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SELECTED ENVIRONMENTAL ASPECTS OF GASIFICATION AND CO-GASIFICATION OF VARIOUS TYPES OF WASTE

Natalia Kamińska-Pietrzak^{1*}, Adam Smoliński²

¹ *Interdisciplinary PhD Studies in the Field of Clean Coal Technologies, Central Mining Institute (Katowice, Poland)*

² *Department of Energy Saving and Air Protection, Central Mining Institute (Katowice, Poland)*

* *Corresponding author: natalia-kaminska-pietrzak@wp.pl, tel.: +48 510 80 58 08*

Abstract

The process of gasification of carbonaceous fuels is a technology with a long-standing practice. In recent years, the technology has been extensively developing to produce energy or chemicals on the basis of obtained gas. Studies focused on the improvement of the gasification process aims at developing the process by increasing environmental safety, the efficiency and the possibilities to utilize various types of alternative fuels (post-consumer waste, various types of biomass waste, by-products and post-process residues, sewage sludge) independently or by co-gasification with coal. The choice of the gas purification system, the process operating parameters and introducing the necessary modifications to the existing technologies are essential steps while processing these kinds of feedstock, with regard to their individual characteristics. This paper discusses selected environmental aspects of the gasification and co-gasification of municipal solid waste, sewage sludge, various types of biomass waste and post-process residues. Selected alternative fuels are also characterized, focusing on the influence of their presence in the feedstock in terms of production and the emission of polychlorinated organic compounds, tars, heavy metals and toxic elements.

Keywords

gasification, co-gasification, plastics, sewage sludge, biomass waste, heavy petroleum residue, Refuse Derived Fuel, dioxins, heavy metals, tar

1. INTRODUCTION

Gasification is a thermochemical process that converts carbonaceous fuels into a combustible gas consisting of CO, H₂, CH₄, CO₂ and other substances in smaller amounts. Gaseous products may be used in combustion as well as the production of many large volume chemicals such as ammonia, methanol, formaldehyde, OXO alcohols and aldehydes, for the synthesis of hydrocarbons by the Fischer-Tropsch process and in various carbonylation, hydrogenation or hydrotreating processes.

Gasification is a process that facilitates using both solid and liquid fuels, this makes it possible to process post-process and post-consumer waste of various types. Homogeneity of the physical and chemical properties of the fuel directed to a gasification reactor is an advantageous feature, but even in the case of major differences in chemical composition or physical properties (for example, between particular components of municipal waste fraction or in the co-processing), the technology permits obtaining far greater feedstock flexibility than combustion (Nikodem 2007). The gasification of various types of waste (municipal or post-process), or co-gasification with conventional fuel, is an effective method for recovering its energy content, and the resulting gas combustion, as opposed to direct gas combustion, does not cause

technological problems regarding the selection of a narrowly specialized stoker.

Waste for which gasification is considered are mainly sewage sludge, biomass waste from wood, pulp and food industry or agriculture, municipal solid waste or their combustible fractions, as well as heavy petroleum residues.

Sewage sludge is a waste derived from the treatment of municipal and industrial wastewater. The content of individual substances in sludge is largely dependent on their origin. They mainly consist of organic (carbohydrates, proteins and fats) and mineral substances. Their common characteristic is a high content of moisture, which reduces the transport efficiency and must be removed. Gasification requires the relatively easy sewage sludge treatment prior to use – the process may be carried out even at 75% moisture content in the fuel, while sludge pyrolysis requires its reduction to about 15% (Manara, Zabaniotou 2012). Sewage sludge is subjected to dehydration (concentration, mechanical dehydration and drying) as well as stabilisation and hygienization (Kordylewski 2005). Currently, a small amount of sludge is utilised by combustion or gasification, however, thermochemical processing technologies are treated as a prospective method for sewage sludge usage. A characteristic feature of sewage sludge as fuel is high content of volatile matters, as well as

nitrogen and heavy metals. Caloric value of dried sewage sludge is 12–14 MJ/kg (Kowalik 2000).

