APPLICATION OF STEAM-PLASMA PROCESS FOR PYROLYSIS OF ORGANIC, INCLUDING MEDICAL AND OTHER HAZARDOUS WASTES

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Plasma technologies and equipment, widely accepted in metallurgy, welding and deposition of structural and functional coatings, are currently finding ever more applications. They seem to be highly promising for meeting two extremely important challenges of modern society:

- environmental protection with destruction of hazardous wastes, in particular organic wastes, this being extremely urgent;
- development of new alternative methods for generation of various types of energy carriers.

Indeed, a considerable share of wastes generated in incredibly large amounts, is made up by organic substances (plastic containers and products, medical wastes, car tires, etc.). Scope of these wastes is huge and many of them particularly, plastics, practically do not decompose under the regular conditions. These wastes often are hazardous for man and the environment. In keeping with the Basel convention on the control of transboundary movements of hazardous wastes and their disposal [1, 2], one of the most hazardous categories, taking the first place in the list of 45 types of hazardous wastes, are those of public health institutions as they contain toxic and infected substances. According to published data [3, 4, 5] over 3 mln, tons of medical wastes are annually generated in the US, up to 1 mln. tons in Russia and China, and around 600 thousand tons in France. Tentative (calculated) amount of medical wastes in Ukraine is equal to approximately 350 thousand tons per year. Not less hazardous are also such wastes as pesticides prohibited or unsuitable for application (by official data about 20 thousand tons of them have accumulated in Ukraine), and a number of other highly-toxic kinds of wastes. The problem of their annihilation, or what is even better, their recycling, is still unsolved and is becoming ever more urgent.

At present, there is a new problem dealing with so called “birds flue”, when it’s necessary to process huge amount of birds carcasses.

Many specialists believe that solution of the problem of medical waste recycling is not possible without their processing being preceded by separation into groups with each component used as raw material. However, in connection with the extreme complexity and high cost of such a separation, it is, probably, more rational to process the above wastes under the impact of a high temperature, which ensures destruction of all the components of the wastes. On the other hand, such an impact in an open atmosphere cannot but lead to generation of harmful substances, in particular, one of the most hazardous classes of substances, which have been often mentioned by ecologists and other specialists, namely halogenated dioxins and dioxin-like substances (DO). The above substances are super-oxidants, particularly deleterious and hazardous synthetic chemical products, byproducts of a number of chemical productions and other associated microemissions resulting from man’s industrial and economic activity, practically not mentioned in manuals or scientific publications before the 90s of the previous century. Unlike the simplest dioxins, the halogene dioxins consist of chlorinated or bromated benzene rings connected by oxygene bridges. These are the so-called polychlorodibenzodioxins and polychlorbezofurans and polybromdibenzodoxins and polybromdibenzofurans, respectively. They are particularly hazardous in connection with the fact, that despite their insolubility in pure water and in pure air, they readily dissolve in water containing humic acids or fulvoacids from soil humus. This is related to the high ability of DO to form complexes with the humus components. DO form complex compounds with air aerosols, and due to their high adhesion ability, they are readily carried not only over earth, but also by air. In the soil DO decompose for 20 to 30 years or more, while in the water DO decomposition lasts 2 or more years [6].

DO extreme health hazards should be considered separately. Being present in the habitat, DO, in view of their high affinity to protein, accumulate in the human body. Production of chlorine- and bromium-containing preparations is the main source of DO penetration into the habitat. The action of DO present in the environment even on the level of traces is also hazardous in that they are practically not revealed by regular methods of analysis. On the other hand, accumulating in a living organism DO are the cause of many oncology diseases, hypercholesteremia, etc.

Analysis of natural objects for DO requires using special and often not readily available methods (concentration and isolation of background substances, detection using gas chromatography and high-resolution mass-spectrometry).

Over the recent years low-temperature combustion of various kinds of wastes has been a typical sources of habitat contamination with halogenated DO, in addition to the above-mentioned productions. Testing shows that DO are resistant to high-temperature impact. More over, at the temperature of 800C formation of bromium-containing DO and not their destruction takes place, while irreversible destruction of halogenated DO occurs only at the temperature of 1200 – 1400 C for 4 to 7 hour, this being quite complicated and expensive from the engineering viewpoint.

