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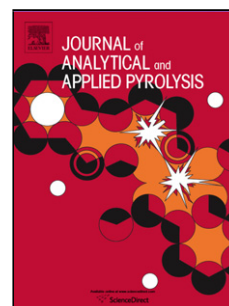
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# Gasification and Pyrolysis of *Posidonia oceanica* in the Presence of Dolomite

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## HIGHLIGHTS

- *Posidonia oceanica* thermal decomposition is studied.
- Combustion, pyrolysis and gasification at different experimental conditions are performed.
- The combined effect of the presence of oxygen, air, water vapor and dolomite in the decomposition bed is analysed.
- Conditions where maximum ratio  $H_2/CO$  is observed are optimized.

## ABSTRACT

In the present work, a very detailed study of the reforming of syngas produced in the decomposition of *Posidonia oceanica* is done. The effect of the presence of different amounts of dolomite is analysed. Also pyrolysis is studied, in nitrogen atmosphere, and gasification in the presence of air, oxygen and different amounts of steam. A detailed discussion on formation and destruction of tars is done. Furthermore, the effect of the heating rate in the decomposition and the residence time of the evolved gases are discussed. Syngas with ratio  $H_2/CO$  from 0.3 to ca. 3 can be obtained from this interesting material. Marine species (microalgae) are usually studied with the aim of cultivate them for gas or oil production, but in this paper we draw attention to the possibility of using a natural resource with a very small impact in the ecosystem.

Keywords: marine seagrass, gasification, reforming, dolomite, *Posidonia oceanica*

## 1. Introduction

Thermochemical conversion pathways of biomass for the production of primary energy by direct combustion, as well as other thermal processes, have a remarkable drawback among others: **tar formation**.

A gas obtained by these means from biomass with 5% moisture containing about 10 g / m<sup>3</sup> tar contains between 3% and 10% of the total energy of the biomass [1]. Furthermore, tars are problematic because they condense on equipment at moderate temperatures causing blocking of filters and plugs of valves and tubes. In addition, tars are corrosive, carcinogenic and produce catalytic deactivation.

Primary treatments can be performed involving the optimization of the gasifier design and operating conditions (biomass feed point, temperature distribution of the gas channel, particle size distribution...) to obtain a syngas with less concentration of tars. Nevertheless, these treatments are limited due to the operating temperature and the technical conditions of the processes, in such a way

that these treatments may be not sufficient to remove tars, especially if the gas is going to be used for chemical synthesis or extraction of biofuels for transport [2].

The definition of the term *tar* is not consistent if we look at the literature, but it seems that includes heavy aromatics and excludes benzene [3]. In general, tars are compounds included in one of the following groups:

- Heterocyclic compounds, tars containing heteroatoms, very soluble in water such pyridine, quinoline, isoquinoline, dibenzophenol.
- Light aromatics, hydrocarbon having a single ring, soluble and condensable such toluene, ethylbenzene, phenol, cresol, xylenes and styrene.
- Light polyaromatic compounds with 2 or 3 rings which condense at high temperatures and relatively high concentrations such indene, naphthalene, methylnaphthalene, biphenyl, acetonaphthalene, fluorene, phenanthrene and anthracene.
- Heavy aromatic hydrocarbons with more than 3 rings that condense at high temperatures and low concentrations as is the case of fluoranthene, pyrene, chrysene, perylene and coronene.

The three main substances in waste biomass (cellulose, hemicellulose and lignin), are formed by polysaccharides and decompose forming tars by three mechanisms published in the literature to result in these polyaromatic hydrocarbons: i) by direct combination of aromatic rings; ii) by HACA ( $H_2$ -abstraction- $C_2H_2$ -addition) sequence in which aromatic rings breakdown forms hydrogen radicals to which follows the addition of ethylene to produce the spread aromatic ring cyclization [4]; and iii) formation of cyclopentadiene phenol precursors as an intermediate of the reaction and subsequent cyclization and combination via radicals.

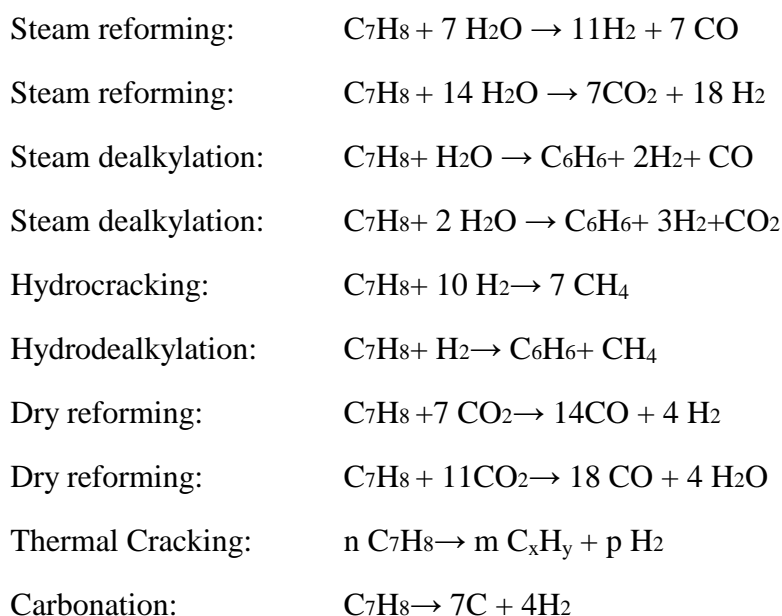
During pyrolytic decomposition of cellulose occur predominantly furan aldehydes and small molecules. Recombination of these species through competitive reactions results in levoglucosane as the main primary tar, and also to furfural, glycolaldehyde and hydroxyacetone. Hemicelluloses give rise to the formation of xylans, xilopirosanes, acetone, methanol and furfural. Lignin results in the formation of guaiacols, catechols and phenols and generally predominantly oxygenates.

Secondary treatment consists in the use of catalysts (acidic, basic, redox) at high temperature producing gas cleaning by removing tars, particles,  $H_2S$ ,  $HCl$ , and alkali compounds. Secondary treatment can be physical (filters with hot dry gas or wet absorption allowing steam reforming and partial oxidation) and catalytic. The most studied processes are partial oxidation, steam reforming, absorption, adsorption and catalytic ceramic filtration.

Catalytic reforming or steam reforming can be performed with natural catalysts (dolomite, olivine, calcite, magnesite, zeolites) or on metal based catalysts (Ni, Ru). Often in the reaction bed conditions occur reactions that deactivate the metal catalyst [5]. Therefore dolomite is usually used when mixing biomass with catalysts.

For a complete reforming it is usual to use a dual reactor configuration, with a primary catalyst dolomite bed where tar levels are reduced to acceptable levels, and if necessary, a second catalyst is introduced to treat the effluent stream, usually Ni catalysts [6]. Adding olivine and Ce<sub>2</sub>O improves the action of the catalyst Ni [5].

Toluene is the species used as laboratory scale model for studying mechanisms of the reactions and catalytic reforming. The most widely used model is known as the Component Model presented in different papers [7-9]. Blanco et al. [10] characterize tar from the pyrolysis and gasification of refuse derived fuels, and has also been used to characterize the possible decomposition reactions of both primary and secondary tars [11, 12]. The reactions involved in the toluene reforming process are then:



### 1.1. Tar cracking through catalytic reactions

Dolomite is a calcium magnesium compound whose overall chemical formula CaMg (CO<sub>3</sub>)<sub>2</sub> with a content of 20% of MgO, ~ 30% CaO and ~ 45% by weight of CO<sub>2</sub>, with a small amount of mineral impurities.

The dolomites in their original form are not suitable as catalysts, therefore must undergo a calcination process during which the carbonate is decomposed into CaO and MgO thus eliminating CO<sub>2</sub>. The total calcination of dolomite occurs at temperatures between 800 and 900 ° C. These temperatures restrict the use of dolomite as catalyst. Calcined dolomite also loses its status as a catalyst for conversion of tars under conditions in which the partial pressure of CO<sub>2</sub> is greater than the equilibrium decomposition pressure of dolomite; this feature should be considered in pressurized gasification processes.