Waste biomass is a group with widely varied composition and physical properties. Biomass waste can be classified according to origin (plant, animal) or structures which are dominant (cellulose, lignin, fats, wax or albumens). Biomass wood waste (sawdust, shaving), straw and paper industry waste, in which cellulose structures are dominant, are also recognized as fuel. The prevalence of small-scale systems for gasification and co-gasification of lignin and cellulose biomass, and the results of research papers devoted to biomass gasification and co-gasification (Van der Drift, Van Doorn, Vermeulen 2001; Myren et al. 2002; Paasen, Kiel 2004; Pinto et al. 2007, 2009; Abu El-Rub, Brammer, Brem 2008; Mastellone, Zaccariello, Arena 2010) indicate that the technology is effective and safe for the environment. Also pulp industry waste may be disposed of without posing further problems regarding the emissions of unwanted compounds. Some of them, such as “black liquor” – the precipitate formed as a result of the wood pulping process, due to the alkali content can be a catalyst for the reaction, and may allow more complete utilization of the chemical energy contained in the co-gasified fuel (Kuang et al. 2007; Jaffri, Zhang 2007; Zhan, Zhou, Wang 2010).

Types of biomass waste other than wood are characterized by a generally higher content of chlorine, sulphur and ash (Paasen, Cieplik, Phokawat 2006). Some of them, especially the shells of different types of nuts and fruit seeds, due to the content of metal oxides having a catalytic activity, permit achieving higher grades of carbon conversion and gas production yield during the co-gasification process with coal (Di Donato et al. 2011). Waste with a low content of cellulose and lignin, such as used fats or oil seed pomace, is fuel with different properties. The long chains of hydrocarbon fragments contained in fats, especially with a large number of unsaturated bonds between carbon atoms, favour the formation of large quantities of liquids and gas rich in hydrocarbons (Pinto et al. 2005; André et al. 2005). Due to the relatively low reactivity and the lower gas yield, research focuses on processing feedstock rich in fats with the addition of catalysts or their co-gasification with fuel containing metal oxides catalysing the reaction of hydrocarbons with a gasifying medium (Pinto et al. 2005, 2009).

Only a moderate part of research on gasification and co-gasification of the biomass waste concerns animal waste. The high fat and heteroatoms content present in the tissues of animal organisms is the cause of large amounts of impurities. Depending on their type, this entails the need to expand node gas purification (Cascarosa et al. 2011). An essential aspect of the waste treatment of animal waste, as in the case of sewage sludge, is the microbiological risk. Therefore, thermochemical processes of energy recovery contained in this type of waste are a prospective and desired direction of their disposal.

Plastic waste is another group of alternative fuels with different properties. The share of plastics in municipal waste from developed countries stands at around 8%. World production increased from 1950 to 2008 from 1.5 million tonnes to 245 million tonnes (Biois... 2010). This involves the need to develop methods of disposal combined with the recovery of a portion of materials or energy used to produce them.

Gasification technology of plastic waste, as a method of energy recycling is not sensitive to polymer changes occurring under the influence of light, in contrast to the methods of material recycling. Gasification also does not require such thorough cleaning of waste, as in the case of chemical or material recycling. Taking into account the consumption of water and energy for material recovery or monomers recycling and greenhouse gas emissions, gasification can be considered a relatively environmentally beneficial form of recycling (The Environment... 2004). Plastics are present in municipal solid waste in extremely varied sizes and forms, and therefore, the larger elements of the waste should be fragmented (to less than 5 cm diameter), while the films – should be subject to concentrating by concentration and clumping. Predominant part of plastic fractions from waste dumps is waste polyethylene that can successfully undergo gasification process (Chiemchaisri, Charnnok, Visvanathan 2010). Polyolefin waste provides a good feedstock for thermochemical processes because it consists almost exclusively of carbon and hydrogen, and typically contain small amounts of impurities and has a high calorific value (e.g. 43.5 MJ/kg of high density polyethylene and 44 MJ/kg of polypropylene) (The Environment... 2004; Kordylewski 2005). The share of plastics in the fuel increases the amount of hydrocarbons and tar in the gas (Chiemchaisri, Charnnok, Visvanathan 2010; Pinto et al. 2012). The high content of halogens is also a major difficulty in the thermochemical processing of certain types of plastics.

Heavy petroleum residue is a fuel with a relatively low reactivity, so research on its gasification and co-gasification focuses on finding efficient catalysts that can enhance the conversion of the contained carbon (Zhan, Zhou, Wang 2010; Ohtsuka 2009; Revankar, Gokarn, Doraiswamy 1987). Heavy residue has a low volatile content compared with coal or biomass. It contains, however, large amounts of sulphur and heavy metals. The calorific value of heavy petroleum residue is 36.2 MJ/kg (Zhan, Zhou, Wang 2010).

Fuel produced from mixed waste (municipal and industrial) is referred to collectively as Refuse Derived Fuel, RDF. Table 1 shows the characteristics of selected materials found in municipal waste.