Therefore, destruction of organic wastes should preferably be performed with application of technologies that prevent formation of the above substances during processing. In this connection, the most well-known technologies of combustion and disposal widely used for many years are more and more in conflict with the current requirements of ecological safety and these technologies are rejected in most of the countries of the world in construction of new garbage-disposal plants. On the other hand, the above organic wastes can be an additional source of producing synthetic fuel in the form of synthetic gas or diesel fuel in the amount of up to 700 kg from one ton of wastes.

As shown by analysis performed by the authors [7, 8], application of technologies based on the use of plasma arc energy appears to be one of the most promising directions, now taking the leading positions in the world in processing and destruction (recycling) of hazardous wastes. Despite the fact that the technologies of plasma processing of various kinds of hazardous wastes began to be implemented comparatively recently, many companies, including those in the leading industrialized countries, are active exactly in this area. According to published data [7, 8], plasma recycling of wastes is currently actively pursued in the USA, Russia and India.

Plasma technology as an alternative to any combustion methods consists in transferring (decomposition) of complex molecules of all substances into very simple molecules under the conditions of super-high temperatures and in the absence of free oxygen.

This technology has a number of obvious advantages:

- Plasma jet temperature is capable for complete destroying of any organic or biological materials, securely annihilating any most toxic poisons, remelting and evaporating the most high-melting inorganic substances, and considerably reducing the volume of wastes as a whole. Even components resistant to a high temperature cannot withstand the plasma treatment process.
- Plasma gasification process (pyrolysis) ensures ecologically clean processing of raw materials (wastes) without formation of resins, dioxins, aerosols, etc., as well as complete extraction of carbon from the waste material, while in other combustion processes up to 30% carbon remains in the fixed residue. The process of plasma gasification provides the highest possible degree of cleaning of the treated materials up to 99.99% and higher.
- The product of plasma gasification is a high-calorie combustible gas (mixture of H_2 + CO) and neutral fixed residue in the form of glassified slag.
- Gas and slag from plasma gasification of carbon-based wastes have commercial value. The above gas may be used when and as it is required: it can be used immediately, stored (preserved) for future use, or transported to a remote user. Gas can be an effective fuel source for power generation, or raw material to produce synthetic motor fuel, etc.
- Ash removed from the reactor in the liquid state, is safe at disposal. Slag melt can be granulated at tapping and used in construction, and the metal melt can be used for producing alloys, master alloys, refining remelting, etc, although the amount of this metal residue usually is quite small.
- Plasma gasification ensures a huge reduction of the solid substance weight. The ratio of waste material weight to the fixed residue ash is up to 400: 1, i.e. degree of processing is more than 99.7%. Other technologies usually provide not more than 5:1, i.e. 60%.
- Plasma gasification units are modular units, taking up a quite small space. They provide easy service, repair ability, adaptability to certain requirements and fast increment of productivity, if required. They may be placed inside the existing infrastructures or under the ground, this facilitating their acceptance by society.
- Plasma torch is an independent heat source, allowing flexible control over the gasification process, i.e. instantaneous response to a change in the processed material composition;
- Cost of construction and sustaining the plasma process of gasification looks to be lower than that of any regular modern combustion system.
- Results of testing performed by a large number of companies, are indicative of the fact that when plasma gasification technologies are used, the concentration of toxic emissions both into the atmosphere and in the fixed residue, is lower than the currently valid standards.

With the advent of plasma technologies waste landfills are becoming the technique of the past.

On the other hand, despite the above-mentioned significant advantages of plasma processes, they have certain drawbacks, preventing a successful promotion of these technologies and equipment to the market.

In practice, electric arc generators, using both inert and oxygen-containing gases, are used as the heat source. In any case, zones of extremely high temperatures (from thousands up to dozens of thousands of degrees) and high parameters gradients are always present in the working space. These circumstances lead to difficult-to-resolve problems, related to selection of the structure and material of reactor walls (materials, that are high-temperature resistant and chemically inert to the wastes, are required), as well as to the technological accuracy and reproducibility. Reaction rates are exponentially dependent on temperature, so that the processed materials being in different temperature zones leads to a great scatter in the material processing rates and process results, respectively.