At high partial pressure of CO<sub>2</sub>, the calcination of dolomite takes place in two steps:





At low partial pressure of CO<sub>2</sub> (<200 Torr) calcination occurs in one step:



In literature we can find that the primary tars converted to gases increases markedly with temperature. Various research groups have conducted extensive studies examining the loss of effectiveness of calcined dolomite in the conversion of tar and other non-metallic oxides catalysts.

In general, studies have shown that dolomite is an effective catalyst for reforming tar [13]. The high molecular weight hydrocarbons are efficiently reformed to moderately high temperatures (> 800 °C) in gasification processes using mixtures of steam and oxygen as gasifying agent, however the outlet concentration of methane is not visibly affected and benzene and naphthalene often fail to be completely renovated.

In the present paper, it is done a very detailed study of the effect of the reaction atmosphere and the heating rate in the decomposition of a biomass feedstock, considering a variety of factors that can influence on the gas composition, i.e., presence of catalysts at different loads, effect of humidity and presence of different oxygen atmospheres. A detailed discussion on formation and destruction of tars is done. Furthermore, the paper deals with the decomposition of a biomass not previously studied in literature such is the case of the alga *Posidonia oceanica*. The possible uses of the syngas produced in the different conditions are also discussed. Marine species (algae and microalgae) are usually studied with the aim of cultivate them for gas or oil production, but in this paper we draw attention to the possibility of using a natural resource with a very small impact in the ecosystem.

This research is a continuation of work presented earlier [14], where the decomposition of different biomass feedstock (esparto grass, straw, waste from urban and agricultural pruning, marine seagrass and waste from pruning forest) was done. To determine the effect that the presence of dolomite catalyst has on the effluent gas reforming it has been selected specie of reference: *Posidonia oceanica*. The reasons for the choice are varied but the most influential are having a behavior and composition slightly different from other species and that there is no study in the literature of thermal degradation of this species. *Posidonea oceanica* is a marine seagrass (usually considered as an algae) endemic of the Mediterranean coast of the province of Alicante. The wastes of the *Posidonia oceanica* deposited on the beaches of Alicante province accounted for during the year 2009 a total of 600,000 tons (Source: Provincial Council of Alicante), so it is a natural resource as a source of biomass.

## 2. Materials and methods

An scheme of the equipment used to carry out the present work can be found in our previous work [14, 15]. It was 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 much controlled speed to a furnace while a constant flow of gas is

passing through. In all runs the temperature of the oven was 850 °C. Gas samples were collected using Tedlar bags and then analyzed by gas chromatograph with flame ionization detector (GC-FID) and with thermal conductivity detector (GC-TCD).

Elemental analysis of the *Posidonia oceanica* marine seagrass [14] indicated the presence of 0.71 % of Nitrogen, 34.85 % C, 4.54 % H, 0.62 % S and 59.28 % O, with a net calorific value of 14,61 MJ/kg. The runs are performed by mixing the dolomite with the biomass prior to its decomposition in the bed.

## 2.1. Description of runs

Runs were performed at two different input speeds to the furnace ( $V_{\text{slow}}=0.5$  mm/s and  $V_{\text{high}}=1.9$  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.

A total of 58 runs were performed in five different sequences:

- 1) Fourteen combustion runs at sub-stoichiometric amounts of air and in the presence of different amounts of dolomite (varying ratio  $D/B$ =dolomite/biomass). These runs performed in oxidative atmosphere were performed in such a way that the oxygen ratio ( $\lambda$ , defined in the next equation) is maintained at  $\lambda =0.25$  in both cases:

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

where: %O, %H, %S, %C = weight percentage of oxygen, hydrogen, sulphur and carbon in the biomass sample,  $m_{\text{air}}$ = air flow rate (kg/s),  $m_{\text{sample}}$ = weight of the biomass (kg),  $L$ = length of tube occupied by the biomass (m),  $v$ = linear velocity of introduction of the tube (m/s)

A value of  $\lambda$  lower than one involves combustion in sub-stoichiometric conditions while values of  $\lambda$  higher than unity represent excess air. In the runs performed,  $v=0.5$  and 1.9 mm/s. In order to maintain the ratio  $\lambda =0.25$ , the corresponding value of  $m_{\text{air}}$  was used. In this sense, the residence time of the volatiles evolved is higher at the lower feeding rate, what can influence in the gas evolution.

- 2) A second series of fourteen runs were performed in pyrolytic conditions, with nitrogen as carrier gas, and introducing different amounts of dolomite as well. Furthermore different runs were performed at  $V_{\text{slow}}$  and  $V_{\text{high}}$ .
- 3) Gasification of the biomass sample in the presence of oxygen saturated with steam introducing different amounts of dolomite, at  $V_{\text{slow}}$  and  $V_{\text{high}}$ . Ten runs were performed in this series.

- 4) Gasification of the marine seagrass in the presence of oxygen and different amounts of steam, maintaining the ratio dolomite/biomass, at  $V_{slow}$  and  $V_{high}$ . Ten runs were performed in this series.
- 5) Gasification of the *Posidonia oceanica* in the presence of air and different amounts of steam, maintaining the ratio dolomite/biomass, at  $V_{slow}$  and  $V_{high}$ . Ten more runs were done.

The runs were conducted at five different relative humidity values. For this purpose, we have designed a device through which the gas stream is branched off as a bypass, one stream is bubbled through a water column saturating the working temperature, then mixed with the original stream with a manual valve controlling the amount of saturated flow. With a humidity and temperature probe mix of both streams is adjusted to the desired moisture in the stream to be introduced into the reactor. In this way, we can observe the effects of different levels of moisture produced in the composition and properties of the syngas.

## 2.2. Catalyst preparation

Dolomite used is known as dolomite "Malaga" whose composition approximate weight % is: 30-35% CaO, 20-24% MgO, 45-48% CO<sub>2</sub>.

To make a reliable physical characterization and due to the heterogeneity of these minerals, it is essential to make a correct sampling. For this purpose, a 1 kg dolomite sample was picked. After grinding, dolomite was sieved to a size between 2.0 and 1.0 mm. These fractions were introduced into a furnace to be calcined at absent CO<sub>2</sub> atmosphere at 900 ° C for 5 hours. At this temperature takes place also the calcite decarbonation. Once the calcination step is finished, dolomite is introduced in closed containers to prevent carbonation and humidification.

Calcined dolomite was characterized by determination of particle size distribution and specific surface. It has been measured the particle sizes distribution in a COULTER LS 230 equipment whose result can be seen in Figure 1. This data can be used to determine other properties of the catalyst from the studies by Orió et al. [16] where these properties with other techniques which are determined by N<sub>2</sub> adsorption and known Hg porosimetry relate diameter particle  $d_p$  and Thiele module, that are the factors conditioning the effectiveness factor of the catalyst. The results are presented in Table 1.

The calcined dolomite (CaO-MgO) is mainly involved in the following reactions:

- Steam reforming of tar.
- Steam gasification of coke deposited on the surface of the dolomite and generated in the thermal cracking of hydrocarbons. This reaction regenerates the solid surface.
- *Water-gas shift*, in the direction of formation of hydrogen and carbon dioxide. Gas concentration very close to equilibrium is reached, which is not achieved with the thermal effect of a catalytically inert solid such as silica sand.

The variables that affect mainly the conversion of tar dolomite are the temperature and time of gas-solid contact.

### 3. Results and discussion

#### 3.1. Influence of catalyst presence and loading

The catalyst effect is analyzed using different reaction atmospheres: air in substoichiometric ratio of O<sub>2</sub> ( $\lambda = 0.25$ ), nitrogen and a mixture gas O<sub>2</sub>/ H<sub>2</sub>O saturated with relative humidity close to 100% and a gasification ratio (GR) close to 1. Gasification ratio is defined as:

$$GR = (\text{Kg O}_2 + \text{Kg H}_2\text{O}) / \text{kg biomass (dry ash-free basis)}$$

The experiments were performed with two speeds of introduction, 0.5 mm/s (V<sub>slow</sub>) and 1.9 mm/s (V<sub>high</sub>) for all atmospheres, in order to analyze the effect of residence time.

