GASIFICATION STUDY OF CYNARA CARDUNCULUS TO PRODUCE HYDROGEN RICH GAS

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ABSTRACT: The need to substitute fossil fuel feedstocks with endogeneous biomass to produce energy with lower environmental impact makes necessary to develop innovative and technologically more advanced processes for energy production. Gasification of Cynara cardunculus L. (cardoon) alone and mixed with Eucalyptus was carried out in a bench scale fluidized bed gasifier to study the influence of operating parameters that could lead to a gas rich in hydrogen. The gasification tests were carried out using a mixture of oxygen and steam, as gasifying agent, to avoid the dilution effect of nitrogen that exists in air.

The effect of catalysts addition to the bed on gas composition was analyzed as well as the influence in the level of contaminants like H_2S, HCl, NH_3 and tars in the gas produced.

Steam and temperature had a positive effect by promoting the hydrogen production. The higher heating value of the gas produced was determined to be in the range 12 – 15 kJ/nm^3 in a dry-nitrogen-free basis.

Cardoon contains N, S and Cl which may give rise to problems during the gasification process and to the eventual use of the syngas produced. The results obtained showed that the presence of contaminants could be decreased through retention in the solid phase and by employing a condensation system to separate out pollutants in the liquid phase. This paper will fully present and discuss the results obtained with the gasification of cynara cardunculus and eucalyptus in a fluidized bed gasifier.

Keywords: gasification, fluidised bed, catalysts, cardoon

1 INTRODUCTION

In Portugal the abundance of forestry biomass is not sustainable and may not be enough to reach the targets established to decrease GHG emissions. Options to produce short rotation woody crops (SRWC) adapted to maritime climates include various species, such as: poplar and willow, among others. Cynara cardunculus L. is an herbaceous perennial plant of the Compositaea family that grows naturally in harsh habitat conditions with high temperatures and water shortage in summer, and then, unproductive and stony soils. C. cardunculus is a strong plant that endures the dry summer period with high biomass growths. Plant vegetative cycle begins by seed germination with the first rains after summer. During the winter it develops a leaf rosette. The stalk starts elongation in spring and the first capitula appear in June–July. During the summer, the aboveground part of the plant dries off and the underground part enters in dormancy until a new cycle begins with the leaf burst from the roots with the autumn rainfall [1].

The actual average production is 20 tons:ha per year, but 30–35 t:ha per year of dry material may be attained in the near future, corresponding to about 40% stalks 25% leaves, and 35% capitula [1]. The harvested biomass is practically dry, thus eliminating one of the disadvantages of agricultural or forestry biomass production for industrial uses, where high moisture levels affect transport, storage and conservation. The great productivity of C. cardunculus L. under hot summer temperatures and dryness makes it potentially interesting to regions with these ecological conditions, such as southern Europe.

The European Union countries have been involved in encouraging the use of renewable energies and the use of biomass and wastes for energy production, with the aim of reducing the dependency on imported fossil fuels and at the same time to reduce CO_2 emissions to prevent global warming, since growing new plants on a sustainable basis is believed to use up most of CO_2 released.

The use of biomass as an energy source is as old as the history of mankind. Wood was burned to provide heat at all times. The interest in the biomass gasification has started at the beginning of this century and many studies have been undertaken leading to the development of various types of gasification technologies. Despite its environmental and social benefits, the biomass use for energy is currently very limited, which is considerably lower than its potential. This is mainly due to higher fuel cost compared to the use of fossil fuels and to technological problems, particularly related to gasification. In fact, the outstanding issues are high cost collection, delivery and preparation of biomass, the efficient, reliable and economic removal of the tars from the gas, and the release of alkali metals from ashes. Nowadays, biomass gasification has been reconsidered thanks to the growing concern related to pollutants emissions from fossil fuel-fired installations and also due to the following reasons: technical progresses, positive contribution to energy balance, especially for developing countries, a net reduction in CO_2, SO_2 and heavy metals emissions, the potential use of agriculture and agro-industrial residues as well.

