Hydrogen production from the co-utilisation of coal and biomass

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Abstract
In this work, co-gasification and co-pyrolysis of binary blends of a bituminous coal (PT) and two types of biomass (olive stones, OS; chestnut, CH) were conducted at atmospheric pressure in a fixed bed reactor. Pyrolysis was performed under nitrogen, and gasification under steam/oxygen atmosphere. In the fixed bed reactor, the particles of the different fuels are in close contact, providing an optimum means for evaluating possible synergetic effects. Pyrolysis tests showed the lack of interaction between the components of the blend. Mass distribution and gases produced during the pyrolysis tests can be predicted from those of the individual components and their mass fractions. During the gasification tests, interactions between the components of the blends were observed. An increase of tar production above the theoretically calculated value, as the percentage of the biomass increased in the blends was observed. The gases produced during gasification of PT-OS blends followed the linear-additive rule, with the exception of CO_2. However, in the case of PT-CH blends, the main gases produced (CO_2, CO and H_2) deviated from the additive rule.

Keywords: gasification, biomass co-firing

INTRODUCTION

Nowadays, hydrogen is considered as an energy carrier for the future. The use of hydrogen can reduce the actual dependence of the energy system on fossil fuels, and can contribute to reduce the negative effects of greenhouse gas emissions (Midilli, 2005; European Commission, 2003). European energy systems are characterised by their dependence on imported fossil fuels and by the rising energy demand. The use of these fuels has a great impact in the environment due to the pollutant emissions produced during their combustion. In the present scenario, the current challenge in the energy production is to reduce the dependence on fossil fuels and to achieve a sustainable energy system. The use of renewable energy is a matter of interest, as it represents a diversification of energy sources. Renewable energies are indigenous sources; therefore the increase of their use will have positive implications in the security of supplies. Additionally, the use of renewable energies has a lower environmental impact than fossil fuels, so their implementation will contribute to preserve the equilibrium of ecosystems. In order to achieve this, a target of obtaining 12% of Europe's primary energy demand from renewable sources by 2010 has been established (European Commission, 1997).

About half of worldwide hydrogen production comes from natural gas reforming (Dunn, 2002) and 98% of the total production comes from fossil fuels. The use of natural gas as a feedstock has the drawback of the volatility of the natural gas prices. For this reason, there is an increasing interest in lower and stable cost fuels to produce mixtures of hydrogen and carbon monoxide by means of gasification. Attractive features of this technology include the ability to produce a high-quality syngas product, which can be used for energy or chemicals production (Song, 2005). Gasification can also accommodate a wide variety of gaseous, liquid, and solid feedstocks. Among the latter, coal, biomass, and wastes such as petroleum coke, heavy refinery residuals and municipal sewage sludge have all been used in gasification operations (González, 2006; André, 2005; Priyadarsan, 2005;

Filippis, 2004; Ponzio, 2007). A hydrogen economy -a future energy system based on hydrogen and electricity- from renewable sources is essential for the long-term.
Of the different renewable energy sources, biomass holds most promise for increasing use in the next few years. Moreover, biomass is considered as a neutral carbon fuel because the carbon dioxide released during its utilisation is an integral part of the carbon cycle.
Currently, there is emerging consensus that in the short term hydrogen will be produced from fossil fuels, including the processes of CO_2 capture and storage. Co-gasification of coal with biomass presents the advantage of a net reduction in CO_2 emissions, if CO_2 capture is contemplated in the process. Biomass gasification is one of the least expensive methods of producing hydrogen from renewable resources. A wide variety of agricultural wastes and other biomass sources can be used to produce hydrogen (Faaij, 2006; Albertazzi, 2005). In addition, bio-solids such as sewage sludge could be effectively used for syngas production (Menéndez, 2004). Biomass gasification technologies have recently been successfully demonstrated at large scale. However the actual operation experience is limited, due to the difficulties to study a wide range of conditions. For this reason, more research is needed at a laboratory scale to gain more knowledge and confidence in this technology.

In this work the co-gasification and co-pyrolysis of mixtures of coal and two types of biomass were carried out. Pyrolysis tests were performed using nitrogen, while mixtures of steam, nitrogen, and oxygen were used for gasification tests. During both type of tests, the mass yields distribution in char, liquid and gas was calculated, and the gas composition was measured. The objective of this work is to study the possible synergistic effects between coal and biomass during pyrolysis and gasification, with a special view to the production of hydrogen.

