Co-gasification of different rank coals with biomass and petroleum coke in a high-pressure reactor for H₂-rich gas production

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Abstract

Four coals of different rank were gasified, using a steam/oxygen mixture as gasifying agent, at atmospheric and elevated pressure in a fixed bed reactor fitted with a solids feeding system in continuous mode. Independently of coal rank, an increase in gasification pressure led to a decrease in H₂+CO production and carbon conversion. Gasification of the different rank coals revealed that the higher the carbon content and reactivity, the greater the hydrogen production. Co-gasification experiments of binary (coal-biomass) and ternary blends (coal-petcoke-biomass) were conducted at high pressure to study possible synergetic effects. Interactions between the blend components were found to modify the gas production. An improvement in hydrogen production and cold gas efficiency was achieved when the coal was gasified with biomass.

Keywords: co-gasification; biomass; coal; hydrogen; high-pressure

1. Introduction

The continued use of coal as a fuel in the long term is subject to its being employed in a clean and efficient way. One of the most promising alternatives is gasification technology, which has the advantage that it is highly versatile, it can be used with a wider range of fuels (coal, biomass, petroleum coke, etc.), and there is a greater variety of applications for the obtained product. The syngas produced from it can be used to generate electricity (IGCC), chemical feedstocks, hydrogen, etc., depending on the demand of the market. Energy systems based on the use of hydrogen are considered to offer great promise for the future. Some of the advantages of hydrogen energy include its low environmental impact and its attractive future application in fuel cells technology for producing electricity (Midilli et al., 2005). Nowadays, 98 % of the hydrogen produced comes from fossil fuels, mainly from natural gas reforming (approx. 50 %) (Dunn, 2002). However, due to the uncertainty of natural gas supplies and the volatility of its price, in the medium term, systems based on coal gasification may offer a

better alternative. Coal gasification is a well established technology for producing syngas ($\text{CO}+\text{H}_2$), a process in which hydrogen production can be increased by means of the water-gas shift reaction (WGS), $\text{H}_2\text{O}+\text{CO} \leftrightarrow \text{H}_2+\text{CO}_2$. With this technology, a highly concentrated stream of hydrogen can be generated, provided that CO_2 capture is undertaken at the same time. Some studies have shown that electricity generation based on the combination of hydrogen fuel cells and CO_2 capture are less costly compared to post-combustion systems (Damen et al., 2006; Damen et al., 2007).

Co-gasification of biomass with coal, which is considered a bridge between the energy production systems based on fossil fuels and those based on renewable energy sources, could contribute to reducing CO_2 emissions and our dependency on fossil fuels. In addition, the use of biomass in combination with coal in the same power plant would avoid the typical problems associated with small biomass-fired power plants, i.e., high specific cost, low efficiency, while at the same time it would reduce the risk of a biomass shortage (Valero and Usón, 2006). The high thermochemical reactivity of biomass and its high volatile matter content suggest that some synergetic effects can be expected in the simultaneous thermochemical treatment of biomass and coal. Whether such effects will occur is dependent upon certain gasification conditions such as feedstock type, direct particle contact, pressure, temperature, reactor type, etc. (McLendon et al., 2004).

Currently, co-gasification of coal and biomass is being conducted at IGCC electricity generating power plants like the Willem-Alexander power station in Buggenum (Netherlands), where residual wastes from the agricultural sector, such as sawdust, grape and sunflower seeds, and peanut shells are cogasified with coal. Similarly, at ELCOGAS in Puertollano (Spain), the world's largest IGCC facility to use coal and petcoke as feedstock, there is an ongoing project aimed at evaluating the effects of adding small percentages of biomass (up to 10 wt.%) on the performance of the plant (Casero and García-Peña, 2007).

The co-utilisation of biomass and waste with coal on a large scale, or even at pilot scale, is very difficult to carry out as it involves a wide range of experimental conditions, the duplication of experiments and the validation of general trends. Hence, the results attained at bench-scale, such as the ones reported in the present work, are used to provide overall tendencies that will help to choose the most suitable operating parameters for pilot plants.

In this work, the effect of coal rank on gas production and other process parameters during gasification under atmospheric and elevated pressures was studied. In addition, co-

gasification experiments on binary (coal-biomass) and ternary (coal-petcoke-biomass) blends were carried out to study the effect of blending different types of fuels. For these purposes, a novel pressurized fixed bed gasifier, using steam/oxygen mixtures as gasifying agent, fitted with a solids feeding system in continuous mode, was employed.

