Krupa-Żuczek K., Nowak A.K.*, Wzorek Z., Gorazda K.

Cracow University of Technology, the Faculty of Chemical Engineering and Technology, Warszawska 24, 31-155 Kraków, *e-mail:akn@chemia.pk.edu.pl, phone: +48 126282716, fax: +48 126282036

The characteristic of solid waste after biomass incineration for energy purposes

Abstract

The study included the analysis of the material generated by the combustion of a mixture of annual plant biomass, i.e. grass from Natura 2000 areas mixed with post-slaughter waste in the form of meat-bone meal. The grass used in the process cannot be used for feeding animals due to its low nutrition value and high degree of lignification. The analyzed materials were obtained in the process of waste biomass combustion for energy purposes. The combustion process was carried out on an industrial scale in a paper production plant. The ashes were analyzed by fluorescence and X-ray diffraction and by AAS spectroscopy. The combination of above methods allowed to evaluation of elemental composition as well as the phases of the solids. The amorphous structure of the obtained vitrificate was confirmed using the XRD method. The results show that the material have two potential uses. First for the purpose of disposing of heavy metals by closing them in the vitreous. Fly ash can be used as a substitute for raw materials for the production of fertilizer. This is indicated by the relatively high levels of potassium, calcium and phosphorus. Potassium is in this case a desirable element, both in the formation of vitreous structures and in the macroelement.

Keywords: biomass, vitrificat, fly ash, waste grass, MMK

1. Introduction

The energy industry in Poland is still based mainly on fossil fuels like hard coal and brown coal. For environmental reasons and due to the adaptation of the Polish legal system to the European Union requirements, there is a change in a feedstock profile in this branch of industry. Pro-ecological measures have been undertaken in connection with:

- the occurrence of the effect of winter smog,
- an increase in the amount of generated waste suitable for thermal utilization,
- problems concerning the possible utilization of agricultural products (grass) from the regions of *Nature 2000* [1-3].

An additional aspect in favour of the thermal usage of plant biomass for energy purposes is the implementation of a directive of the European Parliament and of the Council 2009/28/EC of 23 April 2009 which reduces the emission of pollutants generated as a result of combustion of conventional fuels. The EU obliged the member states by 2020 to fulfil the 3x20% principle regarding the reduction of emitted greenhouse gases by 20% in relation to the year 1990. The other obligation refers to the reduction of energy consumption by 20% and an increase in the application of renewable energy sources by 15% [2,4-6].

Biomass which may constitute a potential energy source is an organic substance of both plant and animal origin, e.g. wood, energy plants, as well as organic waste from wood, agricultural and animal industry. According to the Directive of the European Parliament and of the Council 2009/28/EC biomass is "the biodegradable part of products, waste and residues from biological origin from agriculture (including vegetable and animal substances), forestry

and related industries including fishery and aquaculture, as well as the biodegradable part of industrial and municipal waste".

Both the depletion of conventional energy sources and the technological advancement encourage to search for alternative solutions to managing the excess of currently produced biomass, allowing for obtaining energy. Apart from the traditional organic feedstock used for energy purposes, like firewood, all the residues from numerous branches of industry, agriculture, forestry, and even municipal waste and sewage sludge, become an energy source [7].

The biomass potential may be used in the energy industry in a direct way, as a fuel in the processes of both incineration and co-incineration, as well as a feedstock for producing biogas and biofuel, aiming at generating electrical energy [8].

The biomass composition may be expressed with the formula $CH_{1.45}O_{0.6}$ which points to a high heat of combustion of this ty pe of material. Biomass, however, is a more environmentally-friendly feedstock. As a result of its incineration such an amount of carbon(IV) oxide is produced that is absorbed by plants during the photosynthesis process. This type of fuel constitutes one of the most important sources of renewable energy in Poland and great expectations have been placed in biomass as a high-energy potential feedstock [5,8-10].

What speaks for the use of biomass energy is also a negligible amount of carbon footprint, which is a measurement of anthropogenic emission of carbon dioxide, assigned to biomass and considering its whole life-cycle. Lowering of this parameter at a stage of energy generation contributes to a positive assessment of the life-cycle of all the goods making use of the biomass energy [10,11].

