Fragmentation and agglomeration of biomass in fluidised bed pyrolysis and combustion

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Abstract. The results of experiments on primary fragmentation of wood biomass particles during fast pyrolysis in an inert medium at different temperatures are presented. Growth of temperature and initial size in the range $T = 800 - 950^\circ C$ increases the probability and intensity of fragmentation in the process of rapid pyrolysis of wood particles. Oblong particles are more prone to fragmentation than quasi-circular (cubic) particles with the same equivalent diameter. The critical diameter of fragmentation for spruce wood particles at a process temperature of $950^\circ C$ is $d_{v0} = 18-19$ mm at the ratio of longitudinal and transverse size $h/a = 1$ and is in the range of 7 - 9 mm at $h/a = 8$. Study of microstructure and chemical composition of coke particles (fragmentes) by microscope with SEM analysis showed existence of thin outer layer (0-15 µm) on the particle faces, containing increased quantity of mineral components. Microspheres with a size of 13-23 µm and increased content of sulfur were detected on the particle faces, resulting at $950^\circ C$. Coinciding of maximum and minimum of chlorine, sodium and potassium content in the outer layer denotes on existence of sodium and potassium chlorides on the surface of coke particles. Results of experimental studies of physical and chemical processes occurring between the fuel ash and the bed materials under prolonged temperature exposure were obtained. The aim of these studies was to determine the time and proportion of agglomerated (sintered) particles of several types of biomass depending on the bed temperature. The experiments were carried out in a furnace on biomass ash, sand and mixture of sand and ash. First experiments showed a clear dependence of the temperature of agglomeration beginning on the potassium concentration in the bed and gave the boundary values of the concentrations and temperatures in the bed.

1. Introduction

Studies of primary fragmentation and its effect on the entrainment and mechanical burn out in the fluidized bed boilers during combustion of various fuels were carried out by many researchers, and in most cases they are presented by the data of laboratory studies of different types of coal. Publications as a result of experiments on primary fragmentation of biomass are few. We can distinguish papers [1–5], devoted to research on particle devolatilization and fragmentation of some tree species (Casuarina Equisetifolia, Robinia Psuedoacacia) and wood pellets. Researches of coal and biomass fragmentation are most often focused on the study of particle grinding during heat treatment in a fluidized bed laboratory test rig. The obvious disadvantage of such work is that the data obtained are not the result of the study of the particles heating process exactly, since they are superimposed by the influence of mass transfer and attrition. Mass transfer, in turn, is strongly dependent on the hydrodynamic...
conditions of the fluidized bed, which can vary markedly in different test rigs. The first results of studies of primary fragmentation of wood biomass (spruce) particles during fast pyrolysis in an inert medium at different temperatures without influence of mass transfer and attrition were presented in [6, 7]. These results are added by new experimental data on primary fragmentation of wood particles and agglomeration in present paper. One of the significant problems of burning biomass, especially agricultural waste and some industrial waste, in a fluidized bed is the agglomeration of the bed. It can lead to the enlargement of the bed material, uneven temperature in the bed, deterioration and even full defluidization. An overview of the current state of the art in the field of physical and chemical processes, the influence of various factors and methods of early detection and control of bed agglomeration is presented in [8]. The key factors contributing to the agglomeration are the ratios CA/(K + Na), (Na + K)/(Ca + +Mg), CA/P, the presence of chlorine in the fuel composition, and the combustion temperature. There is a lot of experimental studies of physical and chemical processes occurring between the fuel ash and the bed materials under prolonged temperature exposure, with determination of the chemical composition of the resulting agglomerates and their physical structure. The aim of these studies was to determine the time and proportion of agglomerated (sintered) particles of several types of biomass depending on the bed temperature.

2. Research technique
Experiments on fragmentation were carried out using a laboratory tube furnace "SNOL" with a chamber diameter of 35 mm, equipped with a system of supply and measurement of inert gas flow and scanning electron microscope "Vega3LMH". The wood quasi – circular (cube) and oblong spruce particles of square cross – section with the ratio of longitudinal and transverse dimensions h/a =1 and h/a =8, respectively, and the initial equivalent diameters \(d_{e0} = 16.9-24.9\) mm for quasi-circular particles and \(d_{e0} = 7.3-18.9\) mm for oblong particles at process temperatures 800, 850, 900 and 950°C were studied. The effect of temperature, initial size and shape on the primary fragmentation of large wood particles was evaluated using known criteria of fragmentation: the percentage of fragmentation events \(SF\) [2], the fragmentation degree \(N_f\) [1, 9], variation factor of the feed particle \(F_d\) [9], and fragmentation index \(S_f\) [9] (\(SRI\) [1]). Fragments of coke particles, derived by fast pyrolysis of cubic wood particles with edge lengths A = 8 and A = 13.5 mm were studied by microscope with SEM analysis. System of dispersion analysis “Tescan”, devised by “Oxford Instruments” was used. Experimental setup and methods are described in [6, 7] in more detail.

