A model of pyrolysis in a staged scheme of low-grade solid fuel gasification

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Abstract. The development and evolution of the theory of solid fuel combustion took place in the mid-20th century. The most studied research subject was sized fossil coal. At the same time the research on the fuels with a high yield of volatile matter (biomass) was limited due to insufficient data on kinetics of physical and chemical processes that occur at their heating. Obviously, the creation of a prospective low-tonnage technology for staged gasification of wooden biomass is possible only when a detailed mechanism of these processes is well understood and their kinetic parameters are known. This paper presents the initial results of the development of a model of wood pyrolysis in a screw reactor as the first stage of the multistage gasification process. One of the currently set goals in this research is to develop a mathematical model of heat and mass transfer processes to perform optimization calculations.

Introduction

Modern world trends to involve low-grade solid resources in the energy production are getting urgent for Russia and particularly for the regions that lack their own generating capacities [1]. The development and main evolution of the theory of solid fuel combustion occurred in the mid-20th century and the most studied research subject was sized fossil coal. At the same time the research into fuels with a high yield of volatile matter (biomass) was limited due to insufficient data on kinetics of physical and chemical processes that occur at their heating. It is obvious that a prospective low-tonnage technology for staged gasification of wooden biomass can only be created on the basis of comprehension of a detailed mechanism of these processes and knowledge of their kinetic parameters. At present the mechanisms of wood pyrolysis, gasification and combustion are dealt with in many studies [2-4]. This is explained by a growing interest of the world energy in renewable energy sources. Some technical difficulties, however, hinder the wide-scale adoption of the technology. These are:

- The number of operating parameters, that affect the operation of gas generator is great (exceeds 11). This circumstance complicates optimization of operating conditions of the plant.
- Low temperature of the third stage of the process prevents the complete coal residual combustion, thus leading to a decrease in the efficiency of gasification and formation of a great amount of coke and ash waste.
- Operation of modern gas consuming equipment (internal combustion engine, fuel cell, gas micro-turbine, etc.) requires additional gas cleaning from tar to a level of < 5 - 100 mg/nm3. Fine gas cleaning makes the technology considerably more expensive. It is necessary to optimize stages II and III of the process to obtain virtually tar free gas.

This paper presents the initial results of the development of a model of wood pyrolysis in a screw reactor as the first stage of the multistage gasification process.

In terms of design the pyrolyzer represents a recuperative heat exchanger where a mix of stack and recirculation gases is considered as a heat carrier. To prevent sintering of particles the screw transportation of fuel is used.
To describe kinetics of pyrolysis and transportation of volatile products inside wood particles and their transfer to gas phase, the research was conducted using the simultaneous thermal analysis system: the weighting system of Netzsch STA 449 F1, quadruple mass-spectrometer QMS 409 C Aeolos and the system of pulse gas supply PulseTA (Unique research high-temperature plant). For the indicated plant we have developed the original techniques for interpretation of measurements, including the techniques for a technical analysis of fuels and determination of the kinetic coefficients and pyrolysis mechanism.

The model was verified by both the data of publications and the results of full-scale experiments using a laboratory plant for multistage gasification of low-grade solid fuel [5].

One of the goals set in this research is the development of a mathematical model of heat and mass transfer processes. The model will allow us to do optimization calculations. Thus, geometrical sizes of the pyrolyzer, thermal-physical properties of solid and gas phases, operating parameters of the plant can vary to perform the optimization calculations. Here the temperature profiles and rates should be calculated with a relatively low error within a short time period.

**Model of pyrolyzer**

Detailed numerical modeling of the pyrolyzer with an output of 30 kW was done in the Comsol Multiphysics Software that also enables us to optimize the design and operating parameters of the pyrolysis process in the screw reactor. The sizes applied in modeling the screw pyrolyzer are presented in Fig.2. 40 per cent of interior space is filled with solid mass, which should provide easy circulation of emerging gases around the screw. The screw represents a spiral with a wall 3 mm thick, which is wound on a hollow shaft. The interior space of the pyrolyzer with solid fuel and formed products is separated from heating gases by a wall 5 mm thick. The diameters of the interior space of the pyrolyzer and its external case are 149 mm and 200 mm, respectively.

![Figure 1. View of the screw pyrolyzer. The color highlights the area with porous solid fuel.](image)

Modeling is performed for a homogeneous medium, considering physical properties (porosity, permeability etc.) of the solid phase, through which the pyrolysis products move:

\[
\frac{\rho}{\varepsilon} \left( u_1 \cdot \nabla \right) \frac{u_1}{\varepsilon} = \nabla \cdot \left[ -p I + \frac{\mu}{\varepsilon} \left( \nabla u_1 + \left( \nabla u_1 \right)^T \right) - \frac{\mu}{3\varepsilon} \left( \nabla \cdot u_1 \right) I \right] - \left( \frac{\mu}{k} + \beta \right) u_1 + F \quad (1)
\]

\[
\nabla \cdot (\rho u_1) = Q_{\text{ev}} \quad (2)
\]

The flow of stack gases was considered to be non-isothermal laminar:

\[
\rho \left( u_2 \cdot \nabla \right) u_2 = \nabla \cdot \left[ -p I + \mu \left( \nabla u_2 + \left( \nabla u_2 \right)^T \right) \right] - \frac{\mu}{3} \left( \nabla \cdot u_2 \right) I + F \quad (3)
\]

\[
\nabla \cdot (\rho u_2) = 0
\]

The effective heat transfer in pyrolyzer was considered according to the equation

\[
\rho C_p u \cdot \nabla T + \nabla \cdot (-k_\text{eff} \nabla T) = Q \quad (5)
\]

In the area of high temperature heads we took into account the radiation heat transfer:

\[
Q = \varepsilon_\text{s} (T_2^4 - T_1^4) \quad (6)
\]

The temperature profile included the areas of heating gases, separating steel wall, released pyrolysis products, porous medium and steel screw.

