



Technical sciences

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PHYSIC-CHEMICAL ASPECTS OF ENERGY SUBSTITUTION TECHNOLOGIES IN MODERN PRODUCTION PROCESSES OF PRINTING ENTERPRISES

Introduction

Ukraine's integration into the global economic space requires new approaches to the formation and implementation of the organizational and economic foundations of the energy development of the national economy's branches within the framework of the “green economy” concept. These processes take into account the main challenges:

- Exhaustion of traditional energy sources.
- The prices increasing for traditional energy carriers.
- The resource efficiency increasing.
- The implementation of balanced consumption and production models.
- The tendency towards low-carbon development.

In particular, the printing industry enterprises require significant thermal energy to ensure the efficient operation of glue, steam and water boilers, as well as to ensure the specified heat and mass transfer modes in the technologies of stabilization of printing products, varnishing and adhesive fixation of structural joints.

The energy resources used at each enterprise are a conscious choice within the framework of the appropriate project management system. You can

choose currently more traditional sources of energy, or ecologically cleaner ones: energy from the sun, wind, and water (Fig. 1.) Each of the options has significant differences in the material and technical base of its support, its advantages and disadvantages.

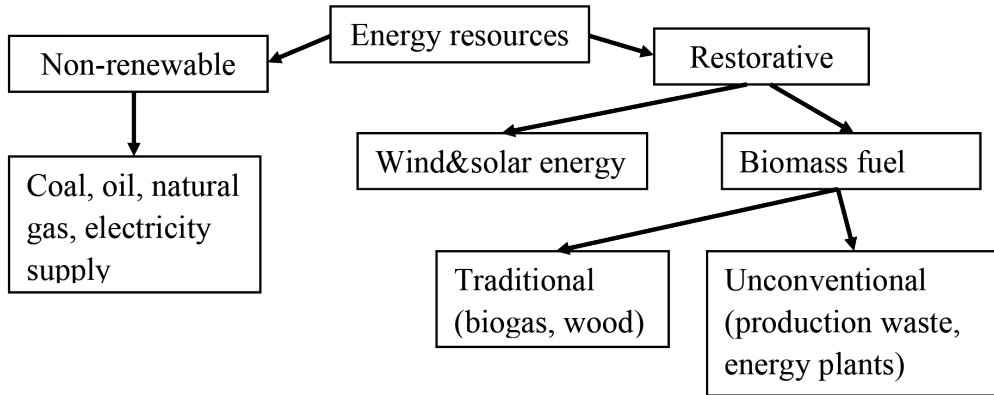


Fig.1. Energy resources structure elements

How energy replacement projects will be implemented is determined not only by the specific conditions of the organization of production processes, but also by the results of scientific research into the physical and chemical aspects of energy flows, which are provided by the technological processes of wide range of printing products manufacturing. Only a deep, convincing physical and chemical justification of the processes of energy substitution can provide a conscious decision regarding the organization of rational energy supply schemes of the enterprise. In the new economic conditions, in connection with a sharp increase in the cost of non-renewable energy resources, the development and use of local, relatively cheap alternative fuels becomes an urgent task. The most powerful local energy resource for most printing enterprises is plant biomass and waste from its processing, as well as waste from own production¹.

In the process of functioning of any enterprise, a large amount of various production wastes containing carbon are formed, consisting of spent fuel and lubricants, rubber and technical products, packaging (containers), plastics, household waste, technological waste of used raw materials, aspiration products, etc. The involvement of this type of renewable energy resources would significantly reduce the need for traditional types of fuel.

¹ Shtefan E. 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.