To further control the biomass/air ratio and the heating speed of the samples, oxidizing gas flows is calculated for gasification experiments as sub-stoichiometric air for a value of the equivalence ratio of  $\lambda=0.25$  as we proposed in our previous work [14].

In this way, it can be done a comparative study maintaining the same conditions. Experiments were carried out with different ratios of dolomite / biomass (D/B), beginning with a run without dolomite, and with D/B equal to 0.25, 0.5, 0.75, 1 and 2 in order to observe the effect of this ratio on the properties of syngas.

#### 3.2. Effect of catalyst in combustion with substoichiometric air

As has been indicated, study of the influence of the amount of catalyst (dolomite) in the reformed fuel gas was carried out. The results obtained for the runs performed both at low input speed (V<sub>slow</sub>, 0.5 mm/s) and high (V<sub>high</sub>, 1.9 mm/s) are shown in Figure 2. Figure shows the volume percentages of each compound in the total gas. The Figure also presents the ratio H<sub>2</sub>/CO calculated by dividing molar % of each compound. Net calorific value of the gas was obtained by the following expression, reflected in the work of Nogueira and Silva [17] and deduced from the formula of Dulong, where the expressions in parentheses represent % by volume in the gas:

$$NCV_{\text{gas}} = 0.126 * (CO) + 0.358 * (CH_4) + 0.108 * (H_2) + 0.59 * (C_2H_4) + 0.637 * (C_2H_6)$$

Details of all analysis performed in the different runs can be found in Supplementary Material (Table S1 for V<sub>slow</sub>, Table S2 for V<sub>high</sub>).

In view of the results the following conclusions can be extracted:

- Concentration of CO<sub>2</sub> decreases with increasing ratio D/B for the two speeds while the CO concentration has variations at both speeds.
- Concentration of H<sub>2</sub> and methane increases with the ratio D/B.



- In the same way an increase occurs in the ratio  $H_2/CO$ , this occurs for both sample introduction speeds.
- The calorific value has certain fluctuations as a function of D/B but generally increases as this ratio increases.
- Generally, it is observed a cracking of the high molecular weight substances only at high D/B, for both speeds.

From the data presented in Tables S1 and S2 it can be concluded that hydrocarbons concentration decreases, even disappearing species such  $C_3$  through  $C_6$ , except benzene. Specifically, tars ( $C_7$ - $C_8$  onwards, toluene and xylenes) fall appreciably their concentration. Notably reduced tar is remarkable with increasing ratio D/B for both speeds but in percentage the decrease is greater at high speed, that is, with shorter residence time.

### 3.3. Effect of Catalyst on pyrolysis ( $N_2$ atmosphere)

The influence of the presence of varying amounts of dolomite in the pyrolysis in the absence of oxygen of *Posidonia oceanica* is discussed in this section. The same flow rates used in combustion runs are used for pyrolysis, in order to maintain similar experimental conditions. Also the values of the ratios D/B used are the same. The results can be read in Tables S3 and S4 and the corresponding Figure 3.

The following considerations are drawn:

- With increasing ratio D/B the  $CO_2$  concentration decreases for both input speeds, the CO concentration increases at high speed and decreases at low speed; nevertheless methane and ethene increased with both speed.
- For D/B greater than 0.75 the cracking of the fractions of 3 and more carbons occur.
- The NCV increases for both speeds but is most pronounced at high input (i.e., high heating rates).
- The ratio  $H_2/CO$  ratio increases with increasing D/B, but more noticeable at low input speed.
- The reforming of the gas is very prominent, disappearing most species with increasing the ratio D/B. The amount of benzene decreases although it does not disappear.
- Tars were also reformed and decrease with increase in the amount of catalyst.

### 3.4. Effect of gasification catalyst mixture in the presence of $O_2/H_2O$

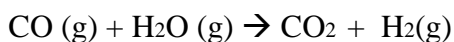
Gasification in oxygen and water vapor is now being studied. Flow rate of the gases are adjusted to maintain the value of  $\lambda$  at 0.25, considering the values of the humidity present.

For these conditions is more interesting to fix the value of GR (kg  $O_2 + H_2O$  vs. kg of biomass present), which is reflected in the results for each set of experiments. For simplicity in the configuration of the equipment, it was decided to adjust the moisture to the saturation value for each working temperature and varying the proportion of oxygen.

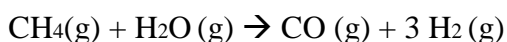
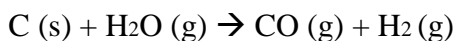
The results obtained can be seen in Tables S5-S6 and Figure 4.

From the results we can conclude:

- The concentration of CO<sub>2</sub> has variability but generally increased for both input speeds. This is because in the presence of dolomite and water the following reaction occurs:



Bearing in mind also the following reactions:



the very high increase in the concentration of H<sub>2</sub> for both input speeds when ratio D/B increased is warranted.

- Moreover, methane concentration reduces and the other hydrocarbons practically disappeared even for low ratios D/B.
- The NCV increases with the ratio D/B for both speeds and the ratio H<sub>2</sub>/CO is tripled or quadrupled, also growing for both speeds.
- Tar formation is lower for low speeds, even without dolomite. With increasing the ratio D/B tar cracking becomes very important, almost disappearing toluene and xylenes at low speed input.

Operating under these conditions it is already clear that the combined effect of the presence of the catalyst and water produced an effective breakdown of tars that is much larger with slightly longer residence times.

### 3.5. Effect of the ratio Dolomite/Biomass combined

In the following Figure 5 it can be seen the effect that the relationship D/B produced in the reforming of syngas as a function of the ratio H<sub>2</sub>/CO and all atmospheres with both input rates.

In view of the results we can conclude:

- For all reaction atmospheres and both speeds, the increase in the ratio D/B improves, in general, the ratio H<sub>2</sub>/CO observing an increment very pronounced to values of 0.75 in the ratio and having in all cases a maximum value to a stationary ratio D/B of 1, from which the growth is very small or even decreases.
- Higher ratios H<sub>2</sub>/CO for small D/B are obtained for gasification with O<sub>2</sub>/H<sub>2</sub>O. The presence of water vapor saturating the gas combustion is the factor that causes the improvement due to reactions which are favored by the catalyst in the presence of H<sub>2</sub>O.

- For low input speed, higher ratio  $H_2/CO$  are observed, suggesting that increased residence time improves  $H_2/CO$  under these conditions, however, for intermediate D/B (0.5-0.75) the trend is reversed and the ratio is improved at the shorter residence times.
- In sub-stoichiometric air atmosphere, it is observed a similar trend to that discussed for the  $O_2$  with respect to the D/B, but there is a clear difference between the residence times, because at  $V_{slow}$  the values of  $H_2/CO$  are much higher. The gas obtained under these conditions could be used to produce electricity of combined cycle turbines or alternative internal combustion engines.
- In the pyrolysis process higher ratios  $H_2/CO$  are obtained with short residence times, reaching a maximum value of D/B about 1. Pyrolysis at  $V_{slow}$  shows the worst ratios  $H_2/CO$ . The use of pyrolysis gas would be obtaining electricity.

### 3.6. Influence of moisture content

In view of the results obtained in experiments with atmospheric  $O_2/H_2O$ , it seems clear that the presence of water in the reaction gas in the presence of dolomite produces a reformed gas by improving their qualities for future use and reducing the concentration of tars in the syngas.

To better understand this effect and check the extension of the same in the atmospheres studied, an analysis of the effect of different levels of relative humidity is performed.

This series of runs has set the D/B close to unity in view of the above results, since it is the optimal ratio of catalyst/biomass if we focus on improving the ratio  $H_2/CO$  and increased NCV.

The relationships H/C and O/C have been of great importance to determine experimental conditions gasification processes, as they are representative of the inertia of formation hydrocarbon volatiles and carbon oxides. But in the case of the reformed gas, and even in the process of gas phase recombination occurring at high temperatures, species  $CO_x$  and  $C_nH_m$  may come from the decomposition of biomass and also from gas phase reactions or products derived from the catalytic action of the dolomite. Therefore, as already indicated, the ratio of gasification is a notable parameter in these runs, as it reflects the relationship between the amount of water and  $O_2$  and the amount of biomass, irrespective of the process which has resulted in the formation of  $CO_2$  and  $CO$ .