Another fundamental problem in industrial acceptance of large-tonnage plasma units with a long cycle of continuous operation consists in the need to use quite powerful (above 100 kW) indirect-arc plasmatrons, having rather limited actual continuous service life, related to inevitable erosion of the most widely used copper electrodes. The industry currently widely uses arc plasmatrons with a relatively short continuous operation cycle (usually only several hours).

On the other hand, the actual paths for essential extension of the above operating life of the most widely used copper electrodes are not clearly seen now. In this case, we are not considering other structures, capable of really providing a much longer operating life, as a cathode self-restored from the gas phase, tungsten, consumable graphite, as being rather complicated and exotic for these technological processes.

Erosion rate of copper electrodes (cathode and anode), which eventually is what determines the plasmatron service life, is related to many factors, and, particularly, arc current. Depending on the near-electrode process dynamics, the erosion characteristics of the anode and cathode may both coincide completely and demonstrate a considerable discrepancy. One of the main issues is providing the unchanged level of specific electrode erosion at long-term operation in the sub-critical current range.

*To solve the above problems, a new technology, eliminating combustion, is proposed, which is based on the use of water steam with high thermodynamic parameters (temperature around 1100 C) for pyrolysis (high-temperature gasification) of the above wastes (**Fig. 1**).*

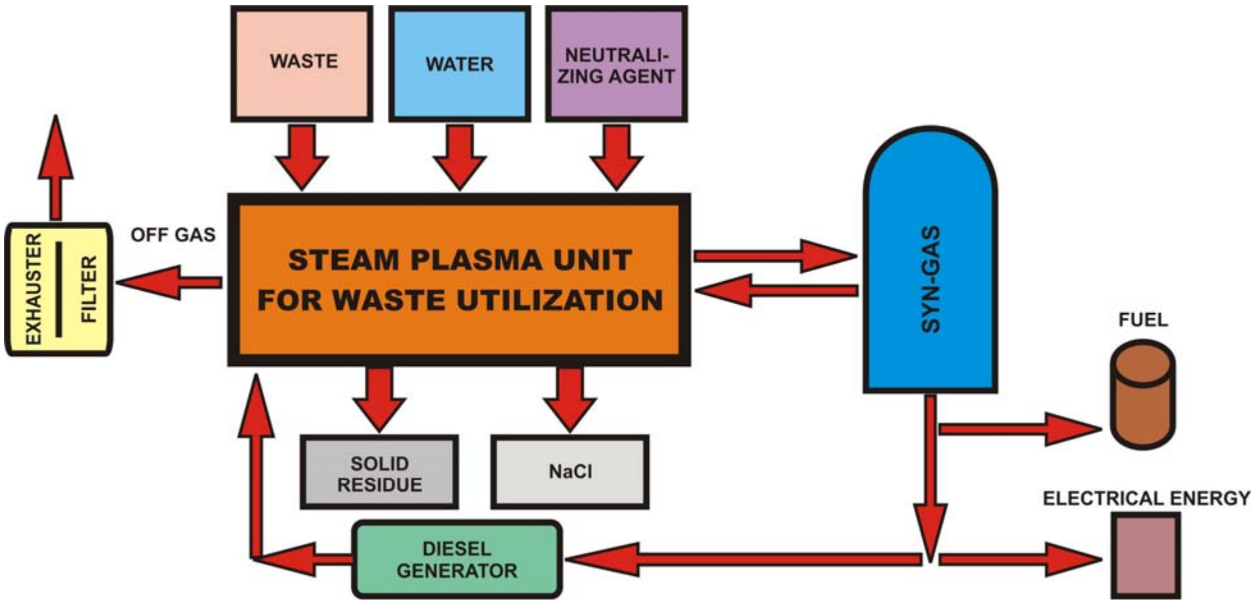


Fig. 1. Schematic of the process of steam-plasma processing of wastes

Performed evaluation shows that processing (plasma gasification) of 1kg of medical wastes (tentative composition being 60% cellulose + 30% plastics + 10% liquid) requires about 1 kW-h of power, which is consumed for dissociation of these substances with generation of synthetic gas ($CO + H_2$) in the amount of 1.1 – 1.4 nm^3 from one kilogram of wastes. In this case the following pyrolysis reaction proceeds:

- cellulose $C_6H_{10}O_5$ + heat =>CH_4 + 2CO +3H_2O => nCO + mH_2
- polyethylene CH_2-CH_2-]n + H_2O + heat => CH_4 + yH_2 + zCO =>nCO +mH_2

