1. Introduction

Effective treatment of municipal solid waste (MSW) is a challenge to environment protection and natural resources, especially for developing countries such as China (Zhou et al., 2006). MSW consists mainly of lignocellulosic, polymer based and inorganic materials (Sharpyov et al., 2003) with lignocellulosics having a share of above 30% (David et al., 2003). Since such waste has a high calorific value and low pollutant emissions, its conversion to marketable fuels has become a worthy goal not only from an economic but also an environmental standpoint (Lacava et al., 2006; Liuzzo et al., 2007). Implementation of oxygen-enriched air combustion has not been studied. Therefore, there is a need to obtain a better understanding of the differences between oxy-fuel combustion and conventional air-fired combustion. The present study aimed at comparing the combustion behavior of several common lignocellulosic materials in CO2/O2 and N2/O2 atmospheres.

During MSW decomposition, the behavior of lignocellulosic materials has a great effect on the combustion (Grammelis et al., 2009). The combustion of lignocellulosics in air and pyrolysis in an N2 atmosphere have already been studied (David et al., 2003; Fang et al., 2006; Liu et al., 2002; Loulou et al., 2003; Sorum et al., 2001; Wu et al., 1997), whereas combustion in oxygen-enriched atmosphere and CO2/O2 atmosphere, especially for those concerning the thermogravimetric analysis, have not been studied. Therefore, there is a need to obtain a better understanding of the differences between oxy-fuel combustion and conventional air-fired combustion. The present study aimed at comparing the combustion behavior of several common lignocellulosic materials in CO2/O2 and N2/O2 atmosphere.

2. Methods

2.1. Materials

The paper mixture (P) was prepared by mixing magazine paper (MP), cardboard (CB), newspaper (NP) and copy paper (CP) in equal proportion (25 wt.%). The plant residue mixture (PR) consisted of equal amounts (25 wt.%) of bamboo, palm leaf, redbud leaves and bombax sawdust. Orange peel, pomelo peel, banana skin and bagasse were mixed in equal amounts to represent the fruit waste mixture (FW) fraction of MSW. The fruit and plant mentioned above are common in Guangzhou, China.

The materials were finely pulverized by DFY-300 pulverizer (Wenling Linda Machinery Co. Ltd., Zhejiang Province, China).
and passed through a sieve with a mesh size of 178 μm. The uniformity of paper mixture, pericarp mixture and foliage mixture was ensured by a micro rotary mixer (Nanjing qunqong drying equipment factory, Jiangsu Province, China). The samples were dried at 105 °C for 3–4 h and stored in desiccators. The initial weight of the samples for all runs was 6 ± 0.5 mg. The proximate and ultimate analyses of the dried samples are shown in Table 1.

2.2. Thermogravimetric analysis (TGA)

The combustion characteristics were studied using a NETZSCH STA 409 PC Luxx simultaneous thermal analyzer (Bavaria, Germany). The analyzer and the mensuration of the samples have been described in detail previously (Tang et al., 2011). Baseline data were obtained by the experimental runs with empty crucibles, and the measured values were subtracted from the values obtained with crucibles containing samples. Combustion in different atmospheres (80N₂/20O₂, 70N₂/30O₂, 60N₂/40O₂, 50N₂/50O₂, 80CO₂/20O₂, 70CO₂/30O₂, 60CO₂/40O₂, 50CO₂/50O₂) were performed at 100–1000 °C at a heating rate of 20°C/min. The flow rate of the mixed gas was 0.006 m³/s (100 ml/min). The experiments in each case were repeated twice, and the repeated experiments had high correlation degrees.

