MECHANISM OF PRIMARY FRAGMENTATION OF COAL IN FLUIDIZED BED

by

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In order to lay a foundation of a credible primary fragmentation model, a theoretical analysis of the thermo-mechanical processes in a devolatilizing solid fuel particle was carried out. The devolatilization model comprises heat transfer, chemical processes of generation of gaseous products of combustion (volatiles), volatile transfer, and solid mechanic processes. A spatial and temporal analysis of the stresses within the particle showed that the radial stress is caused primarily by the pressure of generated volatiles. This stress monotonously decreases from the particle center towards the particle surface, without changing its sign. The tangential stress is caused primarily by the thermal shock. Close to the surface, it changes its sign. In the particle cross-section, the radial stress prevails close to the particle center, whilst the tangential stress is dominant in the surface region. At the points where these stresses exceed the particle tensile strength, cracks occur. Cracks extend tangentially close to the surface, and radially close to the center of the particle.

Key words: *devolatilization, primary fragmentation, coal, fluidized bed*

Introduction

The initial phase of most coal conversion processes, such as combustion, gasification, and liquefaction, is the decomposition of substances exposed to high temperatures. The devolatilization is a thermal decomposition in presence of oxygen. These processes involve a complex series of reactions, such as breaking connections, recombination, and generating the mobile entities [1, 2]. The devolatilization also leads to changes in the physical properties of the coal – it leads to softening, swelling, and agglomeration [3, 4]. The products of the thermal decomposition of coal are volatile compounds and the solid residue (char). The volatile compounds gaseous at room temperature are called volatiles, and those liquid at room temperature are labeled as tar. The processes of pyrolysis and devolatilization on one hand, and char combustion on the other hand, differ significantly – during devolatilization combustion takes place only in the gas phase; the char combustion involves the reaction of oxygen and carbon from the solid phase. Also, the devolatilization lasts considerably shorter than the char combustion [5].

One of the most important consequences of the heat and mass transfer in a coal particle during the devolatilization in fluidized bed (FB) is breakage of the particle, namely primary fragmentation. The primary fragmentation is defined as a change of the number and size of particles during the devolatilization of solid fuels. This process is caused and accompanied by complex processes of heat and mass transfer, as well as elastic phenomena in porous material of the fuel. The primary fragmentation affects the distribution of fuel and temperature gradients, particle size distribution of ash, and unburned emissions in the fly ash in an FB furnace.

In order to predict the behavior of particles during the primary fragmentation, it is necessary to consider what was happening in the interior of a particle from the start of the devolatilization, and to describe the transfer processes that precede and directly cause the primary fragmentation. The resulting analysis of the stresses generated in the particle indicates the breakage mechanism and some basic geometric patterns of the primary fragmentation. The presented analysis and discussion were a base to a primary fragmentation model, described elsewhere [6].

Thermo-mechanical processes inside a solid fuel particle devolatilizing in FB

The devolatilization is described by eqs. (1)-(12). As this system of equations cannot be solved analytically, so the numerical procedure of control volumes was applied. For numerical purposes, the char particle is divided into many segments (usually more than 100) of equal volume. The quantities of interest (temperature, amount of volatiles, their flow, and pressure) are calculated for the medium diameter of each layer. The exception is the surface layer (whose volume is half of the volume of other layers) where the calculation is performed for the surface of the particle. Integration of the equation of non-stationary heat transfer was done for each control volume in time steps τ, $\tau + \Delta\tau$.

The assumptions of the model are: the solid coal particle is a porous sphere with constant chemical and thermal characteristics, the pressure of environment is atmospheric, the particle was on room temperature before introducing to the FB, the process is thermally neutral, and there is no thermal influence of volatile combustion.