The runs in this series were conducted with five relative humidity values for each operating temperature. To this we have designed a device through which the gas stream is branched off as a bypass, as explained before. In this way we can observe the effects of different levels of moisture produced in the composition and properties of the *syngas*. Ahead the results are shown.

#### 3.6.1. Effect of relative humidity in gasification $O_2/H_2O$

In the runs performed, GR relations remain about 1 for low input speeds and decrease to around 0.9 for top speed. All runs in this series were made in such a way that the value of the  $\lambda$  ratio is maintained between 0.2 and 0.3, with the aim to compare overall results.

The results are shown in Tables S7-S8 and in Figure 6. From the results it can be concluded that:

- Humidity increase produces a reduction in the concentration of CO, methane and hydrocarbons C<sub>2</sub>.
- It is found an increase in the amount of produced CO<sub>2</sub> and becomes particularly marked the increase in the concentration of H<sub>2</sub>, both explained by the water-shift reaction  $\text{CO (g) + H}_2\text{O (g)} \rightarrow \text{CO}_2 + \text{H}_2 \text{(g)}$
- CO decrease and H<sub>2</sub> increase produced an increase in the H<sub>2</sub>/CO at both input speeds as humidity increased.
- Likewise, the decrease in high-energy species such as hydrocarbons and CO produced NCV decreased with increasing moisture for both input rates.
- The gas reforming is nearly complete for hydrocarbons up to C<sub>6</sub>, with the exception of benzene whose concentration is reduced to less than half but not completely reformed.
- For tars, the reforming is very remarkable with decays of around 50%.

### 3.6.2. Effect of relative humidity in combustion air

It is also necessary to analyze the effect of relative humidity using air as gas and maintaining the ratio D/B=1. For each input speed, the air flow is adjusted so  $\lambda$  is maintained between 0.2 and 0.3, values that are suitable in the literature [18]. Results are shown in Figure 7, together with the more detailed Tables S9-S10.

The trend is the one expected, i.e., increased concentrations of CO<sub>2</sub> and H<sub>2</sub> and decreased CO and hydrocarbons with the consequent reduction of NCV and very noticeable increase in ratio H<sub>2</sub>/CO for both speeds. Hydrocarbons' reforming is near total and tar reforming is close to 40%.

### 3.6.3. Effect of relative humidity in pyrolysis with N<sub>2</sub>

It is interesting to complete the study presented by analyzing the influence of moisture when it is the only supply of oxygen to the reaction atmosphere. In this case, the D/B is maintained at 1 (previously determined optimal) and the effect is studied at the two inlet velocity conditions used throughout the study. In Tables S11 and S12 the results are presented, as well as in Figure 8.

In view of the results it can be seen that:

- By increasing the relative humidity, the concentrations of CO<sub>2</sub> and H<sub>2</sub> increase, decreasing the concentrations of hydrocarbons and CO. This results in an increase of the ratio H<sub>2</sub>/CO and decreasing NCV.

- The reforming of hydrocarbons occurs even at low relative humidities, being more important for this atmosphere the catalytic effect of dolomite than the combined effect exerted by the water vapor present in the reaction atmosphere.
- Tar reforming occurs to a great extent with increasing moisture.
- All these effects are observed at the two input speeds, although gas conditions obtained are better at  $V_{high}$  than at  $V_{slow}$ , which can be justified by the combined effect of increased heating rate while less residence time in pyrolysis, which produces a better effluent gas reforming.

#### 3.6.4. Steam combined effect

To analyze the effect of the presence of different amounts of water vapor in the reaction atmosphere in the presence of the catalyst, the ratio D/B is fixed to the optimum value in accordance with the above results, and the relative humidity is varied with two different input speeds, obtaining the results shown in Figure 9.

Regarding the percentage of water vapor we can indicate the following conclusions:

- The presence of increasing percentages of water vapor in the reaction gases in the presence of dolomite increases the ratio  $H_2/CO$  for all reaction and residence times. Other authors observed similar trend [19] treating coals.
- The higher values of  $H_2/CO$  are obtained for gasification with sub-stoichiometric air and low residence times, also observed with longer residence times. Partial oxidation processes by the presence of oxygen, together with high temperatures that cause an autothermal reforming and a steam reforming causes these results.
- Pyrolysis processes show the same trend, with a significant noticeable difference between high and low residence time, presenting at high inlet velocities the maxima in  $H_2/CO$ . Autothermal reforming processes at high temperatures and steam reforming are the processes that are reforming the syngas under these conditions.
- Processes with  $O_2$  present the lowest values of the ratio  $H_2/CO$ . But in Figure 9 we can observe that the air and pyrolysis curves have a form which indicates that the value of the ratio  $H_2/CO$  reaches a maximum for increasing vapor concentration values but the increase is not linear, in such a way that a higher concentration of vapor does not produce appreciable improvements in the ratio  $H_2/CO$ . However gasification curves with oxygen, and for both speeds, have a tendency that seems to suggest that higher proportions of steam produced a significant increase in the  $H_2/CO$ .

In all sets of runs, through the effect of dolomitic catalyst and the humidity, it is observed for all atmospheres (air,  $N_2$  and  $O_2/H_2O$ ) the reforming of the gas by the destruction of species  $C_3-C_6$ . The decrease in the concentration of tars is observed both with increasing ratio D/B and the moisture present in the reaction. Another of the most notable effect is that the presence of water vapor in

increasing proportion improves the catalytic effect of the dolomite more extensively, in all atmospheres studied.

For practical purposes the two most interesting variables that determine the possible subsequent uses of syngas are NCV of the gas and the ratio  $H_2/CO$ . The NCV is an important parameter when gas use is geared toward generating electricity in thermal power plants with Rankine cycle or combined cycle plants (Bryton-Rankine).

The processes to enrich the fuel mixture effluent gases are meaningful if we work with warped turbines systems with subsequent gas combustion in steam boilers. But if gas will be used for direct injection in alternative internal combustion engines it is most interesting to have a poor gas that will allow us a constant revolution rate of torque at minimum fuel consumption; in this case, enrich the mixture increasing its NCV not make much sense if the end use will be to obtain electricity. A low calorific value fuelled distributed combustion with swirl for gas turbine applications has been described in literature [20]. If the end use of the syngas is the movement of a vehicle, the reforming of the gas to increase the NCV would be more justified. If the reforming is performed to improve the ratio  $H_2/CO$  for further use in chemical synthesis or liquid biofuels (Fischer-Tropsch) it would be interesting to analyze the results comparing all experimental conditions.

## 5. Conclusions

During the study performed about the thermal decomposition of *Posidonia oceanica* in different conditions, it can be concluded that:

- The presence of increasing percentages of water vapor in the reaction gases in the presence of dolomite increases the ratio  $H_2/CO$  and decreases the NCV of the gas for all reaction atmospheres and residence times.

- The highest values of the ratio  $H_2/CO$  and less NCV are obtained for combustion in sub-stoichiometric air and low residence time. Partial oxidation processes by the presence of oxygen, together with high temperatures that cause an autothermal reforming and a steam reforming causes these results. Pyrolysis has the same trend but a significant difference is observed between high and low residence time, being the  $H_2/CO$  much higher at high input speed.

- The possible use of syngas goes from heat engines use with internal and external combustion (low values of  $H_2/CO$ ) to the processing fluid for obtaining biofuels and methanol by Fischer-Tropsch, either for ammonia, synthetic natural gas and hydrogen ( $H_2/CO > 2$ ).

- In the Fischer-Tropsch synthesis the oxygen is a poison for the catalysts used. For this reason if atmospheres are used with an amount of oxygen is very likely that small amounts of unreacted species appear, so it would be necessary a post-treatment aimed to remove the oxygen gas. It seems therefore interesting to use pyrolysis as technique if the syngas is to be used by this route of chemical synthesis.

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## FIGURES AND TABLES

Table 1. Physico-catalytic properties of prepared dolomite

Figure 1. Particle size distribution of the catalyst prepared.

