DOI: 10.2429/proc.2017.11(1)011 2017;11(1)

Sebastian WERLE[1], Łukasz ZIÓŁKOWSKI[1], Marta POGRZEBA[2], Jacek KRZYŻAK[2]
Izabela RATMAN-KŁOSIŃSKA[2] and Daniela BURNETE[3]

PROPERTIES OF THE WASTE PRODUCTS FROM THE HEAVY METAL CONTAMINATED ENERGY CROPS GASIFICATION PROCESS

WŁAŚCIWOŚCI PRODUKTÓW ODPADOWYCH ZE ZGAZOWANIA ROŚLIN ENERGETYCZNYCH ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI

Abstract: The phytoremediation ability of the energy crops is widely known. Unfortunately, the possibility of the effective, safe and ecological way for treatment such contaminated plants is still unresolved. It is postulated that one of such methods can be gasification - conversion process of organic matter into a combustible gas mixture. This process is associated with the formation of solid and liquid waste products. The paper presents the results of basic physico-chemical properties of solid (ash) and liquid (tar) waste products formed during the heavy metal contaminated energy crops gasification. Plant cultivation was carried out with the modification: 1) N, P, K fertilizer application and 2) inoculum made from specially selected microbial cultures application. The gasification process was carried out in a laboratory fixed bed reactor. Three types of energy crops were used: *Miscanthus* x *giganteus, Sida hermaphrodita, Spartina pectinata*. The experimental plots were established on heavy metal contaminated arable land located in Bytom (southern part of Poland, Silesian Voivodship). The influence of the type of additives on the liquid and solid waste products quality was analyzed. The results show that the addition of fertilizer (N, P, K) to soil couses that zinc content in ash is higher in comparison to control samples (biomass cultivated on soil without fertilization). The opposite situation is observed for lead. The application of the inoculum promotes the migration of lead into solid. In both cases, the cadmium content in ash is lower than detection limits. In the case of tars, there is no significant impact of the additive application on the heavy tars content.

Keywords: energy crops gasification, heavy metals, tars, ash

Introduction

Energy crops are in the area of interest because of multiple ways of advantageous utilization. They can be used for biofuels (solid, liquid and gaseous) and biocomponents production. Examples of commonly used plants are *Salix* L., *Miscanthus* x *giganteus*, *Spartina pectinata*, *Panicum virgatum*, *Sida hermaphrodita*, *Rosa multiflora* [1].

In Poland, agro-biomass is not widely used, which becomes a reason for underdeveloped cultivation techniques, lack of methods of preventing crop diseases and other detrimental external factors. That has a great impact on the volume of production and the quality of fuel. Other factors that affect an agro-fuel production are soil fertility, quality of agricultural treatment and field preparation (e.g. number of weeds). However, the current state of the Polish agro-energy sector gives number of opportunities for relatively easy and quick progression.

[1] Institute of Thermal Technology, Silesian University of Technology, ul. S. Konarskiego 22, 44-100 Gliwice, Poland
[2] Institute for Ecology of Industrial Areas, ul. L. Kossutha 6, 40-844 Katowice, Poland
[3] Institutul de Studii si Proiectări Energetice, Lacul Tei 1-3, 020371 Bucharest, Romania
Contribution was presented during ECOpole'16 Conference, Zakopane, 5-8.10.2016

Energy crops utilization can be useful in more than one field. Phytoremediation is one of the techniques used for remediation of contaminated areas. Soil contamination can be found close to landfills, heavy-metal/oil industry areas. There are energy crops which can be grown on contaminated areas and have a potential to accumulate contaminants. The reasonable method of contaminated biomass utilization is gasification [2].