The thermal balance, defining the temperature profile along the particle radius, is described by non-stationary heat transfer (1) [7]:

$$\frac{\partial}{\partial \tau}[\rho_c c_c T(r, \tau)] = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 \lambda_c \frac{\partial T(r, \tau)}{\partial r}\right] \tag{1}$$

The initial temperature is constant, considering that the particle is taken from room temperature environment and introduced to the FB:

$$T(r, 0) = T_0 \tag{2}$$

The convective boundary condition is:

$$h\left[T_b - T(R, \tau)\right] = \lambda_c \left[\frac{\partial T(r, \tau)}{\partial r}\right]\bigg|_{r=R} \tag{3}$$

The temperature profile of the coal particle changes in time: before the devolatilization, the particle has a uniform temperature distribution, at the beginning of the process the temperature differences between temperatures of particle center and surface are severe, and at the end of the process a uniform temperature distribution is there again – the particle at the FB temperature (fig. 1).
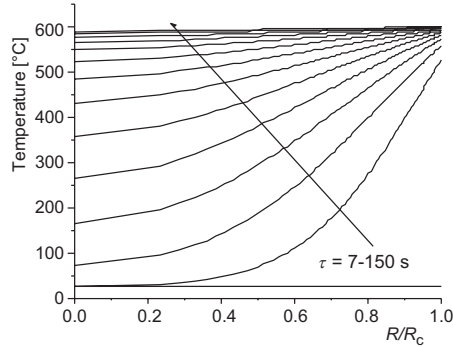
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Figure 1. Temperature profile of a Kolubara coal particle (D_c = 15.3 mm, τ = 0-150 s, T_b = 600 °C); the model results
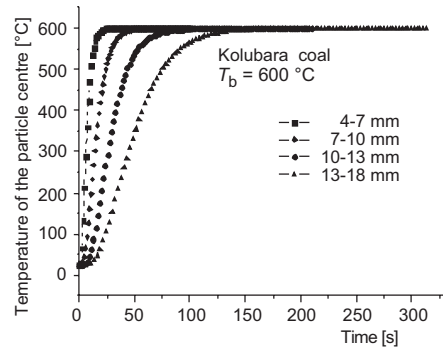

Figure 2. Temperature history of a Kolubara coal particle center (T_b = 600 °C); the model results

The temperature of the coal particle center changes during the devolatilization, which is pronounced for larger particles (fig. 2).

The devolatilization comprises a number of chemical reactions, where each of them is represented by a separate first-order equation, eq. (4). The rate of the chemical reactions is defined by Arrhenius' law:

$$\frac{\mathrm{d}VM_i(r,\tau)}{\mathrm{d}\tau} = k[Vol_i - VM_i(r,\tau)] \tag{4}$$

The amount of generated volatiles is given by eq. (5), whilst eq. (6) defines rate of devolatilization [8]:

$$VM(r,\tau) = Vol\left\{1 - \int_o^\infty \exp\left[-\int_0^\tau k(E)\mathrm{d}\tau\right]\left[\sigma\sqrt{2\pi}\right]^{-1}\exp\left[-\frac{(E-E_0)^2}{2\sigma^2}\right]\mathrm{d}E\right\} \tag{5}$$

$$\Gamma(r,\tau) = \frac{\partial VM(r,\tau)}{\partial\tau} \tag{6}$$

Figure 3 shows the change in amount of generated volatiles along the radial position within the particle – from the center ($r/R = 0$) to the surface ($r/R = 1$), for a Kolubara coal particle, with diameter 15.3 mm. The arrow points the time – from $\tau = 7$ s since the beginning of devolatilization until $\tau = 150$ s.

Devolatilization means generating and releasing a large (in comparison with the particle volume) volume of gaseous prod-

Figure 3. The amount of generated volatiles from a Kolubara coal particle (D_c = 15.3 mm, T_b = 800 °C), depening on the radial position; the model results

ucts, followed by increase of pressure and concentration gradient. Depending of nature of the process and the pore diameter, three mechanisms of mass transfer in the coal particle are pos-
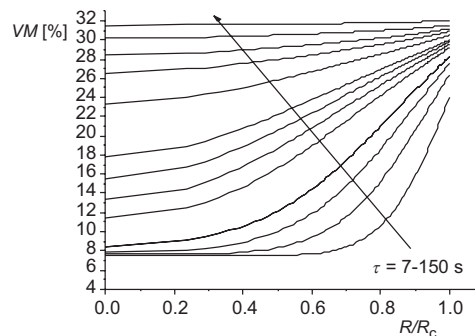
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sible: convective transfer, bulk, and Knudsen diffusion. In this model, only the convective transport was taken into account. If the process is assumed to be a quasi-stationary, mass balance of volatiles are described by eq. (7):

$$\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 N) = \rho_o \Gamma \tag{7}$$

The mass flow of volatiles is described by eq. (8) [9]:

$$N = -\frac{M}{R_g T}\frac{1}{r^2}\left(D_{diff} + \frac{\beta o P}{\mu}\right)\left[\frac{\partial(r^2 P)}{\partial r}\right] \tag{8}$$

Integration with boundary condition $P(R, \tau) = P_0$ gives pressure profile as function of time and radial position.

