Thermal analysis in numerical thermodynamic modeling of solid fuel conversion

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Abstract Detailed kinetic models dominate in combustion modeling. However, their application is often complicated by insufficient knowledge of a mechanism and reaction rates for heterophase interactions especially as applied to gasification. The novel approach using thermodynamic model of extreme intermediate states (MEIS) could make up an efficient alternative. MEIS is strictly deterministic and simple in structure. Along with the search for the final equilibrium, it allows partial equilibria to be found and various macroscopic phenomena to be taken into account, e.g., transport phenomena and kinetic rates. The core problem in MEIS construction is formulation of macrokinetic constrains whose form depends on the problem statement and accessible information on the process. Thermal analysis has been deployed to infer proper constraints for modeling of wooden biomass gasification. The advantage of the method consists in much higher availability of the initial information compared with detailed kinetics. Model results are in good agreement with experiment.

Keywords Fuel processing · Thermodynamic modeling · Macrokinetic constrains · Biomass gasification · Thermal analysis

Introduction

The area of numerical modeling of solid fuel combustion and gasification processes is dominated by detailed kinetic models. However, their improvement as applied to fuel gasification is constrained by the lack and considerable variability of rate constants for heterophase reactions as well as by the lack of theoretical understanding of the mechanism of many such interactions. Application of models is often complicated by variability of fuel properties both in the initial state and in the course of fuel conversion. Making a great number of assumptions, which is inevitable in detailed kinetic modeling, decreases the universal nature of the models and causes their strong dependence on specific conditions of the process [1, 2].

The absence of knowledge about chemical reactions mechanism and reliable quantitative characteristics of the process impedes making substantiated conclusions on the ways to optimize the equipment intended for thermochemical conversion of solid fuels. Thus, the optimal conditions are determined using empirical specifying coefficients. These coefficients are obtained by statistical processing of experimental data which provides their satisfactory accuracy along with comparative simplicity. However, an essential drawback of this approach is empirical origin of the coefficients which hampers application of the models to arbitrary processes and fuels [3].

Numerical description of heterophase processes is comparatively easily performed with the use of thermodynamic models based on the search for final equilibrium states [4]. An advantage of the traditional models of final equilibrium is the absence of necessity to know the accurate mechanism of heterogeneous reactions and considerably higher reliability of the applied constants. At the same time, the final equilibrium models have some drawbacks inherent in thermodynamic description in general. The main of them is systematic overestimation of the conversion degree that hinders estimation of product yields at intermediate stages of conversion.

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A promising approach to specify thermodynamic solutions is the models of extreme intermediate states suggested at MESI. They develop the methodology of classical equilibrium thermodynamics and at the same time make it possible to take account of macrokinetic constraints of the processes to be modeled [5, 6].

Models of extreme intermediate states

The MEIS are formulated as a problem of mathematical programming and in the case of objective optimality criterion have the form [5, 6]:

Find

$$\text{extr} F(x), \tag{1}$$

subject to

$$Ax = b \tag{2}$$

$$x_j \geq 0 \forall_j \tag{3}$$

$$D_t = \{x : x \leq y\} \tag{4}$$

$$F(x) = \Sigma_j F_j(x) x_j \tag{5}$$

$$x_k \leq \varphi(x, y) \tag{6}$$

where x and y are the vector of system components amount and its initial value, respectively; A is the matrix of content of chemical elements in the system components; $b = Ay$ is the vector of elements amount; $D_t = D_t(y)$ is the region of thermodynamic attainability from the initial state y; $F(x)$ and $F_j(x)$ are the thermodynamic function of state for the whole system and its separate component. The choice of function of state (Gibbs or Helmholtz energy, entropy, internal energy) depends on conditions of interaction between the system to be modeled and the environment. Equation (2) sets the condition of material balance and in combination with Eq. (3) determines the region of physical values of variables x. Equation (4) specifies thermodynamically attainable region from state y. The sign "$\leq$" in (4) denotes that the state x can be attained from the state y by a path, along which the function $F(x)$ monotonously change. Closing relation (5) establishes relation between characteristic thermodynamic function and vector of composition. Expression (6) represents a macrokinetic constraint written in a general form.

