Biomass/Coal Co-Pyrolysis and Co-Combustion Characterization

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ABSTRACT

The intricate pyrolytic mechanism and combustion behavior were studied for some individual solid fuels, including corn stover, a kind of US eastern bituminous coal and some plastics, using Micro-scale combustion calorimeter (MCC). And the co-pyrolysis and co-combustion performance the blends of these feed stocks, including biomass with coal, biomass with plastic, and coal with plastic, in various proportions, were investigated in this paper. Since the volatile contents decomposed from biomass boosted the ignition and combustion of coal, which changed the temperature distribution of heat releasing phases. Different blending ratios of biomass and coal were chosen and studied to investigate the synergy effects of different during the co-pyrolysis and co-combustion processes.

MCC was used to quantify the dynamic heat output from the combustion of the gases produced during the pyrolysis process. The measurement of heat output as a function of temperature was used to calculate the heat of combustion of fuels. A previously developed and validated pyrolysis model was used to calculate the heat of pyrolysis of samples.

Based on these test results, the synergy of different fuels and their blends were compared with each individual performance. This research focuses on developing advanced fuel blends through modifying their energetic response as a function of temperature. The co-pyrolysis and co-combustion of multiple fuels, such as the blend of coal and biomass, has emerged as an alternative fuel route to improve the economics, environmental impact and performance of gasifiers and boilers. The result of this paper can instruct the engineering practices of pyrolysis and combustion for coal/biomass blends.

Keywords: biomass; coal; blend; pyrolysis; combustion; synergy

1. Introduction

Biomass was used as a substitute energy resource for centuries. Its environmental advantages with global environmental pressure revitalized the usage of it as one of the ubiquitous renewable energy sources. Biomass can be converted into heat, electricity, chemicals, etc., by different technologies through different technical routes. Currently, thermo-chemical processes for agricultural biomass to energy transformation seem promising and feasible. Biomass and coal undergoing pyrolysis and combustion has historically been of primary interest in the areas of energy recovery and gasification applications.

Pyrolysis (thermal decomposition or de-volatilization) is the initiate thermo-chemical process before combustion. Fuels, such as biomass and coal, decompose or pyrolysis over a wide and exclusive range of temperatures. However in all applications, a consistent output fuel stream or power output is desirable over the decomposition temperature range. This research focuses on developing advanced fuel blends through modifying their energetic response as a function of temperature. The co-pyrolysis and co-combustion of multiple fuels, such as the blend of coal and biomass, has emerged as an alternative fuel route to improve the economics, environmental impact and performance of gasifiers and boilers(Reed 1981; Collot 1999; Williams 2001; Vuthaluru 2003; Vuthaluru
While the blending of biomass and some plastics may be have some potential benefits on utilizing biomass for energy or electricity.

Several researchers have investigated co-pyrolysis of coal/biomass blends. Coal and biomass are consumed by both pyrolysis reactions and char oxidation. A larger fraction of biomass is likely to release as volatile gases during combustion. This large volatile yield occurs over a relatively short time and can influence the time required for complete combustion when compared to a coal particle of similar size. Research works of realizing efficient coal-biomass co-firing have been studied in some literatures (Robinson 1998; Collot 1999; Andrew 2005; Kumabe 2007). However, problems related to co-firing of fuel blends are less understood due to the intricate pyrolysis and combustion behavior of multiple fuels blends. The energetic characterization of coal-biomass blends is not as well understood as the other aspects of their pyrolysis process kinetics (Collot 1999; Manyà 2002; Sadhukhan 2008; Gomez 2009; Bradley 2011). This is primarily attributed to lack of validated pyrolysis energetics models and consistent experimental methodologies for the accurate energetic characterization of solid fuels (Agarwal 2012).

The reactivity of a fuel requires a total energy balance on the fuel, which includes the energy required for pyrolysis of the material as well as the heat released from combustion of the evolved gases and char. In our previous work, a method was developed to quantify energy for pyrolysis of materials using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and a pyrolysis model. This approach was validated with liquid chemicals, plastics, and composite materials. Recently, a microscale combustion calorimeter (MCC) has been developed to measure the heat release rate from milligram size samples as a function of temperature (Lyon 2004). This has also primarily been used on plastic materials and has not considered the effects of energy required for pyrolysis in the evaluation of fuels.

