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ENERGY-SAVING TECHNOLOGIES FOR DISPOSAL OF WASTE WITH PRINTING DESIGN ELEMENTS

Introduction

Waste is an objective consequence of the civilization development, which creates many problems and requires decisive environmental action. But, on the other hand, waste is a resource that, in a market economy, can contribute to the overall energy balance. Municipal solid waste (MSW) (household waste and waste from other sources, such as retail, administration, education, health services, accommodation and food services, etc.). This fraction includes a wide range of products from different materials - organic, plastic, metal, paper, glass, bulky items, batteries, exhaust oils/lubricants, light bulbs, etc.). It represents around 10 % of the total waste generated by mass. More than 90% of MSW has varnish and paint coatings due to printing design. The removal of such paint elements by sorting technologies presents a significant technical challenge¹.

Therefore, the main task of the disposal systems for printing (packaging) products is a scientifically sound choice of technologies for innovative projects in order to ensure minimum or complete absence of emissions, as well as maximum production of target end products or raw materials. These tasks can be most fully achieved by using a system of sorting, identification and separate processing of waste types, in particular, plastic film packaging and packaging using modern resource-saving technologies. To do this, it is advisable to conduct

¹ Shtefan, Y., Roik, T., Zorenko, O., & Shostachuk, O. (2021). Methods of Digital Control of Printing Processes. Technology and Technique of Typography (Tekhnolohiia i Tekhnika Drukarstva), (2(72), 54–63. [https://doi.org/10.20535/2077-7264.2\(72\).2021.242474](https://doi.org/10.20535/2077-7264.2(72).2021.242474)

a preliminary physic - chemical and physic - mechanical analysis of products, as well as the calculation of technological, environmental and social parameters of their disposal, taking into account the characteristics of energy efficiency of equipment. In order to improve waste management, actions are prioritised following the «waste hierarchy» (Fig. 1).

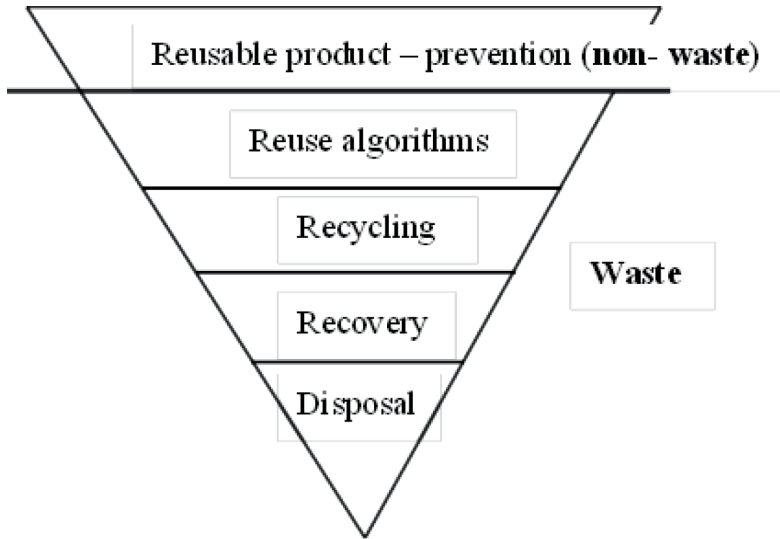


Figure 1. Waste hierarchy according to the Waste Framework Directive (2008/98/EC)

Global demand for food, feed and fibre in aggregate is expected to increase by 70 % by 2050. However, finite resources are becoming increasingly scarce and expensive to extract, whilst renewable resources are often harvested at unsustainable rates.

Technological aspects

Best environmental practices in several areas of waste management are already set out in European legislation and other European reference documents, such as Best Environmental Management Practices (BEMP) - best practices in environmental management and aims to help local waste management authorities and waste management companies move towards a «circular» economy².

This report - BEMP was prepared by the Joint Research Centre of the European Commission in support of the implementation of the sectorial cer-

² Dri M., Canfora P., Antonopoulos I. S., Gaudillat P., Best Environmental Management Practice for the Waste Management Sector, JRC Science for Policy Report, EUR 29136 EN, Publications Office of the European Union, Luxembourg, 2018, ISBN 978-92-79-80361-1, doi:10.2760/50247, JRC111059

tification strategy EMAS (Eco Management and Audit Scheme) for the waste management sector.

