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Fixed-Bed Gasification Process – The Case of the Heavy Metal Contaminated Energy Crops

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Energy crops phytoremediation process is one of the techniques used for remediation of contaminated areas. After cleaning soil, contaminated biomass is produce. It should be utilize in the safe way. Among available energy crop conversion technologies, the most suitable seems to be gasification, which gives the possibility of controlling the fate of the extracted HMs. The gasification process of heavy metal contaminated biomass in fixed bed installation has many advantages in comparison to the combustion process. It produces a gaseous fuel, which can be used to produce energy in different types of installations.
In the work properties of the heavy metal contaminated (HMC) samples of Miscanthus x giganteus, Sida hermaphrodita and Spartina pectinata was presented. The data were collected from an HMC arable area in Bytom, Upper Silesia, Poland and the former sewage sludge deposit site in Leipzig, Saxony, Germany. The study investigated the impact of different treatments on biomass elemental compositions to determine its suitability for energy production. Both sites were treated as follows: (i) C – Control, no treatment, (ii) treated with standard mineral (NPK) fertilizer (ammonium sulphate and Polifoska – 4 % N, 22 % P_2O_5, 32 % K_2O) applied directly to the soil before planting, (iii) treated with the commercial microbial inoculum Emfarma Plus® (EFP), ProBiotics Poland. Gasification results shows that the highest values for the Lower Heating Value (LHV) are obtained for an air ratio of 0.18. The highest increment of the LHV is observed for biomass treated by NPK in comparison to control samples.

1. Introduction

Polluted soil is a serious environmental problem. According to the European Environmental Agency (2007), the 32 European countries have reported occurrences of 250,000 polluted sites. It mostly polluted with heavy metals. 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. These methods are poorly developed yet. HM are non-degradable and generally strongly retained in the soil. Phytoremediation appears to be an economically attractive in situ technique (Kirkham, 2006). 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 (Jensen et al., 2009).
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. In previous works, Tang et al. (2015) concluded that the analysed energy crops are characterized by the yield equal to: 11.7 t/ha in the case of Sida hermaphrodita, 9.5 t/ha in the case of Spartina pectinata, 15.0 t/ha in the case of Miscanthus x giganteus and 13.3 t/ha in the case of Panicum virgatum. Phytoremediation results show that Miscanthus x

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giganteus is a more tolerant species to the total contaminated soil with Zn and Pb to Sida hermaphrodita (Zilveberg et al., 2014). It was proven that Spartina pectinata and Panicum virgatum are very suitable for heavy metals phytostabilization (Pogrzeba et al., 2016).
The investigation of the phytoremediation process has focused on the development a microbiological method stimulating the biomass yield and phytoremediation effect of heavy metal contaminated sites.
Phytoremediation produces secondary waste, which has to be appropriately managed due to the high content of HM. The biomass can be processed using biochemical or thermal conversion methods. Gasification is the process of solid feedstock conversion into gaseous fuel (Billaud et al., 2016). A typical biomass gasification process includes the following steps: drying, pyrolysis, partial combustion, and gasification of decomposed products (Gabbrielli et al., 2016). In order for gasification to convert the solid fraction into gas, steam, air or oxygen are required. Gasification process is characterized by higher energy recovery and lower-cost for atmospheric emission control in comparison to combustion and prevents emissions of sulphur and nitrogen oxides as well as *heavy-metal oxides*. Heavy metals present in biomass can be retained in the solid residue, trapping some of sulphur, nitrogen and chloride introduced by the feedstock.
The aim of the study was to investigate the possibility of using Miscanthus x giganteus, Sida hermaphrodita and Spartina pectinata in energy crop production on HM contaminated sites.
The impact of different treatments (fertilization and inoculation) on biomass elemental compositions (carbon, hydrogen, nitrogen and oxygen content) and moisture, ash and volatile content to determine its suitability for energy production was determined. Multicriterial gasification tests of Sida hermaphrodita was performed.

2. Materials and methods

2.1 Site description

The biomass was collected from a HMC arable land in Bytom, Poland (50°20'43.0"N 18°57'19.6"E) and former sewage sludge dewatering site in Leipzig, Germany (51°25'23.7"N 12°21'56.2"E). Polish site was an agricultural land affected in the past by dust from a lead and zinc smelter, which caused the HMs soil contamination, especially zinc, cadmium and lead. The soil has content of Pb, Cd and Zn that exceed the limits set by Polish law for arable lands (Dz.U. 2016. nr.0 poz.1395), which excludes such areas from food production. German site is a former sewage sludge dewatering site, which was in operation from 1952 to 1990. Following its closure, approximately 650,000 t of sewage sludge remained in several basins.