Table 1. Selected characteristics of municipal waste (Tillman 1991)

Components	C	H	O	N	Cl	S	Moisture [% mas.]	Ash [% mas.]	Combustion heat [MJ/kg]
Paper	33.0	4.6	33.0	0.1	0.13	0.21	16	13	12.7
Plastics	56.4	7.8	8.1	0.85	3.0*	0.3	15	9	18–45
Rubber and leather	43.1	5.4	11.6	1.34	5.0	1.2	10	22	19.6
Wood	41.2	5.0	35.0	0.24	0.1	0.07	16	3	16.2
Fabric	37.2	5.0	27.1	3.1	0.3	0.3	25	2	15.3
Garden waste	23.3	3.0	17.5	0.9	0.13	0.15	45	10	9.3
Food waste	18.0	2.5	12.9	1.1	0.4	0.06	60	5	7.6

* Depending on the type of plastic involved, 0–0.45 chlorine.

The waste undergoes partial processing, so that the RDF fuel mixture has sufficient heating value and does not contain inert ballast, bulky waste, toxic substances, and other undesirable elements during thermochemical processing. A typical procedure prior to the energetic use of waste is based on the following steps (Spliehoff 2010; Kordylewski 2005)

- magnetic separation of ferrous and non-ferrous metals

- manual separation of non-combustible fractions and bulky components
- mechanical sorting into fractions (using air or drum classifiers)
- fragmentation
- drying
- concentration (pelleting or briquetting)

An important issue in the case of gasification of RDF from municipal waste is the variable calorific value, density and moisture content of the fuel. Another aspect is the variable content of harmful elements and compounds. Industrial wastes are mostly homogenous – containing one type of waste with small variations in its composition. Preliminary, the processing of industrial waste for energy recycling does not require most of the steps followed regarding municipal waste.

2. EMISSIONS OF POLYHALOGENATED ORGANIC COMPOUNDS

The two elements belonging to the group of halogens most frequently present in municipal waste and sewage sludge are chlorine and fluorine. Both elements at an atomic level cause severe steel corrosion and react with a protective oxide layer on a metal surface (Bałtorek-Giesa, Jagustyn 2009). Conditions for gasification hinder the formation of molecular halogen for hydrides, therefore by-products of gasification containing halogens are mainly HCl and HF. The above-mentioned compounds have a considerably lesser corrosion effect, however, they should be separated from the gas stream. The capture of these compounds is performed using conventional acid gas absorbents (e.g. calcium oxide). The content of chlorine in the form of chloride affects the melting point of some inorganic compounds. Creating eutectic salts with a low melting point results in binding fuel particles in the agglomerates. Fuel containing in its composition more than 0.5% chlorine are considered as highly slagging (Bałtorek-Giesa, Jagustyn 2009). The most serious problem, however, is the formation of harmful chemicals classified as Persistent Organic Pollutants (POPs), particularly polychlorinated furans, polychlorinated dibenzodioxins, polychlorinated biphenyls and hexachlorobenzene (Kołsut 2002). Some of polychlorinated dibenzodioxins (commonly referred to as dioxins) have a high toxicity to living organisms (2, 3, 7, 8 – tetrachlorodibenzodioxin is one of the most toxic compounds obtained by synthesis). Reducing the formation of polychlorinated compounds and increasing their capture is particularly important in terms of environmental protection.

It is assumed that the main source of the formation of dioxins in the thermochemical processing of waste is the fraction of plastics. Despite the currently increasing trend of good design with the widest possible use of materials prone to recycling, not all of the material used should be gasified. Polyolefine, polystyrene or polyethylene terephthalate waste can be processed without the risk of thermochemical emissions of polychlorinated organic compounds when they provide a uniform flow of waste (e.g. energy recovery in production plants). The content of halogens, especially chlorine, makes it difficult for the development of plastic fraction of municipal waste (processed consumer goods waste, are often heterogeneous in terms of material, and their removal during

a typical work sorting – impossible) by gasification. Waste containing large amounts of chlorine also include rubber and processed tanned leather, as well as various animal biomass (e.g. food waste) and sewage sludge (Tillman 1991).

