Benefits And Drawbacks of Energetic Valorisation of 
*Eucalyptus Globulus* Stumps by Thermochemical Processes

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In the pulp and paper industry in Iberian Peninsula there is an intensive use of *eucalyptus globulus* that has a fast growth and a high productivity. There are large areas of forest dedicated to its growth. After 9 to 12 year rotation cycles trees are cut and the stumps are left in the fields. After 2 or 3 harvesting cycles these tree stumps are removed from the fields and considered low value biomass wastes. This corresponds to depletion on organic matter and of valuable minerals related to soil fertility. The use of these biomass wastes in thermochemical conversion processes like gasification or combustion may be a valuable alternative solution as it allows taking profit of these wastes energetic content. The solid by-products obtained by thermal conversion (ashes) may be incorporated in soils to return the valuable minerals and to ensure a good forest management system.

Stumps removed from eucalyptus stands were used in combustion trials to improve the burning conditions and in gasification tests with different experimental conditions to obtain syngas suitable to be used in furnaces (chemical recover) of pulp industries. Stumps combustion and gasification processes were compared in terms of stumps energetic valorisation, gaseous emissions and gasification gas utilisation.

1. Introduction

*Eucalyptus globulus* has a fast growth and a high productivity and thus it is largely used in the pulp and paper industry in Iberian Peninsula. It is produced in 9 to 12 year rotation cycles, being the trees cut and the stumps left in the fields. However, after 2 or 3 harvesting cycles eucalyptus stumps are removed from the fields and considered low value biomass wastes. Several authors have studied the chemical and fuel properties of stumps and have found that they are suitable to produce energy in a profitable way (Pérez et al. 2006, Gominho et al. 2012). However, Anerud (2010) stated that the presence of excessive contaminants usually found in stumps could lead to high inorganic contents, reducing its value as fuel and causing operating problems during stumps valorisation by thermochemical processes. Despite stumps quality as a fuel, this author also analysed another important issue, the potential environment negative impacts due to stumps removal from the soil.

Eucalypt stumps energy content, encourages the study of theirs valorisation by combustion and/or gasification processes. Combustion and gasification of different biomass species is a well-known subject, however the consequences of using stumps are poorly studied. Eucalyptus combustion has been studied by several authors, however, the combustion of eucalyptus stumps may bring some challenges due to stumps particular mineral composition and properties. Smit and Meincken (2012) studied the performance of vine stumps combustion at lab scale. These authors reported that vine stumps were suited for domestic heating and cooking, though the performance of combustion process was worse when compared with wood pellets and charcoal.

Eriksson et al. (2012) co-gasified Scots pine stumps mixed with root biomass and observed that the gas obtained was similar to that produced by wood pellets gasification. However, due to high contents of stumps extractives, the material obtained after gridding was very sticky, which caused some difficulties during feeding
and gasification, Moilanen and Nasrullah (2011) studied the char gasification reactivity and ash sintering properties of stump chips and reported that stump chips had lower reactivity than other biomass feedstocks. Though the energy content of eucalyptus stumps encourages the study of their valorisation by combustion and/or gasification, these processes need to be further studied, as there are still some challenges. It is important to identify potential operation problems during combustion and gasification. The particular properties of stumps and their mineral matter that may contain alkaline elements like calcium, sodium, or potassium may lead to sintering and agglomeration, which would cause erosion and degradation of the combustor and gasifier building materials and difficult the overall performance of combustion and gasification. The results obtained during the study of the effect of experimental conditions on combustion and gasification are reported, focusing on energy conversion, gaseous emissions, gasification gas yield and quality.

2. Experimental Part

Eucalyptus stumps, whose proximate and elemental analysis are shown in Table 1 were gasified and burnt. Eucalyptus stumps ash content was present in low concentrations, similar to values found in forest residues. The main elements quantified were Si and Ca. The contents of Ca, Mg and P are rather higher than those found in Scots pine stump-root, Eriksson et al. (2012), however lower contents of K, Al, Mg, P, Fe and Na were quantified. Table 1. S, N and Cl contents in eucalyptus stumps were lower than those usually found in forestry biomass and in other eucalyptus stumps, Gominho et al. (2012).

Table 1: Eucalyptus stumps proximate and elemental analysis.

