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Thermogravimetric analysis of combustible waste components

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August, 2010

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Abstract

In order to gain fundamental knowledge about the co-combustion of coal and waste derived fuels, the pyrolytic behaviors of coal, four typical waste components and their mixtures have been studied by a simultaneous thermal analyzer (STA). The investigated waste components were wood, paper, polypropylene (PE) and polyvinyl chloride (PVC). Strong interactions were observed between PVC & wood, PVC & paper and PVC & coal. Interactions were also observed between PE & wood, PE & PVC, PE & paper and PE & coal, but to a smaller degree. No interactions were observed between coal & wood, coal & paper and wood & paper. Since PVC was the only waste component to interact strongly with coal, the interaction between coal and a real waste mixture might be similar to the interaction observed between PVC & coal.
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1. Introduction

The production of waste worldwide is increasing, leading to a growing problem with disposal of the waste and a wish for better utilization than simple landfills [1]. Additionally there is a strong focus on global warming and the desire for using CO2-neutral fuels. Since municipal solid waste contains approximately 80 % CO2-neutral fuel, an efficient method for combustion of waste is desirable. One such method is co-combustion of waste with coal in existing pulverized coal-fired power plants. This is the most common combustion technology on power plants worldwide [2] and has already been used successfully with biomass [3].

To design a process with which to efficiently co-combust coal and waste, it is desirable to be able to predict the combustion behavior of the mixture. Pyrolysis is an important sub-step of combustion which affects the volatile release and char reactivity. This is a major reason that we study the co-pyrolysis behavior [4,5]. Since waste is a very heterogeneous mixture with a large variance in its composition, it is difficult to investigate possible interactions between coal and waste. An alternative is to investigate the existence of possible interactions between coal and the single components of waste, and between the individual components of the waste. A number of articles have investigated the co-pyrolysis of various waste components, their mutual mixtures and their mixtures with coal [4,6-9], but systematic investigation of multiple component systems are scant. Consequently a general study of the co-pyrolysis of coal and the major components of waste is desirable. The objective of the present work is therefore to do a thorough investigation of how different mixtures of coal and major waste components interact during pyrolysis in order to predict how co-combustion of coal and real waste mixtures might be modeled.

2. Experimental

2.1 Materials

Heikkinen and Spliethoff [10] describe the major components of municipal solid waste (MSW) to be: paper (approx. 20 % of MSW), plastic (approx. 12 % of MSW) and wood (approx. 4 % of MSW). Furthermore the major plastic types were estimated to be polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyvinylchloride (PVC) [8,11,12]. Since the pyrolytic behavior of PE, PP and PS is alike when investigated by thermal analysis [13], the waste components investigated here are paper, wood, PE and PVC. The coal used was Columbian bituminous coal, the wood was sawdust from beech wood (dp ≈ 400 μm) and the paper was plain, white printing paper (dp ≈ 40 – 200 μm). The composition of the coal and the wood can be seen from Table 1.
Table 1: Fuel properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Coal</th>
<th>Wood</th>
<th>Properties</th>
<th>Coal</th>
<th>Wood</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (wt% wet)</td>
<td>12.2</td>
<td>7.4</td>
<td>Si (wt% dry)</td>
<td>3.79</td>
<td>0.001</td>
</tr>
<tr>
<td>Ash (wt% wet)</td>
<td>11.3</td>
<td>0.83</td>
<td>Al (wt% dry)</td>
<td>1.29</td>
<td>-</td>
</tr>
<tr>
<td>Volatiles (wt% wet)</td>
<td>31</td>
<td>78</td>
<td>Ti (wt% dry)</td>
<td>0.07</td>
<td>-</td>
</tr>
<tr>
<td>LHV (MJ/kg)</td>
<td>24.7</td>
<td></td>
<td>P (wt% dry)</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>C (wt% dry)</td>
<td>70.6</td>
<td>49.5</td>
<td>Fe (wt% dry)</td>
<td>0.81</td>
<td>-</td>
</tr>
<tr>
<td>H (wt% dry)</td>
<td>4.78</td>
<td>6.1</td>
<td>Ca (wt% dry)</td>
<td>0.22</td>
<td>0.002</td>
</tr>
<tr>
<td>O (wt% dry)</td>
<td>-</td>
<td>44.3</td>
<td>Mg (wt% dry)</td>
<td>0.13</td>
<td>-</td>
</tr>
<tr>
<td>N (wt% dry)</td>
<td>1.59</td>
<td>0.13</td>
<td>Na (wt% dry)</td>
<td>0.06</td>
<td>-</td>
</tr>
<tr>
<td>S (wt% dry)</td>
<td>0.8</td>
<td>0.011</td>
<td>K (wt% dry)</td>
<td>0.22</td>
<td>0.001</td>
</tr>
<tr>
<td>Cl (wt% dry)</td>
<td>0.02</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.2 Pyrolysis

