Effects of blending, staging and furnace temperature on co-firing of coal and biomass-bagasse

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ABSTRACT

This manuscript reports on emissions generated from laboratory-scale batch combustion of a high-volatile content bituminous coal, sugar-cane bagasse, and blends thereof. The average bulk equivalence ratio during the volatile combustion phase was calculated to be sub-stoichiometric. Characterization and quantification of major fixed gases, light volatile hydrocarbons, semi-volatile polycyclic aromatic hydrocarbons (PAH) and particulate matter are reported. The work consists of two parts.

The first part of the thesis investigated the effects on emissions generated for increasing the amount of bagasse in the coal-bagasse blend at furnace temperature of 1000 ºC in atmospheric pressure air. Coal emitted two times more CO₂ and particulate mass than bagasse. In contrast, coal emitted half the amounts of CO, light hydrocarbons and PAH than bagasse. The fuel blends experienced synergistic combustion behavior during their volatile matter combustion phase. As biomass was added to coal, CO₂ and particulate yields were curtailed in linear proportion to the amount of biomass. CO and PAH yields from the blends showed little change, although linear additivity predicted that these emissions would have been much higher. Light hydrocarbons emissions from blends showed no clear trend.

The second part of the thesis studied batch combustion of fixed beds of coal, bagasse and blends thereof in a two-stage laboratory furnace. The primary and secondary furnace temperatures were varied from 800ºC to 1000ºC. The effects of the fuel blending, the combustion staging, and of the operating furnace temperatures on emissions of pollutants were assessed. Total CO₂ emissions from coal were the highest, whereas CO emissions from bagasse were the highest. Combustion of the volatile matter of the blend resulted in lower yields of PIC, than combustion of its neat constituents, suggesting synergistic behavior. Though carbon monoxide (CO) and unburned volatile and semi-volatile hydrocarbons from the coal and the blend did not exhibit a clear trend with temperature, such emissions from bagasse experienced increasing trends with temperature. The secondary stage typically reduced CO, light hydrocarbons and PAH by further oxidation of effluents coming from the primary furnace. Overall, minimum yields of PIC were obtained when the fuels were burned blended, in staged furnace, operated around 900 ºC.
Acknowledgement

I thank my research advisor Prof. Y. A. Levendis for his guidance and untiring support through out the course of the work. I am also grateful to Dr. Marcia Bragato for training and familiarizing me with the laboratory procedures as well as for sharing ideas and knowledge of experimental work. Thanks are also due to Dr. Carlson for the analysis of the samples and the useful tips given for sampling methods. My research at Northeastern was supported by a scholarship from Boston Science Partnership at Northeastern University. The chemicals and accessories required for the experiments were purchased with the funds provided by Mechanical and Industrial Engineering Department of Northeastern University. I thank Mr. Jeffrey Doughty, Mr. Kevin McCue, Mr. Jonathan Doughty, Dr. Briggs and Mr. Richards Weston for their help in solving technical difficulties. The confidence of my parents, Mr. Arvind D. Joshi and Mrs. Rashmi A. Joshi, and my friends, Mr. Amit Bhole and Mr. Palaniappan Nagappan, in me was the driving force of my commitment towards the research work.
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Chapter 1

Introduction

The world energy consumption is increasing with the new developments and scientific progress made. In the process of betterment of life and comfort, increasing pressure is being put on the conventional energy sources like coal, fossil fuels. But, with the decent of limited sources conventional fuels, new energy sources are gaining increasing attention. The new energy sources like wind energy and solar energy require significant initial investments in terms of money and labor. Hence, along with these options, simpler and cheaper alternative of utilization of renewable biomass is being put forward by many parts of the world.

The biomass has advantage of zero net CO₂ emission, since all the carbon captured from environment for its growth is again released into atmosphere. Fermentation products like ethanol from corn and sugarcane etc., substitute partially fossil fuels like petroleum products used in internal combustion engines. But due to the greater demands of ethanol, it is feared that food production may be compromised to produce more of profitable ethanol. Methane gas from sewage is used for cooking instead of natural gas. Another broad type of biomass that is used in the energy production is bio-waste like wood dust, bagasse, different nut shells and several types of grass. There waste materials are burned with coal in thermal power plants. They may be mixed or can be combusted separately in the same furnace.

Bagasse is one of such waste materials remained after sugarcane stalks are crushed to extract out the juice for sugar production. Developing countries like Brazil and India are world leaders in sugarcane production (see Figure 1.1). One metric tonne of sugarcane, when crushed, leaves 225 kg of bagasse with 50%
moisture in it [1]. That is, plenty of bagasse is produced in each sugar producing site. Many sugar producing companies burn it to boil the sugar cane juice. In such cases, it is burned in open to dispose it inefficiently. A better way of using this waste product is to mix it with coal and feed it to thermal power plants. In order to study such blending of bagasse with coal, a scientific study is done at laboratory scale horizontal furnace. A detailed report of this study is presented in this thesis.

Figure 1.1. Sugarcane production in year 2006 for entire World and countries which are sugarcane production leaders is represented [2].

The part 1 of the thesis investigated effects of blending bagasse in coal on the emissions of the combustion. Batch combustion experiments on different blends were carried out at 1000°C in horizontal furnace. Emissions of fixed gases CO, CO₂ and O₂ were recorded online during the test. Light hydrocarbons and polycyclic aromatic hydrocarbons (PAH) were qualified and quantified during the volatile matter combustion. Soot was measured to monitor emissions of particulate matter.(PM) Five blends were tested; starting from neat coal the bagasse share of the mix was increased from 0% to 100% bagasse.
The part 2 of this thesis deals with effects of furnace temperature and afterburner on the emissions from the batch combustion of the blends. The furnace temperature was varied from 800°C to 1000°C. Similar to the first part, fixed gases CO$_2$ and CO, light hydrocarbons and PAH were identified and measured.

1.1 References:


Chapter 2

Emissions generated during the co-combustion of coal and bagasse fuel blends.


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Brief. This investigation examined possible synergies in the combustion and emissions of coal and bagasse blends in fixed beds placed in a laboratory furnace.
2.1 Abstract
This manuscript reports on emissions generated from laboratory-scale batch combustion of a high-volatile content bituminous coal, sugar-cane bagasse, and blends thereof, at 1000 °C in atmospheric pressure air. The average bulk equivalence ratio during the volatile combustion phase was calculated to be sub-stoichiometric. Characterization and quantification of major fixed gases, light volatile hydrocarbons, semi-volatile polycyclic aromatic hydrocarbons (PAH) and particulate matter are reported. Coal emitted two times more CO₂ and particulate mass than bagasse. In contrast, coal emitted half the amounts of CO, light hydrocarbons and PAH than bagasse. At the high heating-rate conditions used in this work, the fuel blends experienced synergistic combustion behavior during their volatile matter combustion phase. As biomass was added to coal, CO₂ and particulate yields were curtailed in linear proportion to the amount of biomass. CO and PAH yields from the blends showed little change, although linear additivity predicted that these emissions would have been much higher. Light hydrocarbons emissions from blends showed no clear trend.