Application of MEIS offers an opportunity to study the states of final equilibrium along with the states of partial equilibrium (equilibriua not for all parameters), i.e., in fact the entire set of states that can occur during the studied process, including those located far from the state of final equilibrium. The equilibrium thermodynamic description has a specific feature: the phenomena caused by kinetics of chemical reactions, diffusion and heat exchanges should be taken into account in thermodynamic form. To include

macrokinetic constraints in the mathematical description of the MEIS one shall exclude the time variable using one of the three suggested methods [6, 7]. The form of these constraints may vary depending on problem statement.

To date there have been several approaches to description of macroscopic constraints in MEIS, which suggest: (1) writing additional thermodynamic relations which take into account the constants of equilibrium among individual stages of the studied process mechanism; (2) transforming right-hand sides of kinetic equations, i.e., making a transition from the space of sought variables of the problem to the space of thermodynamic potentials; (3) imposing constraints on the right-hand side of corresponding equations of motion. The first approach is explained by the unity of thermodynamics and kinetics that describe differently the same physical regularities. The approach allows one to take account of the mechanism of processes in thermodynamic studies without its complete knowledge and formalized description. The use of additional thermodynamic constraints makes the region of thermodynamic attainability $D_t(y)$ narrower.

The second approach implies replacement of coordinates in the right-hand sides of kinetic equations by potentials and further substitution of transformed sides into the expression for a derivative of the total characteristic function of the considered system with respect to time. This approach turns out to be laborious and often leads to changes in mathematical character of the problems solved (violation of the objective function convexity, appearance of multivalued solutions).

The third approach is the simplest for some cases in which, for example, the process rate is determined by one or few limiting reactions. Taking account of macrokinetic constraints for irreversible processes reduces the region of thermodynamic attainability and, correspondingly, increases accuracy of thermodynamic estimates of limiting indices of the processes [6].

Until now the constraints on chemical kinetics within MEIS have been applied to comparatively well-studied processes like methanol synthesis or NO_x formation in combustion, in which the mechanisms of main limiting stages are known and for which kinetic coefficients are known with certainty. Introduction of kinetic constraints for description of spatially inhomogeneous systems like moving bed gasification process is complicated by the lack of both kinetic constants and realistic hypotheses on the mechanism of heterophase reactions. Therefore, it is topical within MEIS to develop new methods of kinetic constraints formulation that are based on more accessible conversion characteristics, including those directly measured.

An important role in development of new gasification technologies and improvement of known ones belongs to the physicochemical methods of research. Among them thermal analysis is typical for studies on thermal solid fuel

processes. The data obtained in thermal analysis can provide initial information for thermodynamic modeling and be used to study gasification kinetics.

Problem statement

The problem solved in the work is: determine a potential of the thermal analysis method to provide initial data for numerical thermodynamic models of solid fuel combustion and gasification processes. The model is based on MEIS with macrokinetic constraints. The model is filled with initial data and the constraints are determined on the basis of thermal analysis results. The problems were solved on the example of fixed-bed gasification of wood biomass in downdraft reactor. The process of thermochemical conversion of fuel in reactor can be represented by three sequential stages—drying, oxidation and reductive combustion, separated along the height (Fig. 1).

Each stage (reactor zone) is described by the respective kinetic equation.