2.3. Weighed sum theory

The calculated curve of mixture was obtained by a weighed sum of experimental weight loss curves of individual components, according to Cozzani and Tognotti (1995):

\[
y_{\text{mix}} = c_1\eta_1 + c_2\eta_2 + c_3\eta_3 + c_4\eta_4
\]

where \(y_{\text{mix}}\) was the calculated value of the TG or DTG curve of mixture, and \(\eta_i\) was the measured value of a TG or DTG curve of constituent \(i\) (1 = cardboard, 2 = copy paper, 3 = magazine paper and 4 = newspaper). The coefficients \(c_i\) were the mass fractions of each component in the mixture, \(c_1 = 0.25\).

2.4. Kinetic theory

Since the material to be combusted consisted of several components, each component was assumed to decompose independently of the others (Calvo et al., 2004; Thipkhunthod et al., 2007). The kinetics of each reaction was described by the following equations:

\[
\frac{dx_i}{dt} = A_i e^{(-E_i/RT)} (1 - x_i)^n
\]

\[
x_i = \frac{m_{i,f} - m_j}{m_{i,f} - m_{i,i}}
\]

where \(x_i\) was the reacted mass fraction or normalized mass for reaction \(i\) at time \(j\); \(R\) the gas universal constant; \(T\) the absolute temperature; \(A_i\) the frequency factor for reaction \(i\); \(E\) the activation energy; \(n\) the order of reaction; \(m_{i,i}\) the initial mass of the sample for reaction \(i\), \(m_{i,f}\) the mass of the sample for reaction \(i\) at time \(j\), and \(m_{i,f}\) the final mass of the sample for reaction \(i\).

The NETZSCH-TA4-Kinetic2 software was used to study kinetic mechanism by using nth order reaction model. Different calculated curves were obtained by choosing different reaction parameters of the fitting model. The correlation coefficient was the index for correlation degree between calculated and experimental weight loss curves. The closer the correlation coefficient approached 1, the better the curves coincided. The parameters were optimized so that correlation coefficient was the closest to 1.

The sum of least squares was defined as:

\[
SAQ = \sum_{j=1}^{N} (w_{\text{R},j} - w_{\text{Y},j})^2
\]

With \(w_{\text{R},j}\) the weight of calculated curve obtained by the fitting model at point \(j\), \(w_{\text{Y},j}\) the real weight of experimental curve at point \(j\), \(i\) was from 1 to \(N\). The correlation coefficient was defined as:

\[
\text{correlation coefficient} = \frac{\sum (w_{\text{R},j} - \bar{w}_{\text{Y}})(w_{\text{Y},j} - \bar{w}_{\text{Y}}))}{\sqrt{\sum (w_{\text{R},j} - \bar{w}_{\text{Y}})^2 \sum (w_{\text{Y},j} - \bar{w}_{\text{Y}})^2}}
\]
3. Results and discussion

3.1. Combustion of individual paper samples

The obtained TG (weight fraction remaining) and DTG (weight loss rate) curves for all the paper samples in 80N2/20O2 atmosphere and 80CO2/20O2 atmosphere are presented in Fig. 1(a) and (b) respectively. Below 600 °C, combustion proceeded in almost the same way for all paper samples. The samples lost most of their weight between 300 and 500 °C, and the peaks of DTG curves were located between 341.6 and 348.1 °C, and 426.4 and 446.4 °C, respectively.

The first peak (the maximal peak) revealed the devolatilization of lignocellulosics in both atmospheres. The contributions of cellulose and hemicellulose to the first peak were greater than that of lignin since cellulose and hemicellulose are highly reactive and burn completely at around 340 °C, while lignin burns at a broader temperature range with less weight loss (Benoît et al., 2009; Muthuraman et al., 2010; Vamvuka et al., 2003). The second peak revealed the combustion of chars (Fang et al., 2006; Grammelis et al., 2009). Differences in peak heights showed that samples differed in reactivity even in the same atmosphere. Copy paper was the most reactive among the paper samples whereas peaks were less evident for magazine paper than for the other paper samples, probably due to the partial removal of hemicellulose during pulp production of magazine paper (Gammelis et al., 2009).

