CONVERSION OF OLIVE TREE PRUNINGS IN FLUIDIZED BED: EXPERIMENTS AND GASIFIER MODELING

Susanna Nilsson¹, Alberto Gómez-Barea^{1*}, Manuel Campoy¹, Guadalupe Pinna², Manuel Antonio Silva Perez², Pedro Ollero¹

¹Chemical and Environmental Engineering Department. Escuela Superior de Ingenieros (University of Seville) Camino de los Descubrimientos s/n. 41092 Seville (Spain)

*Corresponding author: Tel.: +34 954 487223; Fax: +34 954 461775; E-mail: agomezbarea@etsi.us.es

²Foundation Advanced Technological Centre for Renewable Energy (CTAER)

Paraje los Retamares S/N. 04200, Tabernas -Almería (Spain) Tel.: +34 950 10 45 46

ABSTRACT: Fuel conversion measurements were conducted in a laboratory fluidized bed (FB) to characterize the most important steps taking place a FB gasifier in the range of $800 \square 900$ °C. The main inputs for the gasifier model to be developed were obtained: product yields from devolatilization (light gas, tar and char) of olive tree pruning (OTP) and gasification kinetics of the produced char with CO_2 and H_2O . In the second part of this work, the obtained experimental data have been employed in a previously developed FB gasifier model to assess the gasification performance with OTP under various operating conditions. The effect of equivalence ratio, temperature of the feed gas, gasifier throughput, fuel moisture and ash content were analyzed. The main outputs from the model (bed temperature, gas composition, char conversion and gasification efficiency) are used to identify the optimal operation condition

Keywords: gasification, fluidized bed, biomass, agricultural residues, modeling

1 INTRODUCTION

Olive tree pruning (OTP) is an important biomass resource in the Mediterranean countries [1,2]. Its heating value and composition make it a suitable fuel for gasification applications. Devolatilization of OTP has been studied in TGA [1-3] and its gasification with air has been studied in fixed bed [2,3]. In this work the gasification of OTP in fluidized bed (FB) with different gasification agents has been modeled. Product yields from the devolatilization of this fuel and kinetics of gasification of the produced char with CO₂ and H₂O have been measured in a laboratory FB. The results from these tests are used as input in the model. Model simulations have been carried out using a previously developed model [4] to evaluate the gasification of OTP, by calculating gasification efficiency, char conversion and tar content in the product gas. Simulations have also been carried out to study the influence of variations in fuel composition and composition of the gasification agent.

2 EXPERIMENTAL

2.1 Experimental setup

Experiments have been carried out in a laboratory fluidized bed (FB) reactor. The experimental setup is represented in Fig. 1. The reactor is made of stainless steel. It has a preheating section, an FB section with 51 mm internal diameter and a freeboard section with 82 mm internal diameter. The reactor is surrounded by a 10 kW electrical oven, with two independent heating zones, one for the bottom bed and one for the freeboard, and is equipped with 4 thermocouples and two controllers, allowing the control of temperature in both zones.

 N_2 , CO_2 , CO and H_2 can be fed to the reactor using mass flow controllers and the flow of air fed is adjusted by a flowmeter. Steam was generated by vaporizing a fixed flow of water. The steam generated was mixed with the N_2 and the mixture was fed to the reactor. The flow of water was adjusted by a peristaltic pump, which was

calibrated before each test. At the exit of the reactor there is a cyclone for collecting any particles entrained from the reactor. After the cyclone there is a gas cleaning line consisting of a series of equipment where steam is condensed and tar is eliminated to protect the gas analyzer. During devolatilization experiments with tar measurements, all the gas coming from the reactor passed through a tar sampling line with six impingers with isopropylic alcohol kept at -20 °C, situated immediately after the cyclone. For continuous measurements of the composition of the exit gas, a Siemens analyzer was employed, using a non-dispersed infrared method for CO, CO₂ and CH₄ and thermal conductivity and paramagnetic methods for H₂ and O₂, respectively. Also a micro GC was employed to measure the concentrations of CO, CO₂, CH₄, H₂, N₂, C₂H₄, C₂H₆, C₂H₂ and C₃ in samples taken from the gas exit line.

