Research Article

Synthesis gas production from various biomass feedstocks

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Abstract: The decomposition of five different biomass samples was studied in a horizontal laboratory reactor. The samples consisted of esparto grass, straw, Posidonea Oceanic seaweed, waste from urban and agricultural pruning and waste from forest pruning. Both pyrolysis in inert atmosphere and combustion in the presence of oxygen were studied. Different heating rates were used by varying the input speed. Major gas compounds were analyzed. The experimental results show that the amount of CO formed is lower in less dense species. It is also found that there is an increase of hydrocarbons formed at increasing feeding rates, in particular methane, while there is a decrease in the production of hydrogen.

Keywords: biomass; gasification; syngas; thermochemical biofuels; seaweed

1. Introduction

The energy from the sun is stored in biomass through the photosynthetic process. Photosynthesis starts with the capture of light by photosynthetic accessory pigments and conversion into electrical energy by the chlorophyll pigments of the reaction centers. In the next stage, not photochemical, although light is required to activate certain enzymes, the stored chemical energy is used to reduce carbon dioxide and the resulting synthesis of carbohydrates.

Biomass is a CO_2 neutral option for energy generation, and the potential for the conversion of biomass into energy is rapidly increasing [1]. According to Maniatis [2], energy from biomass based on short rotation forestry and other energy crops can contribute significantly toward the objectives of the Kyoto Agreement in reducing the greenhouse gas emissions and to the problems related to climate change. Moreover, a number of biomass technologies are available for converting biomass to energy. These processes can change raw biomass into a variety of gaseous, liquid, or solid materials that can then be used for energy generation. This conversion can be done in three ways: thermochemical (break down biomass under high temperature), biochemical (break down biomass under microorganism or enzymatic processes) and chemical (oils from biomass can be chemically converted into a liquid fuel) [3].

In recent years, there have been many developments in the science and technology of thermochemical biomass conversions. Incineration, gasification, and pyrolysis

conversion are among the established and best available thermochemical technologies [2,3]. These thermal processes provide an efficient, environmentally acceptable and cost-effective method of providing a sustainable energy source.

Gasification is the thermochemical conversion of a solid biomass to a gaseous fuel by heating with a gasification agent (i.e., air, oxygen, steam, hydrogen, CO_2, or mixtures of these gases). Gasification of biomass occurs at high temperatures, 600–1000 ºC or higher. The solid carbon content in the biomass is oxidized over several steps: dehydration, pyrolysis, combustion, and reduction producing a gaseous mixture called synthesis gas (or syngas) by a series of reactions, such as combustion, partial oxidation, methanation, and water-gas shift, among others [4]. Syngas contains mostly carbon monoxide and hydrogen with varying amounts of carbon dioxide, methane and water vapor. The composition and amount of syngas produced are determined by the flow rate, type, and properties of the biomass and the gasifier operating conditions including oxidizing agent equivalence ratio, gasification pressure, and gasifier temperature profile.

The obtained gas is easier and more versatile to use than the original biomass, with possible uses in power gas engines and gas turbines, or to produce liquid fuels [5,6]. Modern integrated gas-steam cycles (IGCC) are capable of achieving high thermodynamic efficiencies [7]. The raw product gas exiting a biomass gasifier contains particulates, tars, and other constituents that may interfere with downstream utilization technologies. The concentrations of these constituents will depend on the reactor design and characteristics of the biomass feedstock, and, in certain cases, gas cleaning is necessary, which affects the economic investment.

The main components of the biomass are hemicellulose, cellulose, and lignin. Thermal degradation of these substances produces several volatiles: carbon dioxide, carbon monoxide, water, methane, hydrogen, and hydrocarbons in different proportions. According to Yang et al. [8] lignin produces four times more hydrogen than cellulose and almost three times more than hemicellulose. For this reason, to increase hydrogen concentration in raw gas, it is reasonable to study pretreatments that modify the chemical composition of the biomass feedstock.

In an inert atmosphere, biomass undergoes volatization and char formation, especially from lignin [9,10]. In an air atmosphere, char previously formed is oxidized in a posterior step. Both processes have an influence on the catalytic effect of certain metallic elements (present in a higher amount in herbaceous crops). According to Meszaros et al. [9], the origin of CO is the decomposition of biopolymers: hemicellulose, cellulose and lignin. As well, in a study on woody residues and herbaceous biomass crop (artichoke thistle), Gómez et al. [11] have measured the higher evolution rates of CO and CO_2 between 300 and 400 ºC, the range of temperatures associate with volatilization of polymers. However, for thistle, new CO formation above 600 ºC is detected. This process is associated with the char formation reactions in which the residual O-functional groups are cleaved. This fact is not observed in woody residues. Meszaros et al. [9] relate these data with catalytic properties of certain elements. According to these researchers, biocarbons that form very low ash are not persistent CO emitters. As well, biocarbons with moderate ash content are not persistent CO emitters if their ash lacks the catalytic species such as K, P, Mg and/or Na, which are responsible for the persistent CO emission. This catalytic effect affects hydrogen production too. The herbaceous crops have the more pronounced evolution of hydrogen in the 500–900 ºC temperature range [11]. In this sense, differences between wood and herbaceous biomass in hydrogen and methane production have been shown [12]. In a study performed in a macro-thermobalance, these authors show that charring reactions play a more significant role in the pyrolysis of grass than in the pyrolysis of the wood species, underlining that it is associated with the fact that a larger amount of inorganic ions are present in herbaceous samples, acting as catalysts of charring reactions.

