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Gasification of Selected Biomass Waste for Energy Production and Chemicals Recovery

Marek Dudyński
Modern Technologies and Filtration, Przybyszewskiego 73/77 lok. 8, 01-824 Warsaw, Poland
marek.dudynski@mtf.pl

In this paper we present a novel design of a gasification plant suitable for utilizing difficult waste biomass and producing heat. The plant was designed to be installed in biomass processing factories where it could successfully replace existing boilers and produce technological steam, while processing the biomass waste resulting from factory main production process. We present in details two such plants, which process feathers or tanned leather waste, and analyses the properties of bottom ash resulting from the gasification process. The bottom ash obtained from gasification of tanned leather waste contains chromium oxide, whereas the one obtained from feathers is rich in phosphor and these components can be easily recovered and reused, closing one loop in circular economy. The study proved that gasification allows for effective conversion of energy and in some cases are clearly advantageous over incinerations producing ashes safer and easier to handle.

1. Introduction

In recent times gasification receives a growing attention as a promising waste utilization method and an alternative for incineration, especially in the industrial context (Obernberger and Thek, 2008, Sosnowska et.al. 2014, Arena et.al, 2016). This technology allows for effective conversion of waste into energy and produces a limited amount of pollutants, although maintaining the process stability is more challenging than in case of incineration. In many biomass processing factories, it is possible to replace existing boilers with gasification systems fed with locally produced biomass waste. In this way the energy necessary for running a factory can be derived from utilisation of the waste produced in its main production process (Dudynski et al., 2012).

Table 1: Typical amount of ash resulting from production of 1 tone of technological steam from various fuels (Kordylewski, 2008; van Loo and Koppejan, 2008)

Material	RDF	Coal	Leather	Feather	Dry wood
Ash kg	45	20	12	2.1	1

Table 1 summarizes the typical amount of ash resulting from production of 1 tone of technological steam from various fuels. We can observe the significant reduction of ash amount produced in the process and there are also significant improvements with carbon prints with application of locally produced waste (Kwiatkowski et al. 2013) for energy production as compared with coal or others externally derived fuels. In the present study we analyse two gasification plants which have been successfully operating in Poland for 6 to 10 years. These plants are fed with various types of difficult waste, such as tanned leather residues or feathers, and are located directly at the industrial facilities where the waste are produced. We are dealing with relatively small systems, which process problematic biological waste otherwise difficult to stabilize. It is crucial that the gasification process residues are secure and easy to handle due to the costs consideration and limited number of staff. In the current paper we present the results of a series of analyses of the properties and the chemical composition of materials used as a fuel and compares the composition of bottom ash produced in the processes. These bottom ashes are rich in chromium oxide in the case of tanned leather or phosphorus oxide for feathers waste and it is both technically possible and economically viable to recover these elements for future use. The waste produced in the exhaust gas cleaning units as a result of desulfurization and chlorine removal are classified as dangerous and was not taken into consideration in this study as a possible source of material recovery but due to high stability of the feeding material and their organic origin it is possible to consider in the future to change the status of these waste to non-dangerous and use it for further processing and material recovery.

2. Materials and methods

2.1. The gasification process

All materials, which we are dealing with in plants described in this paper, are quite difficult to process due to their water content and entangling ability (especially wet feathers and leather waste). The fuel is always transported in containers, even though the main part of it is produced locally. It leaves the containers in heaps, which are hard to break apart, and therefore we constructed a special separation system for feeding such a material into the reactor (see Dudyński et al., 2012) for more details). After being fed into the gasifier, the fuel forms a wet and partially compressed pile, which needs time and high temperature to break, gasify and burn out.

The high content of water results also in low heating value of the waste material bellow 10MJ/kg. In order to maintain the desired heat production we were forced in winters to mix our basic fuel with additional material of higher energy content, such as dry wood or wood pellets.

The waste received from the processing plants not only contains high amount of water, but also potentially dangerous chemicals, either of natural origin (like sulphur in feathers and leather) or resulting from the technological process (chlorine in feathers, chromium in tanned leather. Some of these chemicals reduce the flammability of the material (Kozlowski et al., 2006; Ishii et al., 2007) and force us to apply high temperatures in order to obtain the required speed of the gasification process.

