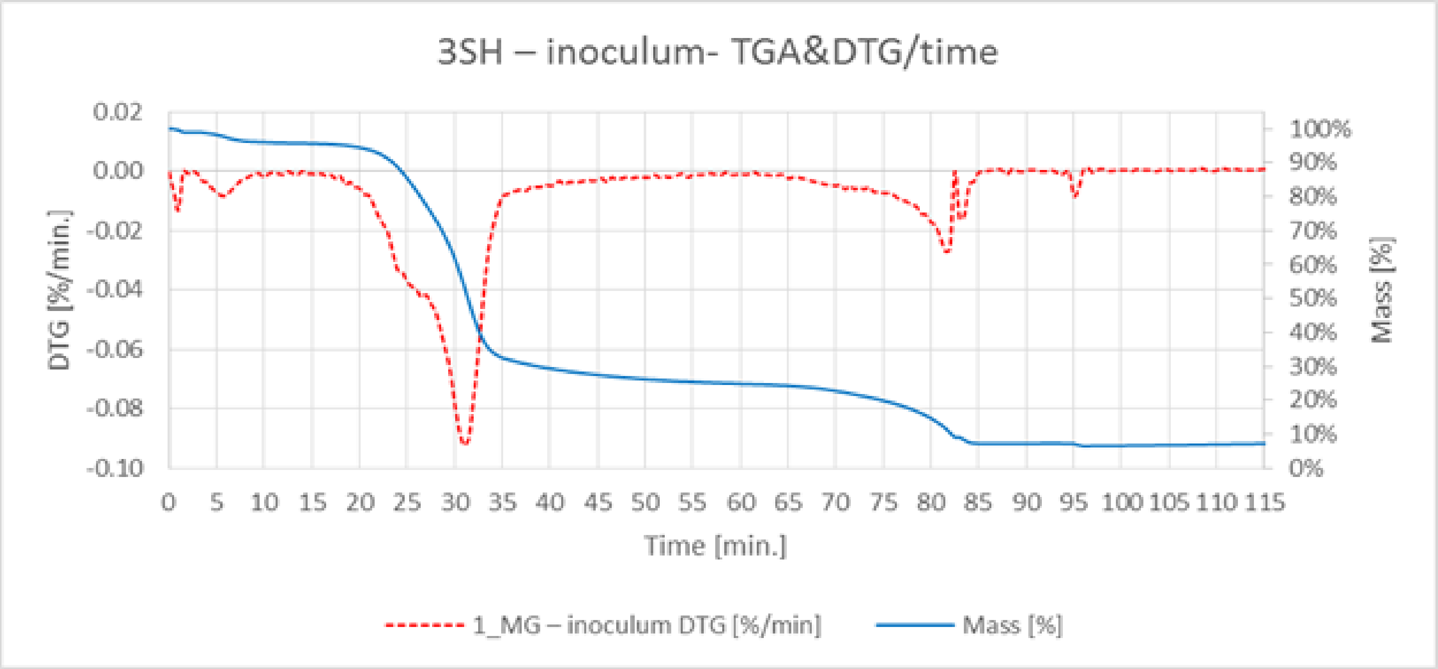
Combined graphs

TG analysis results



Tests result – TGA and DTG versus temperature

TG analysis results



Tests result – TGA and DTG versus time

TG analysis results

- Comparative tables for first, second and third year

Table 1 – *Miscanthus* x *giganteus* crops

First year samples				Second year samples				Third year samples			
Sample	DTG peak [°C]	DTG max. [%/min]	Solid residue [%, wet basis]	Sample	DTG peak [°C]	DTG max. [%/min]	Solid residue [%, wet basis]	Sample	DTG peak [°C]	DTG max. [%/min]	Solid residue [%, wet basis]
Polish crops				Polish crops				Polish crops			
Miscanthus x giganteus	350	0.1050	4.71	2nd_8B/MG/I/P+B/MG/IV/P+B/MG/V/P	341	0.0747	5.248	3rd_1B/MG/I/P	336	0.0858	4.910
				2nd_9B/MG/II/P	341	0.0771	4.856	3rd_2B/MG/II/P	336	0.1009	4.768
				2nd_10B/MG/III/P	341	0.0762	5.103	3rd_3B/MG/III/P	336	0.0940	5.152
German crops				German crops				German crops			
				2nd_17L/MG/III/P	341	0.0711	5.187	3rd_12L/MG/I/P	336	0.0625	5.026
				2nd_18L/MG/IV/P+L/MG/V/P	340	0.0604	5.713	3rd_13L/MG/II/P	346	0.0675	5.146
								3rd_14L/MG/III/P	336	0.0654	5.236