2. Experimental

Four coals of different rank were selected; two Spanish coals: a semianthracite (HV) and a high volatile bituminous coal (PT), a medium volatile bituminous coal from South Africa (SA), and a high volatile bituminous coal from China (DT). In addition, a petcoke (PC) and two biomass samples: olive pulp (OP) and pine sawdust (PS) were selected to carry out the co-gasification experiments. The samples were ground and sieved to obtain a fraction with a particle size of 75-150 μm . The proximate and ultimate analyses and the high heating value of the samples are presented in Table 1.

Figure 1 shows a flow diagram of the experimental device used for the gasification tests. It consists of a stainless steel tubular reactor (13 mm internal diameter, 305 mm height) with a porous plate, which is able to work at a maximum pressure of 20 atm at 1000 °C. Fuel particles are fed continuously into the system from a pressurized hopper, which ensures a steady gas production. The mass flow rate of the solids is controlled using a pneumatically actuated valve.

The reactor temperature is controlled by means of a thermocouple connected to a temperature controller and data recorder. The thermocouple is in contact with the sample bed. The pressure is measured by a pressure transducer and automatically controlled by a micro-valve.

The gas composition of the dried gas fraction (H_2 , O_2 , N_2 , CO , CH_4 and CO_2) was analysed on-line, using a dual channel micro-GC Varian CP-4900 fitted with a thermal conductive detector (TCD). The micro-GC was equipped with a molecular sieve, Molsieve 5Å, and a HayeSep A, columns; helium was used as carrier gas. The system was calibrated employing a standard gas mixture at periodic intervals. The amount of gas generated during the experiments was calculated from a nitrogen balance, since the amount of nitrogen fed in and the composition of the nitrogen evolved were already known. The margin of experimental error was evaluated by calculating the errors produced in the gas composition in experiments repeated several times on different days. The values obtained were all lower than 4%.

In addition to the main gases produced (H_2 , CO , CO_2 and CH_4) expressed in mol of gas per kg of sample on a dry ash free basis, other important parameters such as the gas yield, Y ($Nm^3 kg^{-1}$), gas high heating value, HHV ($kJ Nm^{-3}$), cold gas efficiency, η (%) and carbon conversion, X (%), were calculated. In this work, the gas yield, Y , was calculated as the outgoing dry gas flow rate per mass flow rate of dry fuel. The gas high heating value, HHV , was defined as the gross calorific value of dry gas on a volumetric basis. Cold gas efficiency, η , was defined as the ratio between the energy content of the gas and the energy contained in the solid fuel. Finally, the carbon conversion, X , was defined as the total amount of carbon contained in the gas produced (CO , CO_2 and CH_4) with respect to the total carbon contained in the sample fed in.

The gasification of the coals was carried out isothermally (1000 °C) at pressures of 1 and 15 atm, using a mixture of oxygen and steam (15 and 25 vol.%, respectively) as gasifying agents, carried in an inert flow of N_2 . The total gas flow rate was pre-set to ensure that the O/C value (1.3) and the H_2O/C value (1.1) at the reactor inlet would remain constant. The values of the oxygen and steam introduced with respect to the stoichiometrically necessary, O/O_e and H_2O/H_{2O_e} , were 0.4 and 1.5, respectively.

3. Results and discussion

3.1. Effect of coal rank

Figure 2 shows the main gas production obtained during the gasification experiments of the coals (HV, SA, DT and PT) at pressures of 1 and 15 atm. In order to evaluate the differences between the experimentally obtained gas values and those derived from the thermodynamic equilibrium, a gasification reaction equilibrium model based on the minimization of the total Gibbs free energy was used (Morley, 2005), the results of which are also presented in Figure 2. From the equilibrium values, it can be seen that, independently of the coal rank, syngas production (H_2+CO) is always higher at atmospheric pressure than at 15 atm, whilst the production of CO_2 and CH_4 is favoured when the pressure in the system is increased, since there is a shift in the equilibrium gas phase reactions to the side which has the fewer moles of gas (Eq. (1) dry reforming: $CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$; Eq. (2) steam reforming: $CH_4 + H_2O \leftrightarrow CO + 3H_2$) (Sue-A-Quan et al., 1991; Atimtay et al., 1998).