Key words: coal, biomass, bagasse, combustion, emissions, PAH
2.2 Introduction

Given global trends in electric power generation and consumption, it may be projected that blending of conventional fuels with alternative fuels will be commonly practiced in the future, with biomass playing a major role. For instance, the European Parliament has already approved a directive to increase power co-generation from coal and biomass. The directive states that using biomass as a power source reduces network losses, greenhouse gas emissions, dependency on imported oil, as well as consumption of primary national energy resources [1]. Use of types of biomass that are not intended for food production is preferable. Use of biomass has also the advantage of being a renewable fuel that is considered to be CO$_2$-neutral, as growing plants remove CO$_2$ from the atmosphere by photosynthesis, and equilibrate the CO$_2$ emitted during their combustion [2]. Co-generation of coal and biomass on a weight basis has been reported to reduce air pollution by reducing emissions of volatile organic compounds (VOC) and polycyclic aromatic hydrocarbons (PAH) [3].

Compositions of coal/coal blends for use in power plants are typically established by rule of thumb processes, foreseeing an additive behavior of a blend in relation to its parent compounds. Nonetheless, several investigations have demonstrated that combustion of coal/biomass blends can exhibit non-additive behavior, or in other words may experience synergy [4, 5, 6]. Also, for experiments using coal and biomass blends conducted in diverse apparatuses and conditions, some authors reported non-additive behavior, i.e., synergistic behavior in the total emissions of the blends [7, 8]; while others observed linear correlation between the yield of total volatiles emitted and the amount of biomass in the blend [9, 10]. Neither of those studies, however, identified the species in the emission effluents. These variations in results presumably arise because of disparate burning conditions, including the physicochemical properties of the surrounding gas; heating-rates; blending of the fuels; interactions of the fuel entities; types of biomass and coal used, etc. Nevertheless, an comprehensive explanation of the interaction of the components of mixed fuels has yet to be postulated.
The possibility of synergy in fuel blends is a key issue that still needs resolution, as it can enhance the fuel flexibility of power plants, optimize combustion properties, and generate less pollution. Beneficial synergies will encourage the partial substitution of conventional fuels with biomass, allowing reductions in both the consumption of the conventional fuel and the emissions of greenhouse gases.

This manuscript reports on high heating-rate batch combustion of coal and biomass fuel blends (CBFB) in a horizontal electrically-heated laboratory furnace. Sugar cane bagasse was selected for this study because is a waste biomass. Bagasse is the fibrous residue after the sugar-cane juice is extracted. Burning bagasse, a byproduct of sugar production, reduces waste accumulation. This particular biomass was also selected due to its availability and extensive reports on its properties in the literature [11]. Attention was given to the characterization and quantification of emitted fixed gases, volatile hydrocarbons and semi-volatile polycyclic aromatic hydrocarbons (PAH), some of which are health-hazardous air pollutants [12, 13]. There have been some reports on the speciation of PAH emissions of coal combustion in the literature, some of which from previous work in this laboratory [14, 15]. Also, there are some reports on open air combustion of biomass [18, 19], however few, if any, reports on speciation of PAH emissions from controlled combustion of bagasse were found in the literature.
2.3 Materials and Methods

Pittsburgh #8 HVA bituminous coal, PSOC 1451, and sugar-cane bagasse were burned, with particle sizes of 250>x>212 μm and 212>x>125 μm respectively. Combustion and emissions of this coal have been extensively studied previously by Levendis and co-workers [14, 15, 16]. Proximate and ultimate analysis of both fuels is shown in Table 2.1.

<table>
<thead>
<tr>
<th></th>
<th>PSOC-1451&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Sugar cane Bagasse&lt;sup&gt;a (Dry)&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash (%)</td>
<td>13.84</td>
<td>11.3</td>
</tr>
<tr>
<td>Carbon (%)</td>
<td>71.5</td>
<td>44.8</td>
</tr>
<tr>
<td>Hydrogen (%)</td>
<td>4.7</td>
<td>5.4</td>
</tr>
<tr>
<td>Oxygen (%) (by diff)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>7.0</td>
<td>39.6</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
<td>1.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Sulfur (%)</td>
<td>1.3</td>
<td>0.0</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>34.34</td>
<td>73.8</td>
</tr>
<tr>
<td>Fixed Carbon (%)</td>
<td>51.87</td>
<td>14.9</td>
</tr>
<tr>
<td>Heating Value (Dry)(MJ/kg)</td>
<td>29</td>
<td>17</td>
</tr>
</tbody>
</table>

<sup>a</sup> source: ref [16,17] on Dry Basis ;<sup>b</sup> excludes moisture;

Batch samples of coal/biomass blends were burned in fixed-beds inside a laminar-flow, externally-heated horizontal furnace, see Figure 2.1. The furnace was fitted with a quartz tube, 4 cm in diameter, and 87 cm long. The effluent passed through a venturi (8 mm in diameter) where it was mixed with four jets of preheated air (Figure 2.1). The gases were sampled at the exit of this furnace.
Figure 2.1. Schematic of the laminar-flow horizontal furnace and of the sampling stage.

The furnace was pre-heated to a wall temperature of 1000°C. A porcelain boat loaded with sample was then inserted from the tube's entrance, and it was positioned in the mid-length of the quartz tube, with the aid of a U-shaped quartz tube-made by slicing a tube along its center line, see Figure 2.1. One end of this sliced tube was mounted at the entrance glass-fitting of the furnace. At the start of every experiment, the fitting was opened, and the attached U-shaped tube was extracted from the furnace, the sample boat was mounted at its tip and was quickly inserted in the furnace, the entire operation taking a few seconds. Combustion experiments were conducted in air (21% oxygen), at atmospheric pressure; 4 Lmin\(^{-1}\) of air were supplied to the furnace and an additional 2 Lmin\(^{-1}\) to the venturi. A limited number of pyrolysis tests were conducted in nitrogen to assess the devolatilization fraction of these fuels. The remaining char residues were cooled down, weighed, and subsequently burned in air. Results were in overall agreement with those listed in Table 2.1.

The sampling stage was placed near the furnace to minimize losses (Figure 2.1). Before reaching the sampling stage, the effluent was cooled and inerted by mixing it with a 2 Lmin\(^{-1}\) flow of N\(_2\) to mitigate further reactions from happening once the effluents were out of furnace. Thereby temperatures were brought below 80°C, prior to the sampling stage. Subsequently, condensed phase emissions were trapped on the upper portion of the sampling stage on a 90 mm diameter Whatman glass fiber filter with a nominal pore size of 0.45 μm. Gas-phase polycyclic aromatic hydrocarbon emissions were adsorbed on a bed of Supelco XAD-4 resin, twice as long as wide. After this, during the combustion of volatiles, the effluent was sampled with a micro-syringe in a withdrawal pump for
characterization and quantification of light hydrocarbons by gas chromatography (Agilent 6890 Series GC-FID/TCD system). Semi-volatile hydrocarbons were assessed by extraction of the filters and XAD-4 resins, followed by gas chromatography – mass spectrometry. The detailed procedures for characterization and quantification of light hydrocarbons and PAH are described elsewhere [20 and 21, respectively].

Thereafter, the effluent gas was analyzed on-line for CO and CO$_2$ with a Horiba infrared analyzer and for O$_2$ with a Beckman paramagnetic analyzer. The output of the analyzers was recorded using a Data Translation DT-322 data acquisition board in a microcomputer. The signals from the analyzers were recorded for the duration of the experiment and subsequently were converted to molar fractions.

