

A Detailed Experimental Study on the Thermal Decomposition Behaviour of Wood Pellets under Inert and Oxidative Conditions in a Fixed Bed Reactor

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In this work, spruce wood pellets are pyrolysed in an electrically heated fixed bed reactor. Experimental campaigns have been conducted to investigate the influence of final pyrolysis temperature (600-800°C), heating rate (5-20 K/min) and purge gas composition (none, 100% N₂ and 90/10% N₂/O₂). The instrumentation of the reactor includes transient temperature measurements in the reactor (3 locations in the vertical direction) and inside the pellets bed (3 locations in the radial direction) throughout the thermal decomposition process. Gas measurements are carried out for permanent gases (using a GC), condensables are condensed and collected and the remaining solids are also collected. Hence, the mass balance can be established. The detailed experimental results make them useful for validation of thermal decomposition modelling approaches. The experimental results show evidence of endothermal cellulose decomposition reactions as well as the exothermal char formation process. The occurrence of these two processes overlap at high heating rates and when oxygen is used in the purge gas. The two processes can be separated visually by decreasing the heating rate to 5 K/min. The separation shown in the temperature curves is confirmed by the gas analysis. The yields of CO and CH₄ show a visible shoulder in the higher temperature region. The endothermic plateau visible on the temperature readings can be reduced by increasing the heating rate. Oxygen present in the purge gas will further reduce the visibility of the plateau. The amount of CO₂ formed during experiments shows dependency on the oxygen in the purge gas but appears independent of the applied heating rate. The comprehensive experimental results provide both useful knowledge and a validation basis for further modelling work.

1. Introduction

Combustion of biomass in grate furnaces is widely applied, and many technological approaches are used at different plant scales to achieve a good combustion process and to cope with operational issues connected to the biomass feedstock. This is mainly done through accumulated development and operational knowledge, and to a much smaller degree through modelling supported development. However, there could be a significant potential for improving both design and operation of biomass combustion plants if the appropriate modelling tools were available. To enable reliable predictions of the thermal decomposition process, and the influence of changes in operational conditions, a detailed experimentally based understanding of the phenomena occurring during the thermal decomposition of the biomass is required. This knowledge must then be translated into detailed enough models that can account for the relevant physico-chemical phenomena occurring on the grate.

2. Experimental setup and procedure

The experimental setup is schematically shown in Figure 1. A reactor tube, 500 mm long with an inner diameter of 125 mm and an outer diameter of 129 mm, was placed into a vertical tubular furnace. The furnace consists of three heating zones, each controlled separately by the temperature of the void between the reactor

and the furnace wall. Downstream the reactor the condensable vapours were separated by a cooler and collected in a tank. A gas meter (Ritter TG1 Model 5 drum-type) was used to register the amount of evolved gas before the gas was vented. Between the cooler and the gas meter two coalescent filters were installed to remove aerosols from the gas stream. A split stream of the evolved gas was introduced to a Varian CP-4900 Micro Gas Chromatograph for identification and analysis of gases. Two columns were used, both heated to 333 K (60 °C), column A: Pora Plot Q (PPQ) with helium as a carrier gas and, column B: Molecular Sieve (MS) column with argon as a carrier gas. Upstream the reactor a gas supply system consisting of gas bottles, reduction valves, rotameter and manometer was installed to control the purge gas flow and record the system pressure during the experiment. In addition to the three control thermocouples of the furnace, six additional thermocouples were registering temperatures during the experiments. Three thermocouples were placed on the outer wall of the reactor tube while another three were placed inside the reactor tube in the pellets bed approximately halfway down into the basket, one in the center, one close to the wall and one in between, approximately 15 mm from the center, as Figure 1 shows.



Figure 1: The experimental set-up, the vertical tubular furnace with the reactor tube, inside the reactor tube and the container basket with three thermoelements, and the container basket filled with 250 g pellets

The biomass chosen was 6 mm diameter pellets made from spruce woodchips originating from Southern Norway. The pellets were dried before each run in a muffle furnace at 378 K (105 °C) for at least 24h. The proximate and ultimate analysis of the spruce woodchips used to produce the pellets is presented in Table 1.