The problem formulation

The thermochemical method of processing renewable energy resources using gasification (production of generator gas) allows for the development of autoenergetic technology for the creation of local units within the enterprise for the production of heat and electric energy². Depending on the nature of the contact of biomass particles with the gas phase, gas generation methods can be classified into a fixed-bed system (one or several stages), a fluidized-bed system, and other systems (a system with pushing raw materials, a liquid coolant). We proposed a method of air gasification of plant biomass in a stationary (stationary) layer. The use of air gasification of plant biomass makes it possible to reduce the cost of obtaining generator gas, and the gas formation process takes place at atmospheric pressure. The selected method has a number of significant advantages over other methods of solid fuel gasification: - the possibility of building gas generators of large unit capacity; - the universality of the method, which allows the use of all types of plant biomass, as well as the transition from air blowing to oxygen and vapor oxygen blowing; - low metal capacity; - a small number of stages for the preparation of plant biomass. In a gas generation system with a fixed bed, different temperature zones are formed during the countercurrent (direct flow) movement of gas, which contribute to the transformation of bound carbon into gas. There are combined systems with a fixed bed of raw materials and the use of rotary kilns for solid materials and with a moving bed that is periodically stirred (Garrett Energy Research and Engineering). The choice of the most appropriate gasification method is often determined by the type and conditions of raw material supply, requirements for moisture content and ash elements³. With an ash content of 1-2 % and a moisture content of more than 70 %, for example in wood without preliminary treatment, thermal processing without the introduction of additional fuel is impossible. It is also not recommended to carry out thermal processing of algae with a content of 82 % water or peat with a content of 90 % water without their preliminary preparation. Moisture reduction is achieved by mechanical dehydration or drying. The main parameters of the selected gasification process are presented in Table 1.

2 Shtefan, Ye., & Serogin, O. (2022). Energy-saving technologies for disposal of waste with printing design elements. *Theoretical and practical aspects of modern scientific research : collective monograph. Compiled by V. Shpak; Chairman of the Editorial Board S. Tabachnikov. Sherman Oaks* (p. 91–103). California : GS Publishing Services, 256 p.

3 Shtefan Ye. Practice of Ecological Management of Waste Disposal with Elements of Printing Design/ Shtefan Ye., Seryohin O.O., Ilyenko B.K., Chornyi Yu. A. // Design Energotehnologii i resursosberegeniie. [Energy Technology and Resource Saving]. 2022. №. 3. P. 86–95.

Table 1

Main parameters of the selected gasification process

Parameter name	Unit	Parameter value
Type of gasification process	-	reverse
Fuel moisture (no more)	%	50
Dry gas output from 1 kg of fuel	m ³ /kg	0,8÷2,0
Dry gas output from 1 kg of fuel Fuel consumption	m ³ /kg	depending on the raw material 1,4 ÷ 4,2
Fuel consumption	kg/h	20,0 ÷ 150,0
Temperature in the combustion zone	°C	1200
Outlet gas temperature from the gas generator	°C	550
Gas temperature after the generator gas fine filter	°C	45 ÷ 60
The pressure in the elements of the complex is not higher	kPa	25
Calorific value of gas	kcal/m ³	depending on the raw material 1560 ÷ 1200
Generator power (thermal)	kW	depending on the raw material 100,0 ÷ 400,0

Physic-chemical aspects

Pyrolysis and gasification are attractive in that they make it possible to obtain cheap energy carriers and make a number of industries economically viable⁴. 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

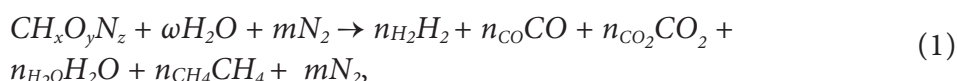
4 Seryogin O., Vasylenko O., Frank J. Riedel, Helmut Aigner . Technological Complex for Processing of Solid Household and Treatment Facilities Waste with Biogas Obtaining. Ecotechnologii i Resursosberezhenie. [Ecotechnologies and Resource Saving]. 2021. № 2, P. 73–79. DOI: 10.33070/etars.2.2021.06.