Heat evolves at combustion of synthetic gas:

$$CO + 1/2O_2 = CO_2,\ \Delta H = -\ 67.63\ \text{ccal}$$

$$H_2 + 1/2O_2 = H_2O,\ \Delta H = -\ 57.82\ \text{ccal}.$$

with the total energy ΔH = -125.45 ccal. per one gram-mole. This corresponds to 2800 ccal/nm^3, which is equivalent to 3.26 kW-h of power. That is, pyrolysis of 1 kg of medical wastes of the above composition, results in generation of energy carrier of 3.59 – 4.56 kW-h capacity converted into power. When the synthetic gas formed during processing is used for powering the plasma pyrolysis unit and allowing for the diesel generator efficiency on 30% level, a practically zero energy balance of the process is achieved, when the energy required for the process is produced completely through combustion of the generated synthetic gas.

At steam pressure in the reaction volume of 0.1 MPa and its temperature of 1100°C, which, by our preliminary estimate, is close to the optimum process mode, the water volume will increase 6330 times, while the enthalpy is 4877 J/g. The required full thermal power for conversion of 1kg/h of water into vapour is equal to 1354.7 W.

Accordingly, ensuring the unit annual efficiency of about 200 tons of wastes, this corresponding to the needs of an average clinic or a mobile plant, requires a plasmatron of about 40 kW power and water flow rate of 30 kg/h. Allowing for the efficiency, converter power factor and requirements of the plasma unit proper the consumed power of the mains will be equal to $40.642/(0.7 - 0.8) \approx 51 \div 58$ kVA.

Amount of steam at the temperature of 1100 °C, pressure of 0.1 MPa and water flow rate of 30 kg/h will be equal to about 190.000 m^3/h. Depending on nozzle diameter in the range from 20 to 100 mm, at the above efficiency it is possible to obtain the flow rate in the range of 6.7 to 168 m/s, respectively.

It should be noted that at present no other technical means are available, except for the plasmatrons, to generate water steam with the required thermodynamic indices, and in this case it is the question of using the so-called "steam" plasma (i.e. plasma, using water steam as the plasma forming gas).

The proposed process, called PLAZER, allows solving many problems of the traditional technologies of plasma gasification.

All currently available units for plasma processing of wastes are characterized by high parameter gradients in the reaction zone, due to the properties of the plasma jets. This circumstance leads to different conditions for waste material volumes being gasified at different rate, while new undesirable compounds can form in the high-temperature zone, for instance, nitrogen oxides, etc. At high-temperature steam pyrolysis, a uniform temperature and concentration mode sets in through the entire reaction zone volume due to the high transport properties of the steam. That is, the process becomes completely monitored and controllable. This is highly important for processing the wastes of a variable composition, when the parameters of steam fed into the reactor are to be controlled to minimize the processing time and maintain the optimum composition of synthetic gas, i.e. a constant set ratio of CO/H_2.

PLAZER provides a highly efficient (up to 100%) processing of organic wastes (including medical and other hazardous wastes) without emission into the environment of such harmful substances as dioxins, resins, phenols, aerosols, etc. The desired product formed, is synthetic gas, which is a valuable energy carrier, as well as safe solid processing products, suitable for further use, for instance, in construction.