The document was developed by the European Commission's Joint Research Centre (JRC) on the basis of desk research, interviews with experts, site visits and in close cooperation with a Technical Working Group (TWG) comprising experts from the sector. This document is based on a preparatory external study carried out by BZL Kommunikation und Projektsteuerung GmbH (Germany) and E3 Environmental Consultants Ltd (UK), whose findings are presented in a Background Report.

The figure 2 illustrates the waste management phases in relation to this report: 1- the ones covered, in 2 the one partially covered and in 3 the ones not explicitly covered.

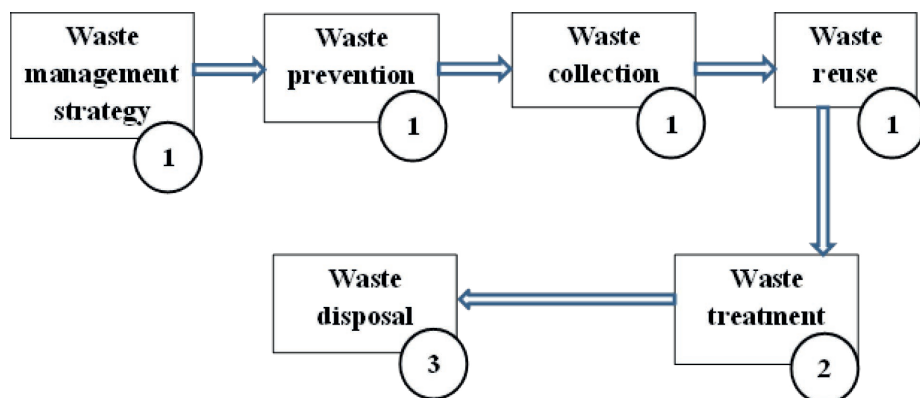


Figure 2. Waste management activities covered in the scope of BEMP.

The main problem is the disposal of «mixed waste», which covers all plastic packaging waste from household waste, and includes rigid and flexible products of various polymer types and colours, which are usually generated with the element of printing design. Given the impossibility of effective separation of printing elements for most mixed waste streams, this mass remains as a residual component, which is usually sent to the final disposal or recovery of energy³. To minimize the component for disposal, attention should be paid to high-temperature disposal methods based on pyrolysis and gasification processes.

It is advisable to consider such methods in combination with technologies for the production of alternative energy carriers and the production of various types

³ Shtefan E., Serogin O. Energy independence problem solving by biomass technologies / Scientific trends: modern challenges. Volume 1 : collective monograph / Compiled by V. Shpak; Chairman of the Editorial Board S. Tabachnikov. Sherman Oaks, California : GS Publishing Services, 2021.- P. 64-70.

of substances and energy on their basis, for example, mechanical, thermal and electrical. So, all mixed waste can be considered as a type of fuel with its inherent calorific value.

Today a certain amount of experience has been accumulated to assess the combustibility of various materials. The lower limit of the calorific value at which they can be burned without additional fuel is from $Q_{H,min} = 3.35 \text{ MJ/kg}$ to $Q_{H,min} = 4.19 \text{ MJ/kg}$ ⁴. The Swedish scientist Tanner found that without additional fuel, various materials can burn with moisture content (W) of not more than 50%, ash (A) of not more than 60% and combustible substances (C) of at least 25%⁵. Figure 3 shows Tanner's triangle, illustrating the area of combustion of a substance without additional fuel⁶. According to Tanner, the lower limit of the calorific value of high-ash and wet material, at which it is possible to burn it without the use of additional fuel, corresponds to the condition: $W = 50\%$, $A = 25\%$, $C = 25\%$.

Based on this relationship, we can conclude that most MSW should be considered, first of all, as a raw material for energy production.