The average bulk equivalence ratio was calculated as \[ \phi_{\text{bulk,ave.}} = \frac{(m_{\text{fuel}}/m_{\text{air}})_{\text{actual}}}{(m_{\text{fuel}}/m_{\text{air}})_{\text{stoichiometric}}} \]. Since in batch combustion the volatile and char combustion phases of these solid fuels happen sequentially, the experimental conditions were set herein with \( \phi \) calculated based on the more intense volatile combustion, during the visible flame period. The volatile matter fractions of both fuels are listed in Table 1, and their compositions were calculated, assuming that the non-volatile residues contained exclusively of carbonaceous char and ash. Thus, the volatile matter of coal consisted of 63% Carbon, 12% Hydrogen and up to 18% Oxygen along with 3% of each Nitrogen and Sulfur, making its chemical formula to be CH$_{2.29}$O$_{0.21}$N$_{0.04}$S$_{0.02}$ on a molar basis. In the case of bagasse, the volatile matter contained 42% Carbon, 7% Hydrogen, up to 50% Oxygen and insignificant amounts of Nitrogen (0.5%) and Sulphur. Thus, on a molar basis, the composition of the bagasse volatiles is CH$_{1.96}$O$_{0.89}$N$_{0.01}$.

In the case of fuel being neat bagasse; the total fuel sample burned was less than one gram (~0.8 g). This sample mass contained 0.59 g of volatile matter, based on the data shown in Table 2.1. Whereas when the fuel was neat coal; the amount of fuel exceeded one gram (~1.15 g). This sample mass contained 0.39
g of volatile matter. Batches of fuel blends were manually mixed prior to insertion in the furnace (see Figure 2.S1, in the Supporting Information Section). Blend composition was defined as a percentage of the mass of the bagasse volatiles in the total mass of the volatiles in the blend. This mass fraction approach has been proved to be rigorous enough to characterize phase behavior of complex systems and accepts variations in molecular composition of blend’s components without losing its predictive power [22,23]. All the tests were conducted at least in duplicate. The neat fuel tests (100% coal and 100% bagasse) were performed in triplicates.

To verify the proportion of emitted compounds determined, carbon balances were done for all tests, following the procedure of Wang et al. [24]. The results showed that more than 90% of the input carbon was accounted for in the products. Considering this satisfactory recovery, the instantaneous emissions of CO and CO$_2$ were used to evaluate the mass of fuel, $m_{\text{fuel}}$, burned in each time interval, which was then used to calculate a time-resolved instantaneous bulk equivalence ratio, $\phi_{\text{bulk},i}$. The rate of devolatilization was assumed to be equal to the rate of combustion of volatiles which was monitored by the rate of evolution of CO, see Figure 2.3.
2.4 Results and Discussion

2.4.1 Preliminary Tests:

Preliminary tests were conducted in two steps, fuel pyrolysis in nitrogen, followed by char oxidation in air. The furnace temperature was 1000 °C. Visual analysis of the filters after pyrolysis showed a blackish residue for neat coal and a light brown residue for neat bagasse. Whereas the coal residue appeared to be mostly soot, the bagasse residue appeared to be condensed oils/tars.

Visual and gravimetric analysis of the sampling filters after char oxidation showed no evidence of particulate formation neither from coal nor bagasse. Also, on-line analysis showed no CO formation during the combustion of the chars. Hence, it was determined from these experiments char combustion of these fuels does not generate particulate matter and CO, under the conditions used herein. These results agree with those of previous studies obtained in this laboratory for batch combustion of coal [14, 15] which showed that under similar combustion conditions the heterogeneous char combustion period does not contribute to PAH emissions either, typically considered as soot precursors.

Subsequent experiments on batch combustion of these fuels showed two distinct combustion phases: burning of the volatile matter in intense luminous diffusion flames, forming over the sample beds, followed by lengthy heterogenous (smoldering) combustion of the remaining beds of chars. Therefore, as it was determined that heterogeneous char combustion did not contribute to CO, PAH and particulate emissions, ensuing experiments focused on the homogeneous combustion of the volatile matter.

2.4.2 Combustion in Air – Emission Yields:

During the volatile matter combustion period of these fuels, and their blends, average bulk equivalence ratios, $\phi_{\text{bulk, ave.}}$, were calculated to be sub-stoichiometric (~0.5). It is worth noticing however, that such flames, of transient and non-premixed (diffusion) nature, are expected to experience large temporal
and spatial gradients of local equivalence ratio and temperature. Indeed, instantaneous bulk equivalence ratios, $\phi_{\text{bulk},i}$, were near unity, see Figure 2.2, or even exceed unity in the case of bagasse, which indicates oxygen deficiencies.

![Figure 2.2](image.png)

**Figure 2.2.** Instantaneous bulk equivalence ratio, $\phi_{\text{bulk},i}$, during combustion of coal and bagasse volatile matter. The time was initialized when the boat was inserted into the furnace, which was preheated to 1000 °C.

A strong hint for the occurrence of synergy in the combustion of fuel blends is evident in the real-time CO emissions shown in Figure 3. In this figure the measured CO profiles from burning coal, bagasse and a 50-50 blend thereof, are superimposed along with a calculated profile for that blend, assuming additive behavior. The measured and calculated CO profiles of the blend were disparate; the profile from bagasse was bimodal whereas those from the blend and the coal were monomodal. Based on thermogravimetric results elsewhere from combustion and gasification of biomass [25, 28], it can be inferred that the first peak in the bimodal CO profile from bagasse may be attributed to the depolymerization of cellulose and the second to the decomposition of the lignin.
Gani et al. [29] also reported a bimodal CO profile from the combustion of biomass and a monomodal profile from a coal/biomass blend. They suggested that the combustion of the volatile matter of biomass may accelerate the evolution rate of volatile matter from coal. However, as the maximum CO emission for the blend herein occurred at almost the same time as the biomass’s second CO peak, it appears that the de-polymerization of cellulose was delayed in the case of the blend. This delay can be attributed partly to the thermal inertia of coal (~2.9 kJ/kg K) which is almost twice that of the cellulose (~1.4 kJ/kg K) component of bagasse [26, 27]. Possible additional, physical contributions to this delay may arise from slower mass diffusion of heated air in the sample in the presence of coal, as a bed of coal has a more compact morphology than a bed of cellulosic material [30]. Finally, possible chemical contributions to this phenomenon are presented in an ensuing section.

![Graph](image.png)

**Figure 2.3.** Experimental CO profiles from the combustion of the volatile matter of neat coal, bagasse and a blend of 50% bagasse. Superimposed is a profile based on the calculated additive behavior of the neat fuels. The time was initiated when the boat was inserted into the furnace, preheated to 1000 °C.
The integrated consumption of oxygen and integrated emissions of main species during the combustion of the volatile matter are shown in Figs 2.S2 and 2.4, normalized by the amount of fuel devolatilized. For fixed gases, the total emissions normalized to the total amount of fuel burned (volatiles + char) were also included in Fig. 2.S2. Moreover, Figs 2.4 and 2.S2 show cumulative amounts of volatile light hydrocarbons (LH) and semi-volatile hydrocarbons (mostly PAH). The amounts of the individual species responsible for most (95% of the total) emissions in each group (LH, PAH) are plotted in Figure 2.S2. LH were monitored during the volatile matter combustion, whereas PAH during the entire combustion period. However both LH and PAH are only attributed to the volatile combustion period, as explained earlier. To facilitate discussion, calculated additive-linear-behavior lines are included in all graphs of Figure 2.4 and Figure 2.S2.