The objective of the present work is to study the thermal degradation products of five different biomass samples in order to study the possibility of obtaining a syngas from the wastes and other gas properties. In order to obtain representative results, a proper sampling was made in accordance with the characteristics of the population statistics. Biomass samples and the sampling technique are described below. The present work allows estimating the possibilities of the gasification of the different biomass feedstocks studied. The amount and composition of the gas produced at the different conditions is studied, with the objective to use the gas for internal combustion engines or as synthesis gas for other purposes.

2. Materials and methods

The equipment used to carry out the present work, shown in Figure 1, has been exclusively developed to accurately control the ratio of oxygen in combustion processes. It consisted of a moving tubular reactor with the samples carefully placed along the tube, which is introduced at a very controlled speed to a furnace while a constant flow of gas is passing through. More details of the equipment can be found elsewhere [13]. In all runs, the temperature of the oven was 850 ºC. The temperature profile inside the reactor was also measured [8]. Gas samples were collected using Tedlar bags and then analyzed by gas chromatograph with flame ignition detector (GC-FID) and with thermal conductivity detector (GC-TCD).
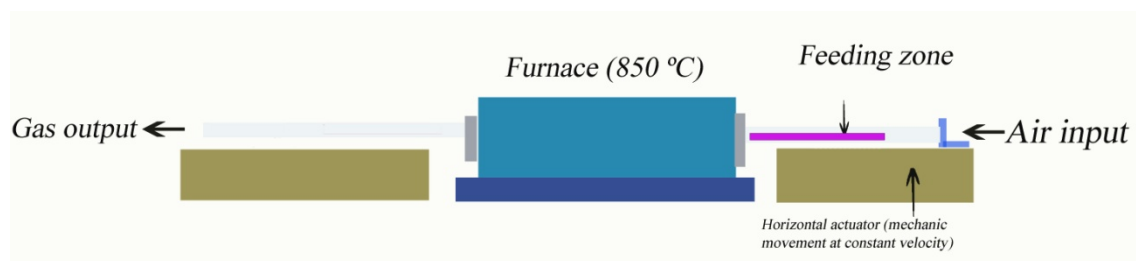

Figure 1. Scheme of the laboratory horizontal furnace used.

Biomass samples under study represent biomass residues or Mediterranean endemic plants. Below are the studied species:

- EG: Esparto grass (*Stipa tenacissima*, L. or *Macrochloa tenacissima*, Kunth), Mediterranean grass with high PCI and easy regeneration. There has been a simple random sampling.
- Straw (Straw *Triticum*, *Hordeum*, and *Avena sativa*), the main cereal crop residue. There has been a simple random sampling.
- POS: Posidonia Oceanica seaweed. There has been a simple random sampling.
- WUAP: Waste from urban and agricultural pruning. In the sampling of agricultural waste and garden clippings, urban target species are those that represent 90% of the cultivated area of the counties with irrigated and rainfed land in the province of Alicante (Spain) and 85% of susceptible ornamental pruning in the gardens of towns with more than 2000 inhabitants in the province of Alicante. Among the species are *Prunus Amygdalus, Citrus sinensis, Citrus limon, Prunus armeniaca* and *Olea europaea* as the major components. It performs a stratified random sampling with proportional allocation.
- WPF: Waste of pruning forest where they have chosen 5 sampling areas, all located in the province of Alicante. Among the species are *Pinus pinaster, Pinus nigra, Pinus halepensis,*

Cedrus deodara, Quercus Ilex and *Juniperus phoenicea* as the major components. It takes a stratified simple sandom sampling with Neyman allocation.