<table>
<thead>
<tr>
<th>Elemental Analysis (% daf)</th>
<th>Mineral Matter</th>
</tr>
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<tbody>
<tr>
<td>C</td>
<td>49.9</td>
</tr>
<tr>
<td>H</td>
<td>5.8</td>
</tr>
<tr>
<td>N</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>S</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>Cl</td>
<td>0.055</td>
</tr>
<tr>
<td>Ash</td>
<td>1.5</td>
</tr>
<tr>
<td>Moisture</td>
<td>24.1</td>
</tr>
<tr>
<td>HHV (MJ/kg daf)</td>
<td>22.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Proximate (% w) as received</th>
<th>% w/w (dry basis)</th>
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<tbody>
<tr>
<td>Na</td>
<td>0.037</td>
</tr>
<tr>
<td>Si</td>
<td>0.243</td>
</tr>
<tr>
<td>Mg</td>
<td>0.048</td>
</tr>
<tr>
<td>P</td>
<td>0.037</td>
</tr>
</tbody>
</table>

*a daf - dry and ash free basis*

Combustion and gasification tests were done in bench-scale fluidized bed reactors with an internal diameter of 0.8m and a total height of 1.5m, already described, Abelha et al. (2013). Both reactors had the possibility to be external heated, as they were placed inside electrical furnaces. Primary air was introduced at the bottom of the combustion reactor through a distributor plate located above the wind box and secondary air was fed inside the bed. All the runs were done at atmospheric pressure. Combustion temperature ranged from 650 to 800°C. Excess air varied between 10 and 40%. After the cyclone located at the top of the combustor, combustion gases were sampled to determine on-line the contents of O2, CO2, CO, N2O, NOx and SO2.

Air and steam were fed through a gas distributor at the bottom of the gasification reactor to achieve a good fluidisation inside the bed. Previous studies about the effect of steam/biomass ratio and of equivalent ratio (ER) led to the selection of steam/biomass ratio of around 1 and ER of about 0.2. Gasification temperature ranged from 750 to 900°C. Gasification gas was sampled after the cyclone for the determination of tar content according to CEN/TS 15439, using isopropanol (2-propanol). Though the presence of on-line CO and CO2 analysers for the control of the gasifier, gasification gas was also collected in bags to be analysed by gas chromatograph for the quantification of H2, CO, CO2, CH4, and other heavier hydrocarbons with 2, 3 or 4 carbon atoms, referred as CnHm. Though the low S and N contents of eucalyptus stumps, Table 1, gasification gas was also sampled to determine the contents of H2S and NH3, respectively by methods 11 and CTM-027 of EPA (Environmental Protection Agency).

3. Results Discussion

The main objective of this work was to study the energetic valorisation of eucalyptus stumps by combustion and gasification, thus the energetic conversion, $\eta$, calculated as the ratio between the gas energetic content and the energy content of the fuel (gas energy/fuel energy) was calculated for both processes. As expected, in
Figure 1 is observed that combustion led to lower energy conversions than those obtained with gasification for the same range of temperatures tested. The rise of temperature led to an increase in energetic conversion for both combustion and gasification. Thus, the highest value for combustion was obtained at 800ºC, being this value similar to that obtained for gasification at a lower temperature, 750ºC. For gasification the highest energetic conversion was obtained at 890ºC.

Figure 1: Effect of temperature on stumps energetic conversion by combustion and gasification.

According to Figure 1 data, eucalyptus stumps combustion should be done at 800ºC to achieve a high energy conversion. However, this criteria should not be the only one to select combustion temperature, as combustion gaseous emission were affected by combustion conditions, namely temperature and excess air and it is important to evaluate if combustion gaseous emission are in accordance with legislation. Hence in Figure 2 is presented the effect of excess air and temperature on the emissions of CO, SO2 and NOx during eucalyptus stumps combustion. The results presented refer to the bottom and top limits of combustion temperatures tested, 650 and 800ºC. Though only these two temperatures are shown in Figure 2, the same trends were also observed for the intermediate temperatures studied, though different concentrations were obtained.

The rise of excess air favoured CO oxidation to CO2 and thus there was a decrease in CO content. In Figure 2 is also observed a reduction in SO2 release. It could be expected that the increase of excess air would favour SO2 release, as observed for NOx emission, which rose when higher excess air contents were used, due to the promotion of oxidation reactions. However, SO2 formation and destruction is a complex issue, being affected by temperature and by inorganic compounds capable of retaining sulphur inside the bed. In fact, most of sulphur was retained in the solid phase, as conversions of Fuel-S to SO2 were below 15-20%. Though for temperatures lower than 800ºC the retention of SO2 via CaO formation is expected to be small and so is the Ca sulphating reaction, the presence of chlorine in the gas phase could have favoured the sulphur retention by Ca compounds. Other elements present in eucalyptus stumps inorganic matter like Na and K, might also have affected sulphur retention in the solid phase as alkali sulphates. The same tendencies were obtained for both 650 and 800ºC. For both temperatures there was a mild increase in NOx and both SO2 and CO decreased with the rise of excess air. However, at 800ºC the release of CO and SO2 was favoured as the increase of temperature promoted C and S release from biomass. It was also observed some NOx decrease for the temperature of 800ºC. These results are in good agreement with other obtained for other biomass species, Abelha et al. (2013).

