Determination of porous structure parameters of coal particles to describe thermal conversion processes

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Abstract. The results of determination of parameters of porous structure of coal and char particles are presented. They were determined using gas adsorption method and thermal decomposition of particles in air oxygen. The porous structure parameters allow predicting char reactivity change at different temperatures as well as during conversion in accordance with Random Pore Model (RPM-model).

Introduction

Porous structure of coal and char is a complex system having various peculiarities [1]. It is known that porous structure of coal consists of a system of macro- (with diameter ≥ 50 nm), meso- (diameter: 2–50 nm) and micropores (with diameter ≤ 2 nm) and it depends on metamorphism degree. It is assumed that [2, 3] micropores with diameter of less than 1 nm are empty spaces between coal-based macromolecules, mesopores correspond to microcracks and macropores are considered to be empty spaces caused by gas evacuation during the metamorphism process or cracks resulted from destruction of structure of coal seam caused by disposition of subsurface rocks.

Micropores constitute from 85 to 95 % of internal surface area and from 60 to 75 % of pore volume. An important feature of pore structure is its interconnection, bindings and connections to external surface which influence on availability of internal porous volume for gas reactant diffusion. Internal surface area of coal having well developed micropore structure can be used effectively in case it has large pores and cracks deeply penetrating the particle starting from external surface. Fuel particle can have well developed micropore structure and hence large specific internal surface area. But if it has weak connections with external surface trough large pores or micropores are blind ones, then this huge internal surface area cannot be available for internal interaction with gases. This is explained by the fact that diffusion of gas reactant can take place within thin film only that is close to external surface of particle especially at high temperature.

Both initial pore structure of coal matter and its behavior during thermal conversion can

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significantly influence energy process, combustion reaction rate as well as combustion efficiency. Of great importance is the impact of porous structure on low temperature thermal process (e.g., combustion and gasification in fluidized bed etc.) where gas-reactant can reach significant internal surface area (by 100-1000 times) of coal matter compared to contour surface area that affects combustion only at external diffusion regime that is typical for high temperatures (1500-1800 °C compared to 850-900 °C).

Porous structure of coal matter and its parameters needed for modeling of thermal processes are not quite well studied. In view of this the objective of the work is to determine parameters of porous structure of coal particles using methods of gas adsorption (water vapor, carbon dioxide) and thermal conversion. Doing so, pore structure parameters are to be defined within the approximation of Bhatia’s random pore model with the aim of further calculation of low temperature energy process.

1 Determination of porous structure of coal matter using gas adsorption

Samples of Donetsk anthracite (A), bituminous Donetsk Gas-type (G) and Donetsk Long-Flame (LF) type coal as well as bituminous Lviv-Volyn Gas-type (LV-G) coal were taken for experimental study (Table 1).

| Grade       | %H     | %A     | %V     | %S   | %C     | %H     | %O     | %N     |
|-------------|--------|--------|--------|------|--------|--------|--------|--------|
| Donetsk A   | 1.5    | 32.8   | 6.0    | 1.3  | 92.0   | 1.8    | 0.8    | 2.8    |
| Donetsk G   | 2.2    | 40.3   | 23.1   | 3.3  | 79.0   | 5.5    | 1.5    | 9.1    |
| Donetsk LF  | 3.9    | 27.9   | 26.2   | 3.5  | 74.5   | 5.5    | 1.6    | 13.6   |
| LV-G        | 2.1    | 43.1   | 22.4   | 3.4  | 79.9   | 5.4    | 1.6    | 8.9    |

It is assumed that determination of surface area using water vapor adsorption ($S_{H_2O}$) is quite representative method to evaluate reacting surfaces of particles relevant to internal kinetic regime and pore diffusion control regime [3, 4]. Note that meso- and macropores provide access for the gas-reactant to micropore structure.

Characteristics of pore structure of coal and char particles were determined based on penetration of gas and water vapor inside porous media of particles. To determine specific surface area $S_{sp}$ and pore volume $V_{sp}$, sorption methods were used [3, 5, 6]. They allowed calculating specific surface area based on quantity of adsorbed matter as well as to calculate pore volume – based on quantity of capillary-condensed liquid. Water vapor and carbon dioxide, penetrating micropores, were used as adsorbate. Benzol can also be used to study mesopores and large micropores (with diameter more 0.8 nm), nitrogen or argon – to study meso- and macropore penetration. Internal surface area and pore volume determined using water vapor can represent reacting surface for char intrinsic reactivity and pore diffusion control regime [3–5, 7].