Before experiments, all biomass feedstocks where crushed to a particle size between 75 to 125 μm and conserved in a dry ambient. Table 1 presents the elemental analysis of the samples (carbon, hydrogen, nitrogen and sulfur) performed by oxidation of the sample to 1000 °C and subsequent detection of combustion products (CO_2, H_2O, N_2 and SO_2). The equipment used was a Perkin-Elmer 2400 (Perkin-Elmer, UK). The equipment is calibrated by using known compounds and has an accuracy of ca. ± 0.03%. Note that the amount of sulfur is negligible in all species but the POS, probably due to the presence of sulphur salts in the seawater (approx. 1–8%). Table 1 also presents the humidity of the samples as collected, the ash content and the Net Calorific Value (NCV) determined using a calorimetric bomb AC-350 LECO Instruments.

Table 1. Elemental analysis of the biomass samples (% dry wt.), humidity, ash content and calorific values.

	Esparto grass	Straw	Posidonea Oc.	Agric. Urban pruning waste	Forest pruning waste
N	0.5	0.21	0.71	2.09	0.65
C	38.16	42.93	34.85	48.06	40.12
H	5.4	6.16	4.54	5.81	5.44
S	0	0	0.62	0	0
O (by difference)	55.94	50.7	59.28	44.04	53.79
Humidity (% wt.)	7.8	6.4	9.8	12.9	9.6
Ash (% wt.)	2.4	1.1	4.9	2.4	1.8
Net calorific value (Kcal/Kg)	4425.8	4118.2	3363.7	3551.6	3939.1

Four experiments were performed with each of the five studied biomass feedstocks combining pyrolytic (nitrogen) and oxidative (air) atmosphere with two different input speeds (0.5 mm/s and 1.9 mm/s). Blank runs were performed, introducing a thermocouple in the oven to measure the heating rate at the different input speeds. The runs performed at the lower speed heated at approximately 9 K/s (540 K/min), and the faster input produced a 17 K/s (1020 K/min) heating of the thermocouple.

The conditions during runs performed in oxidative atmosphere were performed in such a way that the oxygen ratio (λ, defined in the next equation) is maintained at $\lambda = 0.25$ in both cases:

$$\lambda = \frac{(m_{O_2})_{actual}}{(m_{O_2})_{stoic}} = \frac{m_{air} \cdot 23}{\dfrac{m_{sample} v}{L} \left(\dfrac{\%C}{12} + \dfrac{\%H}{4} + \dfrac{\%S}{32} - \dfrac{\%O}{32} \right) \cdot 32}$$

where:

%O, %H, %S, %C = weight percentage of oxygen, hydrogen, sulphur and carbon in the biomass sample

m_{air} = air flow rate (kg/s)

m_{sample} = weight of the residue (kg)

L = length of tube occupied by the residue (m)

ν = linear velocity of introduction of the tube (m/s)

A value of λ lower than one involves combustion in sub-stoichiometric conditions while values of λ higher than ONE represent excess air.

In the runs performed, ν = 0.5 and 1.9 mm/s. In order to maintain the ratio λ = 0.25, the corresponding value of m_{air} was used. In this sense, the resident time of the volatiles evolved is higher at the lower feeding rate, which can influence the gas evolution.

Note that a biomass could produce a very little amount (yield) of syngas of a very interesting ratio H_2/CO (composition) and, on the contrary, it is possible to get a high yield of gas of a poor composition. In this way, in the runs two different parameters are determined for each compound:

- Gas yield: amount of compound (mg) evolved by 100 g of biomass sample
- Gas composition: percentage of each compound (volume) evolved by unit volume of gas.