Measured SO2 and NOx emissions were always below Portuguese legislation limits of 500 mg/m3 and 650 mg/m3, respectively. On the other hand, CO contents were only below the value of 500 mg/m3 imposed by legislation when excess air was around or higher than 30%. The selection of 650ºC for combustion temperature has the advantage of keeping the emissions of CO at low levels and at the same time of preventing bed sintering and agglomeration that may occur during long times of operation. The good operation of combustor during longer times and emissions and emissions in accordance with legislation is probably enough to justify the lower energetic conversion achieved at 650ºC.
Gasification is another viable option for the energetic valorisation of eucalyptus stumps, producing a versatile gas with several different utilisations: as a fuel and as raw material for chemical synthesis. Gasification enables the use of lower quality biomass, like stumps, as the optimisation of gasification process can decrease the environmental effects of their use in conventional combustion processes.

No operational problems were observed during eucalyptus stumps gasification in presence of air and steam. In Figure 3 is observed that the increase of temperature led to an increase in H₂ and to a decrease in hydrocarbons contents, especially CₙHₘ, because hydrocarbons were converted into CO and H₂ by cracking and reforming reactions promoted at higher temperatures, which also explains the increases in those gases observed in Figure 3. At higher temperatures CO conversion into H₂ and CO₂ is also expected to occur by
water gas shift reaction, which is in accordance with the rise observed in Figure 3 for H₂ and CO₂ contents and the milder increase in CO.

In Figure 4 may be observed that the rise of temperature allowed reducing tar content in syngas, as cracking and steam reforming reactions were favoured. Thus, syngas yield also increased. Data presented in Figure 4 refer to the total gas produced, which contained around 40 to 50% of N₂ due to the use of air. Because of this, only a mild effect was observed in gas yield. Due to the same reason, the diluting effect of N₂, no great changes were observed in gasification gas density and HHV (higher heating value). In fact the gas produced presented a low HHV, being considered as a poor quality gas, suitable neither for transportation nor for more demanding utilisations, but suitable for instance for local uses in boilers or furnaces. A better quality gas would be produced if instead of air, oxygen or air enriched in oxygen has been used. These results agree with those published for other biomass species, Abelha et al. (2013) and Pinto et al. (2008).

The results presented in Figures 3 and 4 showed that the eucalyptus stumps gasification temperature should be around 850-900ºC, for ER about 0.2 and steam/biomass of around 1, as a better gas quality with lower tar content was obtained. The highest energetic conversion was also obtained for this range of temperatures, Figure 1. For the selected gasification conditions H₂S and NH₃ contents were within the values imposed by most utilisations (boilers, engines and turbines), which is not surprising due to the dilution effect of N₂ and the low S and N contents in eucalyptus stumps. However, as mentioned before, the high N₂ contents prevent the use of this gasification gas in utilisations either than boilers or furnaces. On the other hand, the use of such high temperatures during gasification may lead to some bed agglomeration during long operation periods, having in mind stumps mineral matter presented in Table 1. So far such problems were not observed, but this subject needs to be further studied in future work.

4. Conclusions

The results observed so far showed that both combustion and gasification are viable options for the energetic valorisation of eucalyptus stumps. For combustion an excess air of at least 30% should be selected and the temperature should be kept around 650ºC, though lower energetic conversions were obtained, to prevent fouling and slagging and eventual agglomeration of combustion bed and consequent stops for cleaning or repairing.

Gasification led to higher energetic conversions than those obtained with combustion for the same range of temperatures tested. Gasification has also the advantage of being a less pollutant and more efficient technology, producing a clean fuel gas that may be burned without the potential problems mentioned before.
for stumps combustion. The main gasification drawback is the fact that it is not yet a fully proven technology at commercial scale when applied to wastes such as stumps. The results obtained so far led to the following conditions for air-blown gasification of eucalyptus stumps: temperature around 850-900ºC, ER about 0.2 and steam/biomass about 1, as high energetic conversions and suitable gas quality were obtained. These results can be applied in various regions of the world, being not limited only to the country of eucalyptus stumps origin.

Besides the comparison of combustion and gasification processes in terms of stumps energetic valorisation and gaseous emissions, other issues need to be evaluated before the selection of one of those technologies, namely the characterisation of solid by-products produced by combustion and gasification of eucalyptus stumps to determine the contents of unconverted carbon and the composition of mineral fraction in terms of major oxides such as: Ca, Fe, Mg, Na, K and P. This information is important to evaluate the impact of these solids incorporation in the soil to decrease soils depletion by stumps removal from the fields, these are the objectives of future research work.

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References