The process of solid fuel drying is described by the equation of the first order:

$$r = \rho_{\mathrm{m}} A_{\mathrm{H_2O}} e^{\left(\frac{-E_{\mathrm{H_2O}}}{\mathrm{RT}}\right)}. \tag{7}$$

The process of volatile release that occurs at the stage of oxidation represents superposition of individual sequential and parallel reactions. Here, we face the methodological difficulty of separating them. Therefore, the process of volatile release is as a rule described by the overall reaction (8) and the kinetic equation of the first order (9):

$$\mathrm{Fuel} \rightarrow \mathrm{CO} + \mathrm{CO_2} + \mathrm{H_2O} + \mathrm{CH_4} + \mathrm{H_2} + \mathrm{tar} + \mathrm{char} \tag{8}$$
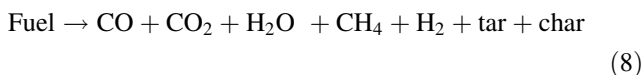
$$r = \rho_{\mathrm{w}} A e^{\left(\frac{-E_{\mathrm{A}}}{\mathrm{RT}}\right)}. \tag{9}$$

At the stage of reductive combustion charcoal burns out. This process can be described by the first order kinetics:

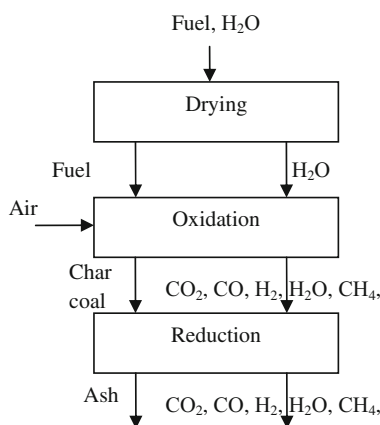**Fig. 1** A scheme of thermochemical conversion of solid fuel in a downdraft reactor

$$r = \rho_{\mathrm{ch}} A e^{\left(\frac{-E_{\mathrm{A}}}{\mathrm{RT}}\right)} \tag{10}$$

where r is the reaction rate constants, kg m^{-3} s and ρ_{m}, ρ_{w}, ρ_{ch} are the bulk densities of moist wood, dry wood, and wood char, respectively.

The processes in gasifier can be simulated with the help of thermal analysis, though in part only. In thermal analysis, the stages of drying, devolatilization, and charcoal burnout are separated in time; however, the gaseous media composition and temperature change course differ from those in a gasifier bed. There are elaborated methods to infer kinetic coefficients for each stage by processing thermograms obtained at different heating rates.

These coefficients can be applied to solve direct kinetic problem. In our study, they are used to derive specific consumption of raw fuel.

The other aim of our study is to derive kinetic constraints applicable for inclusion into MEIS. To do that we utilize the third mentioned above method of kinetic constraints formulation based on immediate setting of the limitation.

Determination of apparent kinetic constants

The kinetic profile and Arrhenius constants were determined with the NETZSCH thermokinetics software, in particular Friedman analysis of non-isothermal processes [8]. Processing of experimental data in this software suggests the use of multi-variant nonlinear regression on the basis of 18 different types of kinetic mechanisms with visual optimization of nonlinear regression parameters [9].

The Friedman method is applied to one-stage reaction of the first order (11) that can be described by Arrhenius equation (12). Measurements that were made at different heating rates have the same degree of conversion at different temperatures. Thus, the value of mass loss in thermogravimetric analysis can be converted to degree of conversion (ξ), according to Eq. (13).

$$A_{\mathrm{solid}} \rightarrow B_{\mathrm{solid}} + B'_{\mathrm{gaseous}}, \tag{11}$$

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -A e_{\mathrm{m}}^{\left(\frac{-E}{\mathrm{RT}}\right)} \tag{12}$$

$$\xi_{\mathrm{j}} = \frac{m(t_{\mathrm{S}}) - m(t_{\mathrm{j}})}{m(t_{\mathrm{S}}) - m(t_{\mathrm{F}})} \tag{13}$$

where $m(t_{\mathrm{S}})$ is a signal at the initial time instant t_{s}, $m(t_{\mathrm{j}})$ is a signal at time instant t_{j}, $m(t_{\mathrm{F}})$ is a signal at the final time instant t_{F}.

Friedman suggested using the logarithm of rate of change in conversion degree $\frac{\mathrm{d}\xi}{\mathrm{d}t}$ (with specified ξ_{j}) as a

function of corresponding temperature, and writing it in the form:

$$\ln \frac{\mathrm{d}m}{\mathrm{d}t} = \ln A - \frac{E}{RT} + \ln f(\xi_j). \tag{14}$$

The practical value of this method lies in the fact that it is not necessary to know accurate kinetic model of the process to determine kinetic parameters.