3. Results and discussion

3.1. Carbon oxides, hydrogen and light hydrocarbons yields

Figures 2 to 5 show the results for the different runs in terms of gas yields. It can be seen that in all runs the majority species are CO_2 and CO, as expected in the pyrolysis and combustion of biomass.
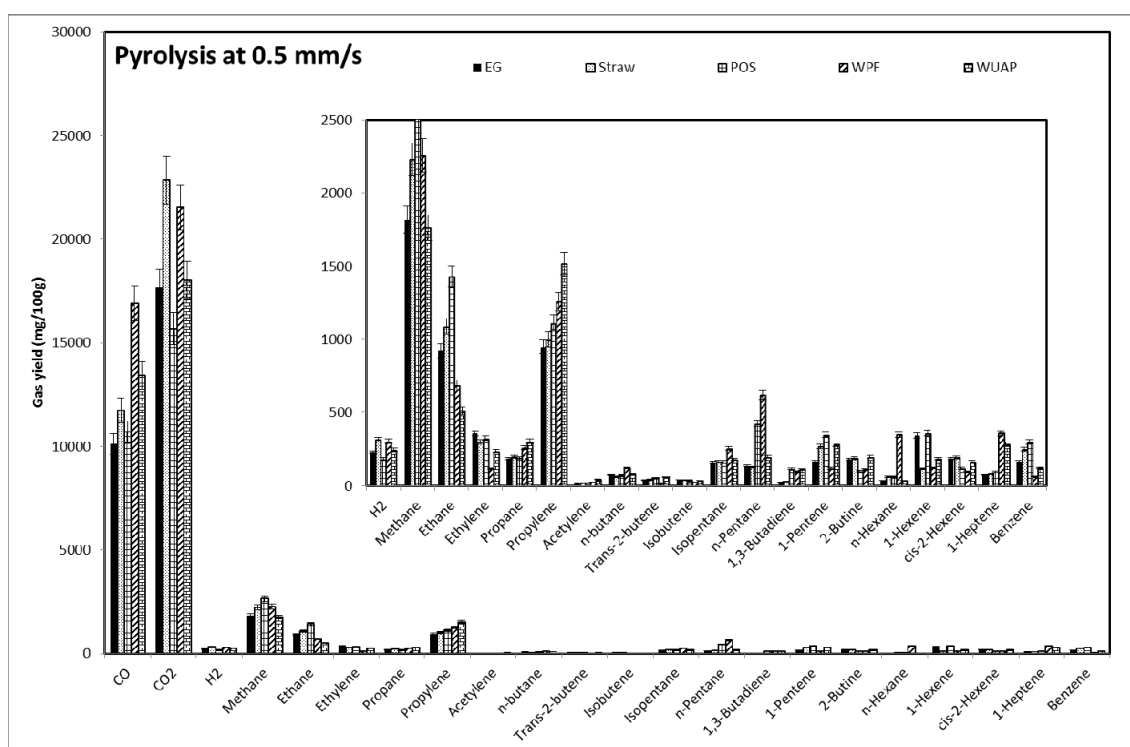

Figure 2. Gas yield for the different biomass feedstocks in nitrogen tmosphere and slow feeding rate.
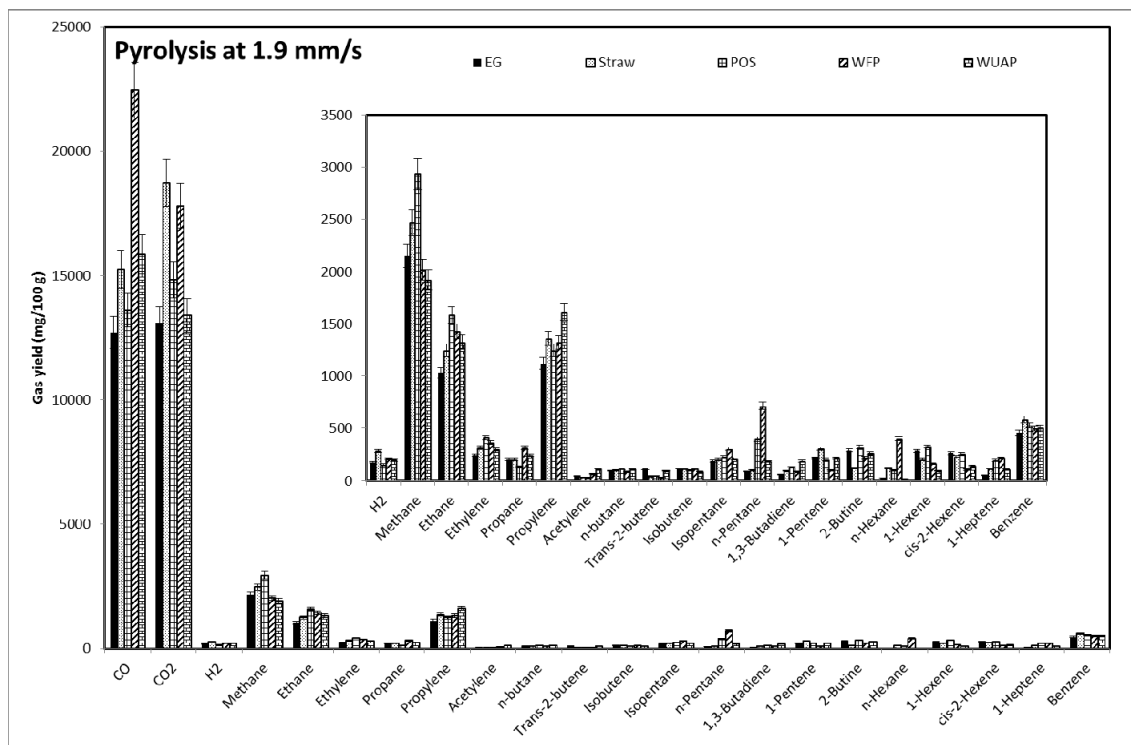
Figure 3. Gas yield for the different biomass feedstocks in nitrogen atmosphere and fast feeding rate.
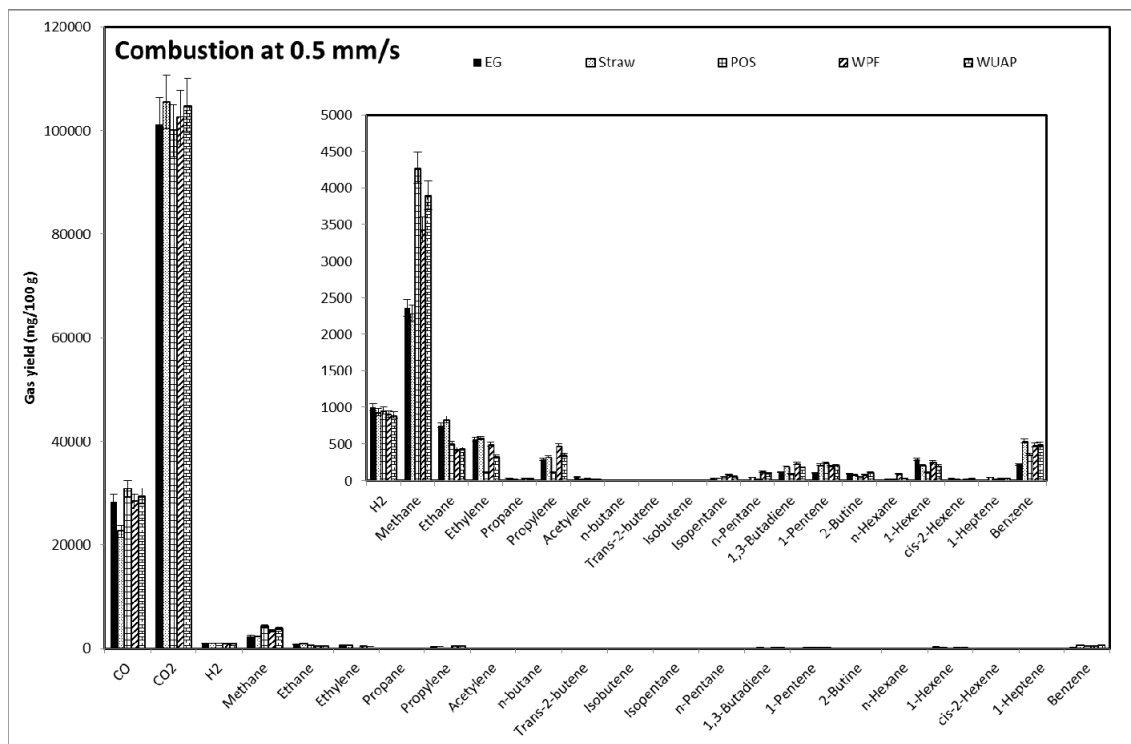