Table 1: Proximate and ultimate analysis of the spruce woodchips used to produce the pellets used in this study (d.b.). a - by difference

Volatiles matter (wt%)	Ash content (wt%)	Fixed carbon ^a (wt%)	Higher heating value (MJ/kg)	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O ^a (wt%)
88.12	0.31	11.57	20.13	48.78	6.27	0.13	0.01	44.81

A container basket with 250 g of pre-dried spruce wood pellets (shown in Figure 1) were placed in the reactor tube and the reactor was closed. The pellets were then dried at 393 K (120 °C) for at least 60 minutes with a rotameter controlled purge gas flow rate of 2.2 L/min. After drying, the reactor was heated at constant heating rate to the selected carbonization temperature and was kept at this temperature for 180 minutes. The container basket had holes in the bottom so that the purge gas was forced through the fuel bed like in a grate-fired furnace.

The furnace control temperature in the three different sections, the gas meter reading, and the system pressure were recorded each minute during this time period until devolatilization was finished. Thereafter the parameters were recorded every 10 minutes until carbonization was finished. The temperature given by the thermocouples on and inside the reactor was sampled automatically with 5 second intervals using the FLUKE Hydra Series II, while the gas chromatograph (GC) sampled gas about every 1.5 minutes using the SOPRANE II software. At the end of the experiments, the furnace heaters were switched off, and the system was left to cool overnight with a small N₂ purge. Five different experiments and one replicate experiment were performed to study the effects of the carbonization temperature, heating rate and the composition of the purge gas. Experimental conditions are shown in Table 2.

Table 2: The different specifications of the performed experiments

Experiment	1	2	3	4	5	6 (replicate)
Carbonization temperature [K]	1073	873	873	873	873	873
Heating rate [K/min]	10	20	10	5	10	10
Purge gas composition [vol%]	None	100% N ₂	100% N ₂	100% N ₂	10% O ₂ 90% N ₂	10% O ₂ 90% N ₂

3. Results

3.1 Mass balance and temperature profiles

Table 3 shows the amount of pre-dried wood pellets in the bed before the experiments, the amount of charcoal, liquid condensate (including the mass on the two filters and in their drains), accumulated gas, and consumed O₂ from the purge gas after the experiments, as well as the deviation in the mass balance. The consumed O₂ was calculated by assuming a constant purge gas flow of 2.2 L/min during the entire experiment. The deviation shows the losses, i.e. how much weight that was needed for closing the mass balance. N₂ is not included in the Table, as there is no consumption of N₂ during the experiment.

Table 3: The mass balance for the experiments. The sums are for the reactants and the products of each experiment, respectively. N₂ is not included.

Experiment	1	2	3	4	5	6
Wood pellets [g]	250.1	250.1	250.0	250.0	250.1	250.0
Consumed O ₂ in syngas [g]	0	0	0	0	56.0	58.2
Sum reactants [g]	250.1	250.1	250.0	250.0	306.1	308.2
Charcoal [g]	58.0	59.7	61.2	63.0	40.0	43.1
Liquid condensate [g]	108.8	107.9	113.0	120.0	119.8	109.5
Gas [g]	64.6	51.2	46.0	38.4	107.4	125.4
Sum products [g]	231.4	217.9	218.7	220.9	264.7	270.2
Deviation between sums [%]	-7.5	-12.5	-11.9	-11.4	-12.7	-9.8

There are several reasons why the mass balance closures did not reach 100% for the experiments. There were significant amounts of condensate left in the cooler house and coils, the pipes, and in the filter houses that were not measured. This is expected to give the largest contribution to the missing mass. Another possible contributor is uncertainty in the measured permanent gas composition. Figure 2 shows the temperature profiles during experiment 1 for three positions inside the bed, the three sections of the outer reactor wall, and the control temperatures (TC) of the furnace. The figure shows that the wall temperatures follow the control temperatures with a small delay due to heat transfer limitations.

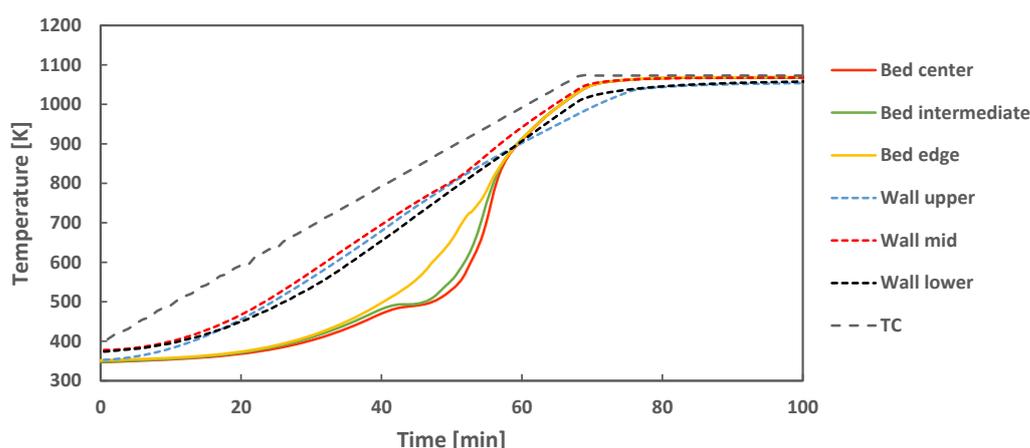


Figure 2: The temperature profile at the edge, an intermediate position, and the center position of the fuel bed, the control temperature of the three sections of the furnace (TC) and the temperatures of the outer reactor wall for experiment 1