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”. 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 determines⁵:

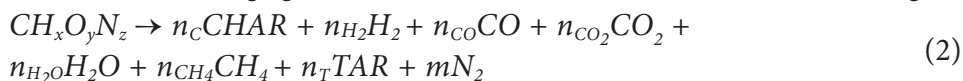
- The equilibrium composition of the synthesis gas.
- The relative amounts of oxidizing agent and heat required for the gasification process.
- The optimal values of the calorific value of the synthesis gas and the efficiency of the process.

Schematically, the equilibrium thermodynamic system can be represented as follows (Fig. 2).

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



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 modeling, 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.

⁵ Osmak A., Seregin A. Thermodynamic modeling of processes of thermochemical conversion of solid fuels. PROCEEDINGS OF UNIVERSITY OF RUSE. 2019, Vol. 58, book 10.1. P. 28–32.

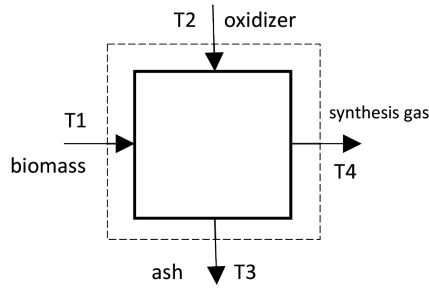
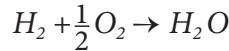
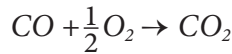
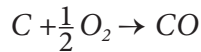
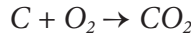
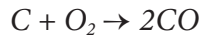


Fig. 2. Scheme of an equilibrium thermodynamic system

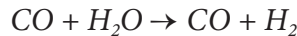
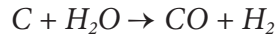
Combustion reaction:



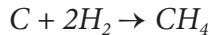
Boudoir reaction:



Water vapor reactions:



Methanation reactions:



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

In thermodynamic modeling, it is assumed that all reactions reach equilibrium, and the equilibrium constants are calculated according to equation (2):

$$K_j = \prod_i (x_i)^{v_i} \left(\frac{P}{P^0} \right)^{\sum_i v_i}, \quad (3)$$

where x_i is the mole fraction of the i component in the ideal system, v 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:

$$\ln(K_{P,T}) = \ln(K_{P,T^0}) + f(T). \quad (4)$$

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

$$\ln K = -\frac{\Delta G_T^0}{RT}, \quad (5)$$

$$\Delta G_T^0 = \sum_i v_i \Delta \bar{g}_{f,T,i} \quad (6)$$

where R is the universal gas constant, ΔG_T^0 is the Gibbs function in the initial state, $g_{f,T,i}$ 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:

$$f_1 = 0 = n_{CO} + n_{CO_2} + n_{CO_4} - 1, \quad (7)$$

Material balance of hydrogen:

$$f_2 = 0 = 2n_{H_2} + 2n_{H_2O} + 4n_{CH_4} - x - 2\omega, \quad (8)$$

Material balance of oxygen:

$$f_3 = 0 = n_{CO} + n_{CO_2} + n_{H_2} - \omega - 2m - y, \quad (9)$$

Enthalpy balance:

$$\sum_{j=react} \bar{h}_{f,i}^0 = \sum_{i=prod} n_i (\bar{h}_{f,i} + \Delta \bar{h}_{T,i}), \quad (10)$$

where $\bar{h}_{f,i}$ is the formation enthalpy, which is zero for all chemical elements in the initial state (298 K, 101.3 kPa); $\Delta \bar{h}_{T,i}$ is the difference in the enthalpies between the calculated and initial state of the system and can be approximated according to equation:

$$\Delta \bar{h}_T = \int_{298}^T \bar{C}_p(T) dT, \quad (11)$$

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

$$\int_{298}^T \bar{C}_p(T) dT = a + bT^2 + cT^3 + dT^4 + k, \quad (12)$$

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 extrema 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 modeling, the Gibbs free energy is minimized, which is minimized in the equilibrium state. Gibbs free energy of the system is defined as follows:

$$G = \sum_{i=1}^N n_i \mu_i, \quad (13)$$

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

$$\mu_i = \bar{G}_i^0 + RT \ln\left(\frac{\theta P_i}{P^0}\right), \quad (14)$$

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 (14) can be rewritten:

$$\mu_i = \bar{G}_i^0 + RT \ln(y_i), \quad (15)$$

where y_i is the mole fraction of the i component.