At temperature >600 °C, copy and magazine paper and cardboard, exhibited a slight weight loss until the final temperature of 1000 °C was reached (Fig. 1(a)). Their DTG curve showed a third peak at 733.0–812.1 °C in a 80N2/20O2 atmosphere and at 919.2–927.7 °C in a 80CO2/20O2 atmosphere. According to Fang et al. (2006) and Betancur et al. (2009), the mass loss at the range of 800–1000 °C was mainly caused by a reduction reaction between semi-coke and carbon dioxide. Liao and Ma (2010) proved that decomposition at around 730 °C in air was due to the degradation of calcium carbonate and other minerals.

Non-combustible constituents usually reduced the combustion efficiency (Sorum et al., 2001). The ash contents of the different paper samples were quite different (Table 1). Magazine paper showed the highest residual weight among four individual paper samples (about 24% in 80N2/20O2 and 31% in 80CO2/20O2 at 1000 °C) (Fig. 1(a)), due to clays and other additives used as filling material to obtain a smooth and lustrous finish (Gammelis et al., 2009).

Besides the ash contents, the atmosphere also affected residual weight. The samples burned more fully in 80N2/20O2 than in 80CO2/20O2 atmosphere (Fig. 1(a)), in agreement with curves of mass loss rates obtained by Fang et al. (2006) and Tang et al. (2011).

3.2. Combustion of paper mixture

A study on the behavior of mixture was also conducted in order to check possible interactions between components. TG and DTG curves of the calculated and experimental results for a mixture of

\[ \text{Corr Coeff} = \frac{1 - \frac{\text{SAQ}}{\sum_{i=1}^{N} W_{Y0}^2 - \left( \sum_{i=1}^{N} W_{Y0} \right)^2}}{N} \]  (5)
four different papers in both atmospheres were compared in Fig. 2(a) and (b) respectively.

As shown in Fig. 2, the shape of the calculated curves approximated the experimental ones under both atmospheres, with three peaks in the DTG curves. The slight deviations in peak heights suggest a low extent interaction between the various paper samples. In the high temperature range under 80N2/20O2 atmosphere, the calculated curve deviated from the experimental one by about 50 °C. This deviation was attributed to the thermal effect and char produced by the decomposition of a paper fraction influencing the thermal degradation of the others (Benoît et al., 2009). On the whole, the mixing process affected the combustion of each component to some extent, and the combustion representing the sum of the individual components only roughly reflected the combustion of the paper mixture.

TG curves and DTG curves of paper mixture in 80N2/20O2 and 80CO2/20O2 atmospheres were also compared in Fig. 2(a) and (b) respectively. The TG curves under 80N2/20O2 and 80CO2/20O2 atmospheres matched well at the initial stage, but the ignition temperatures (Ti) of paper mixture were 315.8 °C in 80N2/20O2 atmosphere and 318.3 °C in 80CO2/20O2 atmosphere. Li et al. (2009) reported that ignition of pulverized coal in CO2/20O2 atmosphere (Ti = 458 °C) was much delayed compared with that in N2/O2 atmosphere (Ti = 432 °C). The ignition of the paper mixture also shifted to a higher temperature in CO2/20O2 atmosphere, but not as dramatic as observed for coal. The first and the second peaks of DTG curve under different atmospheres were located at the same temperature with different weight loss rates. The weight loss rates under 80N2/20O2 atmosphere were larger than those under 80CO2/20O2 atmosphere. At temperature >600 °C, the location of the third peak of paper mixture was affected by the atmosphere. The mineral degradation peak in 80N2/20O2 atmosphere (747.2 °C) appeared much earlier than the CO2 reduction peak in 80CO2/20O2 atmosphere (927.0 °C). The effect of atmosphere on paper mixture’s ignition temperature, weight loss rate and the corresponding temperature of peaks was the same as that on the individual paper.