EXPERIMENTAL

In this work, a bituminous coal (PT) was used. This coal was ground and sieved to obtain a fraction with a particle size of 1-2 mm. Additionally, two types of biomass were used, olive stones (OS) and chestnut tree residues (CH). Raw olive stones were ground and sieved to obtain a particle size fraction of 1-2 mm. Cylindrical pellets of 4 mm diameter and 1 mm height were made using the chestnut tree residues. Proximate and ultimate analyses of the samples used are given in Table 1.

TABLE 1: Proximate and ultimate analyses of the samples

	Proximate analysis (%)				Ultimate analysis (%, daf)				
Sample	Moisture	Ash (db)	Volatile matter (db)	Fixed carbon (db)*	C	H	N	S	O*
PT	4.2	39.3	23.8	36.9	74.5	5.1	1.6	1.5	17.3
CH	8.5	1.2	80.7	18.1	50.3	2.9	0.1	0.0	43.7
OS	7.7	0.6	82.4	17.0	50.9	6.0	0.1	0.0	43.0

*calculated by difference

The gasification and pyrolysis tests were performed in a quartz tubular fixed bed reactor (20 mm internal diameter, 455 mm height). A sample mass of 4 mg was used in all the tests. A thermocouple in contact with the sample bed, measured the reaction temperature, which was controlled to ± 5 °C. The pyrolysis tests were carried out under nitrogen (150 cm^3/min). The gasification experiments were performed under steam (70 vol. %) and oxygen (5 vol. %), carried by an inert flow of N_2,

using a total flow rate of 150 cm^3/min. Prior to the commencement of the experiments, N_2 was passed through the sample bed for 30 min.
During these tests, the samples were heated at 14 ºC/min from room temperature up to 1000 ºC, and this temperature was maintained until the end of the gas production. The liquid fraction was separated by means of condensers containing an ice bath. The non-condensable gases were collected in Tedlar® sample bags with a polypropylene fitting for sampling. H_2, N_2, CO, CO_2, CH_4, C_2H_4 and C_2H_6 were analysed in a gas chromatograph Perkin-Elmer Sigma 15 with a TCD detector. A Teknokroma 10FT Porapak N, 60/80 and a Teknokroma 3FT Molecular Sieve 13X, 80/100 columns, were used. The system was calibrated with a standard gas mixture at periodic intervals.

At the end of each test the liquid and solid fractions were weighed and the amount of gas generated during the experiment was calculated from a nitrogen balance, since the nitrogen fed and its composition in the gases evolved are known.

RESULTS AND DISCUSSION

Pyrolysis tests

Table 2 resumes the mass yield of the different mass fractions (gas, liquid, char) during the pyrolysis tests. As was expected, biomass, CH and OS, produce a low char yield during pyrolysis, due to the weaker strength of the macromolecular structure of these types of materials (Shafizadeh, 1982). When coal PT is blended with biomass, there is a clear reduction on char yield, due to the low amount of char produced during the pyrolysis of biomass.

TABLE 2: Mass distribution during pyrolysis tests

	Experimental Fraction Yields (%)			Theoretical Fraction Yields (%)		
Sample	Gas	Liquid	Char	Gas	Liquid	Char
PT	19.7	7.8	72.5	19.7	7.8	72.5
10% OS	23.6	9.0	67.4	21.2	9.8	69.0
20%OS	24.9	11.2	63.9	22.6	11.8	65.6
30%OS	25.6	13.2	61.2	24.1	13.8	62.1
100%OS	34.3	27.9	37.8	34.3	27.9	37.8
10%CH	21.3	11.0	67.7	21.2	9.8	69.1
20%CH	23.1	12.3	64.6	22.6	11.7	65.7
30%CH	24.9	14.0	61.1	24.1	13.7	62.2
100%CH	34.4	27.3	38.3	34.4	27.3	38.3

If there is no interaction between the components of the blends during the pyrolysis tests, the fraction yields could be calculated from those corresponding to the individual fuels and their respective fractions in the blend. Table 1 includes the calculated fraction yields. As can be seen in this table, the experimental and theoretical values are in agreement, showing that there is no appreciable interaction between the components, despite the experimental device used that ensured an intimated contact between particles. These results are in agreement with those encountered by other authors using

different experimental devices, such as thermogravimetric analysers (Pan, 1996; Biagini, 2002), fluidized beds (Collot, 1999), drop tube reactors and horizontal tubular reactors (Meesri, 2002).