The results of the study of porous structure for coal of different metamorphism degree (Donetsk anthracite – A, Donetsk Gas-type – G, Donetsk Long-Flame – LF, LV gas-type – LV-G) and its char obtained during pyrolysis and pyrolysis along with partial gasification are given in Table 2.

Note that when in furnace, coal particles are being affected by heat treatment which forms porous structure of char particle. Pyrolysis is a first stage of fuel thermal conversion or treatment process. In a fluidized bed and pulverized-coal combustion, fast pyrolysis (having $10^3$ K/min rate) takes place. During investigation the pyrolysis was conducted at $T_{pyr} = 1123$ K, partial gasification – at $T_{gasif} = 1173$ K at CO$_2$ concentration of $C_{CO_2} = 1.96$ kg/m$^3$. 


Table 2. Characteristics of pore structure of coal having different metamorphism degree.

| Grade | \(A^d\) | Before thermal treatment | After pyrolysis | After pyrolysis and partial gasification |
|-------|---------|--------------------------|----------------|----------------------------------------|
|       | \(A^d\) | \(S_{H_2O} \cdot 10^{-3}\), m\(^2\)/kg | \(V_S \cdot 10^5\), m\(^3\)/kg | \(S_{H_2O} \cdot 10^{-3}\), m\(^2\)/kg | \(V_S \cdot 10^5\), m\(^3\)/kg | \(X_g\) |
| A     | 32.8    | 150.0                    | 5.8            | 70.0                                   | 3.8                              | 154.0 | 6.0 | 0.12 |
| G     | 40.3    | 122.0                    | 6.2            | 191.0                                  | 6.5                              | 246.0 | 8.1 | 0.17 |
| LF    | 27.9    | 156.0                    | 8.1            | 201.0                                  | 9.2                              | 278.0 | 10.3 | 0.15 |
| LF-G  | 43.1    | 119.0                    | 6.7            | 141.0                                  | 6.2                              | 243.0 | 6.9 | 0.26 |

It was found that pyrolysis negatively affects char micropores structure of anthracite decreasing \(S_{H_2O}\) and \(V_S\) by \(\sim 50\%\). Specific surface area of bituminous Gas-type coal and pore volume increases while making pyrolysis. The reason for that could be appearance of new micropores resulted from volatile yield. Partial gasification, that takes place in internal kinetic regime (in whole volume of coal particle) [3, 8] at \(T_{gasif} = 1173\) K, results in development of char porous structure. As to anthracite, negative effect of pyrolysis is overridden by developing closed micropores. \(S_{H_2O}\) of G-type coal increases by \(1.8 – 2.0\) times. This confirms the development of micropores of organic matter, which becomes suitable for further gas interaction with char.

The investigation made confirms that for high metamorphism coal having carbon more than 91\% the well developed system of micropores constitute more than 80\% of internal volume that is typical and it is like to so called «anthracite structure». As to coal of low degree of metamorphism with carbon content of 75–80\% (LF, LF-G, G-type), the porous media can be characterized as „open-to-access structure”. Such coal has large internal volume – voidage between coal macromolecules as well as maximal macropore volume. At the same time the volume of micro- and mesopore is small enough.

2 Determination of pore structure on the basis of thermal conversion

Determination of pore structure parameters and its change during the burning-out of solid fuel is one of the important experimental tasks. It is also of great importance to define reliable kinetic constants for designing fluidized bed (FB) facility where the combustion process of relatively coarse particle (1 – 5 mm) takes place at low temperatures (compared to PC-combustion: 800 – 900 °C). In many cases FB combustion of particles occurs in pore diffusion control regime or in a transition zone between the last one and internal kinetic control regime. In view of this it is necessary to consider burning of coal particle as one having internal porous structure.

Usually, particle being burned is simply considered as that having no porous structure and shrinking core models or single/double film models were used to describe the process. Another models such as progressive conversion or single pore models were used to partially account for pore structure.

In details pore structure of coal matter can be modelled while applying stochastic approach to porous structure that is characterized by some average parameters. One of such model is well known Bhatia’s random pore model [8, 9].

Note that kinetic constants are initial input for calculating thermal process during CFD-modelling.

In this work the experimental results on combustion kinetic of bituminous coal in air oxygen are given. Parameters of internal porous interaction are determined based on RPM-model.
2.1 Experimental technique

Experiments were carried out on bench-scale facility designed to study char reactivity. The key element of the facility is cylindrical reactor (with inner diameter of 36 mm) working as plug-flow reactor for gas phase and perfect-mixing reactor for solid phase (keeping FB condition). Special feature of the facility is the possibility to inject pulse of gas-reactant (air oxygen) into the reactor. Effectiveness of pulse injecting the fluidizing agent on thermal treating of coal in FB is proved in [10]. Gas-reactant pulse is injected in flow of gas-inert (argon/nitrogen). The volume of gas-reactant pulse is selected to avoid complete sample burning-out (usually sample is of 0.1–0.5 g) during the pulse. Temperature increase in test should not exceed several centigrade by Celsius [11]. In such a way stepwise decrease of sample weight (by 1–3 % of weight during pulse) takes place while keeping practically isothermal condition during thermal conversion. Then the dependence of specific combustion rate as a function of conversion is determined at constant temperature.