Replacement of N2 by CO2 influenced combustion negatively as it led to a slightly later ignition, a lower maximum weight loss rate and a shift of the third peak to higher temperatures. Therefore, in order to match the combustion performances in air, some improvement measures such as higher oxygen concentration (Bejarano and Levendis, 2008) will be required during CO2/O2 combustion.

3.3. Oxygen-enriched combustion

As shown in Figs. 3 and 4, curves of combustion of paper mixture were similar when the temperature was lower than 300 °C.

![Fig. 4. Oxygen-enriched combustion of paper mixture in CO2/O2: (a) weight fraction remaining curves; (b) weight loss rate curves.](image)

![Fig. 5. Combustion of lignocellulosic materials in 80N2/20O2 and 70CO2/30O2 atmospheres: (a) weight fraction remaining; (b) weight loss rate curves.](image)
In both N₂/O₂ atmosphere and CO₂/O₂ atmosphere, with increasing oxygen concentration, ignition became easier, a lower temperature (T₁) was needed to reach that maximum peak of the DTG curves, and the curves gradually shifted to a lower temperature range. For example, with the increase in the oxygen concentration from 20% to 50% in CO₂/O₂ atmosphere, T₁ decreased from 318.5 to 310.8 °C, and T₁ decreased from 349.8 to 341.3 °C. As the oxygen concentration was increased from 20% to 50%, the maximum weight loss rate (R₁) increased from 22.03% to 25.09%/min in N₂/O₂ atmosphere and from 20.82% to 23.57%/min in CO₂/O₂ atmosphere. Lai et al. (2011) also observed that the maximum mass loss rate was increased when the oxygen concentration increased. The increase in the maximum mass loss rate was perhaps due to the force of the fusion layer being reduced in the presence of oxygen and the quick release of volatiles (Blasi, 1993; Liu et al., 2009). As the oxygen concentration increased, the peak corresponding to chars combustion (R₂) also became more apparent and the corresponding temperature (T₂) decreased. The variation of this peak with oxygen concentration was the same as that of the first peak corresponding to volatile release, while this similarity was not observed for the third peak in the high temperature range.

With the same oxygen concentration, the values of the first two peaks in CO₂/O₂ atmosphere were smaller than those in N₂/O₂ atmosphere, indicating that the replacement of N₂ only by CO₂ had an inhibitory effect on paper combustion (Tang et al., 2011). Such an inhibitory effect was attributed to the higher specific heat capacity of CO₂ compared to N₂ (Bejarano and Levendis, 2008; Li et al., 2009); however, the combustion performance can be improved by increasing the oxygen concentration. As shown in Figs. 3 and 4, the TG and DTG curves of the paper mixture in 70CO₂/30O₂ atmosphere were comparable to those in 80N₂/20O₂ when the location of the third peak was ignored. This conclusion agrees with the results of pulverized bituminous coal obtained by Molina and Shaddix (2007), who had observed that the devolatilization properties of bituminous coal in a mixture of 70CO₂/30O₂ were similar to those in air.

### 3.4. Combustion of plant residue and fruit waste mixtures

Fig. 5 shows TG and DTG curves of the combustion of plant residue and fruit waste mixtures alone with the curves for paper mixture for comparison purposes. Table 2 shows the characteristic parameters obtained during combustion of the three lignocellulosic material mixtures in 80N₂/20O₂ and 70CO₂/30O₂.

As shown in Fig. 5, for the plant residue and fruit waste mixtures, the respective TG curve and DTG curve in 80N₂/20O₂ and 70CO₂/30O₂ matched well which again proved that to achieve the same combustion performances as in air, the oxygen mole fraction in the atmosphere should be increased to 30%.

