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Corresponding Author: Dr. Vitaliano Chiodo, Ph.D

Corresponding Author's Institution:

First Author: Susanna Maisano, PhD

Order of Authors: Susanna Maisano, PhD; Francesco Urbani; Francesco Cipitì; Vitaliano Chiodo, Ph.D

Abstract: The Gasification process is considered one of the most promising and efficient techniques to hydrogen production from biomass as carbon neutral emitter. Aim of the work was to rationalize the potential use waste feedstocks: Citrus peels (from orange fruits industries) and Posidonia Oceanica (Mediterranean seaweed) as fuels for energy recovery, thus, a direct comparison between two biomasses and a traditional woody biomass (White pine) was carried out. Gasification experiments were performed in a bubbling fluidized bed reactor at 1023 K, 1 bar, ER=0.3, and various steam to biomass inlet ratio ($0.5<S/B<1.0$) in order to investigate the influence of these parameters on syngas composition and hydrogen yield. Experimental results highlighted an improvement of the gasification performances in terms of syngas and H2 production with increasing of Steam to Biomass (S/B) inlet ratio (2.10 to 2.70 Nm3/kgbiomass and 0.26 to 0.66 Nm3/kgbiomass respectively) than gasification tests performed with only air (1.90 to 2.10 Nm3/kgbiomass and 0.17 to 0.20 Nm3/kgbiomass respectively). In particular, Posidonia Oceanica showed the best rates both of syngas and of hydrogen yields (2.70 Nm3/kgbiomass and 0.66 Nm3/kgbiomass, respectively), while from the thermal efficiencies point of view, citrus peels resulted the most suitable biomass with recorded the highest LHV syngas, CGE and CCE values (4.8 MJ/Nm3, 68.0% and 98.4%, respectively).

Dear Editor,

considering your kind invitation to submit a research contribution for the Special Issue of *International Journal of Hydrogen Energy* (IJHE), it is our pleasure to present the manuscript entitled "*Syngas production by BFB gasification: Experimental comparison of different biomasses*" (by Susanna Maisano, Francesco Urbani, Francesco Cipitì and Vitaliano Chiodo) for its evaluation.

The article is original. The stated authors, who are all aware of its content and approve its submission, have written it. The article has not been published previously and it is not under consideration for publication elsewhere.

The novelty of the work is certainly the recovery feedstocks investigated; indeed, the aim of this work has been to rationalize the potential use of waste feedstocks (Citrus peels and Posidonia Oceanica) as fuels for energy recovery through gasification in a BFB reactor.

Best regards,

(for the Authors)
Vitaliano Chiodo

1. Panagiotis Tsiakaras (Professor)

University of Thessaly, School of Engineering , Volos-Greece

E-mail: tsiak@mie.uth.gr

Phone: +30 24210 74065

1. Marta Gandiglio (Researcher)

Politecnico di Torino

E-mail: marta.gandiglio@polito.it

Phone: +39 0110904560

3. Cataldo De Blasio (Associate Professor)

Aalto University, Espoo Finland

E-mail: de.blasio@aalto.fi

Phone:+358 50 4147 028

4. Simona Bennici (Research Scientist)

Institute de Science des materiaux de Mulhouse

E-mail: simona.bennici@uha.fr

Phone: +33 (0) 389336729

HIGHLIGHTS

- The thermal behavior of different biomasses was investigated;
- H_2 production from Posidonia Oc. and Citrus peels by steam gasification was investigated;
- Different S/B ratios for the syngas production were evaluated;
- The highest hydrogen yield (0.66 Nm^3/kgbiom) was obtained from Posidonia Oc.;

Syngas production by BFB gasification: Experimental comparison of different biomasses

Susanna Maisano, Francesco Urbani, Francesco Cipitì and Vitaliano Chiodo*

Institute CNR-ITAE, via Salita S. Lucia sopra Contesse 5, 98126 - Messina – Italy

*corresponding author. Tel. +39.090.624203 email address: vitaliano.chiodo@itae.cnr.it

