Short Communication

Select Polymer Wastes as Possible Sources of Solid Recovered Fuels

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Abstract

The basic fuel properties of select polymer wastes such as moisture content; elemental composition; caloric value; content of combustible, non-combustible, and volatile substances, and results of stechiometric calculations of total and partial combustion of particular polymers are presented in this manuscript. The tests were based on polymers commonly used in many branches of the economy, for example in the construction, automobile, pharmaceutical, and packaging industries, as well as in gardening.

Keywords: waste, polymers, recycling, energy recovery, thermal degradation of plastics

Introduction

Plastics are widely used in all branches of the economy and in households. Owing to their diversity and unique chemical and physical properties as well as easy ways to modify them using special additives, they are universal material. Unfortunately, such a diversity makes their reuse complicated [1-4]. The basic sources of polymer waste are municipal waste, unused post-production waste, recycling of cars,t etc. It is estimated the hat share of plastics in total mass of municipal waste is in the range 7 to 14%. It is also estimated that approximately 800,000 mg of plastic wastes are created in Poland each year. According to GUS data in 2011 in Poland, 1,606,700 mg of plastic waste was identified in the stream of municipal wastes [4-7].

The “big five” of plastics, the most widely represented in the market, are polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), and polyethylene terephthalate (PET) [7-9]. Most of the recycling technologies use a uniform polymer. Fractions of the plastic waste that are not suitable for recycling is usually stored in municipal landfills. However, energetic potential of the plastics makes it possible to use them in thermal processes, like gasification, pyrolysis, or combustion [9-11]. Co-combustion in a cement kiln could be used as one of the methods to utilize polluted and mixed polymer waste. In cement kilns ideal conditions for co-combustion of fuels from wastes could be found. The following factors have a great impact on this fact [10-12]: High temperature (1,400ºC), large length of the furnace, the long time fuels stay in the furnace, and alcaic environment. Owing to the parameters listed, thermal degradation of wastes in cement furnaces is considered to be a method that is safe for the natural environment. Due to lack of stability of the content of wastes, manufacturers of cement who use them as fuels in the process of co-firing determined their own standards concerning fueling properties. In the Polish cement industry the following criteria are binding [12]: heating value (W_d) more than 14 MJ/ kg, chlorine concentration (Cl) below 0.5%, sulfur concentration (S) below 2.0%, content of total PCBs (polychlorinated biphenyls) and PCTs (polychlorinated terphenyls) to 50 ppm, heavy metal concentrations below 2,500 ppm, content of chromium and mercury to 100 ppm, (including mercury content to 10 ppm), and water content to 10%. In the case of solid waste obtained as fuel, apart from the parameters listed above, cement plants also consider such factors as temperature of ignition, moisture content, fly ash content, grain size distribution, etc. [12].

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Table 1. Basic fuelling properties of select polymer wastes.

Properties	Unit	Type of polymer waste			
		PE	PP	PVC 1	PVC 2
Moisture content	%	0.13	0.09	0.03	0.01
Bulk density	kg/m^3	380	380	183	259
Heat of combustion	MJ/kg	46.87	46.78	17.28	22.36
Gross Heating Value	MJ/kg	43.37	43.33	16.54	21.80
Content of volatile elements	%	94.24	98.78	83.83	96.68
Content of combustible elements	%	99.30	98.78	70.20	71.74
Content of ash	%	0.57	1.13	16.15	3.30
Flash point	ºC	318	270	283	218
Smoking target temperature	ºC	342	280	-	-
Chrome	ppm	<11.30	<1.00	<11.30	<11.30
Carbon (C)	%	88.36	87.51	36.26	38.40
Hydrogen (H)	%	15.75	15.64	5.06	2.73
Sulfur (S)	%	0.21	0.20	0.05	0.35
Nitrogen (N)	%	0.49	0.44	1.63	0.61
Chlorine (Cl)	%	0.19	0.20	0.30	0.30
Oxygen (O)	%	0.00	0.00	56.67	42.74

Fuel properties for plastics should be carefully examined due to the potentuially high environmental impact of its combustion [13, 14]. On the other hand in some cases it could be as a source of high environmental relief [15-17].

Method

Characteristic of Tested Wastes

In order to test the suitability of polymer waste for power production, four types of polymer waste were examined. The following types of waste were analyzed: polyethylene, polypropylene, and two types of polyvinyl chloride (PVC 1 – wall panels, PVC 2 – foil). These polymer wastes were selected because they are commonly used in many branches of the economy: construction, gardening, medicine, automobile industry, and in households. Selected wastes comprise three main groups of polymers, which participate in the market demand in the following way: polyethylene (29%), polypropylene (19%), and polyvinyl chloride (12%) [10, 11].