Determination of combustion kinetic constants (energy activation, pre-exponential factor) is made during stepwise increase of temperature (by 25–50 °C) accounting for change in combustion rate.

In the given work the process of interaction of char of low ash bituminous coal ($A^d = 12.35 \%$, $V^d = 27.6 \%$) with air oxygen was studied. Subject of study is the impact of temperature and gas-reactant condition on burning-out. Tests were carried out within wide range of gas-reactant pressure $P = 0.1–1.2$ MPa and temperature $T = 360–800$ °C (633–1073 K) for particle sizes of $d = 0.1–0.16$ mm.

Secondary treatment of test data was done to evaluate internal surface area parameters in accordance with RPM-model. Kinetic constants were determined as follows [11, 12]:

$$W_m = \frac{1}{1-X} \cdot \frac{dX}{dt} = \frac{1}{m} \cdot \frac{\Delta m}{\Delta t} = K_0 \cdot \exp \left( -\frac{E}{R \cdot T_p} \right),$$  \hspace{1cm} (1)

$$W_m = \frac{1}{m} \cdot \frac{\Delta m}{\Delta t} = K'_0 \cdot \exp \left( -\frac{E}{R \cdot T_p} \right) C_0^{n};$$  \hspace{1cm} (2)

$$W_m = \frac{1}{m} \cdot \frac{\Delta m}{\Delta t} = \Lambda \cdot k_0 \cdot A_c \cdot \exp \left( -\frac{E}{R \cdot T_p} \right) C_0^{n},$$  \hspace{1cm} (3)

where $W_m$ – specific (per unit of current weight) reaction rate, 1/s; $X$ – sample conversion, unit fraction; $t$ – burning-out time, s; $K_0$ – pre-exponential factor, 1/s; $K'_0$ – reaction rate constant, (1/s)/(kg/m$^3$); $k_0$ – rate coefficient, m/s; $\Lambda$ – gravimetric stoichiometric coefficient, unit fraction; $E$ – activation energy, J/mol; $R = 8.314$ – ideal gas constant, J/(mol·K); $T_p$ – particle temperature, K; $\langle C_0 \rangle$ – average concentration of gas-reactant (air oxygen) in reactor, kg/m$^3$; $n$ – apparent reaction order; $A_c$ (or $A_s$) – specific external (or internal) surface area of particle (per unit of weight of particle), m$^2$/kg, for spherical particle – $A_c = 6/(\rho_p^a d)$, where $\rho_p^a$ – apparent particle density, kg/m$^3$; $d$ – equivalent particle diameter, m.

Kinetic characteristics were determined on the basis of experimental curves ($\ln W_{m0} = f(1/T)$). The values of ($k_0$ and $E$) were defined using least-squares method (LSM).

Secondary treatment of test data was made to determine RPM-model parameters. In this case experimental data related to combustion rate as a function of conversion $W_{m0}=f(X)$ at constant temperature were processed in accordance with the following RPM-model equations [8, 9]:

$$W_m = \frac{1}{1-X} \cdot \frac{dX}{dt} = \frac{1}{m} \cdot \frac{\Delta m}{\Delta t} = K_0 \cdot \exp \left( -\frac{E}{R \cdot T_p} \right),$$  \hspace{1cm} (1)

$$W_m = \frac{1}{m} \cdot \frac{\Delta m}{\Delta t} = K'_0 \cdot \exp \left( -\frac{E}{R \cdot T_p} \right) C_0^{n};$$  \hspace{1cm} (2)

$$W_m = \frac{1}{m} \cdot \frac{\Delta m}{\Delta t} = \Lambda \cdot k_0 \cdot A_c \cdot \exp \left( -\frac{E}{R \cdot T_p} \right) C_0^{n},$$  \hspace{1cm} (3)

