PHYTO2ENERGY

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

WP3 – Lab tests & FTIR Analysis

ISPE

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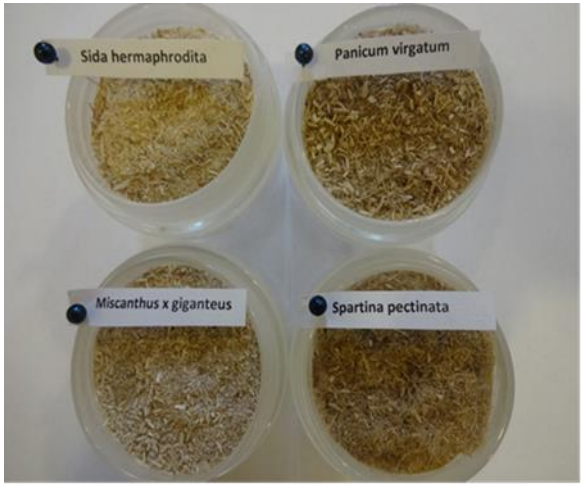
Lab tests & FTIR analysis - Overview

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 :

- *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

Lab tests & FTIR analysis - Overview

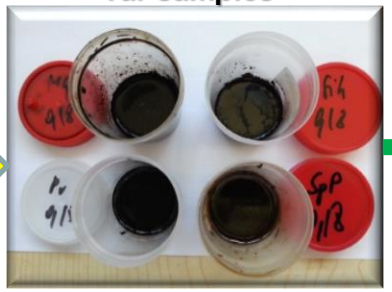
Biomass samples

Spartina pectinata
Miscanthus x giganteus
Sida hermaphrodita
Panicum virgatum

Gasification process SUT Laboratory

GAS

Tar samples



Ash samples

Laboratory analyses

ICECHIM

Results

Lab tests

A. Lab tests

- Analyses of the biomass samples (*Miscanthus* x *giganteus*, *Sida hermaphrodita*, *Panicum virgatum, Spartina pectinata*) were done
- Analyses included the heavy metals content, such as cadmium (Cd), zinc (Zn), lead (Pb), in biomass samples.
- Also, the analyses presented the influence of the inoculum and NPK fertilizer on the properties of each biomass type regarding other elements: potassium (K) and sodium (Na).
- The lab test for biomass, ash and tar were:

Biomass analyses	Carbon	Hydrogen	Nitrogen	Oxygen	Sulphur	Chlorine	Pb	Cd	Zn	Mg	Ca	P	K	Na	Loss on ignition	Moisture	Volatiles	Residuum at calcination
Ash analyses	Pb	Cd	Zn	K	K_2O	Ca	Na	Mg	Fe	Fe_2O_3	P	P_2O_5	CaO	MgO	Cl-	pH	EC	Density
Tar analyses	Pb	Cd	Zn	K/K_2O	Ca/CaO	Na	Mg/MgO	Fe/Fe_2O_3	P/P_2O_5	Cl^-	pH	Density						

FTIR analysis

B. FTIR analysis

FTIR (Fourier Transform Infrared Spectroscopy) 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 OH, C=O, alkanes and species like CH_4, CO_2, CO.

- For all analysed biomass samples the FTIR spectrum were recorded and were identified characteristic absorption bands.
- For all analysed ash samples the FTIR spectrum was recorded and identified characteristic absorption bands.
- For all analysed liquid residues samples the FTIR spectrum was recorded and identified characteristic absorption bands.

FTIR spectrum	OH	CH_2 from saturated compound	C=O	aromatic ring	C-C-O-	C-H from aromatic ring