The temperatures in the pellets bed are different from those of the reactor walls. This is due to heat transfer limitations and possibly reactions consuming and generating heat. The heating of the pellets bed starts with a somewhat longer time lag than that of the reactor wall, which is due to heat transfer limitations and the thermal inertia of the pellets bed itself. Shortly after the bed starts to heat up a temperature plateau is observed, which is followed by a very rapid temperature increase. These heating rates in the pellets bed are higher than the set-point heating rate of the furnace. Calculations of the heating rate showed that the heating rate spiked very fast for the innermost parts of the bed where the medial position reached a heating rate of about 80 to 100 °C/min. A higher heating rate for the reactor broadened the spike of the calculated heating rates. The possible reason of this behaviour is found in the pyrolysis kinetics of wood. Rath et al. (2003) found two reaction steps when investigating biomass pyrolysis heat of reaction in a Differential Scanning Calorimeter. The first one is the primary biomass pyrolysis, the second is an exothermic reaction that is almost independent of the reaction conditions. Park et al. (2010) found the presence of two sequential thermal regimes separated by a plateau. The two regimes correspond to an initial endothermic decomposition where the mass loss occurs and a secondary exothermic reaction where the intermediate solid converts to the final char. The temperatures during this stage can overshoot the surface temperature, which is not observed in our work as the thermocouple was not placed inside pellets but in the void between individual pellets. Park et al. reported that the plateau is caused by the endothermic cellulose decomposition. Another effect that will cause a plateau in the gas phase temperature during devolatilization, is the fact that the volatile gas that is released from the solid has a lower temperature than the surrounding fluid. This will be explained in the following, where we have assumed that the heat of devolatilization is zero and that devolatilization occurs at a given temperature, T_{devol} . A layer of a solid piece of fuel will start to devolatilize when that layer reach T_{devol} . Since the solid is initially at a lower temperature than T_{devol} , a heat flux from the surrounding fluid is required to drive the devolatilization process. The heat flux to the devolatilization zone of the particle depends on the temperature difference between the devolatilization zone and the surroundings. This means that the gas released from the solid, which will have a temperature equal to the particle temperature, will be significantly cooler than the surrounding fluid. It will therefore cool the surrounding fluid – potentially causing a temperature plateau that lasts until the devolatilization process is finalized. When the cooling effect of the devolatilization process is over, only the char is left, which is then easily heated due to no outflowing cool gas. Due to the strong temperature difference that has been built up during the devolatilization phase, and the low thermal inertia of the char, the char will now heat up very quickly, and the heating rate will initially be significantly faster than the heating rate of the reactor walls. The heating rate will then decrease as the char temperature approaches the temperature of the reactor walls. Di Blasi et al. (2014) investigated the temperature overshoot of different biomass types in a fixed bed pyrolysis reactor and found that the temperature overshoot is present for all kinds of biomass, but the degree is dependent on the biomass type and external reaction conditions, with softwood showing the least and hazelnut shells the most exothermicity. Looking at the global heat figures, endothermic cellulose decomposition seems to counteract the exothermic reaction heats from hemicellulose and lignin conversion (Di Blasi et al.). Hence, the rather modest overshoot can be explained by the cellulose-rich softwood pellets that exhibits the least exothermicity as well as the higher heating rate of the reactor compensating for the temperature difference at the thermocouple measurement point while the overshoot occurs.