That is why works have been undertaken aiming at constructing an installation for incinerating plant and animal biomass. In the course of studies into the processes of biomass incineration process waste was obtained, i.e. fly ashes and vitrificates. The fly ashes were collected from two points on the flue gas treatment installation – a filter and a settling tank [12-14].

Technological solutions based on the incineration and co-incineration of waste of both plant and animal origin are a part of waste management aiming at not only the neutralization of solid waste but also reducing its volume and mass. There is more than 320 kg of solid residues per one ton of incinerated waste [15-19], whereas there is only 40 kg per one ton of incinerated plant waste. The ash obtained in the calcination process has the ability to accumulate both valuable and harmful substances [20,21].

Thus it was necessary to apply the vitrification process in order to neutralize environmentally-harmful compounds and fly ash. In the case under discussion vitrification consisted in a controlled energy delivery and reaching a temperature of 1200-1300°C. At such a high temperature the calcined material undergoes thermal decomposition with the release of gaseous products and the incineration process takes place. Due to the process of rapid cooling the obtained ash has the structure of glass. Owing to the application of the vitrification process a material is obtained with inorganic compounds built into the glass structure, which is additionally resistant to external factors and chemical agents [19,21, 22].

2. The material for research

The analyzed material was the ash resulting from the incineration of annual biomass and meat-bone meal. The plant biomass was obtained from dried grass and weeds which had not undergone any agricultural treatment and which came from the regions of low air pollution and distant from road routes. The biomass was characterized by a significant mass fraction of hay originating from the region *Nature 2000*.

Three types of materials were analyzed:

- the ash from the settling tank
- the ash from the filter
- the vitrificate

3. Research methods

Both in the raw material and in ash the following were determined: the total phosphorus content after a sample mineralization in a mixture of nitric(V) and hydrochloric acids in the ratio of 3:1, the content of soluble phosphate forms in hydrochloric acid with a concentration of 1mol/dm^3 , in neutral ammonium citrate, and in water. The obtained solutions were studied with the help of the differential photometric method consisting in the formation of a yellow-coloured phosphorus-vanadium-molybdenum complex and the photometric measurement of absorbance at a wavelength of 430nm.

The determination of calcium content – the titration method – relies on dissolving the sample in nitric(V) acid, precipitating phosphates in the form of bismuth(III) phosphate(V), and then determining the calcium content during complexometric titration with EDTA in the presence of fluorexon.

The determination of humidity – with the aid of a moisture balance by RADWAG company at a sampling time of 5s and a temperature of 105° C.

The contents of potassium and heavy metals were determined by the AAS method with the Perkin Elmer AAnalyst 300 following the sample mineralization with a concentrated nitric(V) acid.

Phase composition was determined by XRD method with the use of Philips X'pert PW1830 apparatus. Content analysis by the X-ray fluorescence method was carried out on MiniPal4 apparatus by PANalytycal.

4. Results and discussion

In the first stage of the research analyses of the material by the XRF method were performed which showed that the studied material contained the following elements: aluminium, silicon, phosphorus, sulphur, potassium, calcium, and iron, as well as titanium, vanadium, chromium and manganese, though in significantly smaller amounts (Fig. 1.).

a)



b)

c)

Fig. 1. Analysis result by X-ray fluorescence of: a) vitrificate, b) ash from the settling tank, c) ash from the filter

An initial, qualitive analysis of the materials composition measured by XRF method showed significant amounts of silicon present in all ash samples. The concentration of this element in excess of 30% is most likely due to the type of fuel mixture used. This value is justified because the biomass used for incineration for energy purposes not only contains silica but also is enriched during the preparation stage (eg mowing, pelleting and then comminuting before entering the burner). This is confirmed by the results obtained by X-ray diffraction analysis, where clear and numerous effects from SiO₂ crystals were observed. Considering the analyzed ashes and the obtained vitrificats as potential raw material for fertilizers production, the attention should be paid on to the presence of calcium and phosphorus as macronutrients and magnesium, sulfur and potassium as micronutrients. Potassium is a desirable element, not only as a fertilizers component, but also in the process of binding heavy metals due to its low melting point, which will have a beneficial effect on vitreous. In the smallest dust that was extracted from the air purifying filters sulphur in combination with calcium produces gypsum, considered as a waste material. XRF analysis showed only trace amounts of heavy metals. Only iron occurs in slightly higher quantities in all analyzed biomass combustion products. In further studies, using the powder X-ray diffraction method and the AAS method, analyzes were carried out to confirm the results obtained by this method



b)

a)



c)