Polychlorinated dibenzodioxins and polychlorinated dibenzofurans are emitted from combustion or gasification processes that are carried out at a temperature below 1200°C. These compounds are contained in fuel or formed by the rearrangement of chemical degradation products of chlorinated aromatic hydrocarbons or in heterogeneous reactions of hydrocarbons, occurring in the mixture of exhaust gas and fly ash, which are catalysed by copper compounds (Kołsut 2002). For each of these mechanisms it is assumed that the formation of dioxins extends outside the furnace (at a temperature range of 200–450°C). Dioxin precursors (in rearrangement, as well as *de novo* synthesis) are incompletely reacted carbon compounds contained in the fuel. One of the basic methods of reducing the formation of dioxins in the gasification process is, therefore, to operate the process at a high temperature or using a catalyst in order to achieve the complete conversion of hydrocarbons formed in the pyrolysis. Conesa, Fullana, Font (2005) in their study dedicated to the formation of dioxins during the thermochemical processing of bone meal, compared the levels of concentration of polychlorinated dibenzodioxin (PCDDs) obtained during pyrolysis and combustion. During pyrolysis at a temperature above 1100°C, the resulting amounts of PCDD were greater than in the case of combustion at the same temperature, but below 850°C dioxin emission from pyrolysis was lower. Paasen, Cieplik and Phokawat (2006) compared the amount of harmful compounds formed secondarily in the process of gasification of sewage sludge and RDF which consisted of paper and plastic waste. Sewage sludge contained in the dry ash-free state contained 0.3% of chlorine and RDF contained 1.5% of chlorine. The fuel was subjected to the air gasification process in a reactor with a bubbling fluidized bed. For both fuels, dioxin content in the synthesis gas decreased significantly when the gasification temperature was increased to above 800°C. During gasification of RDF at 725°C the gas contained 74.22 ng dioxin/m³, for gasification at 825°C the content decreased to 4.50 ng/m³. The content of dioxin in the gas produced during the gasification of sewage sludge was lower, and at 750°C amounted to 1.98 ng/m³. Increasing the gasification temperature by 100°C resulted in its reduction to 0.38 ng/m³. The total content of polychlorinated dibenzodioxins and polychlorinated dibenzofurans in the gas produced from the gasification of sewage sludge at 750°C was 1.9 ng/m³, and for RDF – 373.0 ng/m³. During the gasification of waste at a temperature above 800°C, the ratio of chlorine in the emerging HCl to chlorine contained in the fuel varies considerably and amounted to 9% of the sludge and 48% for the RDF. Tar produced during gasification of RDF also contained much larger amounts of chloro-organic compounds. The chlorine content in the tar from the gasification of RDF was 4124 mg/m³, while the tar resulting from the gasification of sewage sludge was 56 mg/m³.

Adlloch et al. (2000) presented the composition and efficiency recognized the harmful compounds produced secondarily by the co-gasification of coal and municipal solid waste. Gasification was carried out by oxygen-enriched air in the High Temperature Winkler (HTW) demonstration plant with

a fluidized bed. In the resulting raw gas, chloride content amounted to 6.98 mg/m^3 fluoride – less than 0.09 mg/m^3 , and the total content of polychlorinated dibenzodioxins and dibenzofurans – 0.012 ng/m^3 . Flue gases from the combustion of the resulting gas contained 1.38 mg/m^3 HCl, HF below 0.02 mg/m^3 and 0.002 ng/m^3 polychlorinated dioxin and furans. The content of polychlorinated dioxins and furans at the same level (0.005 ng/m^3) was observed in exhaust gas following the combustion of product gas from the gasification of post-consumer packaging films. Exhaust gases also included $1.25 \text{ } \mu\text{g/m}^3$ chlorinate and polychlorinated biphenyls and chlorophenols. Flue gases from the same plant, which was supplied thanks to the fraction of plastic waste from sorting contained 0.03 ng/m^3 PCDD/PF, however, two times lower content of chlorophenols was observed and the total content of polychlorinated biphenyls, chlorobenzenes and chlorophenols was $0.99 \text{ } \mu\text{g/m}^3$ (Adlhoch et al. 2000). Polychlorinated dibenzodioxins and dibenzofurans, except for gas, were also included in the slag and dust. The authors determined the stream of PCDD/PF derived with the slag during an hour to be approximately equal to the stream of these compounds in the raw gas.