Biomass for energy purpose could be specifically produced in plantations, named energy crops or as in a present ongoing project short rotation woody crops (SRWC) and could overcome some of the drawbacks mentioned above related to a more intensive use of biomass for energy production.

Of the various energy conversion technologies that could be applied to fuels from energy crops with the aim of reducing their impact on the environment, one of the most promising appears to be gasification. The gaseous product obtained can be used either for energy or for chemical synthesis. However, it could contain undesirable components such as: heavy hydrocarbons, tar, solids and gaseous pollutants, which may have a direct bearing on its final end-use applications.

Several methods can be used to reduce the undesirable components, either by using gas cleaning systems or by minimising the release of such constituents during gasification by the addition of catalysts or sorbents.

Catalysts may be used in gasification processes to improve the quality of the product gas by cracking tar that result from incomplete gasification of pyrolysis products. Catalysts may also influence the composition of the product gas by reducing hydrocarbons contents or by changing the ratio of CO to H_2 to values more suitable for chemical synthesis.

Catalytic gasification has been studied by several authors, and there is a vast the number of publications about this subject in the literature [2-8].

The catalyst may be incorporated in the gasification reactor or could be used as a follow-up process [9]. Several catalysts have been studied: dolomite and other natural minerals, alkaline catalysts (LiCl, NaCl and KCl), Ni-based catalysts and precious metals. Dolomite has been much studied, because it is inexpensive and has proven to be a suitable for tar reduction. Corella et al. [4] reported tars reductions of about 80% in presence of dolomite and with suitable gasification conditions. Garcia et al. [6] and Pinto et al. [7] reported that the good performance of Ni and Mg based catalyst in tar destruction, which was higher than that of dolomite. Even better results may be obtained with precious metal catalysts, however, they high costs make them prohibitive to be used at industrial scale.

2 EXPERIMENTAL PART

The gasification runs were undertaken on a bench-scale atmospheric fluidised bed gasifier, presented in Figure 1. The gasifier is a bubbling fluidised bed reactor made of refractory steel, circular in cross-section with an inside diameter of 80 mm and a height of 1 500 mm and operates at atmospheric pressure. The gasifier is heated by an electrical furnace, which provides the heat for reactions. The gasifier has three independent heating zones which are controlled via PID.

The fuel is supplied to the gasifier above the bed by a continuous feeding system, composed of a set of two screw feeders and a variable speed motor. The controlling feeder discharges from the silo, is previously calibrated for the mixture to be studied, through an electronic frequency controller. The fuel in the silo is permanently agitated to facilitate discharge of solid fuel, by a mixer connected to the shaft of the screw through two cogwheels. The screw feeder connected to the gasifier rotates at a fixed and fast speed to avoid the pyrolysis of the feedstock during feeding. In order to avoid the clogging of the tube which could be caused by pyrolysis of the feedstock, prior to its entry to the gasifier the feeder is externally water cooled. A nitrogen flow is used to help the waste feeding and to avoid a back flow of the gas.

Temperature and pressure are measured in various points along the reactor.

The gas produced leaves the reactor, passing through a cyclone to remove particulates. Tar and condensable liquids carried away by the gas are removed in a quenching system, including a condenser, a liquid collector and two glass wool filters. Then, the gas passes through a paper filter prior to be injected into on-line CO and CO_2 analysers. The gas produced is also collected in bags to be analysed on a gas chromatograph to determine its composition, particularly H_2, CH_4, and other heavier hydrocarbons, whose total concentration is given as C_nH_m.

The operating conditions used in the experimental work carried out are presented in Table 1.

Figure 1: Bench-scale gasification set-up.

The results of laboratorial analyses performed with cynara cardunculus and eucalyptus samples are shown in Table 2, which lists the main characteristics: proximate and ultimate analyses, and higher heating value.

Table I: Operating conditions.