We substitute equation (15) into equation (13):

$$G = \sum_{i=1}^N n_i \Delta \bar{G}_i^0 + \sum_{i=1}^N n_i RT \ln\left(\frac{n_i}{n_{tot}}\right), \quad (16)$$

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:

$$\sum_{i=1}^N n_i a_{ij} = A_j, \quad j = 1, 2, 3, \dots, k \quad (17)$$

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 (17) and the Gibbs free energy equation (16), we write the form of the Lagrange function.

$$L = G - \sum_{j=1}^k \lambda_j \left(\sum_{i=1}^N n_i a_{ij} - A_j \right). \quad (18)$$

The partial derivatives of equation (18) are equal to zero. The fulfillment of this condition allows us to find the extremum point.

$$\frac{\partial L}{\partial n_i} = 0 \quad (19)$$

Equation (19) can be transformed into a matrix form taking into account the limitations of the material balance (17). The values of n_i must satisfy the condition $0 \leq n_i \leq n_{tot}$. Equation (19) is solved by iterative methods, or by Newton's method.

In thermodynamic modeling 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.

Main theoretical and practical results

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 modeling 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 conversion⁶.

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 an 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 variables. For a

⁶ Zainal Z.A., Ali R., Lean C.H., Seetharamu K.N. Prediction of performance of a downdraft gasifier using equilibrium modelling for different biomass materials. *Energy Conversion and Management*. 2001. Vol. 42. P. 1499–1515.

formalized description of the kinetic block in thermodynamic models, three methods are used:

- ▶ record additional balance ratios that limit the individual stages of the mechanism of the process under study;
- ▶ transformation of the right-hand sides of kinetic equations into thermodynamic potentials;
- ▶ entering constraints directly on the kinetic equations.

The first approach 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 abovementioned 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 and the UPF-02, UPP-1 pyrogenerators have been designed, manufacturing and successfully tested. 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. The material flows directions (by arrows) and equipment schematic lay out are shown at Figure 3: I – feedstock; II – thermal energy; III – liquid fractions of pyrolysis; IV – pyrocarbon; V – pyrolysis and generator gas, respectively; VI – electricity; VII – ash. Converter consists of: 1 – pyrolysis generator; 2 – heat exchanger; 3 – filter for purification of pyrolysis and gasification products; 4 – gas compressor; 5 – gas tank; 6 – internal or external combustion engine; 7 – electric current generator; 8 – gas generator.

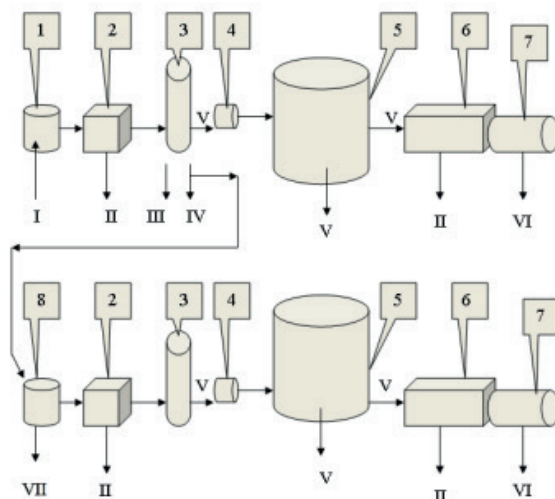


Fig. 3. Scheme of the combined converter.

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