Abstract

The Gasification process is considered one of the most promising and efficient techniques to hydrogen production from biomass as carbon neutral emitter. Aim of the work was to rationalize the potential use waste feedstocks: Citrus peels (from orange fruits industries) and Posidonia Oceanica (Mediterranean seaweed) as fuels for energy recovery, thus, a direct comparison between two biomasses and a traditional woody biomass (White pine) was carried out. Gasification experiments were performed in a bubbling fluidized bed reactor at 1023 K, 1 bar, ER=0.3, and various steam to biomass inlet ratio (0.5<S/B<1.0) in order to investigate the influence of these parameters on syngas composition and hydrogen yield. Experimental results highlighted an improvement of the gasification performances in terms of syngas and H_2 production with increasing of Steam to Biomass (S/B) inlet ratio (2.10 to 2.70 $Nm^3/kg_{biomass}$ and 0.26 to 0.66 $Nm^3/kg_{biomass}$ respectively) than gasification tests performed with only air (1.90 to 2.10 $Nm^3/kg_{biomass}$ and 0.17 to 0.20 $Nm^3/kg_{biomass}$ respectively). In particular, Posidonia Oceanica showed the best rates both of syngas and of hydrogen yields (2.70 $Nm^3/kg_{biomass}$ and 0.66 $Nm^3/kg_{biomass}$, respectively), while from the thermal efficiencies point of view, citrus peels resulted the most suitable biomass with recorded the highest LHV syngas, CGE and CCE values (4.8 MJ/Nm^3, 68.0% and 98.4%, respectively).

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1. Introduction

The energy increasing demand and environmental impact due to the utilization of fossil fuels have resulted in calls for more alternative energy sources. Different scenarios of alternative energy sources use are developing. Among these, biomass and biofuels, are promising candidates that are able to ensure programmable and constant energy production [1-4].

According to the biomass classification, biofuels can be divided in to primary and the secondary ones. Primary biofuels (wood and residues of forest and agricultural crops) is the traditional biomass without any treatment, while secondary biofuels (biohydrogen, bio-oil, bioethanol etc…) are obtained from biomass through several processes or technologies [5]. Furthermore, secondary biofuels can be divided into three generations depending mainly on; i) nature of the feedstock used to produce it and ii) processing method adopted for the conversion [2,6]. In particular, the third generation is connected with algal biomass, that represents a new direction of bioenergetics through fuels synthesis (biodiesel, biohydrogen, bio-oil and biochar) [5,7,8]. In this context, gasification process, that converts carbonaceous materials with assistance of a gasifying agent (air, oxygen, steam and CO_2), is one of the most flexible technologies due its higher efficiency and its suppleness to use a wide range of feedstocks (biomass, coal, wastes, etc.) [9]. The outlet stream gas obtained can be used to generate electrical energy through gas turbine or gas engine or fuel cell systems [10-12]. Nevertheless, the gasification stream gas depends on several factors such as reactor type, flow rate of feedstock, gasification agent, residence time, pressure and temperature of reactor. Hence, different technologies that use different reactor configuration, such as fixed bed, bubbling fluidized bed, circulating fluidized bed have been studied in these years [13]. Among the market ready technologies, updraft gasification is one of the most suitable technologies for treating high moisture content biomass, but the high tar concentration in the outlet gas has limited its application. In this way, the fluidized bed gasifier (BFB) resulted to have many advantages, such as easy scale-up, flexibility regarding feedstock type and size, uniform temperature distribution and high carbon conversion efficiency; therefore, it is suitable for the gasification of biomass [11,13,14].

The suitable gasifying agent’s selection is another important factor that influences gasification performance. Indeed, the gasifying agent reacts with biomass breaking carbohydrate compounds (such as hemicellulose and cellulose) that are decomposed into smaller molecules (i.e., carbon dioxide, methane etc…). Air is the most used in the gasification process, however oxygen is often chosen in order to increase the heating values of the outlet gas stream (syngas). Steam is another agent used for its ability to extract the most amount of hydrogen from biomass; nevertheless, it requires additional power input. Occasionally, CO_2 is used as the gasification agent to enhance CO_2 recycling and to reduce CO_2 concentration in the atmosphere [15].

