

AGING OF MECHANICALLY ACTIVATED WOOD Effect on the Burning Ability

by

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One of the aspects for optimizing the powdered biofuel combustion technology is to ensure proper relationship between powder production and its delivery into the reactor. This paper focuses on the effect of a time delay between production and use of powdered fuel on its combustion efficiency using pine sawdust as an example. It was established that the ignition delay time increases with an increasing delay between powdered fuel production and use (i.e., the effect of sample aging takes place). A correlation between the ignition delay time, the amount of lignin radicals, and the sample's ability to release volatile combustible matter is demonstrated.

Key words: *mechanochemistry, material aging, pine sawdust, lignin radicals, ignition delay*

Introduction

Number of known limitations of fossil fuels [1] make us return to renewable energy sources. According to experts, biomass is one of the most promising energy sources [2]. Biomass is produced in large quantities as a waste product in a number of wood processing and agricultural industries. This feedstock could be utilized as an energy source in small-scale power stations operating using the principle of the conventional coal-fired power station, however, some preparatory measures need to be taken for that.

The combustion of coarse lumps of plant-based feedstock is characterized by low combustion rate and low local combustion temperature. One of the methods to increase the combustion rate of plant biomass is to burn it in the form of highly dispersed particles flow, where such pulverized biofuel approaches the coal powder combustion characteristics [3] and so allows co-firing of them [4]. Known that the stage involving formation and ignition of volatile products of thermal decomposition is strongly depend on surface property [5]. In this connection, it is extremely important to properly choose the feedstock pretreatment conditions to simplify this process as much as possible.

Today, mechanical activation is the first stage in almost all the technological biorefinery procedures: from bioethanol production manufacturing ordered mesoporous carbons [6, 7]. In rough approximation, mechanical activation is used to increase the rate of heterogeneous chemical reactions by increasing the reaction surface. In addition, however, deep me-

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chanical treatment significantly alters the feedstock micro-structure [8] and then can be used as the driving force of mechanochemical processes [9, 10].

In particular, mechanical stress causes homolytic cleavage of chemical bonds and thus causes the formation of radicals – parts of a molecule with an unpaired electron, often detectable by electron paramagnetic resonance (EPR) technique [11, 12]. This experimental method based on specific property of unpaired electron selectively absorbs microwave energy in certain magnetic field. The EPR allows to measure two main characteristics: quantity of radicals (by EPR signal intensity) and the nature of them (by specific form and position of measured signal).

Lignin known as one of the key components of wood (its content is up to 30% depending on certain wood species). In terms of its chemical nature, lignin is a polyphenol having an irregular rigid branched structure, which allows it to act as reinforcement for the plant cell wall [13]. However, structural rigidity of lignin makes it less resistant to disintegration compared to cellulose, the key component of wood, so the EPR signal observed during grinding of wood feedstock belongs to lignin radicals [11, 12].

The objective of this study is to check the stability of mechanically induced lignin radicals and test the hypothesis whether there is a correlation between concentration of these radicals and combustibility of the sample. A combination of methods were applied for this purpose: continuous-wave EPR, an author-build method for measuring the ignition delay time of powdered fuel samples under isothermal conditions, and the set of standard simultaneous thermal analysis (STA) methods (for determining the temperature of volatile compounds formation). Note that we did not perform such test on other types of biomass, because it is long-time work and it will be subject of future study.

Experimental methods

Pine sawdust procured from the Kurtamyshsky forestry (Kurgan region, Russia) was used in this study. The data on its technical characteristics are summarized in tab. 1.