Due the temperature gradient and mass transfer through the particle, radial and tangential stresses are generated. They are given by eqs. (9) and (10):

$$\sigma_r = \frac{E_J}{(1+\upsilon)(1-2\upsilon)}\left[(1-\upsilon)\frac{du}{dr} + 2\upsilon\frac{u}{r}\right] - \frac{E_J \alpha \Delta T}{1-2\upsilon} \tag{9}$$

$$\sigma_t = \frac{E_J}{(1+\upsilon)(1-2\upsilon)}\left[\upsilon\frac{du}{dr} + \frac{u}{r}\right] - \frac{E_J \alpha \Delta T}{1-2\upsilon} \tag{10}$$

The equilibrium equation is:

$$\frac{d}{dr}\left[\frac{1}{r^2}\frac{d}{dr}(r^2 u)\right] = \frac{\alpha(1+\upsilon)}{1-\upsilon}\frac{d\Delta T}{dr} - \frac{(1+\upsilon)(1-2\upsilon)}{E_J(1-\upsilon)}B(r) \tag{11}$$
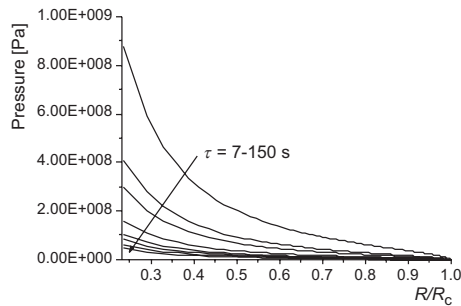

Figure 4. The pressure of volatiles in a Kolubara coal particle ($D_c = 5.7$ mm, $T_b = 700$ °C), depending on radial position within the particle; the model results

The force of the released volatiles is defined by (12):

$$B(r) = \frac{2\varepsilon_{pore}}{R_{pore}}P(r,\tau) \tag{12}$$

The pressure of the released volatiles reaches its maximum in the center of the particle at the beginning of devolatilization (fig. 4). The influence of original particle diameter and FB temperature on the pressure in the particle center was also examined. Figure 5 shows the change of the pressure of the volatiles in the particle center, depending on the original diameter of the particle. The smaller particles are subjected to the higher pressure in the particle center, which rapidly decreases soon after the beginning of the devolatilization. Figure 6 illustrates the change of the pressure of the volatiles in the particle center, depending on the FB temperature. As expected, the pressure is higher for the higher FB temperature.

A huge amount of volatiles generated in a relatively small particle cause a high pressure that influences mostly radial stress. The radial stress (fig. 7) rapidly increases at the

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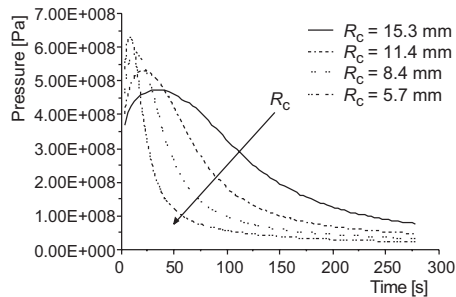THERMAL SCIENCE, Year 2016, Vol. 20, Suppl. 1, pp. S125-S132

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Figure 5. The pressure of volatiles in Kolubara coal particles, on FB temperature of 600 °C, depending on the particle diameter, the model results
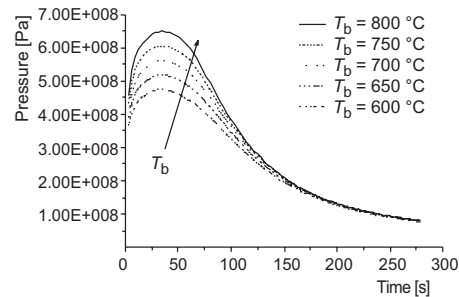
Figure 6 The pressure of volatiles in Kolubara coal particle (D_c = 15.3 mm), depending on the FB temperature, the model results