Figure 4. Gas yield for the different biomass feedstocks in air atmosphere and slow feeding rate.
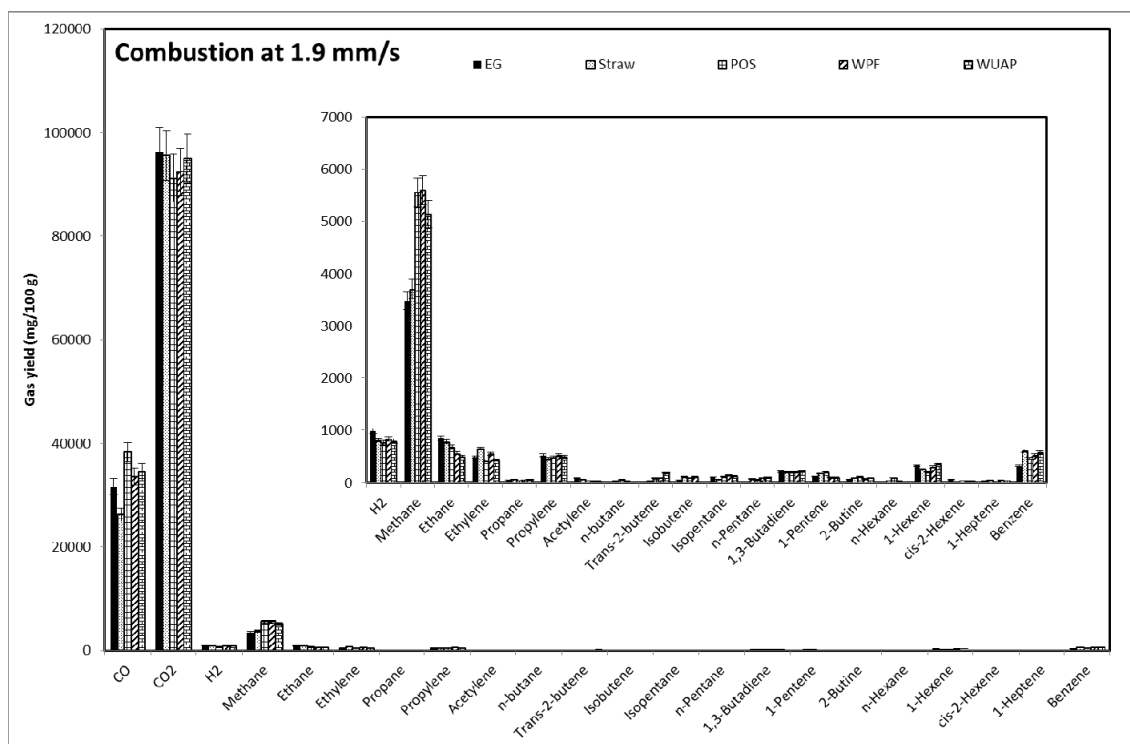
Figure 5. Gas yield for the different biomass feedstocks in air atmosphere and fast feeding rate.