Figure 2. Sub-stoichiometric combustion of *Posidonia oceanica* in air in the presence of dolomite at 0.5 mm/s ( $V_{slow}$ ) and 1.9 mm/s ( $V_{high}$ ).

Figure 3. Pyrolysis in nitrogen of *Posidonia oceanica* in the presence of dolomite at 0.5 mm/s ( $V_{slow}$ ) and 1.9 mm/s ( $V_{high}$ ).

Figure 4. Gasification of *Posidonia oceanica* with saturated O<sub>2</sub> in the presence of dolomite at 0.5 mm/s ( $V_{slow}$ ) and 1.9 mm/s ( $V_{high}$ ).

Figure 5. Effect of D/B ratio on H<sub>2</sub>/CO

Figure 6. Gasification of *Posidonia oceanica* with O<sub>2</sub>/H<sub>2</sub>O in the presence of dolomite at 0.5 mm/s ( $V_{slow}$ ) and 1.9 mm/s ( $V_{high}$ ) varying the humidity.

Figure 7. Gasification of *Posidonia oceanica* with air in the presence of dolomite at 0.5 mm/s ( $V_{slow}$ ) and 1.9 mm/s ( $V_{high}$ ) varying the humidity.

Figure 8. Pyrolysis of *Posidonia oceanica* in nitrogen in the presence of dolomite at 0.5 mm/s ( $V_{slow}$ ) and 1.9 mm/s ( $V_{high}$ ) varying the humidity.

Figure 9. Effect of relative humidity ratio on H<sub>2</sub>/CO

In supplementary material:

Table S1. Sub-stoichiometric combustion of *Posidonia oceanica* in air in the presence of dolomite at 0.5 mm/s.

Table S2. Sub-stoichiometric combustion of *Posidonia oceanica* in air in the presence of dolomite at 1.9 mm/s.

Table S3. Pyrolysis of *Posidonia oceanica* in nitrogen in the presence of dolomite at 0.5 mm/s.

Table S4. Pyrolysis of *Posidonia oceanica* in nitrogen in the presence of dolomite at 1.9 mm/s.

Table S5. Gasification of *Posidonia oceanica* with O<sub>2</sub> / H<sub>2</sub>O in the presence of dolomite at 0.5 mm/s.

Table S6. Gasification of *Posidonia oceanica* with O<sub>2</sub> / H<sub>2</sub>O in the presence of dolomite at 1.9 mm/s.

Table S7. Gasification of *Posidonia oceanica* with O<sub>2</sub>/H<sub>2</sub>O in the presence of dolomite at 0.5 mm/s varying the humidity.

Table S8. Gasification of *Posidonia oceanica* with O<sub>2</sub>/H<sub>2</sub>O in the presence of dolomite at 1.9 mm/s varying the humidity.

Table S9. Gasification of *Posidonia oceanica* with air in the presence of dolomite at 0.5 mm/s varying the humidity.

Table S10. Gasification of *Posidonia oceanica* with air in the presence of dolomite at 1.9 mm/s varying the humidity.

Table S11. Pyrolysis of *Posidonia oceanica* in nitrogen in the presence of dolomite at 0.5 mm/s varying the humidity.

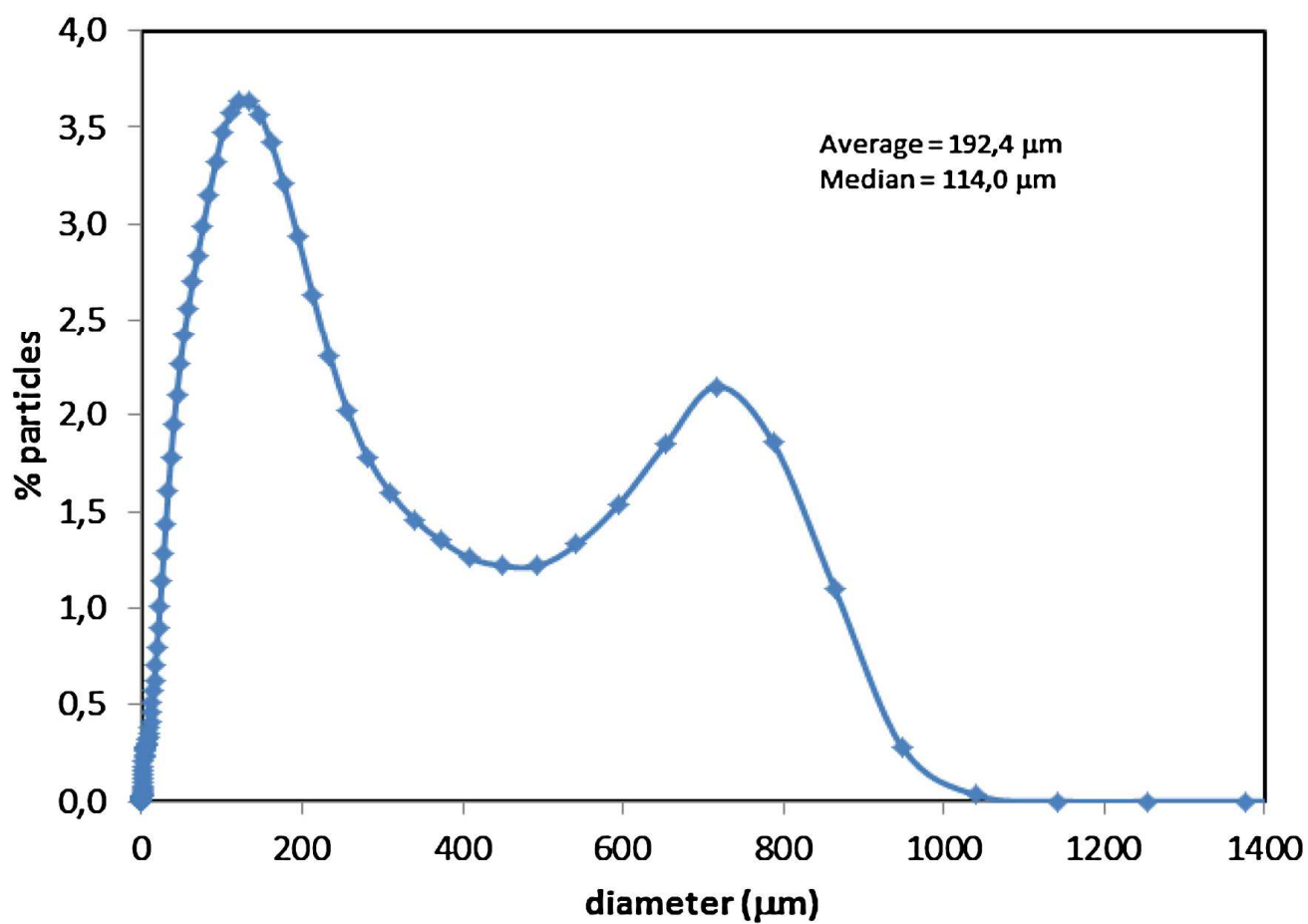
Table S12. Pyrolysis of *Posidonia oceanica* in nitrogen in the presence of dolomite at 1.9 mm/s varying the humidity.