Gasification is a thermo-chemical conversion of solid feedstock into a gaseous fuel. Because of the low amount of the oxidizer used in the process and the reducing atmosphere, gasification prevents sulphur and nitrogen oxides emission, also it is possible to accumulate part of the contaminants in the solid residues. Gasification is a way to utilize contaminated biomass while useful syngas is produced. Syngases are mostly low-calorific gases (depends on the feedstock and gasification agent) that can be used in power boilers, industrial furnaces, gas turbines or piston engines [3]. Biomass gasification gases, as a fuel that might be received from local energy sources shows a great potential as fuel for CHP plants [4, 5]. Combined heat and electricity generation in distributed energy systems with internal combustion piston engines is a good option for local communities due to a relatively low investment cost and the high efficiency of electricity production. What is more, the market of commercial solutions for low-calorific value gases (e.g. biogas, syngas) is constantly growing [6].

Werle shows [7] that it is possible to obtain a combustible gas from the gasification of sewage sludge at a relatively high process efficiency and low environmental impact. However, it was found, that still unsolved problem is solid and liquid waste products generated during the process [8]. These products can be the source of a variety of toxic organic [9] and inorganic [10] substances. In this study the results of basic physico-chemical properties of solid (ash) and liquid (tar) waste products formed during the heavy metal contaminated energy crops fixed bed gasification process.

Feedstock and apparatus

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 Zaklady Chemiczne "Police" S.A., Poland) were applied,
- 3 plots with commercially available microbial inoculum solution (EmFarma Plus, ProBiotics Magdalena Gorska, 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 shutdown 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. The feedstock samples is presented in Figure 1.

Fig. 1. Samples of gasified energy crops

Proximate analysis of the studied plants are presented in Table 1 and the proximate analysis in Table 2. The heavy metal concentration of the analysed feedstock is presented in Table 3.

Table 1

Ultimate analysis of the analysed feedstock

Plants	**Carbon**	**Hydrogen**	**Nitrogen**	**Oxygen**	**Sulphur**
	[% d.m.]				
SH	46.2 ±2.3	6.69 ±0.33	0.430 ±0.020	46.5 ±2.3	0.200 ±0.001
SH_{NPK}	46.4 ±2.3	7.22 ±0.36	0.380 ±0.019	45.8 ±2.3	0.200 ±0.001
SH_{EFP}	47.0 ±2.4	7.06 ±0.35	0.300 ±0.016	45.4 ±2.3	0.200 ±0.001
MG	46.9 ±2.4	7.32 ±0.37	1.380 ±0.069	44.2 ±2.2	0.200 ±0.001
MG_{NPK}	45.5 ±2.3	6.88 ±0.34	1.130 ±0.056	46.3 ±2.3	0.200 ±0.001
MG_{EFP}	46.5 ±2.3	7.13 ±0.36	1.490 ±0.074	44.7 ±2.2	0.200 ±0.001
SP	46.7 ±2.3	6.33 ±0.32	0.320 ±0.016	46.5 ±2.3	0.200 ±0.001
$P_{NP}S_{K}$	46.3 ±2.3	6.77 ±0.34	0.380 ±0.019	46.4 ±2.3	0.200 ±0.001
SP_{EFP}	47.0 ±2.3	7.07 ±0.35	0.590 ±0.029	45.1 ±2.3	0.200 ±0.001

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

Table 2

Ultimate analysis of the analysed feedstock

Plants	**Moisture**	**Volatiles**	**Ash**
	[% d.m.]		
SH	9.8 ±0.5	75.8 ±3.8	2.7 ±0.1
SH_{NPK}	9.1 ±0.5	76.9 ±3.8	2.4 ±0.1
SH_{EFP}	9.4 ±0.5	76.6 ±3.8	4.8 ±0.2
MG	8.6 ±0.4	74.9 ±3.8	5.5 ±0.3
MG_{NPK}	8.3 ±0.4	76.5 ±3.8	4.2 ±0.2
MG_{EFP}	8.2 ±0.4	75.3 ±3.8	4.9 ±0.3
SP	8.3 ±0.4	77.9 ±3.9	3.7 ±0.2
$P_{NP}S_{K}$	8.4 ±0.4	77.5 ±3.9	3.4 ±0.2
SP_{EFP}	9.5 ±0.5	75.7 ±3.8	3.4 ±0.2