The same trends were observed in the experimental results. However, in this case, the production of H_2 and CO was lower than that of equilibrium, whereas the production of CO_2

and CH₄ was higher (Pinto et al., 2003). This shows that during the experiments, equilibrium conditions were not reached, probably due to insufficient gas residence time in the reaction zone. The differences observed seem to indicate that kinetics play an important role during gasification, especially the kinetics of heterogeneous char-gas reactions, which are characterized by lower reaction rates than those of the gas phase reactions.

In addition to its influence on equilibrium, the effect of pressure on coal devolatilisation must also be considered. Considerable differences may appear in the morphology and reactivity of the chars produced during the devolatilisation stage, and these are bound to affect the heterogeneous reactions and the composition of the gas. At atmospheric pressure a higher and faster release of volatile matter occurs, leading to a reduction in the amount of char produced (Saxena, 1990; Griffin et al., 1994). Furthermore, this char will not only be more reactive, due to a higher textural development, but it will also display a lower degree of carbon ordering. However, a rise in the pressure system, will lead to a lower fuel devolatilisation, as the pressure exerted from the inside by the volatile matter is counteracted by the external pressure, giving rise to a higher amount of char with a higher and more ordered carbon content (Chen et al., 2008; Wu et al., 2000; Miura et al., 1989). For this reason, chars produced at 15 atm will be less reactive and, taking into account the higher reactivity of carbon towards oxygen than to steam (Eq. (3) carbon oxidation: $C + O_2 \rightarrow CO_2$; and Eq. (4) carbon steam gasification: $C + H_2O \leftrightarrow CO + H_2$), this may explain why more CO₂ and less H₂ and CO were produced at 15 atm than at atmospheric pressure, since H₂ and CO are mainly produced through steam gasification reaction.

Furthermore, it can be observed that the production of the oxygenated species (CO and CO₂) increased with the coal carbon content (HV > DT > SA > PT), a trend also deducible from the equilibrium values. This could be due to the fact that the main gases produced during gasification depend on the carbon content of the fuels, and their potential to produce these gases increases with the carbon content. Thus, coal PT exhibits the lowest value of gas production, especially of CO, since it has a lower carbon content than the other coals. It was also observed that in the case of bituminous coals, those with the highest carbon content produce the highest amount of hydrogen. Coals DT and SA produced more H₂ than the HV coal, which has the highest carbon content. This is possibly because these two coals are more reactive than coal HV and, therefore, they react more easily with steam to produce more H₂ during gasification (Fung and Kim, 1983).

Table 2 shows the main characteristics (experimental and equilibrium) of the gas produced during coal gasification at atmospheric pressure. In this table it can be seen that the semianthracite (HV) gas yield, in dry basis, presents the highest value. This is attributed to its high carbon content, and to the fact that the total gas flow rate was pre-set to maintain constant the O/C ratio. As a consequence of the higher total gas flow rate used, the gas produced by the semianthracite is more diluted by the N₂ introduced and has a low *HHV*. When considering the bituminous coals, DT and SA have a higher *HHV* than PT, since these coals produced more hydrogen. Lower rank coals (PT, DT and SA) showed higher carbon conversions to gas since they are more reactive than semianthracite (Takarada et al., 1985). Therefore, these coals react more easily with the oxygen and steam present in the gasifying agent. Cold gas efficiency follows a similar trend to *HHV*, the highest values corresponding to the DT and SA coals. The HV semianthracite has the lowest value despite its higher gas yield; this is due, on the one hand, to the lower *HHV* of the produced gas and, on the other hand, to the high *HHV* of the semianthracite.

Table 3 shows the main characteristics (experimental and equilibrium) of the gas produced during gasification of the coals at 15 atm. A similar behaviour to that obtained at atmospheric pressure can be observed, with coals DT and SA producing the gas fraction with the highest *HHV*. In this table, again, it can be seen that semianthracite HV produced the highest gas yield due to the dilution effect. In addition, the *HHV* and cold gas efficiency of the gas produced were lower than those calculated at equilibrium conditions, and this difference is greater than at atmospheric pressure. This is because the theoretical values only take into account the effect of pressure on the equilibrium reactions, and ignore the reactivity of the char. Tables 2 and 3 also show that carbon conversion was higher at atmospheric pressure than at 15 atm, and that the differences in carbon conversion between the coals (bituminous and semianthracite) were higher at atmospheric pressure than at 15 atm. In this case, the negative effect that the increase in pressure had on coal devolatilisation was more pronounced in coals with a higher volatile matter content and there was a decrease in their final carbon conversion (Wall et al., 2002).