Table 2: Average characteristics of biomass feedstock used in the gasification plants (Godinho et al., 2011; Dudynski et al., 2012)

Parameters proximate analysis	Leather	Feathers
Moisture	65.0%	51,6%
Volatiles	27.1%	42.7%
Fixed carbon	5.9%	5.0%
Ash	2.0%	0.7%
Ultimate analysis (ash and moisture free)		
C	49.3%	61.77%
H	8.52%	5.68%
O	24.7%	11.74%
N	12.42%	18.53%
S	1.83%	2.16%
Cl	0.45%	0.12%
Cr	2.77%	0%
HHV	7.25MJ/kg	11.94MJ/kg

In order to deal successfully with such materials, we developed a novel gasification plant equipped with multilayer and multipoint hot air injection system (Dudyński, 2000, 2008). At the very bottom of the gasifier the 400K air is applied through a moving cone grate. The second ring injecting hot air is located slightly above the grate. Such construction prevents the unburned material to mix with the ash and the vapours to condensate at the bottom of the gasifier which causes many problems in winter. At the same time such configuration improves the energy recovery completely burning the coal remaining in the ashes. Due to the reductive character of the gasification process the chemical compounds present in the solid residues have a lower oxidation number as compared to those resulting from combustion, which for example in case of chromium oxides determines whether the ashes are toxic or not. In the gasification process described here only the waste produced in the exhaust gas cleaning units were considered hazardous. Approximately 40 to 50% of the air used for gasification is delivered through these two lower injection systems and most of CO_2 and H_2O necessary for gasification is produced in bottom area of the reactor. The remaining air is delivered through 32 nozzles located at 1/3 of the total height of the gasifier, approximately at the bottom of the pyrolysis zone. Compressed air of 420K is delivered through the nozzles and part of it is directly combusted with the pyrolysis gases, creating hot gases which later drive the pyrolysis and drying process. Hot gases with temperatures between 900-1100K are fed into combustion chamber and burn in the conditions of mild combustion (Dudynski et al., 2012) resulting in very low levels of NOx and CO in exhaust gases (Kwiatkowski et al*. 2013a).* The flue gases pass through steam boiler and are directed to the desulfurization and filter system. Such design is realization of the concept of local energy centres integrated to the biomass processing factories transforming the locally produced waste into energy (heat or electricity) consumed locally. As a backup system we use the wood pellets boiler providing the additional energy necessary in winter and guaranteeing security of production with lowest CO_2 costs for environment.

2.2 Leszno gasification plant

The steam producing gasification plant located in Leszno Gorne, south-west Poland, was integrated with a leather processing factory. The 2 MW plant has successfully operated for over 10 years, when the production of leather was stopped in this location. Like all the other reactors analysed in this study, the gasifier had a standard up-draft construction and used air as a gasifying agent. The waste derived fuel, fed into the reactor at an average rate of 950 kg/h, consisted of moist tanned waste mixed with wood or textile wastes. The syngas produced in the gasifier was combusted in a separate chamber. The exhaust gas was directed into a heat exchanger, where it was used to produce steam. The plant provided 80% of heat necessary for running the factory. The average chemical and technical properties of waste used as a fuel in all considered gasification plants are presented in Table 2.

Initially the plant was fed with tannery waste mixed with fresh woodchips and the resulting bottom ash was further processed to chrome paint (see also Dettmar at al. 2010). Eventually the process became too costly due to the presence of sand and the woodchips were replaced with wood pellets and sometimes with locally derived low ash RDF containing mainly textile wastes which improved the ashes quality allowing the further processing of the chromium oxide.

2.3 Olsztyn gasification plant

The 3.5 MW gasification plant located in Olsztyn, north-east Poland, is integrated with an industrial slaughterhouse and operates on poultry feathers. It has been previously described in (Dudyński et al. 2012). The fuel produced by the slaughter- house consists of mainly turkey and chicken feathers, but contains also poultry entrails, nails, blood, beaks and whole carcasses. The mixture varies strongly in composition and moisture content, resulting in difficult process stability maintenance. The plant utilizes 1200 kg/h of feathers and 50-70 kg/h of wood pellets and produces steam later used in the slaughterhouse and meat processing plant (see Kwiatkowski et al. 2012a) for analysis of material and energy flows). The plant has successfully replaced previously operating coal-fired boiler

Table 3: Operational parameters of the Leszno and Olsztyn plant during a representative week.

Parameter	Value for Leszno	Value for Olsztyn
Fuel (wet 70% moisture)	Tannery waste 750kg/h	Feathers 1320kg/h
Wood pellets	200kg/h	57kg/h
Steam production	2800kg/h	3000kg/h
Ash production	35kg/h	6kg/h
Flue gas	7500kg/h	7750kg/h
Quicklime for flue gas treatment	21kg/h	31kg/h
Temperature of syngas	800 C	800C
Temperature of hot flue gases	950C	998C
Temperature of flue gases (boiler outlet)	120C	139C
Steam parameters	0.86MPa/173.4C	0.86MPa/173.4C

In fact the bottom ash is only a small fraction of the total solid waste produced in the Olsztyn plant. The feathers contain very large amount of sulphur (exceeding 2.5% of dry mass) and chlorine, and the major part of solid residues is produced in the desulfurization and dechlorination units. In the current study we do not focus on the desulfurization and dechlorination waste, as it is only a major problem in one particular design of a gasifier. The aim of this study was to compare the bottom ash resulting from gasification of different types of waste and the possibility of retrieving the important elements contained in the material.