For the pyrolysis measurements a NETZSCH STA 490C with platinum/rhodium crucibles was used to measure weight loss as a function of time. Sample masses of 3-15 mg and heating rates of 20 K/min were used with a flow of 100 ml/min N₂. The normal sample mass was 3-5 mg. Larger sample masses were used to investigate the influence of variations in sample mass due to temperature gradients caused by thermal lag or reaction enthalpy. The samples were heated to 120 °C, kept at constant temperature for 30 minutes and heated further to 800 °C. Mixtures were prepared by weighting equal amounts of each component on top of each other in the crucible followed by mixing. This method of mixing was found to be adequate by testing the repeatability of the measurements. Sample mass loss through the mixing process is negligible. From the thermogravimetric (TG) data, derivative thermogravimetric (DTG) curves were created with a program provided by NETZSCH. Both TG- and DTG-curves were smoothed as much as possible using aforementioned program’s smoothing function to simplify comparison between different curves. The TG-curves were normalized with the initial weight at 120 °C.

To check whether interaction occurs during co-pyrolysis, an expected weight loss curve was calculated based on a weighted average of the components [14]:

\[ m\%_{\text{calc}} = w_1 \cdot m\%_1 + w_2 \cdot m\%_2 + \ldots + w_i \cdot m\%_i \]  

(1)

Here m% is the percentage-wise remaining mass of the mixture, m%_{calc}, and the pure components, m%(i), respectively. The factor wᵢ is the mass percentage of component I in the initial mixture. Small deviations from this calculated curve is to be expected due to various uncertainties, while larger deviations will indicate interaction. The size of the deviation needed to conclude the presence of interactions depends on the repeatability of the measurements. Generally the difference between the experimental and the calculated value of m% should be less than 2-4 % if the deviation is to be considered negligible [5,15-17].
3. Results and discussion

3.1 Single components

The TG- and DTG-curves for the pyrolysis of single components are shown in Figure 1. As can be seen from Figure 1, a low weight loss is observed for coal while much higher weight losses are observed for the waste components, the greatest being for PE. For all curves, the weight loss increases with increasing temperature. It can be seen that the decomposition begins at relatively low temperatures for wood, paper and the first decomposition of PVC while the decomposition of coal and PE and the second decomposition of PVC begins at much higher temperatures. The following specific trends for the different components were observed.

Figure 1: TG- and DTG-curves for the pyrolysis of coal (••), wood (— ---), paper (- -), PE (• ---), and PVC (—-).
3.1.1 Coal
As can be seen from Figure 1, a slow reaction at high temperatures over a wide temperature interval is observed. The difference in the pyrolytic behavior for different sample masses has been investigated, but only a slight variation in the peak temperature for the DTG-curve, Tpeak, is observed when the sample mass is increased from 5 mg to 10 mg.

Coal has many different kinds of bonds – many of which are resonance stabilized – so a slow decomposition reaction over a wide temperature range is expected [18-20]. The bonds are also more stable compared to the other components investigated, so the decomposition is expected to take place at high temperatures. Additionally, a low weight loss is expected since coal has a relatively high content of ash and fixed carbon [20,21] .

3.1.2 Wood
Wood consists mainly of cellulose, hemicellulose and lignin [22]. On DTG-diagrams, hemicellulose is generally seen as a low-temperature shoulder on the cellulose peak, while the decomposition of lignin is a slow reaction and occurs over a wide temperature range that is not clearly visible [7]. At the DTG-diagram in Figure 1, this behavior is clearly seen with a sharp peak around 375 °C and a low-temperature shoulder at around 320 °C.