3.2. Effect of blending fuels

The effect of partly replacing fossil fuels (coal, coal-petcoke blends) with biomass during gasification was also studied. Co-gasification tests on binary blends of coal PT combined with two different biomass samples: olive pulp, OP, and pine sawdust, PS, and on ternary blends

(PT-PC-Biomass) were carried out. The feedstock mass flow rate was pre-set to ensure that the values of the O/C and H₂O/C ratios would remain constant at the reactor inlet. A mixture of oxygen and steam was used as gasifying agent carried in an inert flow of N₂, at a total flow rate of 200 Ncm³ min⁻¹.

Figure 3 shows the production of the main gases during the high-pressure co-gasification of the binary blends of coal PT and the biomass (950 °C, 15 atm, 5 and 55 vol.% of O₂ and H₂O_v, respectively). This figure shows that the production of H₂ and, especially, of CO, increased with additions of up to 10 wt.% biomass. A slight increase in CO₂ production was also observed. An increase in gas production was predictable, as biomass fuels are much more reactive than coal. However, what is surprising about this increase in gas production is that it occurs when a low percentage of biomass is used.

Table 4 summarises the main gasification parameters of the PT-biomass binary blends. In this table it can be seen that the carbon conversion of the coal-biomass blends was higher than that corresponding to the individual coal. Assuming that no interactions occur between the fuels, and that the biomass reaction is complete, the maximum carbon conversions that can be expected, based on the coal carbon conversion, would be 64.6 and 66.4 % for blends with biomass percentages of 5 and 10 wt.%, respectively. However, the experimental results showed that the values obtained were between 7.3 and 10 % higher than the theoretical values, indicating that interactions occurred between the coal and biomass fuels, as a result of which there was a rise in coal carbon conversion (Sjöström et al., 1999).

Table 4 also shows there was a slight decrease in the H₂/CO ratio, as the increase in the H₂ concentration was not as great as that of CO (Kumabe et al., 2007; André et al., 2005). The increase in gas yield resulted from the higher rate of conversion during the co-gasification tests (Sjöström et al., 1999). An increase in cold gas efficiency was also attained due to the higher gas yield and its higher *HHV* (Lapuerta et al., 2008; André et al., 2005). The interactions that occurred between the coal and biomass may have been due to the high reactivity of the biomass fuels. When coal is fed into the reactor with biomass, the latter will react rapidly, releasing a high amount of volatile matter via the thermal or oxidative cleavage of the weakest covalent bonds in the organic matter. This matter then rapidly decomposes and forms a high number of free radicals, which react not only with organic matter of the biomass, but possibly with the coal also, thereby favouring decomposition and oxidation/gasification reactions in the coal. Furthermore, the hydrogen-rich light molecules produced from the devolatilisation of the biomass and the cracking of volatiles may react with the volatiles

produced from coal, thereby preventing recombination reactions and the formation of less reactive secondary char (Sjöström et al., 1999). The alkali metals present in the mineral matter of the biomass, such as Na, K and Ca, may also favour heterogeneous gasification reactions inside the coal (Brown et al., 2000; Collot et al., 1999; Miura et al., 1989).

Two different biomass samples, olive pulp, OP, and pine sawdust, PS, were also added in a percentage of 10 wt.%, to the 50-50% binary blend of coal PT-petcoke PC, which is currently used as feedstock at the Elcogas IGCC power plant. Figure 4 shows the main gases produced during the co-gasification experiments of the ternary blends of PT-PC-Biomass (45-45-10 %) (1000 °C, 15 atm, 5 and 55 vol.% of O₂ and H₂O_v, respectively). In this figure it can be seen that the H₂ obtained during the gasification of the binary blend PT-PC was almost unaffected when 10 wt.% of fuel was replaced by biomass. Nevertheless, a slight decrease in CO production was observed, as the production of CO₂ increased. This different reactive behaviour compared to those attained from binary blends of coal PT-biomass gasification could be due to the lower amount of volatiles released by ternary blends, which would have a greater availability of oxygen to be oxidized leading to an increase in CO₂ production to the detriment of CO. These results seem to indicate that there is negligible or no interaction between the biomass and the PT-PC blend. However, from Table 5, where the main gasification parameters of the ternary blends are summarised, it can be seen that when biomass was added to the blend of fossil fuels, an increase in the gas yield occurred. This led to a gas with a higher cold gas efficiency, although the high heating value of the gas from the ternary blends was lower than that of the binary blend (PT-PC). This was mainly due to the higher amount of CO₂ produced.