2.4.2.1. Bulk equivalence ratio, $\phi$: the average bulk $\phi$'s observed during the volatile matter combustion were about 0.53 for both coal and bagasse. Even though, under the same conditions, bagasse released more volatiles than coal, the amount of air consumed by bagasse also increased compared to coal. This was expected since the volatile mass fractions account for 34.3% of coal and 73.8% of bagasse, as shown in Table 2.1. However, the blends exhibited non-linear behavior, see Fig. 2.S2. The resulting bulk equivalence ratios during the combustion of their volatiles were higher than those of the neat fuels. Particularly for the 50% bagasse blend, the calculated average bulk $\phi$ was 0.66, resulting in a 20% increase from linear-additive behavior. High average bulk $\phi$ values suggest that fuel blending enhanced the volatile matter combustion phase. In fact, the instantaneous bulk $\phi$ for the 50% bagasse blend was calculated to reach values as high as 1.6, which is even higher than that of the neat bagasse (1.5).

2.4.2.2. Particulates: Particulate emissions of blends obeyed a nearly-linear behavior, with deviations from additivity within 7%. Neat coal emitted two times
more particulate mass than neat bagasse. Therefore, partial substitution of coal with biomass has the potential of reducing particulate emissions.

2.4.2.3. **Consumed O\textsubscript{2}** showed almost linear additive behavior with the exception being a 26\% departure below the expected value for the 26\% bagasse blend during the total combustion test (see Figure 2.4.2). This experiment was conducted in duplicate and results of both experiments supported this negative departure from linearity.

![Figure 2.4. Combustion yields, presented in descending order of quantity, against increasing percentage of bagasse volatile matter in the total volatile matter of each blend. Legend: – calculated additive linear behavior; g/g fuel = gram species per gram fuel volatiles burned during the volatile combustion phase, or fuel burned in total period (volatile matter combustion + char combustion), as noted. Furnace temperature was kept at 1000\°C.](image)

2.4.2.4. **CO\textsubscript{2} emissions**: Yields of CO\textsubscript{2} were lower from bagasse than from coal, which was expected based on the lower carbon content of the former fuel. Part of the CO\textsubscript{2} was emitted during the devolatilization period and part during the char combustion period, in agreement with the fuels proximate analysis shown on Table 1. During devolatilization, CO\textsubscript{2} yields from the blends were lower than
additive behavior would predict, with maximum departure being 19% for 50% bagasse blend, see Figs 2.4 and 2.S2. This behavior agrees with the observed values of $\phi_{\text{bulk,ave.}}$, which were higher than those of the neat fuels, see Fig. 2.S2, indicating that the blends experienced a fuel-richer volatiles combustion than either neat coal or neat bagasse. If the total combustion period (volatiles+char) is considered, CO$_2$ emissions from blends experienced smaller, but positive, departures from the linear additive behavior, see Fig. 2.S2.

2.4.2.5. CO emissions: In stark contrast to the CO$_2$, CO emissions experienced an opposite trend. Yields of CO were two times higher from neat bagasse than from neat coal, see Figs 2.4 and 2.S2, suggesting a very different mix of devolatilization products for the former high-oxygen content fuel. Like the case of other oxygenated fuels and, even, lignite coals, CO is a prominent product of bagasse pyrolysis. Seeker et al. [31] and McLean et al. [32] reported that bituminous coals, such as the one used herein, form condensed phase matter in their devolatilization products whereas lignites do not. Such findings were attributed to the chemical composition of the coals. Cellulosic materials (bagasse consists of nearly 75% cellulose [25]), are formed by a series of glucose rings polymerized by glycosidic bonds, which comprise one atom of oxygen bonded to two carbon atoms [33]. As a fuel’s oxygen content decreases, glycosidic linkages are increasingly substituted by aliphatic hydrocarbon moieties and glucose rings are substituted by aromatic ones [30, 34]. If devolatilization process of a fuel starts by oxidative cleavage of the weakest covalent bonds in its organic matter, as was suggested by Sjöström et al. [35], the first step should be depolymerization [33, 34]. In this case, the high yields of CO emitted during combustion of oxygen-rich fuels, such as bagasse and lignites, originate from thermally degradative CO elimination from the fuel, rather than oxidation by atmospheric oxygen. The next observation regarding the CO plots of Figure 2.4 and Figure 2.S2 is that the entire CO emission yields arise from the combustion of the volatile matter alone, see Figure 2.2, as the generated diffusion flames have fuel-rich regions. As mentioned earlier, no CO emissions were observed
during the comparatively slow, heterogeneous char combustion phase. Whereas CO may indeed be the primary combustion product of char oxidation at its surface, it readily oxidizes in the bulk gas in the furnace to CO$_2$.

A final and rather important observation on CO emissions concerns the blends’ yields. They showed strong deviation from the linear-additive behavior, with CO yields ranging from 47% to 74% lower than linear behavior predicted. The departure from linear behavior strongly supports the hypothesis of synergy between the two fuels, under the current experimental conditions. Such behavior may be explained by considering the CO-emission profiles of Figure 2.3, where the blend’s profile appeared to peak at the same time as the profile of neat coal. A hypothesis may be put forward that de-polymerization starts mainly from bagasse, then intermediary radicals form by the broken glycosidic bonds and react with thermally-activated sites on the surfaces of coal, instead of generating CO. So the reaction pathway is presumably changed, generating aliphatic radicals in place of CO, and at the same time enhancing the coal’s devolatilization. This radicals-solid interaction would also explain why the average bulk equivalence ratios of the blends were found to be above additive-linear behavior. MacPhee et al, [36] monitored interactions between macerals in blends of high- and low-volatile coals. They observed synergy during devolatilization, which they attributed to interactions of the volatile matter of high-volatile coal with the solid material of the low-volatile coal.

2.4.2.6. Light Hydrocarbons: Cumulative light hydrocarbon yields from the combustion of volatiles of neat bagasse were almost three times higher than the corresponding yields from neat coal, see Figs 2.4 and 2.S2. This may be explained based on the higher instantaneous bulk equivalence ratios, $\phi_{\text{bulk, i}}$, of bagasse. The main emissions from bagasse were, in decreasing order: indene, benzaldehyde, phenol, methane, ethane, acetophenone, ethylene, acetylene, propylene and benzene. Benzene and acetophenone were the only compounds with lower yields from bagasse than from coal, see Fig. 2.S2. Also styrene was detected in all tests, but due to styrene’s high instability [37] the analysis method
used herein could not reproducibly quantify its yields. For blends, however, light hydrocarbons yields as a whole showed complex behavior with the 25% bagasse blend emitting 16% above the expected linear additive behavior and blends with 50% and 75% bagasse resulting in emissions 44% and 53% below, respectively. This complex behavior was also found for individual species: benzene was emitted above the linear additive behavior; phenol was almost on the line; indene, methane, ethylene and propylene emissions were below the line, and benzaldehyde, ethane, acetophenone, and acetylene had some points above and others below the line. The observed variations in the behavior of the light hydrocarbons can be understood if one considers that, under the high heating rate conditions used in this work, light hydrocarbons were being formed by the gaseous intermediaries while some solid moiety was yet present. In this scenario light hydrocarbons generation become site dependent, that is, the physico-chemical properties of surfaces where reactions take place will likely interfere with the yields and the kinds of products formed.

