ESTIMATION OF LHV, RELEASED HEAT AND EXERGY OF A COMBUSTION REACTION OF SPENT COFFEE AND EUCALYPTUS WOOD CHIPS

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Abstract. This work presents a study about estimation of lower heat value, released heat and exergy for a process of biomass combustion composed by spent coffee and eucalyptus wood chips. Parameters of reaction as, spent and chip concentration in biomass blend, moisture, air excess and temperature of combustion products are presented. A thermodynamic modeling is proposed for the process, being presented the equations of LHV, released heat, air-fuel ratio and exergy. The influence of the reaction parameters on LHV, released heat, air-fuel ratio and exergy are presented and analyzed in a graphic form. It is expected that the results and conclusions of this work will assist in the biomass boiler operation.

Keywords: LHV, Exergy, Biomass, Combustion

1. INTRODUCTION

The use of waste from production processes is necessary for industries due to several factors such as: environmental issues, costs of waste allocation and mainly as a source of thermal energy (MACEDO, 2006). Similarly, the soluble coffee industry faces a problem such as the disposal of its main residue, the spent coffee. It is estimated that each ton of green coffee is generated 480 kg of sludge (CABRAL and MORIS, 2010).

One of the solutions found for the volume of tailings resulting from the process is the biomass boiler firing. Thus, by burning this residue, one can take advantage of the energy released by the combustion process to provide steam to the process.

In some facilities, inefficient use of generated steam or excess moisture in coffee production is necessary or complementary to another fuel to supply soluble coffee production (VIOTTO, 1991).

In this work, the combustion of the blend of spent coffee and eucalyptus wood chips (complementary fuel) is analyzed. Both the analysis of 1st and 2nd laws of thermodynamics of the combustion process of spent coffee are unusual.

A modeling (1st and 2nd laws of thermodynamics) of combustion process to obtain values of lower heat power (LHV), released heat and exergy are presented. Excess air, combustion temperature, blend ratio, and moisture are considered for obtaining analytical expressions.

2. MATHEMATICAL MODELLING

According to (Torrent et al., 2016), a complete combustion reaction of biomass using atmospheric air can be expressed by (Eq. 1):

\[ CH_yO_z + \delta(O_2 + 3.76N_2) \rightarrow CO_2 + \frac{\gamma}{2}H_2O + 3.76aN_2 \] (1)
where $C$, $H$, $O$, and $N$ are, respectively, carbon, hydrogen, oxygen and nitrogen, with the coefficients $y$, $z$, the ratios $H/C$ and $O/C$, and $\varepsilon$ can be obtained by (Eq. 2):

$$\varepsilon = 1 + \frac{y}{2}$$

(Keating, 2007) propose the reaction, (Eq. 3) for coal and other solid fuels:

$$n_C C_s + n_H H_2 + n_O O_2 + a(O_2 + 3.76N_2) \rightarrow bCO_2 + cH_2O + dN_2$$

where $C_s$, $H_2$, $O_2$, and $N_2$ are respectively solid carbon, hydrogen gas, oxygen gas and nitrogen gas; $n_C$, $n_H$, $n_O$, $a$, $b$, $c$, $d$ are the stoichiometric coefficients of the combustion reaction.

In order to identify the stoichiometric coefficients of the reaction it is necessary to perform the elemental analysis of the biomass (spent coffee and eucalyptus chips). In the analysis value are presented $C$(%), $H$(%), $O$(%), $N$(%) and $S$(%), where $N$ and $S$ are despicable in biomass.

Table 1 shows the elemental composition and physical-chemical characteristics in the dry base of the spent coffee and eucalyptus chips.