BIOMASS analyses

- Lab test results - Analyses for the biomass samples for 3 years

Miscanthus x giganteus		Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	P (mg/kg)	K (mg/kg)	Na (mg/kg)
First year samples	*Miscanthus x giganteus*	35	1.55	83.28	<DL	<DL	<DL
Second year samples	MG – inoculum	49.48	1.01	114.64	436.70	2339.7	35.35
	MG-control	37.88	1.09	165.43	540.35	2461.7	32.49
	B/MG/I/P + B/MG/IV/P + B/MG/V/P	231.52	5.12	570.56	561.40	1687.7	82.14
	B/MG/II/P	161.95	3.91	630.20	652.91	1851.8	78.27
	B/MG/III/P	192.83	4.63	637.97	793.75	1982.8	100.63
	L/MG/III/P	2.92	1.08	229.78	1392.2	5100.1	329.84
	L/MG/IV/P + L/MG/V/P	3.35	0.63	119.10	508.77	3534.3	153.48
Third year samples	B/MG/I/P	31.98	1.458	195.628	221.85	3110.41	27.78
	B/MG/II/P	32.53	1.333	205.814	196.09	2319.77	26.23
	B/MG/III/P	41.98	1.450	208.265	220.60	3533.93	47.70
	L/MG/I/P	2.18	1.749	330.284	964.46	4310.86	2304.94
	L/MG/II/P	2.53	1.608	342.569	839.96	4211.51	2053.94
	L/MG/III/P	2.20	2.166	392.089	802.12	4249.51	2555.15

Sida hermaphrodita		Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	P (mg/kg)	K (mg/kg)	Na (mg/kg)
First year sample	*Sida hermaphrodita*	56.84	5.20	146.50	<DL	<DL	<DL
Second year samples	SH – inoculum	47.38	6.95	205.66	497.12	3313.1	70.67
	SH-control	34.50	7.13	181.57	544.67	3303.1	84.01
	B/SH/I/P + B/SH/IV/P + B/SH/V/P	N/A	6.08	747.07	925.90	2944.1	120.18
	B/SH/II/P	N/A	4.03	1023.9	602.34	1687.4	99.39
	B/SH/III/P	47.07	3.96	542.92	426.65	1781.7	115.70
	L/SH/I/P+ L/SH/IV/P + L/SH/V/P	2.68	1.00	79.63	374.19	3850.3	255.64
	L/SH/II/P	1.91	1.06	117.85	884.89	4303.5	258.22
	L/SH/III/P	1.93	1.53	129.30	545.46	2052.5	298.04
Third year samples	B/SH/I/P	34.79	4.141	153.798	145.74	1797.83	57.05
	B/SH/II/P	25.21	3.882	131.984	103.54	2159.23	61.70
	B/SH/III/P	26.17	6.140	185.097	171.23	1932.51	73.43
	L/SH/I/P	3.71	0.916	83.390	206.52	1610.43	1450.47
	L/SH/II/P	2.65	0.712	94.299	290.90	1640.10	1727.67
	L/SH/III/P	2.97	0.975	82.436	269.24	900.50	1721.12

BIOMASS analyses

- Lab test results - Analyses for the biomass samples for 3 years

Spartina pectinata		Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	P (mg/kg)	K (mg/kg)	Na (mg/kg)
First year sample	*Spartina pectinata*	92.66	1.25	147.70	<DL	<DL	<DL
Second year samples	SP – inoculum	96.62	0.68	224.04	477.40	1140.0	43.48
	SP-control	134.52	0.86	149.45	328.40	667.12	40.81
	B/SP/I/P + B/SP/IV/P + B/SP/V/P	111.25	0.90	287.14	351.37	2076.5	80.88
	B/SP/II/P	111.58	0.95	294.72	364.86	2119.4	81.02
	B/SP/III/P	115.17	1.10	366.94	458.38	2197.9	84.02
	L/SP/II/P	7.08	0.65	369.71	828.18	3699.1	356.04
	L/SP/III/P	4.54	0.61	396.26	1064.58	4017.70	492.74
	L/SP/I/P+ L/SP/V/P	0.50	0.04	44.91	3.52	0.99	0.77
Third year samples	B/SP/I/P	56.09	0.558	109.760	170.55	2267.72	45.28
	B/SP/II/P	52.95	0.600	105.967	162.72	2397.29	48.35
	B/SP/III/P	57.52	0.625	133.948	263.92	2258.27	64.56
	L/SP/I/P	3.41	0.699	352.134	367.47	2079.29	1812.13
	L/SP/II/P	1.96	0.775	266.442	293.37	2672.80	1926.66
	L/SP/III/P	2.24	0.674	236.940	284.23	2048.22	1970.94