TG analysis results

Table 2 – *Sida Hermaphrodita* crops

First year samples				Second year samples				Third year samples			
Sample	DTG peak [°C]	DTG max. [%/min]	Solid residue [%, wet basis]	Sample	DTG peak [°C]	DTG max. [%/min]	Solid residue [%, wet basis]	Sample	DTG peak [°C]	DTG max. [%/min]	Solid residue [%, wet basis]
Polish crops				Polish crops				Polish crops			
Sida hermaphrodita	336	0.0980	7.84	2nd_5B/SH/I/P+B/SH/IV/P+B/SH/V/P	345	0.0891	4.772	3rd_7B/SH/I/P	346	0.0940	4.306
				2nd_6B/SH/II/P	346	0.0983	4.674	3rd_8B/SH/II/P	346	0.0899	4.676
				2nd_7B/SH/III/P	350	0.106	3.875	3rd_9B/SH/III/P	336	0.0906	4.956
German crops				German crops				German crops			
				2nd_14L/SH/I/P+L/SH/IV/P+L/SH/V/P	326	0.0858	6.4	3rd_18L/SH/I/P	346	0.0849	4.764
				2nd_15L/SH/II/P	326	0.0888	5.4	3rd_19L/SH/II/P	346	0.0897	4.214
				2nd_16L/SH/III/P	346	0.0816	5.409	3rd_20L/SH/III/P	346	0.0761	4.824

TG analysis results

Table 3 – *Spartina pectinata* crops

First year samples				Second year samples				Third year samples			
Sample	DTG peak [°C]	DTG max. [%/min]	Solid residue [%, wet basis]	Sample	DTG peak [°C]	DTG max. [%/min]	Solid residue [%, wet basis]	Sample	DTG peak [°C]	DTG max. [%/min]	Solid residue [%, wet basis]
Polish crops				**Polish crops**				**Polish crops**			
Spartina pectinata	345	0.0980	7.51	**2nd_11B/SP/I/P+B/SP/IV/P+B/SP/V/P**	350	0.0957	4.832	**3rd_4B/SP/I/P**	341	0.0867	4.680
				2nd_12B/SP/II/P	346	0.0858	4.58	**3rd_5B/SP/II/P**	341	0.0777	4.840
				2nd_13B/SP/III/P	346	0.0864	4.77	**3rd_6B/SP/III/P**	346	0.0834	4.454
German crops				**German crops**				**German crops**			
				2nd_19L/SP/II/P	340	0.0692	5.768	**3rd_15L/SP/I/P**	346	0.0828	4.696
				2nd_20L/SP/III/P	331	0.0655	6.364	**3rd_16L/SP/II/P**	341	0.0833	4.636
				2nd_21L/SP/I/P+L/SP/V/P	345.5	0.0669	5.692	**3rd_17L/SP/III/P**	341	0.0786	4.934

TG analysis results

Table 4 – *Panicum virgatum* crops

First year samples				Third year samples			
Sample	DTG peak [°C]	DTG max. [%/min]	Solid residue [%, wet basis]	Sample	DTG peak [°C]	DTG max. [%/min]	Solid residue [%, wet basis]
Polish crops				**Polish crops**			
Panicum virgatum	345	0.0927	11.66	3rd_10B/PV/II/P	341	0.0876	4.624
				3rd_11B/PV/III/P	341	0.0945	4.540
German crops				**German crops**			
				3rd_21L/PV/I/P	346	0.0789	4.526

TG Analysis - Conclusions

- Analyzing the data presented in the comparatives tables, it can be concluded that in case of the inoculum application, the *Sida hermaphrodita* from Bytom Poland, is characterized by **the highest reactivity.**
- *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.
- The NPK fertilizer and 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 inoculum used during cultivation of perennial dicotyledonous plants can positively influence of such treated feedstock.
- Taking into consideration chemical structure of the energy crops, *Miscanthus* x *giganteus*, and *Sida hermaphrodita* 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.

Thank you for your attention!