<table>
<thead>
<tr>
<th>Table 1 – Biomass characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spent Coffee$^{(1)}$</td>
</tr>
<tr>
<td>$C$(%)</td>
</tr>
<tr>
<td>$H$(%)</td>
</tr>
<tr>
<td>$O$(%)</td>
</tr>
<tr>
<td>Ash (%)</td>
</tr>
<tr>
<td>Moisture (%)$^*$</td>
</tr>
<tr>
<td>45</td>
</tr>
<tr>
<td>Eucalyptus Chips$^{(2)}$</td>
</tr>
<tr>
<td>$C$(%)</td>
</tr>
<tr>
<td>$H$(%)</td>
</tr>
<tr>
<td>$O$(%)</td>
</tr>
<tr>
<td>Ash (%)</td>
</tr>
<tr>
<td>Moisture (%)$^*$</td>
</tr>
<tr>
<td>45</td>
</tr>
</tbody>
</table>

(1) Silva et. Al., 1997
(2) Macedo, 2006
* Value adopted in this work.

Using Table 1, the stoichiometric coefficients of Eq. 3 can be obtained using the expressions given in Table 2:

<table>
<thead>
<tr>
<th>Table 2 – Stoichiometric coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition of moisture (kg)</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>Ash</td>
</tr>
<tr>
<td>Water</td>
</tr>
</tbody>
</table>

From the stoichiometric coefficients obtained in Table 2, it is possible to rewrite the combustion equation (Eq. 3) for a generic, ash-free biomass with moisture, Eq. (4):

$$n_C C_s + n_H H_2 + n_O O_2 + n_w H_2O + a(O_2 + 3.76N_2) \rightarrow bCO_2 + cH_2O + dN_2$$

Spent coffee and eucalyptus wood chips are burned at the same time, so it is necessary to rewrite Eq. 4 by adding the two biomasses and their respective proportions, Eq. (5):

$$\alpha(n_C C_s + n_H H_2 + n_O O_2 + n_w H_2O)_{SC} + \beta(n_C C_s + n_H H_2 + n_O O_2 + n_w H_2O)_{EC}$$

3Moran and Shapiro, 2006
where the indices S.C. e E.C. refers to the spent coffee and eucalyptus chips, and \( \beta \) are the biomass proportions in the reaction, being \( a, b, c \) and \( d \) determined by the stoichiometric balance of the reaction, where:

\[
a = \frac{[2b + c] - (2a n_{O,S.C} + a n_{O,E.C} + 2b n_{O,E.C} + b n_{O,E.C})]}{2}
\]

\[
b = a n_{C,S.C} + b n_{C,E.C}
\]

\[
c = \frac{(2a n_{H,S.C} + a n_{H,E.C} + 2b n_{H,E.C} + b n_{H,E.C})}{2}
\]

\[d = 3.76a\]

The excess air can be added to the combustion reaction; thus, it arrives at Eq. (6):

\[
\alpha(n_C + n_H H_2 + n_O O_2 + n_e H_2 O)_{S.C.} + \beta(n_C + n_H H_2 + n_O O_2 + n_e H_2 O)_{E.C.}
\]

\[\hspace{1cm} + \lambda a(O_2 + 3.76 N_2) \rightarrow \hspace{1cm} \nu CO_2 + \beta H_2 O + \gamma N_2 + h O_2\]  \hspace{1cm} (6)

being \( \lambda \) the excess of air, \( e, f, g \) and \( h \) are determined by the stoichiometric balance of the reaction, where:

\[
e = a n_{C,S.C} + b n_{C,E.C}
\]

\[
f = \frac{(2a n_{H,S.C} + a n_{H,E.C} + 2b n_{H,E.C} + b n_{H,E.C})}{2}
\]

\[g = 3.76a \lambda\]

\[h = \frac{(2a n_{H,S.C} + a n_{H,E.C} + 2b n_{H,E.C} + b n_{H,E.C}) + 2a \lambda - 2e - f}{2}\]

2.1 Energy Analysis

Applying the 1st Law of thermodynamics on combustion reaction (Eq. 7), it arrives:

\[
\dot{Q} = \sum_{\text{Prod}} \dot{n}_i [\overline{H}_f^o + \Delta \overline{h}_f] - \sum_{\text{React}} \dot{n}_j [\overline{H}_f^o + \Delta \overline{h}_f]
\]  \hspace{1cm} (7)

where \( \overline{H}_f^o \) is formation enthalpy of the element and \( \Delta \overline{h}_f \) is the enthalpy change of the element between the evaluated temperature and the reference temperature, \( \Delta \overline{h} = \overline{h}(T) - \overline{h}(T_0) \).

