GASIFICATION OF GRAPEVINE PRUNING WASTE IN AN ENTRAINED-FLOW REACTOR: GAS PRODUCTS, ENERGY EFFICIENCY AND GAS CONDITIONING ALTERNATIVES

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ABSTRACT

Owing to its higher efficiency and versatility, gasification is seen as a necessary evolution in the development of biomass energy systems. This technology has been primarily tested in fixed bed (updraft and downdraft) and fluidised bed reaction systems, with less information available about the potential of entrained-flow reactors. This latter design benefits from a relatively simple mechanical structure, robustness against severe gasification conditions and also reduced investment and operating costs. This paper describes the development of a pilot scale entrained-flow reactor and evaluates its performance in the gasification of wood waste left over from the pruning of grapevine (*Vitis vinifera*). The original biomass was initially analysed for its chemical composition and thermal behaviour. A series of gasification trials were conducted to evaluate the effect of temperature and relative biomass/air ratio (F_{rg}) on the yield, composition, heating value of the resulting syngas. The cold gas efficiency of the system was determined for different operating conditions from the heating value and yields of the resulting producer gas.

The results showed that the use of higher temperatures caused a small increase in overall gas yields (from 1.76 $Nm^3 kg^{-1}$ at 750ºC to 1.96 $Nm^3 kg^{-1}$ at 1050ºC) and a notable rise in its heating value (from 3.65 $MJ kg^{-1}$ at 750ºC to 4.95 $MJ kg^{-1}$ at 1050ºC), primarily derived from an increase in the concentration of hydrogen. The experimental results show a reduction in the fuel properties of the producer gas when using biomass/air ratios (F_{rg}) below 2.5, which was attributed to the partial combustion of the producer gas. However, this effect was largely counteracted by the production of higher gas yields (3.39 $Nm^3 kg^{-1}$ for F_{rg} = 2.16 compared to 1.96 $Nm^3 kg^{-1}$ for F_{rg} = 4.05), owing to the higher conversion of the fuel at low biomass/air ratios. Optimum gasification conditions (cold gas efficiency up to 83.06 %) were reached when using high reaction temperatures (1050ºC) and low F_{rg} (2.19). This paper also provides a final review about the formation of unwanted tars and particulates in gasification processes, its effect in energy applications, and the use of alternative technologies (thermocatalytic cracking, reforming, water-gas shift) for the conditioning and upgrading of the resulting gas stream.

INTRODUCTION

Most countries in the world are taking measures aimed at reducing their energy dependence on fossil fuels (coal, petroleum and natural gas). The purpose of this is twofold: on the one hand, the limitation of greenhouse gas emissions responsible for global warming; on the other, a reduction in the exposure to economic risks associated with the rising prices of these increasingly scarce natural resources. A cost-effective approach to meet these objectives requires implementing energy efficiency practices and also giving priority to low-carbon technologies, including renewable energies sources (del Río, 2009; San Miguel *et al.*, 2010). As an example of the extent to which these measures are going to affect our future, the European Union (EU) recently agreed on an ambitious "Plan on Climate Change" that includes a binding obligation to reach 20% of its energy mix from renewable sources by 2020 (EU, 2008).

Biomass, obtained from dedicated energy crops or as a by-product of agricultural, forest management and industrial activities, has an important role to play in this transformation. Biomass energy technologies are usually grouped into two categories: biological (such as fermentation and anaerobic digestion); and thermochemical (including combustion, gasification and pyrolysis). In the latter group, biomass combustion for power generation has reached a high degree of maturity, as evidenced from the large number of plants currently in operation worldwide (Van den Broek *et al.*, 1996). However, the energy efficiency of this technology is limited (typically between 15-25 %, depending on plant size and design) and the operating and investment costs are high, resulting in low financial returns (Sondreal *et al.*, 2001; Dornburg and Faaij, 2001; Caputo *et al.*, 2005).

Gasification incorporates significant advantages over conventional combustion processes with respect to its energy efficiency and versatility (Dornburg and Faaij, 2001; Caputo *et al.*, 2005). Despite its success during periods of energy scarcity, gasification technology became obsolete after the Second World War owing to the lower price of natural gas and petroleum derivates. Economic and environmental considerations are giving gasification a second opportunity due to its potential to valorise not only biomass but also a wide range of other organic materials like plastics, tyres and municipal solid wastes (MSW). The scientific production in this field, with thousands of papers and numerous monographs in the last few years (Knoef, 2005; Rezaiyan and Cheremisinoff, 2005; Badeau and Levi, 2009), demonstrates the high expectations created around this technology, while the limited commercial activity evidences the technical and economic difficulties encountered in its practical development.

Gasification involves the transformation of a carbonaceous material into a combustible gas as a result of its exposure to high temperatures (850-1200ºC) under mildly oxidising atmospheric conditions (substoichiometric oxygen, steam, CO_2). This gas, typically referred to as producer gas or syngas, contains variable concentrations of combustible hydrogen and carbon monoxide, as well as nitrogen, carbon dioxide, methane and other light hydrocarbons. Owing to its heating value, the syngas may be fed to an internal combustion engine for power generation. Electrical efficiencies up to 30-40 % have been reported in conventional biomass gasification plants, reaching up to 60-65 % in total efficiency when incorporating cogeneration (EQTEC, 2009). Electrical efficiencies for integrated gasification combined cycles (IGCC) are in the order of 45-55 % (Deschamps *et al.*, 2008). Syngas may also be used in the production of synthetic liquid fuels and lubricants (via Fischer-Tropsch), as a source of hydrogen after purification and gas separation, and as a raw material for the synthesis of industrial chemicals (methanol, ammonia) (Bridgwater, 2003).

Gasification may be conducted in different types of reactors the most widely used being fixed beds (both in updraft and downdraft configurations) and fluidised beds (both in bubbling or circulating configurations). Less information is available on the use of entrained-flow reactors (also referred to as free fall and drop tube reactors), a design characterised for its mechanical simplicity and robustness (Biagini *et al.*, 2005; Lapuerta *et al.*, 2008; Zhao *et al.*, 2009). Owing to the temperature patterns and atmospheric conditions generated inside the reaction chamber and also to differences in heat transfer efficiencies, reactor design has a notable effect on the quality and composition of the resulting syngas (Knoef, 2005; Han and Kim, 2008). For instance, particulate and tar levels in updraft gasifiers are typically much higher than in downdraft and fluidised bed reactors. Reactor design also determines its capacity to operate under unfavourable conditions generated as a consequence of the high temperatures, the formation of tar deposits and the corrosive conditions occurring during the gasification of biomass.