2. Methods

Instrumentation

A micro-scale combustion calorimeter (MCC) was used to quantify the dynamic heat output from the combustion of the gases produced during the pyrolysis process.

![Fig. 1 Schematic diagram of Micro Combustion Calorimeter(MCC)(Lyon)](image)

The measurement of heat output as a function of temperature was used to calculate the heat of combustion of fuels. Solid fuel materials were put in the crucible on the testing platform in the pyrolyzer, which was heated at setup heating rate in inert gas (pyrolysis) or 20% O₂ (oxidation). The gases released from the fuel sample were lead to the combustion chamber where they were
mixed with excess oxygen to completely burnout. The oxygen consumption was recorded to calculate the heat released from solid fuels.

**Theory**

The pyrolysis (also known as thermal decomposition) reaction of carbonaceous materials is very intricate, because the decomposition of carbonaceous materials involves a large amount of parallel and series reactions. TGA could provide some general information on the overall reaction kinetics, rather than individual reactions. It could be used as a tool for providing comparison of kinetic data of various reaction parameters such as temperature and heating rate. Other advantages include only a single sample, and few data are required for obtaining kinetics over an entire temperature range in a continuous manner. In present work, kinetic parameters from TG data were obtained from the following rate expression derived from Arrhenius equation.

$$\frac{d\alpha}{dt} = \frac{A}{\beta} e^{-\frac{E}{RT}(1-\alpha)^n}$$  \hspace{1cm} (1)

where \(\alpha\) is the conversion rate of reactant, \(t\) (min) is the time, \(A\) (min\(^{-1}\)) is the pre-exponential factor (frequency factor), \(\beta = \frac{dT}{dt}\) is the heating rate (\(^{\circ}\)C s\(^{-1}\)), \(E\) (J/mol) is the activation energy, \(R\) (J/mol K) is the universal gas constant (8.314), \(T\) (K) is the temperature, \(n\) is the reaction order.

The solid fuel was put in crucibles during controlled pyrolysis in an inert gas stream. The fuel gases released from the fuel are mixed with excess oxygen and completely oxidized in combustor chamber at high temperature, and the instantaneous heat of combustion of the flowing gas stream is measured by oxygen consumption calorimetry. The heat of combustion of the solid fuel \(Q\) is liberated per unit time \(t\) in MCC is limited by the rate at which the thermally decomposing solid releases fuel because the gas phase combustion reactions in the flame are rapid by comparison. Thus, the heat release rate \(dQ/dt\) (W) is proportional to the mass generation rate (g s\(^{-1}\)) of volatile fuel, the mass loss rate of the solid:

$$Q_c(t) = \frac{dQ_c(t)}{dt} = h_{c,v}^0(t) \frac{dm_v(t)}{dt} = -h_{c,v}^0(t) \frac{dm_s(t)}{dt}$$  \hspace{1cm} (2)

where a superscripted dot indicates the time derivative; \(h_{c,v}^0\) (J g\(^{-1}\)), the enthalpy (heat) of complete combustion of the volatile pyrolysis products of mass \(m_v\), and \(m_s\) is the instantaneous residual mass of solid. Using the principle of oxygen consumption calorimetry, we can achieve the Eq.(3) as:

$$Q_c = \int_0^\infty Q_c(t)dt = c \int_0^\infty \Delta m_{o2}(t)dt$$  \hspace{1cm} (3)

Eq. 3 provides a means for relating the total oxygen consumed to the total heat released by combustion of the pyrolysis products.

**Materials and Preparation**

Samples used in this study included biomass as corn stover (CS) and some US eastern bituminous coal (EC). The proximate and ultimate analyses for these samples are provided in Table 1 and Table 2, respectively.