3.1.3 Paper
Since paper is produced from wood, it would be expected that the pyrolysis curves of wood and paper are similar. As can be seen from Figure 1, this is only partly the case. The curves have similar shape and decomposition temperature. However, the curve for paper has a clear second decomposition reaction at approximately 620 ºC, and on the DTG-diagram only a weak shoulder can be seen. The reason for the high-temperature decomposition is probably related to unknown chemicals added to the paper during the production. Similar high-temperature peaks have also been observed in the literature [23]. The weak shoulder indicates that the paper sample most likely contains less hemicellulose than the wood sample [15] – probably because the paper is produced from a different type of wood.

3.1.4 Polyethylene
PE is a type of plastic, and in the literature most plastics (including PE) are observed to decompose over a narrow temperature range [4,7,9,16]. At Figure 1 a steep decomposition curve is observed at approximately 485 ºC which is consistent with this. Additionally the final mass loss is close to 100 % which is in accordance with the literature [10,12,13,24]. No deviation was seen as a result of variations in sample mass from 5 mg to 9 mg.

3.1.4 Polyvinyl chloride
The decomposition of PVC is different from most other plastics and occurs in two general steps: the breaking of the Cl-bonds (reaction PVC(I)) and the breaking of the C-C bonds of the back bone (reaction PVC(II)) [5,7,10,11,24]. These two different reactions are clearly seen in Figure 1. An investigation of the influence of mass variations showed a clear deviation for reaction II. As can be seen from Figure 2, an increase in mass from 5 mg to 10 mg results in a faster reaction with a decrease in
Tpeak of approximately 7 ºC. This might be due to an exothermic reaction taking place just prior to reaction I, or just inhomogeneity of the sample.

Figure 2: TG-curves for the pyrolysis of PVC with two different sample masses, 5mg (- -) and 10mg (—).

3.2 Waste mixtures

A very strong interaction was observed for the co-pyrolysis of PVC/wood and PVC/paper, where the two expected peaks for the pure components have combined into a single peak. Clear deviations are also observed for the mixtures PE/wood, PE/PVC and paper/PE, while no interaction seems to occur for the co-pyrolysis of wood/paper. The latter is in accordance with the literature where no interaction is observed [7,10]. An overview of the observed interactions for the waste mixtures can be seen in Table 2.

Table 2: Deviations for waste mixtures

<table>
<thead>
<tr>
<th>Components</th>
<th>Observed deviations (TG)</th>
<th>Observed deviations (DTG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE/wood</td>
<td>- Increase in final weight of 10.5 %</td>
<td>- Decomposition of PE is delayed by 2 ºC and is slower than expected</td>
</tr>
<tr>
<td>PE/PVC</td>
<td>- Increase in final weight of 7.5 %</td>
<td>- Faster reaction for PVC(I)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Peak from PVC(II) and PE delayed 8 ºC</td>
</tr>
<tr>
<td>PVC/wood</td>
<td>- Increase in final weight of 2.5 %</td>
<td>- The two expected peaks has combined into a single peak</td>
</tr>
<tr>
<td>PVC/paper</td>
<td>- Shape of curve different from the expected</td>
<td></td>
</tr>
<tr>
<td>Paper/PE</td>
<td>- Increase in final weight of 9.5 %</td>
<td>- Slightly slower reaction for the second peak (corresponding to PE)</td>
</tr>
<tr>
<td>Paper/wood</td>
<td>- No observed interaction</td>
<td>- No observed interaction</td>
</tr>
</tbody>
</table>

3.2.1 PE/wood

The DTG-diagram (Figure 3) for the co-pyrolysis of PE and wood shows the expected two peaks for pure PE and wood respectively. A slight elevation of the pyrolysis temperature for the second peak (from PE) is observed and the reaction is slower than the calculated results. Also a strong decrease in final weight loss is observed at the TG-diagram in Figure 3. Since neither wood nor PE is expected to
give deviations based on variations in sample mass, these deviations might be a result of interaction between the two components.

When comparing the results with observations of co-pyrolysis of PE and wood in the literature, major differences are found. Dong et al. [12] observed no interactions while Zhou et al. [17] observed interaction in the form of lowered pyrolysis temperature for the second peak. Zhou et al. [17] think the interaction is caused by biomass catalyzing the decomposition of the polymer chain in PE.