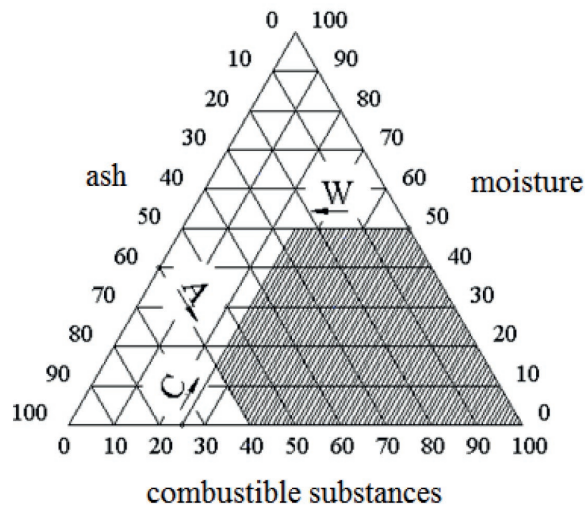


Figure 3. Tanner's triangle

This MSW disposal method will make it possible to turn waste into a valuable raw material, allowing the creation of an energy-chemical production facility that ensures

4 Serogin O., Vasylenko O., Pivovarov C. Processing and disposal of unsorted, unsegregated municipal solid waste / Journal of Food and Packaging Science, Technique and Technologies, №15, 2020/ - P.20-22.

5 Shtefan E., Serogin O. Energy independence problem solving by biomass technologies / Scientific trends: modern challenges. Volume 1 : collective monograph / Compiled by V. Shpak; Chairman of the Editorial Board S. Tabachnikov. Sherman Oaks, California : GS Publishing Services, 2021. - P. 64-70.

6 Serogin O., Vasylenko O., Pivovarov C. Processing and disposal of unsorted, unsegregated municipal solid waste / Journal of Food and Packaging Science, Technique and Technologies, №15, 2020/ - P.20-22.

its deep processing and, on this basis, the supply of highly liquid, competitive goods to the cycle of a closed economy, such as: electricity; thermal energy; combustible gases; rare gases; gases for organic synthesis; motor fuel; resins and oils; solvents; inks for printing inks; electrode graphite; carbon black; metallographic products and carbon plastics; carbides; abrasive materials and products from them; mineral fertilizers; sorbents and filtrates; metals, including: Al, Li, Ba, Ti, Ni, Ge, Co, Va, Cr, Mn, etc.; technical and drinking water; construction materials, etc.

Calculations show that this approach will allow not only minimizing the costs of disposal of various wastes and hazardous substances. Of the well-known technologies for the utilization of MSW, pyrolysis and gasification are attractive in that they make it possible to obtain cheap energy carriers and make a number of industries economically viable⁷.

Pyrolysis is the process of decomposition of complex hydrocarbon substances under the influence of high temperatures without access to ambient oxygen into simpler hydrocarbons.

The preferential production of one or another pyrolysis product (gas, coke or liquid products) is determined by the requirements of the consumer and can be achieved by appropriate hardware for the pyrolysis process. Taking into account the endothermic nature of the process, pyrolysis plants are distinguished by the method of heat supply to the reactor: external (by burning part of the resulting gas, tar or coke); internal (by supplying a limited amount of oxygen or air to the reactor to burn part of the raw material); circulating of hot gases or solid coolant using.

Depending on the temperature, pyrolysis technologies are divided into: low-temperature – up to 5500 °C; medium temperature – up to 8000°C; high-temperature - over 8000°C.

To expand the possibilities of controlling the pyrolysis process (obtaining products with desired characteristics and reducing the yield of toxins), it is advisable to use various catalysts.

In addition, it is advisable to combine a pyrolysis plant with a solid (coke) residue gasification plant with liquid or solid ash removal, or with a micro metallurgical process.

Gasification is a thermochemical process of converting various hydrocarbons into fuel, the so-called «generator gas»⁸.

7 Seryogin O., Vasylenko O., Frank J. Riedel, Helmut Aigner . Technological Complex for Processing of Solid Household and Treatment Facilities Waste with Biogas Obtaining / Energy Technologies and Resource Saving, ISSN 2413-7723, №2, 2021.- P.73-79. DOI: 10.33070/etars.2.2021.06

8 A combined two-stage Process to «Zero-Residue» Solution Processing and Disposal of unsorted, unsegregated Municipal Solid Waste. Frank Riedel. Presentation at ATHENS2014 International Conference on Sustainable Solid Waste Management

Thermal analysis allows one experiment to determine almost the entire set of technical characteristics of the fuel, with the exception of the release of volatiles. However, there is no standard method for determining these characteristics, due to the high diversity of the studied fuels; therefore, the issue of developing such a method is relevant.

