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Biomass ignition in mills and storages – is it explained by conventional thermal ignition theory?

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Abstract – Self-ignition temperatures determined in the framework of conventional thermal ignition theory does not explain why biomass is much more susceptible to spontaneous ignition in power plant mills or storages. Examining the onset of reactions at low temperatures may provide a better understanding of the process, which can then be incorporated into refined models of self-ignition for biomass and other organic solids. In the present study, the slow, transient heating of several lignocellulosic biomasses and a bituminous coal from ambient temperature to around 300° C were investigated in a lab scale tube oven, with sample sizes between 11–40 g. Tests were carried out under oxidizing (20 % O_2) and inert atmospheres. Judged by off-gas measurements of CO and CO_2, a reaction onset could be seen at temperatures below 100° C. Under oxidizing atmosphere, reactions were more intense and set off earlier, suggesting that a heterogeneous oxidation is the dominating mechanism in self-ignition. It could also be shown that both mechanisms compete for reactive material. While oxidation was exothermic, pyrolysis was largely thermally neutral in these experiments. Reaction behavior was seen to depend highly on the material, and the results indicate that higher ash contents may promote reaction onset. However, further work is needed to arrive at a comprehensive model of self-ignition.

1. Introduction

Biomass is increasingly replacing coal for heat and power generation on large, centralized boilers fired with pulverized fuels. Changing from one fuel to another is however not completely straightforward: experience shows that wood pellets ignite more readily than coal in power plant mills or storages. A theory of thermal ignition was developed by Semenov [1] and Frank-Kamenetskii [2]. Although these models meant to describe the thermal runaway in reactive gas mixtures, they have subsequently been applied to the ignition of solids in oxidative atmosphere as well [3–5]. Data compiled from these and similar works [6–8] showed coal, rather than biomass, to be more susceptible to ignition.

While this 'classical' method has seen some criticism [9], systematic studies on transient processes leading up to thermal runaway are rare, and typically follow different experimental procedures among the authors: Ren et al. [10] observed temperature rise by self-heating of coal in adiabatic setups, where temperature increased by several Kelvin within a few hours. A conceptually similar study was presented by Della Zassa et al. [11], showing temperature increase by up to 50 K in sewage sludge kept in insulated vessels over several days. Using external, forced heating, Moqbel et al. [12] suggested using several additional characteristic temperatures below the self-ignition point to characterize the process. Fernandez Anez et al. [13] recorded CO and CO_2 emissions for samples placed in an oven with temperatures below the self-ignition point, and found the formation of these gases to increase with temperature.

Compared with TGA-experiments, they found off-gases to appear before considerable weight loss was measurable. In fact, monitoring of CO and CO_2 is an accepted method of detecting the onset of spontaneous reactions.

The ongoing investigation outlined here takes a somewhat different approach. We aim at explaining self-ignition through the different sub-processes, e.g. pyrolysis, heterogeneous oxidation, heat and mass transfer; and their respective interdependencies. The work presented will mainly focus on the former two, pyrolysis and heterogeneous oxidation.

2. Experimental Procedure

Experiments were carried out in a closed lab-scale tube oven. Inlet and outlet ports at opposite ends allowed control of the gas atmosphere. The basic design of the experimental setup used can be seen in Fig. 1. The samples to be tested were placed in a cylindrical wire mesh holder (length: 150 mm, diameter 30 mm), which was suspended in the oven. The sample holder was filled completely, but without compressing the sample. Owing to their different bulk densities as a fixed bed, the sample materials were therefore tested at different masses. The oven was flushed with defined mixtures of oxygen and nitrogen at a total flow rate of 2.5 L/min. Oxygen concentrations of 20 % (oxidation) and 0 % (pyrolysis) were used. The temperature was increased at a rate of 1 K/min to typically 300 °C (exceptions are mentioned) and the oven was held at this temperature until the reaction had ceded. Temperatures of sample and oven, as well as CO, CO_2 and O_2 in the off-gases were monitored in 10 second intervals. The reported values are dry gas measurements.