Tanigaki, Manako and Osada (2012) studied the gasification of municipal waste by oxygen-enriched air in the direct ash melting system. By obtaining carbon conversion rates at 91.7 and 95.3% they observed PCDD/PF performance decrease. Increasing the conversion of hydrocarbons involved in the formation of dioxins can also be achieved by using high temperature entrained-flow gasifiers. Birgan, Matsumoto and Kitagawa (2012) subjected poultry manure (waste with a very high chlorine content) supercritical water gasification, and observed levels of dioxin concentration to be of a much lower level than the acceptable level of emission. Plasma gasification is also a prospective technology, particularly in the case of waste with a high content of halogens. Plasma is a state in which molecules or atoms are present in the gas and are partially ionized. High temperature resulting from the discharge provides the possibility of thermal degradation of organic compounds that do not decompose during conventional gasification processes (including condensed aromatic hydrocarbons and heterocyclic compounds). Plasma gasification leads to the significant reduction of emissions of dioxins and furans, and is recognized as the most environmentally friendly thermo-chemical treatment of waste. The most effective method to remove dioxins, regardless of the technology used, is captured by a specialized multi-stage adsorption filter.

3. FORMATION OF TAR

Tar is a mixture of aromatic hydrocarbons with a molecular weight greater than benzene. The amount of their formation and composition is strongly dependent on the composition of the fuel or the fuel mixture directed to the process (Pinto et al. 2012). Alternative fuels, which additionally cause an increase in the yield of the tars, are mainly plastics, biomass waste rich in fats and sewage sludge.

Polymers, which are the main component of plastics, consist of repeating structure fragments, therefore, their thermal decomposition occurs with the release of large amounts of light hydrocarbons. The content of these compounds in gas, which are to be used for energy purposes, is desirable because it increases the calorific value. However, hydrocarbons

form by side reactions of repolymerizing compounds of higher molecular weight including aromatic hydrocarbons. Gasification of plastics is thus linked to the formation of considerable amounts of tar. Paasen, Cieplik and Phokawat (2006) compiled the results of experiments with the fuel-air gasification of RDF (paper + plastics), and sewage sludge. The process was carried out in a reactor with a bubbling fluidized bed at more than 800°C and at atmospheric pressure. The gas formed from RDF contained almost three times more tars precursors – ethylene and benzene (respectively: 4.6 mg/m^3 and 9309 mg/m^3) and more than twice as much tar – 26.4 mg/m^3 . The formation of large amounts of tar is one of the reasons that the co-gasification of plastic fractions of municipal waste with other fuels is considered. Currently, many researchers focus on the beneficial aspects of co-gasification of plastic waste with wood biomass or energy crops and coal (Pinto et al. 2012; Chiemchaisri, Charnnok, Visvanathan 2010; Adlhoch et al. 2000). In degradation of tars that are side products in the gasification process, increased gasification temperatures (Brage et al. 2000; Li, Suzuki 2009; Anis, Zainal 2011), and the optimum flow rate of gasifying agent (Ledesma et al. 2000) is important. Obtained amounts of tar slightly decrease with decreasing process pressure (Mayerhofer et al. 2011). A particularly high percentage reduction of tar is achieved with the addition of catalysts (Anis, Zainal 2011). Guan et al. (2009) obtained gas free of tar through the use adding dolomite (at a mass ratio of steam to waste equal to 0.42 in 800°C at atmospheric pressure). In the same system, without the use of a catalyst, raising the temperature to 900°C resulted in a decrease in mass efficiency of tars to 3.6%.

Tars formed as by-products in the process of gasification plastics generally have low levels of heteroatoms and low polarity. A study focused on emissions from the gasification of plastic waste, published by the Environmental and Industry Council and the Canadian Plastics Industry Association (2004) indicate a relatively high content of tars in the resulting gas. Both in the case of post-consumer packaging films, and the fractions of the plastic waste from sorting, about 6% of the carbon was contained in the feedstock. Resulting hydrocarbons do not contain large amounts of polar groups, thus the amount of carbon that remains in the effluent water from the process did not exceed 0.2%. Straka and Bučko (2009) subjected post-consumer tyre waste and coal to a steam air gasification process in a fixed bed reactor (at 800°C and 2.7 MPa). During the gasification of tyre waste (mainly consisting of rubber, oil and soot) tar formed with a yield of 40.5% and when coal was processed the yield of tar was 17.5%. In the co-gasification of both materials, beneficial effects of reducing the amount of generated tars were observed. The addition of 10% post-consumer tyre waste did not cause a noticeable change in the amount of tar generated (comparing to coal gasification only), but contained in its composition less oxygen functional groups.