As was mentioned above, gas composition was determined by means of GC analysis. As an example, Figure 1 shows the concentration of the main gases produced during the pyrolysis tests of the individual components (H_2, CO, CO_2 and CH_4). C_2H_6 and C_2H_4 concentration was below 0.1 % during all the tests (pyrolysis and gasification) and are not included in the plots and tables. At low temperatures, during the primary pyrolysis, CO and CO_2 are the main species released; while at higher temperatures, gas production is due mainly to the generation of H_2 during the condensation of the carbon structure as the secondary pyrolysis proceeds (Strezov, 2007; Ladner, 1988)

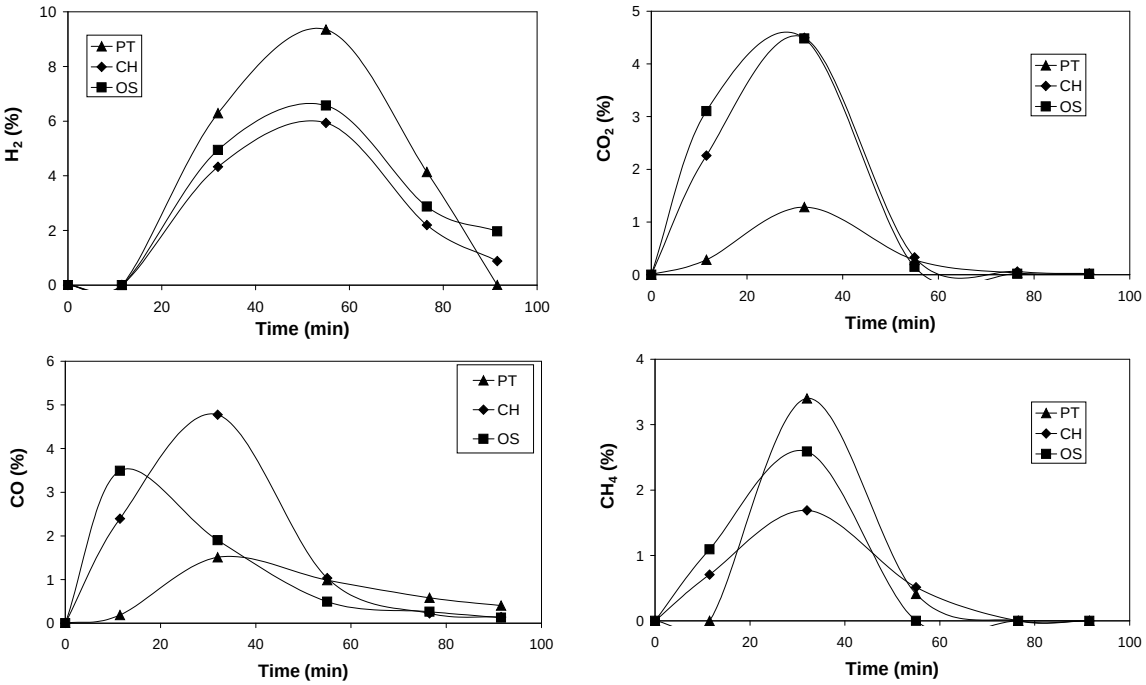
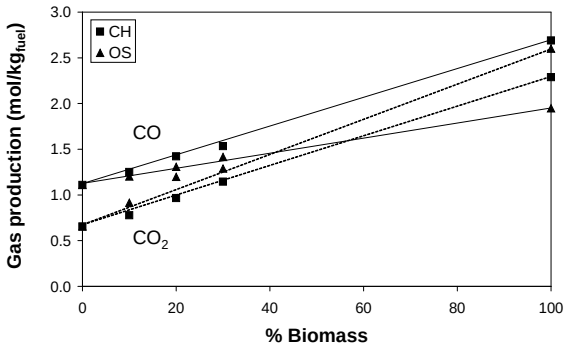


FIGURE 1: H_2, CO, CO_2 and CH_4 composition during pyrolysis tests of the individual fuels.

These plots can be used to determine the amount of each gas produced during pyrolysis by integration of the curves. Figure 2 shows the amount of the main gases produced during the pyrolysis tests. As can be seen, hydrogen is the main gas produced during the pyrolysis tests. PT coal produces higher amount of H_2 and CH_4, while biomasses produce more CO and CO_2. This is due to the high oxygen content of biomass that promotes the production of oxygenated species.