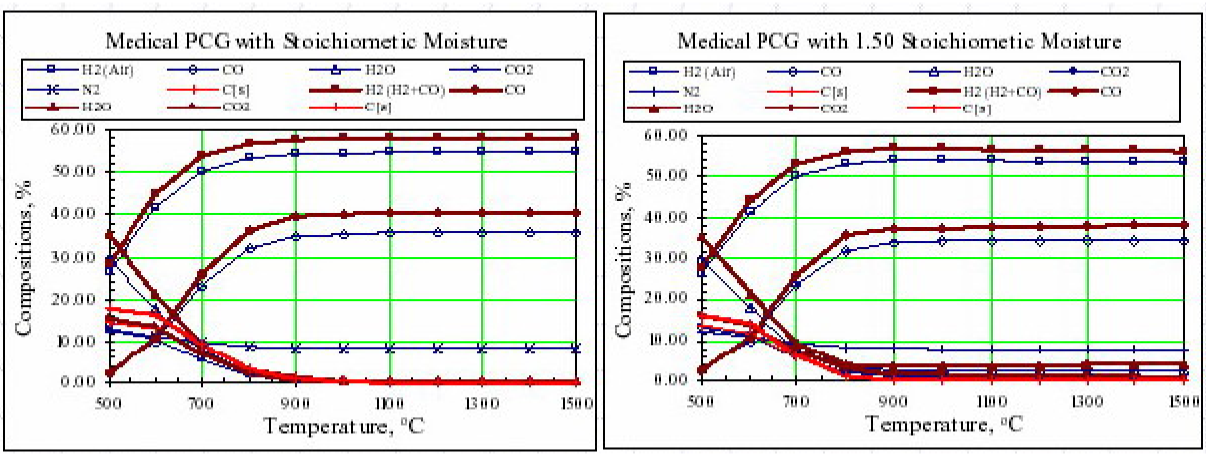
Such hazardous elements as chlorine, fluorine, etc. present in the composition of many plastic materials, are bound and readily removed during processing. At gasification of carbon-containing substances by water steam at high thermodynamic parameters, the gas phase does not contain sulfur compounds – it remains entirely in the fixed residue (slag).

Absence of ballast nitrogen and free oxygen in the reaction chamber eliminates the problem of nitrogen oxide formation. This, allowing for the absence of argon or other gases, provides a high quality of the obtained synthetic gas, and does require additional measures for its separation and cleaning.

The process of steam-plasma gasification is not sensitive to humidity of the processed wastes. It does not loose its destructive effectiveness with the change of humidity and composition of the solid substance.

With application of steam-plasma conversion, a much higher degree of waste material conversion (irrespective of its composition) into the desired product of synthetic gas is to be anticipated. This will provide new engineering means for specifying more stringent ecological norms on toxic emissions, including dioxins.

At steam conversion temperature over 900°C (as is seen from thermodynamic analysis [9] given in **Fig. 2**), equilibrium carbon is absent from the system. Therefore, the issue of complete gasification of carbon from all the compounds is determined solely by process kinetics, i.e. time of the solid phase contact with the reactive heat carrier – in this case water steam with high thermodynamic parameters. It is obvious that with temperature increase the reaction rate (and efficiency, respectively) will rise with the proportional reduction of overall dimensions of the unit. Upper temperature level will be determined chiefly by the reactor material resistance.



a b

Fig. 2. Change of the composition of gas converted by plasma at processing of medical wastes under the conditions of stoichiometric (a) and 1.50 of stoichiometric humidity (b) [9].

Use of synthetic gas produced during processing, for self-sufficient powering of the unit proper entails an essential lowering of power consumption in waste processing, thus making the process practically energy self-sufficient and in addition, simultaneously organizing production of power and liquid fuel.

The operating life of the steam plasmatron (steam plasma generator) is much longer than the operating life for regular one, and development of 300 kW steam plasmatron with the continuous operating life of 300 h, is quite real in the authors' opinion.

Equipment used in the process implementation is characterized by reduced overall dimensions (3 to 5 times, compared to the best analogs). This equipment can be made both in the stationary and in the mobile variants (on a truck bed or carriage bays, sea or river ships, etc.), thus providing a real engineering facility for waste recycling in the site where it is generated and accumulated.

Various organic wastes, including highly-toxic and hazardous can be proposed as an object of recycling by the PLAZER process:

- Medical wastes – syringes, gloves, dressing materials, organic wastes, etc.;
- Birds carcasses to be processed as a result of birds flue;
- Homeless animals (dogs, cats, groundhogs etc.) carcasses;
- Used plastic bottles and containers;
- Car tires;
- Pesticides and chemical pest killers;
- Wood chips;
- Other organic wastes.

The above merits and advantages of the PLAZER process allow overcoming the disadvantages of other known processes and are a reliable basis for its promotion in the market. The equipment can be both used in Ukraine, and proposed for export, as the need for such an equipment is in place all over the world. By preliminary estimates, the requirements of just the Ukrainian market in medium-efficiency industrial units for steam-plasma recycling of organic, also medical and other hazardous (highly toxic) wastes of 1000 tons per year are equal to approximately 300 to 350 units. The needs of the European and world markets (taking into account the known data on wastes accumulated in the health care establishments) are practically unlimited.

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