Several natural biomass samples and a bituminous coal were investigated as listed in Table 1. All samples were in pulverized form. Due to the fibrous nature of most biomass samples, it was not attempted to test samples at uniform particle sizes. The particle sizes reported here correspond to sieving fractions. Preliminary tests with pine wood sieved into two fractions (50–200 µm and 600–1000 µm) showed some variation between different particle sizes, but these were small compared to the effect of the material type. Packed beds are treated as porous solids here, i.e. it is expected that their behavior is not so much governed by the individual particle size, but more by the free internal surface area, the size of the channels and the contact area among particles. These factors in turn influence the reactive surface area, the transport of reactant and product gases, and the thermal conductivity of the bed.
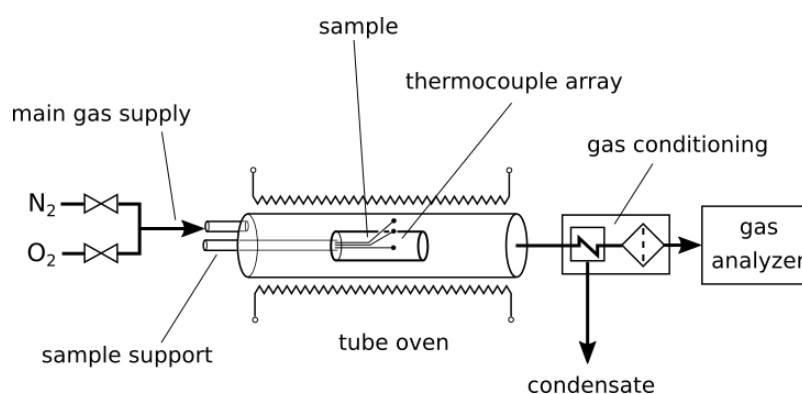

Figure 1. Principle layout of the experimental setup.

Table 1. Materials used in the tests. Different sample masses are due to different bulk densities. See text for a discussion of size and sample mass.

Material	Particle size [μm]	Sample mass [g]	Water [wt-%]	Volatiles [wt-%]	Ash [wt-%]
Beech wood	0–200	17	8.4	70.6	2.5
Pine wood	50–200	12	5.6	80.8	0.3
Wheat straw	200-400	11	8.0	71.2	3.9
Sunflower husk pellets	125-850	40	9.2	68.6	4.7
Bituminous coal	0-125	40	6.6	33.9	8.8

Additional tests were carried out on lignin and cellulose. Both materials were acquired from Sigma-Aldrich in finely pulverized form. The sample masses were 40 g for lignin and 30 g for cellulose.

The temperature in the sample center was used to describe the reaction progress. As outlined previously [14], emissions were scaled by sample mass. Using the known gas flow rate through the oven, it was possible to convert the measured emissions to a molar formation rate. The formation rate is reported in moles per unit time per original sample mass, thereby neglecting sample mass loss in the early stages.

3. Results and Discussion

3.1. Onset of reaction for different material types

A main interest in this work is to describe the onset of reactions, before a noticeable temperature overshoot occurs. Measuring a relevant quantity of product gases CO and CO_2 was used as a criterion here. A value of 10 ppm measured concentration of the respective gases could be easily distinguished from any noise on the signal, and was therefore used as a comparison. Since the product gas concentrations scale with the mass of the sample, we used a threshold of 1 ppm measured per gram of sample, which leads to 'onset'-thresholds of 11–40 ppm, depending on the material. Results of this analysis are summarized in Table 2. By this evaluation, a reaction is already readily detectable around 100 °C for most materials. It is also worthwhile to point out that the respective thresholds are reached at lower temperatures for oxidative conditions than under pure nitrogen atmosphere.

As CO and CO_2 appeared gradually, the definition of a reaction onset based on a certain measured or released amount is to some degree arbitrary. Further results from the off-gas measurements are therefore summarized in Fig. 2. The cellulose and lignin experiments were carried out to ambient temperatures of up to 350 °C. The coal oxidation experiment was run only up to 250 °C oven temperature, since a significant temperature overshoot and high CO and CO_2 concentrations were already measured at this point. All other experiments were run according to the procedure described above.

Table 2. Reaction onset based on a threshold of 1 ppm measured per gram of sample for oxidizing and pyrolyzing conditions.