Based on these considerations, this paper describes the construction of a pilot scale gasifier based on the entrained-flow technology and its testing in the valorisation of a residual biomass obtained from the pruning of grapevine. The original biomass was initially analysed for its chemical composition, thermal behaviour and fuel potential. A series of gasification trials were conducted to investigate the effect of temperature and relative biomass/air ratio (F_{rg}) on the yield, composition and heating value of the resulting gases. Reaction conditions were optimised in order to maximise cold gas efficiency of the system. The paper also provides a final discussion about potential applications of the resulting syngas and alternative conditioning technologies that could be applied to maximise its fuel properties and commercial value.

MATERIALS AND METHODS
Biomass supply and characterisation
Waste biomass from the pruning of grapevine (*Vitis vinifera*) has been used in this work. This agricultural by-product is generated in large amounts in the wine making regions of Mediterranean countries, with an estimated yearly production of between 1.0-1.5 t ha^{-1} (Lapuerta *et al.*, 2008). Prior to being used, the biomass was ground and sieved to a particle size < 500 μm. The homogenised product was characterised for its chemical composition (CHNS) using a Leco CHNS-932 analyser and for its thermal behaviour and proximate composition using a TA Instruments Q500 thermogravimetric analyser (TGA). Low heating values (LHV) were determined in a Parr 1351 analyser (UNE-164001-EX).

Entrained-flow reactor
The reaction system employed in this work was designed and developed at the University of Castilla - La Mancha (UCLM). As illustrated in Figure 1, it consists of three stages: a feeding unit, an electrically heated entrained-flow reactor and a gas conditioning system.

The feeding system consists of a hermetically sealed stainless steel box connected to the top of the reactor via a calibrated screw feeder. Secondary inlet ports connected to a compressor and a steam generator allow the injection of air and steam, respectively, at a controlled flow rate. The entrained-flow reactor consists of a hollow tube (1.2 m long, 60 mm internal diameter, 7.5 mm wall thickness) made of alumina and placed inside an electric furnace designed to control the process temperature (up to 1250ºC). An ash collector is located at the bottom of the reactor to recover solid products (ash and char). The reaction gases pass though a cleaning system (a cold trap) aimed at reducing the concentration of particulates and condensable tars. A valve system allows the connection of the gas outlet whether to a burner (coupled to a CCD camera) or to a water-gas shift reactor. On the other hand, the gas outlet can be derived into a tar sampling system. (composed of a particle filter, and an impinger train). Lastly, gas characterisation was performed using a calibrated double channel (molecular sieve 5A and PoraPlot Q) Agilent 3000 micro-GC with thermal conductivity detector.
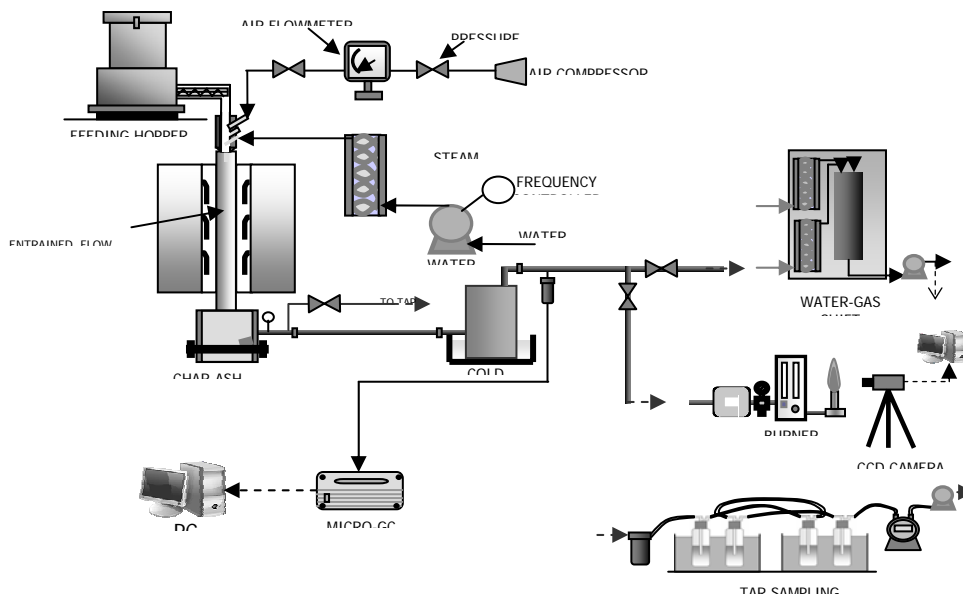

Figure 1. Flowchart of the reaction system developed for the gasification of biomass.

Gasification procedure

Previously ground and homogenised biomass was loaded into the feeding box. Air (the gasification agent used in all tests) was injected into the reactor at a constant flow of 2.08 kg h^{-1}, which implies 1.57 seconds of spacial residence time (reactor volume 3.39 dm^3). The reactor was heated to its final temperature between 750ºC and 1050ºC. When the set conditions were reached, the biomass was fed into the reactor at rates (m_f) ranging between 0.90 - 1.69 kg h^{-1}, equivalent to 0.82 - 1.54 kg h^{-1} on a dry and ash free basis (m_f daf). The reactor was allowed to stabilize (usually 20-30 min) before analysing the composition of the gas products. Tables 1 and 2 describe the gasification conditions employed to investigate the effect of temperature and relative biomass/air ratio (F_{rg}), respectively. Gas yields were calculated from the concentration of nitrogen in the producer gas, which was used as an internal standard (molar balance calculations).