Panicum virgatum		Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	P (mg/kg)	K (mg/kg)	Na (mg/kg)
First year sample	*Panicum virgatum*	88.96	1.34	122.40	<DL	<DL	<DL
Second year samples	PW – inoculum	143.47	1.38	247.92	370.27	470.14	33.63
	PW-control	161.49	1.28	209.76	368.94	377.01	35.28
Third year samples	B/PV/I/P	143.50	1.640	259.679	283.94	444.22	43.89
	B/PV/II/P	157.08	1.925	283.844	227.73	389.94	45.83
	B/PV/III/P	166.61	1.849	269.824	340.62	351.27	52.63
	L/PV/I/P	3.32	0.800	273.984	707.42	2194.53	2557.45
	L/PV/II/P	2.66	1.150	448.644	737.86	1639.85	2528.94
	L/PV/III/P	1.89	0.612	206.391	733.29	1806.50	2342.48

ASH analyses

- Lab test results - Analyses for the ash samples for 3 years

Miscanthus x *giganteus*		Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	P (mg/kg)	K (mg/kg)	Na (mg/kg)
First year sample	*Miscanthus* x *giganteus*	240	<0.6	219	1900	8000	600
Second year samples	MG – inoculum	132	<0.6	1110	3280	63200	1137
	MG-control	240	<0.6	219	1900	8000	600
	B/MG/I/A + B/MG/IV/A + B/MG/V/A	1342	<0.6	3308	2449	24600	<83
	B/MG/II/A	947	<0.6	3603	2320	26300	2537
	B/MG/III/A	1164	<0.6	2909	4115	30700	<83
Third year samples	B/MG/I/A	41.62	1.52	1065	2379	31232	461
	B/MG/I/A no catalyst	27.84	bdl	803	6506	38668	7318
	B/MG/I/A with catalyst	54.40	0.76	1096	5372	24546	4765
	B/MG/II/A	43.56	1.26	1094	2004	25508	981
	B/MG/III/A	51.61	1.64	1222	2279	36082	591
	L/MG/I/A	31.59	3.88	1176	5183	33339	1212
	L/MG/II/A	11.85	3.47	1599	7815	41308	1221
	L/MG/III/A	7.37	2.54	1243	5044	35222	859

Sida hermaphrodita		Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	P (mg/kg)	K (mg/kg)	Na (mg/kg)
First year samples	*Sida hermaphrodita*	226.7	2.3	794.2	3300	13300	1100
Second year samples	SH – inoculum	122	<0.6	744	510	32900	<83
	SH-control	226.7	2.3	794.2	3300	13300	1100
	B/SH/I/A + B/SH/IV/A + B/SH/V/A	171	<0.6	2471	4139	29600	<83
	B/SH/II/A	81	<0.6	5805	3957	36300	<83
	B/SH/III/A	296	<0.6	2370	2114	27600	<83
	L/SH/I/A+ L/SH/IV/A + L/SH/V/A	6.6	<0.6	502	7490	5780	<83
	L/SH/II/A	11.1	<0.6	629	10305	6090	7167
	L/SH/III/A	6.6	<0.6	539	1629	18800	<83
Third year samples	B/SH/I/A	76.44	12.38	2020	3622	25761	1296
	B/SH/II/A	66.27	7.67	1288	2173	29648	1180
	B/SH/III/A	33.69	1.84	895	4234	29150	1322
	L/SH/I/A	12.00	8.40	515	2576	10694	821
	L/SH/II/A	3.43	1.19	338	2153	10442	612
	L/SH/III/A	7.30	1.35	395	2350	6794	941