Table 1. Pine sawdust characteristics

Cellulose [%]	Lignin [%]	Resins [%]	Pentosans [%]	Humidity [%]	Ash [%]	Fixed carbon [%]	Volatile compounds [%]
44.66 ±0.90	29.62 ±0.05	4.89 ±0.02	6.3 ±0.01	1.66 ±0.02	0.61 ±0.04	23.60 ±0.1	85.61 ±0.16

The experimental pine sawdust samples were prepared using the following procedure. In order to comminute the coarse fractions, the original sawdust was passed through a Desi 11 disintegrator (Desintegrator Tootmise OU, Estonia). This stage is not necessary and can be replaced for example by coarse filter or coarse sieve. Further, samples were dried in laboratory oven at 105 °C during two hours and then residual humidity was controlled by Radweg WPS 50 SX, see tab. 1. Next, immediately before the experiment, the samples were subjected to additional mechanical activation in an APF-4 laboratory planetary ball mill (developed at the Institute of Solid State Chemistry and Mechanochemistry, SB RAS, Novosibirsk, Russia) under the standard activation conditions: centripetal acceleration was 20 g. The 50 g feedstock per 800 g of grinding media was loaded into the jars. The mechanical activation procedure was selected so as to prevent feedstock charring: four cycles activation for 2.5 minute + cooling for 5 minute were conducted.

Figure 1 shows the particle size spectrum of the original (before activation) and mechanically activated samples as a function of minimal size distribution $x_{c_{min}}$. The data were obtained on a CAMSIZER XT particle size analyzer (Retch technology). It is seen that in our

conditions result of milling only small shift of particle size to small radius – here we used conditions not for grinding, but only for activation.

The samples before and after mechanical activation were studied by EPR on an E-109 Varian X-band EPR spectrometer at ambient temperature. Quantitative measurements of spin concentrations in the sample were conducted using Cu^{2+} sulfate pentahydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as an EPR standard, the field position (measured as dimensionless g -factor) was determined with respect to Mn^{2+} in MgO . Experimental mistake was calculated from repeated measurement of standard sample, which has a signal amplitude similar to the interested one.

The ignition delay time under isothermal conditions was measured in a vertical tubular reactor (set-up designed at the Institute of Thermophysics, Siberian Branch of the Russian Academy of Sciences); its thorough description can be found in [14, 15]. The set-up was a vertical heat-insulated steel pipe capable of maintaining constant temperature in the range of 500-1000°C. Along the entire length of the combustion chamber, there were photodiodes whose purpose was to measure the ignition delay time as a difference between the time of sample injection into the upper portion of the tube and the response time from one of photodiodes. According to [15], the optimal set-up temperature for detection of the pine sawdust ignition at used geometry was chosen at 520 °C. To improve the quality of measurements and to demonstrate an experimental error, each measurement was repeated to ten times.

The STA involving thermogravimetric measurements, differential scanning calorimetric studies, and mass spectrometry-based evolved gas analysis was also performed. The STA 449F1 Jupiter® set-up coupled with a QMS 403D Aeolos® quadrupole mass spectrometer (NETZSCH, Germany) was used. The experiments were conducted in the temperature range of 50-800 °C in a synthetic air atmosphere (80 vol.% Ar, 20 vol.% O_2). The flow rates of argon and oxygen were 40 mL and 10 mL per minute, respectively. An accurately weighed sample (10.0 ± 0.2 mg) was placed in an unlidded crucible made of Al_2O_3 . The heating rate was 20 °C per minute. The experimental data were analyzed using the Proteus analysis software package [NETZSCH Proteus Thermal Analysis v.6.1.0 – NETZSCH-Geratebau GmbH – Selb/Bayern, Germany, 2013].

Results

The EPR study of paramagnetic centers in plant biomass

In accordance with the literature data, the EPR spectrum of ground pine sawdust contains a broad line belonging to organometallic complexes [16, 17] and a narrow line near 3320 Gs, which position ($g = 2.0043$) and width (9.43 Gs) corresponds to lignin radicals (putatively having a quinoid structure) [11, 18]. Figure 2 shows the complete EPR spectrum of mechanically activated pine sawdust, the portion of the spectrum near $g = 2$ (near 3320 Gs) is shown on the right-hand side. Asterisks denote the signal from the EPR standard (Mn^{2+} in MgO).