Table 1. Experimental conditions employed to investigate the effect of gasification temperature

Temperature (ºC)	F_{rg}	m_f (kg h^{-1})	m_f (daf) (kg h^{-1})	m_a (kg h^{-1})	Residence time (s)
750	3.80	1.56	1.38	2.08	1.57
850	3.80	1.56	1.38	2.08	1.57
950	3.80	1.56	1.38	2.08	1.57
1050	4.05	1.69	1.49	2.08	1.57

Table 2. Experimental conditions employed to investigate the effect of the relative biomass/air ratio (F_{rg})

Temperature (ºC)	F_{rg}	m_f kg h^{-1})	m_f (daf) (kg h^{-1})	m_a (kg h^{-1})	Residence time (s)
1050	2.16	0.9	0.79	2.08	1.57
1050	2.92	1.22	1.08	2.08	1.57
1050	3.33	1.39	1.23	2.08	1.57
1050	4.05	1.69	1.49	2.08	1.57

RESULTS AND DISCUSSION

Characterisation of the grapevine biomass

Figure 2 shows the TG/DTG curves of the grapevine biomass performed under inert (nitrogen) and oxidising (air) atmospheric conditions. The nitrogen curve shows three distinguishable areas of mass loss. The first one (stage 1) takes place at temperatures around 100ºC and is attributed to the elimination of highly volatile organics and unbound moisture. Weight loss in this first stage is 5.4 wt%. The second one (stage 2) occurs at temperatures between 200-400ºC and corresponds to the combined pyrolysis of the biomass components. It has been described in the literature that hemicellulose degrades at comparatively lower temperatures (220-315ºC) than cellulose (315–400ºC), while lignin decomposes over a broad temperature range (250-700ºC) (Yang *et al.*, 2007). The non-symmetrical shape of the derivative plot in stage 2 evidences two overlapping reactions, which may be associated with the degradation of hemicellulose (at lower temperatures) and cellulose (at higher temperatures). The shape of the DTG curve, with a maximum at 309ºC, suggests a higher proportion of the latter component in the original biomass. Weight loss in this second stage amounted to 61.1 wt% of the original biomass.

The third area of weight loss (stage 3), at temperatures above 400ºC, evidences the progressive degradation of temperature resilient elements, including heavy lignin fractions and solid chars derived from the carbonisation of the original biomass components. The residue at 900ºC consists of a mixture of char and inorganic ash. Weight loss between 400-900ºC was 12.4 wt%, leaving a residue that represents 20.6 wt% of the original biomass.

The thermal analysis of grapevine biomass in air is very similar to that in nitrogen at temperatures below 350ºC. The TG/DTG plots show the elimination of water and volatile components at temperatures around 100ºC (stage 1) and the subsequent thermal degradation of the biomass components (hemicellulose and cellulose) at temperatures above 200ºC (stage 2). At higher temperatures, the thermal degradation process is overlapped by the onset of combustion that takes place at 350-500ºC. A second less marked peak centred at 590ºC has been associated with the

oxidation of combustion resilient lignin derivates and also to the thermal transformation of inorganic fractions, possibly alkaline-earth sulfates and carbonates. Complete combustion is reached at temperatures above 650ºC, resulting in complete elimination of organic matter and leaving a residue of incombustible ash that represents 6.0 wt% of the original biomass.
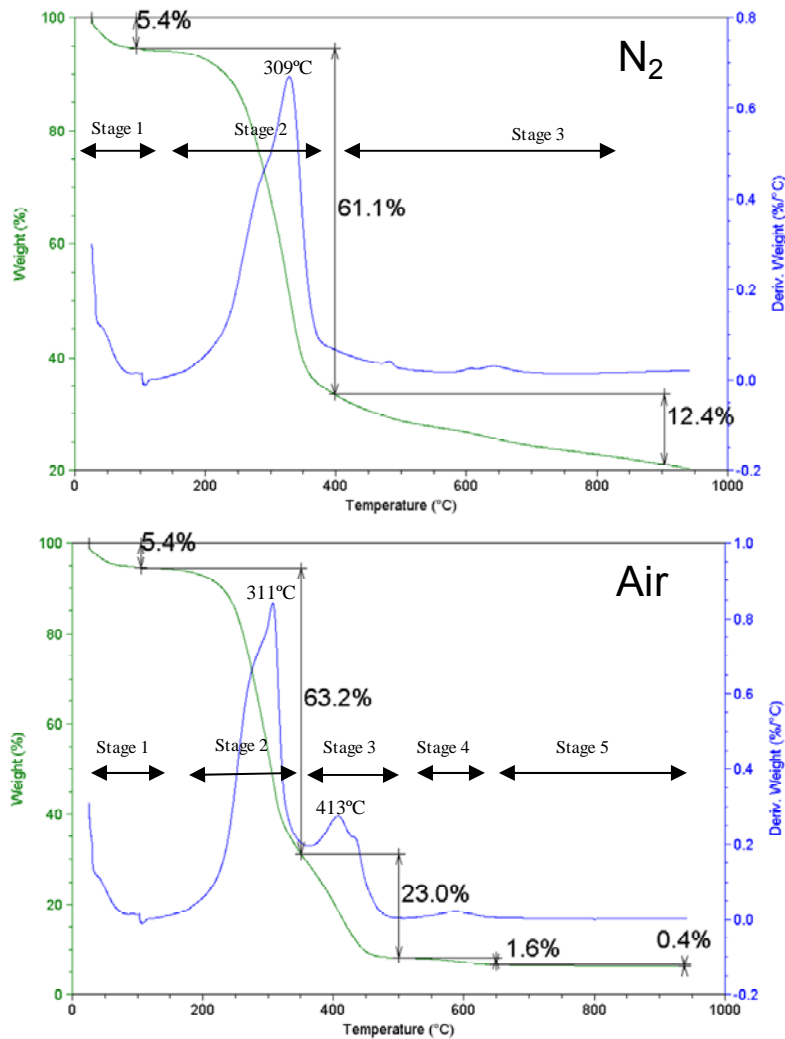

Figure 2. Thermogravimetric analysis of grapevine biomass under inert (top) and oxidising atmospheres

Table 3 illustrates the proximate composition of the as-received grapevine biomass and its elemental composition on a dry ash free basis. As evidenced in the TG analyses, the biomass exhibited relatively low moisture and fixed carbon contents (5.4 wt% and 16.1 wt%, respectively), with a dominant contribution of the volatile fraction, which represented 72.5 wt% of its original mass. The biomass also contained 6.0 wt% ash.