3.2 Effect of the purge gas and its composition and heating rate

Figure 3 (left) shows the temperature profiles for experiment 1, 3 and 5 measured in the center of the pellets bed. As previously mentioned, experiment 1 was carried out without purge gas. A small amount (2.2 L/min) of inert gas (nitrogen) was used as purge gas in experiment 3, while in experiment 5, the purge gas contained 10 v/v% oxygen in nitrogen. All three experiments have the same heating rate (10 K/min). The figure shows a similar pattern for experiment 3 and 5 as for the reaction carried out without purge gas, but with a slightly longer time lag at the beginning of the reaction for experiment 1, probably due to slower heat transfer (no flow from below). The temperature profile during the first part of the heating (until the reaction temperatures reach the plateau after about 40 minutes) of the experiments for experiments 3 and 5 are identical, while the second part is slightly different. It can be assumed that the temperature differences between experiments 3 and 5 in this part are due to exothermal reactions involving oxygen in experiment 5. In the experiments with purge gas, the plateau is decreasing, and this can be attributed to the purge gas flow levelling the temperature differences in the voids of the pellets bed. In case of experiment 5, the plateau has completely disappeared, which is most likely the effect of the previously mentioned oxygen consumption. The slightly higher temperatures measured in experiment 5 compared to experiment 3 are also due to in general higher bed temperatures caused by the oxygen consumption.

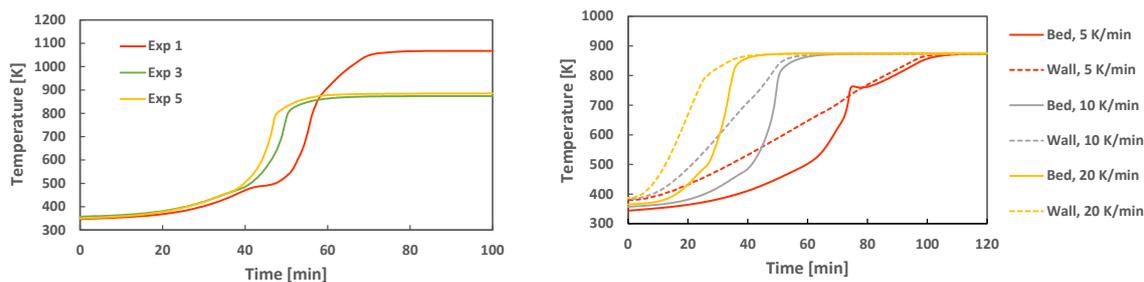


Figure 3: **Left:** The temperature profile during heat-up in the center of the pellets bed for experiments 1, 3 and 5, **Right:** The temperature profile during heat-up at the reactor wall and in the center of the fuel bed for experiments 2, 3 and 4 with heating rate 20, 10 and 5 K/min, respectively

Figure 3 (right) shows the temperature profiles for experiments 2, 3 and 4 measured at the reactor wall and in the center of the pellets bed. The same amount (2.2 L/min at room temperature and atmospheric pressure) of N_2 purge gas was applied in all three experiments. The heating rates in these experiments were 20, 10 and 5 K/min, respectively. The figure shows that the temperatures measured in the bed show significantly different values. The slower the heating rate, the flatter is the temperature increase in the first part of the run. While the experiments with 10 and 20 K/min are similar, experiment 4 with 5 K/min shows different characteristics. After a slower start, the exothermic part of the decomposition process looks more severe, with a visible temperature overshoot. The overshoot occurs at almost 100 K lower temperature than the set-point, while the other experiments do not show similar behaviour. Based on previously discussed kinetics, it is assumed that the decomposition reactions are the same in all the experiments. In experiments 2 and 3, due to the higher heating rate set for the reactor, the wall temperature stays above the biomass bed temperature. The overshoot is hence not visible for experiments 2 and 3. In case of experiment 4, with the lowest heating rate, the reactor did not have time to heat up enough until the point when the exothermic reactions started, and the bed temperature overshoot the temperatures measured at the wall. Furthermore, the figure shows that after the devolatilization is finished in experiment 4, the char bed is heated at the same rate as the reactor walls, which indicates that the exothermal heat increase of the bed originates during the devolatilization process. Higher heating rates during pyrolysis normally gives a higher heat transfer rate into the biomass particles, which is expected to increase the amount of volatile matter released per time unit. A connected pressure build-up inside the biomass particles would alone also increase the potential for secondary reactions as increasing pressure alone means increasing residence time and increased partial pressures inside a particle, but since a high heating rate causes a large volume flow out of the particle, this will have a reverse residence time effect. Pellets will also behave differently from e.g. wood chips, due to higher density and lower porosity, likely increasing the flow speed out of the particle and decreasing the residence time of volatiles inside the particle.

