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Gasification of Olive Wastes under Different Atmospheres. Part I. Olive Powder

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Abstract: *A greater production of renewable energy is required based on the imminent depletion of fossil fuels and the environmental problems arising from their misuse. Biomass is in a privileged position due to numerous advantages such as decentralization, the potential of using agro-industrial waste, zero balance of* CO_2 *and the possibility of creating jobs in rural areas.*

Gasification processes of olive residue from the production of olive oil using air and steam at different temperature were carried out. The composition of the gas produced and its heating value are reported.

Based on the results the predominant chemical route and optimal gasification conditions were identified. A feasibility study focused on the design of a pilot scale gasification plant was performed.

Keywords: *Gasification, olive residue, renewable energy.*

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I. Introduction

This fact has been demonstrated in previous papers in which the techniques was applied to reactions of olive pits (Luna et al. 2017)

As we know, fossil fuels are exhaustible raw materials and reserves are decreasing fast due to uncontrolled consumption. Not surprisingly, the IEA [1], after assessing in detail the global reserves, has found that they have reached their maximum production point. The problem of lack of reserves must be added the environmental problem due to their consumption, derived from the massive emission of greenhouse gases into the atmosphere. Moreover, geopolitical conflicts that carry energy dependence are apparent every day, and need action that will diversify the energy sources and give greater participation to renewable energy.

Including biomass stands out for its well-known advantages:

- It is a renewable source of energy and its use does not contribute to accelerate global warming; in fact, it reduces carbon dioxide and waste conversion processes.
- The replacement of petroleum, help to mitigate the greenhouse effect and pollution.
- The bio-fuels contain negligible levels of sulfur and nitrogen and the emissions do not contribute to cause "acid rain", or emission of sulfur and nitrogen oxides.
- The conversion of forest, agricultural and urban waste for power generation significantly reduces the problems derived from management of these wastes.
- Biomass is a local resource that is not subject to fluctuations in energy prices, caused by changes in the international market of fuel imports.
- The use of biomass resources can stimulate rural economies, creating more job options and reducing economic pressures on agricultural and forestry production.

Among the thermochemical conversion processes biomass gasification is characterized by retaining much of the energy content of the starting material in the form of synthesis gas, while pyrolysis results in a charcoal with a high carbon content, being gases generally of lesser interest. Depending on the subsequent application given to the fuel produced, one process or the other may be selected.

In this paper we describe comparatively the results obtained during the thermal treatment of waste from the extraction of olive oil, changing the atmosphere (inert and oxidant, provided in the latter case by air or steam). The influence of experimental conditions on the composition of the gas generated in processes, its heating value, and carbon and energy yields are studied. In all cases the temperature of 900°C was used, based on previous experiences from gasification with steam, which showed that temperature was optimal for the production of H_2 and CO in the resulting gas [2-3].

II. Materials and Experimental Methods

RAW MATERIAL

As starting material olive pulpe and skin (powder), ground to a particle size of 0,5 mm was used. This material was provided by the Finca la Orden (Guadajira, Badajoz). The elemental and immediate analyses were performed according to the relevant technical standards [4].

III. Eexperimental Method And Materials

The experimental apparatus used for testing pyrolysis and gasification has been described in detail in previous work [3]. Basically it consists of the following constituents:

1. Gases: Commercial N_2 (> 95% w/w) and air (taken from the environment, by means of a compressor), were used. The steam was generated by passing water through a coil introduced into an electric furnace. By a peristaltic pump (Masterflex) a known volume of water contained in a glass vessel is propelled. The oven temperature charge of producing water vapor was maintained around 300 ° C.
2. Heating System and temperature control: It consists of a cylindrical furnace within which is housed the reactor which reaches temperatures up to 1200 ° C. A temperature control system to determine the working conditions thereof, as well as the determination of the temperature. Said furnace (CI ElectronincsTF / 3 / IZ / F / 240 V) is made of ceramic material, provided with resistors and lined sheet, and has the following dimensions: 20 cm length, 4.4 cm internal diameter and 22 cm outside diameter.
3. Reactor: It consists of a cylindrical stainless steel reactor provided with a mesh basket hanging from a stainless steel wire and can be moved along the tube. The dimensions thereof are as follows: 75 cm long, 4 cm internal diameter and 4.3 cm outer diameter. Laterally an entry for the feed gas (in this case, N_2), and in the bottom of the reactor there is an outlet for gases and condensable products.
4. Gases and tars were condensed in a series of cold traps. The gas fraction, mainly composed of H_2, CO, CO_2 and CH_4, was analysed chromatographically with a 4000 HRGCKonik gas chromatograph provided with a thermal conductivity detector and a double injector connected to two columns: a 4.5 m stainless steel column (2.1 mm ID) packed with Carboxen 1000 of 60/80 mesh, and a 3 m stainless steel column (2.1 mm ID) packed with Porapak Q of 100/120 mesh. Helium and nitrogen were used as carrier gases respectively.

In addition to the determination of the molar production of gas and the calorific value, the value of YC (carbon yield), defined as the ratio of moles of carbon of the gas generated and those of initial biomass were calculated.

IV. Resultas And Discusión

Gases composition (H_2, CO, CH_4 and CO_2) for experiments carried out at 900°C are shown in Figure 1. Important differences for each process can be observed.

During thermal decomposition of biomass, and depending on the specific atmosphere and the conditions of pressure and temperature, different thermo dynamical balances occur, among which the following may be highlighted [5-7]: a) reactions of partial and total oxidation with oxygen in the air (Eqs. 1 and 2), b) Bourdouard reaction (3), steam reactions (4,5), reaction hydro gasification reaction(6), and reforming of methane (7).

$$C + \tfrac{1}{2}O_2 \leftrightarrow CO \qquad \Delta H= -123\ MJ\ kmol-1\ (1)$$
$$C + O_2 \leftrightarrow CO_2 \qquad \Delta H= -406\ MJ\ kmol-1\ (2)$$
$$C + CO_2 \leftrightarrow 2CO \qquad \Delta H= +172\ MJ\ kmol-1\ (3)$$
$$C + H_2O \leftrightarrow CO + H_2 \qquad \Delta H= +131\ MJ\ kmol-1\ (4)$$
$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H= -41\ MJ\ kmol-1 \quad (5)$$
$$C + 2H_2 \leftrightarrow CH4 \qquad \Delta H= -75\ MJ\ kmol-1\ (6)$$
$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H= 206\ MJ\ kmol-1\ (7)$$

The reaction enthalpies are given in standard conditions (298 K; 1,013 bar); taking the enthalpy of formation of carbon 12.5 kJ mol^{-1}.

From Figure 1, it is evident that the atmosphere plays an important role in the profiles and consequently in the composition of the generated gas. First, based on the concentration pattern it can be seen that in general during the pyrolysis process, gas production is reduced.

Usually in the early stages of the process; methane is generated along a more extended period, different from that found in previous experiences [7] (in any case, concentrations are very low). In the gasification with water vapor, is particularly remarkable high values of H_2 and CO_2 concentration, which indicate a clear contribution of water balances and water gas shift.

The concentration profiles of CO, are higher in the case of air, probably because there is in this case a source of formation of this gas (partial combustion and Bouduard reaction, the latter especially present at this temperature). The participation of the latter balance can be related to the high profile of CH_4 found with this agent.

Based on the values of molar production (Figure 2), it is clear that steam gasification is the most interesting. The high velocity of gas generation corresponding to these reactions compared with the other, makes moles accumulated values much higher with this agent than those with oxygen or inert atmosphere.