Experimental studies have been conducted with the integrated thermal analyzer manufactured by the firm NETZSCH. It includes the device for simultaneous thermal analysis STA 449 Jupiter, the quadrupole mass spectrometer QMS 403 C Aeolos and the device for pulse thermal analysis PulseTA.

The measurement technique included the following steps: preparation of a sample by the standard quartering method, placement of the 10–20 mg sample in alumina crucible and its heating from 35 to 1,000 °C at different heating rates (5, 10, and 20 °C min^{-1}) in the inert atmosphere (Ar—99,995 %, 40 mL min^{-1}). The pyrolysis products obtained were recorded in the range of mass numbers from 1 to 200 with ionization by 70 eV electron impact. Mass spectrometer signal was calibrated by pulse supply of corresponding calibration gases.

The sample of pine (*Pinus sibiricus*), 0.2 mm large, was used as a material. Figure 2 shows the obtained thermograms for wood pyrolysis (solid lines).

The kinetic analysis according to Friedman was used to establish relationship between the logarithm of rate of change in the biomass conversion degree and temperature (Fig. 3). The found macrokinetic constants for wood pyrolysis were then used in the multi-variant nonlinear regression method of kinetic analysis to determine the apparent mechanism of pine wood pyrolysis.

As is seen from Fig. 3, the activation energy depends on the conversion degree, which is indicative of the multi-
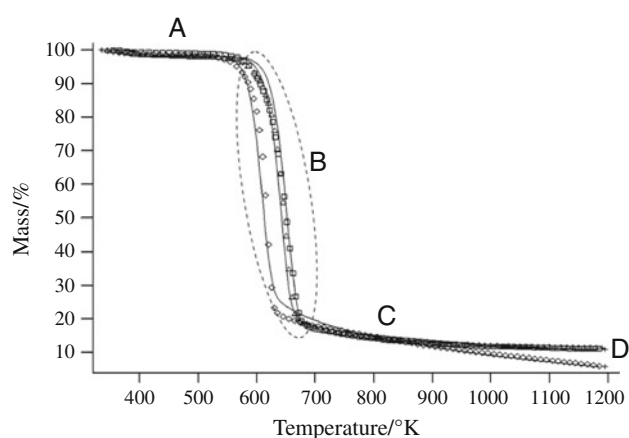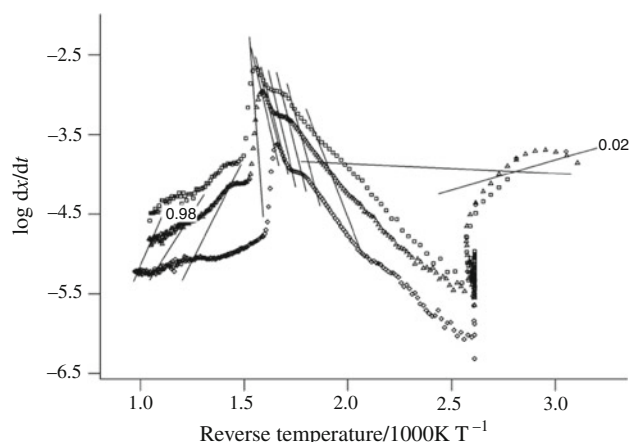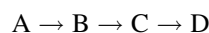

Fig. 3 Isoconversional lines by Friedman's method

stage process. The process demonstrates deceleration. An apparent kinetic scheme of the pine pyrolysis process providing the best fit in the nonlinear regression has the form:

$$A \rightarrow B \rightarrow C \rightarrow D$$

where A is the raw wood, B is the dry wood, C is the char, and D is the ash. This kinetic model was applied by Hobbs in his works [2]. The kinetic constants for each stage of the determined mechanism are presented in Table 1.