2.2. Feedstock description

Table 1: Ultimate and proximate analysis of the analysed feedstock

%mass	Bytom site								
	MG_C	MG_{NPK}	MG_{EFP}	SH_C	SH_{NPK}	SH_{EFP}	SP_c	SP_{NPK}	SP_{EFP}
C	46.90	45.50	46.50	46.20	46.40	47.00	46.70	46.30	47.00
H	7.32	6.88	7.13	6.69	7.22	7.06	6.33	6.77	7.07
N	1.38	1.13	1.49	0.43	0.38	0.30	0.32	0.38	0.59
O	44.20	46.29	44.68	46.48	45.80	45.44	46.45	46.35	45.14
Moisture	8.60	8.30	8.20	9.80	9.10	9.40	8.30	8.40	9.50
Volatiles	74.90	76.50	75.30	75.80	76.90	76.60	77.90	77.50	75.70
Ash	5.50	4.20	4.90	2.70	2.40	4.80	3.70	3.40	3.40
	Leipzig site								
C	45.40	44.60	45.20	44.10	44.90	44.60	43.90	44.90	43.40
H	7.28	6.96	6.84	7.22	6.77	6.96	6.73	6.35	6.77
N	2.15	2.06	1.47	0.38	0.65	0.66	0.85	0.90	1.06
O	45.17	46.18	46.29	45.80	48.45	47.29	48.32	47.65	48.57
Moisture	8.20	8.00	8.00	8.90	8.50	9.400	8.20	8.10	8.30
Volatiles	74.00	74.40	74.30	74.10	74.30	75.70	72.70	73.40	72.10
Ash	6.50	6.30	5.80	3.90	2.80	3.30	8.70	7.80	9.30

Legend:
MG_C - Miscanthus x giganteus –control; MG_{NPK} - Miscanthus x giganteus -nutrients NPK; MG_{EFP} - Miscanthus x giganteus – Em Farma Plus; SH_C - Sida hermaphrodita- control; SH_{NPK} - Sida hermaphrodita - nutrients NPK; SH_{EFP} - Sida hermaphrodita - – Em Farma Plus; SP_C - Spartina pectinata – control; SP_{NPK} - Spartina pectinata - nutrients NPK; SP_{EFP} - Spartina pectinata - Em Farma Plus

Both sites were treated as follows: (1) C – Control, no treatment, (2) NPK standard fertilization (ammonium sulphate and Polifoska – 4 % N, 22 % P_2O_5, 32 % K_2O) (3) EFP - Commercial microbial inoculum Emfarma Plus® ProBiotics 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. 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). Results show that *Sida hermaphrodita* is characterized by the lowest content of ash. The volatile matter content and moisture content are similar for all feedstock. The percentage of carbon, hydrogen and oxygen are also quite similar for all biomass types. *Miscanthus* x *giganteus* is characterized by the highest content of nitrogen.

2.3. Gasification experiment

Gasification experiment was conducted using a fixed-bed gasification facility, as illustrated in Fig. 1. (Werle and Wilk, 2011).

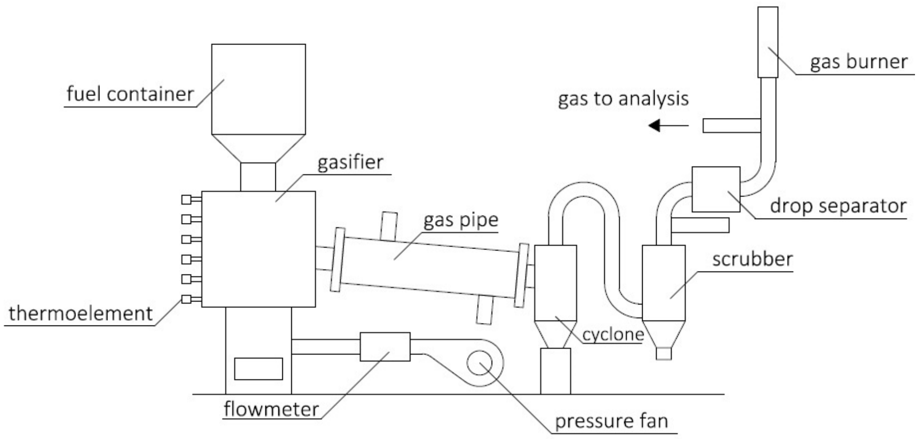

Figure 1: Schematic diagram of the experimental system (Werle and Wilk, 2011)