It is noteworthy that carbon oxides yields vary between the different samples. The results of WUAP are remarkable where the amount of these species are higher than the rest, especially the carbon monoxide. Elemental analysis of this waste has the highest percentage of carbon (48.06%), so it is not surprising that there is a greater amount of carbon species.

It is also worth noting that the CO_2 yield in the fuel gases from Straw is the largest of all the samples. This species is the one that has the second highest concentration of carbon (42.93%).

Moreover, the amount of CO formed is lower in less dense species and where there has been a better distribution of heat around the particles during the process. In this way, it can be seen that the species presenting more CO yield are WUAP and WPF.

As for the minority species, the most important are methane, ethane, ethylene and propylene, as major hydrocarbons, and hydrogen.

Comparing the data obtained at 0.5 mm/s and 1.9 mm/s, it is noteworthy that the amount of CO formed at the high heating rate regime is increased with respect to the low heating rate runs. CO production is even higher than that of CO_2 in the pyrolysis of Straw, WUAP and WFP. CO and CO_2 production are practically equal in the pyrolytic decomposition of EG and POS.

This behavior may be due to poorer heat transfer within the biomass during high heating rate runs, and also to the possible reactions between species enhanced by the higher gas residence time. The most important reactions produced in these pyrolytic conditions lead to the formation of CO and CH_4:

    i. $C + CO_2 \leftrightarrow 2\ CO + 164.9$ kJ/kmol

    ii. $C + H_2O \leftrightarrow CO + H_2O + 122.6$ kJ/kmol

    iii. $CO + H_2 \leftrightarrow CO + H_2O + 42.3$ kJ/kmol

iv.　　$C + 2\,H_2 \leftrightarrow CH_4 + 0\ kJ/kmol$

v.　　$CO + 3\,H_2 \leftrightarrow CH_4 + H_2O - 205.9\ kJ/kmol$

vi.　　$C + CO_2 + H_2O \leftrightarrow 2H_2 - 41\ kJ/kmol$

These reactions are favored [14] with increasing gas distribution around the particles; a fact that occurs when there is increased generation of species from the interior zone of the particles outward at high speeds of introduction of sample or smaller feed rates of gas. According to Fushimi et al. [15] a higher heating rate causes a rapid evolution of volatiles, producing a porous char that increases final conversion of biomass and increases the reaction rate in steam gasification.

Roberts et al. [16] studied coal pyrolysis and related heating rate effects with structural and superficial char properties. Mermoud et al. [17], working with large wood char particles, concluded that a lower heating rate produces a dense charcoal and a minor amount of volatiles. Moreover, the charcoal obtained at different heating rates exhibits very different gasification kinetics. The gasification rate in dense char is smaller than that of low-density char. Gasification results are in accordance with data obtained by other researchers working with biomass [13,18]. As commented, an increase in the heating rate diminishes hydrogen production and favors methane and carbon dioxide production.

Supported by the above, it is also found that there is an increase of hydrocarbons formed at increasing feeding rates, in particular methane, while a decrease in the production of hydrogen with increasing velocity is observed.

In the same sense, Barneto et al. [13], using the same experimental equipment that is used in the present work, sustain that a slow heating rate produces more hydrogen than a rapid heating rate and remark that this behavior could be related to the reactivity of the char produced during the first stage of the gasification process.

In the combustion runs, the formation of CO_2 is the most favored at 0.5 mm/s, and hence, this is the predominant species. The amount of CO formed is much higher in this process than that observed in pyrolysis. Similarly, there is a distribution of species very similar to those of the pyrolysis experiments and also an increase in the proportion of H_2.

It is also noteworthy that, in hydrocarbons, the amount of benzene is clearly increased compared to experiments performed at the same rate of entry in the absence of oxygen.