An interaction similar to this paper’s is observed by Aboulkas et al. [25] for the co-pyrolysis of PE and olive residue. The cause of the interaction is thought to be either that coke from the biomass stabilizes PE, or that gasses from the pyrolysis of the biomass react with PE. Similar mechanisms might be the reason for the interactions observed in the present work. The coke or the gasses from coal pyrolysis may stabilize PE and result in less mass loss during pyrolysis.

3.2.2 PE/PVC

For the co-pyrolysis of PE and PVC, the expected peaks from the pure components were observed on the DTG-diagram, but with some deviations from the expected, as can be seen from Figure 4. The pyrolysis of PVC(I) was observed to be faster than expected, while the combined peak for PE and PVC(II) was delayed approx. 8 °C. Based on measurements with different sample masses of the PE/PVC-mixture, it can be concluded that the deviation for the PVC(I)-peak might be caused by variance in mass, while the interaction at the PE/PVC(II)-peak is not.

Similar interaction is also observed by Heikkinen et al. [7] and Miranda et al. [11]. Heikkinen et al. [7] observed the interaction for non-mixed samples, indicating a gas-solid interaction [8]. This is opposed to the conclusions made by Miranda et al. [11], proposing that the interaction is caused by the polyen-chain from PVC stabilizing PE and thereby delaying the pyrolysis.
3.2.3 PVC/wood & PVC/paper

The DTG-curves for the co-pyrolysis of PVC and wood are shown in Figure 5. The DTG-curves for PVC/paper are not shown since the curves are very similar to PVC/wood. A very large interaction is observed: the two expected low-temperature peaks from wood and PVC(I) have fused to one single peak.
with \( T_{\text{peak}} \) close to the expected PVC-peak. The high-temperature peak from PVC(II) shows almost no deviation. A decreased final weight loss can also be observed from the TG-data. Similar interactions have also been observed for measurements where the components were not mixed. This indicates that the interaction is likely caused by gas-solid reactions [8].

The observed interactions have also been shown in literature with similar deviation degree for even small fractions of PVC [8]. Since the interaction occurs for both PVC/wood and PVC/paper, it is concluded that the interaction is related to cellulose, hemicellulose or lignin. This is supported by Matsuzawa et al. [8] where similar interactions have been observed for PVC/cellulose. The mechanism of the interaction at the PVC peak is thought to be that cellulose inhibits cyclization and cross-linking during the decomposition of PVC [8]. HCl from PVC acting as a catalyst for the dehydration and decomposition of the glucose-monomers of the cellulose is thought to be the reason for the interaction at the cellulose peak [8].

### 3.2.4 Paper/PE

The DTG-curve in Figure 6 for the co-pyrolysis of paper and PE shows the expected peaks from the pure components, but the second peak (from PE) is lower than expected. The TG-curve in Figure 6 shows strong deviation from \(-490 \, ^{\circ}\text{C}\) in the form of a decreased weight loss and the final weight loss (\(\approx 17.5 \, \%\)) is much lower than the calculated (8 %). Since no significant variation is observed for measurements of two different sample masses of the paper/PE-mixture, the observed deviations are believed to be caused by interaction. Since paper is thought to be the major component in RDF [26] and PE is the most commonly used type of plastic [11], this interaction might be important for predicting the behavior of the co-pyrolysis of coal and waste.

![Figure 6: TG-curves for the pyrolysis of calculated paper-PE (— —) and experimental paper-PE (—), and DTG-curves for the pyrolysis of calculated paper-PE (•••) and experimental paper-PE (• —).](image)