2.2 Material

The fuel employed was olive tree pruning (OTP), which is a heterogeneous fuel containing both branches and leaves from olive trees. In order to enable small, but homogeneous samples, the OTP was ground to particle size below 0.5 mm. Pellets were prepared from the resulting material using a pelletizing machine. The pellets produced had a diameter of 6 mm. The proximate and elemental composition of the OTP employed is given in Table I. The bed material employed was bauxite with particle size between 250 and $500 \, \mu m$.

2.3 Operating conditions

The experiments were carried out at 800, 850 and 900 °C. The amount of OTP employed in each test was 3-8 g depending on the test temperature. The gas velocity employed was approximately 3 times the minimum fluidizing velocity of the bed material. Devolatilization was studied using N_2 as fluidizing gas. Tests with CO_2 - N_2 mixtures were carried out to study the gasification of char with CO_2 and H_2O - N_2 mixtures were employed to study the gasification with steam. CO_2 and steam concentrations in the range of 10-40% were studied. Also

steam gasification experiments with 5 and 10% H₂ were conducted to investigate the inhibition effect of H₂.

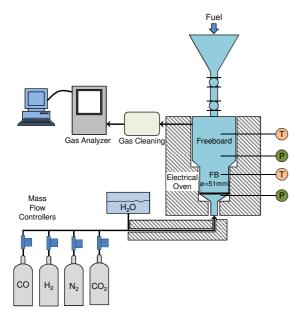


Figure 1: Experimental setup

Table I: Proximate and elemental composition of OTP

HHV (MJ/kg)	19,08	
Moisture (% as received)	8,11	
% drybasis		
Ash	4,95	
FixedCarbon	16,29	
Volátiles	78,76	
С	47,22	
Н	6,36	
N	0,99	
S	0,06	
0	40,42	

2.4 Experimental procedure

The procedure employed during the devolatilization experiments was as follows. Prior to the tests, the reactor was heated by setting the test temperature in the oven. During the heating period a continuous flow of air was fed. Once the desired temperature was reached, the fluidizing gas was switched to N₂ and when no more oxygen was detected by the analyzer, a batch of OTP was fed through a pipe that ends near the bed surface. When the CO, CO₂, CH₄ and H₂ concentrations measured by the gas analyzer were nearly zero, devolatilization was considered to be complete. Then the gas feed was switched to air in order to burn the remaining char.

During the char gasification tests, the char was generated in situ in the bed using the same procedure as in the devolatilization experiments. After the devolatilization was completed, the gas feed was switched to the desired gasification gas mixture. Gasification conditions were maintained until the concentrations of the product gases (CO, CO₂ and H₂) at the exit were close to zero and too low to allow accurate measurements. Afterwards the fluidizing gas was switched to air to burn the remaining char.

2.5 Data treatment

During the devolatilization experiments gas samples were taken at a location just before the gas analyzer. The samples were analyzed using a micro GC, measuring the concentrations of CO, CO₂, CH₄, H₂, N₂,C₂H₄, C₂H₆, C₂H₂ and C₃.The devolatilization stage lasted for 1-3 min depending on the test temperature and during this period seven gas samples were taken at different times. From the analysis of the different samples, data of concentrations of the light gas species at different times were obtained. In order to express the concentrations as a continuous function of time, the data were fitted using polynomial functions. The total yields of the different light gas species were calculated by integration over the complete time of devolatilization. The char yield was determined from the continuous measurements of CO2 and CO in the gas analyzer during the char combustion stage.

The liquid collected from the tar sampling train was analyzed by two different techniques: (1) solvent distillation for gravimetric tar determination (gravimetric tar) and (2) gas chromatography—mass spectrometry (GC–MS) for the quantification of 36 aromatic tars (from benzene to perylene).

