

PYROLYSIS AND PARTIAL OXIDATION OF COAL PARTICLE IN SUPERCRITICAL WATER

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INTRODUCTION

Potentially experiments on coal conversion in supercritical water (SCW) may be useful for development ecologically efficient technologies of coal conversion into valuable hydrocarbons, liquid and gaseous hydrocarbon fuel, hydrogen and heat [1]. It is known [2] that combustion of a solid coal particle is a complex multi-stage process that includes: 1) coal decomposition into volatile hydrocarbons and coke residual; 2) gas-phase combustion of volatiles; 3) heterogeneous combustion of coke residue. The third process has the slowest rate and limits the time of complete combustion of coal dust in burners. On another hand, the process of combustion can be separated into diffusion stage of oxidizer feeding to the fuel and the kinetic stage of chemical reactions of coal oxidation and decomposition processes. Coal conversion in SCW under conditions of coal partial oxidation by oxygen in the SCW/O₂ mixture includes extraction of hydrocarbons from coal, oxidation and hydration of carbon due to water decomposition and oxygen-bearing components of coal, pyrolysis of organic mass of coal, and burning. The coal combustion occurs at temperatures considerably lower than in common systems. Therefore we can expect that the total combustion rate is governed by the rate of heterogeneous combustion of coal (kinetically limited combustion). Due to a high diffusion rate in supercritical water [3] oxygen would penetrate into particle pores, so the burning would occur throughout the particle. This is confirmed by our results.

I. DRY AND WET PYROLYSIS OF COAL PARTICLES

Investigations were performed with coal of the following elementary composition per a combustible mass: C (77.7%), H (5.5%), O (13.7%), N (2.6%), S (0.5%). After coal grinding in a vortex chamber, a mixture of particles was obtained. It was defined by the measured function of coal particles distribution that the average radius of particles was $r_0 = 14 \mu\text{m}$.

To reveal the role of SCW in extraction process we studied first the vacuum extraction of volatile substances from coal. Coal was supplied into the reactor (up to a half of reactor volume). The reactor was evacuated to ~ 100 Pa at the room temperature and then was slowly heated by outer heater up to 800°C . The rate of temperature increase was $2.1^\circ\text{C}/\text{min}$. Substance were sampled from the reactor continuously. They were analyzed by quadrupole mass-spectrometer MS-7303. The content of volatile substances was determined from mass-spectra based on methods given in papers [4, 5].

Temperature dependencies of the mass of extracted coal substances with respect to the mass of coal combustible substances (i.e., the mass of coal without ash (-5%) and moisture (-12%)) at particles heating in vacuum (~ 100 Pa) are shown in Fig. 1. Each point in Fig. 1 corresponds to the total amount of substance, extracted since the beginning of experiment, (cumulative sum).

In Fig. 1 we should note two distinctive temperatures: $T = 350^\circ\text{C}$ and $T = 600^\circ\text{C}$. At $T = 350^\circ\text{C}$, a drastic change in dependency for water extraction is observed. Apparently, all