To the author’s knowledge, no references with similar components can be found in the literature, but Grammelis et al. [4] have compared TG-data for RDF with an artificial waste mixture of 88 % paper, 3.6 % PE and 8.3 % PVC, which was thought to represent RDF well. For this in their experiment, similar interactions were observed for the PE-peak. Since the interaction observed by Grammelis et al. [4] was dissimilar to the interaction observed for paper and PVC, the interaction might be comparable to results for co-pyrolysis of the paper/PE mixture. Chattopadhyay et al. [23] observed interaction at the PE peak between paper and a mixture of the plastic types PE, PP and PET. Since the pyrolytic behavior of these three plastic types seems similar when using thermal analysis [13], the results by Chattopadhyay et al. [23] might also to some degree be comparable to results for only paper and PE. Both Grammelis et al.’s [4] and Chattopadhyay et al.’s [23] observed interaction was contrasting to the results in this study, showing a premature pyrolysis for both the paper and the PE in the mixture. No literature was found where a delay of pyrolysis for the two components was observed. Grammelis et al. [4] and Chattopadhyay et al. [23] suggest that interaction at the PE peak might be caused by either gas freed [23] or the remaining ashes [4] from the paper. Though the interactions observed here are different, this might still be the explanation.

3.3 Mixtures of waste and coal

A strong interaction was observed for the co-pyrolysis of coal & PVC. No interaction was observed for the mixtures of coal & wood and coal & paper, while only a small deviation was observed for the co-pyrolysis of coal & PE. The lack of interaction between coal and biomass is in accordance with the literature, where no interaction is observed [15,27,28]. An overview of the observed interactions can be seen in Table 3.

### Table 2: Deviations for coal/waste mixtures

<table>
<thead>
<tr>
<th>Components</th>
<th>Observed deviations (TG)</th>
<th>Observed deviations (DTG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal/wood</td>
<td>- No observed interaction</td>
<td>- No observed interaction</td>
</tr>
<tr>
<td>Coal/paper</td>
<td>- No observed interaction</td>
<td>- No observed interaction</td>
</tr>
<tr>
<td>Coal/PE</td>
<td>- The curve is displaced to the right.</td>
<td>- Decomposition is delayed by 5 °C and is faster than expected</td>
</tr>
<tr>
<td>Coal/PVC</td>
<td>- The curve is displaced to the right in the interval from 280 – 350 °C</td>
<td>- Different shape of first peak for PVC(I)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Decomposition of PVC(I) is delayed by 16 °C and is slower than expected</td>
</tr>
</tbody>
</table>

#### 3.3.1 Coal/PE

A small deviation from the expected is observed for the co-pyrolysis of coal and PE. The DTG-peak in Figure 7 (corresponding to both coal and PE) is slightly higher and occurs at higher temperatures than calculated. Measurements with different sample masses of the mixture indicate that the observed deviation might be caused by this, but the trend in deviation caused by variance in sample mass was not clear enough to conclude that there is no interaction between the fuels.

An interaction between coal and PE is observed by Cai et al. [16]. These interactions are thought to be caused by H-radicals from PE reacting with radicals released from the coal, thereby inhibiting re-polymerization of coal radicals and increasing the weight loss.
3.3.2 Coal/PVC

As can be seen from Figure 8, a strong interaction is seen for the co-pyrolysis of coal and PVC. In most of the temperature range, the weight loss is as expected, but in the temperature interval from approximately 280 °C to 360 °C a significant delay is observed. The DTG-diagram also shows that the
observed DTG-peak in the temperature interval is moved ~20 °C towards higher temperature and that the pyrolysis peak is much lower and broader than calculated. These deviations are much greater than those described for the variance in sample mass for PVC, so this is most likely not the cause of the observed deviations. Measurements were also performed with samples, where the two components were put on top of each other without mixing. These samples show a much smaller deviation from the expected than the mixed samples. This indicates that the cause of the interaction is partly related with a solid-solid reaction [8].

No article has been found that describes the co-pyrolysis of coal and PVC. Since the interaction occurs before the coal pyrolysis, the interaction is most likely caused by a reaction between raw coal and PVC. A possible explanation might be that the released HCl from PVC is temporarily bound in the complex structure of the coal, but it is uncertain whether the coal is able to contain as much HCl as must be released in this experiment.

5. Conclusion

A series of experiments were carried out to investigate the co-pyrolysis of mixtures of coal, wood, paper, PE and PVC. From the experiments it was found that strong interactions were observed between wood & PVC, paper & PVC and coal & PVC. Interactions of lesser degree were also observed for coal & PE, paper & PE, wood & PE and PE & PVC, while no interactions were observed between coal & paper, coal & wood and paper & wood. Since PVC was the only waste component to interact strongly with coal, it might be assumed that the only major interaction between coal and waste will be similar to the interaction between coal and PVC.
References