During the char gasification experiments, the amount of char reacted up to a certain time was determined from the CO and CO_2 concentrations measured by the gas analyzer. The effect of gas mixing was taken into account to correct the gas concentrations measured during the char tests. Blank tests with CO_2 injection into the fluidized bed were performed to assess the effects of gas mixing in the exit line.

2.6 Experimental results

The yields of char, tar, light gas and water measured during the devolatilization of OTP at different temperatures are shown in Fig. 2.

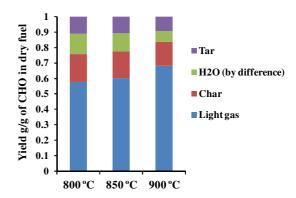


Figure 2: Distribution of products measured during the devolatilization of OTP at different temperatures

The temperature did not have a large effect on the total yield of tar, but affected its composition significantly. The gravimetric tar, that contains the most heavy tar compounds, decreased by almost 50% while the yield of aromatic tars increased almost 30%, when increasing the temperature from 800 to 900 °C. The major aromatic tars measured were benzene, toluene and naphthalene. The yields of benzene and naphthalene increased with temperature, while the toluene decreased.

The composition of the light gas at different temperatures is given in Fig. 3.

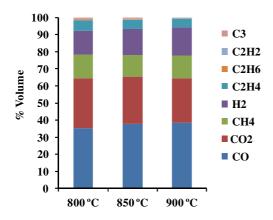


Figure 3: Composition of the light gas obtained during devolatilization of OTP at different temperatures

The yields of char, tar, water and different light gas species were fitted to a quadratic function of temperature, to be employed in the model. This type of expression gave good fit for all the experimental yields.

The rates of gasification of char with CO_2 and steam were expressed using n^{th} -order kinetics. The following expression was employed for CO_2 :

$$r_{co_2} = k P_{co_2}^n F(x) \tag{1}$$

For the gasification with steam, also the inhibition caused by H_2 was considered:

$$r_{H_2O} = kP_{H_2O}^n \left(1 - P_{H_2}\right)^m F(x) \tag{2}$$

F(x) is a function that expresses the variations of the reaction rate with char conversion, x. F(x) was expressed using the random pore model [5] and the same expression of F(x) could be used for both the gasification with CO_2 and steam. It was found that the experimental data were well represented by the kinetics expressions for gasification with CO_2 and steam (Eqs (1) and (2)).

3 MODEL

3.1 Model description

The model employed has been described in detail elsewhere [4]. The inputs used by the model are: proximate and elemental analysis of the fuel and its HHV, gasifier geometry: diameter and length of the fluidized bed and freeboard sections, properties of the bed material (density and size), feed rates of fuel and gasifying agent and the composition of the gasifying agent. The model also employs the experimental data presented in the Experimental section, including devolatilization yields and composition of the light gas as a function of temperature and the kinetics of char gasification as a function of gas composition, temperature and char conversion. The model employs a fluid dynamics submodel to estimate the suspension density of the bed in the bed and freeboard zones. It takes into account attrition and fragmentation of particles during calculation of char conversion. Distribution of char conversion in the bed and freeboard are calculated taking

into account the residence time of char particles. The temperature in the gasifier and the composition of the gas are calculated using energy and mass balances, kinetic models and equilibrium calculations.

3.2 Model results

Simulations were carried out to calculate the optimal operating conditions and to evaluate the effect of variations in the ash and moisture contents of the fuel and variations of its HHV. Also the effects of preheating of the fluidizing gas and the usage of enriched air instead of air have been evaluated.

As an example of the results, Fig. 4 shows the cold gas efficiency as a function of temperature, for the gasification with air. Different gasification temperatures are achieved by varying the equivalence ratio i.e. varying the feed rate of air for a fixed rate of fuel.