Table 3. Proximate and elemental analysis of grapevine biomass

Proximate composition [a] (% wt.)			
Moisture	Fixed carbon	Volatile matter	Ash
5.4	16.1	72.5	6.0

Elemental composition [b] (% wt.)				
C	H	N	S	O
49.3	5.6	0.77	0.06	44.3[c]

[a] as received   [b] dry ash-free basis   [c] by difference

The elemental analysis evidences a high oxygen content (44.3 wt%), an element which does not contribute to its calorific value. Carbon amounted to 49.3 wt% and hydrogen to 5.6 wt%, while the concentrations of nitrogen and sulphur were marginal (0.77 wt% and 0.06 wt%, respectively). Based on its elemental composition, the stoichiometric air/fuel ratio of this biomass was calculated to be 0.201 kg biomass/kg air (as received basis). Relative biomass/air ratios (F_{rg}) employed in the gasification trials were determined according to expression (1),

$$F_{rg} = [m_f / m_a] / F_{stoi} \tag{1}$$

where: m_f = biomass feeding rate (kg h^{-1}). m_a = air mass flow rate (kg h^{-1}).
    F_{stoi} = stoichiometric fuel/air ratio for grapevine = 0.201 (kg biomass kg^{-1} air).

The experimental lower heating value of the biomass as received was 15.82 MJ kg^{-1}, equivalent to 16.83 MJ kg^{-1} on a dry ash-free basis. These values are comparable to other biomass types reported in the literature (Sheng and Acevedo, 2005; Friedl *et al.*, 2005).

Gasification of biomass in the entrained-flow reactor
Effect of gasification temperature
Figure 3 illustrates the effect of gasification temperature (in the range 750-1050ºC) on the chemical composition and heating value of the resulting gases. The experimental trials were conducted according to the conditions described in Table 1. The results show that high temperatures notably favoured the formation of hydrogen, with values rising from 4.59 % at 750ºC to 10.55 % at 1050ºC. The concentrations of other species (CO, CO_2, CH_4) were less significantly affected by temperature, although a small rise in CO (from 21.46 vol % at 750ºC to 22.64 vol % at 1050ºC) and CH_4 (3.35 vol % at 750ºC and 4.30 vol % at 1050ºC) and a drop in CO_2 values (14.25 vol % at 750ºC and 12.74 vol % at 1050ºC) were apparent at higher temperatures.

Changes in gas compositions (primarily the rise in hydrogen content) cause a progressive increase in the heating value (LHV) of the resulting producer gas from 3.65 MJ kg^{-1} at 750ºC to 4.95 MJ kg^{-1} at 1050ºC.
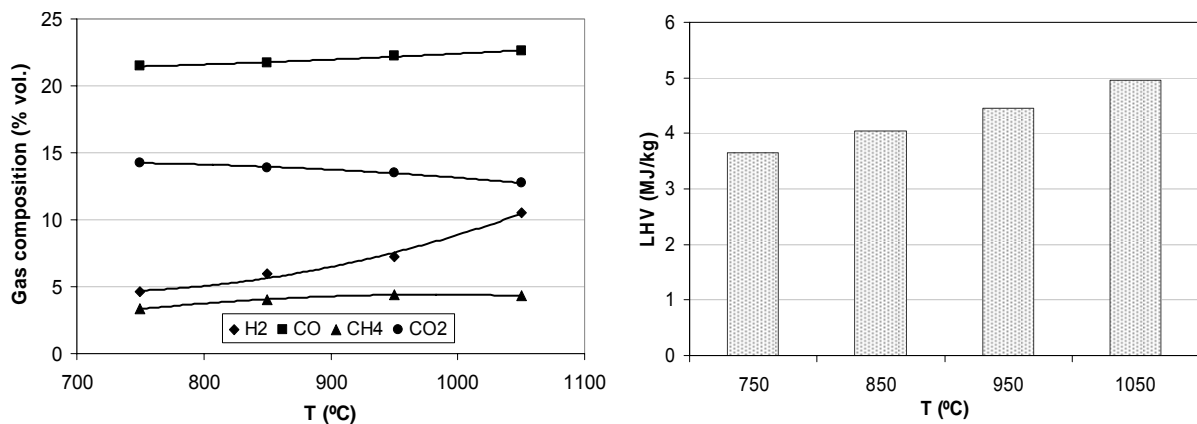

Figure 3. Composition (H_2, CO, CH_4) and LHV of the syngas resulting from the gasification of grapevine pruning waste at different temperatures

The results in Figure 4 show a small but noticeable increase in overall gas yields from 1.76 Nm^3 kg^{-1} at 750ºC to 1.98 Nm^3 kg^{-1} at 1050ºC. This extra gas derives from the additional biomass devolatilisation that takes place at higher temperatures, the secondary reforming of these volatile products, and also from the additional gasification of the tars and chars derived from the initial carbonisation of the biomass. All these reactions are favoured at high temperatures, as discussed in more detail below.

Cold gas efficiency (η_g) represents proportion of the chemical energy contained in the original biomass that is transformed into chemical energy in the producer gas. Cold gas efficiency values were determined according to expression (2):

$$\eta_g (\%) = \frac{\dot{m}_{pg} \cdot LHV_{pg}}{\dot{m}_{f\ d.a.f.} \cdot LHV_f} \cdot 100 \tag{2}$$

where: LHV_f and LHV_{pg} represent the low heating value of the fuel (biomass) and the resulting producer gas (MJ kg^{-1}), respectively; and m_{pg} and $m_{f\,d.a.f.}$ (kg h^{-1}) correspond to the mass flow rates of the producer gas and the biomass, respectively.
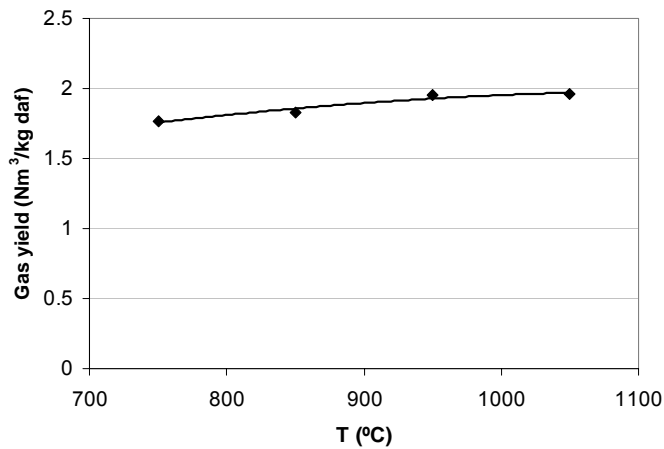

Figure 4. Gas yields generated from the gasification of biomass at different temperatures.