The shapes of the spectra of the samples before and after mechanical activation remain almost unchanged. However, quantitative measurements indicate that the concentration

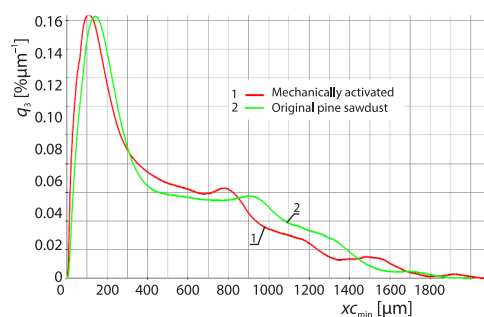


Figure 1. Particle size spectrum for the original – 1 and mechanically activated – 2 pine sawdust samples

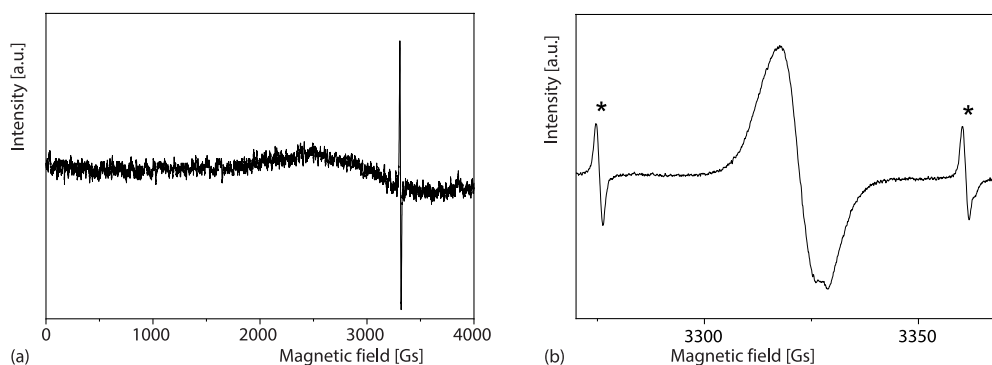


Figure 2. The EPR spectrum of the mechanically activated pine sawdust; (a) complete EPR spectrum and (b) its fragment

of organic radicals after mechanical activation increases by approximately one order of magnitude: from $(1.7 \pm 0.4)10^{16}$ s/g to $(1.4 \pm 0.5)10^{17}$ s/g (this error is related to accuracy of the measurement method). The measured values show good agreement with the literature data [11]. In order to further confirm that the observed signal belongs to lignin radicals, we conducted a series of qualitative experiments. Thus, we compared the shape and the intensity of the EPR signals after the following samples had undergone mechanical activation:

- pure lignin procured from Aldrich (CAS Number 8068-05-1),
- sawdust obtained from the lignin-rich hard portion of pinewood, and
- cellulose-rich sawdust pulp after lignin was separated using an alkali. In all three cases, the signal shape was the same, while its intensity declined in the series $1 > 2 > 3$.

Next, we studied the stability of *excessive* lignin radicals that emerged immediately after mechanical treatment. Figure 3 shows the decay kinetics of the EPR signal from the mechanically treated pine sawdust at room temperature in air-free atmosphere (left-hand side) or in an open measuring cell. The inset in the right-hand side figure shows the constancy of the signal shape immediately after grinding and one day later.