beginning of the devolatilization, whilst spatially it uniformly decreases from the particle center to the surface. This stress does not change its sign during the devolatilization. On the other side, the tangential stress (fig. 8) increases also rapidly, but the spatial distribution is somewhat different. The tangential stress is changing the sign close to the surface. Therefore, within the particle interior, the radial stress prevails close to the center, and tangential stress prevails next to the particle surface. That means that the particle can be divided into two zones: the inner and outer layer, where the stresses differ according to the direction and sign, and the breakage has a different character and timing.
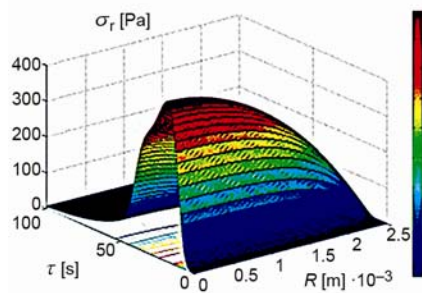

Figure 7. Radial stress (D_c = 5 mm) heated up to 1026 °C, heating rate 100 °C per second, depending on time and radial position [10]
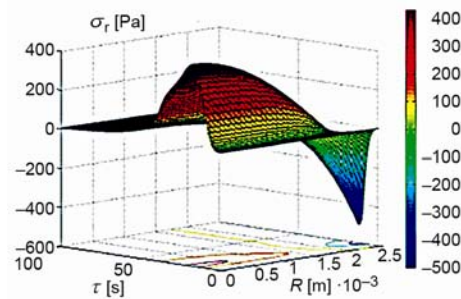
Figure 8. Tangential stress (D_c = 5 mm) heated up to 1026 °C, heating rate 100 °C per second, depending on time and radial position [10]

Mechanism of primary fragmentation

A crack in the devolatilizing solid fuel particle occurs when the stresses exceed the tensile strength of the fuel material, at the point of irregularities in the particle structure. The compressive strength of a solid fuel particle depends on physical and chemical characteristics of the fuel. When it comes to coal, the tensile strength is associated with the coal rank and maceral composition, which is defining the pore structure [11, 12]. Laboratory investigations showed that the coal tensile strength depends of the size of the particle, the coal rank, and distribution, type and condition of discontinuities in the coal structure [13]. As the newly formed

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crack propagating though the particle, it connects with other cracks and existing pores. In some cases this scenario leads to the fragmentation, in some not.

On the basis of the presented analysis of the thermo-mechanical processes, a certain facts, related to the primary fragmentation, can be emphasized.

– The particle cracks under the influence of stresses generated due to severe temperature gradient in the outer zone of the particle (leading to increase of thermal stress), and devolatilization in the inner zone of the particle (leading to pressure increase).
– The initiation, progression and merging of cracks precede the fragmentation. The initial cracks are, actually, the existing irregularities in the material structure. A crack is initiated when the stresses outgrow the material tensile strength.
– In the outer zone, the tangential stress prevails, hence the particle breaks tangentially – exfoliates. The thickness of this zone depends mainly on the heating rate and thermal diffusivity of the particle.
– During the heating, the volatiles from the interior of the particle start to release and move through the porous structure, making cracks and puncturing its path in direction of lower pressure.
– The volatiles next to the particle surface, reach the devolatilization temperature earlier, and the first start to move towards the surface. The volatiles generated close to the center, start to move later, either towards the surface of already opened crack, depending on what is closer.
– The existing pores and newly formed cracks are merging and connecting, leading in some cases to the fragmentation [6].

Similar spatial analysis has been conducted before [10, 14, 15], for example the calculation of Dacombe *et al.* [15] taking into account only the thermal stress. Also, the primary fragmentation experiments [15-18] fit into this theory. It was shown that there are two types of fragments after the devolatilization: smaller fragments (in regard to the initial particle size) originating from the outer zone of particle, and larger fragments, originating in breakage of the inner zone of the particle. The smaller fragments are generated soon after the devolatilization start, whilst the larger ones are being produced later.