One of the methods for describing the gasification processes of low-grade solid fuels is thermodynamic modelling, which determines⁹:

1. The equilibrium composition of the synthesis gas.
2. The relative amounts of oxidizing agent and heat required for the gasification process.
3. The optimal values of the calorific value of the synthesis gas and the efficiency of the process.

Schematically, the equilibrium thermodynamic system can be represented as follows (Figure 4):

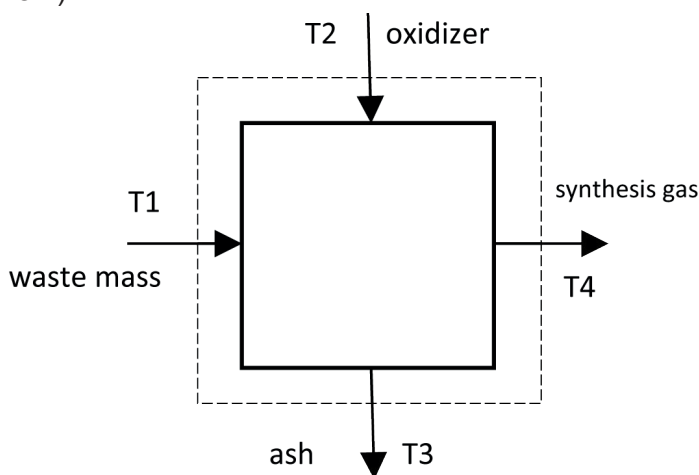
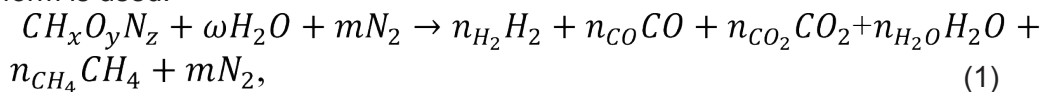


Figure 4. – Scheme of an equilibrium thermodynamic system

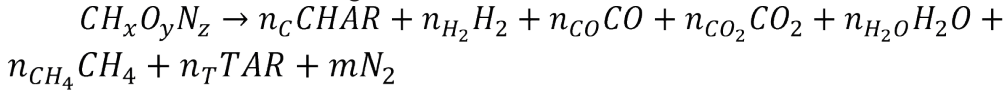
To describe the conversion process, a one-stage generalized reaction of the form is used:



where x, y, z is the number of atoms of hydrogen, oxygen and nitrogen reduced to 1 carbon atom, ω is the amount of moisture reduced to 1 mole of the organic mass of fuel, kg / mol, m is the amount of nitrogen.

⁹ Osmak A., Seregin A. Thermodynamic modeling of processes of thermochemical conversion of solid fuels / PROCEEDINGS OF UNIVERSITY OF RUSSIA - 2019, volume 58, book 10.1. P. 28-32

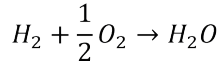
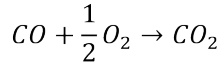
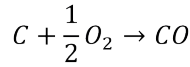
In the case of pyrolysis, one can write a similar one-stage generalized reaction, which will have the following form:



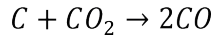
where CHAR – coke, TAR – resin. Moreover, their gross composition can be expressed by the formula $CH_{x1}O_{y1}N_{z1}$ and $\rightarrow CH_{x2}O_{y2}N_{z2}$, respectively.

Writing such equations is the first step in thermodynamic modelling, from which we can assume the main reactions that occur during the thermochemical conversion of solid fuel. Thus, the conversion mechanism is written in the form of several gross reactions in which fuel and coke are carbon and have the following form:

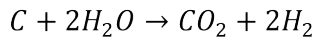
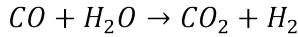
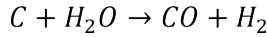
Combustion reaction: $C + O_2 \rightarrow CO_2$



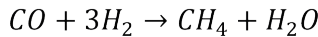
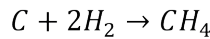
Boudoir reaction:



Water vapour reactions:



Methanation reactions:



These reactions proceed both with absorption and with the release of heat.