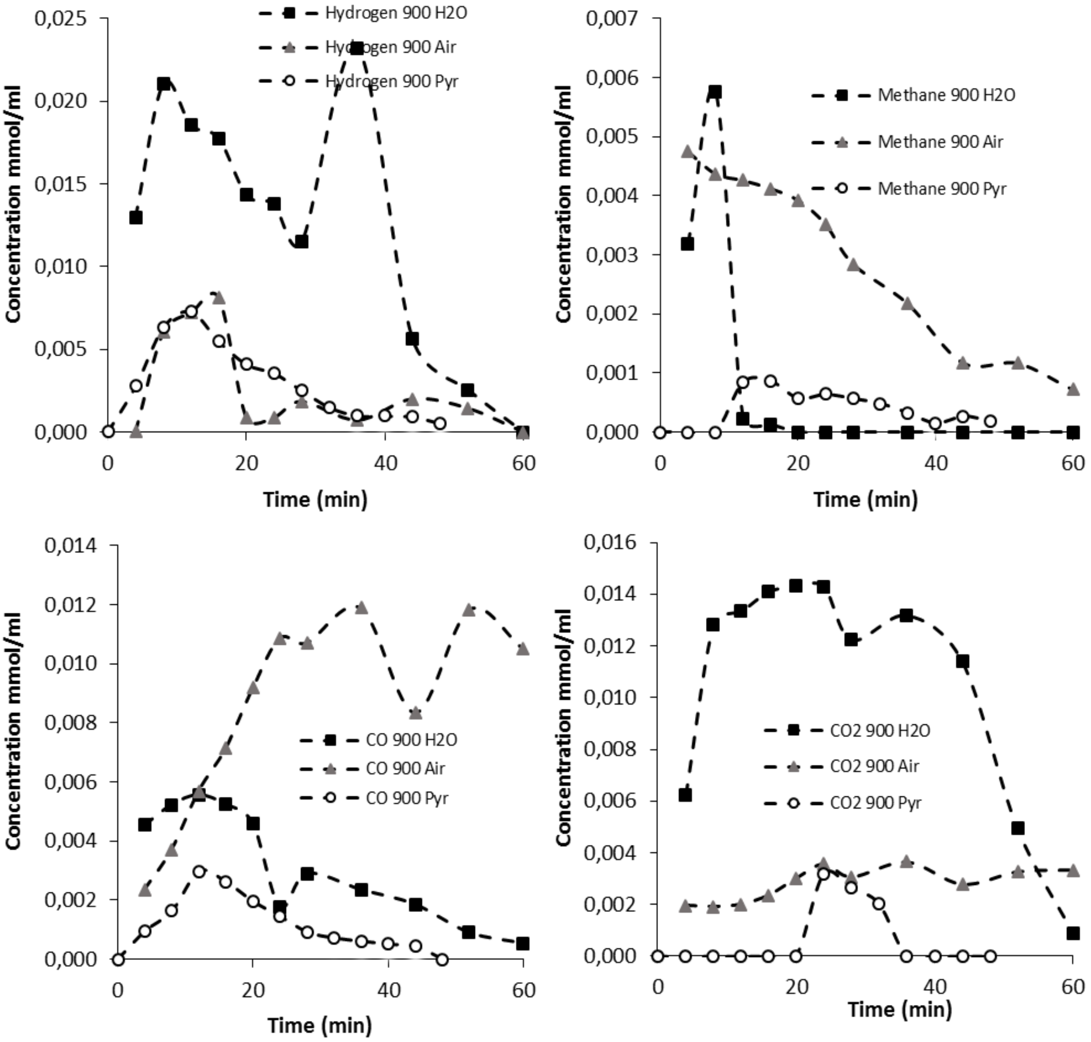

Fig. 1Concentration of gases (mol L-1) vs. time (min)

Finally, in Table 1 the molar fractions obtained for each case, LHV and carbon yields are shown. For example, if a high calorific value gas is required, it will be more interesting to perform a gasification using steam where values of 1140,94 kcal m^3N are achieved, in agreement with values reported in other works.