Table 3

Heavy metal concentration in analysed feedstock

Plants	Pb	Cd	Zn
	[mg/kg d.m.]		
SH	N/A*	6.1 ±0.3	747 ±37
SH_{NPK}	N/A*	4.0 ±0.2	1024 ±51
SH_{EFP}	47.1 ±2.4	4.0 ±0.2	543 ±27
MG	232 ±12	5.1 ±0.3	571 ±29
MG_{NPK}	162.0 ±8.1	3.9 ±0.2	630 ±32
MG_{EFP}	192.8 ±9.6	4.6 ±0.2	638 ±32
SP	111.3 ±5.7	0.9 ±0.05	287 ±14
SP_{NPK}	111.6 ±5.7	1.0 ±0.1	295 ±15
SP_{EFP}	115.2 ±5.7	1.1 ±0.1	367 ±18

*N/A - not available

The heavy metal content in solid biofuels is regulated in EU by the European Standard [11]. According to this document, the limits established for heavy metal content in solid biofuels are as presented in Table 4.

Table 4

Heavy metal content in solid biofuels according to [11]

Heavy metal [mg/kg d.m.]	Limit
Lead	≤ 10
Cadmium	≤ 2.0
Zinc	≤ 100

Comparing the results from the lab tests for biomass samples with the limits from the table above, results the following conclusions:

- the lead and the zinc content in all biomass samples exceeds the limits established in the standard,
- the cadmium content in majority of biomass samples exceeds the limits established in the standard.

The experimental study was conducted using laboratory-scale fixed-bed gasification facility [12]. The scheme of the installation is shown in Figure 2.

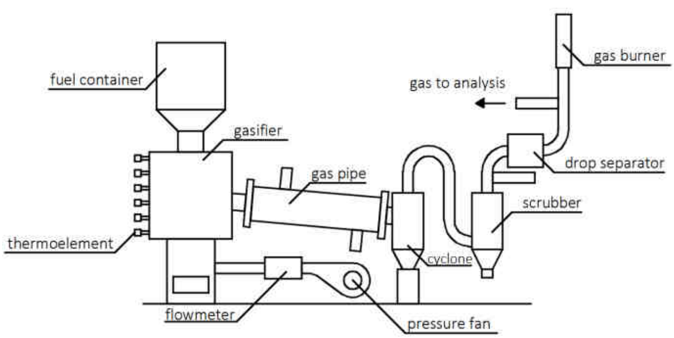

Fig. 2. Scheme of the gasification installation

The main part of the system is a fixed-bed gasifier with the maximum weight of the feedstock of 5 kg. The gasified material was fed into the reactor form the fuel container above. Gasification agent (air) was fed from the bottom by pressure fan. Air flowmeter allows to set the desirable air excess ratio in the gasifier. Produced gas passes basic gas cleaning equipment and the sample to analysis is taken. The internal temperature profile in the reactor is measured by six thermoelements located along the vertical axis of the reactor.

There are four main zones in the reactor: drying zone (water is evaporated), pyrolysis zone (thermal decomposition to volatiles and solid char), reduction zone (where main combustible gas components are produced) and combustion zone (where part of the biomass is combusted to generate heat for endothermic reactions).

Gasification process was carried out for six air excess ratios: 0.12, 0.14, 0.16, 0.18, 0.23, 0.27. The gas composition was measured. The results of this aspect was presented earlier [2].