ASH analyses

- Lab test results - Analyses for the ash samples for 3 years

Spartina pectinata		Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	P (mg/kg)	K (mg/kg)	Na (mg/kg)
First year sampes	*Spartina pectinata*	120.1	9.8	297.7	3100	4100	500
Second year samples	SP – inoculum	377	<0.6	802	510	8830	<83
	SP- control	120.1	<0.6	297.7	3100	4100	500
	B/SP/I/A + B/SP/IV/A + B/SP/V/A	599	<0.6	2511	1917	32900	<83
	B/SP/II/A	584	<0.6	3003	2057	25100	<83
	B/SP/III/A	477	<0.6	1918	1596	26300	<83
Third year samples	B/SP/I/A	84.16	0.52	589	1644	20225	652
	B/SP/II/A	81.89	0.94	507	1501	17555	395
	B/SP/III/A	109.21	0.92	784	2221	25904	645
	L/SP/I/A	9.80	1.05	1433	4028	16381	1113
	L/SP/II/A	3.79	0.74	1103	1869	24311	1074
	L/SP/III/A	3.67	0.50	937	1574	21368	1061

Panicum virgatum		Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	P (mg/kg)	K (mg/kg)	Na (mg/kg)
First year samples	*Panicum virgatum*	120.1	<0.6	252	3100	2200	450
Second year samples	PW – inoculum	474	<0.6	1297	497	6470	<83
	PW-control	120.1	9.8	252	3100	2200	450
Third year samples	B/PV/II/A	196.35	2.28	1343	3137	5904	756
	B/PV/III/A	206.84	3.38	1110	2475	3528	629
	L/PV/I/A	5.79	1.31	859	3541	10328	702

TAR analyses

- Lab test results - Analyses for the tar samples for 3 years

Miscanthus x giganteus		Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)
First year samples	*Miscanthus x giganteus*	67.60	<DL	30.67
Second year samples	MG – inoculum	51.8	2.3	75.9
	MG-control	67.6	0.6	30.67
	B/MG/I/T + B/MG/IV/T + B/MG/V/T	51.2	0.6	39.6
	B/MG/II/T	12.4	0.6	19.2
	B/MG/III/T	64.4	5.17	221
Third year samples	B/MG/I/T	11.10	0.588	<DL
	B/MG/I/T no catalyst	5.61	<0.300	<DL
	B/MG/I/T with catalyst	4.11	<0.300	<DL
	B/MG/II/T	9.46	0.789	<DL
	B/MG/III/T	7.89	0.438	<DL
	L/MG/I/T	9.26	1.13	<DL
	L/MG/II/T	5.43	0.353	<DL
	L/MG/III/T	5.93	0.827	<DL

Sida hermaphrodita		Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)
First year samples	*Sida hermaphrodita*	30.51	<DL	14.26
Second year samples	SH – inoculum	44.9	2.35	12.1
	SH-control	30.51	0.6	14.26
	B/SH/I/T + B/SH/IV/T + B/SH/V/T	46	2.93	100
	B/SH/II/T	80	3.55	184
	B/SH/III/T	34.2	0.6	138
	L/SH/I/T+ L/SH/IV/T + L/SH/V/T	30.5	0.6	54.5
	L/SH/II/T	111	9.3	278
	L/SH/III/T	89.1	5.95	185
Third year samples	B/SH/I/T	3.74	0.572	<DL
	B/SH/II/T	3.31	1.06	<DL
	B/SH/III/T	2.35	1.330	<DL
	L/SH/I/T	10.40	0.961	<DL
	L/SH/II/T	9.36	0.659	<DL
	L/SH/III/T	4.05	<0.300	<DL