Bed agglomeration experiments were carried out in a furnace on biomass ash, sand and a mixture of sand and ash with a sample weight of 5 g. A layer of materials was poured on a substrate with a height at the level of 2 – 3 particle diameters (1 – 2 mm). The temperature range was 670 – 900 °C. Exposure of samples ranged from 15 minutes to an hour at a constant temperature. Then the samples were removed, cooled, and the nonsintered material was weighted.

3. Results and discussion
Analysis of these experiments, taking into account the fragmentation criteria, showed that the increase in the process temperature in the range of 800 – 950 °C intensifies the primary fragmentation of wood particles (figures 1 -4). This applies both to the proportion of particles fragmented and to the composition of the resulting coke particles. Figure 2 shows that the values of variation factor \(F_d\) ≈ 0.9 for cubic particles with \(d_{e0} = 16.9\) throughout the range of temperature, although it was not fragmented. It denotes that shrinkage for these particles is ~ 10 %, and may play a significant role in fragmentation of wood particles. The change of fragmentation characteristics depending on the initial particle diameter is consistent with the existing data and ideas about the nature of the effect of fuel particle size on fragmentation: with the increase in the initial size of wood particles the tendency to fragmentation increases (figures 5, 6). The critical fragmentation diameter at a temperature of 950°C may be determined using the dependence of \(SF\) on the initial diameter \(d_{e0}^{CT}\) (figure 6). Taking the value of \(d_{e0}\), for which \(SF = 50\%\), to be the critical fragmentation diameter, this diameter \(d_{e0}^{CT}\) is in the range of 7-9 mm for particles with h/a = 8, and \(d_{e0}^{CT} = 18 – 19\) mm for particles with h/a =1. Smaller values of
the critical diameter for elongated particles, as well as a comparison of main criteria dependence for particles with \( h/a = 1 \) and \( h/a = 8 \) (figures 1-6) indicate a greater tendency of elongated particles to the fragmentation in relation to the cubic particles (quasi-circular form), ceteris paribus.

It is known, that fragmentation due to a pressure inside particles (volatile stresses) is dominant for high volatile fuels, and thermal stresses play a lesser role. Oblong particles have less surface/volume ratio and less specific surface for volatiles outlet as compared to cubic particles. Therefore, the gas pressure inside the particle will rise faster, reaching higher maximum values. This should result in higher maximum volatile release stresses inside oblong particle comparing to cubic particle with the same equivalent volume diameter \( d_{eq} \).

**Figure 1.** The fragmentation degree as a function of temperature.

**Figure 2.** The variation factor of the feed particle as a function of temperature.

**Figure 3.** Fragmentation index as a function of temperature.

**Figure 4.** Percentage of fragmentation events as a function of temperature.
The study of fractured unregimented coke particles using an electron microscope showed that their structure repeats the structure of the original wood particles with the preservation of the inherent softwood structural elements: tracheids, modularity rays, simple and bordering pores [6]. Fracturing of cubic particles is characterized by the presence of a few large cracks dividing the particles into large fragments. Crack formation occurs by sequential longitudinal ruptures of the tracheid walls. These cracks originate on the surface and propagate to the center of the particle. Photo shows fractured, but not fragmented particle \(d_{v0} = 16.9\) mm remained intact due to the core not affected by cracking (figure 7). Destruction of the tracheid walls inside the particle was observed to occur in the planes of both longitudinal and cross sections. Crack origin is more probable at the place of irregularities on particle surface, especially in the places of exit to particle outer surface the boundaries of late (autumn) and early (spring) wood gain. Figure 8 shows the rupture on the surface of small non-fragmented coke particles \(d_{v0} = 9.9\) mm on the boundary of gains.

Thin layer (0-15 µm) was found on coke particle surface by microscope. This superficial layer differed by orientation of surface relative to the tracheid axis, looked like pollution and had increased content of mineral components. The screening of surface layer cuts showed that pollution like
formations with higher mineral content could be found on tracheid walls at the 180 µm in depth from butt end surface of coke particles and were not found out of tracheid walls outside on the flank surface of coke particles. Pollutions were not visualized quite at the flank surface in a number of cases. Pollution like formations are not compact everywhere and are possible to be a local part on the surface of tracheid walls at some area (it is typical of the flank surfaces).

Microspheres with a size of 13-23 µm and increased content of sulfur were detected on the particle faces, resulting at 950°C. External layer surface including microspheres surface mostly has irregular round –convex inclusions several microns in size or consists of them entirely.

Coinciding of maximum and minimum of chlorine, sodium and potassium contents in the outer layer denotes on the existence of sodium and potassium chlorides on the surface of coke particles. The thin layer differed in appearance from the appearance of the tracheid walls and did not cover the entire surface of the particles. It is unlikely that this layer could be outside pollutions because distribution of such pollutions shouldn’t depend on the face orientation relative to the tracheid axis, contrary to one observed in examined coke particles. Thus, probability of above lay formation in fast pyrolysis process may be presumed. Assumption related to the lay and microspheres formation based on leakage of molten alkali chlorides and chemical compounds, containing S, accordingly has been provided in [9]. Leakage of molten mineral components could lead to beginning of fluidized bed agglomeration already at the stage of devolatilization and fragmentation of wood particles combustion.