With respect to carbon conversion, similar effects to those of binary blends gasification were obtained, though to a lesser extent. This might be because the maximum possible carbon conversion expected during the ternary blends gasification (assuming 100% biomass conversion) was 94%, whereas, in fact, the carbon conversion attained was 97.3% (PT-PC-OP), and 98.2% (PT-PC-PS). In the case of binary blends with 10 wt.% of biomass (cf. Table 2), the maximum carbon conversion (assuming 100% biomass conversion) was 66.4%, and the experimental conversion obtained was 76.4% (PT-OP and PT-PS). In the case of ternary blends, biomass seems to have a lesser effect on gas production and on the other process parameters. This could be due to the fact that the PT-PC blend shows a different behaviour than when only coal is gasified (Fermoso et al., 2009). As was previously stated, in the case of the PT-Biomass binary blends, the most reactive component may undergo partial oxidation,

leading to a rise in CO production. However, in the case of the ternary blends, more oxygen is available in the devolatilisation zone of the reactor, since petcoke, which releases small amounts of volatile matter, is also fed into the reactor. This means that the volatile matter released by the biomass can be more easily oxidized, leading to the formation of fewer free radicals. As a result, the radicals interact less with the small amount of volatiles released by the PT-PC blend.

In sum, it can be said that under the conditions used in this work, when fuels with very different reactivities (coal, petcoke, biomass, etc.) are gasified as a blend, interactive effects may take place due to volatile-volatile and volatile-char interactions, and possibly due to mineral matter catalytic effects. This leads to an increase in carbon conversion and greater cold gas efficiency.

4. Conclusions

Four different rank coals were gasified at different pressures. Regardless of coal rank, gasification at atmospheric pressure led to the production of a greater amount of H₂ and syngas, and better cold gas efficiencies and carbon conversions than those obtained at 15 atm. The increase in pressure exerted a negative effect on the gasification process, and this effect was more pronounced in the case of low rank coals.

Co-gasification experiments on binary and ternary blends showed interactions between their components and the gas production was modified. The addition of a small amount of biomass (up to 10 wt.%), led to greater H₂ and CO production.

Acknowledgements

This work was carried out with financial support from the Spanish CDTI (Project CENIT PiIBE) and ELCOGAS, S.A. J.F. acknowledges funding from the PCTI Asturias, and M.G.P acknowledges funding from the CSIC I3P Program, co-financed by the European Social Fund.

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Table 1. Proximate and ultimate analyses and high heating values of the samples

Fuel type	Sample	Rank *	Proximate Analysis (wt.%, db)		Ultimate Analysis (wt.%, daf)					HHV (MJ kg ⁻¹ , daf)
			Ash	V.M.	C	H	N	S	O ⁺	
Coal	HV	sa	8.8	8.6	90.6	2.8	1.7	1.9	3.0	35.1
	SA	mvb	14.9	25.6	78.6	4.9	1.9	0.7	13.9	32.9
	DT	hvb	10.9	29.0	81.9	5.0	0.8	1.2	11.1	32.4
	PT	hvb	36.3	24.7	71.2	4.8	1.5	1.7	20.8	29.1
Petcoke	PC		0.3	9.6	87.6	3.8	1.5	6.2	0.9	35.1
Biomass	OP		7.6	71.9	54.3	6.6	1.9	0.2	37.0	21.6
	PS		1.4	86.5	49.8	6.6	0.2	0.0	43.4	20.2

* sa: Semianthracite; mvb: Medium volatile bituminous coal; hvb: High volatile bituminous coal
dry basis (db); dry ash free basis (daf); ⁺ calculated by difference

Table 2. Gasification parameters of different rank coals (1000 °C, 1 atm, 25 vol.% H₂O_v and 15 vol.% O₂)