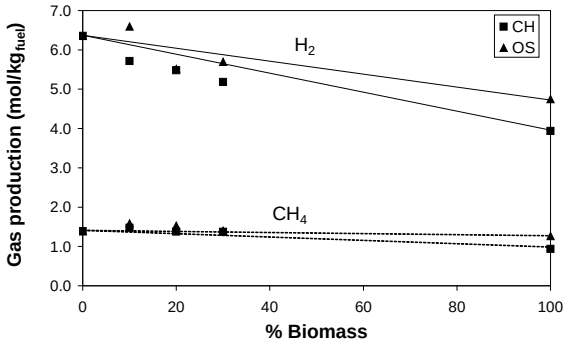


FIGURE 2: Gas produced during pyrolysis tests of the blends.

When the percentage of biomass increases in the blend, more CO and CO_2 are produced. On the other hand, a decrease on H_2 and CH_4 production is observed when coal PT is blended with biomass. It can be observed in Figure 2 that the formation of gases is proportional to the percentage of the components in the blend. These results indicate the absence of interactions between coal and biomass during pyrolysis in the fixed bed reactor.

Gasification tests

During the gasification tests, a reduction in tar yield is observed respect to the pyrolysis tests, due to the partial gasification of this fraction. Figure 3 shows the tar mass yield during gasification tests of PT-CH and PT-OS blends. An important production of tars during biomass gasification (CH, OS) was obtained. This phenomenon has implications in biomass gasification processes, as it produces a reduction in gas yield and operational problems. When coal PT is blended with biomass, there is an increase in tar production respect to the individual coal. This increase is higher than the additive rule value, showing that there is some degree of interactions between both fuels during gasification, which influences the tar production. The deviation increases with the percentage of biomass, and is higher in the case of PT-CH blends.

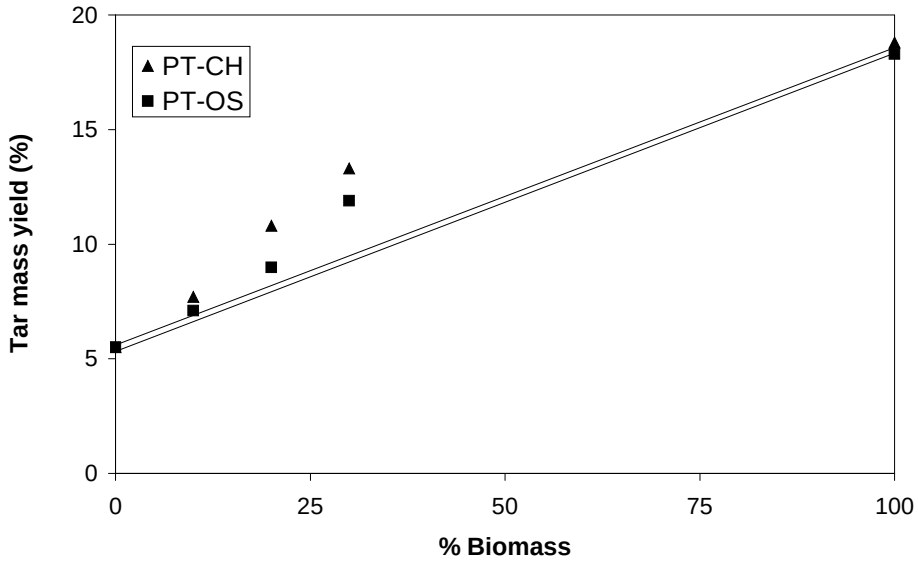


FIGURE 3: Tar mass yield during gasification tests of the blends.

Gas production during gasification tests was calculated with the same methodology used during pyrolysis, and the results obtained for the individual fuels are resumed in Table 3.

TABLE 3: Gas production during gasification of the individual fuels

	Gas production (mol/kg_{fuel})			
Sample	H_2	CO	CO_2	CH_4
PT	22.1	14.1	16.3	1.3
CH	9.4	7.4	19.0	1.0
OS	14.2	6.2	18.2	1.2

An increase in hydrogen is observed, respect to the pyrolysis tests, due to the reaction of the carbonaceous material with the steam. CO and CO_2 production increased due to the oxidation and gasification of the carbon. In both types of tests, gasification and pyrolysis, a similar amount of CH_4 is produced, suggesting that it has a pyrolytic origin. The amount of gas produced during the gasification tests of PT-CH blends is shown in Figure 4.