Experimental Parameter	Variation Range
Reaction temperature (ºC)	770 - 860
Freeboard temperature (ºC)	850
Flow rate of biomass (g/min)	≈5.0
Particle size of Cynara	Pellets
Particle size Eucalyptus (mm)	125 – 2.0
Flow rate of steam (g/min)	2.4 -5.0
Flow rate of oxygen (g/min)	0.72– 1.69
Equivalence ratio (w/w)	0.1 – 0.25
Steam / Biomass ratio (w/w)	0.4 – 1.0
Pressure	Atmospheric

The cardoon samples were prepared as pellets, prior to their use in the gasifier, due to its very low density and irregular form, which caused great difficulties of feeding it to the gasifier. All parts of cardoon were used, which includes stalks, leaves and capitula (with seeds).

Table II: Fuel analysis.

	Cynara	Eucalyptus
HHV (MJ/kg db)	18.84	17.12
Moisture (%)	13.1	9.8
Ash (% db)	6.2	2.1
Vol. Matter (% db)	76.9	87.0
Fixed Carbon (% db)	16.9	10.9
Carbon (% db)	49.3	52.6
Hydrogen (% db)	6.1	5.2
Nitrogen (% db)	1.7	0.3
Sulphur (% db)	0.29	0.07
Chlorine (% db)	0.47	0.01
Oxygen & errors (% db)	36.5	39.7
Al_2O_3 (% of ash)	0.80	0.32
CaO (% of ash)	10.4	49.3
Fe_2O_3 (% of ash)	1.16	5.20
K_2O (% of ash)	13.7	14.0
MgO (% of ash)	5.39	6.30
Na_2O (% of ash)	21.5	3.78
SiO_2 (% of ash)	15.5	1.30
P_2O_5 (% of ash)	1.92	2.40

Note: db - dry base

3 DISCUSSION OF RESULTS

The study included the influence of several gasification process variables as given below:

- Blends of cardoon with eucalyptus
- Temperature
- Equivalence Ratio, using oxygen
- Steam vapour ratio
- Use of catalysts

Each parameter effect was correlated with the following parameters:

- Composition of gasification gas
- Gasification parameters: Gas Production (GP); High Calorific Value (HCV); Energetic Conversion (EC)
- Sulphur Emissions: in the raw gas and in the gas after the condensation systems
- Chlorine emissions in the raw gas and in the gas after the condensation systems
- Tar Production
- Ammonia emissions: in the raw gas and in the gas after the condensation systems.

However, in this paper, only the results obtained regarding the effect of cardoon amount in the mixture composition, i.e., different amounts of cardoon and eucalyptus, as well as the influence of the use of catalysts, will be reported and analyzed. The results obtained with the variation of the other parameters, like steam, temperate, etc, will be discussed and reported in a future paper.

The gas composition is presented in a nitrogen and water vapour free basis. The values of C_nH_m presented correspond to the sum of the hydrocarbons with more than one carbon atom, such as: C_2H_4, C_2H_6, C_3H_8 , C_4H_{10}.

It was also calculated the gas yield, gas HHV and energy conversion. Gas yield corresponds to the quantity of dry gas without nitrogen, formed by each gram of biomass, in a dry ash free base. The high calorific value is the volumetric calorific value calculated also in the dry base without nitrogen. The energy conversion is the relation between the quantity of energy content in the gas (product of the gas flow by its calorific value) and the quantity of input energy in the fuel feed of biomass blends (product of fuel flow by its calorific value).

3.1 Influence of cardoon amount

Several fuels blends were tested with various amounts of eucalyptus added to cardoon to avoid bed agglomeration problems of the sand bed observed for were verified for the gasification of 100% cardoon. The influence of cardoon amount on the evolution of gas main components is presented in Fig. 2.