In thermodynamic modelling, it is assumed that all reactions reach equilibrium, and the equilibrium constants are calculated according to equation:

$$K_j = \prod_i (x_i)^{v_i} \left(\frac{P}{P^0}\right)^{\sum_i v_i}, \quad (2)$$

where x_i is the mole fraction of the i component in the ideal system, v_i is the stoichiometric coefficient (positive value for products, negative value for reaction reagents); P^0 – pressure in the initial state, 101.3 kPa.

The temperature dependence of the equilibrium constant can be expressed as follows:

$$\ln(K_{P,T}) = \ln(K_{P,T^0}) + f(T). \quad (3)$$

Equation (2) and (3) is used to describe the equilibrium state of an ideal system:

$$\ln K = -\frac{\Delta G_T^0}{RT}, \quad (4)$$

$$\Delta G_T^0 = \sum v_i \Delta \bar{g}_{f,T,i} \quad (5)$$

where R is the universal gas constant is the Gibbs function in the initial state, is the Gibbs function of the i component at a given temperature.

Given the generalized reaction (1), the equations of material and energy balance are compiled.

Material carbon balance:

$$f_1 = 0 = n_{CO} + n_{CO_2} + n_{CH_4} - 1, \quad (6)$$

Material balance of hydrogen:

$$f_2 = 0 = 2n_{H_2} + 2n_{H_2O} + 4n_{CH_4} - x - 2\omega, \quad (7)$$

Material balance of oxygen:

$$f_3 = 0 = n_{CO} + n_{CO_2} + n_{H_2O} - \omega - 2m - y. \quad (8)$$

Enthalpy balance:

$$\sum_{j=react} \bar{h}_{f,i}^0 = \sum_{i=prod} n_i (\bar{h}_{f,i} + \Delta \bar{h}_{T,i}), \quad (9)$$

where is the formation enthalpy, which is zero for all chemical elements in the initial state (298 K, 101.3 kPa); is the difference in the enthalpies between the calculated and initial state of the system and can be approximated according to equation:

$$\Delta \bar{h}_T = \int_{298}^T \bar{C}_P(T) dT, \quad (10)$$

where is the specific heat at constant pressure, which depends on temperature and can be determined empirically by equation:

$$\int_{298}^T \bar{C}_P(T) dT = a + bT^2 + cT^3 + dT^4 + k, \quad (11)$$

where k is the integration constant; a , b , c , d are the coefficients of the corresponding gases, which are presented in the reference books of physical and chemical quantities.

When methods are used to search for extreme of thermodynamic functions, a list of substances capable of participating and forming during chemical transformations is set as initial information, and it is not necessary to know the reactions that occur in the process under study. Most often, during thermodynamic modelling, the Gibbs free energy is minimized, which is minimized in the equilibrium state. Gibbs free energy of the system is defined as follows:

$$G = \sum_{i=1}^N n_i \mu_i, \quad (12)$$

where G is the Gibbs free energy, is the amount of the i th component of the system, μ_i is the chemical potential, which is determined by the formula (13):

$$\mu_i = \bar{G}_i^0 + RT \ln\left(\frac{\theta P_i}{p^0}\right), \quad (13)$$

where θ is the fugacity coefficient, $\bar{G}_i^0$ is the standard Gibbs free energy.

The fugacity coefficient and pressure are usually the same when the pressure approaches zero. Then equation (13) can be rewritten:

$$\mu_i = \bar{G}_i^0 + RT \ln(y_i), \quad (14)$$

where y_i is the mole fraction of the i component.

We substitute equation (14) into equation (12):

$$G = \sum_{i=1}^N n_i \Delta \bar{G}_i^0 + \sum_{i=1}^N n_i RT \ln\left(\frac{n_i}{n_{tot}}\right), \quad (15)$$

Next, we find the values of n_i that minimize the Gibbs energy using the Lagrange multipliers $\lambda_j = \lambda_1, \dots, \lambda_k$. At the same time, the limitations of the material balance for the elements are imposed on the thermodynamic system, which has the form:

$$\sum_{i=1}^N n_i a_{ij} = A_j, \quad j = 1, 2, 3, \dots, k, \quad (16)$$

where a_{ij} is the number of atoms of the j element in 1 mole of the i component, A_j is the total number of atoms of the j element in the reaction mixture.