<table>
<thead>
<tr>
<th>Table 1: Proximate analysis (dry basis)</th>
<th>Table 2: Ultimate analysis (dry basis)</th>
</tr>
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<tbody>
<tr>
<td><strong>Fuel</strong></td>
<td><strong>EC</strong></td>
</tr>
<tr>
<td>Ash, %</td>
<td>10.50</td>
</tr>
<tr>
<td>Sulfur, %</td>
<td>0.88</td>
</tr>
<tr>
<td>Volatile, %</td>
<td>28.28</td>
</tr>
<tr>
<td>Fixed Carbon, %</td>
<td>61.22</td>
</tr>
<tr>
<td>Heat Value, BTU/lb</td>
<td>14073</td>
</tr>
<tr>
<td>Heat Value(_{MAR}), BTU/lb</td>
<td>15724</td>
</tr>
</tbody>
</table>

Corn stover was dried and grinded as fine samples for the MCC. The corn stover particles were sieved through calibrated sieves within 400-500 μm range. Corn stover samples were dried again at 110°C in air before experimentation. Eastern coal was received as
pulverized powder with mean diameter lower than 400 μm sieve. The EC sample was received in a wet state (about 30% moisture by weight), and thus was thoroughly dried in air at 110 ºC for 4 hours before use.

More test samples were prepared by blending EC with biomass samples in different ratios (80:20, 50:50 and 20:80) by weight, to investigate co-pyrolysis and co-combustion synergies between coal and biomass samples. Thus, in total five samples were developed and ten tests executed including, EC, CS-Raw and EC/CS-Raw blends.

Analysis procedure

The heat of pyrolysis, \( \Delta h_p \), is defined as the difference of heat of formations of pyrolysis gas and the active solid material. Hence, the heat of pyrolysis is positive for an endothermic decomposition process. The heat of combustion, \( \Delta h_c \), is defined as amount of heat released from the combustion of volatiles released during the solid fuel pyrolysis (Lyon 2000). Many studies in the literature have calculated the heat of pyrolysis of materials using the STA instrument (Frederick 1975; Henderson 1982; Strezov 2000; Rath 2003; Strezov 2004; Gomez 2009).

The heat of pyrolysis was calculated as the area difference between the apparent and sensible specific heat capacity curves, \( \Delta h_p \approx \text{Area}_{as} \), or as the area difference under the apparent and specific heat flow DSC curves. In recent study (Agarwal 2012), it was validated and concluded that the heat of pyrolysis is different from the area difference under the apparent and sensible specific heat curves, or area difference under the apparent and sensible heat flow DSC curves for the degradation of a charring material. While the heat of pyrolysis, \( \Delta h_p \), is defined on the basis of per unit volatile mass lost, and can be calculated by applying the STA data onto a pyrolysis mathematical model.

MCC data was analyzed by calculating the \( \Delta h_p \) and \( \Delta h_c \) properties. The \( \Delta h_p \) property was calculated by integrating the HRR signal, \( Q' \), over the pyrolysis temperature range and dividing it by the heating rate of the sample, as shown in Eq.(4) and described elsewhere.

\[
\Delta h_p = \int_{t_a}^{T} \frac{Q'}{(dT/dt)} \, dt
\]  

(4)

The \( \Delta h_c \) property has been termed as the heat of combustion of sample in many literature studies (Lyon 2000; Lyon 2004). This property, similar to HRR, is based on the initial mass of the sample. However, previous study of our research group (Agarwal 2012) shows the heat of reaction or heat of combustion should be calculated on the basis of volatile mass for charring materials. Thus, the \( \Delta h_c \) property can be calculated as per Eq. (5).

\[
\Delta h_c = \Delta h_p \left( \frac{1}{1-Y_c} \right)
\]  

(5)

3. Results and Discussion

MCC signal analysis

Big difference between the energy density of the samples is seen from comparing HRR signals of EC and CS samples in Fig. 1. As known from the previous discussion, the amount of volatile matter released from EC pyrolysis is substantially lower than that released by biomass samples (~20% volatile matter for EC in compared to ~80% for CS samples). With a relatively very low devolatization rate for EC sample, the peak height for HRR signal of EC was comparable in comparison to biomass samples shown in Fig. 1.

The MCC heat release rate (HRR) signals of EC and CS are shown in Fig. 1. The HRR, similar to the DSC signal, is measured on the basis of per unit initial mass of the sample. As observed from Fig. 1, EC has one HRR peak for both pyrolysis and combustion, while CS has two separate peaks, even one of them is not very clear during the pyrolysis process. As expected, this signifies that the rate of production of pyrolysis gases is proportional to the heat generated during the combustion of those gases.
As observed from Fig. 1, the peak HRR value of EC pyrolysis (24.91 W/g) found in at about 470°C, while the peak HRR of EC oxidation (70.32 W/g) is found at about 554°C. The biggest peak HRR value of CS pyrolysis (31.22 W/g) is found at about 333°C, and the minor one (22.1 W/g) is found at about 296°C. CS oxidation has two separate peaks, one (39.67 W/g) at about 296°C, and a sharp one (100.66 W/g) at about 419°C.