Figure 5 shows a notable increase in the cold gas efficiency of the process when using higher temperatures. This is attributed to the superior heating value (LHV) of the producer gas and, to a lower extent, to the increased gas yields generated at high temperatures.
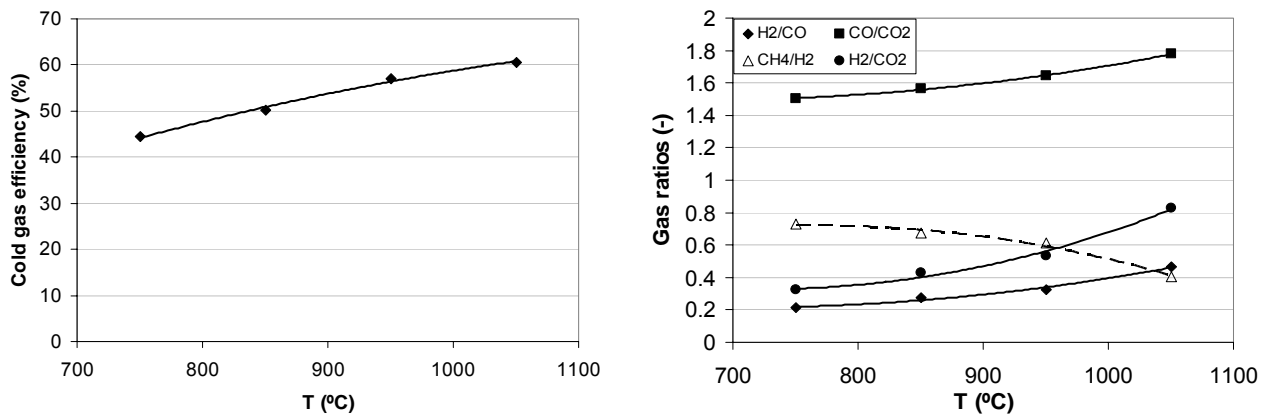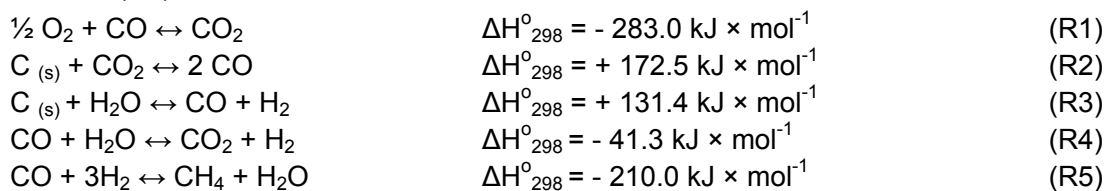

Figure 5. Cold gas efficiency (left) and gas ratios (right) from the gasification of grapevine pruning waste at different temperatures

The results described in this section confirm that the lower gasification temperature (750°C) is sufficient to attain almost complete devolatilization of the original biomass in the entrained-flow reactor. The rise in the CO/CO_2 ratio observed in Figure 5 at higher temperatures evidences the reducing atmospheric conditions of the process, derived from the complete exhaustion of oxygen (R1) in the upper parts of the reactor. The superior H_2/CO, H_2/CO_2 and CO/CO_2 ratios observed at 1050°C also confirm the favourable influence of temperature on the Boudouard (R2), steam reforming (R3) and water-gas shift (R4) reactions and the limited contribution of the methanation reaction (R5).

½ O_2 + CO ↔ CO_2	ΔH^o_{298} = - 283.0 kJ × mol^{-1}	(R1)
C$_{(s)}$ + CO_2 ↔ 2 CO	ΔH^o_{298} = + 172.5 kJ × mol^{-1}	(R2)
C$_{(s)}$ + H_2O ↔ CO + H_2	ΔH^o_{298} = + 131.4 kJ × mol^{-1}	(R3)
CO + H_2O ↔ CO_2 + H_2	ΔH^o_{298} = - 41.3 kJ × mol^{-1}	(R4)
CO + 3H_2 ↔ CH_4 + H_2O	ΔH^o_{298} = - 210.0 kJ × mol^{-1}	(R5)

Effect of the relative biomass/air ratio (F_{rg})

This section describes the effect of relative biomass/air ratio (F_{rg}) on the performance of the gasification process at 1050°C. As described in Table 2, biomass/air ratios were modified by changing the biomass feeding rate between 0.9-1.69 kg h^{-1} for a constant air flow of 2.08 kg h^{-1}. The experimental results in Figure 6 show a lower concentration of combustible gases (CO, H_2, CH_4) and a higher proportion of CO_2 when using low F_{rg} values. This may be attributed to partial combustion of the original biomass and the combustible gases caused by the higher proportion of oxygen in the process. Consequently, the heating value (LHV) of the resulting syngas increased significantly when using higher biomass/air ratios (3.93 MJ kg^{-1} at F_{rg} = 2.16 compared to 4.95 MJ kg^{-1} at F_{rg} = 4.05).