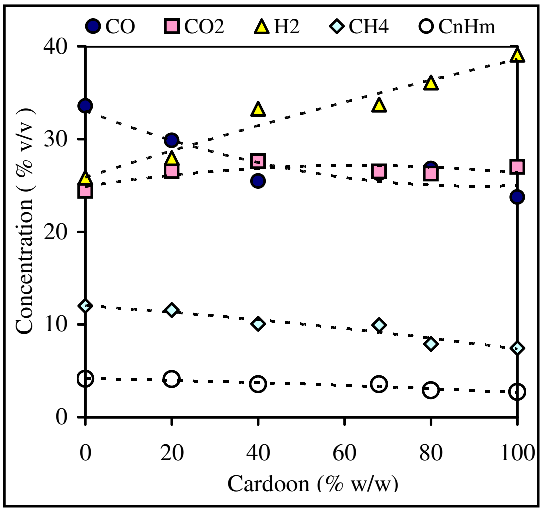

Figure 2: Effect of cardoon/eucalyptus mixture on gas composition. Other experimental conditions were: T = 830 ºC; ER = 0.1; r = 1.0 (daf); biomass flow rate = 5.0 g /min

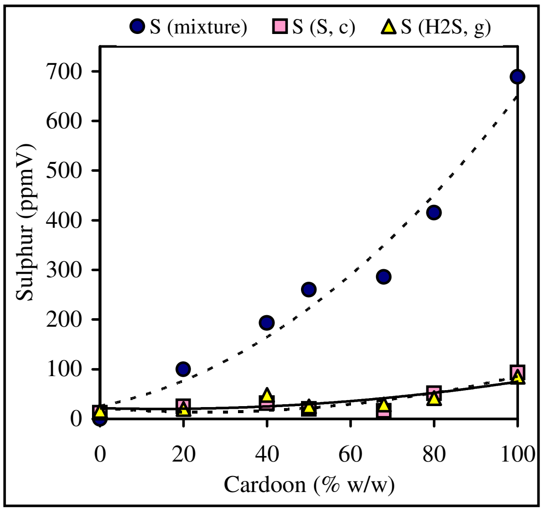

Figure 3: Effect of cardoon/eucalyptus mixture on gas composition. Other experimental conditions were: T = 830 ºC; ER = 0.1; r = 1.0 (daf); biomass flow rate = 5.0 g /min

The results showed that for higher cardoon fractions in the biomass blends, it is obtained a gaseous fuel with with higher hydrogen content and lower concentrations of hydrocarbons. The production of CO increases for very low amounts of cardoon. It may be concluded that, from the perspective of gas composition, cardoon has a beneficial effect, as it contributes to increase the production of H_2 and minimizes the production of CH_4, C_nH_m and CO.

Fig. 3 presents the influence of mixture composition in the variation of sulphur converted to the gas phase. S (S, c) is the sulphur species condensed in the quenching system and S (H_2S, g) is the H_2S in gas after passing the condenser.

The addition of cardoon increases H_2S in the gas and the S fraction condensed, as expected, which is due to the higher concentrations of sulphur present in the cardoon than in eucalyptus.

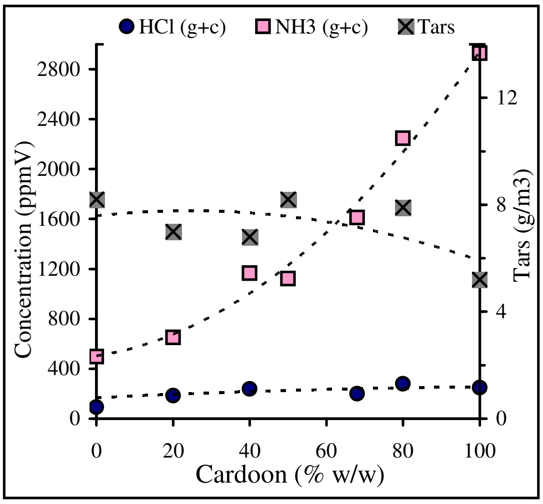

Figure 4: Effect of cardoon/eucalyptus mixture on chlorine, ammonia and tars emissions. Other experimental conditions were: T = 830 ºC; ER = 0.1; r = 1.0 (daf); biomass flow rate = 5.0 g /min

Practically, all the Cl remains in the liquid condensation systems as HCl. A much higher level of Cl was found in cardoon than in eucalyptus, which may explain the increase of the chlorine content, in the "raw" gas from mixtures of cardoon with eucalyptus.