Given the limitations of the material balance with respect to elements (16) and the Gibbs free energy equation (15), we write the form of the Lagrange function:

$$L = G - \sum_{j=1}^N \lambda_j (\sum_{i=1}^N n_i a_{ij} - A_j). \quad (17)$$

The partial derivatives of equation (17) are equal to zero. The fulfilment of this condition allows us to find the extreme point

$$\frac{\partial L}{\partial n_i} = 0 \quad (18)$$

Equation (18) can be transformed into a matrix form taking into account the limitations of the material balance (16). The values of n_i must satisfy the condition $0 \leq n_i \leq n_{tot}$. Equation (18) is solved by iterative methods, or by Newton's method. In thermodynamic modelling of the processes of thermochemical conversion of solid fuels, a number of assumptions are used:

1. The carbon contained in the fuel passes into the gas phase in the form of gaseous products of CO, CO₂, CH₄, and also H₂, H₂O, O₂ are part of the synthesis gas. The yield of hydrocarbons C₂ and higher is considered insignificant and is not taken into account in the calculation. Unreacted carbon is represented by coke and soot. In this case, the reaction time is sufficient to achieve equilibrium.

2. Resin formation is neglected.

3. Ash is considered an inert substance in the conversion process, although in practice it has a significant thermal and chemical effect on the system under study at temperatures above 700 °C.

4. Gases have ideal properties.

Thermodynamic models allow us to evaluate the maximum theoretical efficiency of the process and describe the equilibrium composition of the system.

The process of thermochemical conversion is influenced by three macrokinetic restrictions:

1. The restriction associated with the fact that the gasification process tends to the boundary of the formation of free non-gasified carbon. Upon reaching this boundary, an equilibrium is established between the solid and gas phases.

2. The limitation associated with the thermal regime of the process, which, regardless of the reaction parameters determines the efficiency of the process and the composition of the resulting synthesis gas.

3. The restriction associated with the fact that after the onset of a stationary state, additionally added heat to the system is mainly used to heat the reaction products, and not to change their composition.

Taking into account the above macrokinetic limitations in thermodynamic modelling allows us to bring the models under development closer to a realistic description of the processes under study. Usually, the restrictions used take into account the formation of nonequilibrium products and (or) the features of the course of the individual stages of the conversion¹⁰.

Another method for describing nonequilibrium processes is the calculation of multicomponent chemical reactions in the form of a sequence of time-dependent intermediate thermodynamic states. The method combines taking into account the kinetics of the reaction in the form of Arrhenius dependence and the thermodynamic method of minimizing Gibbs energy.

In an equilibrium thermodynamic description, the account of the phenomena caused by the kinetics of chemical reactions, diffusion, and heat transfer should be carried out in terms of a macroscopic description in which the time variable is expressed in terms of other system variables¹¹. For a formalized description of the kinetic block in thermodynamic models, three methods are used:

1. Record additional balance ratios that limit the individual stages of the mechanism of the process under study;

2. Transformation of the right-hand sides of kinetic equations into thermodynamic potentials;

¹⁰ Prediction of performance of a downdraft gasifier using equilibrium modeling for different biomass materials / Z.A. Zainal, R. Ali, C.H. Lean, K.N. Seetharamu // Energy Conversion and Management. 2001. V. 42. P. 1499 – 1515.

¹¹ Там само.

3. Entering constraints directly on the kinetic equations.

The first method is due to the unity of thermodynamics and kinetics, which describe the same physical laws in different ways. This method allows one to take into account the mechanism of processes in thermodynamic studies, without requiring its full knowledge and formalized description. The introduction of additional thermodynamic limitations of chemical and transfer processes expands the field of effective use of this approach.

The second method consists in replacing the coordinates in the right-hand sides of the kinetic equations by potentials and the subsequent formulation of the converted parts into an expression for the characteristic function of the system in question. This approach is time-consuming and is due to the use of a large number of assumptions, which in the general case are not substantiated, therefore, have almost not received practical application.

The third approach is the simplest and consists in the fact that the speed of the process is determined by the limiting reaction, for which kinetic coefficients are known with great reliability. Taking into account macrokinetic constraints for irreversible processes drastically reduces the studied area of thermodynamic reachability and, accordingly, increases the accuracy of thermodynamic estimates of process limit values.

Calculations show that the economic efficiency of waste disposal increases significantly when pyrolysis and gasification processes are combined.