Fig. 2. Difractograms of: a) vitrificate, b) ash from the settling tank, c) ash from the filter

The studies by the XRD method (Fig. 2.) proved that each of the described materials forms different systems of compounds, and so:

- the ash from the settling tank contains iron-calcium-potassium phosphate and silica,
- the ash from the filter consists of quartz and negligible amounts of calcium sulphate dihydrate,
- the vitrificate is characterized by an amorphous form typical of glass.

Table 1 presents research results for selected parameters, obtained by means of the AAS method and standardized methods. The data show that the ash after the incineration of meat-bone meal and plant biomass in a form of annual grass may be used as a substitute for a phosphorus-bearing feedstock. Special attention should be paid to the ash collected from the filter due to the phosphorus and calcium content and better afterburning of the material. An additional advantage of this type of material is a low content of heavy metals. The vitrificate,

on the other hand, contains smaller amounts of the described compounds, which may be evidence of closing them within a sparingly soluble glassy form.

Parameter	Analyzed material		
	Ash from the settling	Ash from the	Vitrificato
	tank	filter	viumcate
Volatile matter [%]	13.29	7.34	0
Humidity content [%]	2.67	1.87	0.12
Total phosphorus content [%]	1.45	5.69	1.01
Calcium content[%]	6.94	7.06	2.51
Potassium content [%]	1.65	6.52	0.12
Iron content [%]	0.52	0.22	0.20
Magnesium content [%]	1.54	2.78	0.38
Zinc content [%]	0.05	0.03	0
Cadmium content [%]	0.008	0.002	0.0006
Lead content [%]	0.002	0.003	0.0002
Copper content [%]	0.003	0.005	0.0006
Chromium content [%]	0.008	0.004	0.002

Table 1. Characteristic of materials

5. Conclusions

The conducted research shows a different character of waste after the biomass incineration. This is connected with the origin of waste, hence the distribution in the installation for incinerating and treatment of process waste.

The values obtained for the parameters 'volatile matter' and 'humidity content' indicate that the process occurred in accordance with the assumptions made at the stage of the installation design.

The undertaken operations allow to identify new approaches to make use of the waste after biomass incineration for energy purposes and to recycle elements to the production cycle. This gives new possibilities for feedstock substitution and implementing the principles of sustainable development in heat power engineering.

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References

- Polish law, Act of 20 February 2015 on Renewable Energy Sources, Dz.U. 2015 poz. 478 (in Polish)
- Central Statistical Office of Poland, Energy from renewable sources, Energia ze źródeł odnawialnych w 2014 r. Warszawa 2015, www.stat.gov.pl (2015). Accessed_10 December 2015 (in Polish)
- 3. Taubman, J.: Carbon and alternative sources of energy, Węgiel i alternatywne źródła energii. Wydawnictwo Naukowe PWN, Warszawa, 2011 (in Polish)
- Piekarczyk, M., Kotwica, K., Jaskulski D.: Influence of using ash from barley straw combustion on chemical properties of lightweight ground, Wpływ stosowania popiołu ze słomy jęczmienia jarego na chemiczne właściwości gleby lekkiej, Fragm. Agron. 28(3), 91–99 (2011) (in Polish)
- 5. Jarosz, Z., Faber, A., Borzęcka-Walker, M., Pudełko, R.: Evaluation and regionalisation of potential of biomass as byproduct from grain production, Szacowanie i regionalizacja potencjału biomasy ubocznej z produkcji zbóż. Stowarzyszenie ekonomistów rolnictwa i

agrobiznesu, Roczniki Naukowe, tom XVI, zeszyt 3, 99-103 http://ageconsearch.umn.edu/bitstream/201832/2/16-3-Jarosz.pdf (2014). Accessed 10 May 2017(in Polish)