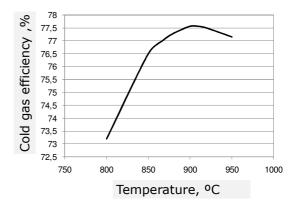


Figure 4: Cold gas efficiency as a function of temperature calculated from the model for the gasification of OTP with air.

The results indicate that the optimal operating temperature is close to 900 °C. The cold gas efficiency is a consequence of the char conversion in the bed, as well as the amount of volatiles burnt by the air fed, which is a direct function of the equivalence ratio. The results from the simulations carried out at different temperatures indicate that the char conversion is mainly a function of the operating temperature. The variations in gas composition between different simulations have shown to have small effects on the char conversion.

Table II shows the operating parameters and results from the model calculations for the gasification with air at $850~^{\circ}\text{C}$ and for an OTP feed rate of 660~kg/h (ER=0,35).

The simulations carried out varying the composition of the fuel have shown that small variations of the moisture content, ash content or HHV of the fuel influence significantly the gasification efficiency and gas quality.

Table II: Results from the simulation of gasification of OTP with air at 850 °C.

ER	0.357
Product gas flow (Nm ³ _{dry gas} /h)	1528
CO (%v/v, dry gas)	20.18
H ₂ (%v/v, dry gas)	15.37
CO ₂ (%v/v, dry gas)	10.72
CH ₄ (%v/v, dry gas)	2.37
$N_2(\%v/v, dry gas)$	51.27
H ₂ O (%v/v, dry gas))	10.93
Tar (g/Nm³, dry gas)	2.70
LHV gas (MJ/Nm ³ , without tar)	5.06
Bottom discharged solids (kg/h)	17.9
Fly ash elutriated (kg/h))	22.4
C in flyash (%)	25.5
Carbonconversion(%)	96.4
Charconversion(%)	89.5
Cold gas efficiency (%)	72.2

4 CONCLUSIONS

The gasification of olive tree pruning in fluidized bed has been studied, both by experiments and modeling. Devolatilization experiments provided results of product yields and composition of light gas and tar at different temperatures. Char gasification experiments resulted in kinetic expressions for the gasification reactions with CO₂ and H₂O as a function of gas composition, temperature and char conversion. The experimental data have been employed in a gasifier model to simulate the gasification of olive tree pruning in fluidized bed, and to evaluate the influence of operation conditions such as equivalence ratio, fuel composition, preheating of the fluidizing gas and the use of enriched air.

5 NOMENCLATURE

F(x) Function that expresses the variation of reactivity with char conversion, -

 p_{CO2} Partial pressure of CO₂ in the feed gas, bar p_{H2O} Partial pressure of H₂O in the feed gas, bar p_{CO} Partial pressure of CO in the feed gas, bar Partial pressure of H₂ in the feed gas, bar

x Char conversion, -

Abbreviations

OTP Olive tree pruning FB Fluidized bed

ER Equivalence ratio, kg O₂/kg O₂ for complete oxidation of the fuel

6 REFERENCES

- [1] M. Lapuerta, J.J. Hernández, J. Rodríguez, Biomass and Bioenergy Vol 31 (2007) pag. 13.
- [2] V. Skoulou, A. Zabaniotou, G. Stavropoulos, G. Sakelaropoulos, Int J Hydrogen Energ Vol 33 (2008) pag. 1185.
- [3] O. Ioannidou, C.G. Jung, A. Zabaniotou, Catal

- Today Vol 167 (2011) pag. 129.
- [4] A. Gómez-Barea, B. Leckner, Fuel Vol 107 (2013) pag. 419.
- [5] S. K. Bhatia, D. D. Perlmutter, AIChE Journal Vol 26 (1980) pag. 379.

7 ACKNOWLEDGEMENT

The financing help of Foundation Advanced Technological Centre for Renewable Energy (CTAER) in the project PI-0918/2012 is acknowledged. The experimental work made by Manuela Barragán is acknowledged.