**Table 1. Physico-catalytic properties of prepared dolomite**

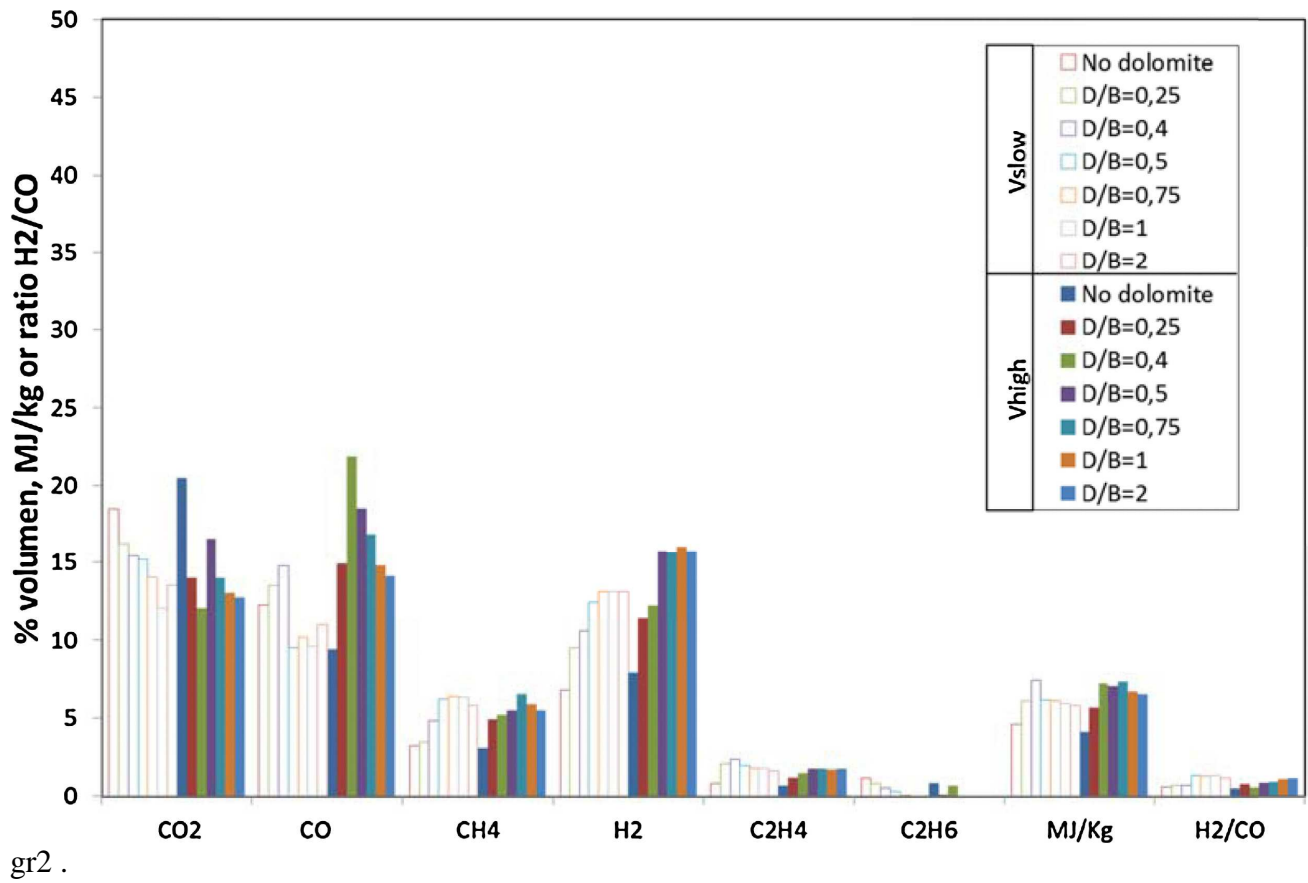
Particle diameter (mm)	0.18 to 0.22
Specific surface area (m <sup>2</sup> /g)	9.2
BET surface area (m <sup>2</sup> /g)	11.0
Area (micropores) (m <sup>2</sup> /g)	0.91
Area (17-3000 Å pores) (m <sup>2</sup> /g)	18-20



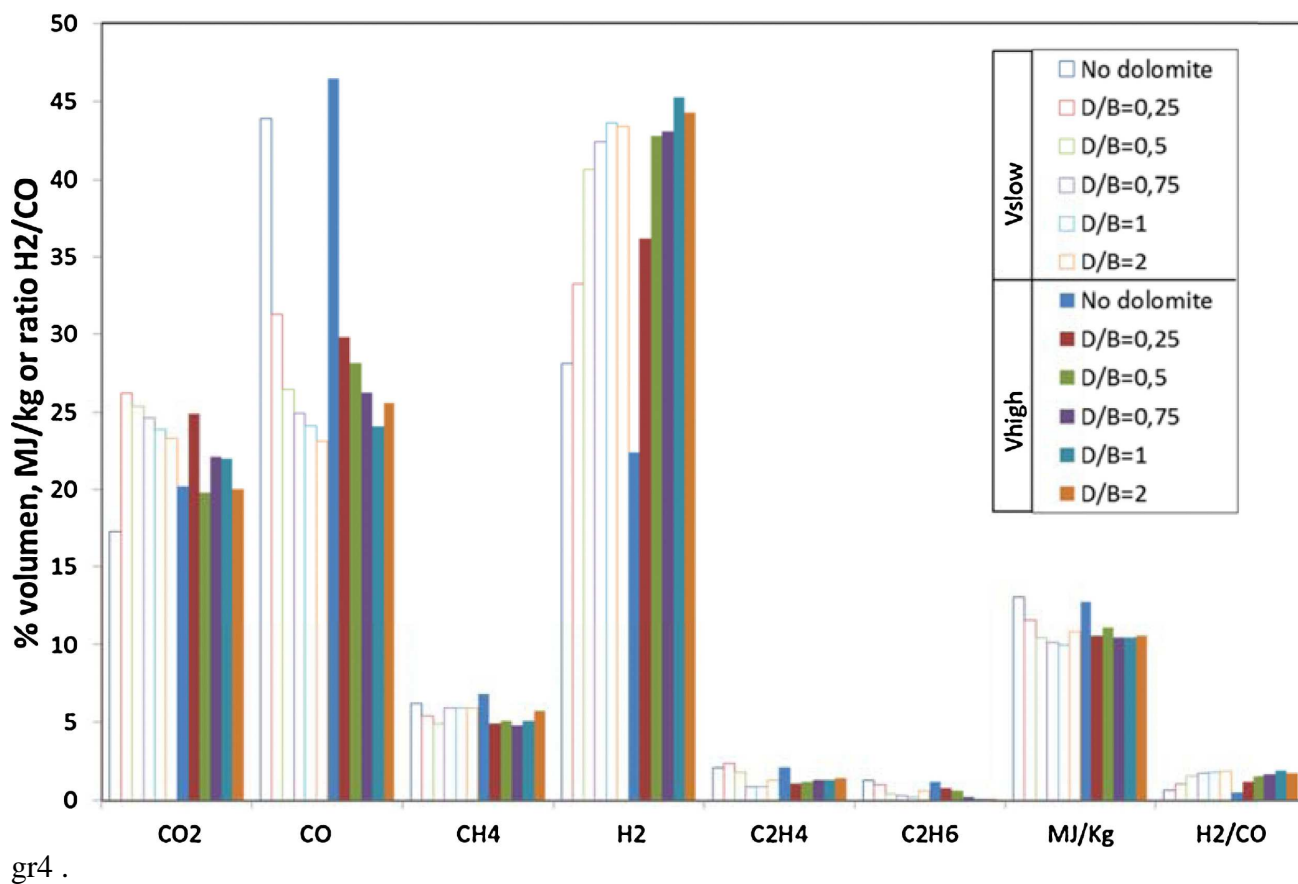
Volume (pores 17-3000k) ( $\text{cm}^3/\text{g}$ )	0.073
Average micropore diameter ( $\text{\AA}$ )	141
The total pore area ( $\text{m}^2/\text{g}$ )	15.9