The heating value is one of the main thermochemical properties of a solid fuel having 2 variations higher heating value (HHV) and lower heating value (LHV). The LHV assumes that water produced by the reaction remains in the vapor phase, whereas the HHV considers that it is in the liquid phase, (Madanayake et al., 2017). The HHV can be calculated by impiral equation (Friedl et. al., 2005), Eq. 8:

\[
HHV = 0.51 C^2 - 232 C - 2230H - 51.2 \cdot H \cdot C + 131 N + 20600
\]  \hspace{1cm} (8)

However, eq. 8 is valid for values of elements in the dry base and without ash, thus it reaches Eq. 9:

\[
HHV = -3.55 \left( \frac{C \cdot 100}{100 - Ash} \right)^2 - 223 \left( \frac{C \cdot 100}{100 - Ash} \right) - 2230 \left( \frac{H \cdot 100}{100 - Ash} \right) - 51.2 \left( \frac{H \cdot 100}{100 - Ash} \right) + 131 \left( \frac{C \cdot 100}{100 - Ash} \right)
\]
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\[ +13\left(\frac{N}{100} - Ash\right) + 20600 \]  

To determine the LHV values of the moist biomass and used Eq. 10 (Rendeiro et al., 2008):

\[ LHV_w = (1 - w) \cdot (HHV) - \left(\frac{9 \cdot (1 - w)}{100} \cdot 2442.3\right) - w \cdot 2442.3 \]  

\[ LHV_{w,blend} \] can be calculated by Eq. 11 (Mehmood, 2012):

\[ LHV_{w,blend} = \alpha \cdot LHV_{S,C} + \beta \cdot LHV_{E,C} \]  

The heat released by the reaction can be calculated by Eq. 12:

\[
\dot{Q} = e [\Delta h]_{CO_2} + f [\Delta h]_{H_2O,g} + g [\Delta h]_{N_2} + h [\Delta h]_{O_2} - \beta [\Delta h]_{H_2O} + n_{H, E,C} [\Delta h]_{H_2} + n_{O, E,C} [\Delta h]_{O_2} + n_{w, E,C} [\Delta h]_{H_2O} \\
- \alpha [p_{C, S,C} [\Delta h]_{C} + n_{H, S,C} [\Delta h]_{H_2} + n_{O, S,C} [\Delta h]_{O_2} + n_{w, S,C} [\Delta h]_{H_2O}] - \lambda h [3.76 [\Delta h]_{N_2} + \lambda [\Delta h]_{O_2} + LH V_{w, blend}  
\]  

According to (Weston, 1992), often with solid fuels, the biomass enters the reaction at room temperature (reference temperature) while the products emerge at high temperatures reaction \( T \) and the air enter at temperature \( T_E \). Thus, Eq. 13 can be reduced to:

\[
\dot{Q} = -LHV_{w, blend} + e [\Delta h(T)]_{CO_2} + f [\Delta h(T)]_{H_2O,g} + g [\Delta h(T)]_{N_2} + h [\Delta h(T)]_{O_2} - \lambda h [3.76 [\Delta h(T)]_{N_2} + \lambda [\Delta h(T)]_{O_2}  
\]  

Using the JANAF thermochemical tables, presented by Keating, 2007, it is possible to create a polynomial for enthalpy and entropy as a function of reaction temperature. The polynomials below are valid for a temperature range of 500k to 2000k, being \( \Delta h = cal/gmole \) and \( \Delta s = cal/gmole \cdot K \):  

\[ \Delta h_{CO_2} = -6 \cdot 10^{-7} T^3 + 3.3 \cdot 10^{-3} T^2 + 8.15127 T - 2844 \]  

\[ \Delta s_{CO_2} = 122.982 \ln(T) - 76.152 \]  

\[ \Delta h_{H_2O} = 1.3 \cdot 10^{-3} T^2 + 7.1785 T - 2285.6 \]  

\[ \Delta s_{H_2O} = 10.095 \ln(T) - 54.636 \]  

\[ \Delta h_{N_2} = 5 \cdot 10^{-4} T^2 + 6.72997 T - 2107.2 \]  

\[ \Delta s_{N_2} = 7.8653 \ln(T) - 45.479 \]  

\[ \Delta h_{O_2} = 5 \cdot 10^{-3} T^2 + 7.34917 T - 2367.5 \]  

\[ \Delta s_{O_2} = 8.3444 \ln(T) - 48.349 \]  