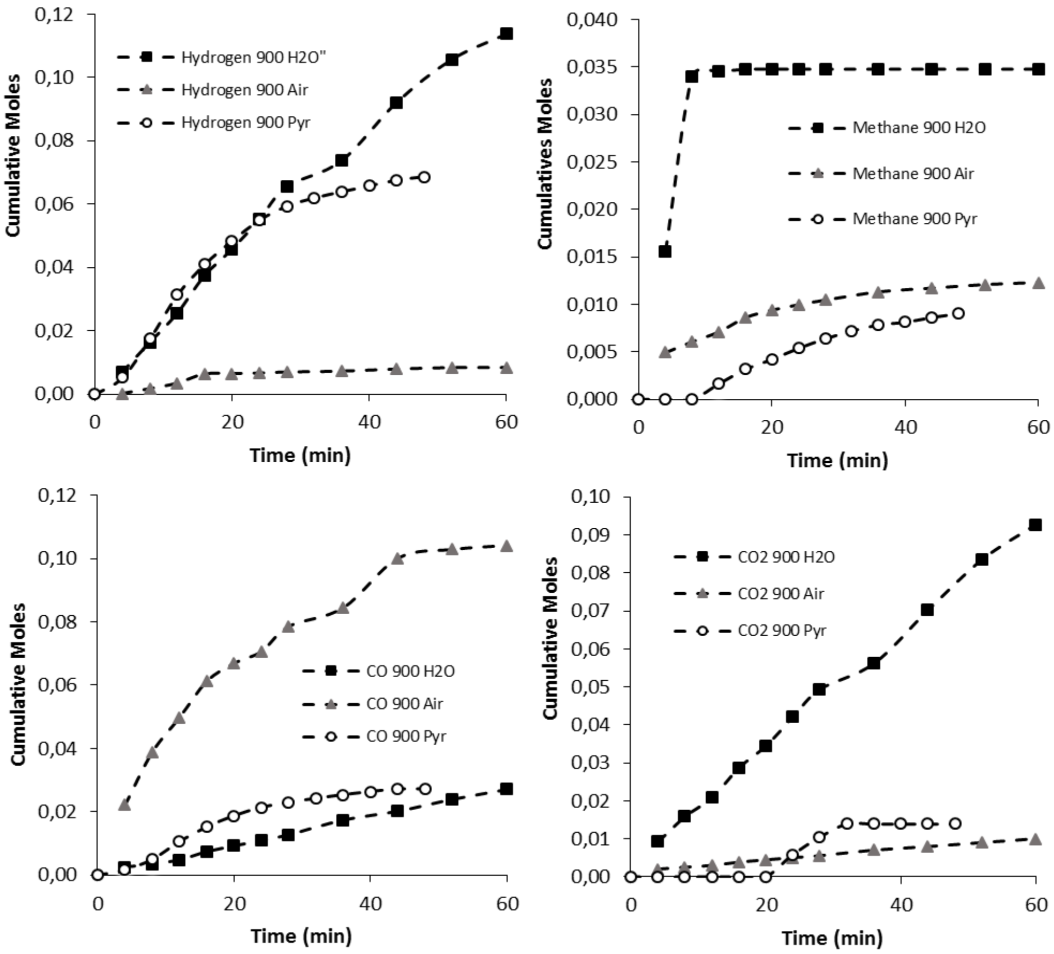

Fig. 2. Cumulative amount of generated gases (mol).

Table 1. Molar Fractions, lower heating value (LHV) and carbon performance.

	MOLE FRACTION (%)				**LHV (kcal/m^3 N))**	**CY (%)**
	H_2	**CO**	**CH_4**	**CO_2**		
PYR	6,86	7,72	0,90	1,39	688,15	3,43
AIR	4,33	6,45	5,60	11,77	1081,72	0,0022
STEAM	27,79	4,52	7,28	24,88	1140,94	13,15

If the object is to produce a gas stream rich in hydrogen it will obviously be more interesting gasification with steam, despite the additional cost to be taken into account due to the vaporization of water. Pyrolysis is the route looking for lower gas production and increased performance of the solid phase.

V. Conclusiones And Final Considerativos

The atmosphere is a definite variable in gasification of olive powder. Water vapor is by far the agent that allows a gas with a higher amount of H_2, because of the prominence of the balance water-gas and water gas shift. In this case, the lower proportion of methane, possibly due to the participation of methane reforming reaction, causes the LHV being lower. In the case of gasification with air, high calorific value gases are obtained, fundamentally due to the contribution of methane.

The pyrolysis process gives low carbon yield and gas generation is located almost in the initial period.

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