The obtained kinetic scheme and rate coefficients were used in simulation of TG curves. The result is graphically represented in Fig. 3, showing a good agreement with the experimental.

Besides, the above thermal analysis data were also applied to construct the dependence of change in the elemental fuel composition on the conversion degree (Fig. 4). These data were used to evaluate thermodynamic properties of wood fuel at different stages of its conversion by standard engineering technique.

Thermodynamic modeling with macrokinetic constraints

Thermodynamic model was to reproduce data of the full-scale experiment on the laboratory-scale solid fuel conversion bench. The bench has an insulated downdraft reactor interconnected with the blocks of air blow supply, cooling and analysis of conversion products [10].

Fig. 2 Comparison of TG curves for pyrolysis at various heating rates, 5, 10, and 20 K min^{-1}: Simelated—*dotted lines* and measured—*solid lines*

Table 1 Macrokinetic constraints of pyrolysis

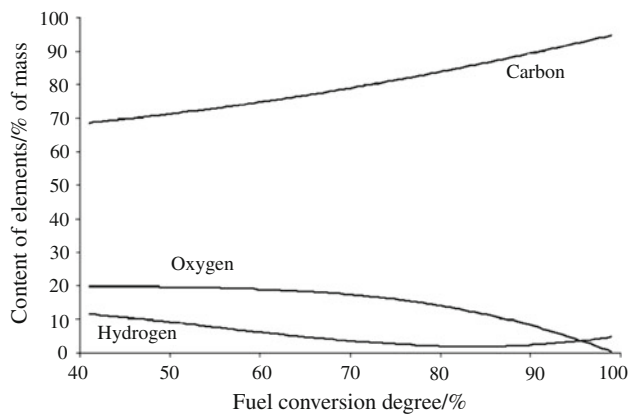| Stage	Log A/s^{-1}	$E_A/\mathrm{kJ\ mol^{-1}}$
Drying	−1.2	10.1
Devolatilization	9.4	146.2
Char burnout	−5.4	3.5

Fig. 4 Change in the elemental composition of wood biomass in the conversion process

Pine 2–4 mm in size was loaded into the reactor with directed flows. Stationary conditions were obtained and the data required for construction of material and energy balances (gas temperature at reactor inlet and outlet, composition of gas and tarry products) were measured. Gas composition was determined by the gas chromatography method with the aid of the SRI 8610C chromatograph. The tar composition was first determined gravimetrically and then with thermal analysis combined with mass-spectrometry. Charcoal of different degree of conversion was sampled after the experiment. Elemental composition of the charcoal was determined by thermal analysis. Then material and energy balances were calculated. Convergence of the balances made up 1–3 %.

The applied thermodynamic model maximizes entropy for the system with lumped parameters. The pressure and system enthalpy are fixed parameters. The model has the following form:

Find

$$\max S(x), \tag{15}$$

subject to

$$A(x) = b \tag{16}$$

$$D_z(y) = \{x : x \leq y\} \tag{17}$$

$$S(x) = \sum_j S_j(x)x_j \tag{18}$$

$$x_j \geq 0 \tag{19}$$

$$x_k \geq \phi(x, y). \tag{20}$$

In these expressions $S(x)$ and $S_j(x)$ are entropies of the system and its jth component; the type of dependences $S_j(x)$ is determined by the phase, which the corresponding substance belongs to.

Along with the mathematical formulation of MEIS (15–20), let us define the logic structure of the model. The process of moving bed gasification occurs in an open spatially inhomogeneous system. Therefore, it is necessary to make decision on the methods for considering theses features. The problem statement is illustrated in Fig. 6. Inhomogeneity of the fuel bed throughout the reactor height can be taken into consideration by conditional division of the bed into zones R0,…,R4. When describing the processes in the open system the state coordinates are flows: variables x_j are interpreted not as amounts of components, but as flows through a definite reactor section at the height that is specified by reactor division into zones. The flows of fuel F_f and air blow F_b with the temperature T_f and T_b, respectively, enter the initial zone R0. The object of modeling is a component composition of gas that passes through the reactor section at the boundaries of zones R0–R4, denoted in Fig. 5 as $F_0,…,F_4$. Transient modes of the reactor are not considered and a steady-state conversion process is presumed.