Testing Methodology

The purpose of the tests was to determine basic fuel properties of polymer waste in order to to use them as a source of energy. Scope of tests included the following parameters [13-16]: moisture content (W), content of combustible elements, content of ash (A), heat of combustion (W_g), heating value (W_d), elementary composition (C, H, S, N, Cl, O), and concentration of chromium (Cr). Preliminary processing of the polymer wastes consisted of decomposition into analytical graining. All the markings were carried out in accordance with a valid standard and each of the tests was repeated a few times [18-21].

Results and Discussion

Energetic evaluation of the polymer wastes may supply many properties. However, the following are considered the most important: elemental composition, ash content (ballast), and – first of all – moisture content and calorific value (Table 1).

Moisture content is one of the basic parameters that determine suitability of fuel for energetic purposes. It significantly influences caloric value of fuel and plays an important role in the process of combustion. Moisture content has an impact on the process of combustion as it causes increases in the volume of the stream of exhaust gases. Tested polymer wastes are characterized by low moisture content (below 1%) which is a value inside the range of error limit. A characteristic value for fuel is its calorific value. It depends on the type and amount of the combustible particles in the fuel and moisture content. The higher calorific value, the more heat is obtained while burning the same amount of the solid fuel. Analyzed wastes

Table 2. Content of dry and wet exhaust flue gases for λ=1.4.

Components	Dry exhaust flue gas [kmol/kmol dry flue gas]				Wet exhaust flue gas [kmol/kmol wet flue gas]			
	PE	PP	PVC 1	PVC 2	PE	PP	PVC 1	PVC 2
CO_2	0.1030	0.1030	0.1742	0.1805	0.0928	0.0927	0.1520	0.1676
SO_2	0.0001	0.0001	0.0001	0.0006	0.0001	0.0001	0.0001	0.0006
N_2	0.8335	0.8336	0.7674	0.7609	0.7507	0.7507	0.6697	0.7066
O_2	0.0633	0.0633	0.0580	0.0577	0.0570	0.0570	0.0506	0.0536
HCl	0.0000	0.0000	0.0002	0.0002	0.0000	0.0000	0.0002	0.0002
H_2O	-	-	-	-	0.0993	0.0995	0.1273	0.0714

have a high heating value. In the case of PE and PP it is triple the minimum required by cement plants (14 MJ/kg). Furthermore, analyzed waste of polyvinyl chloride has a caloric value of 17-22 MJ/kg, which is close to that of fossil fuels like hard coal, which has calorific value of 16.7-32.7 MJ/kg [22]. From the ecological point of view, ash content is an important issue, because it contains heavy metals. Content of non-combustible mineral substance in fuel and its content influence the quality of fuel (heat of combustion) and its suitability for energetic purposes, and determines exploitation parameters of the hearth.

Tested polymer wastes contain relatively little ash. For polyolefin (PE, PP) it amounts to 0.57-1.13%, and for PVC 1 ash content falls between 3.30-16.15%. Content of volatile elements is one of the most characteristic features of solid fuels, as they are composed of gas products and tar fumes created as a result of thermal decomposition of the solid fuel without access to air. The amount of volatile elements decreases with the increase of the level of carbonization of soil fuel [6]. Fuels with high amounts of volatile elements give a long flame during burning and require additional air supply to assure non-smoke combustion. Tested polymer waste has a highly volatile particle content that exceeds 90%.

An important issue from the energetic point of view is flash point. In order to initiate the combustion process, fuel should be heated to the temperature at which ignition shall start. Flash point depends on the content of volatile elements in fuel. Analyzed polymer fuel melts in temperatures below the flash point and then decomposes, creating volatile elements with low molecular mass. The lowest flash point was noted for PVC 2, which amounted to 218ºC, and the highest flash point was noted for PE, which reached 318ºC. Content of chromium in the polyethylene waste and polyvinyl chloride waste reached 11.30 ppm, and in polypropylene waste chromium content fell below the level of determination. Tested polymer waste contains 10 times less chromium than the value acceptable by cement plants.

Analysis of elementary composition of polyethylene and polypropylene waste showed that tested waste consisted mainly of carbon, which complies with their construction, as they belong to polymer compounds characterized by long carbon chains–C–C–C–. Performed tests show that PE and PP have a high carbon content of approximately 89%, which confirms the possibility of effective burning. Polyolefin waste may be initially classified for the gasification process, during which synthetic gas is obtained (CO, H_2). The presence of other chemical elements such as hydrogen, sulfur, nitrogen, chlorine, and oxygen is slight and can come from additives such as plasticizers, dyes, etc. In the wastes of polyvinyl chloride high oxygen content was observed in approximately 42-57%. Carbon content reached 36-38%. Content of sulfur in the polyvinyl chloride waste does not exceed values required by cement plants. The value obtained during tests is 6 times lower. Similarly, chlorine content is 1,5 times lower than the level required by cement plants and determined for the co-firing process. Table 2 presents results of stoichiometric calculations assuming that burning is total and complete. In flue gases the following products are dominant: CO_2, SO_2, N_2, O_2, and H_2O. Other substances created during partial and incomplete burning appear in slight amounts and will not have a significant influence on the balance of elements. The relation of excessive air was determined as λ=1.4 in order to assure minimum 6% content of oxygen in flue gases, which is required by law for the process of thermal transformation of waste [23].