2.4.Measurement methods

The fuels and post-gasification bottom ashes were analysed using standard analytic methods, standing in accordance to the EU Directive. The composition of ashes was determined by the x-ray fluorescence method, whereas the leachability tests were performed using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and other standard analytic techniques.

3. Results and discussion

The ashes produced from each of the fuels had unique composition. For example the ashes obtained from tannery waste contained mostly chromium (III) oxide (55.91 wt%) and silicon dioxide (23.58 wt%), and contained very small amounts of calcium oxide (1.20 wt%) and phosphorus pentoxide (1.59 wt%), whereas the ashes obtained from feathers contained mostly phosphorus pentoxide (40.35 wt%) and calcium oxide (35.97 wt%) and obviously no chromium oxide.

The data concerning the properties of post-incineration ashes obtained from tannery waste, which was found in the literature (Louhab et al. 2006), clearly indicates the presence of toxic chromium (VI) oxide. The content of CrO_3 in bottom ashes amounts for 260 ppm, whereas in cyclone ash - 680 ppm. The amount of chromium oxide in bottom ash during incineration vary from 17% to over 20% of the ash mass with chromium (VI) consisting up to 30% of the chromium mass in clear contrast with gasification where we have chromium oxide entirely in the chromium (III) form. Chromium (VI) oxide is highly toxic, corrosive and considered carcinogenic, moreover it is dissolvable in water and therefore can easily contaminate soil through leaching, if disposed of to landfill.

The analysis of leachability properties (Dudynski et al., 2013) indicates that the post- gasification bottom ashes obtained in the processes of utilizing tannery waste or feathers are non- hazardous and with additional precautions even inert, according to the standards set out by the Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste. Therefore the ashes obtained in such process can be recycled without particular precautions with order to recover the important chemicals as: chromium III in case of leather waste or phosphorus for feathers bottoms ashes. There is also possible to recover natural hydroxyapatite from the solid deposits in the combustion chamber and boiler (Sosnowska et al. 2015, Kwiatkowski et al. 2016).

There are interesting conclusions concerning the differences in bottom ashes produced during gasification and incineration of RDF in (Rocca et al., 2012). The researchers have analysed in detail the composition, mineralogy, buffering capacity and leaching properties of the ashes obtained in both processes. They found that the incinerated RDF ash consisted of an assemblage of several crystalline phases while the gasified RDF ash was mainly characterized by amorphous glassy phases. The authors assumed that the differences in leaching of contaminants between the two types of ashes is related to kinetic effects since the leaching availability of major components from the glassy matrix of the gasification bottom ash proved limited compared to that of the incineration ash. Their explanations fit very well with our data.

Our analysis showed that the post-gasification bottom ash contains very small amounts of carbon (e.g. 1.2% for the bottom ash obtained through gasification of feathers) as compared to incineration residues. This clearly indicates that gasification is very efficient in terms of energy conversion.

Quite surprisingly the presence of sand turns out to cause numerous problems during the daily operation of the biomass gasification system. The sand which enters the reactor as an effect of careless fuel handling tends to accumulate at the bottom of the gasifier which is also filled with biomass ashes rich in sodium and potassium salts that lower the sand melting point (Miles et al., 1996). The removal and handling of the mixture of ashes and glassy phase is very difficult and problematic. It shows that the handling of the fuels shall be organized and designed in such a way as to avoid introducing the sand into process and for the systems with chemicals recovery is much better to use wood pellets or others high quality ash free waste as textiles then wood chips or others waste wood containing sand.

4. Conclusions

In this paper we have presented a novel design of a gasification plant suitable for utilizing biomass waste and producing heat, which has been successfully operating in a number of biomass processing plants. We have described in detail two such plants, which process feathers, tanned leather waste, wood and RDF, and analysed the properties of bottom ash resulting from the gasification process. We have compared the composition and leaching characteristics of the biomass and RDF post-gasification bottom ash, RDF post-incineration ash and coal post-combustion ash.

It has been proven that gasification is an effective and promising way of utilizing difficult industrial waste, such as tannery residues and feathers. It is suitable for processing such hazardous organic waste into energy and results in production of limited amount of non-hazardous solid residues. The advantage of local gasification plants designed for particular type of biomass feed is that the composition of bottom ash is relatively stable and it can be potentially profitably reused as fertilizer or in recovery of particular chemicals. Such reuse of bottom ashes was a part our operational plan and only for temporary economic reasons this practice was sometimes suspended.

In particular cases the bottom ashes from gasification process are clearly less dangerous than the ones resulting from direct combustion of the same material (e.g. due to the type of chromium compounds, carbon content etc.). In general the release of constituents through leaching is smaller for gasification ashes which are linked to the mineralogy of the ashes. It is also worth to note that the level of dioxins in the bottom ashes resulting from gasification of feathers is very low even though the material contains a significantly high amount of chloride.

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