Regarding tars, it is not possible to foresee a well defined tendency as a function of blends composition. However, in the test with 100% cardoon, a lower tar concentration was obtained (5.2 g/m^3). This value was even lower than those usually obtained during gasification of other biomass species in the same installation.

There is a clear increasing tendency of NH_3 emissions with the increase of cardoon share in the blends. This may be related with the fact that nitrogen content in cardoon is 6 times higher than that of eucalyptus. As mentioned before, almost all ammonia produced remains in the liquid phase of the gas cooling system. These results can be seen in Figure 4.

3.2 Influence of catalysts

Several tests were performed to evaluate the influence of using different catalyst in the production of tars and in the gas yields. The catalysts used were: dolomite, olivine and G72-D (a commercial Zn based catalyst). Dolomite and olivine were used as received and also in calcined form. Two different amounts of catalyst were tested, 15% and 30 % of the weight of the sand bed. In all the experimental runs, the operating conditions were the following: cardoon/eucalyptus = 50/50%; T = 830 ºC; ER = 0.1 daf; steam/biomass = 1.0 daf; biomass flow rate = 5.0 g/min.

The influence of the catalysts used on gas composition can be observed in Fig. 5.

The use of catalysts slightly increases the production of H_2 and CO_2 and decrease CO levels. Simultaneously, it appears that there is a slight decrease of CH_4 and other hydrocarbons. Although the small extent of such effects, the results obtained seem to point out, that utilization of these catalysts promotes the water gas shift reaction. In addition the results obtained show that there are no significant differences between the several catalysts relating to the gas composition

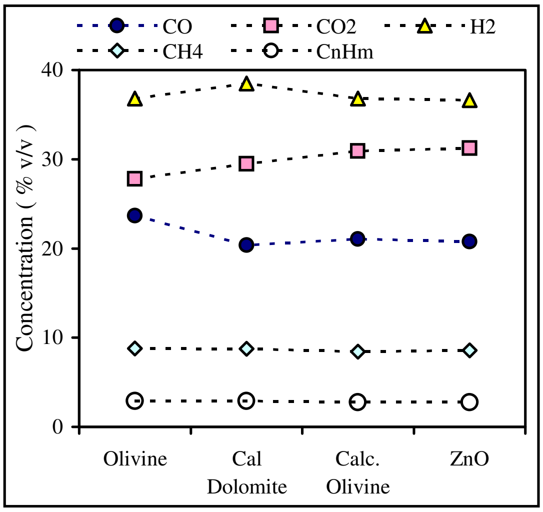

Figure 5: Effect of catalysts (15% w/w of bed) on gas composition.

In Fig. 6 it is presented the influence of different catalyst in sulphur released into the gas phase, as sulphur species condensed in the quenching system S (S, c) and remaining in the gas after passing the condenser as H_2S.