2.4.2.7. PAH and other high molecular compounds: Combustion of neat coal resulted in two times less total PAH emissions than combustion of neat bagasse, see Fig 2.4 and 2.S2. As many as 31 and 41 PAH compounds were observed in the effluents of coal and bagasse, respectively. In other words, combustion of bagasse emitted both higher amounts and more species of PAH than coal. Emissions of selected individual PAH compounds are shown in Fig. 2.S2. In decreasing order of emission, the most prominent PAH were: naphthalene, acenaphthylene, phenanthrene, fluoranthene, pyrene, dibenzofuran, benzofuran, biophenyl, fluorene, 9H-fluoren-9-one, acephenanthrylene, benzo[b]fluoranthene, 1-methyl-naphthalene; 2-methyl-naphthalene, benz[a]anthracene and benzo[a]pyrene. Therefore, higher yields were found for lower molecular mass products, in line with the PAH growth mechanism by H-abstraction-C2H2-addition, HACA [38, 39]. A reaction scheme may be envisioned by considering the solid fuel as a polymeric matrix, which starts its combustion by depolymerization, and latter by reaction of the remaining monomers. Hence, a solid fuel's
depolymerization would supply a radical pool that would react with the remaining monomers and by doing so would generate PAH and, ultimately, particulates, as PAH are considered precursors to particulate formation. It is interesting to note that while bagasse’s PAH yields were double those from coal; bagasse’s particulate yields were half of those from coal, see Figs 2.4 and 2.S2. These results suggest that the global growth rate for particulates is lower for bagasse than for coal. Existing models for particulate formation indicate that yields of particulate result from two opposite processes: growth and oxidation [39, 40]. Considering the higher oxygen content of bagasse, it is possible that bagasse’s particulate growth was impeded by locally oxidizing conditions in the diffusion flame of its volatile matter.

Combustion of the fuel blends resulted in drastic reductions in total and in individual PAH yields, up to 62%, see Figs 2.4 and 2.S2. The only exceptions were emissions of oxygen-containing compounds (dibenzofuran, benzofuran and 9H-fluoren-9-one), which experienced mixed behavior. Thus, in the experimental conditions of this work, the presence of coal favored the particulate growth for the blends, which consumed the PAH and reduced their yields. Perhaps the partially de-polymerized matrix of coal would supply a pool of islands of stability that promote the growth of particulates by the HACA mechanism [30, 39]. This would provide a much faster growth rate, even under the locally-oxidizing conditions in the combustion of high-bagasse content blends.

An error analysis was conducted to assess reproducibility of the results for the combustion of neat coal and neat bagasse, where experiments were carried out in triplets. One standard deviation in the yields of carbon dioxide was within 13% of the average. Yields of light hydrocarbons and PAH were recorded in very small scales (10^{-6} to 10^{-9} grams/gram-of-volatiles). In such cases the standard deviations were within 35% of the average.
In summary, under the high heating rate conditions studied here, a possible sequence of events during combustion of coal/biomass fuel blends, in fixed beds, is initial depolymerization (due to thermal degradation) followed by generated radicals attacking the remaining solid fuel surface forming PAH and, ultimately, generating particulate matter. If, after the initial depolymerization, the remaining solid matrix still possessed a sufficient amount of aromatic rings, at the presence of coal, the growth rate of the particulate was more prevalent than its oxidation. Otherwise, the presence of oxygen in the bagasse volatile matter flame prevented the particulate growth and predominant products were PAH and CO.
2.5 References


[37]. http://physchem.ox.ac.uk/MSDS/ST/styrene.html


2.6 Supporting Information

**Figure 2.S1.** a) Bituminous Coal of 250 – 212 μm granulometry  b) Sugar cane bagasse in 212 - 125 μm size cut  c) Bituminous coal and sugar cane bagasse mixed in equal proportions of their volatile matter content. The main scale reads 100μm.
Figure 2.S2. Combustion yields, presented in descending order of quantity, against increasing percentage of bagasse volatile matter in the total volatile matter of each blend. Legend: • measurements, --- calculated additive linear behavior; g/g fuel = gram species per gram fuel volatiles burned during the volatile combustion phase, or fuel burned in total period (volatile matter combustion + char combustion), as noted. Furnace temperature was kept at 1000°C.
Chapter 3

Temperature effects on the two stage co-combustion emissions of coal and bagasse fuel blends

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3.1 Abstract

Batch combustion of fixed beds of coal, bagasse and blends thereof took place in a two-stage laboratory furnace. The primary and secondary furnace temperatures were varied from 800°C to 1000°C, and average bulk equivalence ratios were sub-stoichiometric. The effects of the fuel blending, the combustion staging, and of the operating furnace temperatures on emissions of pollutants were assessed. The furnace effluent was analyzed for fixed gases, volatile and semi-volatile hydrocarbons, with emphasis to polycyclic aromatic hydrocarbons (PAH), as well as for particulate matter. Results showed that whereas carbon dioxide was generated both during the volatile matter and the char combustion phases, carbon monoxide and other products of incomplete combustion (PIC) are generated during the volatile combustion phase. Total CO₂ emissions from coal were the highest, whereas CO emissions from bagasse were the highest. Combustion of the volatile matter of the blend resulted in lower yields of PIC, than combustion of its neat constituents, suggesting synergistic behavior. Though carbon monoxide (CO) and unburned volatile and semi-volatile hydrocarbons from the coal and the blend did not exhibit a clear trend with temperature, such emissions from bagasse experienced increasing trends with temperature. The secondary stage typically reduced CO, light hydrocarbons and PAH by further oxidation of effluents coming from the primary furnace. Overall, minimum yields of PIC were obtained when the fuels were burned blended and when the combustion was staged, with both stages operated in vicinity of 900 °C.
3.2 Introduction

The concept of co-firing biomass and coal is receiving increasing attention in Europe and United States [1]. Biomass being low on cost and available in plenty becomes a ready source of fuel for blending in coal-fired power plants. Its use reduces the net carbon dioxide released to the atmosphere. Increasingly stringent constraints considered on carbon emissions promote the use of biomass. Typically 2 to 20% of biomass is mixed with coal on an energy basis. As Biomass usually has about half the energy content (e.g. 17 MJ/kg for sugarcane bagasse) of coal (29 MJ/kg for bituminous coal) its required mass is nearly twice as that of coal it substitutes, to keep a boiler's power output constant [2], see Table 3.2.

The co-firing of coal and various types of biomass has been studied extensively in the literature for combustion effectiveness and emissions of pollutants like NOx, SOx and CO [3]. Biomass has proved to be a good option for partial coal substitution, considering that it is low in cost and it is a renewable energy source [1]. Nevertheless, some practical aspects of co-firing, such as ash deposition rates and corrosion in boilers have received attention [4]. Recent studies conducted by Zabetta et al [5] and Kruczek [6] have reported that the main cause of increased fouling and corrosion in case of co-firing biomass in utility boilers is because of the alkali contents of the bio-fuels. Such problems were mostly attributed to the lower melting temperatures of the alkali elements, particularly potassium and phosphorous, see Table 3.1, as well as to reactions of furnace wall silicates with the alkalis. Table 3.1 lists the amounts and compositions of ash, of a typical coal, the Pittsburgh # 8 bituminous coal, and the sugarcane bagasse (the two fuels used in this study) with those of other biomasses, such as red oak wood chips, Danish wheat straw, imperial wheat straw and switchgrass. Bagasse stands out from the other biomass fuels as having by far the lowest potassium oxide content. It also has lower phosphorus content than most other types of biomass. It is also obvious that bagasse has very low ash content, which will load the power plant’s particulate control devices the least. Finally, unlike
most other sources of biomass, bagasse has the advantage of being a waste fuel, so its production does not compete for land and irrigation with production of food.