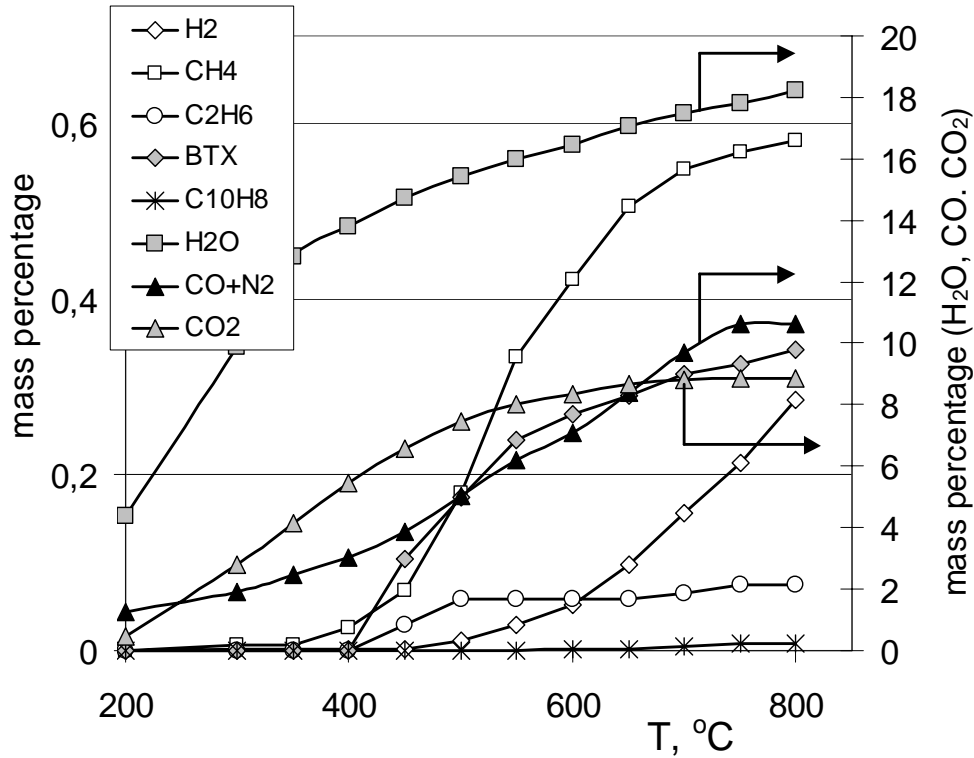


Figure 1: Temperature dependency of volatile substance yield from coal particles at heating in vacuum.

adsorbed water leaves coal particles, and with an increase in T , water extrusion from coal pores starts (we mean pores of the nanometer size). It is interesting that hydrocarbon and porous water extractions from coal start simultaneously at $T \sim 350^\circ\text{C}$. Possibly, hydrocarbons are dissolved in porous water and extruded from pores.

Taking into account the initial oxygen mass fraction in coal ($\sim 13.7\%$) one can see from data in Fig. 1, that 89.4% of initial oxygen is converted at $T = 800^\circ\text{C}$ from coal into CO_2 (47%) and CO (34%). On the contrary, the amount of hydrogen extracted from coal at $T = 800^\circ\text{C}$ did not exceed 0.78% of initial H in coal. The main amount of hydrogen was extracted in H_2 . Actually, the amounts of O and H, stayed in coal at $T = 800^\circ\text{C}$ are even higher than it was determined above because some part of oxygen and hydrogen was formed at dissociation of porous water. As it is known [6], at $T > 650^\circ\text{C}$ in SCW solutions of hydrocarbons, water decomposition occurs. This leads to hydrogenation of pyrolysis products and increasing the fraction of molecular hydrogen in products. It is obvious in Fig. 1 that starting from $T = 600^\circ\text{C}$, the higher amount of H_2 is extracted with a rise in temperature.

In general, thermal extraction of volatile substances from coal in vacuum is characterized by a very low yield of hydrocarbons and H_2 . On the contrary, oxygen of organic substances is converted into CO_2 and CO almost completely.

In experiments on wet pyrolysis coal particles after weighting was supplied into the reactor together with some amount of water. Then the reactor was heated with the rate $0.55^\circ\text{C}/\text{min}$ up to $T = 550^\circ\text{C}$, at that the pressure in reactor became 30 MPa. Under these conditions reactor was stood 15 min, following that water passed through reactor (20 mg/s during 2 min), and a sample was taken. After sampling reactor was heated with the same rate in 100°C and the cycle “standing-passing-sampling” was repeated.