Conclusions

Polymer waste may qualify as solid recovered fuel that meets the requirements of cement plants for the process of co-combustion. Conditions of combustion in cement furnaces (1,400ºC, burning time of a few second) makes it impossible to create harmful gasous products. On the basis of obtained results we may state that examined waste had low moisture content, which does not exceed 1.0%, polymer waste contains a slight amount of ash (PVC 1) – approximately 16%, content of chloride and sulfur in examined polymer waste does not exceed the values required by the Polish cement industry, all the examined waste has high heating value, which definitely exceeds the required 14 MJ/kg, a desired parameter for solid fuels; the fraction required by cement plants has been determined as 30 mm × 30 mm pieces. Concerning such a criterion, polymer wastes selected from the municipal waste stream before the co-combustion process should be mechanically crushed in order to achieve the required size.

References

1. SAECHTLING H. Plastics. Handbook, 5th edition. Scientific and Technical Publishing Warsaw **2000** [In Polish].
2. CZOP M., BIEGAŃSKA J. Impact of selected chemical substances on the degradation of the polyolefin materials. Chemik, **66**, (4), 307, **2012**.
3. JIANG Z., LIU X., JIAO S., HAN J. Study of Thermal Degradation of Polymers. Advanced Materials Research, **652-654**, 1664, **2013**.
4. VAN KREVELEN D.W., TE NIJENHUIS K. Properties of Polymers. Elsevier Science, **2009**.
5. AL-SALEM S.M., LETTIERI P., BAEYENS J. Recycling and recovery routes of plastic solid waste (PSW). Waste Manage. **29**, (10), 2625, **2009**.
6. FORTELNÝ I., MICHÁLKOVÁ D., KRULIŠ Z. An efficient method of material recycling of municipal plastic waste. Polym. Degrad. Stabil. **85**, (3), 975, **2004**.
7. COLOMBA DI BLASI. Modeling and simulation of combustion processes of charring and non-charring solid fuels. Prog. Energ. Combust. **19**, (1), 71, **1993**.
8. KOZŁOWSKI E., KROP E., CZACHOWSKA-KOZŁOWSKA D., WIATOWSKI M.. Processes of decomposition of used plastics. Chemical Industry, **84**, (12), **2005** [In Polish].
9. LEION H., MATTISSON T., LYNGFELT A. Solid fuels in chemical-looping combustion. International Journal of Greenhouse Gas Control, **2**, (2), 180, **2008**.
10. CZOP M., KOZIELSKA B. Physicochemical properties of waste mix from polyolefin group. Archives of Waste Management and Environmental Protection. **12**, (1), 47, **2010** [In Polish].
11. CZOP M. Analysis of impact of selected chemical substances on the properties of polyolefin waste. Pol. J. Environ. Stud. **21**, (5A), 48, **2012**.
12. CZOP M., GEBAUER E. Testing of basic fuel parameters of the upholstery wastes in the light of their utilization in cement furnace. Archives of Waste Management and Environmental Protection. **12**, (4), 15, **2010** [In Polish].
13. PIKOŃ K. Environmental Impact of combustion. Appl. Energ. **75**, (3-4), 213, **2003**.
14. PIKOŃ K. Environmental aspects of municipal waste to energy systems, conference proceedings, Second International Symposium on Energy form Biomass and Waste, International Waste Working Group, ISBN 978-88-6265-004-5, Venice, **2008**.
15. PIKOŃ K., GASKA K. Greenhouse gases emission mitigation relevant to changes in MSW management system., JAPCA J. Air Waste Ma., **60**, (7), 782, **2010**.
16. PIKOŃ K. Polyethylene in MSW management system, Archives of Waste Mangement and Environmental Protection, ISSN 1733-4381, **9**, 29-46, **2009** [In Polish].
17. NADZIAKIEWICZ J., PIKOŃ K., STELMACH S. Removal of hydrocarbon pollutants from syngas by using plasma-catalytic reactor, Przemysł Chemiczny **91**, (6), 1270, **2012** [In Polish].
18. PN-ISO 334: Solid mineral fuels. Determination of total sulfur. Eschka method, **1997**.
19. PN-ISO 587: Solid mineral fuels. Determination of chlorine using Eschka mixture, **2000**.
20. PN-G-04523: Solid mineral fuels. Determination of nitrogen – Semi-micro Kjeldahl method, **1992**.
21. ISO 609: Solid mineral fuels. Determination of carbon and hydrogen - High temperature combustion method, **1996**.
22. NADZIAKIEWICZ J. Combustion of soild wastes, Gonme editorial, Katowice **2001** [In Polish].
23. Order of the Minister of Economy dated 21 March **2002** concerning requirements for the thermal processes of transformation of wastes (Journal of Acts **2002** No. 37 Item 339).