In the reactor bed R0, the components are mixed and in R1 the fuel is dried and heated. The constraints on the rate of fuel consumption throughout the reactor height (a specification of the general Eq. (21) are set as inequalities limiting the fuel conversion degree at the boundaries of reactor zones and are taken in the form:
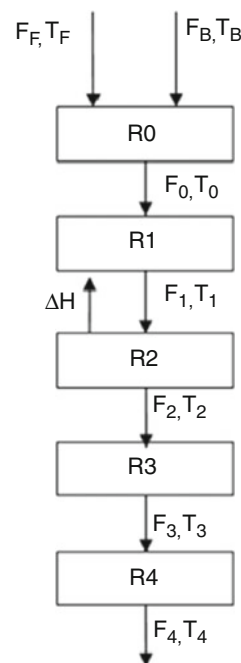
$$m(x_{OMW}) = m(y_F), \tag{21}$$

$$m(x_{B1}) \geq 0.6m(y_F), \tag{22}$$

$$m(x_{B2}) \geq 0.3m(y_F), \tag{23}$$

$$m(x_{B3}) = 0, \tag{24}$$

Fig. 5 Graphical interpretation to the problem statement

where $m(x_j)$ is the mass of component x_j; *B1*, *B2*, and *B3* are indices of char coals passing through the reactor sections with flows F_1, F_2, and F_3, respectively; the coefficients 0.6 and 0.3 correspond to the conversion degrees 40 and 70 % (the share of decrease in the initial fuel mass) that are chosen arbitrarily. Equation (22) characterizes invariability of the organic mass of wood (OMW), before the fuel is dried up. Note that in the model fuel is represented by a pair of variables: one—for OMW, the other—for moisture. Change in the elemental fuel composition depending on the conversion degree is assumed based on the data of thermoanalytical measurements, whose technique and results were described above. The fuel composition for the chosen conversion degrees is specified according to these data, as shown in Table 2. Initial data on the composition and temperature of flows F_F and F_B are assumed on the basis of the full-scale experiment on the laboratory bench. The specific fuel consumption at R0 is estimated using thermal analysis and Friedman's kinetics. The key initial data include the values from Table 3.

Fuel drying, its heating and reaction ignition are due to the reaction heat release in the underlying beds. Therefore, the model takes into account heat flow between zones R2 and R1 that is oppositely directed to the material flow. The parameters of heat flow are estimated based on the experimental data by the relation:

$$\Delta H = \frac{H_A(T_A) - H_B(T_B)}{l_{A,B}} \Delta l,$$

where ΔH is the heat flow, W; H_A and H_B are the system enthalpy at sections A and B, respectively, that is calculated in terms of the gasification process rate; l is the height of the corresponding reactor zone. This method allows the quality of the model to be estimated via comparison of the

Table 2 Fuel composition

Fuel conversion degree/%	Carbon/%	Hydrogen/%	Oxygen/%
0	52.7	4.9	42.4
40	72.5	3.9	23.6
70	81.1	1.9	17.0

Table 3 Calculation inputs

Moisture/mass%	14.3
Specific fuel consumption rate/kg m^{-2} h^{-1}	392.4
Specific air consumption rate/m^3 kg^{-1} (fuel)	0.78
Specific steam consumption rate/kg kg^{-1} (fuel)	0.06
Initial temperature of fuel/°C	20
Air-blast temperature/°C	193

calculated field of temperatures with the temperature at checkpoints T_A and T_B.

Results and discussion

The calculation results are presented in Table 4 and Fig. 6. In the table, the calculated gas composition is compared with the experimental one.

