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THERMODYNAMIC MODELING OF PROCESSES OF THERMOCHEMICAL CONVERSION OF SOLID FUELS

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Abstract: *The thermochemical conversion of solid fuels is a multi-stage process that combines a large number of elementary reactions, the experimental separation of which is difficult. Therefore, the construction of an adequate mechanism of this process is a necessary task. In this regard, most researchers use enlarged mechanisms, and the kinetics of the conversion of solid fuels is approximated by a first-order reaction in a one-step process, without taking into account the individual kinetics of gum formation, volatilization, and coke conversion. This fact leads to a significant deviation of the calculated temperature profiles, gas composition, etc. in numerical simulation of the process under study from experimentally obtained data.*

Keywords: *synthesis gas, biomass, thermochemical conversion.*

INTRODUCTION

In the case of a comprehensive study of the properties of the fuel, the use of a large number of parallel samples in determining the technical characteristics increases the error in their determination. This fact makes it relevant to search for a universal and express method. One of these methods is a comprehensive thermal analysis.

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.

EXPOSITION

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

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 1):

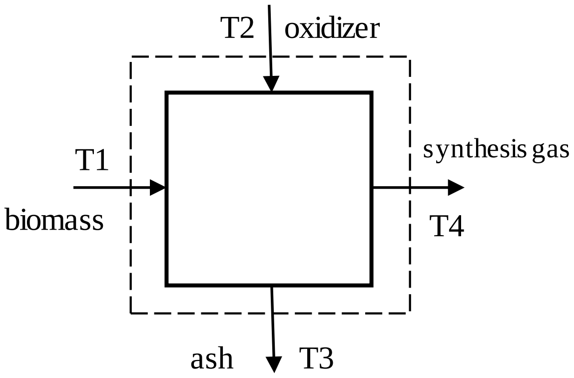

Fig. 1. Scheme of an equilibrium thermodynamic system.

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

$$CH_xO_yN_z + \omega H_2O + mN_2 \rightarrow n_{H_2}H_2 + n_{CO}CO + n_{CO_2}CO_2 + n_{H_2O}H_2O + n_{CH_4}CH_4 + mN_2, \quad (1)$$

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:

$$CH_xO_yN_z \rightarrow n_C CHAR + n_{H_2}H_2 + n_{CO}CO + n_{CO_2}CO_2 + n_{H_2O}H_2O + n_{CH_4}CH_4 + n_T TAR + mN_2$$

CHAR - coke, TAR - resin. Moreover, their gross composition can be expressed by the formula $CH_{x1}O_{y1}N_{z1}$ and → $CH_{x2}O_{y2}N_{z2}$, 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:

Combustion reaction:

$$C + O_2 \rightarrow CO_2$$

$$C + \frac{1}{2}O_2 \rightarrow CO$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

Boudoir reaction:

$$C + CO_2 \rightarrow 2CO$$

Water vapor reactions:

$$C + H_2O \rightarrow CO + H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$C + 2H_2O \rightarrow CO_2 + 2H_2$$

Methanation reactions:

$$C + 2H_2 \rightarrow CH_4$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

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):

$$K_j = \prod\nolimits_i (x_i)^{v_i} \left(\frac{P}{P^0}\right) \sum\nolimits_i v_i, \quad (2)$$

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

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

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

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

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

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:

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

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 (10):

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

where $\bar{C}_P(T)$ is the specific heat at constant pressure, which depends on temperature and can be determined empirically by equation (11):

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

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 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 [2], 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, n_i is the amount of the ith 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):

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

Next, we find the values of n_i that minimize the Gibbs energy using the Lagrange multipliers $\lambda j = \lambda 1, \ldots, \lambda k$,. At the same time, the limitations of the material balance for the elements are imposed on the thermodynamic system, which has the form:

$$\sum_{i=1}^{N} n_i \, a_{ij} = A_j \text{ , j = 1, 2, 3,…,k,} \tag{16}$$

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.

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

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

$$\frac{\vartheta L}{\vartheta n_i} = 0 \tag{18}$$

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 modeling of the processes of thermochemical conversion of solid fuels, a number of assumptions are used [3-4]:

1. The carbon contained in the fuel passes into the gas phase in the form of gaseous products of CO, CO_2, CH_4, and also H_2, H_2O, O_2 are part of the synthesis gas. The yield of hydrocarbons C_2 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 [5-6].

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 conversion.

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 [7].

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 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;
3. 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.

CONCLUSION

- Thermodynamic models without macrokinetic restrictions allow us to study the equilibrium state of the system, determine the maximum efficiency of the process, and the composition of the gas phase.
- The use of macrokinetic constraints in thermodynamic models allows the most realistic description of the process under study.
- For the formation of macrokinetic constraints, thermal analysis data can be used.

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