Sample	Experimental				Equilibrium			
	Coal				Coal			
	HV	SA	DT	PT	HV	SA	DT	PT
Rank [*]	sa	mvb	hvb	hvb	sa	mvb	hvb	hvb
H ₂ /CO	0.9	1.0	0.9	1.0	0.8	0.9	0.9	1.0
CO/CO ₂	2.2	2.3	2.3	1.9	3.2	2.6	2.9	2.2
Y _g (Nm ³ kg ⁻¹)	4.6	4.0	4.3	2.7	4.9	4.1	4.6	2.7
HHV (kJ Nm ⁻³)	4876	5225	5114	5102	5295	5256	5372	5148
η (%)	70.7	74.6	77.1	73.6	81.4	76.5	85.2	75.7
X (%)	87.6	93.7	93.0	92.5	100.0	100.0	100.0	100.0

* sa: Semianthracite; mvb: Medium volatile bituminous coal; hvb: High volatile bituminous coal

dry basis (db); dry ash free basis (daf); ⁺ calculated by difference

Table 3. Gasification parameters of different rank coals (1000 °C, 15 atm, 25 vol.% H₂O_v and 15 vol.% O₂)

Sample	Experimental				Equilibrium			
	Coal				Coal			
	HV	SA	DT	PT	HV	SA	DT	PT
Rank [*]	sa	mvb	hvb	hvb	sa	mvb	hvb	hvb
H ₂ /CO	0.9	1.0	0.9	1.2	0.8	0.9	0.9	1.0
CO/CO ₂	1.9	1.8	1.8	1.4	2.9	2.4	2.7	1.9
Y _g (Nm ³ kg ⁻¹)	4.7	4.0	4.3	2.7	5.0	4.1	4.6	2.8
HHV (kJ Nm ⁻³)	4595	4929	4811	4529	5094	5113	5269	4794
η (%)	67.2	70.0	72.2	66.0	79.5	75.2	84.1	72.4
X (%)	87.3	92.8	92.1	88.6	100.0	100.0	100.0	100.0

^{*} sa: Semianthracite; mvb: Medium volatile bituminous coal; hvb: High volatile bituminous coal
dry basis (db); dry ash free basis (daf); ⁺ calculated by difference

Table 4. Gasification parameters of binary blends of coal PT with biomass: olive pulp, OP, and pine sawdust, PS (950 °C, 15 atm, 55 vol.% H₂O_v and 5 vol.% O₂)

Sample	PT	PT-OP		PT-PS	
Composition (wt.%)	100	95-5	90-10	95-5	90-10
H ₂ /CO	2.3	2.0	1.9	2.0	2.0
CO/CO ₂	1.0	1.2	1.3	1.2	1.2
Y _g (Nm ³ kg ⁻¹)	2.07	2.28	2.33	2.19	2.34
HHV (kJ Nm ⁻³)	6223	6458	6656	6559	6614
η (%)	69.0	78.3	82.4	76.6	82.3
X (%)	62.7	72.3	76.4	71.9	76.4

Table 5. Gasification parameters of ternary blends coal PT- petcoke PC-Biomass (olive pulp, OP, and pine sawdust, PS) (45%-45%-10%); (1000 °C, 15 atm, 55 vol.% H₂O_v and 5 vol.% O₂)

Sample	PT-PC	PT-PC-OP	PT-PC-PS
Composition (wt.%)	50-50	45-45-10	45-45-10
H ₂ /CO	1.6	1.7	1.7
CO/CO ₂	1.9	1.7	1.7
Y _g (Nm ³ kg ⁻¹)	3.66	3.99	3.98
HHV (kJ Nm ⁻³)	7132	6644	6752
η (%)	97.7	101.7	103.0
X (%)	93.3	97.3	98.2

Figure 1. Flow diagram of the experimental device.

Figure 2. Main gases production during the gasification of different rank coals (HV, SA, DT and PT) at pressures of 1 and 15 atm (1000 °C, 15 vol.% O_2 and 25 vol.% H_2O_v).

Figure 3. Main gases production during the high-pressure co-gasification of binary blends of coal PT-Biomass (olive pulp, OP, and pine sawdust, PS) (950 °C, 15 atm, 5 vol.% O₂ and 55 vol.% H₂O_v).

Figure 4. Main gases production during the high-pressure co-gasification of ternary blends (45-45-10%) of coal PT – petcoke PC – Biomass (olive pulp. OP, and pine sawdust, PS), (1000 °C, 15 atm, 5 vol.% O₂ and 55 vol.% H₂O_v).