Under the same atmospheres, differences in weight loss during combustion of paper, fruit waste and plant residue mixtures were obvious (Fig. 5). Paper and fruit waste mixtures showed three peaks in the DTG curves, while the plant residue mixture exhibited only two peaks. Paper lost most of its weight between 300 and 500 °C, and its peaks in the DTG curves were located around 350, 440 and above 700 °C, respectively. The fruit waste mixture lost most of its weight between 200 and 500 °C, and its peaks in the DTG curves appeared around 230, 320 and 465 °C, respectively. In addition, paper had the maximum weight loss rate at the first peak, while the fruit waste mixture achieved that rate at the second peak.

Table 2 showed ignition temperature (T₁) and maximum combustion rate (R₃ = Max (R₁, R₂, R₃)) of the lignocellulosic materials. T₁ of the fruit waste mixture in both atmospheres (about 220 °C) was much lower than that of paper (about 315 °C) and plant residue mixtures (about 290 °C). The lignocellulosic materials differed significantly in the maximum combustion rates (R₃), but reached these rates in the narrow temperature region of 322–350 °C. The highest R₃ was observed for paper and the lowest for fruit waste. Although the values of the peak around 450 °C differed little, the peaks of the fruit waste and plant residue mixtures were much broader than that of the paper mixture. This observation indicates that most of the chars of the fruit waste and plant residue mixtures were combusted in this temperature range and explains the absence of the third peak corresponding to chars gasification at temperature >600 °C of DTG curves for the fruit waste and plant residue mixtures. The content of minerals in fruit waste and plant residue was negligible, thus only paper had a peak corresponding to degradation of minerals at around 740 °C in N₂/O₂ atmosphere. Fig. 5(a) showed a residual weight of about 5% of the fruit waste mixture, which indicated a more complete burnout of the fruit waste mixture than that of paper (about 18%) and plant residue (about 9%).

### 3.5. Kinetic analysis

Table 3 shows the kinetic parameters and correlation coefficients under the nth order reaction model. The lignocellulosic mixtures in N₂/O₂ atmosphere or CO₂/O₂ atmosphere were modeled considering three parallel reactions, which agreed well with the findings of Sorum et al. (2001) and Grammelis et al. (2009). On the whole, the apparent activation energy values of the paper mixture were the highest and the values of the plant residue mixture were the lowest. At the same oxygen concentration and for the same material, the values of apparent activation energies

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atmosphere</th>
<th>T₁ (°C)</th>
<th>T₂ (°C)</th>
<th>R₁ (%)/min</th>
<th>T₃ (°C)</th>
<th>R₂ (%)/min</th>
<th>R₃ (%)/min</th>
<th>T₄ (°C)</th>
<th>Residual mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper mixture</td>
<td>80N₂/20O₂</td>
<td>315.8</td>
<td>350.9</td>
<td>22.03</td>
<td>441.0</td>
<td>5.07</td>
<td>774.2</td>
<td>2.03</td>
<td>16.68</td>
</tr>
<tr>
<td></td>
<td>70CO₂/30O₂</td>
<td>314.9</td>
<td>349.0</td>
<td>22.20</td>
<td>443.1</td>
<td>5.30</td>
<td>923.2</td>
<td>2.16</td>
<td>18.13</td>
</tr>
<tr>
<td>Fruit waste mixture</td>
<td>80N₂/20O₂</td>
<td>220.7</td>
<td>230.3</td>
<td>8.58</td>
<td>321.9</td>
<td>9.35</td>
<td>472.5</td>
<td>4.13</td>
<td>5.30</td>
</tr>
<tr>
<td></td>
<td>70CO₂/30O₂</td>
<td>217.8</td>
<td>231.1</td>
<td>8.66</td>
<td>322.1</td>
<td>9.33</td>
<td>472.1</td>
<td>4.17</td>
<td>5.44</td>
</tr>
<tr>
<td>Plant residue mixture</td>
<td>80N₂/20O₂</td>
<td>291.5</td>
<td>348.0</td>
<td>13.74</td>
<td>461.8</td>
<td>4.76</td>
<td>—</td>
<td>—</td>
<td>8.86</td>
</tr>
<tr>
<td></td>
<td>70CO₂/30O₂</td>
<td>292.0</td>
<td>348.1</td>
<td>13.73</td>
<td>448.9</td>
<td>4.82</td>
<td>—</td>
<td>—</td>
<td>8.73</td>
</tr>
</tbody>
</table>