2.2 Exergy Analysis

Using the second Law of Thermodynamics, the maximum available work that can be produced can be determined. Thus, exergy is the useful quantity that results from the interaction between the system or process and the environment that surrounds it (Dincer and Rosen, 2013). The flow of exergy can be divided, basically, into distinct parcels (Kotas, 1985):
\[ \dot{A} = \dot{A}_k + \dot{A}_p + \dot{A}_{ph} + \dot{A}_{ch} \] (22)

where \( \dot{A}_k \) is the kinetic exergy, \( \dot{A}_p \) is the potencial exergy, \( \dot{A}_{ph} \) is the physis exergy and \( \dot{A}_0 \) is the chemical exergy. The terms of kinetic and potential exergy can be neglected in this analysis.

### 2.2.1 Chemical Exergy

The chemical exergy charged by the spent coffee or wood chips can be calculated by the coefficient presented \( \lambda \) in Eq. 23 (Szargut et al., 1988).

\[
\varepsilon = \frac{1.042 + 0.2160 \left( \frac{H_u}{C_w} \right) - 0.2499 \left( \frac{O_u}{C_w} \right) \left[ 1 + 0.7884 \left( \frac{H_u}{C_w} \right) \right] + 0.0450 \left( \frac{N_u}{C_w} \right)}{1 - 0.3035 \left( \frac{O_u}{C_w} \right)}
\] (23)

Once calculated \( \varepsilon \) the chemical exergy of spent coffee or wood chips can be determined.

\[ A_{ch} = \varepsilon \cdot (2442 \cdot w + LHV_w) + w \cdot A_{H_2O} \] (24)

where \( A_{H_2O} \) is the chemical exergy of water.

The exergy of fuel can be calculated by Eq. 25:

\[ A_{ch,blend} = \alpha \cdot A_{ch,S.C.} + \beta \cdot A_{h,E.C.} \] (25)

For the calculation of the chemical exergy of the combustion gases it can use the Eq. 26.

\[ A_{ch,CG} = R \cdot T_0 \left[ e \cdot \ln \left( \frac{yCO_2}{yCO_2} \right) + f \cdot \ln \left( \frac{yH_2O}{yH_2O} \right) + g \cdot \ln \left( \frac{yN_2}{yN_2} \right) + h \cdot \ln \left( \frac{yO_2}{yO_2} \right) \right] \] (26)

where \( y \) is the molar fraction of the flue gases and \( ye \) is the molar fraction of the gases that make up the dead state (environment). Thus the calculation of the chemical exergy of the incoming air is negligible, since the air from the inlet has molar fractions similar to the dead state.

### 2.2.2 Physics Exergy

The physical exergy calculation is based on the difference of pressure and temperature between the object of analysis and the environment in which it is inserted, in this case the pressures are atmospheric, so physical exergy is referring to the temperature difference of the input and output components and the environment. As the fuel enters atmospheric pressure and ambient temperature the physical exergy of it is zero. Thus the physical exergy of the incoming air and flue gases can be calculated by Eqs. 27 and 28, respectively.

\[ A_{ph,air} = 3.73a^3L \Delta h(T_1)_{N_2,in} - T_0 \Delta s(T_1)_{N_2,in} + a \Delta h(T_1)_{O_2,in} - T_0 \Delta s(T_1)_{O_2,in} \] (27)

\[ A_{ph,CG} = e \Delta h(T_1)_{CO_2,in} - T_0 \Delta s(T_1)_{CO_2,in} + f \Delta h(T_1)_{H_2O,in} - T_0 \Delta s(T_1)_{H_2O,in} \] (28)

\[ + g \Delta h(T_1)_{N_2,in} - T_0 \Delta s(T_1)_{N_2,in} + h \Delta h(T_1)_{O_2,in} - T_0 \Delta s(T_1)_{O_2,in} \]