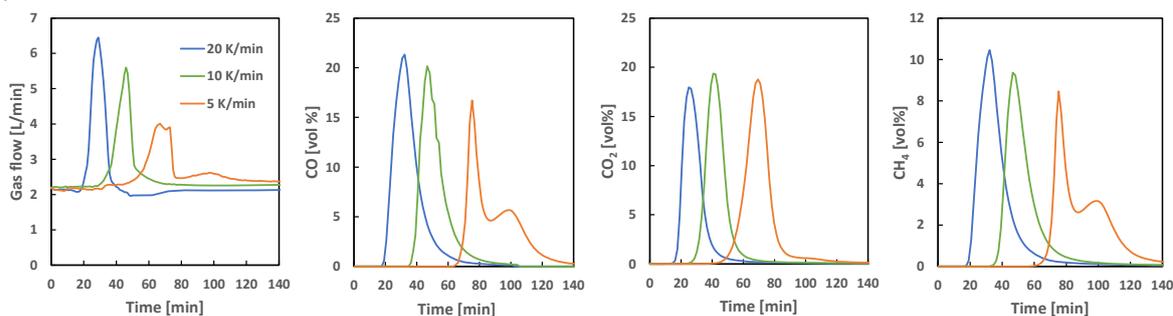


Figure 4: The gas flows (total, CO, CO₂ and CH₄) during experiments 2 (20 K/min), 3 (10 K/min) and 4 (5 K/min)

There will also be a difference in mechanical strength, hence influencing the degree of possible pressure increase before particle rupture or disintegration occurs. Neves et al. (2011) analysed data reported on pyrolysis and found a positive relationship between the yield of permanent gas and the heating rate. In the current work, the charcoal and liquid yields decreased, and the gas yield increased with increasing heating rate. Comparing the results with similar experiments carried out with pine wood (Williams and Besler, 1996), it can be observed that the yield differences between the experiments with different heating rates are somewhat higher in the current work, as well as in the current work the amount of condensate decreased instead of increasing. In addition, in the current work the amounts of gases are significantly lower and the amount of

liquids in the 20 K/min experiment is significantly lower. Chen et al. (2014) pyrolyzed 50 g bamboo samples under similar conditions, and their results are more similar to this work, i.e. the char and liquid yields decreased with increasing heating rate while the gas yields increased. There are, on the other hand, differences in the yields, since they had significantly larger char yield in the 5 K/min experiment and significantly lower liquid yields. The reason can be either the differences in the biomass or in the experimental set-ups. One plausible reason can be that the amount of biomass (250, 25 and 50 g) and hence the evolved volatiles were larger in the current setup. Also, the condenser might not be able to effectively separate all the condensable vapours during the higher heating rate experiments. As mentioned earlier, it is reasonable to assume that the low liquid yield in our work is due to some condensables not being collected. This is presumably also the main reason for not being able to close the mass balances. Figure 4 shows the total gas flow as well as CO, CO₂ and CH₄ flows during experiments 2-4. The figure shows clearly that the gas flow peaks decrease with decreasing heating rate. There are only minor differences in the CO₂ yields, which cannot be separated from normal experimental deviations. This can be explained by the fact that CO₂ is formed during primary pyrolysis (Neves et al.). Since heating rate does not alter the devolatilization process itself at the investigated experimental conditions or the composition of the pyrolysis gas from it, significant changes are not expected. For experiments 2 and 3 (10 and 20 K/min), there are only minor differences in CO and methane yields, both increased somewhat with increasing heating rate. During the 5 K/min experiment a shoulder appears for both gases. The reason is that the chemical reactions separate visibly in time at slow heating rates. The first peak can be attributed (Jakab et al., 1997) to the formation of methane and carbon monoxide during devolatilization, which here corresponds with the overshoot in the temperature curve shown in Figure 5, the second is from the char formation process at higher temperatures. This means that not only the thermal behaviour (temperature curves) was masked at high heating rates in the current experimental setup but the evolution of gaseous products too.

4. Conclusions

Spruce wood pellets were placed in a metal container basket and heated up in a fixed bed reactor under different experimental conditions. The temperatures in and around the pellets bed as well as the amount and composition of the released gases during heat-up were monitored. The experimental results show evidence of endothermal cellulose decomposition reactions as well as an exothermal char formation process. The occurrence of these two processes overlap at high heating rates and when oxygen is used in the purge gas. The two processes can be separated visually by decreasing the heating rate to 5 K/min. The separation shown in the temperature curves is confirmed by the gas analysis. The yields of CO and CH₄ show a visible shoulder in the higher temperature region. The endothermic plateau visible on the temperature readings can be reduced by increasing the heating rate. Oxygen present in the purge gas will further reduce the visibility of the plateau. The amount of CO₂ formed during experiments shows dependency on the oxygen in the purge gas but appears independent of the applied heating rate. The detailed experimental results are valuable for validation purpose in further modelling work.

Acknowledgments

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