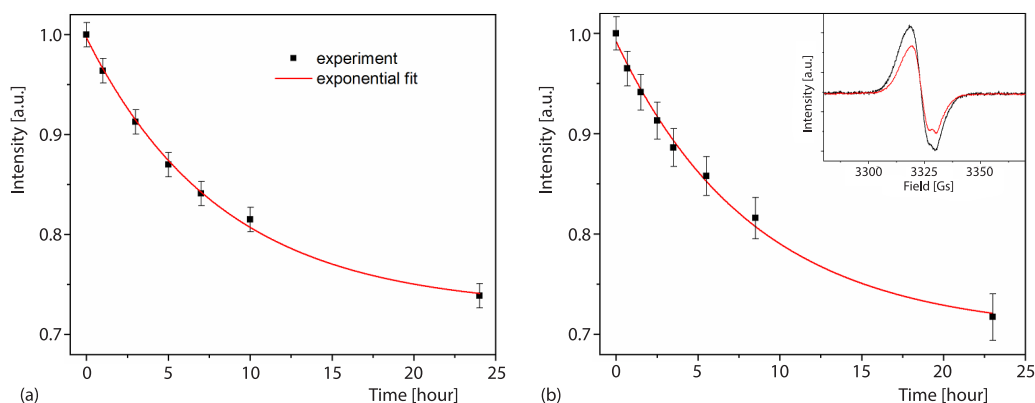


Figure 3. The decay kinetics of EPR signal from mechanically treated pine sawdust at room temperature in the absence of air (a) and in the presence of air (b); the inset shows the signal shape immediately after the mechanical treatment and one day later

These experimental dependences are fitted well by a monoexponential decline curve, with the characteristic time of 8.3 ± 0.6 hours (without unrestricted access to air) and 8.4 ± 0.9

hours (with unrestricted access to air). These values coincide within experimental error, so it is fair to say that this process does not depend on restricting the air access to the measuring cell. It has been reported in literature that oxygen interacts with radicals in green tea polyphenols [19]. However, our findings indicate either that oxygen has no effect on lignin radical decay at all or that this effect is so strong that special experiments in a totally oxygen-free environment need to be performed to detect it. The observed effect may be related to pairwise recombination of mechanically induced radicals as it has been hypothesized in [20].

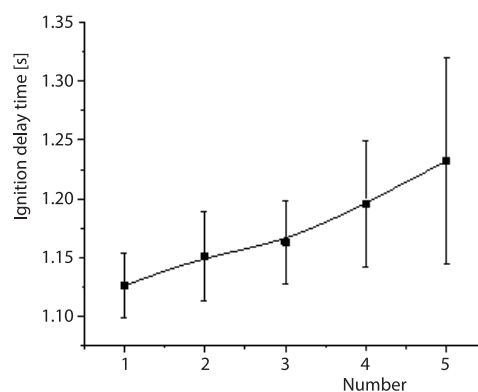


Figure 4. – Ignition delay time as a function of exposure duration

Combustion in a tube furnace

The effects of mechanical activation of pine sawdust on ignition and thermal destruction were studied experimentally. Figure 4 shows the ignition time as a function of time that has passed after grinding (denoted with the control points):

- one hour,
- two hours,
- three hours,
- two days after milling, and
- the original (non-activated) sample.

One can see that ignition delay time increases with *aging* of the samples, approaching the value for the non-activated powder. Within the experimental error, the characteristic time of this process is the same as that for EPR signal intensity decay, suggesting that these processes are inter-related. The STA experiments have additionally confirmed this relationship.

Simultaneous thermal analysis

Thermal analysis curves for the activated pine sawdust samples in a synthetic air atmosphere are shown in fig. 5. One can see that the combustion process involves several stages, which is consistent with earlier findings [21]. In all the samples, residual water is removed during the first stage of decomposition (heating the samples to 150 °C). Further combustion involves two separate stages, each being accompanied by exothermic effects: heat release and simultaneous sample mass loss.

At the second decomposition stage taking place in the temperature range of 200-380°C, low intensity ion currents with mass-charge ration $m/z = 29, 31, 27, 26, 42, 41, 42, 51, 55, etc.$ are observed, which is indicative of incomplete combustion of organic wood components and the release of their destruction products into the gas phase. This phase corresponds to the formation and ignition of volatile combustible compounds. The third stage of thermal destruction takes place in the temperature range of 380-500°C and is accompanied by a more abrupt sample mass loss and significant heat release. It is assumed that this stage is caused by rapid combustion of carbon-rich residue that was formed during the first stage. Ion currents from H₂O, CO, CO₂, and NO fragments (m/z 18, 28, 44, and 30, respectively) indicates the main gaseous products being released during combustion of the samples. The final residual mass of the solid end products of combustion is 4.8% of the initial samples.