The main component of the lab-scale installation was a well-insulated stainless steel reactor (gasifier) with a 150 mm internal diameter with a total height of 300 mm. Biomass from the fuel container was fed into the top of the gasifier. The gasification air was directed from the bottom by a pressure fan. The HMC biomass was then circulated in a counter current direction to the process gases. In the drying zone, water was evaporated from the fuel. In the second zone (pyrolysis), the biomass was thermally decomposed into volatiles and solid char. In the third zone, carbon was converted into the main combustible components of syngas. In the last zone, the remaining char was combusted. The combustion zone provided a source of energy for the gasification reactions in the upper zones. The gasification reactions are mainly endothermic. The internal reactor temperature was measured by six N-type thermoelements located along the vertical axis of the reactor integrated with an Agilent temperature recording system. The syngas was transported from the gasifier and then cleaned by a cyclone, scrubber and drop separator. The volumetric fractions of the main syngas components were measured online using a Fisher Rosemount and ABB integrated set of analyzers (Werle and Wilk, 2012).

The air ratio was calculated taking into account the gasification air flow rate and biomass flow ratio. The lower heating value (LHV) in MJ m^{-3} of the gasification gas was estimated using the formula given below (Kim et al., 2011): $LHV = 0.126 \cdot CO + 0.108 \cdot H_2 + 0.358 \cdot CH_4$

Gasification parameters methodology were characterised in Table 2. *Sida hermaphrodita* was chosen as a representative feedstock to experiment. In the recent years *Sida* attracted attention as a promising plant for bioenergy production (Barbosa et al., 2014). Along with *Miscanthus*, another perennial, high-yield energy plant, *Sida* recently attracted attention due to its wood-like, high-yield biomass (Borkowska and Molas, 2012). Due to the numerous shoots per plant, the biomass yield of *Sida* is higher compared to that of currently used energy plants (Jablonowski et al., 2016).

Table 2: Parameters for the gasification processes

Feedstock	Gasification agent	Air ratio λ	Gasification agent temperature, K	Parameters
SH_C SH_{NPK} SH_{EFP}	Atmospheric air	0.12; 0.14; 0.16 0.18; 0.23; 0.27	298	Temperature distribution, gasification gas composition and LHV of gasification gas

3. Results

3.1 Composition of the gasification gas and the lower heating value of the gasification gas

Figure 2 presents the gas composition of the gasification gas and Figure 3 presents the LHV of this gas as a function of the air ratio. Analyzing this results it can be observed that during the test with the air ratio equal to 0.18, the main combustible components in the produced gas (and the LHV) reaches its maximum.