Material	Temperature at 1 ppm/g (sample) [° C]			
	CO (oxidation)	CO_2 (oxidation)	CO (pyrolysis)	CO_2 (pyrolysis)
Beech wood	149	106	182	119
Pine wood	130	98	204	130
Wheat straw	154	110	175	117
Sunflower husk pellets	113	85	148	92
Bituminous coal	90	59	156	78
Lignin	131	79	167	82
Cellulose	210	190	250	206

For all experiments shown, more CO_2 than CO was detected, with the CO:CO_2-ratio increasing, but not exceeding 1, as the temperature increased. However, no clear pattern was observed in this behavior. For the analysis reported here, the sum of both gases was considered as a measure of the conversion of fuel carbon, and thus, reaction intensity. It should also be noted that considerable amounts of tar were released, which could not be sampled.

Figure 1 (a) shows data for oxidation in a low temperature range. Oxidation products appear initially at temperatures below 100° C. The data also indicates an earlier reaction onset in coal than in the biomass materials, which agrees with the findings in the literature [6–8, 13], and also with the previously determined thresholds for thermal runaway under these conditions (coal: 147.5 °C, pine: 227.5 °C, both within ±2.5 K). Of the natural biomasses, sunflower husk is the most reactive in range 50–150 °C, followed by pine, beech and wheat straw. The latter two are almost indistinguishable here. Lignin is seen to react strongly, whereas cellulose shows no reaction at all in this range. At higher temperatures (Fig. 1 (b)), notably above 200° C, this picture changes. Between temperatures of 230° C and 260° C, pine, beech and wheat show a sharp acceleration in the release rates of CO and CO_2, that levels of again at even higher temperatures (> 280° C). Coal qualitatively shows the same behavior, while it is absent in this temperature interval for lignin, cellulose, and sunflower husk pellets.

For the pyrolysis experiments, Figs. 2 (c)-(d), a similar discrepancy between the ranking of the materials at low and high temperatures is seen, albeit on a much smaller scale. While starting at low temperatures, coal pyrolysis is weak throughout the range tested. Of the biomasses, sunflower husk is the most reactive, followed by wheat, beech and pine. At temperatures below 200° C, the observed release rates of CO and CO_2 under pure nitrogen atmosphere are loosely in order of the ash content (compare Table 1), but not directly proportional to it. Of the biomass components, lignin is again more reactive than cellulose at low temperatures.
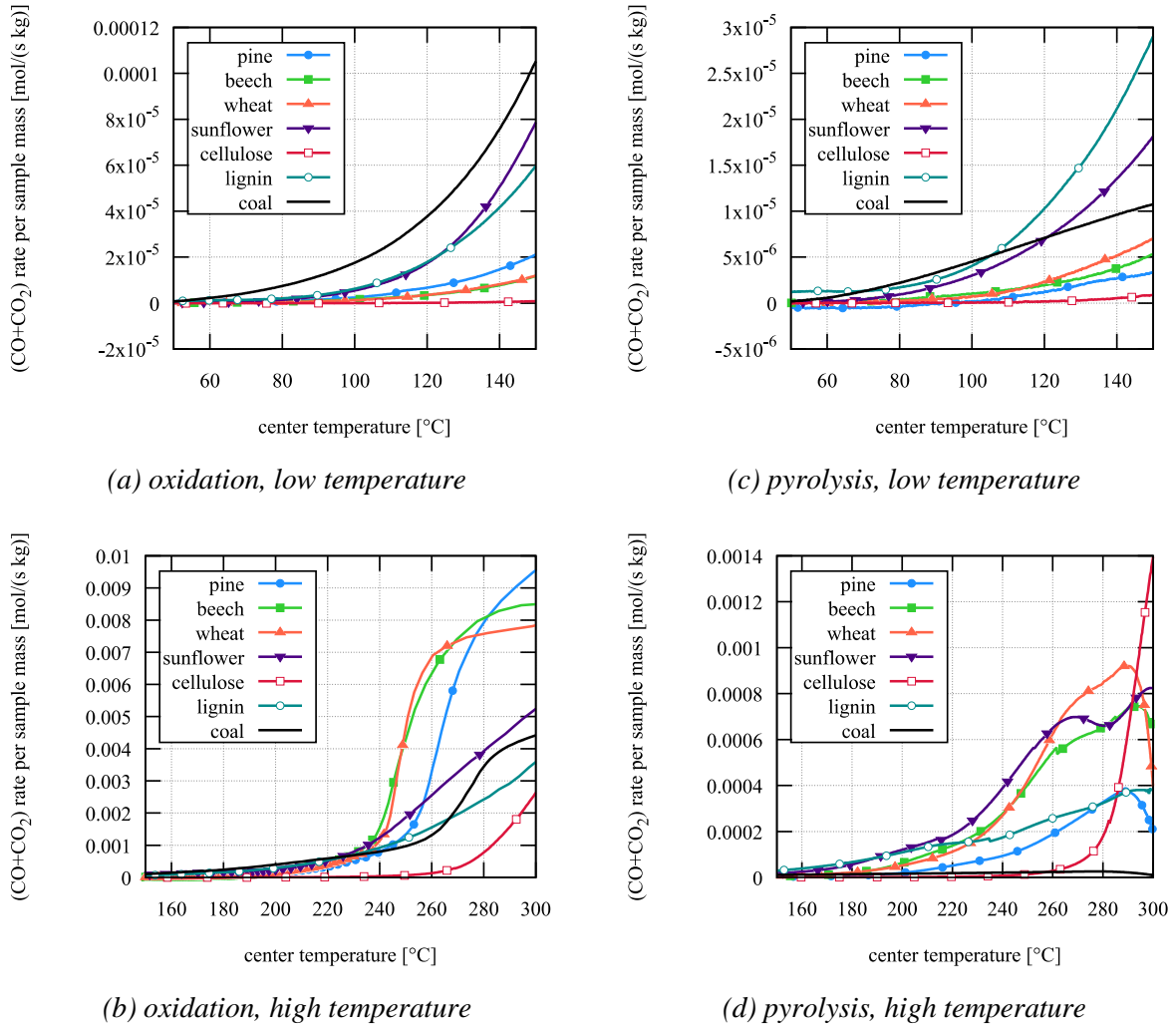
(a) oxidation, low temperature