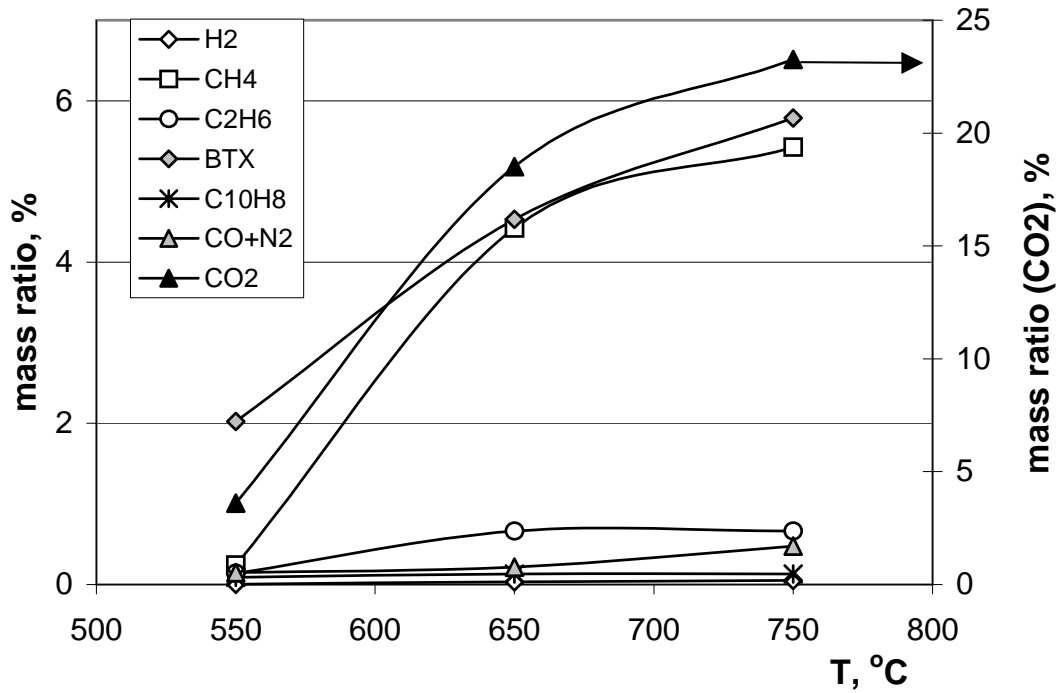


Figure 2: Temperature dependencies of substance extraction from coal particles in SCW.

The cumulative sums of the extracted substances mass in respect to the mass of combustible substances of coal depending on sampling temperature are presented in Fig. 2. It is obvious in Fig. 2, that with a rise of T , the yield of CO_2 , CH_4 and BTX (benzene, toluene and xylene) fraction increased drastically. In products of extraction, there is almost no CO. Apparently, it is explained by water-gas-shift reaction



where formed hydrogen participates in hydrogenation of hydrocarbons in coal.

The amount of oxygen in CO_2 at $T = 750^\circ\text{C}$ reaches $\sim 17.2\%$, for the initial mass share of oxygen in coal of $\sim 13.7\%$. This proves water dissociation. The amount of hydrogen in hydrocarbons extracted from coal in SCW at $T = 750^\circ\text{C}$, was 0.45% in BTX (gross formula C_1H_1) and 1.4% in CH_4 , i.e., 26.5% from the initial amount of hydrogen in coal (at the initial mass share of H $\sim 5.5\%$ in the initial coal) were extracted. Besides, due to dissociation of water molecules, the amount of hydrogen in extracted products (relative to the initial amount of hydrogen in coal) increased by 7.1% . This value was received from balance of oxygen in the beginning (in coal) and in the end (in CO_2) of the process of extraction.

In general, oxygen extraction from coal in SCW happens more intensively than in vacuum (see Figs. 1, 2). The amount of oxygen in hydrocarbons extracted from coal in SCW is approximately one order higher than that at extraction in vacuum.

II. OXIDATION OF COAL PARTICLES IN SCW-OXYGEN FLUID

The partial and complete oxidation of coal particles by supercritical water-oxygen fluid was studied in a semi-batch reactor. The experimental procedure is as follows. We take a vertical cylindrical reactor and put a cylindrical shell with the face ends made of porous stainless steel (pore diameter < 10 microns). We put a sphere-treated particle of coal inside the shell. The reactor was filled with water and heated up to the operation temperature T , and the pressure P

was up to 30 MPa. After the reactor was heated, we feed to reactor (shell) the water-oxygen fluid of the same temperature. The fluid was directed upward. After a certain feeding duration, the reactor was filled promptly (for $15 \div 20$ s) by water without oxygen. This was made to limit strictly the residence time for coal in SCW/O₂ t_{ox} . Then the reactor was cooled down and the shell with the remains of the coal particle was slide out.

We measure the initial mass M_0 and diameter d_0 of the coal particle, its final mass M_f and diameter d_f . To get a high reproducibility, we watched the initial density accurately, and the density scattering was less than 3 %. The experimental temperature of reactor ranged from 400 to 750 °C, the mass portion of oxygen in fluid was from 0.13 up to 5.26 %, the feeding time t_{ox} – from 413 to 1763 s. A coal particles with diameter $d_0 = 1.4 \div 4.8$ mm were used in the experiments. The streamline regime was laminar, Reynolds number Re estimated on particles diameter d_0 did not exceed 23. Measurements of diameter d_f and mass M_f of coal



Figure 3: Exposed particle cut.