TAR analyses

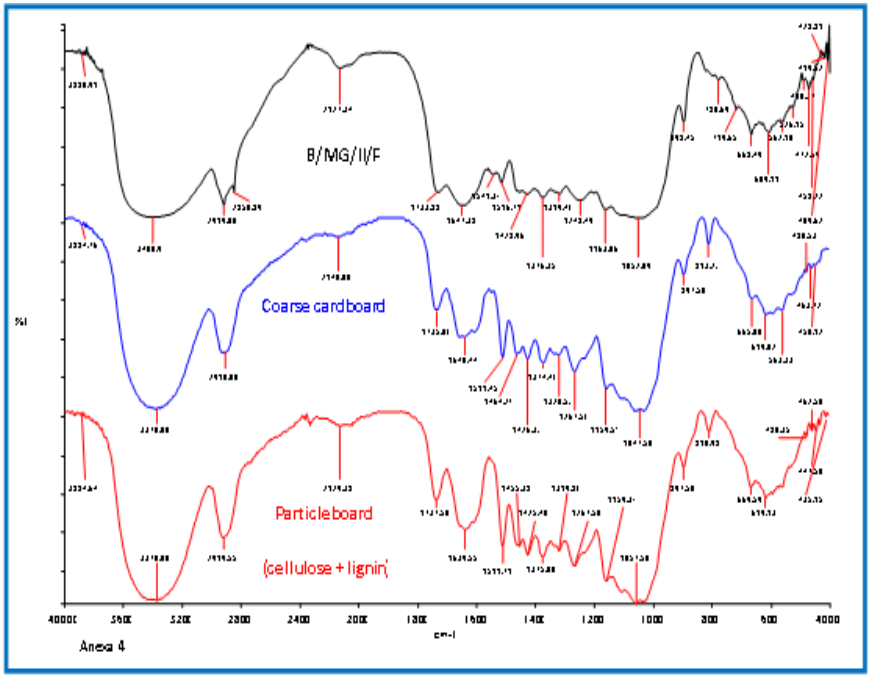
- Lab test results - Analyses for the tar samples for 3 years

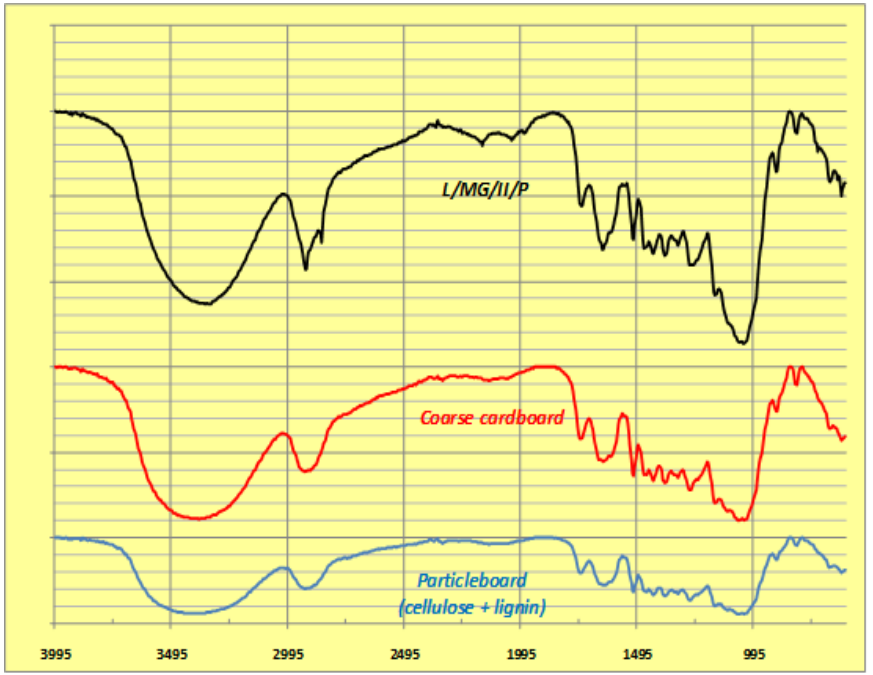
Spartina pectinata		Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)
First year sampes	*Spartina pectinata*	23.29	<DL	15.84
Second year samples	SP – inoculum	3.22	0.6	6
	SP-control	23.29	0.6	15.84
	B/SP/I/T + B/SP/IV/T + B/SP/V/T	91.1	3.88	225
	B/SP/II/T	71.7	1.55	174
	B/SP/III/T	61.5	3.78	177
Third year samples	B/SP/I/T	19.90	0.497	<DL
	B/SP/II/T	17.00	<0.300	<DL
	B/SP/III/T	9.54	<0.300	<DL
	L/SP/I/T	6.41	1.110	<DL
	L/SP/II/T	5.30	0.309	<DL
	L/SP/III/T	4.49	<0.300	<DL