In this context, the recycling of residual biomasses or wastes used in order to produce syngas for energy production could represent a good opening for waste disposal management and promotion of olso environmental benefits, too. Indeed, the using of residues could reduce the costs of feedstock supply and the amount of landfilled materials. Thus, authors would report the main results of an investigation on the effect of gasification process applied to different waste materials Posidonia Oceanica (Mediterranean sea plant) and Citrus peels (residues derived from orange fruits industries).

Posidonia Oceanica is the most abundant seaweed in the Mediterranean area, that contains cellulose, hemicellulose and lignin concentrations of 38 wt%, 21 wt% and 27wt%, respectively [16,17]. Despite it is an essential element in the equilibrium marine ecosystem, its residues represent environmental social and hygienic problems in the countries of the EU [18-20]. Hence, energetic applications were proposed in these years, mainly as fertilizer, insulation material and precursor for bio-oil and biochar production through pyrolysis process [7,19,21]. While few works investigated on Posidonia Oceanica gasification providing positive results about the feasibility to convert its residues into syngas [22,23].

Similarly to Posidonia Oceanica about the Citrus peel residues the conversion to bio-oil and/or chemicals was proposed [24-26] mainly due to its high moisture concentration, nevertheless, authors recently explored the potential valorization of Citrus residues by experimental and simulation activities [12,27]. Accordingly, the aim of this work is to rationalize the potential use waste feedstocks (Citrus peels and Posidonia Oceanica) as fuels for energy recovery through gasification in a BFB reactor. In particular, a direct comparison between two biomasses with a traditional woody biomass (White pine) was carried out into three steps: firstly, i) chemical-physical characterization of biomasses by proximate, ultimate analysis, ash analysis and determination of calorific value were carried out; successively ii) thermogravimetric analyses (TGA) were performed to understand their behavior during thermal processes and iii) a series of experimental measurements using the three biomasses and two different gasifying agents, (air and air-steam) were conducted in a pilot bubbling fluidized bed (BFB) gasifier. Finally, results were compared in terms of syngas composition, hydrogen yield, carbon conversion and cold gas efficiency.

2. Methods

2.1. Biomass preparation and characterization

Different kinds of biomasses were selected as raw materials to perform gasification experiments. Particularly, a lignocellulosic material (White-pine wood) was compared with an agro-industrial residue (Citrus peels derived from orange fruit industries) and a Mediterranean sea plant (Posidonia Oceanica). All biomasses were preventively dried both in air and an oven (White-pine wood at 383 K for 6 h, while Posidonia Oceanica and Citrus peels at 353 K for 16 h), shredded and sieved into a grain size range between 0.4<d<1 mm.

Samples were preserved in a dryer in order to assure a dry ambient. Proximate and ultimate analysis was performed to determine physical-chemical characteristics of the samples; results were summarized in Table 1.

Table 1: Ultimate and proximate analysis of biomasses

		White pine	Citrus peels	Posidonia Oceanica
Proximate analysis (wt%)	Moisture	7.6	7.0	12.67
	V.M.	74.2	64.6	60.95
	C.F.	17.4	20.0	12.36
	Ash	0.87	9.0	14.02
Ultimate analysis (wt%)[a]	C	52.71	42.46	46.1
	H	5.95	6.24	6.82
	N	0.54	1.26	1.28
	S	0.2	0.13	0.3
	O[b]	39.53	40.85	31.41
H/C atom ratio		0.11	0.15	0.15
O/C atom ratio		0.74	0.96	0.64
HHV (MJ/kg)		19.3	17.8	18.1
LHV (MJ/kg)		18.3	16.6	17.2

a. as received; b. by difference

Proximate analysis includes the volatile matter determination (by measuring weight loss after heating biomass samples to 1223±20 K in an alumina crucible under N_2 atmosphere, ASTM D-2013), moisture (through the drying of the biomass in a convection oven at 383 K until constant weight), ash (by heating samples at 848±25 K for 3 h, to constant weight in a muffle furnace, Standard E-1755-01), and fixed carbon (calculated by subtracting the percentages of volatile matter, moisture and ash) content.