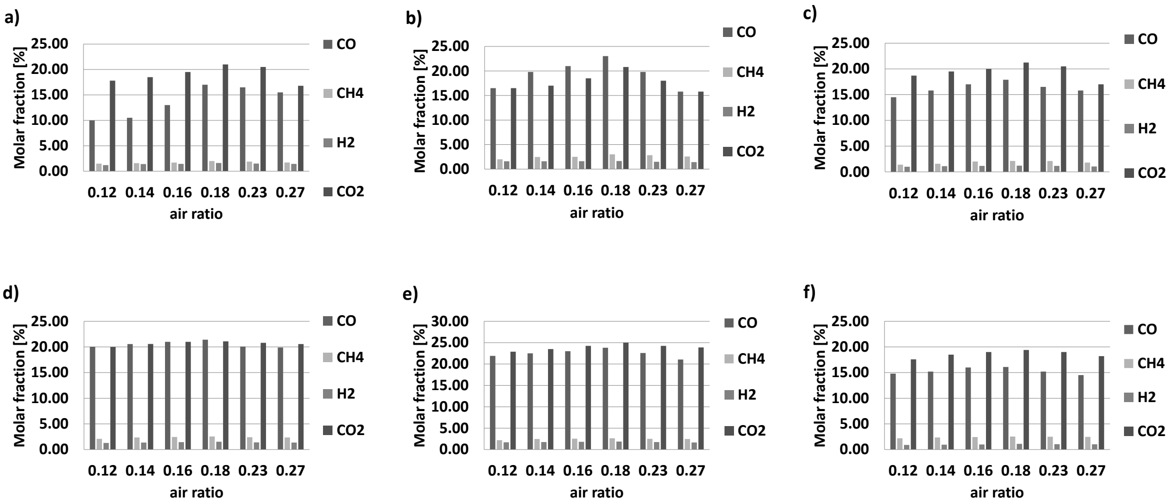

Figure 2: Gas composition as a function of air ratio: a) Bytom SH_C, b) Bytom SH_{NPK}, c) Bytom SH_{EFP} d) Leipzig SH_C, e) Leipzig $SH_{NP}K$, f) Leipzig SH_{EFP}

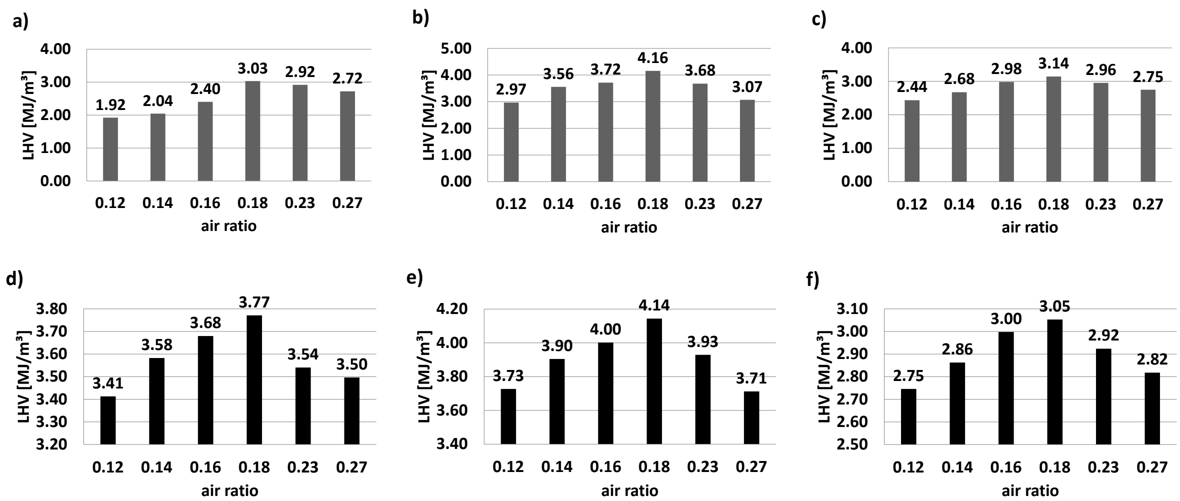

Figure 3: The LHV of the gasification gas as a function of air ratio : a) Bytom SH_C, b) Bytom SH_{NPK}, c) Bytom SH_{EFP} d) Leipzig SH_C, e) Leipzig $SH_{NP}K$, f) Leipzig SH_{EFP}

Air ratio is a parameter that quantifies the amount of air per unit mass of fuel, as compared with the theoretical amount of air needed for complete oxidation. The optimum air ratio that favors gasification (incomplete combustion) resulting in combustible gases like CO, rather than the case of complete combustion with an air supply that mainly produces CO_2 (Taba et al., 2012). CO_2 shows an inverse relation with CO, as the reactions that produce those gases are competing for the same reactants, namely carbon. When gasification air is fed with the fuel into the reactor, the endothermic reaction of air and carbon occurs first (e.g. Boudouard equilibrium $C+CO_2 \rightarrow 2CO$), and the CO in a gaseous state produced from the fuel reacts with the residuals causing next reactions (e.g. water gas shift $C+ H_2O \rightarrow CO+ H_2$). The composition of H_2, CO and CO_2 (and the LHV) in the gasification gas changes according to the amount of the air supplied to reactor (Kim et al., 2011). It can be concluded that gasification gas achieved from biomass cultivated on German site is characterized by the highest content of methane, carbon monoxide and hydrogen. This feature is connected with the lowest moisture content in such feedstock (see Table 1). Basu (2010) has reported that a minimum of 2,260 kJ of energy from the gasifier is required to vaporize 1 kg of moisture in biomass. The gasification of biomass feedstock with lower content of moisture is characterized by the higher overall process efficiency and give the possibility to obtain gas with the higher content of CO, H_2 and CH_4. The gasification gas from the biomass treated by NPK fertilizer is characterized by the higher LHV in comparison to gasifcation gas from biomass treated by EFP. This is due to the fact that fertilized biomass is characterized by lower ash content in comparison to control and inoculated samples. Analyzing the LHV values, it can be observed that gasification process gives the opportunity to obtain valuable gaseous fuel. Such fuel can be effectively utilized in boiler, gas turbines or engines (Werle, 2015).