Table 3.1. Ash composition of different biomass fuels in comparison with bituminous coal. [1, 7]

<table>
<thead>
<tr>
<th>Ash Composition</th>
<th>Melting Point (°C)</th>
<th>BITUM. COAL</th>
<th>BAGASSE</th>
<th>WOOD</th>
<th>D-STRAW</th>
<th>I-STRAW</th>
<th>GRASS (% mass, ash basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>1723</td>
<td>54.4</td>
<td>46.6</td>
<td>44.7</td>
<td>41.5</td>
<td>38.7</td>
<td>58.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2015</td>
<td>24.5</td>
<td>17.7</td>
<td>9.4</td>
<td>1.0</td>
<td>1.4</td>
<td>2.3</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1830</td>
<td>1.1</td>
<td>2.6</td>
<td>0.6</td>
<td>0.0</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1594</td>
<td>9.2</td>
<td>14.1</td>
<td>7.8</td>
<td>0.7</td>
<td>0.6</td>
<td>11.5</td>
</tr>
<tr>
<td>MgO</td>
<td>2852</td>
<td>0.9</td>
<td>3.3</td>
<td>1.3</td>
<td>2.0</td>
<td>1.7</td>
<td>5.4</td>
</tr>
<tr>
<td>CaO</td>
<td>2614</td>
<td>3.0</td>
<td>4.5</td>
<td>16.2</td>
<td>8.1</td>
<td>4.3</td>
<td>11.2</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1275*</td>
<td>0.6</td>
<td>0.8</td>
<td>0.8</td>
<td>0.6</td>
<td>13.5</td>
<td>0.4</td>
</tr>
<tr>
<td>K₂O</td>
<td>350**</td>
<td>2.0</td>
<td>4.2</td>
<td>9.3</td>
<td>32.0</td>
<td>20.5</td>
<td>9.1</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>580</td>
<td>0.3</td>
<td>2.7</td>
<td>1.2</td>
<td>4.4</td>
<td>3.1</td>
<td>4.0</td>
</tr>
<tr>
<td>SO₃</td>
<td>17</td>
<td>2.3</td>
<td>2.1</td>
<td>1.4</td>
<td>3.3</td>
<td>4.3</td>
<td>3.0</td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
<td>98.3</td>
<td>98.6</td>
<td>92.6</td>
<td>93.6</td>
<td>88.0</td>
<td>105.3</td>
</tr>
<tr>
<td>Ash (% mass dry fuel basis)</td>
<td></td>
<td>13.2</td>
<td>2.2</td>
<td>1.3</td>
<td>4.7</td>
<td>4.9</td>
<td>8.1</td>
</tr>
</tbody>
</table>

* Temperature of sublimation
** Temperature of decomposition

Coal and biomass blend devolatilization has been previously studied in a thermogravimetric balance by Haykiri-Acma et al. [8]. They reported non-additive behavior in devolatilization of mixtures of Turkish lignite coal and Hezelnut shell (2 to 20% by weight) in the temperature range of 400 K to 600 K. Jones et al [9] investigated synergy of the bituminous coal and pine wood blends by carrying out batch pyrolysis experiments and thermogravimetric analysis (TGA) in the temperature range of 673 K to 1173 K. The tar emissions demonstrated non-additive behavior for the large scale pyrolysis tests. On the other hand, additive
behavior was recorded in case of the TGA experiments. Another study of biomass by G. Collot et al. [10] in a fluidized bed combustor reported information regarding tar and volatile yields. In this case the absence of synergy was attributed to poor mixing of the two fuels and the authors suggested that introduction of well mixed fuel blends in the furnace may increase the chances of synergy. A number of different coal biomass co-firing studies have discussed the effects of fuel blending on the emissions of CO, NO\textsubscript{x} and SO\textsubscript{x} [2, 3, 11]. However, there are very few investigations regarding the emissions of health-hazardous components, as polycyclic aromatic hydrocarbons and soot from co-combustion of coals with different types of biomass [12, 13].

In this paper, sugarcane bagasse was chosen as the biomass to be blended with bituminous coal. Bagasse is a byproduct of sugar production. It is the dried pulp left after the juice from sugar cane is extracted. In the past, both this bagasse and this bituminous coal were studied individually in this laboratory. Batch pyrolysis and combustion experiments of bagasse were conducted to monitor the emissions of fixed gases, volatile and semivolatile hydrocarbons and soot [14]. Similar studies on the emissions from coal were also conducted previously [12]. Recently, Bragato et al. [15] studied the one-stage batch combustion of blends of several these two fuels at fixed furnace temperatures. At the high heating-rate conditions used in that work, the fuel blends experienced synergistic combustion behavior during their volatile matter combustion phase. As biomass was added to coal, CO\textsubscript{2} and particulate yields were curtailed in linear proportion to the amount of biomass, however, CO and PAH yields from the blends showed little change, although linear additivity predicted that these emissions would have been much higher. In this study the effects of combustion staging and stage temperature were investigated for the neat fuels as well as a 50-50 blend therefrom.

3.3 Materials and Methods
The two fuels involved in the blends were Pittsburgh # 8 HVA bituminous coal (PSOC-1451), and dried sugar-cane bagasse. The bituminous coal was obtained
from the Penn State Coal Sample Bank, whereas bagasse was obtained from a Brazilian sugarcane processing plant. Both the fuel samples were grinded and sieved to particle sizes were 250 to 212 μm for coal and 212 to 125 μm for bagasse. Properties and combustion behavior of the coal has been extensively studied in previous years in this laboratory [12, 13, 16]. Bagasse was chosen for co-combustion because of its easy availability to industries, where it is a biomass residue accounted as waste. Hence the utilization of bagasse in co-firing helps reduce accumulation of waste. Also, there is a fair amount of literature reporting properties of bagasse [17]. Chemical compositions of both fuels are shown in Table 3.2.

Table 3.2- Proximate and Ultimate Analysis of Fuels

<table>
<thead>
<tr>
<th></th>
<th>PSOC-1451&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Sugar cane Bagasse&lt;sup&gt;a&lt;/sup&gt; (Dry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash (%)</td>
<td>13.84</td>
<td>11.3</td>
</tr>
<tr>
<td>Carbon (%)</td>
<td>71.5</td>
<td>44.8</td>
</tr>
<tr>
<td>Hydrogen (%)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.7</td>
<td>5.4</td>
</tr>
<tr>
<td>Oxygen (%) (by diff.)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>7.0</td>
<td>39.6</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
<td>1.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Sulfur (%)</td>
<td>1.3</td>
<td>0.0</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>34.34</td>
<td>73.8</td>
</tr>
<tr>
<td>Fixed Carbon (%)</td>
<td>51.87</td>
<td>14.9</td>
</tr>
<tr>
<td>Heating Value (Dry)(MJ/kg)</td>
<td>29</td>
<td>17</td>
</tr>
</tbody>
</table>

a) source: [16,18] on Dry Basis; b) excludes moisture;

The three fuels burned in this study were coal (~1.5 grams per batch), bagasse (~0.8 grams) and their blend (~0.9 grams). The blend consisted of calculated equal amounts of volatile matter masses of coal and bagasse. The blend was mixed manually. Batch samples of these fuels were burned in a fixed-bed placed inside a laminar-flow, electrically-heated horizontal furnace. The furnace consisted of two stages: (i) a primary furnace, and (ii) a secondary furnace or
afterburner. The full length of the two furnaces was fitted with one quartz tube, 4 cm in diameter, and 110 cm long. The effluent is passed through a venturi (8 mm in diameter) before entering the afterburner, where it was mixed with four jets of preheated air (see Figure 3.1). Half the amount of gases was sampled after the venturi and the remaining half was passed into the afterburner. The second sampling stage was set-up at the exit of the secondary furnace.

