Chemical features of thermal decomposition and combustion of fine coal particles: models and experiment

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Abstract. A brief overview of models describing thermal conversion and combustion of coal is presented. Additionally the properties of coal dust were experimentally studied. The main characteristics of brown coal particles, composition of thermal decomposition products and its change with the temperature were measured. The mass loss rate of coal particles and its temperature dependence were studied. Based on the obtained experimental data, an applicability of available in literature models was analysed.

1. Introduction
Highly efficient combustion of low-grade coals in boilers of thermal power plants is one of the most important and urgent problems of the energy industry [1, 2]. Development of practical recommendations on the choice of optimal and effective modes of combustion of solid organic fuels requires a knowledge of relationships between the different physicochemical properties of coals and the characteristics of various stages of coal thermochemical conversion and combustion [3]. Many experimental studies shown that coal pyrolysis and combustion involves interaction of many chemical and physical processes. Rather large number of models was suggested in literature to describe the chemical reactions during coal thermal transformation, including single-step and multistep kinetic chemical models, the distributed activation energy models, the group-depolymerization, vaporization, and cross-linking model, the chemical percolation model for devolatilization and others [4].

It is well known that a coal is a typical natural porous media [5]. It is very important to understand combustion behaviors of individual coal particles to achieve effective coal combustion control. The reaction processes in the coal combustion can be roughly divided into a devolatilization process, caused by coal pyrolysis, and a char combustion process. In the coal heating process, it is well known that swelling occurs in the coal softening process. Coal pyrolysis and char combustion are accompanied by gas diffusion in pores, which has a significant impact on the product release and the yield [6]. Furthermore, fragmentation occurs, causing the particle diameter to change suddenly in the latter period of the combustion process. However, it is very difficult to understand these coal combustion behaviors, because coal properties vary depending on the coal type, and the reaction occurs at high temperature and under complicated reaction fields [7]. Many models allowing to describe coal particles thermal decomposition processes were suggested.
In this work experimental studies of decomposition and combustion of a coal dust of Pavlovskiy brown coal were performed which include particle size measurements, ash content and calorific value determinations, thermogravimetric analysis, and Fourier-transform infrared spectroscopy of thermal decomposition outlet gases. The obtained results of experimental studies will be used with the aim of comparison of available in literature theoretical approaches to the analysis of reaction processes during coal combustion and comparison of suitable robust models for further detailed studies of coal particles combustion. To this end we did a brief overview of available in literature models and approaches.

2. Coal particle thermal decomposition and combustion models

The combustion of high ash coals is often described by the shrinking core model that considers effects of chemical reaction and diffusion [8, 9]. In this model, a burning char particle is divided into a number of concentric annular volume elements [10]. The model takes into account the initial structural properties of the coal, namely surface area and porosity, and predicts the particle’s burning rate, temperature, diameter, apparent density, and specific surface area during the combustion process [10, 11]. A major shortcoming of this model is that it does not take into account the effects of pore diffusion in the char [12]. Furthermore, in this model, the reaction rate is based on the particle volume. Thus, for fine-sized low-grade coals this model has many limits and can't be commonly used.

To predict the pore structure and surface area during combustion the random pore model is commonly used [13, 14]. As volatiles are driven off from the coal, the structure of coal becomes more porous. Rapid devolatilization leads to a highly porous char while fewer pores are evolved during slow devolatilization, due to a lower volatile yield [14]. These pores are used for gas transport and their surfaces as reaction sites. The pore size in coal particles is not uniform. A particle is assumed to consist of microporous grains, surrounded by macropores [13]. It is considered [8, 13] that reactions occur mainly in the micropores, while the macropores serve to transport gaseous reactants and products. As the reaction proceeds, the size of the micropores increases. The random pore model takes into account the structural changes in coal as it reacts. However the complex nature of chemical processes occurred during coal particle combustion is out of consideration.