---

a T₁ is the ignition temperature.
b T₂ is the temperature associated to R₁.
c R₁ is maximum weight loss rate of the first peak in DTG.
d T₃ is the temperature associated to R₂.
e R₂ is the weight loss rate of the second peak in DTG.
f T₄ is the temperature associated to R₃.
g R₃ is the weight loss rate of the third peak in DTG.

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4. Conclusions

The comparison of the calculated weight fraction remaining curve with experimental weight fraction remaining curve in a N2/O2 atmosphere were slightly lower than those in a CO2/O2 atmosphere. Oxygen-enriched combustion accelerated the reactivity of the samples. The values of apparent activation energy decreased with the increase of the oxygen concentration. Thus, compared with the activation energy values in 80CO2/20O2, the values in 70CO2/30O2 were closer to those in air.

The correlation coefficients in Table 3 were greater than 0.99, so the model and parameter were reliable. Fig. 6 shows the comparison of the calculated weight loss and experimental weight loss and provides evidence that nth order reaction model could simulate the weight loss very well. For paper, Sorum et al. (2001) obtained average apparent activation energy values of 110.3, 244.8 and 45.1 kJ/mol for the three reactions, while the values obtained by Grammelis et al. (2009) were 131.4, 211.2, 39.4 kJ/mol. Considering the effect of the different operating conditions such as heating rate, initial weight of the samples and measurement systems, the difference of kinetic parameters obtained was reasonable.

Table 3
Kinetic parameters and correlation coefficients under different atmospheres.

<table>
<thead>
<tr>
<th>Material</th>
<th>Paper mixture</th>
<th>Fruit waste mixture</th>
<th>Plant residue mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>80N2/20O2</td>
<td>80CO2/20O2</td>
<td>70CO2/30O2</td>
</tr>
<tr>
<td>LogA0 (1/s)</td>
<td>10.2</td>
<td>11.5</td>
<td>11.7</td>
</tr>
<tr>
<td>E1 (kJ/mol)</td>
<td>140.9</td>
<td>157.7</td>
<td>155.3</td>
</tr>
<tr>
<td>n1</td>
<td>3.9</td>
<td>3.9</td>
<td>3.9</td>
</tr>
<tr>
<td>c1 (%)</td>
<td>25.1</td>
<td>30.7</td>
<td>29.8</td>
</tr>
<tr>
<td>LogA0 (1/s)</td>
<td>29.8</td>
<td>32.5</td>
<td>31.4</td>
</tr>
<tr>
<td>E1 (kJ/mol)</td>
<td>246.5</td>
<td>255.8</td>
<td>247.5</td>
</tr>
<tr>
<td>n1</td>
<td>0.7</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>c1 (%)</td>
<td>60.9</td>
<td>60.4</td>
<td>58.7</td>
</tr>
<tr>
<td>LogA0 (1/s)</td>
<td>−6.0</td>
<td>−5.6</td>
<td>−6.0</td>
</tr>
<tr>
<td>E1 (kJ/mol)</td>
<td>81.2</td>
<td>90.5</td>
<td>80.5</td>
</tr>
<tr>
<td>n1</td>
<td>2.4</td>
<td>0.4</td>
<td>2.7</td>
</tr>
<tr>
<td>c1 (%)</td>
<td>14.0</td>
<td>9.0</td>
<td>11.5</td>
</tr>
</tbody>
</table>

Correlation coefficient 0.998304 0.998266 0.998977 0.994227 0.994585 0.999947 0.999274 0.998081 0.998940

Fig. 6. The comparison of the calculated weight fraction remaining curve with experimental weight fraction remaining curve.

References