The boundary conditions selected to solve the problem are:
• Inlet fuel temperature – 20°C;
• Temperature of inlet heating gases – 600°C;
• Fuel flow rate in pyrolyzer – 1 mm/s;
• Rate of inlet heating gases varied in the range – 0.1–1 m/s.

The thermal analysis was applied to study the pyrolysis of a fuel particle (pine). To this end the pine samples (chips, 1x1 cm in size, with an average mass of 145 mg) were heated in the flow of inert gas (argon) up to 600°C at various heating rates (1, 5, 10, 15, 30 K/min). The weight loss of the samples was recorded (Fig.2). Figure 2 shows that the sample is dried to the temperature of 120°C. The amount of moisture produced during heating at a minimum heating rate is higher than at the other heating rates. This can be explained by the fact that the fuel particle stays in the thermal analysis furnace for a much longer time, which fosters water release from the particle depth. In the temperature interval 200 – 400°C the high volatile yield occurs (about 65%). According to the shape of thermal analysis curve of weight loss we can suppose that this process runs in two stages in temperature intervals 200 – 300°C and 300 – 350°C, at a heating rate of 1 K/min. This is caused by the fact that in the beginning the volatiles leave the particle surface without destroying the structure, then at higher temperatures the particle is destroyed and volatiles are formed from its depth. In the temperature interval 400 – 600°C there is a deep decomposition of fuel particle with breaking the carbon skeleton bonds C-C and C-H. Weight loss at the heating rates other than the heating rate of 1 K/min shifts to the region of higher temperatures (by about 50°C). In this case the mechanism of fuel particle decomposition remains the same and ceases to depend on the heating rate.

Thus, the mechanism of fuel particle pyrolysis can be described by two successive stages:

Biomass→Volatile1+Char
Char→Volatile2+ASH

Each stage can be described by the equation of the first order rate:

\[ k = A \exp\left(-\frac{E}{RT}\right), \]  

(7)

where \( k \) – reaction rate constant, \( s^{-1} \); \( A \) – pre-exponential factor, \( s^{-1} \); \( E \) – activation energy, kJ/mole; \( R \) – gas constant, \( T \) – temperature, K.

With further processing of thermal gravimetric curves according to equation (7) we can construct the Arrhenius plot ln(k)-1/T. The plot makes it possible to determine the activation energy and pre-exponential factor (Fig.3).

The kinetic coefficient values calculated for stage 1 were \( E=31/3 \) kJ/mol, \( \ln A=3 \) s-1 and for stage 2 - \( E=23.5/\)mole, \( \ln A=2 \) s-1. The obtained kinetic coefficients were applied in further modeling.
Results and discussion

The constructed calculated mesh consisted of 604 thousand elements of three types (tetrahedrons, prisms and pyramids) and had the minimum size of 0.2 mm. The change in the value of calculated elements corresponded to the gradients of the main parameters to be determined and was carried out automatically by the Comsol Multiphysics Software.

One of the decisive factors of heat transfer and, as a result, the pyrolysis efficiency, is the volumetric rate of heating gases. In the course of numerical experiments the main attention was paid to the calculated model stability under changing boundary conditions.

Figure 4 presents an example of temperature profiles and flow rate of gases formed in the process of pyrolysis that were obtained from the calculation. The emerging local areas of accelerated gas flow in the space between the screw shaft and porous medium are well seen. Consideration of the radiation heat transfer in the model led to a 40-fold increase in the time of calculation. Comparison of calculation results with the model (1)–(5) and (1)–(6) allows us to draw a conclusion about an insignificant contribution of the radiation heat transfer to the total thermal balance of the pyrolysis process in the modeled screw reactor. This made it possible to simplify the model and thus considerably reduce the computational effort, which is critical in the forthcoming optimization problem of working parameters and sizes of a staged gasification scheme to be developed.

Figure 3. The Arrhenius plots obtained at pyrolysis of fuel particles at different heating rates.

Figure 4. Example of calculated temperature values (a) and flow rate of pyrolysis products (b) at an average gas flow rate at the inlet section \( w = 0.1 \text{ m/s} \).
Figure 5 presents changes in the calculated values of solid fuel temperatures and its heating rate determined by the temperature gradient, considering the condition of solid particle travel at a speed of 1mm/s. Non-uniform character of temperature rise is explained by the fact that the volume of fuel packed is crossed by the screw blade that has a higher temperature. Since the largest yield of volatile components occurs in the range of temperatures 200–500 °C (Fig. 2), we can make a conclusion that the chemical kinetics equations determined at $dT/d\tau = 30$ K/min can be applied.

One of the preliminary conclusions of the conducted parametric research is the existence of an asymptote for the relationship between the solid fuel residence time in the temperature conditions required for pyrolysis and the amount of coming heating gases (Fig.4).

Conclusions

A model of heat exchange and aerodynamics was developed for pyrolysis in a staged scheme of solid fuel gasification. The model is intended for high speed optimization calculations. For the range of considered operating conditions we show the possibility of applying stationary experimental relationships ($dT/d\tau = 30$ K/min) to determine the rate of change in the density of solid fuel, volatile yield, etc. The results of the parametric research demonstrated the existence of an asymptote for an optimal amount of heating gases, that ensures the completeness of the first stage of pyrolysis.

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Acknowledgments

The research was performed at Melentiev Energy Systems Institute SB RAS under the support of Russian Science Foundation (Grant № 16-19-10227).