Fig. 2 shows the MCC HRR signals obtained from the pyrolysis and oxidation of EC and CS samples blending ratios of 80:20. The predicted HRR profile for a weighted sum of individual EC and CS sample HRR signals in 80:20 ratio was also generated. Since coal was 80% weight of the sample, the performance of the coal is dominant during the test. The measured pyrolysis HRR profile is a little bit higher than the predicted HRR profile. It shows that there are some synergetic effects between these two fuels when they were blended at 80:20 proportions. And the predicted oxidation HRR profile shows there will be a small sharp peak (30.67 W/g) at about 414°C, while the experimental result did not show this peak at all, which means the presence of coal depressed the second peak of CS. But generally, the predicted HRR profiles are very good of EC and CS fuel blend.
Fig. 3 MCC heat release rate data of blend, EC/CS=50:50, in N\textsubscript{2} and Air

Fig. 3 shows the MCC HRR signals obtained from the pyrolysis and oxidation of EC and CS samples blending ratios of 50:50. The predicted HRR profile for a weighted sum of individual EC and CS sample HRR signals in 50:50 ratio was also plotted. The measured pyrolysis HRR profile is a little bit higher than the predicted HRR profile. It shows that there are some synergetic effects between these two fuels when they were blended at 50:50 proportions. And the predicted oxidation HRR profile shows there will be a big sharp peak (55.63 W/g) at about 416°C, while the experimental HRR profile shows a little peak (19.03 W/g) at about 462°C. The second peak of CS was not only depressed but shifted to 36°C higher.

MCC HRR data of EC and CS samples blending ratios of 20:80 is shown in Fig. 4. Since biomass has dominant weight proportion, the co-pyrolysis and co-combustion profiles are very similar to the biomass individual profiles, with only a small peak after 450°C in both tests. While the presence of coal still has some influence on the whole blending sample, such as a little bit higher (~20%) HRR than predicted in pyrolysis, and the HRR oxidation profile shifted about 8°C higher.

<table>
<thead>
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<th>Table 3: Experimental Result</th>
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<tbody>
<tr>
<td>Fuel</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>Eastern Coal</td>
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<td></td>
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<tr>
<td></td>
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<tr>
<td>Corn Stover</td>
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</table>
The MCC results for heat of combustion and char/ash yield were shown in Table 3, with individual fuels and the different blending ratios.

The measured MCC data indicated a linear relationship between the char/ash yield and the proportion of biomass in the blend, suggesting lack of synergistic effects between the two fuels during co-pyrolysis and co-combustion process. Thus the co-pyrolysis and co-combustion performance can be approximately predicted by the two parent fuels.

![Fig. 5 MCC char/ash yield.](image)

![Fig. 6 MCC Heat Release.](image)

Fig. 6 demonstrates that the heat of combustion and heat of pyrolysis released from the biomass/coal blend reduces with less coal and more biomass. But the MCC data show there are same trend for all the tests of different blending ratios. And the trend is nearly linear, which means no apparent synergy between the two kinds of parent fuels.

4. Conclusions

There are some weak synergetic effects in coal and biomass co-pyrolysis and co-combustion processes, but the effects are not very apparently observed. Co-pyrolysis and co-combustion have no apparently synergetic behavior between the two parent fuels. The measured MCC data indicated a linear relationship between the char/ash yield and the proportion of biomass in the blend, suggesting lack of synergistic effects between the two fuels during co-pyrolysis and co-combustion process. Thus the co-pyrolysis and co-combustion performance can be approximately predicted (for engineering purposes) by the two parent fuels. It was further validated and concluded that the weighted sum prediction for the heat of pyrolysis and the heat of combustion for coal-biomass fuel blends must be conducted on the basis of their individual volatile mass contributions and not on the basis of initial fuel blend proportion.

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