On the initial segment of bed height primarily combustion takes place. Oxygen, however, is not used completely. CO concentration, in particular owing to CO_2 reduction, starts to increase only with oxygen depletion. The zone of reductive combustion, in which the CO_2 concentration would decrease, is not formed, because in the system there is a great quantity of steam acting as an oxidizer in the process. Steam is accumulated in the gaseous phase down to the height of 8 cm owing to evaporation of fuel moisture and combustion of the organic fuel mass. Methane begins to accumulate in the system only with oxygen depletion. Hydrogen formed at earlier stages of the process participates in methane formation. The quantity of gas increases mainly in the range of height from

Table 4 Comparing the calculation and experiment gas composition

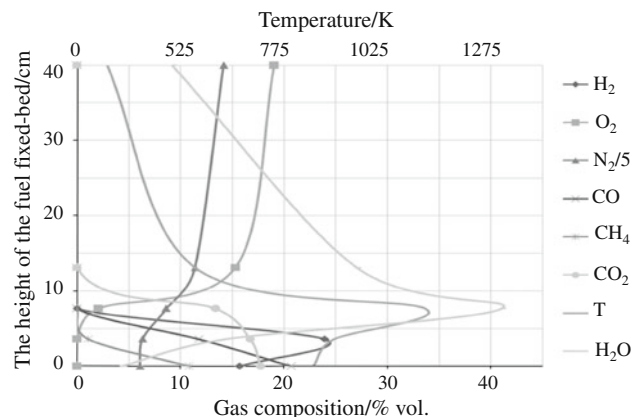| Dry gas composition/vol.%						
Substances	The calculation					The experiment
	R0	R1	R2	R3	R4	
Ar	0.9	0.9	0.9	0.4	0.4	–
H_2	0.0	0.0	0.0	28.0	16.4	20.0
O_2	20.9	20.9	3.5	0.0	0.0	2.9
N_2	78.1	78.1	73.0	37.0	31.7	41.3
CO	0.0	0.0	0.0	13.8	21.6	15.6
CH_4	0.0	0.0	0.0	1.3	11.3	4.2
CO_2	0.0	0.0	22.7	19.6	18.5	14.0

Fig. 6 The calculated gas composition and temperature profiles

4 to 13 cm, which is seen from the decrease in the relative nitrogen content in gas composition.

The temperature values obtained by calculations and experiments for the bed height 40 cm are 73 and 85 °C, respectively, and for the bed height 20 cm are 193 and 211 °C. Somewhat higher calculated temperatures can be explained by the fact that the model does not take into account heat losses through the reactor wall to environment. The height of fuel ignition is adequately predicted by the model. In the experimental data, the height of ignition is 11 cm and in the model is 13 cm.

The experimental composition of producer gas after the reactor does not correspond to the final equilibrium state, since it includes both combustible components and oxygen. Therefore, it is noteworthy that the experimental gas composition occupies an intermediate position between the calculated compositions of R3 and R4. The real process does not reach the final equilibrium.

The lower nitrogen content in the calculated composition indicates that the model overestimated the quantity of formed gaseous gasification products. Evidently it is natural for the following reason. In the experimental composition of products, there is some tar and a certain share of combustible fuel components turns into it, whereas tar is a thermodynamically nonequilibrium product of conversion. The possibility of liquid organic products to form was not considered in the thermodynamic calculation. Obviously the model can be improved by developing kinetic constraints on the tar cracking in situ.

Conclusions

On the whole, the study has shown consistency of the suggested approach to modeling of the gasification process with regard to macrokinetic constraints. It is obvious that the applied body of initial information is incomparably more compact and accessible than the body of initial information necessary for the detailed kinetic modeling of the heterophase process. The data of thermal analysis applied are universal and easily reproducible. The model is compact and allows the component composition profile to be restored by simple measurements made during full-scale experiment. The model, however, has some disadvantages: (1) it does not consider the formation of such nonequilibrium products as tar; and (2) the whole reactor volume was arbitrarily divided into zones and a certain degree of conversion was attributed based on the linear dependence between the specific fuel volume and the reaction rate. These disadvantages can be overcome by introduction of additional macrokinetic constraints on the right-hand side of motion equations. The latter requires a more elaborated dependence between specific volume and conversion degree.

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