Ultimate analysis was performed through a CHNS analyzer (Thermo Fisher Scientific, Flash EA 1112).

High Heating Values (HHV) and Lower Heating Value (LHV) of the different biomasses were calculated with following equations: 1, 2 and 3 [8,28,29]:

$$HHV(OLS) = 1.87(C)^2 - 144(C) - 2802(H) + 63.8(C*H) + 129(N) + 20147 \tag{1}$$

$$HHV(PLS) = 5.22(C)^2 - 319(C) - 1647(H) + 38.6(C*H) + 133(N) + 21028 \tag{2}$$

$$LHV = HHV - hg\,(9H/100 - M/100) \tag{3}$$

The measured HHV value was calculated with an average of two different regression methods, ordinary least-squares regression (OLS) reported in eq. 1 and a partial least-squares regression (PLS) in eq. 2. Otherwise, LHV was calculated with eq. 3, where hg, H and M are latent heat of steam, moisture percentage, hydrogen percentage, respectively, on as received basis.

2.2. Thermo-decomposition analysis

The thermal decomposition behavior of the biomasses was investigated by thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) measurements. In particular, Netzsch Thermische, TASC 414/2, analyzer was used to carry out experiments in order to individuate the suitable operative conditions to maximize biomass oxidation steps.

Samples were heated in a temperature range from 298 K to 1173 K with a heating rate of 10 K/min under nitrogen atmosphere and nitrogen-steam atmosphere (40kPa$_{H2O}$).

2.3. Gasification testing

Gasification tests were carried out by a bench-scale fluidized bed gasifier, a layout of which is shown in Fig. 2. The gasifier is equipped with a bubbling fluidized reactor of height equal a 475 mm and an internal diameter of 27 mm. The freeboard has an internal diameter of 52 mm and is 295 mm height. The feeding system consists of a vessel (1 L of biomass) working in nitrogen atmosphere (50 ml/min) and maintained under stirring and equipped with a screw at adjustable feeding rate.

Silica sand (particle size range between 0.4-0.6 mm) was used as reactor bed material, while the biomass particle size used for tests was 0.4<d<1 mm.

All system temperatures (bottom reactor zone, freeboard, cyclone, inlet gas, etc...) were monitored by thermocouples, while the pressure was controlled through the installation of controllers in different points of the gasifier. The gasification outlet stream before being analyzed by a micro-GC (Gas Chromatographic) analyzer passed through a filter cyclone kept at 673 K to separate solid particles and a cold traps system to collect the condensable gaseous fraction (TAR).

Water (gasifying agent) was fed by an HPLC pump. Qualitative and quantitative analysis of the produced syngas was determined by a micro-GC analyzer (Pollution Vega); the composition was defined as the average of five measurements.

The syngas yield (η_{syn}, the capacity of the gasifier to produce a specified quantity of gas per unit of dry biomass) was determined for all samples by means of the nitrogen mass balance according to Eq. 4 [30]:

$$\eta_{syn} = \frac{\dot{V}_{air} \cdot xN_2air}{xN_2syn \cdot \dot{m}_{biom}} \, [\mathrm{Nm^3/kg_{biom}}] \tag{4}$$

where $\dot{V}_{air}, xN_2air, xN_2syn$ are the air flow rate and the nitrogen volumetric fraction in the air and in the syngas, respectively, while $\dot{m}_{biom}$ is the dry biomass flow rate (kg/s).