However, it is worthwile considering that the reduced heating values of the producer gas obtained at low biomass/air ratios were compensated by the production of significantly higher gas yields, as illustrated in Figure 7. Gas yields at F_{rg} = 2.16 (3.39 Nm^3 kg^{-1}) were 73 % higher than at F_{rg} = 4.05 (1.96 Nm^3 kg^{-1}), whereas differences in heating value only reached up to 26 %.
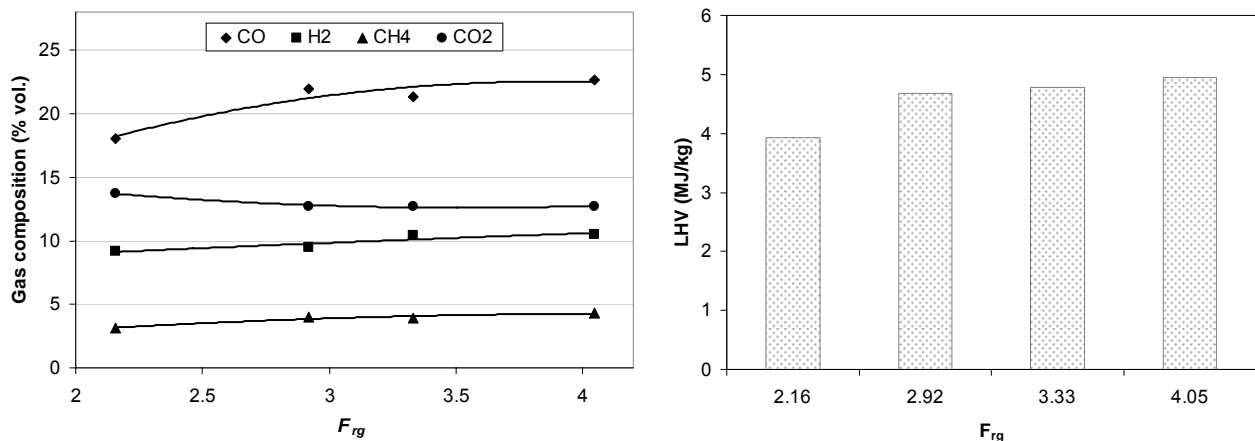

Figure 6. Composition (H_2, CO, CH_4) and lower heating value (LHV) of the gases resulting from the gasification of grapevine pruning waste at different biomass/air ratios
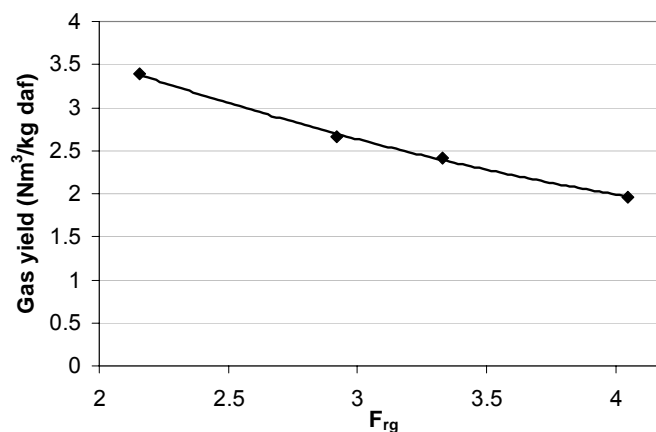

Figure 7. Gas yields from the gasification of biomass at different biomass/air ratios

The results in Figure 8 evidence a decrease in the cold gas efficiency of the process wihen increasing the the relative biomass/air ratio. These results confirm the assumption stated above that higher heating values are largely counteracted by lower gas yields. Cold gas efficiencies as high as 83.06 % were reached at 1050°C and F_{rg} = 2.16, compared to 60.60 % at F_{rg} = 4.05. Despite the higher process efficiencies, the use of very small biomass/air ratios may have negative consequences in terms of lower plant throughput and higher relative operating costs that need to be taken into consideration if the process is to be upscaled.

The reduction in the CO/CO_2 ratios observed (Figure 8) when using low biomass/air ratios (F_{rg} = 2.16) confirm the oxidizing conditions existing inside the reactor, which are attributable to the combustion of part of the gas in the upper parts of the reactor. This excess of oxygen facilitates the oxidation of CO to CO_2. The results in Figure 8 also show that H_2/CO, H_2/CO_2, CO/CO_2 and CH_4/H_2

gas ratios remain stable for F_{rg} values above 2.92. This suggests the reaching of equilibrium conditions in the reactions R1-R5 owing to the high temperatures employed (1050ºC).
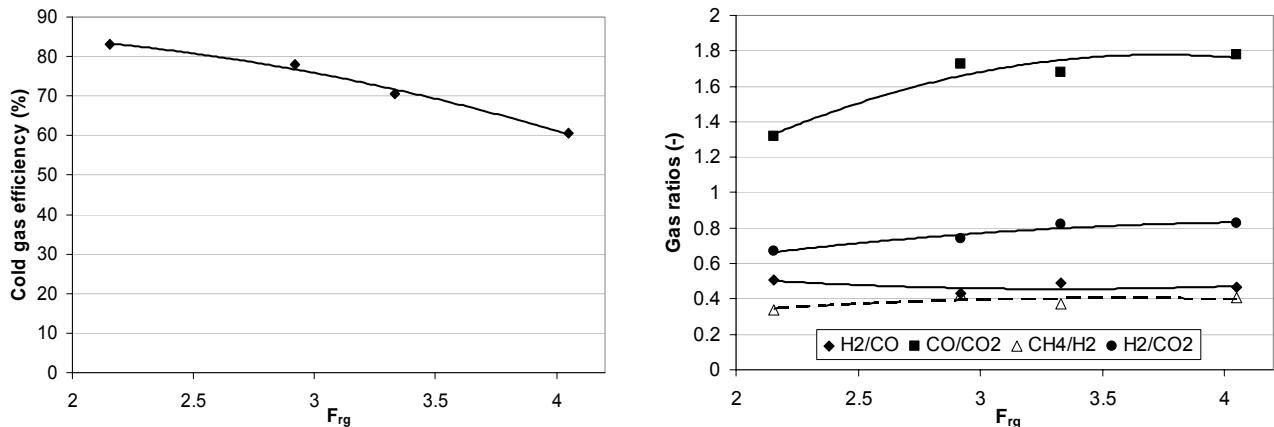

Figure 8. Cold gas efficiency (left) and gas ratios (right) from the gasification of grapevine pruning waste at different biomass/air ratios.

UPGRADING ALTERNATIVES FOR GAS PRODUCTS

The experimental results in this paper describe the suitability of entrained-flow designs in the gasification of biomass. This final section provides a review of alternative technologies in the conditioning of the resulting producer gas for the upgrading of its fuel properties, as a first analysis for subsequent modifications to the original reactor design.

The quality of the gas produced in a biomass gasification process, and therefore its potential to be used in different energy applications, is affected by different factors. On the one hand, the concentration of combustible gases determines the heat of combustion of the producer gas. Carbon monoxide has a higher heating value per unit of volume than hydrogen (LHV = 11.95 MJ m^{-3} vs. 8.42 MJ m^{-3}), although these are still significantly lower than methane (21.20 MJ m^{-3}). The dilution of combustible gases with atmospheric nitrogen is responsible for the even lower heating value observed in most biomass gasification processes. In our case, heating values reached a maximum of 4.95 MJ kg^{-1} at 1050ºC and F_{rg} = 4.05.