particles after being in reactor (i. e., exposed to partial oxidation by SCW/O₂ fluid) showed that even under large reduction in particles mass, $\Delta M = M_0 - M_f$, reduction in diameter, $\Delta d = d_0 - d_f$, was small. Visual analysis of particles photos, taking under proper enlargement, (see Fig. 3) shows that burning-out of particle mass occurred throughout the particle. At the same time the density of particles increased towards its centre, and outer region of particle remained as carbon framework. To illustrate the volume nature of coal particle burning in SCW/O₂ fluid, Figure 4 presents the dependencies between relative changes in diameter $\Delta d/d_0$ and density $\Delta \rho/\rho_0$ of coal particles oxidized in SCW at various temperatures T during a unit of time of particle stay in the reactor.

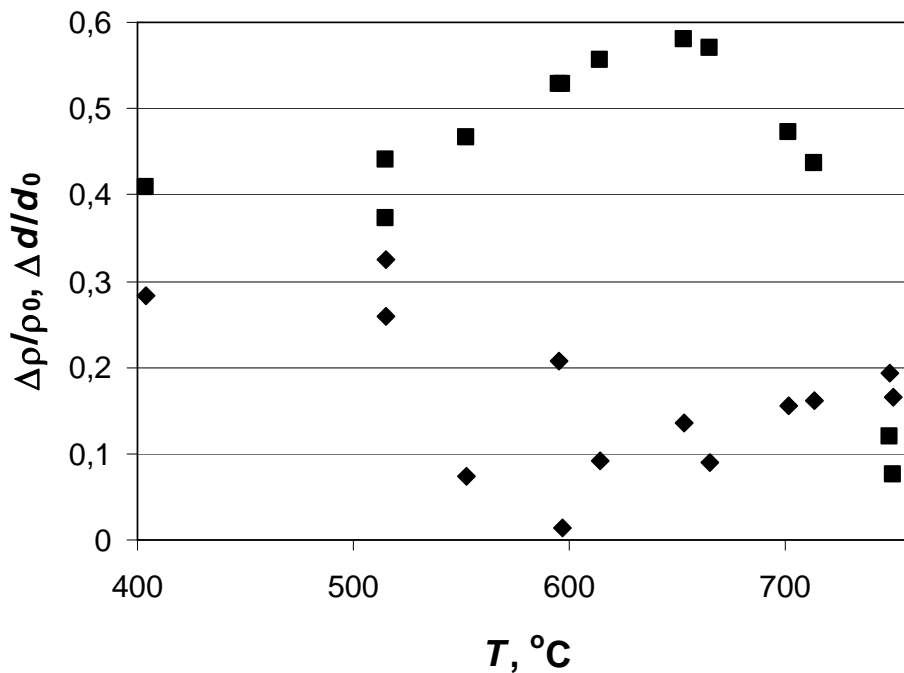


Figure 4: The relative decreases of coal particles density (squares) and diameter (diamonds) after SCW/O₂ oxidation depending on reactor temperature.

Data on Fig. 4 indicate the existence of different physical-chemical mechanisms determining the rate and character of oxidation. Perhaps, a significant decrease in the density of coal particles within $T \approx 400-550^\circ\text{C}$ is caused by a drastic drop in water density at a rise of T and oxygen flow into pores of coal particles due to convective mixing of the initial solution and oxidation products. As a result, the efficient area of O_2 contact with carbon increases. In the range of $T \approx 550-750^\circ\text{C}$, a convective component of O_2 flow towards a coal particle decreases with a growth of temperature. Besides, there may be “screening” of coal particles caused by an increase in the rate of HO_2 radical formation, which form long-living transitional complexes with carbon atoms in the structure of coal particles. Since forced pumping of $\text{H}_2\text{O}/\text{O}_2$ solution by means of hydraulic difference and convective mixing in coal pores is negligibly small, the oxidation rate in coal pores decreases drastically. This leads to the fact that final density of coal particles at $T \rightarrow 750^\circ\text{C}$ almost returns to the initial value (see Fig. 4), and the oxidation rate decreases.