Additionally, after each gasification tests completed, ash and tar samples were collected in order to performed analyses on heavy metals content. In the Figure 3, example of the tar samples is presented.

a) b)

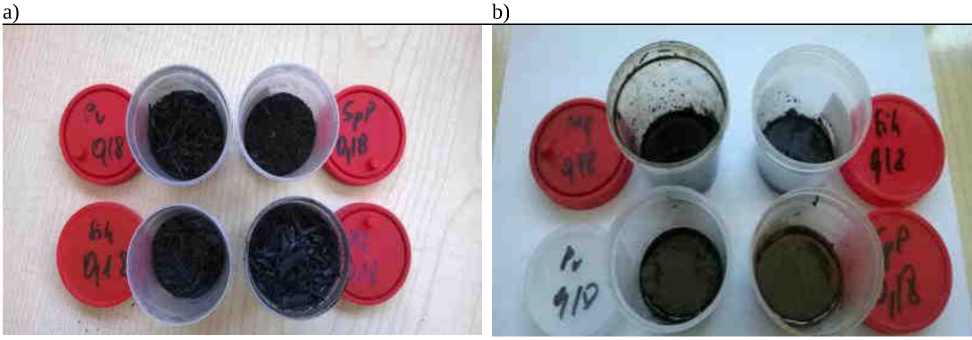

Fig. 3. Analysed samples: a) ash, b) tar

Results of experimental investigation

The key findings demonstrate that gasification process of heavy metal contaminated biomass is characterized by a lower emission of gaseous pollutants into the atmosphere compared to combustion as most of the heavy metals from biomass are moved into solid products. Heavy metal content in tars was much lower in comparison to ash. Taking into consideration the results of the composition the ashes, their potential land application should be carefully analysed. In Tables 5 and 6 the heavy metal concentration in the ash and tar samples is presented.

Analyzing the content of metals in the ashes after gasification, we can see that the maximum content of lead is for MG - 1342 mg/kg while SH_{NPK} has the minimum value - 81 mg/kg. The cadmium concentration is less than < 0.6 mg/kg for all ash samples. For zinc, the maximum content was found for SH_{NPK} - 5805 mg/kg and the minimum content was found for SP_{EFP} - 1918.0 mg/kg.

Table 5

Heavy metal content in ash samples

Plants	Pb	Cd	Zn
	[mg/kg d.m.]		
SH	171.0 ±8.6	< 0.6 ±0.03	2471 ±124
SH_{NPK}	81.0↓ ±4.0	< 0.6 ±0.03	5805↑ ±290
SH_{EFP}	296 ±15	< 0.6 ±0.03	2370 ±118
MG	1342↑ ±67	< 0.6 ±0.03	3308 ±165
MG_{NPK}	947 ±47	< 0.6 ±0.03	3603 ±180
MG_{EFP}	1164 ±58	< 0.6 ±0.03	2909 ±145
SP	599 ±30	< 0.6 ±0.03	2511 ±126
SP_{NPK}	584 ±29	< 0.6 ±0.03	3003 ±150
SP_{EFP}	477 ±24	< 0.6 ±0.03	1918↓ ±96

In case of tar analysis, the content of metals in the ashes after gasification, we can see that the maximum content of lead is for SP sample (91.1 mg/kg), while for MG_{NPK} the lead content is the lowest (12.4 mg/kg). The maximum value of cadmium concentration was registered for MG_{EFP} (5.17 mg/kg), while the minimum values (< 0.6 mg/kg) were found for SH_{EFP}, MG and MG_{NPK} samples. For zinc, the maximum content was found for SP - 225 mg/kg and the minimum content was 19.2 mg/kg for MG_{NPK}.

Analyzing results presented in both tables it should be concluded that most of the heavy metals contained in the feedstock are transferred to solid products, not to liquid phase.

In the case of Poland the first option is regulated in Poland by Decision of Polish Ministry of Agriculture and Rural Development [13]. The maximum level of heavy metals in the fertilizers is 5 mg/kg d.m. for cadmium and 140 mg/kg d.m. for lead. Analyzing the content of lead in the ashes these requirements have been fulfilled only for ashes after SH_{NPK} gasification.