If the scenario where the outer zone fragments due to the thermal stress and the inner zone due to the devolatilization, is accepted, a possibility of consecutive fragmentation of fragments should be considered. In other words, is there a sequel to the first fragmentation; or, at least, an additional exfoliation of the fragments? At the *normal* temperatures in a fluidized bed furnace (up to 950 °C) the temperature difference, leading to the thermal stress, occurs only in the surface layer of the *cold* particle, just introduced to the hot environment. Very soon afterwards (fig. 1), the particle reaches the temperature of the devolatilization start, the first cracks in interior occur. After the first stage of fragmentation, the surface temperature of the fragments is too high for thermal stress to occur. At the same time, the most of the volatiles generated on that temperature is already released (fig. 3). That is the reason that there is no additional *exfoliation*, nor the breakage of the fragments.

In the higher temperature environment (above 950 °C), the procedure is somewhat different: the heating rate is severely higher, hence the temperature gradient and the amount of released volatiles are also high. After the first phase of fragmentation, the temperature gradient is still high enough for the thermal stress to cause cracks and exfoliation of the larger fragments. Also, at such high temperatures, the structure and dynamics of the volatile generation is different, so the consecutive fragmentation is possible. Such a scenario was reported by Senecca *et al.* [19].

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Conclusions

The thermo-mechanical processes occurring in a devolatilizing coal particle are thoroughly discussed in order to the reveal the mechanism of primary fragmentation. The time and spatial analysis of the stresses in the coal particle showed that the radial and tangential component have different causes and behavior. The radial component of the stress is influenced mainly by the pressure of the generated volatiles. The radial stress does not change the sign and it decreases uniformly towards the particle surface. On the other hand, the tangential stress is mainly thermal in character, and it changes the sign close the particle surface. When the particle cross-section is observed, the radial stress prevails close to the center, and the tangential stress close to the surface. Accordingly, the primary fragmentation in these zones has different character and timing. In the outer zone, the particle crack tangentially, and in the inner zone radially.

The cracks occur at the points where the stress exceeds the tensile strength of the coal. The tensile strength of a coal depends on the coal rank and the size of the particle, as well as the distribution, type and state of discontinuities in the coal structure.

On the base of the presented analysis, some geometrical patterns for a primary fragmentation model may be established:
– the particle is divided in two zones with different fragmentation behaviors,
– the cracks start from initial points,
– the cracks are propagating towards the particle surface or another crack,
– the number of the initial cracks depends on the discontinuities in the solid structure of coal, which is related to the coal porosity and composition,
– the distribution of the initial cracks has to be random, and
– there is no consecutive fragmentation of the fragments.

The presented analysis is a solid base for a model of the primary fragmentation.

Acknowledgment

Nomenclature

B – force, [N]
c_c – specific heat capacity, [Jkg^{-1}K^{-1}]
D – diameter of coal particle, [m]
D_{diff} – diffusivity, [m^{2}s^{-1}]
E – activation energy, [Jmol^{-1}]
E_J – Young's modulus of elasticity, [Pa]
E_o – mean activation energy, [Jmol^{-1}]
h – convective heat transfer coefficient, [Wm^{-2}K^{-1}]
k – reaction rate constant, [s^{-1}]
M – molar weight, [kgmol^{-1}]
N – mass flow, [kgm^{-2}s^{-1}]
P – pressure, [Pa]
R_c – coal particle radius, [m]
R_g – universal gas constant, [Jmol^{-1}K^{-1}]
r – radial position, [m]

T – temperature, [K]
u – deformation, [–]
VM – volume fraction of released volatiles in time τ, [%]
Vol – volume fraction of released volatiles in time $\tau \rightarrow \infty$, [%]

Greek symbols

α – thermal expansion coefficient, [K^{-1}]
βo – permeability, [m^2]
Γ – devolatilization rate, [s^{-1}]
ε – porosity, [–, %]
λ_c – thermal conductivity, [Wm^{-1}K^{-1}]
μ – viscosity, [Pa·s]
ρ – density, [kgm^{-3}]

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σ	$-$ standard deviation of Gauss distribution of energy activation, $[\text{Jmol}^{-1}\text{K}^{-1}]$		

Subscripts

b	$-$ fluidized bed
0	$-$ initial
c	$-$ coal

σ_r $-$ radial stress, [Pa]
σ_t $-$ tangential stress, [Pa]
τ $-$ time, [s]
υ $-$ Poisson's ratio, [$-$]

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