The obtained results were generalized based on the idea that the mass reducing rate must depend on key parameters – temperature T , oxygen concentration ρ_{ox} and water ρ_{wt} , and particle size. Since the mass of coal particle decreased mainly due to fall in particle density (see Fig. 4), we take the initial diameter as a characteristic size of the particle. As a result the average mass rate, $W = \Delta M/t_{\text{ox}}$, have been described by the formula

$$W = A d_0^\alpha \rho_{\text{ox}}^\beta \rho_w^\gamma \exp(-E_a/RT) \quad (1)$$

where the coefficients were determined by least-squares fitting of the experimental data. It resulted in the following values: $A = 1.52 \cdot 10^{-6}$, $\alpha = 3$, $\beta = 0.5$, $\gamma = -1$, $E_a = 0$. Here W has the dimensions g/s, d_0 – mm, ρ_{ox} and ρ_w – g/cm³.) The results of the fitting of experimental measured $\Delta M/t_{\text{ox}}$ with the Eq. (1) are plotted in Fig. 5. One can see that the experimental values of $\Delta M/t_{\text{ox}}$ (~ 50 points) are described by (1) pretty well.

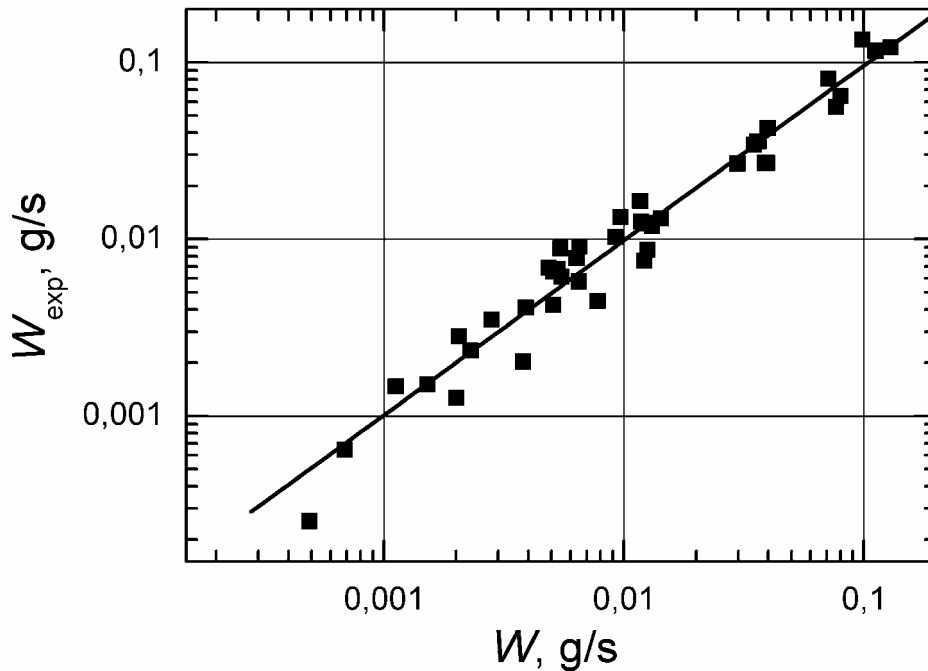


Figure 5: Experimental average mass loss rate at SCWO/ O_2 oxidation of coal particles depending on parameter W .

Note that in these experiments we have not found an explicit temperature dependence of $\Delta M/t_{ox}$: the value of E_a is zero. If we would introduce artificially in Eq. (1) the activation energy $E_a \sim 100$ kJ/mol (typical for coal combustion in oxygen [7]), then fitting of equation to our experimental results would produce the order parameters for water reaction in (1) that must be beyond physical reasons – $\gamma \geq 6$, and $\gamma = 2$ at $E_a = 46$ kJ/mol. Note that actually a growth of combustion rate of coal particle in SCW/O₂ with temperature increase is accounted in Eq. (1) implicitly through a negative value of γ and decrease in the SCW density with growth of T . However, the observed increment in the combustion rate is much smaller than for coal combustion in oxygen [7].

For the experimental condition of this study the mass loss of coal particle cannot be described by the model of surface combustion [8]. Apparently this fact is due to the low combustion rate. It provides for oxygen penetration into coal particle pores. In this case as particle burns its outer region is enriched with carbon, i.e. the ratio C : H increases. This enrichment reduced the burning of particle periphery and promotes deeper penetration of oxygen towards the particle centre.

CONCLUSION

The results obtained in this study show that the mechanisms and kinetics of coal particle oxidation by supercritical water fluid differ greatly from the coal combustion in gas media. We should mention also the practical importance of the fact, that the oxygen addition to SCW increases the water dissociation rate and, as a result, the fraction of hydrocarbons and hydrogen in reaction products.

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