The formation of large quantities of tar in the gasification process also occurs during the processing of biomass waste containing fats (such as bagasse, plant oil, bone meal). Long hydrocarbon chains with unsaturated carbon-carbon bonds existing in fats may be subject to cyclization, dehydrogenation and aromatization reactions, thereby forming aromatics. A significant content of fats in the waste of some types of

biomass makes the process of gasification inefficient enough due to the high yields of liquid products (Pinto et al. 2009). This type of waste may be subjected to co-gasification with other fuels in the appropriate proportion. André et al. (2005) determined that the addition of oil crops bagasse into conventional fuel should not exceed 40%. Cascarosa et al. (2011) observed an increase in the efficiency of tar in a small (1%) addition of bone meal to coal.

Considerable amounts of tars are also created in the air gasification process of sewage sludge (Phuphuakrat et al. 2010; Chen, Namioka, Yoshikawa 2011; Adegroye et al. 2004). A characteristic feature of tars generated in the thermal conversion of such waste is a high content of heteroatoms, especially nitrogen and oxygen. The main groups of compounds present in tar, containing nitrogen are cyanoaromatics and N-heterocyclic aromatic hydrocarbons (Chen, Namioka, Yoshikawa 2011), while oxygen compounds are predominated by phenol (Adegroye et al. 2004). Paasen, Cieplik and Phokawat (2006) also observed that the tar from the gasification of sewage sludge, despite the high temperature process (850°C) and the presence of a gasifying agent contained a large quantity of primary tars that did not undergo further reactions.

The gas produced during the gasification process is subjected to a further purification, this forms tar by so-called secondary methods, involving physical separation from the gas stream or chemical degradation. Particularly undesirable components include polycyclic aromatic hydrocarbons, condensing even at high temperatures and accumulating on the elements of the apparatus. In case of a relatively small content of tar in the gas, only physical methods are commonly used. Condensing tar particles are captured in various kinds of filters, separated in cyclones or absorbed in the selective solvent. Phuphuakrat et al. (2010) tested the effectiveness of removing tars from the gas by using a system composed of two venturi scrubbers and three sawdust absorbers. The removal efficiency of polycyclic aromatic hydrocarbons by the scrubbing system amounted to 96.1%, and absorbers filled with sawdust stopped them completely. After passing through the tested system, the gas contained only light aromatics. The degradation of large amounts of tars can be achieved using chemical methods. Aromatic compounds are thermally or catalytically cracked or reformed with the participation of a gasifying agent. These reactions may be catalysed by various substances e.g. transition metals, platinum metals and their oxides (in the form of supported catalysts), oxides and carbonates of alkali metals, acid type zeolite catalysts and activated carbons (Anis, Zainal 2011).

4. EMISSIONS OF HEAVY METALS AND TOXIC ELEMENTS

One of the important aspects of gasification and co-gasification of different kinds of fuels is the emission of heavy metals and toxic elements and managing the products which contain these substances. Elements present in feedstock undergo complex chemical and physical transformations in the gasification conditions. Figure 1 presents the schematically possible behavior of fuel mineral matter in the gasification conditions.

Non-volatile metals are normally distributed in the slag and ash at the same level of concentration as in the fuel. Me-

tals characterised by partial volatility can be found in the ash and slag, but they also volatilize into the gas phase, and therefore are present in gas or post-process aqueous condensate. Mercury has a high volatility and is the most mobile of the heavy metals contained in the fuel.

The behaviour of heavy metals and other harmful elements during gasification and their content in the individual by-products of gasification cannot be entirely predicted by modelling based on thermodynamic assumptions. Ilyushechkin et al. (2010) in the results of experimental gasification in the entrained flow reactor obtained only partial compliance of their distribution in the fly ash, slag, gas and wastewater. Tanigaki, Manako and Osada (2012) studied the distribution of heavy metals in various by-products from the gasification of municipal waste. Over 90% of the heavy metals with a low melting point (95.2% lead and 92.0% zinc) were found in fly ash, and the high-melting metals such as iron and copper, had the metallic form. Adlhoch et al. (2000) marked the content of mercury, cadmium and thallium in the main co-gasification product of municipal waste and coal, and also in the side products of this process – slag and dust. The process was conducted in a fluidized bed reactor, using oxygen-enriched air as a gasifying agent. The stream of cadmium and thallium metals contained in the feedstock supplied to the generator, was 75 g/h. The amount brought within with the slag was 21 g/h, while with the dust: 26 g/h of cadmium and thallium. The gaseous products of the reaction system resulted in below 0.27 g/h of the two elements together. Mercury was added with the fuel (2.9 g/h), primarily retrieved on the dust filter (2.48 g/h), its stream in the slag was 0.24 g/h, while in the raw gas – 0.05 g/h. Saveyn et al. (2010) noted, however, that during the gasification of sewage sludge, metals such as copper, lead and zinc are contained mainly in the solid residue, while mercury and cadmium have a high tendency to migrate and are usually contained in the condensed liquid product or deposited on the particulate filter. In addition, mercury, due to the tendency to create fine aerosol droplets is often present in the process gas (Marrero et al. 2004).