where $W_m$ – specific (per unit of current weight) reaction rate, 1/s; $X$ – sample conversion, unit fraction; $t$ – burning-out time, s; $K_0$ – pre-exponential factor, 1/s; $K'_0$ – reaction rate constant, (1/s)/(kg/m$^3$); $k_0$ – rate coefficient, m/s; $\Lambda$ – gravimetric stoichiometric coefficient, unit fraction; $E$ – activation energy, J/mol; $R = 8.314$ – ideal gas constant, J/(mol·K); $T_p$ – particle temperature, K; $\langle C_0 \rangle$ – average concentration of gas-reactant (air oxygen) in reactor, kg/m$^3$; $n$ – apparent reaction order; $A_c$ (or $A_s$) – specific external (or internal) surface area of particle (per unit of weight of particle), m$^2$/kg, for spherical particle – $A_c = 6/(\rho_p^a d)$, where $\rho_p^a$ – apparent particle density, kg/m$^3$; $d$ – equivalent particle diameter, m.

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where $W_{m0}$ – reaction rate per unit of initial mass of carbon in sample, 1/s; $X$ – carbon conversion, unit fraction ($X=(m_0-m)/m_0$); $m_0$ – initial mass of carbon in sample, kg; $k_s$ – reaction rate constant, m/s; $C$ – gas-reactant concentration; $S_{0v}$ – specific (per unit of volume) internal surface area of particle, m$^2$/m$^3$; $\varepsilon_0$ – particle porosity, unit fraction; $\psi$ – structural parameter of RPM-model that characterizes pore structure of particle; $L_{0v}$ – specific length of pores per unit of volume, m/m$^3$; $L_0$ – specific length of pores per unit of particle mass, m/kg; $\rho$ – true particle density, kg/m$^3$; $S_0$ – specific internal surface area of particle per unit of mass, m$^2$/kg.

2.2 The results of experimental study on thermal conversion of low ash bituminous coal in a fluidized bed

Char samples held during $t_{pyr} = 60$ min at atmospheric pressure at $T_{pyr} = 900$ °C (1173 K) in a flow of inert gas ($Ar$, $N_2$) in a quartz reactor were used in the experiments. Sample heating rate to final temperature was 8–10 K/min, usual sample weight was 0.5–2.5 g. In case of sample agglomeration, it was crashed till desired particle size.

2.2.1 The dependence of combustion rate for char of bituminous coal from conversion

Experiments to study combustion rate as a function of conversion were conducted at temperatures $T = 500$–550 °C (773–823 K) for particles of $d = 0.1$–0.16 mm at $P = 0.108$ MPa. Their results in a form of $W_{m0} = f(X)$ are given on Figure 1 and in a dimensionless form, suitable for comparison with theoretical calculation, on Figure 2.

Determination of $\psi$ was conducted on the basis of curve fitting, given on Figure 2 in a form of specific rate (related to rate at moment $t = 0$) $(dX/dt)/(dX/dt)_{t=0}$. Curve fitting was made assuming the same value for rates at initial time ($t = 0$), approaching the same maximum for theoretical curve as well as reaching maximum of correlation coefficient ($r^2=0.98$). The following equation was obtained to characterize internal pore structure at $\psi = 25$:

$$\frac{(dX/dt)}{(dX/dt)_{t=0}} = (1-X) \cdot \left[1 - 25 \cdot \ln (1-X) \right]^2$$

(8)

During investigation the dependences of reaction rate per unit of current mass ($W_m$) as a function of conversion were determined. These curves were characterized by small steady state region at $X = 4$–15 %. Further these data ($W_m$ and $W_{m0} = f(X)$) were accounted for.
while defining kinetic constants and tests were carried out keeping small conversion (10 – 15 %) of sample.

**Fig. 1.** The dependence of interaction (reaction rate $W_{m0}$) between char of bituminous coal of interest with air oxygen as a function of conversion $X$ ($d = 0.1 – 0.16$ mm, sample weight $m_{batch} = 0.1$ g; $T = 490$ °C (763 K), $P = 0.108$ MPa).

**Fig. 2.** Comparison of relations of dimensionless combustion rates for chars of bituminous coal as conversion $(dX/dt)/(dX/dt)_{t=0}$ - measurable, obtained in tests, and $(dX/dt)/(dX/dt)_{t=0}$ - theoretical, calculated on the basis of RPM-model ($d = 0.1–0.16$ mm, $m_{batch} = 0.1$ g; $T = 490$ °C (763 K), $P = 0.108$ MPa).
2.2.2 The dependence of reaction rate of char of low ash bituminous coal from temperature

Batch samples having 0.05–0.1 g were used in tests. Total flow rate of gas-reactant trough the reactor was 1.2 – 1.6 l/min (at atmospheric pressure) and 4.5 – 5.5 l/min (at higher pressures). To keep isothermal condition during the test in the reaction zone, at high temperatures (more 500 – 550 °С), char sample was mixed with preliminary burnt-out sand of the same size keeping ratio 1:10 correspondingly.