In many studies a relatively simple kinetic model with non-distributed activation energies was used [8, 15, 16]. This allows for a quick evaluation of the pyrolysis behavior of a large number of coals to assess the effect of coal origin. Activation energy and sometimes pre-exponential factor are usually estimated using this model.

The sequence of burning of a coal substance is very complicated, thus to describe the thermochemical transformation of solid organic fuels more complex kinetic models are preferably used [3, 17, 18]. In a mathematical model of thermochemical transformation of a solid organic fuel the process is subdivided into several relatively independent parallel-consecutive multistep stages: drying and heating of a particle until release or ignition of volatiles; release of volatiles and their combustion near the particle; combustion of the nonvolatile (coke) residue consisting of organic and mineral matter [17]. The physicochemical model in a wide temperature range suggests that drying of a wet material is characterized by moisture evaporation from the bulk of a coal particle, with the evaporation front moving inside the particle as a phase transition front, under the influence of an increase in the temperature of the dry surface. Since the moisture in fuel forms bonds of different strength with the coal matter, it is appropriate to consider two independent fronts of evaporation of hygroscopic and chemically bound moisture, with the latter lagging behind the former. A mathematical model assumes that multistep processes of thermochemical transformation of a solid fuel are additive, the functional groups in thermolysis of the fuel transform independently, the ratio of functional groups in the resin is the same as in the initial coal, and the volatiles released in pyrolysis of coal dust and the nonvolatile coke residue are ideally mixed with the oxidant (air) prior to the chemical reaction [3, 17].

There is also a model like the random pore model called a percolation model [19–21]. This model predicts detailed variations of reaction rate, porosity, and maximum relative particle diameter with particle conversion in the coal combustion process. Percolation models can take into account of the heterogeneous structure and the fragmentation behavior of char particle. They define a particle as an
object arranged in a large number of interconnected lattices. Thus, particles fragment in a reaction process in which lattices are lost and the connection are burned out. A percolation model can take into account both the devolatilization process with particle swelling and the char reaction process with ash agglomeration to express total coal particle combustion behaviors [19]. However, it is very difficult to predict the particle temperature distribution because the temperature in a coal particle varies during very short time. But it cannot take into account in case of fine coal particles analyzing.

There are a lot of models described coal porous media using the fractal theory [22-24]. The article describes pore models with fractal properties similar to real coal pores generated by the random walk algorithm and the improved gas diffusion model for fractal porous media [23]. To predict the variation of pore structure during \( \text{O}_2/\text{CO}_2 \) combustion of coal chars is used the fractal random pore model [24]. This model can more accurate describe coal char combustion, especially at higher conversions.

Recently, papers have appeared with attempts to describe the behavior of particles during co-combustion with gas or coal gasification in a stream [6, 25, 26]. In such studies numerical simulations are usually based on numerous models to describe the kinetics of chemical processes. This combination of models can be very useful, for instance, in the article [6] it was shown that the coal particle size has a strong influence on the gas temperature and the species concentration distribution. The information obtained using mathematical models can help in practical studies of coal particles combustion in industrial power plants.

### 3. Experimental part

As a model coal a coal dust of Pavlovskiy brown coal was chosen for the present studies. The particle sizes of coal dust were analyzed by Analysette 22 Nano Tec (Fritsch, Germany). Ash content was determined using standard method (GOST 11022-95). For this procedure a muffle furnace with a heating temperature of up to 1000°C was used. The lowest calorific value was measured by Calorimeter IKA C 6000 (IKA – Werke GmbH & Co, Germany). Thermogravimetric analysis was performed using TGA-HP150s equipment (TA Instruments, USA). IR specters of thermal decomposition gas products were recorded using the Nicolet iS10 FT-IR Spectrometer (Thermo Electron Corporation, USA). For this aim the spectrometer has a special gas-cuvette and the temperature-maintaining unit. The experiments were carried out in a chamber at atmospheric pressure in the air. Samples were heated up to 800°C with a heating step of 5°C/min. Outlet gases came out into separate gas line heated up to 180°C connected to the spectrometer.