3.2 Syngas production

The poor gas obtained in the pyrolysis and gasification of biomass, once subjected to the cleaning and dehumidification process, can be used either as fuel in internal combustion engines, carrier fluid in gas turbines, as well as fuel in turbine systems steam, or as feedstock for the production of ammonia, methanol, H_2 and other species.

One of the most important parameters used to determine the potential for fuel synthesis gas is the relationship of H_2/CO. Gasification processes for synthesis gas pursue improved relations H_2/CO changing operating conditions and/or gasification atmosphere.

Using the data obtained, it is possible to calculate the volume of gas (L/g) produced during the decomposition. Figure 6 shows a visual plot of CO volume (L/g) vs. hydrogen production (L/g) from pyrolysis and combustion runs at the different input speeds. Size of the bubble in this graph is proportional to the ratio H_2/CO in the syngas produced (it is given as a reference in the one obtained in the combustion of Esparto grass at 1.9 mm/s). In this Figure it can be observed that:

- Combustion runs, logically, produces a higher amount of CO_2. The amount of hydrogen is also higher compared to the pyrolysis. Also the ratio H_2/CO is higher when oxygen is present.
- Runs performed at 0.5 mm/s present, in general, lower hydrogen production. This should be due to the recombination of $CO + H_2O$ giving CO_2 and H_2. This reaction is favored at high temperatures and high gas residence time, as is the situation at 0.5 mm/s.
- Straw is the waste producing the richer H_2 gas.
- POS and WUAP are the species producing lower amounts of H_2. With respect to the ratio H_2/CO it can be observed that:
- The higher ratio is obtained with Straw, being the only value higher than 1 (1.15). Also close to one (0.98) is the value obtained with EG.
- In general, the ratio increases as the feeding rate decreases, i.e., when gas residence time is increased and the heating rate decreases.
- The ratio is increased in combustion runs with respect to that obtained in pyrolysis, at both heating rates studied.
- In general, better ratios of H_2/CO are obtained with the less dense samples, i.e., EG, Straw and POS, although better yields in fuel gases are obtained with the more dense wastes.

With the gas compositions one can calculate [19] both the density and the Net Calorific Value of the evolved gas. Density was calculated using the experimental composition of gas evolved in the stationary state. The results of this calculation indicate that the density does not vary substantially and is always in the range 1.2–1.3 kg/m^3, probably because the temperature of the furnace is always 850 ºC. On the other hand, the NCV of the gas varies between 3100 and 4950 kJ/kg approximately. The highest NCV is obtained in the pyrolysis of WUAP at 1.9 mm/s, and the lowest in the combustion of EG at 0.5 mm/s. In general, higher NCV are obtained in pyrolytic conditions and at the highest input speed.
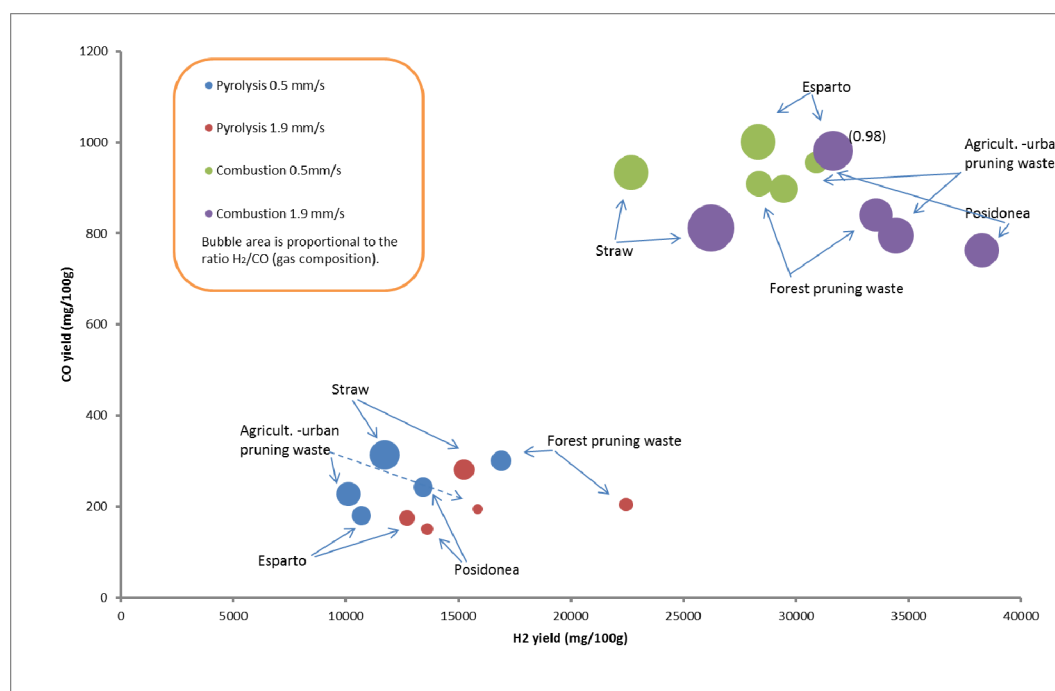

Figure 6. Hydrogen and CO yield for the different biomass feedstocks in air/nitrogen atmosphere and two different input speeds. Bubble graph in which bubble area is proportional to the ratio H2/CO in the gas composition.