Table 6

Heavy metal content in tar samples

Plants	Pb	Cd	Zn
	[mg/kg d.m.]		
SH	46.0 ±2.3	2.9 ±0.2	100.0 ±5.0
SH_{NPK}	80.0 ±4.0	3.6 ±0.2	184.0 ±9.2
SH_{EFP}	34.2 ±1.7	0.60 ±0.03	138.0 ±6.9
MG	51.2 ±2.6	0.60 ±0.03	39.6 ±2.0
MG_{NPK}	12.4↓ ±0.6	0.60 ±0.03	19.2↓ ±1.0
MG_{EFP}	64.4 ±3.2	5.2 ±0.3	221 ±11
SP	91.1↑ ±4.6	3.9 ±0.2	225↑ ±11
SP_{NPK}	71.7 ±3.6	1.6 ±0.1	174.0 ±8.7
SP_{EFP}	61.5 ±3.1	3.8 ±0.2	177.0 ±8.9

The other option considered is to use ashes after gasification as an amendment improving soil quality at post-industrial areas. However there is no direct regulation for using ashes for improving post-industrial soil quality. But in the case of Poland the quality of the ashes (especially heavy metal content) can be assessed using Decision of the Ministry of the Environment on Sewage Sludge [14]. The maximum permissible levels of metals in sewage sludge used for non-agricultural land reclamation are 25 mg/kg d.m. for cadmium, 1000 mg/kg d.m. for lead and 3000 mg/kg d.m. for zinc. Majority of the tested ashes after gasification process met the standards.

Conclusions

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 (*Miscanthus* x *giganteus*, and *Spartina pectinata*).
- Gasification has many more advantages than the classic combustion. It is characterized by a lower emission of gaseous pollutants into the atmosphere. Heavy metals from the biomass are moved to the solid (not liquid) phase. Concentration of heavy metals may be reduced after recovery of heavy metals from solid products, which will help to protect the environment.
- Heavy metal content in tars was much lower in comparison to ash.
- Analyzing the possibility of the use ash as a fertilizer it should be emphasize that only ashes after SH_{NPK} gasification have been fulfilled the requirements.
- Majority of the tested ashes after gasification process met the standards as an amendment improving soil quality at post-industrial areas.

Acknowledgments

The paper has been prepared within the frame of the FP7-People-2013-IAPP (GA No610797) Phyto2Energy Project.

References

[1] Stolarski MJ, Krzyżaniak M, Śnieg M, Słomińska E, Piórkowski M, Filipkowski R. Int Agrophys. 2014;28:201-211. DOI: 10.2478/intag-2014-0009.
[2] Werle S, Bisorca D, Katelbach-Woźniak A, Pogrzeba M, Krzyżak J, Ratman-Kłosińska I, et al. J Energy Inst. 2017;3:408-417. DOI: 10.1016/j.joei.2016.04.002.
[3] Chomiak J, Longwell JP, Sarofim AF. Prog Energ Combust. 1989;15:109-129. DOI: 10.1016/0360-1285(89)90012-9.
[4] Kalina J. Thermal Sci. 2012;16:827-848. DOI: 10.2298/TSCI120126124K.
[5] Skorek-Osikowska A, Bartela Ł, Kotowicz J, Sobolewski A, Iluk T, Remiorz L. Energy. 2014;67:328-340. DOI: 10.1016/j.energy.2014.01.015.
[6] Kalina J. App Therm Eng. 2011;31:2829-2840. DOI: 10.1016/j.applthermaleng.2011.05.008.
[7] Werle S. Energies. 2015;8:8562-872. DOI: 10.3390/en8088562.
[8] Nilsson S, Gómez-Barea A, Cano DF. Fuel. 2012;92:346-353. DOI: 10.1016/j.fuel.2011.07.031.
[9] Aznar M, San Anselmo M, Manyà JJ, Murillo MB. Energy Fuels. 2009;23:3236-45. DOI: 10.1021/ef801108s.
[10] Yang C, Wang J, Lei M, Xie G, Zeng G, Luo S. J Environ Sci. 2010:22;675-680. DOI: 10.1016/S1001-0742(09)60162-5.
[11] ISO 17225-2:2014 Solid biofuels -- Fuel specifications and classes. www.goo.gl/DyYPDD.
[12] Werle S, Wilk RK. Patent nr P-397225 Instalacja zgazowania biomasy, zwłaszcza osadów ściekowych (Patent P-397225. based on the application from 2.12.2011, Biomass gasification installation, mainly for sewage sludge). www.goo.gl/49jUao.
[13] Rozporządzenie Ministra Środowiska z dnia 1 września 2016 r. w sprawie sposobu prowadzenia oceny zanieczyszczenia powierzchni ziemi DzU 2016. nr 0 poz.1395 (Regulation of the Polish Ministry of