(c) pyrolysis, low temperature

(b) oxidation, high temperature

(d) pyrolysis, high temperature

Figure 2. Off-gas release rates of permanent gases CO and CO_2 (sum), scaled by sample mass. Pyrolysis experiments with cellulose and lignin were run up to 350° C ambient temperature. Low and high temperature refer to different ranges of the same experiment. Points are included for clarity and do not represent the sample rate. Note the different scaling on the ordinate axes.

At higher temperatures, the ranking of the materials changes again. Most notably, release of CO and CO_2 from cellulose pyrolyis sharply increases from temperatures above ca. 260 °C. Interestingly, none of the observed behavior seems to correlate directly with the material properties of the samples as listed in Table 1.

3.2. Assessment of heat release and thermal runaway

Additionally to the product gas concentration, the temperature difference between sample center and oven temperatures was evaluated (Fig. 3). A negative difference indicates heat transfer from the surroundings to the sample. A positive difference means that the reaction produces so much heat, that the sample heats itself. This can lead to thermal runaway, if the temperature increase by self-heating is sufficiently high.

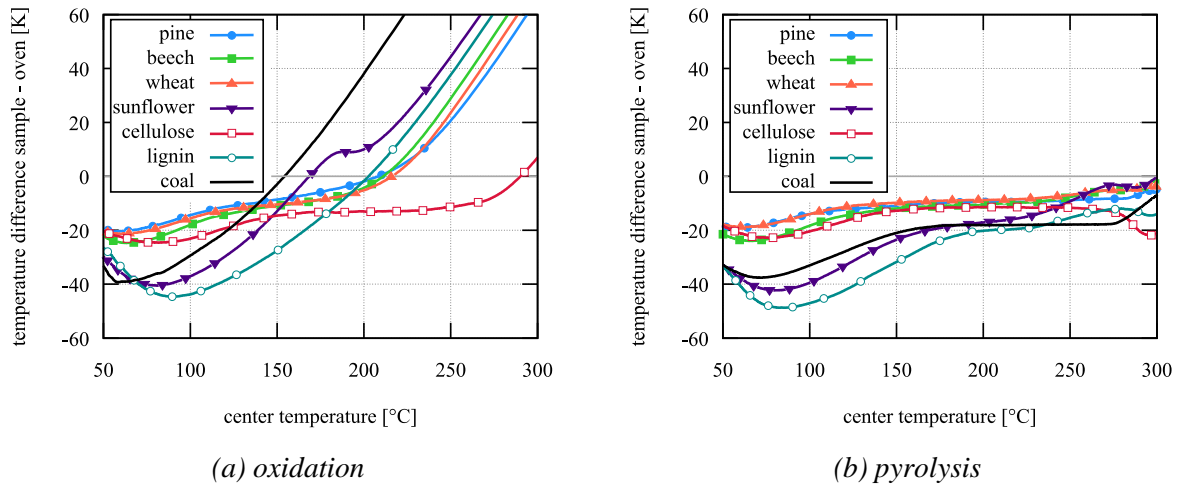*(a) oxidation*   *(b) pyrolysis*

Figure 3. Temperature difference between sample and oven for experiments show in Fig. 2. A positive value indicates a reversal of the heat transfer, i.e. the sample releases heat to its surroundings. Points are included for clarity and do not represent the sample rate.