On the other hand, the presence of unwanted species (particulates, tars, acids) may restrain the use of the producer gas in certain energy applications. Boilers and burners are less stringent in terms of fuel quality requirements than internal combustion engines. Although tolerable amounts vary depending on the specific make and characteristics of the engine, the following values have been reported as a reference (FAO, 1986; Han and Kim, 2008):

-   dust: below 10-50 mg Nm^{-3}, and preferably 5 mg Nm^{-3}
-   tar: below 100-500 mg Nm^{-3}
-   acids: below 10-50 mg Nm^{-3} (measured as acetic acid).

Another aspect that needs to be taken into consideration is the energy efficiency, as this has a direct impact on the economics of the process. Cold gas efficiency represents the ratio between the chemical energy content in the product gas compared to the chemical energy in the original biomass fuel. This parameter is affected not only by the heating value of the syngas but also by its yield. As shown in this paper, higher energy efficiencies may require the use of low biomass feeding rates and may be accompanied by consequently lower syngas heating values. In any of these cases, economic considerations associated with the operating and investment costs of gasification plants of different sizes are prevalent in the design of a biomass gasification process.

Formation and control of tars and particulates

Various reviews have been dedicated to the formation and elimination of tars in biomass gasification processes (Han and Kim, 2008; Devi *et al.*, 2003). Biomass gasification takes place as series of sequential steps that occur simultaneously inside the reactor. In the entrained-flow design employed in this work, the original biomass is dried as it enters the reactor through the top, releasing water that is carried through the system. This is followed by thermal degradation (pyrolysis) of the dry biomass, an endothermic process that results in the release of organic vapours and the formation of char. The

mentioned organic vapours, together with the original biomass, the resulting chars and other combustible gases (CO, H_2, CH_4, etc), may be partly combusted (if oxygen is in excess) (R1), in a series of reactions that supply the energy consumed throughout the process. Excess organic vapours are endothermically reformed as to generate hydrogen and carbon monoxide. The solid char resulting from the pyrolysis of the biomass is also steam (R3) or dry (Boudouard reaction, R2) gasified. The extent of the water-gas shift (R4) reaction affects the H_2/CO ratio in the final producer gas. A wide range of other reactions (hydrogenation, methanation, aromatisation, condensation) determine the final composition of the syngas.

Biomass pyrolysis proceeds at a much faster rate than gasification. Hence, it is the products of the pyrolysis reaction (volatile organics and char), and not the original biomass, that actually react with the gasifying agent to produce the resulting gas. If the reaction temperature is not sufficiently high, the biomass feeding rate is too rapid and/or the contact time of the products inside the reactor is not adequately long, the gasification/reforming reactions will not completely consume the pyrolysis products. This unreacted matter undergoes complex secondary reactions (carbonisation, aromatisation, condensation, etc) that result in the formation of particulates and tars.

It has been described that tar formation represents one of the key technical barriers in the commercial success of biomass gasification (Bridgwater, 1994; Abu El-Rub *et al.*, 2004; Zhang *et al.*, 2004). Tars condense in different areas of the gasification system (reactor, filters, valves), thus blocking the flow and causing major operating problems. Furthermore, quality requirements are very stringent with regard to the concentration of tars in a fuel gas that is to be used in energy or chemical synthesis applications. Tar contents reported by different authors vary roughly between 0.5-100 g Nm^{-3}, depending on reactor design, operating conditions, and biomass properties (Han and Kim, 2008). Minimising tar levels in the syngas requires a combination of two strategies: the first one involves optimising reactor design and operating conditions; the second involves the conditioning of the resulting gas products.

Optimising reactor design and operating conditions.
Reactor design determines the temperature, reaction times and atmospheric conditions at which the original biomass and the secondary products (volatile organics, gas products, chars) are subjected during the gasification process. This affects the equilibrium and kinetics of each one of the steps described above (drying, pyrolysis, combustion, reforming, gasification, etc). For instance, co-current (downdraft) fixed bed reactor designs produce very low tar and particulate contents owing to the fact that the pyrolytic vapours are forced to pass through the high temperature zone after they have been generated. In contrast, counter-current (updraft) reactors generate very high tar contents since pyrolysis vapours are released through an area that is cooler than the one in which they were produced, resulting in very short exposure times to high temperatures. Comparatively, the formation of tars in entrained-flow, and bubbling fluidised bed reactors is lower than in updraft reactors. Tar values are reduced even further in circulating fluidised bed reactors owing to higher exposure time of the volatile organics to high temperatures and favourable heat exchange conditions (Devi *et al.*, 2003; Knoef, 2005).

Tar concentration is also reduced when increasing the oxidising capacity of the process by using higher temperatures; longer residence times of the reaction products (both biomass and pyrolytic products); and higher oxygen concentrations. In gasification processes with high relative biomass/air ratios (F_{rg}), oxygen availability in the gasification area is low, resulting in the formation of high levels of unreacted particulates and vapours. In contrast, the use of low biomass/air ratios and higher temperatures favours the oxidation of the biomass fuel (combustion conditions), resulting in lower tar values but also reduced syngas heating values (Han and Kim, 2008).

Physical methods for gas purification:
Physical gas cleaning technologies for particulate and tar control include those based on phase separation: cyclones, filters, electrostatic precipitators, activated carbon beds. Cyclones and filters, particularly the latter, are highly efficient at removing suspended solids, but have a very limited capacity to separate aerosols and volatile mists. Owing to their low operating temperatures, fabric filters and active carbon beds are rapidly blocked with deposits that are difficult to clean. Ceramic filters may operate at higher temperatures, being highly efficient with solid particulates while minimising the deposition of condensable products (tars) and reducing pressure drops.

A filtering system may be followed downstream by a wet scrubber aimed at removing tars and other organic species from the syngas. Scrubbing with organic solvents (rather than water) has been reported to be particularly efficient with tar separation (50-90 % efficiency to 20-40 mg Nm^{-3}) (Bridgwater, 2003). However, this alternative involves high costs and environmental shortcomings due to the generation of large volumes of contaminated solvents.