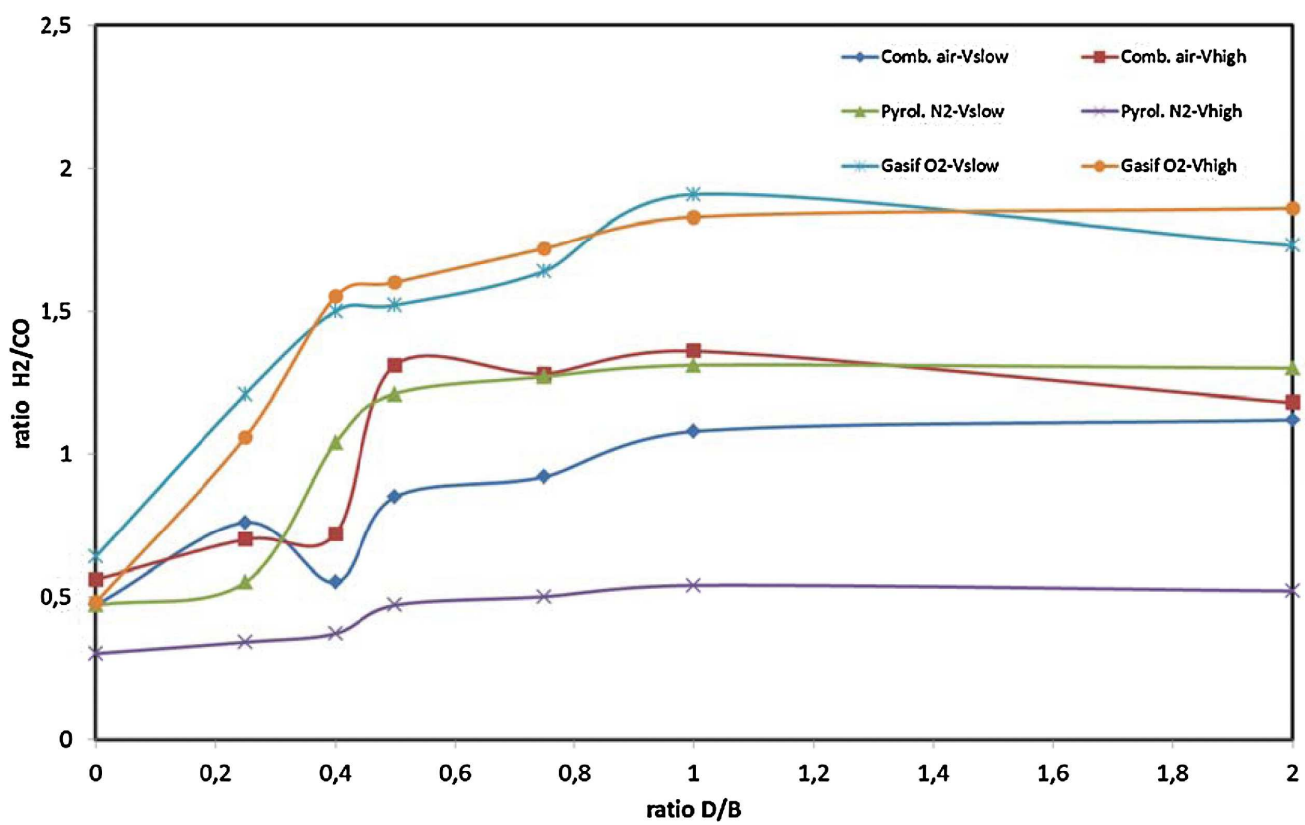


gr1 .

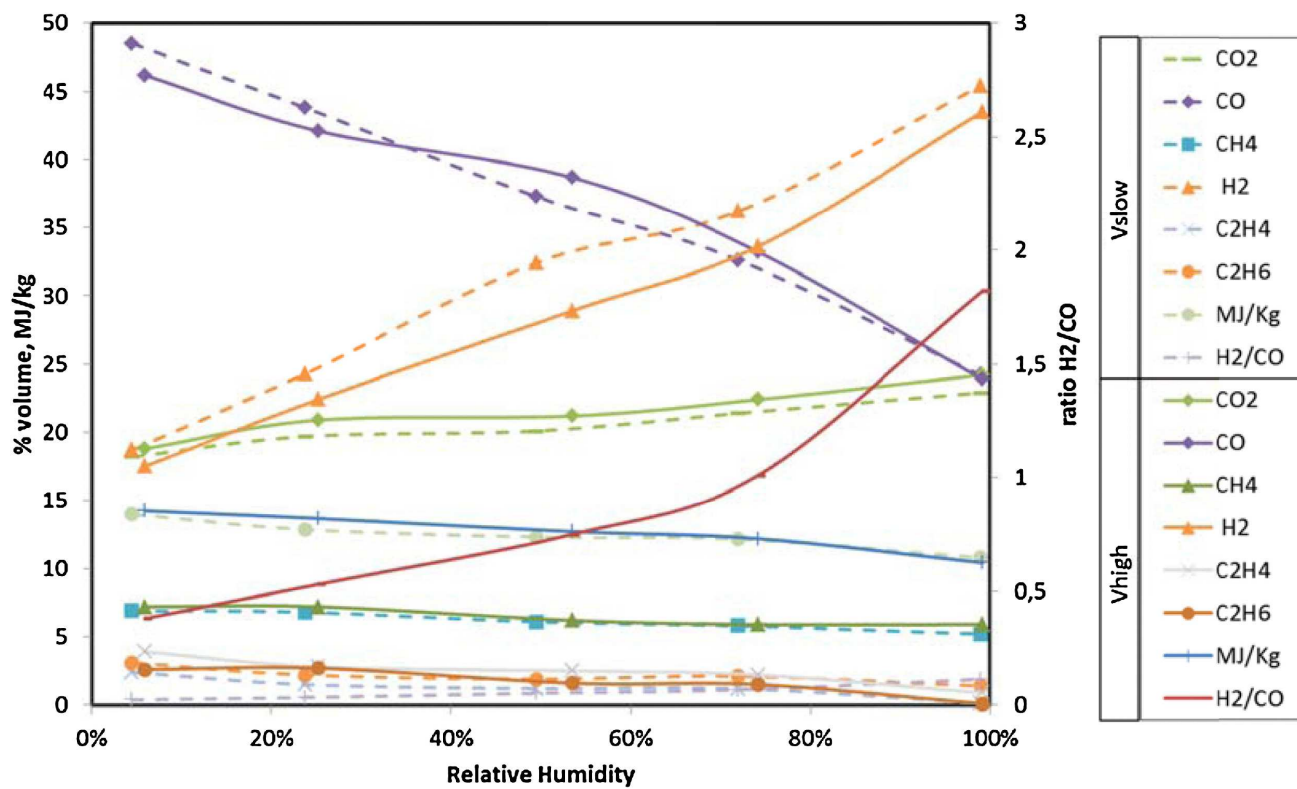




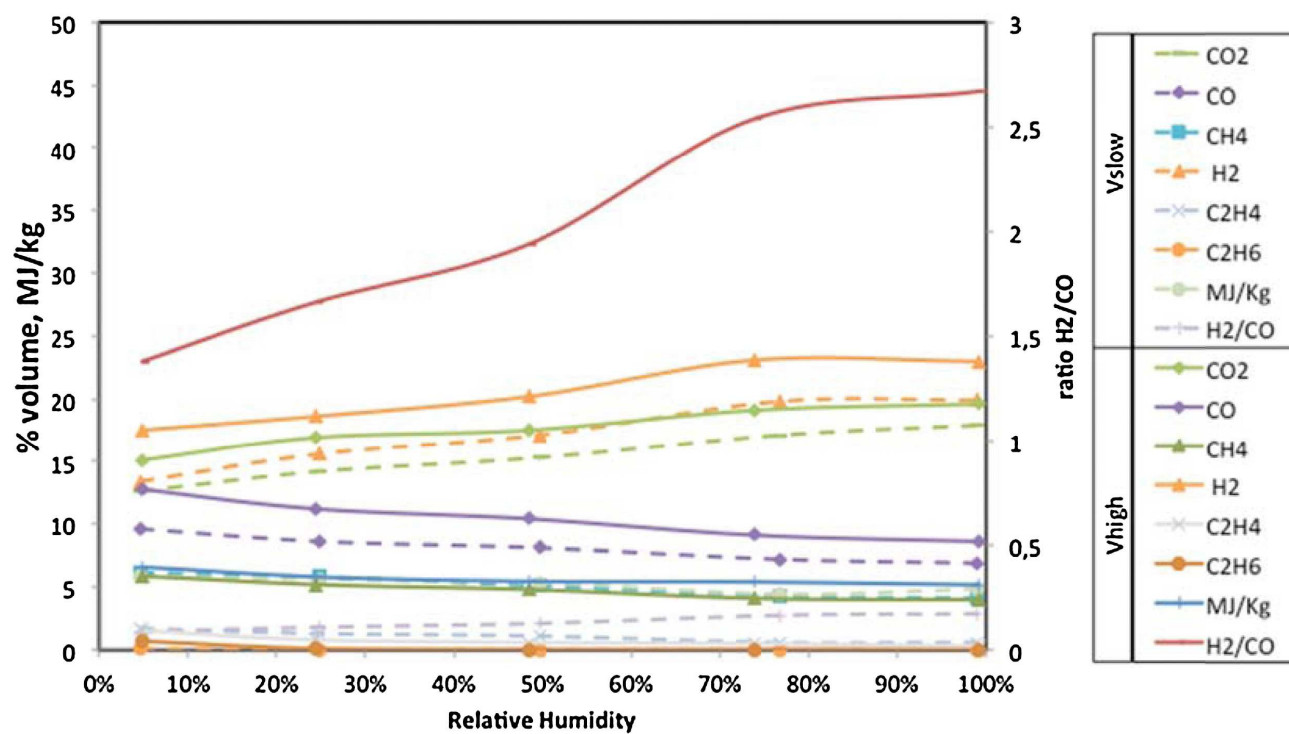




gr5 .