For all samples under both oxidizing and pyrolysis conditions, a minimum is seen between 50 and 120–150 °C, which can be attributed to the evaporation of water bound in the sample. After the evaporation of water is complete, the slope of the curve will steadily increase for oxidizing conditions (Fig. 3(a)) and remain largely flat under pyrolyzing conditions (Fig. 3(b)). A positive gradient on the temperature difference curve is seen as a sign of an exothermal reaction. Comparing the crossing-point temperatures for oxidation, i.e. the point at which $\Delta T=0$ [15], the ranking of materials compares quite well with the onset gas-release (Figs. 1 (a) and (c)), but not so much with that in the later stages (T > 200 °C). Additionally, exothermal reactions in cellulose are seen only at very high temperatures, which suggests that this component has little or no role in ignition at low temperatures. Some materials, most notably sunflower husks, show weakly exothermal behavior also at high temperatures under pyrolysis conditions (Fig. 3 (b)). However, this appears at such high temperatures that it likely does not play a role in the ignition process.

3.3. Competition of oxidation and pyrolysis

To investigate the competition between pyrolysis and oxidation, a second type of experiment was performed with pine wood, Fig. 4. A sample previously pyrolyzed was allowed to cool and reheated again under 20% O_2 ("pre-pyr"). Compared to the fresh sample under the same atmosphere ("ox+pyr"), the onset of CO and CO_2 release was delayed (150 °C and 141 °C vs. 133 °C and 106 °C for a 10 ppm threshold, respectively), and the maximum levels of both gas concentrations were lower. On the other hand, more CO and CO_2 were released under oxygen atmosphere than under nitrogen atmosphere ("pyr"), regardless of a pre-treatment of the sample. Moreover, 199 °C and 133 °C were necessary to reach the respective 10 ppm thresholds for CO and CO_2 without the presence of oxygen in the gas phase.

These observations suggest heterogeneous oxidation occurs below 150 °C, that it is faster and consumes more material than pyrolysis; that both compete for the same reactive material; and that both reactions are to some degree kinetically limited.
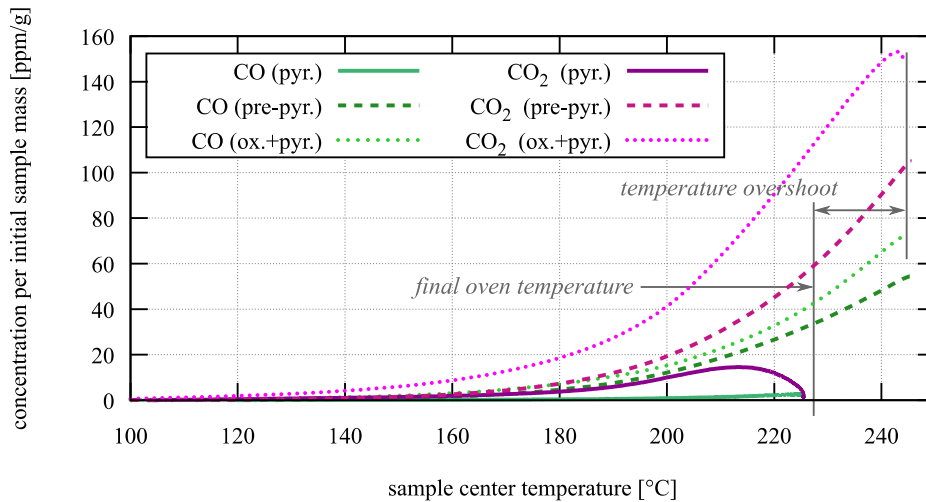
Figure 4. Concentrations of CO and CO_2 (normalized by sample mass) are lower when no oxygen is available (pyr.) and when the material has been pre-pyrolyzed (pre-pyr), compared to oxidation of a fresh sample.