### 4. Results and discussion

Physical and structural parameters of coal particles were measured by different methods and they are presented in the table 1.

| Parameter                   | Value  |
|-----------------------------|--------|
| Particle size               | \(< 120 \mu m)\) |
| Ash content                 | 24.5 % |
| Lowest calorific value      | 3914 kcal/kg |

As it can be seen from the table 1 the particles size is rather small. On the other hand, approximately 1/4 of coal particle consists on mineral components, which are not burned out during heating up to 815°C. The lowest calorific value is higher for fine coal particles than for a raw coal of the same rank (3250 kcal/kg) in according to our previous investigations [27].

TG-FTIR analysis was employed, which combines thermogravimetric (TG) analysis with evolved product analysis by Fourier-transform infrared spectroscopy (FTIR). Obtained experimental results are presented in figures 1 and 2.
All peaks observed (figure 1) were analysed using integrated Thermo scientific FTIR and Raman spectral libraries. Both peaks in ranges of 2250–2400 cm\(^{-1}\) and 600–750 cm\(^{-1}\) are assigned to vibrations in carbon dioxide. Two low-intensity peaks in range of 2050–2250 cm\(^{-1}\) are related to carbon monoxide [28]. Peaks at about 3000 cm\(^{-1}\) are assigned to methane. For all spectra sets of absorption bands were observed between 3000 and 3300 cm\(^{-1}\) and between 1500 and 1900 cm\(^{-1}\). These bands correspond to the H-O stretching and H-O-H bending in water molecules.

![FTIR spectra](image)

**Figure 1.** FTIR spectroscopy of fine coal particles during thermal transformation in air.

Figure 1 show that the trace of CO has already detected at 200°C. On the spectra recorded at 300°C the trace of methane was appeared. Absorbance peak maximums of CO and CH\(_4\) were detected at about 400°C and 450°C, respectively.
As shown in figure 2 the line of mass change has two well-defined step-like zones that are from 35 to 110°C and from 190 to 550°C. In the first zone the rapid decrease in weight with rate of about 4.8 mg/°C is observed. The mass loss rate is comparable with the rate of evaporation of hygroscopic moisture referred in [15]. The rate of weight decreasing in the second zone is about 1 mg/°C. The rest of diagram (from 550 to 800°C) is characterized by the weight-loss rate less than 0.3 mg/°C.

As it can be seen from experimental data the evaporation processes of hygroscopic moisture is almost completed at 200°C. The reaction rate obviously decreases with increasing temperature and with the evaporation of highly volatile components, which is consistent with existing models concepts [16]. The release of carbon containing molecules is strongly depended on temperature.

5. Conclusion
Experimental results such as coal properties, decomposition rates (temperature dependencies of mass loss), and product distributions in gas phase were obtained in our work. Since many various chemical and physical processes are involved in coal particles combustion, such as heating-up of particles, devolatilization, and subsequent char formation, it is difficult to describe all processes by one model. Of particular interest is the prediction of char properties, such as composition, surface areas, and morphology, since these impacts on char combustion. On the other hand, the processes of devolatilization, char formation, and heterogeneous oxidation depend on temperatures and a heating-up rate. A numerical technique for estimating kinetic processes of thermochemical conversion of solid organic fuels [3] was used for analysis of processes in dust-like coal combustion and was found suitable to describe our experimental results. Gas diffusion equations in fractal porous media by numerically simulating movements of molecules in pore models [22] it was found of interest for detailed analysis of gas transport and for analysis of influence of gas diffusion in porous media on thermal decomposition rates and particle combustion. Preliminary analysis of our experimental results on combustion of coal particles demonstrates that percolation model for simulation of coal combustion process [19] can possibly provide reasonable agreement with experimental data and serve as robust procedure for prediction of char and ash formation.

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