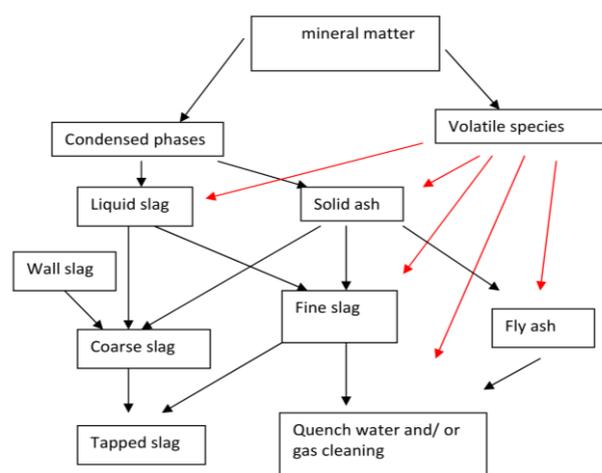


Fig. 1. Possible ways of mineral matter changes during gasification of solid fuels (Ilyushechkin et al. 2010)

The presence of the various elements in each gas or by-product is determined by their properties, including volatility, mechanical strength and solubility in water. Figure 2 shows the division of selected elements according to volatility level.

Some components contained in the fuel can result in changes in the distribution of metals in the main and by-products of gasification as a result of chemical reactions and phase changes. The addition of fuels with high sulphur and chlorine content (sewage sludge, waste plastics, petroleum coke and some types of biomass) increases the volatility of many elements. Di Donato et al. (2011) found that migration of thallium, tin, zinc, cadmium, antimony and arsenic, is caused by the formation of volatile chlorides. Font et al. (2011) observed, however, that the addition of the selected biomass content increases the ratio of a number of elements (including heavy metals) in the slag, and decreases their migration to the fly ash, in studies of carbon co-gasification, residues from the processing of waste oil and oil seed. With the increase in the content of tested biomass fuels (in the range 0–6% by mass) copper, germanium, molybdenum, nickel, lead, arsenic, antimony, thallium, boron and zinc content decreased in the fly ash.

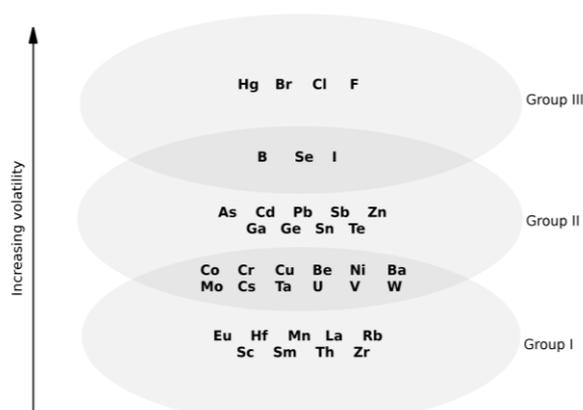


Fig. 2. The division of elements into groups according to the volatility (Erickson 1999)

Heavy metals and the other toxic elements are present in all types of fuels. However, there are groups of waste fuels in which the content of toxic elements is particularly high. Sewage sludge and municipal waste have the highest content of trace elements. Table 2 lists the results of the analysis of heavy metals in a sludge and coal in a dry state.

Table 2. The content of heavy metals in coal and sewage sludge (Bień 2002)

	Pb [mg/kg]	Cd [mg/kg]	Hg [mg/kg]	Zn [mg/kg]	Ni [mg/kg]	As [mg/kg]	Cu [mg/kg]	Co [mg/kg]	Cr [mg/kg]
Coal	20	<1	<2	15	3	5	23	<2	<2
Sludge	211	2	<2	567	32	10	829	3	62

The content of toxic elements in the sludge (especially copper, zinc, lead, chromium) is much higher than that in the fossil fuels. Heavy petroleum residue and fraction of plastic waste and food waste are also considered to be alternative fuels rich in toxic metals (Kordylewski 2005).