The experiments for predicting agglomeration tendency were used for 4 samples of biomass ashes (table 1): from sunflower husks of "Elevator" (Kumertau), ash pellets from sunflower husks (Tambov), ash of demolition wood and ash pellets from peat.

| Name of indicator | Sunflower husks of "Elevator" (Kumertau) (1) | Pellets from sunflower husks (Tambov) (2) | Demolition wood, Moscow region (3) | Pellets from peat (4) |
|-------------------|---------------------------------------------|---------------------------------------------|------------------------------------|-----------------------|
| SiO₂              | 2.94                                        | 14.32                                       | 9.46                               | 50.50                 |
| TiO₂              | 0.05                                        | 0.36                                        | 0.32                               | 0.68                  |
| Al₂O₃             | 0.85                                        | 2.83                                        | 1.52                               | 15.15                 |
| Fe₂O₃             | 0.5                                         | 11.45                                       | 5.11                               | 9.11                  |
| CaO               | 26.98                                       | 11.31                                       | 35.17                              | 11.20                 |
| MgO               | 14.16                                       | 8.19                                        | 4.25                               | 2.71                  |
| K₂O               | 36.46                                       | 25.73                                       | 3.96                               | 1.30                  |
| Na₂O              | 0.74                                        | 3.44                                        | 0.62                               | 0.45                  |
| P₂O₅              | 5.27                                        | 6.81                                        | 2.31                               | 1.77                  |
| SO₃               | 12.05                                       | 7.57                                        | 7.31                               | 7.13                  |
| CO₂               | -                                           | 7.99                                        | 26.8                               | -                     |

The tendency to agglomeration is often determined by the ratio of the proportion of alkali metals to silicon oxides [10]. This ratio for ash sunflower (1) is 12.6, for ash (2) it is 2.05, for ash (3) it is 0.49, and for ash (4) it is 0.035. It is believed that at a ratio greater than 1 agglomeration is extremely likely. It should be noted that all ash samples have rather high melting temperatures. Thus, for ash (1), the most prone to agglomeration, the softening temperature is 1280 – 1300°C.

Preliminary, the works were performed for ash, most prone to agglomeration: ash "Elevator", Kumertau (1). It turned out that this ash without sand (as well as sand without ash) does not agglomerate even at a temperature of 900°C at an exposure of 1 hour. At this temperature, the mixture of sand and ash (1) was almost completely sintered, and the exposure time from 15 minutes to 1 hour did not play a significant role. It was accepted to conduct experiments to determine the effect of
temperature on the fraction of sintered particles with an exposure of 1 hour. It is important to choose the concentration of ash in the sand mixture. To do this, experiments were conducted on mixtures with a fraction of ash from 5 to 50% at a temperature of 850 – 900 °C. It turned out that for ash (1) the influence of the ash fraction was not significant: in all cases, almost complete sintering occurred. At low concentrations of ash in the mixtures it is difficult to ensure good mixing with sand. This may give additional errors in determining the mass of the sintered material. Therefore, it was decided to conduct experiments with the concentration of ash in the mixture of 5%. The adopted value of the concentration of ash mixed with sand 5% is a reasonable representation of the real situation for FB boilers ([11, 12]).

The first experiments were carried out on two types of ceramic substrates and on a fine metal mesh (metal-ceramic filter material). As a result, it was considered appropriate to conduct basic experiments on a metal mesh substrate. Figure 9 shows the dependence of the fraction of the sintered material on the bed temperature. The data for ash (1) and ash (2) are almost the same. At a temperature of about 750 °C, the share of agglomerates already reaches 80%. With the subsequent increase in temperature, the share of agglomerates only slightly increases. This temperature approximately corresponds to the melting temperature of potassium Tetra- and disilicates. Thus, it can be concluded that at a high concentration of potassium in the bed (about 15,000 and 12,000 ppm, respectively, for ash (1) and (2)) agglomeration occurs at 750 °C.

![Figure 9. The share of sintering particles versus bed temperature.](image)

Agglomerates at relatively low temperatures are not strong and can decay. However, even the intensification of mass transfer in the fluidized bed only slows down this process in time. For ash (3) with a potassium concentration of 1636 ppm mass agglomeration begins at a temperature of more than 800 °C, agglomerates are not strong and can be destroyed in the fluidized bed. For ash (4) agglomeration does not occur even at a temperature of 900 °C. Thus, the first experiments showed a clear dependence of the beginning of the agglomeration temperature on the potassium concentration in the bed and gave the boundary values of the concentrations and temperatures in the bed. Currently, experiments are continuing with an artificial increase in the concentration of potassium by adding a solution of KCl. It is planned to conduct studies of the structure of agglomerates using a scanning electron microscope with SEM analysis.
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