### 3. RESULTS

The parameters for construction of curves presented in this work are the following: \( a = 0.3 \), \( b = 0.7 \), \( \lambda = 1.05 \), \( T = 1300K \), \( w = 0.45 \) and \( T_e = 600K \). Figure 1 is presented \( LHV \) as function of moisture for various biomass blend. As moisture increases the \( LHV \) values decrease, increasing the spent coffee content in the blend increases the \( LHV \) values also increase.
Figure 1. LHV as function of the moisture, with various values of biomass blend.

Figure 2 (a) and Figure 2 (b) show the behavior of the heat released as a function of moisture, it can be verified that as moisture increases the heat released decreases. In Figure 2 (a) it is observed that values below 60% moisture the heat lost increases with the spent coffee content, whereas values above 60% moisture the lost heat decreases with the increase of the spent coffee content. With respect to excess air, its increase causes the decrease of the heat lost, Figure 2 (b).

Figure 3 (a) and Figure 3 (b) show the behavior of the enthalpy of the products as a function of the moisture, it can be verified that as the moisture increases the enthalpy of the products decreases. The increase in the content of spent coffee causes increased enthalpy of the products (Figure 3 (a)), as well as excess air (Figure 3 (b)). It can be noted that the released heat is reduced to zero (adiabatic flame temperature), which is dependent on reaction parameters, biomass

The behavior of the lost heat and the enthalpy of the combustion gases as a function of temperature are presented in Figure 4 (a) and 4 (b). It is found that the increase in temperature causes a decrease in the heat released while the enthalpy of the combustion gases increases. Analogously, the increase in the inlet temperature causes the enthalpy to increase.

An exergetic balance of combustion can be seen in Figures 5 (a) and 5 (b), it can be seen that the chemical exergy of the biomass blend is considerably higher than the physical exergy of the combustion gases, chemical exergy of the gases of combustion and physical exergy of the incoming air. It is observed that physical and chemical exergy decreases with increasing moisture, while increasing the temperature of the combustion chamber only causes an increase in the physical exergy of the combustion gases, the physical exergy of the incoming air does not depend on the temperature of the combustion chamber, but rather the air inlet temperature. In relation to the biomass blend, the higher the spent coffee content the higher the exergy of all components of the reaction.
Figure 3. (a) Enthalpy products as function of the moisture, with various values of biomass blend. (b) Enthalpy products as function of the moisture, with various values of air excess.

Figure 4. (a) Heat released products as function of the temperature, with various values of biomass blend. (b) Enthalpy products as function of the temperature, with various values of air excess.

Figure 4. (a) Exergetic balance of combustion reaction as function of the moisture, with various values of biomass blend. (b) Exergetic balance of combustion reaction as function of the temperature, with various values of moisture.
4. CONCLUSIONS

This work presents an estimate of LHV values, released heat and exergy of the combustion reaction of a biomass blend, in the case of spent coffee and eucalyptus chips. A model of the combustion reaction of the first and second Laws of thermodynamics is proposed, the parameters excess air, biomass composition, moisture and combustion temperature are analyzed in order to understand their effects on LHV, released heat and exergy (chemical and physical).

The modeling was based on the elemental analysis of the spent coffee and eucalyptus chips, thus, literature values are used to elaborate a complete combustion reaction with excess air. With this, analytical expressions are obtained for LHV, released heat, biomass exergy, exergy of the air intake and exergy of combustion gases, both chemical and physical.

It is expected that the proposed modeling and the results obtained could help in the understanding of the biomass combustion, mainly in the combustion of biomass blend, in the case of this work spent coffee and wood chips.

5. ACKNOWLEDGEMENTS

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6. REFERENCES


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