The results of experiments submitted by the Environmental Gasification and Industry Council and Canadian Plastics Industry Association (2004) indicate a relatively high content of lead in waste gas from the processing of plastic fraction of municipal solid waste ($44.19 \mu\text{g}/\text{m}^3$), and the lead and chromium (order: 35.27 and $20.08 \mu\text{g}/\text{m}^3$) in the exhaust gas from the processing of post-consumer film. The exhaust gases following the combustion of plastic fraction gasification products contained several times more mercury ($3.82 \mu\text{g}/\text{m}^3$).

The total content of heavy metals (silver, aluminium, cadmium, copper, mercury, lead and zinc) was noted in wastewater from the gasification of both types of waste. The total metal content was $1.4 \mu\text{g}/\text{m}^3$ for films and $2.5 \mu\text{g}/\text{m}^3$ for plastic fraction of municipal solid waste. Wastewater from the gasification of both types of waste contained similar amounts of silver, aluminium, cadmium, copper and mercury. Zinc content was doubled and lead content was several times higher in the case of the gasification of waste mixtures of sorted plastics. Di Donato et al. (2011) observed a particularly high content of heavy metals – lead, zinc, vanadium, nickel and molybdenum in the slag created during the co-gasification of heavy petroleum residue and coal.

An important feature of the by-product solid waste is that heavy metals can be leached out of them. This determines the possible use of waste as well as its storage methods. The contamination of land with heavy metals is a harmful phenomenon. Metals, in contrast to organic compounds, do not decompose, and even if they migrate into water in the form of low toxicity, they are subject to environmental transition to a more toxic form. Pinto et al. (2009) studied the properties of the gasification of solid waste in contact with water having a neutral pH to slightly alkaline (9.1). Despite the benign environment, decreasing the solubility of many metals, the presence of large amounts of leached nickel was observed in caustic. The content of zinc and chromium did not exceed the accepted limits for safe materials, but they were also present in leachate. Moustakas et al. (2009) studied the behaviour of molten slag cooled by water and air in contact for 64 days with aqueous solutions having a pH in the range of 3–8. Chromium, lead and nickel were immobilized in the slag, while copper, manganese, iron and zinc permeated into the solution with a very low pH. Capacities of the slag to immobilize metals were dependent on the particle size (the smaller elements passed easily into the solution). The slag cooling method used also has a significant impact on the leaching of heavy metals. Slag rapidly cooled by means of water, had a better ability to prevent metal migration due to the advantage of a suitable amorphous glass structure. The use of very high gasification temperature allows slag vitrification and thereby the immobilization of heavy metals and the degradation of compounds contained in the organic matter. Additives of calcium or magnesium oxides facilitate the transition of residues in the glass state (Wei et al. 2011). Vitrified solid waste can be safely stored or used in the building industry, as opposed to the ash, slag and dust remaining after conventional gasification or combustion. Vitrification of slag and fly ash can be carried out independently, can be integrated in the installation or occur during the gasification process. Gasification technologies with a direct melting system have been used in the disposal of waste deemed hazardous, but have also created dynamic commercial installations aimed at energy recovery from waste. There are currently dozens of gasification plants with direct melting systems under license from JFE Steel Corporation and Nippon Steel Engineering, the largest of which processes 720 tonnes per day (Arena 2012). Plasma gasification is also a prospective technology. Its great advantage, especially in the case of municipal waste, is the large flexibility for changes in the feedstock, both in the size of waste and the chemical composition and moisture. The largest commercial plasma gasification installation in Ottawa

operates on the technology of Plasco Energy Group and processes 300 tons per day of municipal waste (Plasco Energy Group data).

5. CONCLUSION

Gasification and co-gasification can be an environmentally safe and an effective method for the disposal of various types of waste. Knowledge of waste composition, in particular the content of chlorine or heavy metals, and the presence of plastics and fats, ensures the proper selection of process conditions, catalysts or other additives, and the construction of the gas purification unit. The problem regarding the formation of large amounts of tar occurs in particular in the case of waste with a high level of volatile content or containing polymers. Reducing the by-product yield of aromatic hydrocarbons can be achieved by raising the process temperature and by employing catalysts. The formation of dioxins, significant in the case of fuels with a high content of chlorine, can be visibly reduced thanks to the use of high-temperature gasification. High-temperature processes also allow immobilizing heavy metals present in the slag or in the slag and ash mixture, allowing their safe disposal or their use as an aggregate.

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