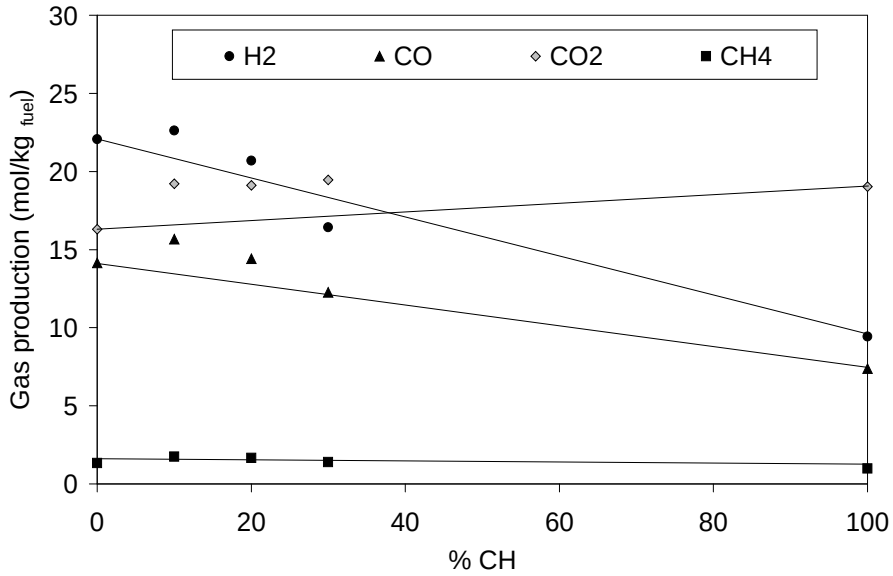


FIGURE 4: Gas produced during gasification tests of PT-CH blends.

As can be seen in this figure, gasification of PT-CH blends produces a similar amount of CO_2 than biomass alone, even using 10% of biomass. H_2 and CO production show a positive deviation from the additive rule for the blends with 10% and 20% of CH. However, the generation of hydrogen is affected in a negative way during the gasification of the blend with 30% of CH. Methane production remains practically constant when the percentage of CH is varied. These results indicate the existence of interactive effects between coal PT and biomass CH during gasification tests.

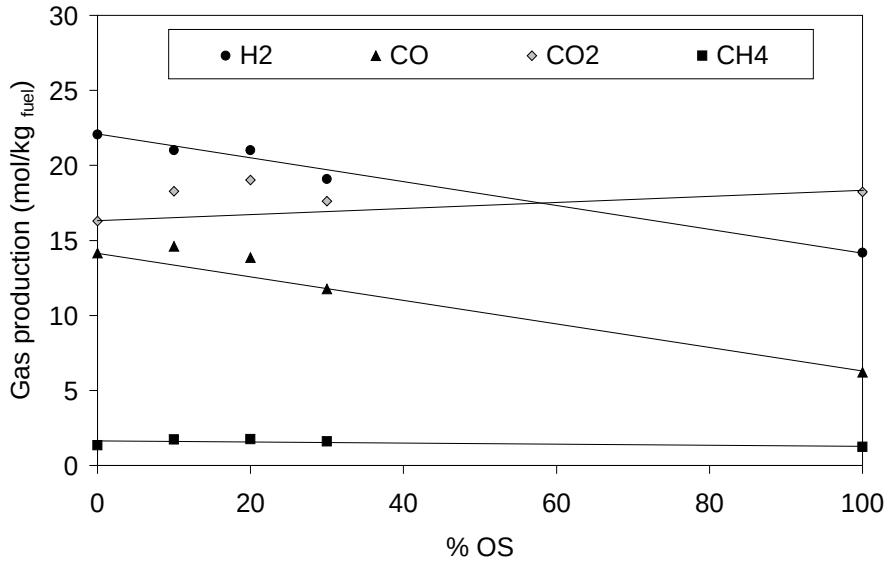


FIGURE 4: Gas produced during gasification tests of PT-OS blends.

Figure 4 shows the gas produced during gasification of PT-OS blends. As with the PT-CH blends, the CO_2 generated lies above the theoretical value calculated assuming that there is no interaction between both fuels. However, H_2, CO and CH_4 production follow the additive rule. These results suggest that a lower degree of interaction exists during gasification of PT-OS blends, in comparison with PT-CH.

CONCLUSIONS

The results obtained during the co-pyrolysis of binary blends of a bituminous coal and two types of biomass show that there is a lack of interaction between the fuels. The mass distribution (char, liquid, gas) can be calculated from those of the individual components and their respective mass fractions. Main gases produced during the co-pyrolysis (H_2, CO, CO_2 and CH_4) were measured and it was observed that they followed the additive rule.