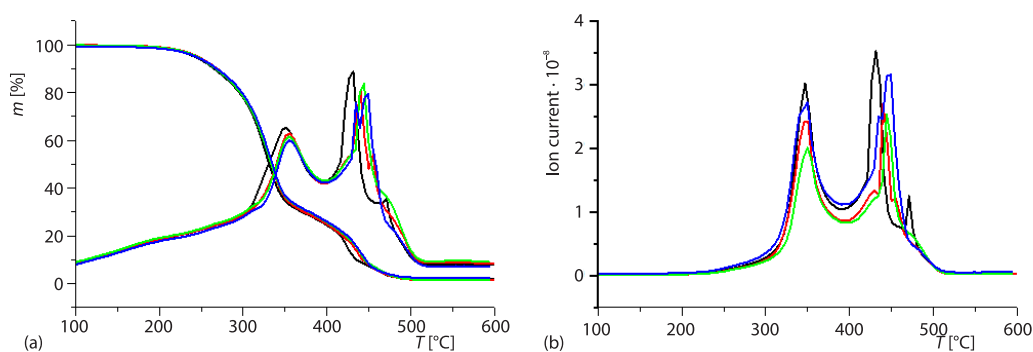


Figure 5. Thermal analysis curves of the *aged* samples stored for 0 hours (black) 3 hours (red), 5 hours (green), or 20 hours (blue) and the MS curves showing CO₂ release in a synthetic air atmosphere at a heating rate of 20 °C per minute

Having compared the thermal analysis curves, one can draw a conclusion that ignition of the *freshly ground* sample takes place at a lower temperature. The onset temperature for this sample is 306 °C, while the onset temperatures for the *aged* samples stored for 3, 5, or 20 hours lie in the range of 321-326 °C. The temperature corresponding to the maximum combustion intensity for the “freshly ground” sample during the first stage is 350 °C, while for the *aged* samples it lies in the temperature range of 354-356 °C. This fact agrees with the data on variation of the ignition delay time during isothermal combustion in a tube furnace.

Discussion

The experimental data suggest that there is a correlation between the ignition delay time, the amount of lignin radicals, and the sample’s ability to release volatile combustible compounds. However, these findings are not sufficient to reveal the nature of this correlation. Let us develop a hypothesis about its nature based on our findings and the facts known from the literature.

Our earlier studies have shown that the calorific value of wood [21] and the amount of volatile products of thermal destruction [10] depend on lignin content in wood. Bahrle *et al.* [22] studied the early stages of lignin pyrolysis and revealed that the release of monomeric units into the gas phase occurs simultaneously with increasing EPR signal intensity in the solid residue. Therefore, one can make a conclusion that thermal destruction of lignin has a radical mechanism [23].

Hence, if lignin actually plays a crucial role in the formation of volatile products of thermal destruction (in turn, these substances are responsible for the combustion properties of the material) and if thermal destruction of lignin occurs via the radical mechanism, the initial radical concentration is expected to eventually affect the combustion properties of the material, which was observed in our experiments.

It is worth mentioning that the characteristic aging time of the samples is approximately several hours (*e.g.*, EPR signal decays by only 25-30% within the period of 24 hours, while signal intensity during the first two hours declines by less than 5%), so the revealed effects can be used in actual practice.

Conclusions

It has been demonstrated that there is a correlation between the physicochemical characteristics of aging of mechanically activated pine sawdust (namely, a correlation between

the EPR signal intensity decay, increasing ignition delay time under isothermal condition in a tube furnace, and increasing temperature of formation of volatile compounds under continuous heating). These data are of fundamental importance for our understanding of the nature of changes occurring during mechanical activation of plant-based feedstock.

Furthermore, the hypothesis about the effect of mechanically induced lignin radicals on formation and ignition of volatile combustible compounds has practical significance for further development of the plant biomass burning technology. It is important that the *aging effect* suggests using such fuel as far as possible after preparation. But there can be a more general conclusion. Based on the hypothesis formulated in this study, one can try to further reduce the ignition delay time (or tune another reactivities) for plant-based feedstock, since the initial radical concentration can be controlled by varying the duration and type of mechanical (or another) activation – if such reactivity based on lignin radicals and such activation can produce them.

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