For the same heating procedure, the difference between sample and oven temperature qualitatively characterizes heat release and transfer (Fig. 5). At temperatures around 150 °C, the slopes for the oxidizing- and the pyrolysis curves begin to differ markedly. Oxidation appears as "more exothermic" and pyrolysis as "more endothermic" at these conditions. Prior pyrolysis did not have a large (net) effect: both "pre-pyr" and "ox+pyr" reach 245 °C maximum temperature, exceeding the oven temperature by 20 K. Possibly, the absence of pyrolysis as a heat sink compensates for prior loss of reactive material in the "pre-pyr" experiment: the pre-pyrolyzed sample shows a similar exothermicity, even though less CO and CO_2 are observed.
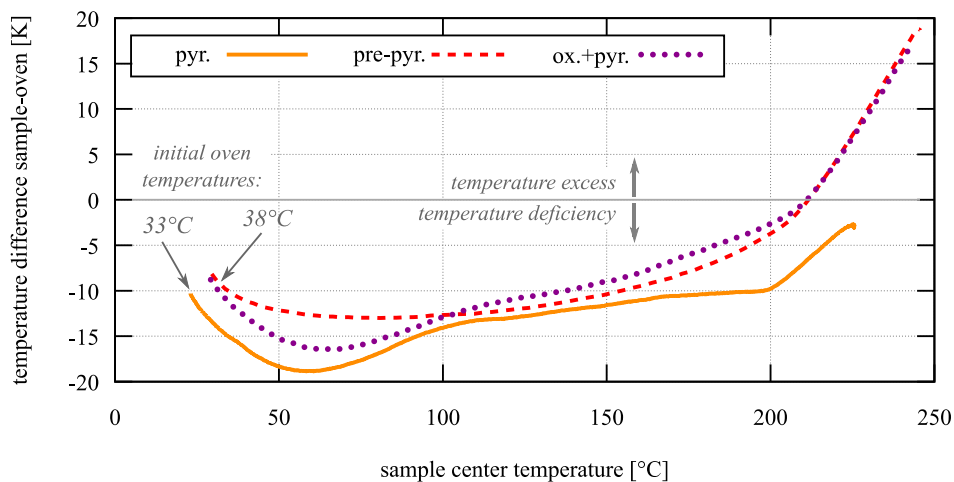

Figure 5. Heating under oxygen (ox.+pyr., pre-pyr.) shows a characteristic overshoot of sample temperature, which is absent under inert atmosphere.

4. Conclusions

For heating at low temperatures, three distinct processes were observed: evaporation of water, pyrolysis, and heterogeneous oxidation. Heterogeneous oxidation appears slightly exothermic and favored over pyrolysis at low temperatures and sufficient oxygen. It could also be shown that both processes act on the same material, i.e. there is a competition between them for available reactive matter.

Comparing different materials, it was seen that their relative reactivity changed when the temperature increases from low (50–150 °C) to intermediate temperatures (150–300 °C). The reactivity ranking of neither pyrolysis nor oxidation could be explained from the volatile, ash, and char distribution. This means that the proximate composition of biomass, as typically used in description of high temperature combustion processes, cannot be used to predict its low temperature reactive behavior. Only at very low temperatures did the ranking of reactivities correspond roughly to the amount of ash, which may point to catalytic effects between the organic and the mineral matter.

Of the typical structural components of biomass, reactions of cellulose do not seem to have a role in ignition. Lignin, in turn, was found to begin reacting at rather low temperatures, a result that is in agreement with the literature, e.g. [16, 17]. The effect of hemicellulose remains to be tested. The high reactivity of sunflower husk pellets may also indicate that extractives promote reactions.

Based on these findings, a more adequate model of self-ignition would have to at least consider separate pyrolysis and heterogeneous oxidation mechanisms. Possibly, evaporation of moisture would have to be included as a heat sink. The competition between pyrolysis and direct oxidation is also necessary to describe the transition from smoldering to flaming, the latter being dominated by a homogeneous oxidation of volatiles released by pyrolytic decomposition. The complex relation between pyrolysis and direct oxidation – competition for reactive material and transition of the dominant reaction mode – is not reflected in conventional ignition models. Separating the two may improve ignition predictions.

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