Based on the analysis of all sets of data obtained as well as previous experience, it was found two typical interaction regions: first one – pore diffusion control at 440–640 °С, the second one – transition region between pore diffusion control and external diffusion control at temperatures higher than 640 °С. In the first region the dependence of logarithm of reaction rate from reciprocal temperature can be best fitted by linear correlation. In view of this kinetic constants were obtained for pore diffusion control region (440–638 °С) (Fig. 3).

![Fig. 3. The dependence of interaction between char of low ash bituminous coal and air oxygen from temperature (440 – 645 °C) and pressure (0.1 MPa, 0.8 MPa, 1.2 MPa) (d = 0.1–0.16 mm, mbatch = 0.05 g).](image)

Kinetic constants (at P = 0.1 MPa), obtained for the above macrokinetic region, are presented in Table 3 and Table 4.

It is seen that the value of activation energy depends on the way of how to fit experimental data (selected correlation) and may change from 124 kJ/mol to 130 kJ/mol (here the dependence of oxygen concentration from temperature and pressure is accounted for).

**Table 3.** Kinetic constants of interaction between char of low ash bituminous coal and air oxygen (for \( W_m = K_0 \exp(-E/R \cdot T) \), \( T = 440–645 °C (713–918 K) \)).

| Particle size, mm | \( K_0 \), 1/s | Activation energy \( E \), kJ/mol | Pressure of gas-reactant in reactor, MPa |
|-------------------|---------------|-----------------------------------|----------------------------------------|
| 0.1–0.16          | 1.557·10^5    | 124                               | 0.1                                    |

Kinetic constants (at P = 0.1 MPa), obtained for the above macrokinetic region, are presented in Table 3 and Table 4.
Table 4. Kinetic constants of interaction between char of low ash bituminous coal and air oxygen with the account of oxygen partial pressure

\[ W_m = K_0 \cdot \exp\left(-\frac{E}{R \cdot T_p}\right) \cdot C_0^n \] at \( n = 0.8; \ T = 440 - 645 \ ^\circ C \ (713–918 \ K) \).

| Particle size, mm | Reaction rate constant, \((1/s)/(kg/m^3)^n\) | Activation energy \(E\), kJ/mol |
|-------------------|-----------------------------------------------|-------------------------------|
| 0.1–0.16          | 2.071 \times 10^6                             | 130                           |

On the basis of the analysis of total sets of experimental results including kinetic constants \((E, K'_0)\) and internal porous parameters \(\psi\) for RPM-model, the following generalized correlation to predict combustion reaction rate as a function of temperature and carbon conversion (within the range of \(T = 440–640 \ ^\circ C \ (713–913 \ K)\)) was obtained:

\[
\frac{dX}{dt} = 2.071 \cdot 10^6 \cdot e^{\frac{130000}{RT}} \cdot C_0^{0.8} (1 - X)^{\frac{1}{2}} [1 - 25 \cdot \ln(1 - X)]^{\frac{1}{2}} \tag{9}
\]

The predicted dependences for burning-out reaction rate as a function of carbon conversion for different temperatures within the above range are given on Figure 4 (at \(T = 450 \ ^\circ C \ (723 \ K)\) and \(T = 520 \ ^\circ C \ (793 \ K)\)).

Fig. 4. Comparative dependences of theoretical (forecast) interaction (reaction rate \(W_{m0}\)) between char of bituminous coal and air oxygen as a function of conversion \(X\) (RPM-model) at different temperature: 1 – \(T_1 = 450 \ ^\circ C \ (723 \ K)\), RPM; 2 – experimental data, \(T = 490 \ ^\circ C \ (763 \ K)\); RPM-model: 3 – \(T = 490 \ ^\circ C \ (763 \ K)\), 4 – \(T_2 = 520 \ ^\circ C \ (793 \ K)\).

It is seen that it is possible to predict reaction rate as a function of both carbon conversion and temperature while modelling the combustion process of fuel particles.

**Conclusion**

1. The experimental dependences were obtained for interaction between char of low ash bituminous coal and air oxygen as a function of carbon conversion, as well as gas reactant temperature and pressure in the reactor.
2. Kinetic constants (activation energy, pre-exponential coefficient, apparent reaction
order) for interaction between char of bituminous coal and air oxygen were determined.

3. Empirical parameters and correlations were obtained allowing calculation of parameters of char porous structure change during conversion within the RPM-model.

4. All sets of parameters were summarized giving general correlation to predict reaction rate as a function of temperature and conversion accounting for developing the porous structure.

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