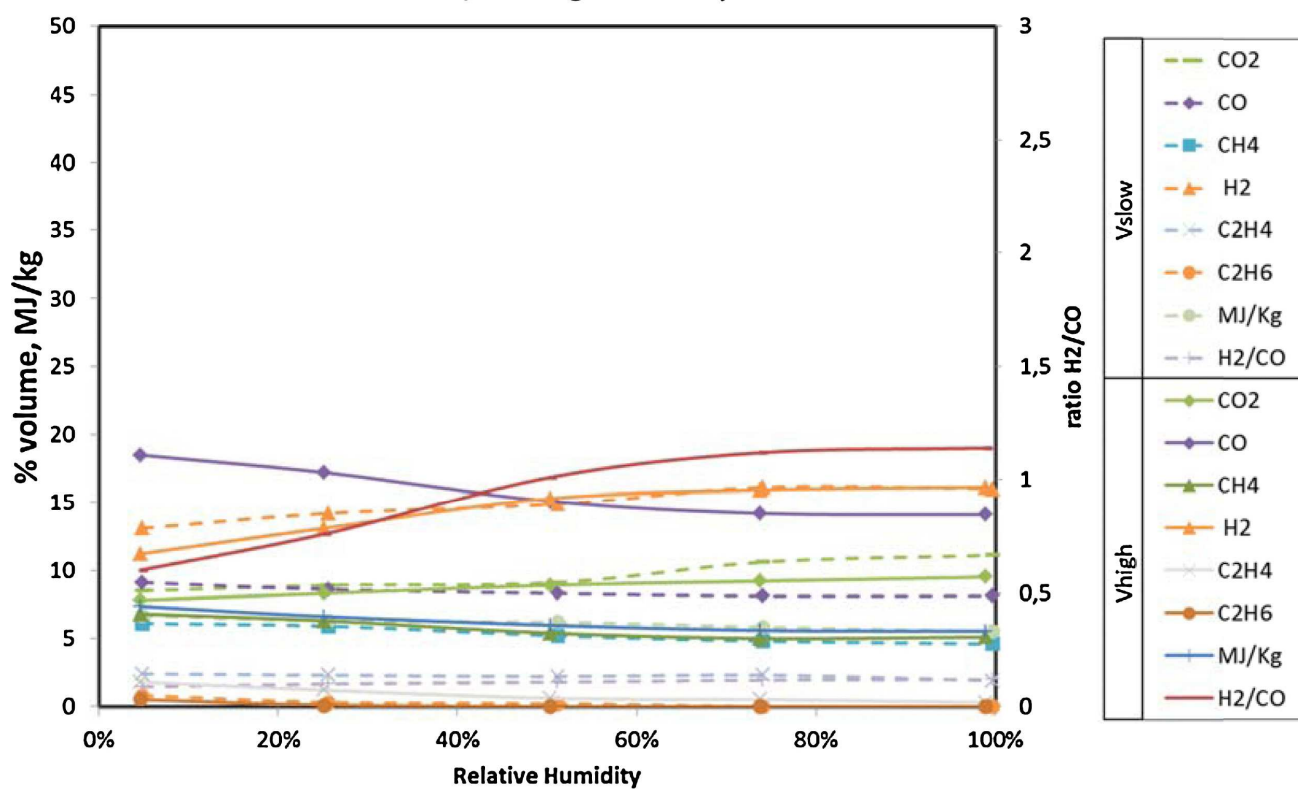


gr6 .

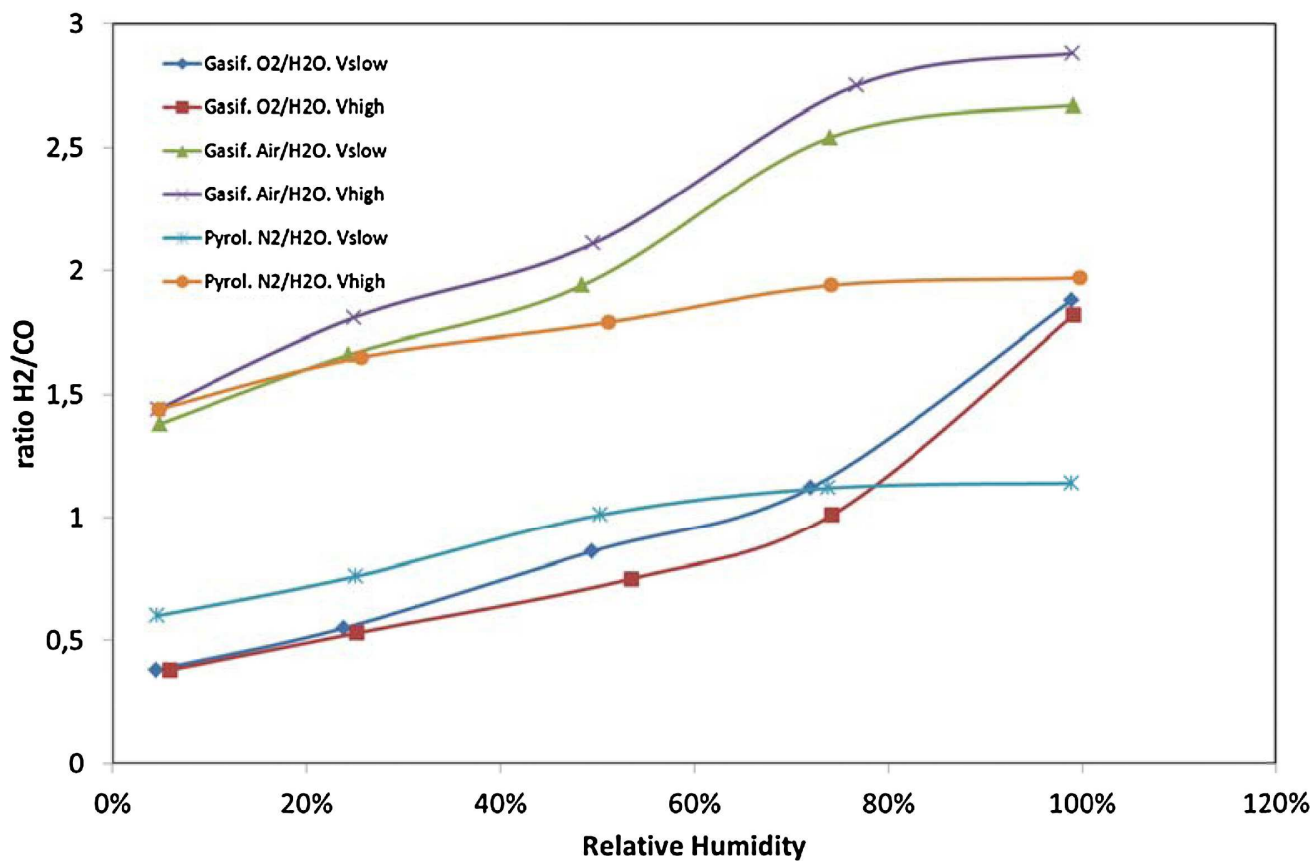


gr7 .



Gasification with water/N<sub>2</sub>. V<sub>high</sub>. Humidity effect

gr8 .



gr9 .