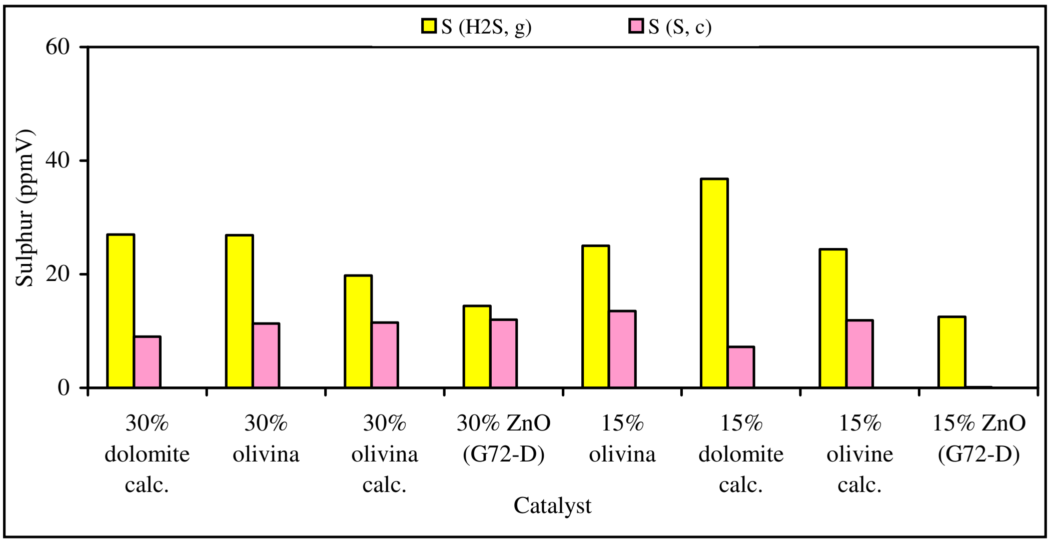

Figure 6: Effect of catalysts (15% w/w of bed) on sulphur emissions.

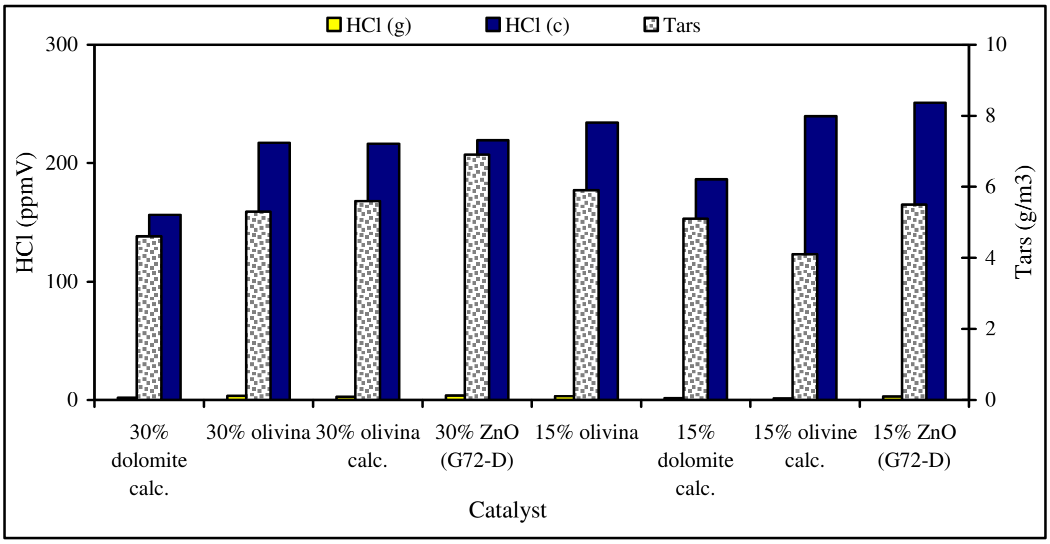

Figure 7: Effect of catalysts on chlorine and tars emissions.

The results obtained with different catalysts appear to show that the amounts of sulphur released to the gas phase are lower than that obtained in the absence of a catalyst. In fact, without catalysts the amount of sulphur retained in the condensate liquids was 25.4 ppmV, while the levels found when using several catalyst were all lower, ranging from 7 to 13.5 ppmV. As for the measured H_2S in the gas after the condensing system, the value found was 20.1 ppmV without catalyst, while in presence of catalysts the concentrations varied between 12.5 and 48.9 ppmV. It may be verified that the best results were achieved with the ZnO catalyst.

Catalyst utilization is also beneficial to control tar production. Tar concentration in absence of catalyst was around of 8.2 g/m^3, which was higher than the values found for the tests with catalyst. These values varied between 4.1 and 6.9 g/m^3 regardless the catalyst type, as can be seen in Figure 7. Tar reductions ranged from 15 to 50%. Reduction of tar content was more effective when using 15% of calcined olivine and calcined dolomite, giving tar reduction of about 50% and 45% respectively.