Environment on procedure how to conduct land surface pollution assessment). <http://isap.sejm.gov.pl/DetailsServlet?id=WDU20160001395+2016%2409%2405&min=1> accessed 2017-05-09.

[14] Rozporządzenie Ministra Środowiska z dnia 6 lutego 2015 r. w sprawie komunalnych osadów ściekowych (Regulation of the Minister of the Environment on municipal sewage sludge dated 25 February 2015). Journal of Laws of Poland, No 2015, Item 257. <http://isap.sejm.gov.pl/ DetailsServlet?id=WDU20150000257> accessed 2017-05-09.

WŁAŚCIWOŚCI PRODUKTÓW ODPADOWYCH ZE ZGAZOWANIA ROŚLIN ENERGETYCZNYCH ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI

[1] Instytut Techniki Cieplnej, Politechnika Śląska, Gliwice, Polska
[2] Instytut Ekologii Terenów Uprzemysłowionych, Katowice, Polska
[3] Instytut Badań Energetyki, Bukareszt, Rumunia

Abstrakt: Zdolność fitoremediacyjna roślin energetycznych jest powszechnie znana. Wciąż jednak niedostatecznie rozpoznanym problemem jest możliwość efektywnego, bezpiecznego i ekologicznego wykorzystania energetycznego takich zanieczyszczonych roślin. Postuluje się, że jednym z takich sposobów może być zgazowanie, polegające na przekształcaniu substancji organicznej w palną mieszaninę gazów. Niestety proces ten wiąże się z powstawaniem stałych i ciekłych produktów odpadowych. W pracy przedstawiono rezultaty badań podstawowych właściwości fizyczno-chemicznych stałych (popiół) i ciekłych (smoły) produktów odpadowych pochodzących z procesu zgazowania roślin energetycznych uprawianych na terenie zdegradowanym ekologicznie. Uprawa roślin prowadzona była z zastosowaniem modyfikacji polegających na dodawaniu do gleby nawozów (N, P, K) oraz aplikowania szczepionki, będącej preparatem złożonym ze specjalnie dobranych kultur mikroorganizmów. Proces zgazowania prowadzono w laboratoryjnym reaktorze ze złożem stałym. Wykorzystano trzy rodzaje roślin energetycznych: miskanta olbrzymiego, ślazowca pensylwańskiego i spartynę grzebieniastą. Rośliny pozyskano z gruntów ornych zanieczyszczonych metalami ciężkimi zlokalizowanych w okolicach Bytomia na Górnym Śląsku. Zbadano wpływ rodzaju dodatku do gleby na jakość powstałego odpadu. Wyniki pokazują, że dodatek nawozu (N, P, K) do gleby powoduje, że w fazie stałej po procesie zgazowania jest wyższa zawartość cynku w porównaniu z próbą kontrolną. Odwrotna sytuacja obserwowana jest w przypadku ołowiu. Aplikacja szczepionki sprzyja z kolei wiązaniu ołowiu, a utrudnia wiązanie cynku. W obu przypadkach zawartość kadmu w popiele jest poza granicą oznaczalności. W przypadku smół nie można stwierdzić istotnego wpływu rodzaju dodatku do gleby na zawartość metali ciężkich.

Słowa kluczowe: zgazowanie roślin energetycznych, metale ciężkie, smoły, popiół