**Figure 3.1.** Schematic of laminar-flow horizontal furnace and the two sampling stages.

Prior to each test, the furnace was pre-heated to the desired temperature. A porcelain boat loaded with sample was then inserted from the quartz tube’s entrance in the primary furnace. The quartz tube had a special arrangement for the boat insertion. The glass-fitting end was attached with a half tube, on which the boat could be rested and positioned centrally in the primary furnace, see Figure 3.1. Therefore, during each experiment, the glass-fitting entrance was opened and the half-sliced tube was drawn out from the quartz tube, the sample boat was placed in it and was inserted in the furnace promptly, the entire process taking a few seconds. Combustion experiments were conducted in air, at atmospheric pressure. A total 6 Lmin⁻¹ of air was distributed in 4Lmin⁻¹ to primary furnace and 2Lmin⁻¹ to the venturi. Both the sampling stages were placed close to the furnace exits. In each sampling stage the effluent was mixed with 2Lmin⁻¹ flow of nitrogen in order to quench and inert the chemical reactions. The condensed phase emissions were captured by Whatman paper filters (90 mm
diameter with a nominal pore size of 0.45 μm) at the entrance of sampling stage. Gas-phase polycyclic aromatic hydrocarbons in the emissions were adsorbed on a bed of Supelco XAD-4 resin, 30 ml in volume in both stages. During the combustion of volatiles, the effluent was sampled with a micro-syringe activated by withdrawal pump placed after the XAD-4 chamber. Semi-volatile hydrocarbons were assessed by extraction of the filters and XAD-4 resins followed by gas chromatography-mass spectrometry. Again, the samples were collected after both furnaces and characterized as well as quantified for light hydrocarbons by gas chromatography (Agilent 6890 Series GC-FID/TCD system). The same effluents were then carried through on-line CO and CO₂ analyzers (with Horiba infrared) to vent. The output signals of the analyzers were recorded using a Data Translation DT-322 data acquisition board for the duration of the experiment and were converted to molar fractions.

The average bulk equivalence ratios during batch combustion of these fuels, defined as $\Phi_{\text{bulk,ave.}} = [(m_{\text{fuel}}/m_{\text{air}})_{\text{actual}}/(m_{\text{fuel}}/m_{\text{air}})_{\text{stoichiometric}}]$, were determined to be in the sub-stoichiometric region. Since the volatile and char combustion phases happen sequentially in batch combustion, $\Phi$ was calculated only for the intense volatile combustion, considered to occur during the visible flame period. During these experiments the volatile matters were determined for both fuels, and their compositions were calculated, assuming that non-volatile residue was composed of char and ash only. In these calculations the chemical formulae of the fuels were assumed to be CH$_{2.29}$O$_{0.21}$N$_{0.04}$S$_{0.02}$ for this coal and CH$_{1.96}$O$_{0.89}$N$_{0.01}$ for bagasse based on the data in Table 3.2. The composition of blends is defined as percentage mass fraction of the bagasse volatile matter to the total mass of bagasse + coal volatile matter.
3.4 Results and Discussions:

3.4.1 Emissions of fixed gases:
Batch combustion of the volatile matter and the char residues of these fuels occurred sequentially. The evolution of CO₂ from samples of bagasse, coal and from the 50/50 mix are shown in Figure 2 at the exits of the primary and the secondary furnaces, both operated at 900 °C.

![CO₂ Online Profile](image)

**Figure 3.2.** Online CO₂ profiles in the effluents of batch combustion of coal, bagasse and blend thereof, at primary and secondary furnace temperatures set at 900°C.

From examination of these plots it is obvious that (a) combustion of volatile matter is briefer and more intense than that of chars; (b) combustion of the coal’s volatile matter generates less CO₂ than that of bagasse’s as coal contains less volatiles; (c) combustion of coal chars is much lengthier than that of bagasse chars, as coal chars contain much more fixed carbon; (d) the effluents of the second furnace contain higher mole fractions of CO₂, as additional combustion takes place therein; (e) the CO₂ mole fractions of blends were found to be in-between those of the neat fuels.

Upon numerical integration of these CO₂ profiles, as well as those of CO, the mass yields of emissions were determined and are displayed in Figs 3 and 4. Some of the key issues regarding the afterburner and furnace temperature effects on the fixed gases emission from the blends are discussed for volatile phase emissions and total combustion emissions. Carbon balances were carried
out for all tests based on the CO$_2$, CO and soot measurements. The balances were satisfactory with more than 90% of the carbon accounted for.

The carbon dioxide yields from entire sample combustion (volatile + char combustion phases) of coal were the highest, followed by those from the blend and then those from bagasse, which has the lowest fixed carbon content. The blend resulted in lower CO$_2$ yields than its constituents during volatile matter combustion, suggesting possible delays in the reactions resulting in CO$_2$ production. Higher CO$_2$ yields in case of afterburner indicate that the fuel intermediated combustion products were provided with extra residence time at same temperature and atmosphere to oxidize completely.

Trends of CO$_2$ emissions can be correlated to those of CO emissions. While volatile matter combustion durations were comparable, the char combustion phase of bagasse lasted for a very short period compared to coal and the blend was of intermediate duration on the time scale. Moreover, the higher instantaneous equivalence ratio for volatile matter combustion phase of bagasse (which peaked at 1.5) than coal (which peaked at 1) [15] suggests deficiency of oxygen leading to more CO production. In most cases, the blend was found to produce less CO that its parent fuels. This phenomenon is attributed to the synergistic effects of co-combustion of coal and bagasse [15]. The CO recorded during the smoldering char combustion was not significant, as any CO generated as a primary product of heterogeneous char oxidation typically gets oxidized homogeneously to CO$_2$ in the bulk gas. Therefore, there was little difference in CO yields from volatile matter combustion to total combustion (volatiles + char). In most cases the secondary furnace treatment reduced the yields of CO as, most likely, some was oxidized to CO$_2$. An occasional data point or two in these plots are inexplicably out of line as the human factor involved in the insertion of fuel and the judgment of the inception and termination of the volatile and char combustion phases in the post processing of data may have caused some errors.
Figure 3.3. Yields of carbon dioxide emitted during the combined volatile matter + char combustion (upper row) as well as during volatile matter combustion only (bottom row) from the primary furnace (left hand column) and the secondary furnace (right hand column) are plotted against the furnace temperature for all three different fuels (C = coal, B = biomass and C/B = blend with equal amount of volatile masses of coal and bagasse).

The increase in the furnace temperature did not affect CO yields from either the coal or the blend to generate clear trends. To the contrary the CO emissions from bagasse were much influenced by the rise in the operating temperature of the furnaces. Perhaps the lower thermal inertia of the cellulose component of
bagasse [19, 20] and the loose morphology of bagasse as compared with that of coal caused the temperature of the bagasse sample beds raise faster.