4. Conclusions

The decomposition of five different biomass feedstocks was studied in a horizontal laboratory reactor. Both pyrolysis in inert atmosphere and combustion in the presence of oxygen were studied.

Significant differences were observed in the composition of the gas evolved as a function of the oxygen ratio. The NCV of the evolved gas presents a loss of calorific power with respect to the biomass samples, of about 45% for pyrolysis and 30 for combustion.

The ratio of H_2/CO for all samples in all studied conditions indicates that gas obtained is appropriate for internal combustion engines.

Gas obtained from Straw in combustion conditions at low feeding rate could be used as low quality syngas for methanol synthesis through Fisher-Trops reactions.

The experimental results show that the amount of CO formed is lower in less dense species. It is also found that there is an increase of hydrocarbons formed at increasing feeding rates, in particular methane, while there is a decrease in the production of hydrogen.

Acknowledgements

References

1. Ohlström M, Mäkinen T, Laurikko J, et al. (2001) New concepts for biofuels in transportation biomass-based methanol production and reduced emissions in advanced vehicles. pp. 3-94.
2. Maniatis K (2001) Progress in Biomass Gasification: An Overview; Bridgewater AV, editor. Oxford: Balckwell Scientific Publications.
3. Faaij A (2006) Modern biomass conversion technologies. *Mitigation and Adaptation Strategies for Global Change* 11: 343-375.
4. Kumar A, Jones DD, Hanna MA (2009) Thermochemical biomass gasification: A review of the current status of the technology. *Energies* 2: 556-581.
5. Reed TBD, A. (1998) Handbook of Boimass Downcraft Gasifier Engine Systems. Golden: Biomass Energy Foundation Press.
6. Klass DL (1998) Biomass for Renewable Energy, Fuels, and Chemicals. San Diego: Academic Press.
7. McKendry P (2002) Energy production from biomass (part 3): Gasification technologies. *Bioresource Technology* 83: 55-63.
8. Yang H, Yan R, Chen H, et al. (2007) Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 86: 1781-1788.
9. Mészáros E, Jakab E, Várhegyi G, et al. (2007) Thermogravimetry/mass spectrometry analysis of energy crops. *Journal of Thermal Analysis and Calorimetry* 88: 477-482.
10. Szabó P, Várhegyi G, Till F, et al. (1996) Thermogravimetric/mass spectrometric characterization of two energy crops, Arundo donax and Miscanthus sinensis. *Journal of Analytical and Applied Pyrolysis* 36: 179-190.
11. Gómez CJ, Mészáros E, Jakab E, et al. (2007) Thermogravimetry/mass spectrometry study of woody residues and an herbaceous biomass crop using PCA techniques. *Journal of Analytical and Applied Pyrolysis* 80: 416-426.

12.   Khalil RA, Mészáros E, Grønli MG, et al. (2008) Thermal analysis of energy crops. Part I: The applicability of a macro-thermobalance for biomass studies. *Journal of Analytical and Applied Pyrolysis* 81: 52-59.
13.   Barneto AG, Carmona JA, GÃ¡lvez A, et al. (2009) Effects of the composting and the heating rate on biomass gasification. *Energy and Fuels* 23: 951-957.
14.   Estrada C (2008) Gasificación de biomasa para producción de combustibles de bajo poder calorífico y su utilización en generación de potencia y calor. *Scientia et Technica* 25.
15.   Fushimi C, Araki K, Yamaguchi Y, et al. (2003) Effect of heating rate on steam gasification of biomass. 1. Reactivity of char. *Industrial and Engineering Chemistry Research* 42: 3922-3928.
16.   Roberts DG, Harris DJ, Wall TF (2003) On the effects of high pressure and heating rate during coal pyrolysis on char gasification reactivity. *Energy and Fuels* 17: 887-895.
17.   Mermoud F, Salvador S, Van de Steene L, et al. (2006) Influence of the pyrolysis heating rate on the steam gasification rate of large wood char particles. *Fuel* 85: 1473-1482.
18.   Li XT, Grace JR, Lim CJ, et al. (2004) Biomass gasification in a circulating fluidized bed. *Biomass and Bioenergy* 26: 171-193.
19.   Horta Nogueira LASL, E.E. (2003) Dendroenergía. Fundamentos e aplicaçoes. Rio de Janeiro: Editora Interciencia Ltda.