Panicum virgatum		Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)
First year samples	*Panicum virgatum*	23.32	<DL	11.63
Second year samples	PW – inoculum	17.3	3.21	15.2
	PW-control	23.32	0.6	11.63
Third year samples	B/PV/II/T	12.7	1.060	<DL
	B/PV/III/T	20.50	1.210	<DL
	L/PV/I/T	4.85	0.974	<DL

FTIR analyses

FTIR spectrum for biomass samples of *Miscanthus x giganteus with NPK fertilizers from Bytom and from Leipzig*





Biomass analyses conclusions

Conclusions:

- ***Biomass***

✓The biomass from Bytom site was distinguished by highest absorption level of lead, cadmium and zinc: Pb→1231.52 mg/kg (B/MG/I/P + B/MG/IV/P + B/MG/V/P) *Miscanthus* x *giganteus*, Cd→7.13 mg/kg (SH-control), and Zn→1023.92 mg/kg (B/SH/II/P) *Sida hermaphrodita*.

✓The biomass from Leipzig site was distinguished by highest absorption level of phosphorus and potassium: P→1392.21 mg/kg (L/MG/III/P) *Miscanthus* x *giganteus* and K→5100.1 mg/kg (L/MG/III/P) *Miscanthus* x *giganteus*.

Ash analyses conclusion

Conclusions:

- ***Ash***

✓The ash resulted after biomass gasification from Bytom site contains the highest quantity of lead Pb→1342 mg/kg ((B/MG/I + B/MG/IV + B/MG/V)/A) *Miscanthus* x *giganteus*, cadmium Cd→12.38 mg/kg (B/SH/I/A) *Sida hermaphrodita*, zinc Zn→5805 mg/kg (B/SH/II/A) *Sida hermaphrodita*, K→63200 mg/kg (B/MG/II/A) *Miscanthus* x *giganteus*;

✓The ash resulted after biomass gasification from Leipzig site contains the highest quantity of phosphorus P→10305 mg/kg (L/SH/II/A) *Sida hermaphrodita*;

Tar analyses conclusions

Conclusions:

- ***Tar***

✓**The highest contents** of heavy metals in the tar samples have the highest values for *Sida hermaphrodita* – NPK fertilizers (L/SH/II/T) from Leipzig site;

- Pb→111 mg/kg
- Cd→9.3 mg/kg
- Zn→278 mg/kg

FTIR analyses conclusions

- *FTIR (1)*

Each biomass sample (*Miscanthus* x *giganteus/ Sida hermaphrodita* with NPK fertilizers, *Miscanthus* x *giganteus/ Sida hermaphrodita* with inoculum) was compared with FTIR standards library spectra. **Thus, all the biomass samples were identified as a coarse cardboard or a particleboard, composed of cellulose and lignin with different fitting degrees:**

✓87% and 85% for L/MG/II/P;

✓86% and 81% for L/SH/II/P;

✓85% and 82% for L/MG/III/P;

✓82% and 78% for L/SH/III/P.

✓95% and 92% for B/MG/I/P;

✓94.5% and 93% for B/SH/I/P;

✓94.8% and 93.6% for B/MG/II/P;

✓92.8% and 91.4% for B/MG/III/P.

Conclusions

- *FTIR (2)*
  - All the biomass samples contain clusters of wooden structure, with approximately equal amounts of cellulose and lignin. **The largest amount of cellulose** was found in Bytom sample *Miscanthus* x *giganteus control* and the lignin was found in the Bytom sample *Miscanthus* x *giganteus with NPK fertilizers*.
  - In comparison with Bytom site, Leipzig site has a more complicated composition matrix and FTIR analysis can not identify all the substances which are contained in biomass samples.

CONCLUSIONS:

- *Sida hermaphrodita* and *Miscanthus* x *giganteus* with *inoculum and NPK fertilizers* have the highest content of heavy metals in biomass, ash and tar samples proving that inoculum and NPK fertilizers increase the plant absorption of heavy metals.
- Taking into consideration this fact, the most attractive species for phytoremediation coupled with thermal utilization of produced biomass seems to be *Miscanthus* x *giganteus*, followed by *Sida hermaphrodita.*

WP3 – Lab tests & FTIR Analysis

Thank you for your attention!