3.2. Temperature distribution in the reactor

The temperature profiles in the reactor were measured by six N-type thermocouples installed at six points along the vertical axis of the reactor. The temperatures were measured at the following distances above the grate, t1: 10 mm, t2: 60 mm, t3: 110 mm, t4: 160 mm, t5: 210 mm and t6: 260 mm. Figure 4 presents the temperature profile inside the reactor. Analyzing presented results it can be concluded that the temperature at t_3 was always the highest temperature in the reactor; t_3 may have been located in the partial oxidation zone, which would have been the hottest area in the fixed bed gasifier. The other monitoring sites may have been located as follows: t6 and t5 in the drying zone, t4 in the pyrolysis zone, t2 in the oxidation (combustion) zone and t1 in the ash zone.

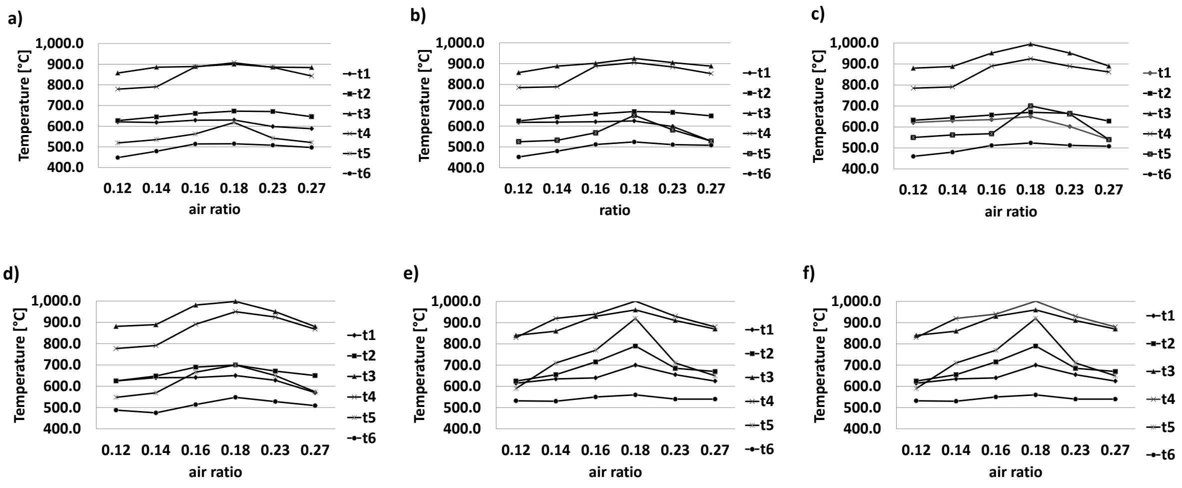

Figure 4: Temperature distribution in the rector as a function of air ratio: a) Bytom SH_C, b) Bytom SH_{NPK}, c) Bytom SH_{EFP} d) Leipzig SH_C, e) Leipzig $SH_{NP}K$, f) Leipzig SH_{EFP}

4. Conclusions

The possibility of using energy crops in fuel production on HM contaminated sites was presented. Collected biomass was characterised based on parameters, which determine its utility as a biofuel feedstock where gasification processing is advantageous. Results show that Sida hermaphrodita is characterized by the lowest content of ash. The volatile matter content and moisture content are similar for all feedstock. The percentage

of carbon, hydrogen and oxygen are also quite similar for all biomass types. Miscanthus x giganteus is characterized by the highest content of nitrogen.
In the recent years Sida hermaphrodita attracted attention as a promising plant for bioenergy production so the gasification of Sida was performed. It was confirmed that the LHV of produced gas is acceptable taking into consideration the usage of this gas. The best air ratio of gasification gas was found for $\lambda = 0.18$, moreover the gas obtained from NPK fertilized biomass had the highest LHV.

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