- Denisiuk, W.: Straw value of energy, Słoma potencjał masy i energii. Inżynieria Rolnicza 2(100), 23-30, http://ir.ptir.org/artykuly/pl/100/IR(100)_2072_pl.pdf (2008). Accessed 10 December 2016(in Polish)
- Karcz, H., Kantorek, M., Grabowicz, M., Wierzbicki, K.: Straw as the fuel in boilers for energy production, Możliwość wykorzystania słomy jako źródła paliwowego w kotłach energetycznych. Inżynieria Środowiska, Piece Przemysłowe & Kotły XI-XII, 8-15 (2013) (in Polish)
 - 8. Vassilev S. V., Baxter D., Andersen L. K., Vassileva Ch. G.: An overview of the chemical composition of biomass, Fuel, Vol. 89, Issue 5, 913–933 (2010) doi.org/10.1016/j.fuel.2009.10.022
- Vassilev, S.V., Baxter D., Andersen L.K., Vassileva C.G.: An overview of the chemical composition of biomass. Fuel, Vol. 89, Issue 5, 913–933 (2010). doi.org/10.1016/j.fuel.2009.10.022
- Kajda-Szcześniak, M.: Evaluation of the quality of briquettes produced on the basis of corn straw and low density polyethylene. Archives of Waste Management and Environmental Protection, Vol. 14, Issue 4, 41-50 (2012)
- Macak, M., Nozdrovicky, L., Maga, J.: Environmental effects of the burning of the straw for energy purposes, Agricultural Engineering International: CIGR Journal, 2015, 218-226
- Varitis, S., Kavouras, P., Pavlidou, E., Pantazopoulou, E., Vourlias, G., Chrissafis, K., Zouboulis, A.I., Karakostas, Th., Komninou Ph.: Vitrification of incinerated tannery sludge in silicate matrices for chromium stabilization, Waste Management, Vol. 59, 237-246, (2017). doi.org/10.1016/j.wasman.2016.10.011
- Bernardo, E., Scarinci, G., Colombo P.: Vitrification of waste and reuse of waste-derived glass. In: Meyers R.A. (ed.), Encyclopedia of Sustainability Science and Technology, Springer, Berlin (2012). 11581-11613
- 14. Celary, P., Sobik-Szołtysek J.: Vitrification as an alternative to landfilling of tannery sewage sludge. Waste Management, Vol. 34, Issue 12, 2520-2527 (2014) doi.org/10.1016/j.wasman.2014.08.022
- 15. Piecuch T.: Termiczna utylizacja odpadów. Politechnika Koszalińska, Koszalin 1998.
- Haugsten K.E., Gustavson B.: Environmental properties of vitrified fly ash from hazardous and municipal waste incineration. Waste Management, Vol. 20, 166-167 (2000) doi.org/10.1016/S0956-053X(99)00325-6
- 17. Rawlings, R.D., Wu, A.R., Boccaccini J.P.: Glass-ceramics: their production from wastes. A review. Mater. Sci., 41, 733-761. (2006). doi:10.1007/s10853-006-6554-3
- 18. Piecuch, T.: Waste thermal utilisation, Termiczna utylizacja odpadów. Politechnika Koszalińska, Koszalin (1998) (in Polish)
- Haugsten, K.E., Gustavson, B.: Environmental properties of vitrified fly ash from hazardous and municipal waste incineration. Waste Management, Vol. 20, Issue 2-3, 167-176 (2000). doi.org/10.1016/S0956-053X(99)00325-6
- Xiao, Y., Oorsprong, M., Yang, Y., Voncken, J.H.L.: Vitrification of bottom ash from a municipal solid waste incinerator. Waste Management, Vol. 28, Issue 6, 1020-1026 (2000). doi.org/10.1016/j.wasman.2007.02.034

- 21. Platače, R., Adamovičs, A.: The evaluation of ash content in grass biomass used for energy production. In: Brebbia, C.A., Magaril, E.R. Khodorovsky, M.Y., Energy Production and Management in the 21st Century, The Quest for Sustainable Energy, WITTPress, 1057-1065 (2014)
- 22. Cubars, E., Poisa, L., Noviks, G., Platace, R., Bumane, S.: Analysis of heavy metal content in the dry matter of different energy crops. Environment. Technology. Resources, Proceedings of the 10th International Scientific and Practical Conference. Volume II, Rezekne, Latvia, 91-95 (2015)