Figure 3.4. Yields of carbon monoxide emitted during the combined volatile matter + char combustion (upper row) as well as during volatile matter combustion only (bottom row) from the primary furnace (left hand column) and the secondary furnace (right hand column) are plotted against the furnace temperature for all three different fuels (C = coal, B = biomass and C/B = blend with equal amount of volatile masses of coal and bagasse).
3.4.2. Light Volatile Hydrocarbons and Semivolatile (PAH) Emissions:

In these experiments 25 different light hydrocarbon (LH) species were detected, the sum of which expressed as yields are shown in Fig. 5. The species of methane, ethane, ethylene, phenol, benzaldehyde, indene and acetophenone were the most prominent, standing apart from others by at least 2 orders of magnitude. A few selected individual components (methane, ethylene and acetylene) contributing major amount of the total light hydrocarbons are shown in Fig. 3.S1 in the Supporting Information Section. The light hydrocarbons were measured at the exits of both furnaces during the volatile phase only. No significant volatile hydrocarbon emissions were expected to be released during the char combustion phase. The highest emissions were seen in case of bagasse. This is well supported by the bagasse’s composition consisting mainly of cellulose and lignin, which present oxygen atoms as part of the ring structure. During thermal decomposition, due to the position of the oxygen atoms at the ring, cellulose and lignin are easier to convert to short molecules, with 2 or 3 carbon atoms, than coal [21, 22].

The additional residence time provided by the after-burner was instrumental in reducing the emissions of light hydrocarbons, particularly those from combustion of bagasse, the concentration of which were higher. Finally, the yields from bagasse show an overall trend of rising light hydrocarbon emissions with furnace temperature. But the little rise for coal and blend emission does not allow for any temperature related inferences to be generally drawn.

The polycyclic aromatic hydrocarbons (PAH) were investigated using XAD-4 absorbent during the entire (volatile + char) combustion at the sampling stages, as explained in the experiment procedure section. Emissions of PAHs are hazardous to health as some are proved to be carcinogenic [23]. As many as 55 different PAH compounds were detected in these effluents, the sum of which is plotted in Fig. 3.5. PAH components (such as naphthalene, acenaphthylene, pyrene, fluoranthene, acephenanthrylene and benzo[b]fluoranthene) contributed
a significant share of total PAH and are shown in Fig. 3.S2 in the Supporting Information Section.

![Graph showing light hydrocarbons and PAH yields vs furnace temperature]

**Figure 3.5.** Total yields of light hydrocarbons and total polycyclic aromatic hydrocarbons in the effluents of the primary furnace (left column) and the secondary furnace (right column) are plotted against furnace temperature and for all three fuels (C=coal, B=bagasse, C/B=blend with equal amount of volatile masses of coal and bagasse).

Similarly to the light hydrocarbons, PAH yields were the highest from bagasse and the lowest from the blend, with coal being rather closer to the values of the blend. In the case of PAH the effect of the secondary furnace was remarkably
effective in reducing their yields. The PAH emissions were also observed to decline with declining operating furnace temperatures. Finally, it is important to note that the blend consistently emitted less than the weighted sum of its constituents, at all furnace temperatures tested, indicating strong synergy in play.

3.4.3. Particulate Matter:
Total amount of particulate matter produced in this setup was determined with the help of fine filter papers located before each sampling stage. The amount of particulate matter trapped in the filter papers increased with the furnace temperature. The increasing trend of PM with temperature is consistent with the PAH trend. Also, the reduction in PAH is balanced with increased PM in the afterburner.
3.4.4. Desired Operating Conditions:
The blending of fuels clearly proves to be useful means of reducing harmful PAH, light hydrocarbon and CO emissions. The lower and, particularly, the higher ends of the temperature range indicated some elevations in the CO, light hydrocarbon and PAH yields. The preferable furnace temperature range appears to be in the range of 900°C to 950°C, in order to minimize emissions. Thus blending and moderate temperature range would be the best choice, based on the results obtained in this particular experimental setup and under the conditions outlined in this manuscript.
3.5 References:


[17]. Erlich C., Ohman M., Bjornbom E., Fransson T. H., Thermochemical characteristics of sugar cane bagasse pellets, Fuel 84 (2005) 569–575..


Figure 3.S1. Major individual constituents of Light Hydrocarbons emissions plotted against furnace temperature for Primary furnace (Left column) and Afterburner (Right column) and three different fuels (C=coal, B=bagasse, C/B=blend with equal amount of volatile masses of coal and bagasse).
Figure 3.S2. Total PAH consisted of summation of several hydrocarbons; few are represented individually, for primary furnace (Left column) and the afterburner (Right column) against furnace temperature for three different fuels (C=coal, B=bagasse, C/B=blend with equal amount of volatile masses of coal and bagasse).
Chapter 4

Conclusions

This thesis puts forward a detailed study of co-combustion of a high-volatile content bituminous coal and waste biomass in the form of sugarcane bagasse, conducted in atmospheric air. Co-firing of coal and biomass is gaining importance in the industry because of lower net CO2 emissions and has additional advantages of less emissions of NOx, SOx. The blending practices have faced problems such as increased ash depositions, fouling and corrosion rates. Bagasse, with low ash contents, is especially suitable to avoid these issues. Sugarcane bagasse is a process waste and its utilization in power generation doesn't put a toll on food production. Coal is the major source of electricity production in the world (40%) and in United States (50%) as well. Considering 11% recovery of dry bagasse from sugarcane processing, the world produced a total of 154 Mt of bagasse and 5370 Mt of coal in year 2006. Therefore a 3% (by weight) blending would have been possible in case of total utilization of all bagasse produced globally in coal fired power plants.

Characterization and quantification of major fixed gases, light hydrocarbons, semi-volatile polycyclic aromatic hydrocarbons (PAH) and particulate matter are reported for emissions from laboratory scale batch combustion in the Chapter 2. Five blends were tested at fixed furnace temperature of 1000°C, starting from neat coal with increasing proportion of bagasse in the blend, till neat bagsse. At the high heating-rate conditions used in this work, the fuel blends experienced synergistic combustion behavior during their volatile matter combustion phase. CO and PAH yields from the blends showed non-linear additivity, whereas CO2 and particulate yields were curtailed in linear proportion to amount of bagasse. Light hydrocarbons emissions from blends showed no clear trend.
Chapter 3 of the thesis investigates the effects of furnace temperature and staging of combustion on the blends. Combustion of the volatile matter of the blend resulted in lower yields of products of incomplete combustion (PIC), than combustion of its neat fuel constituents (coal and bagasse), suggesting synergistic behavior. Total CO$_2$ emissions from coal were the highest, whereas CO emissions from bagasse were the highest. Though carbon monoxide (CO) and unburned volatile and semi-volatile hydrocarbons from the coal and the blend did not exhibit a clear trend with temperature, such emissions from bagasse experienced increasing trends with temperature. The secondary stage typically reduced CO, light hydrocarbons and PAH by further oxidation of effluents coming from the primary furnace.

This work strongly supports blending of bagasse with coal. It is economical to substitute coal by weight, in order to maintain the power output of the furnace constant. Furnace temperature in vicinity of 900°C for staged combustion was observed to minimize the yields of major pollutants.