Tar cracking and reforming of volatile organics:
Tars removed from the gas stream by physical methods do not contribute to the energy efficiency of the gasification process. Hence, a better alternative involves their cracking into smaller molecular weight volatile species that can be readily reformed for the production of hydrogen and carbon monoxide. Tars have been reported to be highly resistant to thermal degradation (temperatures above 1200ºC and long reaction times) (Bridgwater, 1994). Hence, a large number of reviews have been dedicated to describe the catalytic cracking of tars using a wide range of natural and synthetic solids (Bridgwater, 1994; Sutton *et al.*, 2001; Zhang *et al.*, 2004; Han and Kim, 2008).

Catalytic cracking may be conducted using one of two strategies: *in situ*, where the biomass and the catalyst are in intimate contact with each other during the gasification process; or *ex situ*, where the tar containing gas stream is catalytically conditioned in a secondary reactor downstream of the main gasification process. Several papers have been published describing the catalytic conditioning of gasification gases over a wide range of natural and synthetic materials including alkaline minerals (olivine, dolomite, limestone, benotine), acid fluidised catalytic cracking (FCC) type zeolites (Y, Beta, ZSM-5) and acid mesostructured aluminosilicates (Al-MCM-41, Al-SBA-15). The catalytic activity has been related primarily to their acid/alkaline properties of the solid, while their pore size distribution and surface area contributes to the accessibility of the reacting molecules to the internal catalytically active sites. Other aspects that need to be taken into consideration when analysing the potential of these products include: market cost; hydrothermal stability; poisoning (sulphur); deactivation by coke deposition; and thermal regeneration capacity.

Reforming involves the partial oxidation of organic vapours derived from the pyrolysis of the original biomass, resulting in the formation of hydrogen and carbon monoxide. Small molecular weight organic species reform more readily than heavier products, which is why cracking of tarry organic species facilitates their subsequent reforming. Hence, cracking and reforming both contribute to the elimination of heavy tars, maximising the cold gas efficiency of the process. Conventional and advanced nickel based catalysts, like the ones employed in the reforming of natural gas, have also been used to enhance reforming reactions during the gasification process. Noble metals (Pt, Pd, Rh, Ru) have been reported to exhibit stronger reforming activities and are less prone to poisoning than nickel, although their market prices are significantly higher. The preparation of catalyst containing active reforming metals (Ni, Pt) supported over alkaline (MgO, CaO, dolomite) and acid (zeolites) solids has been reported to increase the efficiency of the process owing to the combined cracking and reforming activity of the mix (Zhang *et al.*, 2007; Yang *et al.*, 2010).

Maximising hydrogen content: water-gas shift reaction.
Some papers speculate on the potential of adapting biomass gasification for the generation of pure hydrogen, for use in advanced energy or chemical synthesis applications. This option has not been commercially proven and would require the development of highly cost-effective gas separation and purification technologies. This separation would be alleviated if the biomass gasification process were conducted using pure oxygen (instead of air), thus reducing the diluting effect of nitrogen and the need to remove it from the resulting syngas.

Carbon monoxide is particularly detrimental to the use of hydrogen in advanced energy applications. Poisoning of platinum based catalysts employed in low temperature Polymer Electrolyte Membrane (PEM) fuel cells takes place at CO concentrations as low as 10 ppm. In the water-gas shift reaction, carbon monoxide reacts with water to form carbon dioxide and hydrogen (Ruettinger *et al.*, 2003). Owing to the exothermic nature of this reaction, the equilibrium of WGS is shifted to the formation of hydrogen only at low temperatures. However, the kinetic efficiency is limited at low temperatures. Therefore, a two stage (high temperature + low temperature) system is frequently used. Owing to their low cost, thermal stability and resistance to deactivation, commercial high temperature WGS processes (HTS) use iron based catalysts. Low temperature WGS processes (LTS) use copper based catalysts, which are 1000 times more active but also very sensitive to deactivation and

poisoning. Other materials currently being investigated for their catalytic activity in WGS reactions include: lanthanum (La_2O_3) and cerium oxides (Ce_2O_3), noble metals (Pt, Rh, Ru) supported on different metal oxides. The practical generation of pure hydrogen from biomass gasification is still at a very early stage of development.

Water-gas shift technology may also be used with the less ambitious objective of modifying the fuel properties of the producer gas. Owing to differences in density, heat of combustion, oxygen stoichiometry, flammability and other combustion properties between hydrogen and carbon monoxide, modification of the CO/H_2 ratio has a notable effect on the fuel behaviour of the gas determining its potential in different energy applications.

CONCLUSIONS

Gasification of a grapevine pruning biomass has been succesfully conducted in an entrained-flow reactor designed and constructed at UCLM. Experimental trials have been carried out in order to evaluate the effect of temperature and relative biomass/air ratios in the composition, heating value and yields of the resulting producer gas. The results have shown that the use of higher temperatures favours the formation of hydrogen, resulting in higher heating values of the resulting gas (LHV up to 5.0 MJ kg^{-1}). Gas yields and the concentration of other gases (CO, CH_4 and CO_2) was less notably affected by temperature.

The use of low relative biomass/air ratios (< 2.5) resulted in lower levels of CO and H_2 in the resulting producer gas, and a consequently reduction in its heating value. In contrast, gas yields were significantly higher at low biomass/air ratios, compensating for the reduction in heating value. Hence, the highest cold gas efficiencies were (up to 83 %) were reached when biomass gasification was conducted using low biomass/air ratios (F_{rg} = 2.16) and high temperatures (1050ºC). In addition to these, other considerations like plant throughput, operating costs and investment costs, will need to be taken into consideration when selecting the optimum gasification conditions.

The presence of tars and particulates may limit the potential of the producer gas in certain energy applications (internal combustion engines, gas turbines, fuel cells). There exist different alternatives to the upgrading of gaseous products. An initial filtration or cyclone system may be the most appropriate to remove particulates from the gas stream. This could be followed by a thermocatalytic process intended to promote the cracking and reforming of volatile organics. Producer gas clean from tars and particulates may be subjected to water-gas shift to increase the hydrogen and reduce CO concentrations, as required in certain energy applications.

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