Regarding chlorine, very low levels were found in the gas exiting the condenser, between 1.4 and 3.8 ppmV, which is in agreement with previous results obtained in this system [8]. Higher values were obtained in the condensation system, which varied from 186 to 250 ppmV, but in similar order of magnitude as the values obtained for the test without catalyst (about 180 ppmV). Dolomite appears to be more effective in retaining Cl in the solid phase than other materials tested.

4 CONCLUSIONS

The utilization of cynara cardunculus as feedstock, in a pelletized form, has not found to give rise to any operational problems related with the feeding system.

However, it was observed some tendency of bed agglomeration, which could be attributed to the high content of alkali-earth metals in this biomass specie. This problem might be solved with the addition of dolomite to the bed or through blends of cardoon with other types of biomass, as e.g from forestry origin, as found in several tests following the observation of this tendency.

Addition of biomass species, like eucalyptus, to cardoon gasification, could bring environmental benefits by decreasing H_2S, NH_3 and HCl emissions.

Very small amounts of char were found in bed, which means that almost all cardoon were gasified. From the results obtained it may be concluded that the increase of cardoon share in fuel blend, as a beneficial effect on gas composition as it increases H_2 levels and decreases hydrocarbons and CO concentrations.

The use of different fuel blends appears to have no significant effect on tar levels, although it seems that cardoon alone presents a lower tendency to produce tar.

Utilization of different catalyst did not have much influence on gas composition. However, it may be concluded that, globally, the use of catalysts promotes the water gas shift reaction and appears to be effective for tar abatement, being olivine the most effective catalyst. However, dolomite was the most effective in reducing HCl release to gas phase and ZnO was the most effective in reducing presence of sulphur in the gas phase.

It was possible to control contaminants in the gas phase by adjusting some operating conditions such as temperature and oxygen flow. However, this procedure was not enough for the effective reduction of the levels of tar and hydrocarbons, demonstrating the need for further gas cleaning.

Steam and temperature had a positive effect on promoting hydrogen production. The addition of steam to the gasifier favoured the production of H_2 at the expense of CO, as well as it clearly decreased the level of tar, due to the greater importance of water gas shift reaction in presence of steam.

Cooling down of the gas using a water scrubber could be an interesting solution to retain NH_3 and HCl present in the raw gas produced.

5 ACKNOWLEDGEMENTS

The Authors are grateful to the FCT (Fundação para a Ciência e Tecnologia) for the financial support to do this research work through POCI-PPCDT/ENR/59323/2004 and PTDC/AGR-CFL/64500/2006.

6 REFERENCES

[1] Jorge Gominho, Jesus Fernandez, Helena Pereira, Industrial Crops and Products 13 (2001) pp. 1–10

[2] A. V. Bridgwater, Catalysis in thermal biomass conversion, Applied Catalysis A: General (1994) 116, 5-47.

[3] J. Gil, M.P. Aznar, M.-G. Caballero, J. Corella, Ind. Eng. Chem. Res. (1999) 38(11) 4226-4235.

[4] Corella J, Aznar MP, Gil J, Caballero MA., Energy and Fuels (1999) 13, 1122-1127.

[5] Corella J., Toledo J. M., Padilla R., Energy & Fuels (2004) 18, 3, 713-720.

[6] Garcia L., Benedicto A., Romeo E., Salvador M. L., Arauzo J., Bilbao R., Energy & Fuels (2002) 16, 5, 1222 – 1230.

[7] Pinto F, Lopes H, André R N, Gulyurtlu I, Cabrita I, Fuel (2007) 86, 2052-2063.

[8] Pinto F, Lopes H, André R N, Gulyurtlu I, Cabrita I., Fuel (2008) 87, 1050–1062.

[9] Pinto F, André R N, Franco C, Lopes H Gulyurtlu I, Cabrita I, Fuel (2009) doi:10.1016/j.fuel.2008.12.012.