It should be especially emphasized that the combination of a pyrolysis plant and a gas generator waste disposal process into one technological process will make it possible to bring the use of waste products to almost 100%.

It is advisable to complete the installations with an autonomous power plant or boiler house, which use coke residue, pyrolysis or generator gases, and liquid fractions as fuel.

In the future, the plants can be equipped with modules for the production of synthetic gasoline and diesel fuel according to the scheme: pyrolysis gas $\rightarrow$ methane $\rightarrow$ methanol $\rightarrow$ gasoline. The direct synthesis of gasoline using the Fischer-Tropsch technology from synthesis gas is also possible. Economically attractive are the possibilities for obtaining such gases as, hydrogen, carbon monoxide and dioxide, nitrogen, etc.

It seems very promising to use the products of gasification and pyrolysis, including coke and hot ash, in external combustion engines - «Stirling engines» type (with external heat supply).

For the practical implementation of the above-mentioned waste disposal processes, the following steps are proposed:

- the pilot plant development with a processing capacity of 0.5-10 tons/day;
- the technology for gasification and pyrolysis processing development for various raw materials;
- design and construction of energy-chemical production facilities with a processing 50-150 tons/day (by the expense of profits received from low-capacity power plants).

With the author's participation, the GG-30 gas generator (Fig. 5) and the UPF-02, UPP-1 pyrogenerators (Fig. 6) have been designed, manufacturing and successfully tested.



Figure 5. General view of the gas generator GG-30



a



b

Figure 6. The combustion process of generator gas: a) in a low-pressure burner (a) and in an infrared burner (b)

The test results of these installations served as the basis for the development of a scheme for a combined converter of organic waste into gaseous, liquid and solid substances and energy carriers.

Converter K-47 (Fig. 7) consists of: pyrolysis generator -1; heat exchanger -2; filter for purification of pyrolysis and gasification products -3; gas compressor -4; gas tank -5; internal or external combustion engine -6; electric current generator -7; gas generator -8.

The material flows directions are shown by arrows (Fig. 7): I - feedstock; II - thermal energy; III - liquid fractions of pyrolysis; IV - pyrocarbon; V - pyrolysis and generator gas, respectively; VI - electricity; VII - ash.

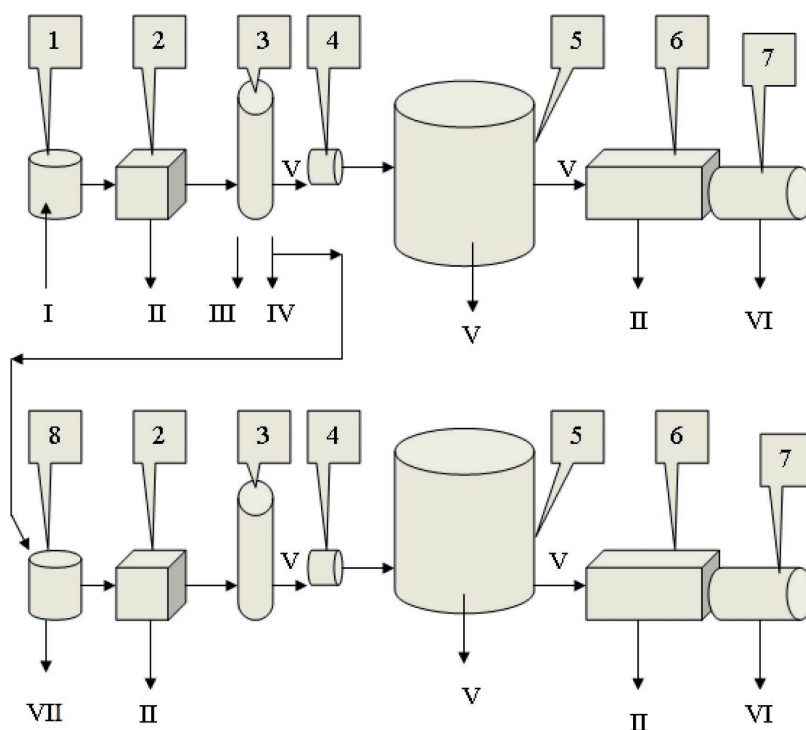


Figure 7. Scheme of the combined converter K-47

The payback period of technological equipment does not exceed 1-2 years.

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