During gasification tests, different degrees of interactions were observed. An increase of tar production above the additive rule was observed as the percentage of the biomass increases in the blends. Gases produced during PT-CH gasification show deviation from the linear rule, especially the CO_2. In the case of PT-OS blends, the gases produced showed a lower degree of interaction.

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References

Albertazzi, S., Basile, F., Brandin, J., Einvall, J., Hulteberg, C., Fornasari, G., Rosetti, V., Sanati ,M., Trifirò, F., Vaccari, A. (2005). The technical feasibility of biomass gasification for hydrogen production. *Catalysis Today*, 106, 297–300.

André, R. N., Pinto, F., Franco, C., Dias, M., Gulyurtlu, I., Matos, M. A. A., Cabrita, I. (2005) Fluidised bed co-gasification of coal and olive oil industry wastes. *Fuel*, 84, 1635-44.

Biagini, E., Lippi, F., Petarca, L., Tognotti, L. (2002). Devolatilization rate of biomasses and coal-biomass blends: an experimental investigation. *Fuel*, 81, 1041-1050.

Collot, A.G., Zhuo, Y., Dugwell, D.R., Kandiyoti, R. (1999). Co-pyrolysis and co-gasification of coal and biomass in bench-scale fixed-bed and fluidised bed reactors. *Fuel*, 78, 667-679.

Dunn, S. (2002) Hydrogen futures: toward a sustainable energy system. *International Journal of Hydrogen Energy*, 27, 235-64.

European Commission, COM (97)599 final (1997). Energy for the future: Renewable sources of energy.

European Commission, EUR 20719 EN (2003). Hydrogen Energy and Fuel Cells. A vision of our future. *Luxembourg: Office for Official Publications of the European Communities*, 36 pp., ISBN 92-894-5589-6.

Faaij, A. P. C. (2006). Bio-energy in Europe: changing technology choices. *Energy Policy*, 34, 322–42.

Filippis, P., Borgianni, C., Paolucci, M., Pochetti, F. (2004). Prediction of syngas quality for two-stage gasification of selected waste feedstocks. *Waste Management*, 24, 633-39.

González, J. F., Gañán, J., Ramiro, A., González-García, C. M., Encinar, J. M., Sabio, E., Román, S. (2006). Almond residues gasification plant for generation of electric power. Preliminary study. *Fuel Processing Technology*, 87, 149-55.

Ladner, W.R. (1988). The products of coal pyrolysis: properties, conversion and reactivity. *Fuel Processing Technology*, 20, 207-222.

Meesri, C ., Moghtaderi, B. (2002). Lack of synergetic effects in the pyrolytic characteristics of woody biomass/coal blends under low and high heating rate regimes. *Biomass and Bioenergy* , 23, 55–66.

Menéndez, J. A., Domínguez, A., Inguanzo, M., Pis, J. J. (2004). Microwave pyrolysis of sewage sludge: analysis of the gas fraction. *Journal of Analytical and Applied Pyrolysis*, 71, 657-67.

Midilli, A., Ay, M., Dincer, I., Rosen, M. A. (2005). On hydrogen and hydrogen energy strategies. I: current status and needs. *Renewable and Sustainable Energy Reviews*, 9, 255-71.

Pan, G.P., Velo, E., Puigjaner, L. (1996). Pyrolysis of blends of biomass with poor coals. *Fuel*, 75, 412-418.

Ponzio, A., Kalisz, S., Blasiak, W. (2007). Effect of operating conditions on tar and gas composition in high temperature air/steam gasification (HTAG) of plastic containing waste. *Fuel Processing Technology*, 87, 223-233.

Priyadarsan, S., Annamalai, K., Sweeten, J. M., Holtzapple, M. T., Mukhtar, S. (2005). Co-gasification of blended coal with feedlot and chicken litter biomass. *Proceedings of the Combustion Institute*, 30, 2973-80.

Shafizadeh, F. (1982). Introduction to pyrolysis of biomass. *Journal of Analytical and Applied Pyrolysis*, 3, 283-305.

Song, X., Guo, Z. (2005). Technologies for direct production of flexible H2/CO synthesis gas. *Energy Conversion and Management*, 47, 560–69.

Strezov, V., Patterson, M., Zymla, V., Fisher, K., Evans, T.J., Nelson, P.F. (2007). Fundamental aspects of biomass carbonisation. Journal of Analytical and Applied Pyrolysis, 79, 91-100.