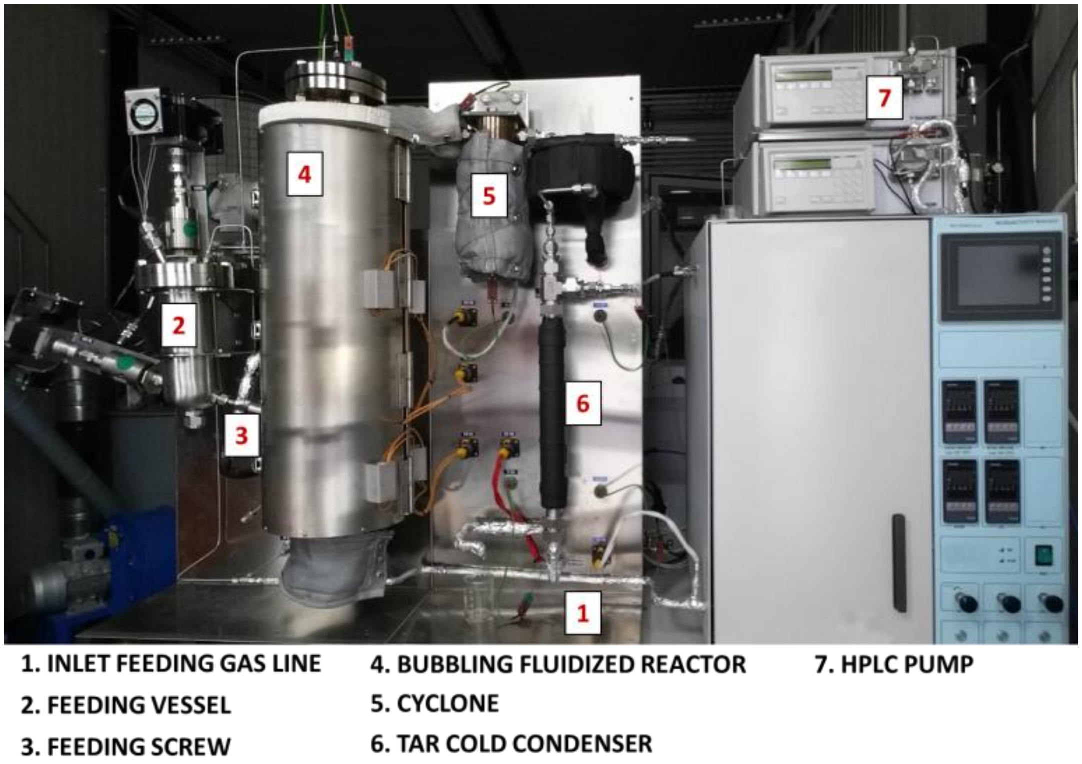

Figure 2: Bench-scale fluidized bed gasifier

While the hydrogen yield (η_{H2})was calculated by the Eq. 5:

$$\eta_{H2} = \eta_{syn} \cdot xH_{2syn} \; [Nm^3/kg_{biom}] \tag{5}$$

Where η_{syn} and xH_{2syn} are the syngas yield and the hydrogen volumetric fraction in the syngas, respectively.

The gasification tests were performed at 1023 K and an equivalent ratio (ER) value equal to 0.3. The biomass feeding rate (0.8 g/min both White pine and Posidonia Oceanica, and 1.035 g/min for Citrus peels) was chosen in order to assure the adequate air flow rate necessary to the fluidization conditions and an equivalent ratio equal to 0.3 (1325 ml/min of air for White pine, 1350 ml/min of air for Citrus peels and 1300 ml/min of air for Posidonia Oceanica). The measurements were carried out changing steam to biomass ratio (S/B) in the range: 0-1 (wt/wt).

The behavior of the different biomasses on gasification performances was also investigated with the following three parameters [31]: the heating value of produced syngas (LHV$_{syngas}$) Eq. 6, the cold gas efficiency (η_{CGE}), Eq.7, and the carbon conversion efficiency (η_{CCE}), eq.8.

$$LHV_{syngas} = \frac{(H_2 mol\% \cdot 10.79 + CO\ mol\% \cdot 12.63 + CH_4 mol\% \cdot 35.8)}{100} \tag{6}$$

The cold gas efficiency (η_{CGE}) indicate the capacity of the gasification system to convert the chemical energy of the biomass into syngas and was calculated according to Eq. 7

$$\eta_{CGE}(\%) = \frac{LHV_{syn} \cdot \dot{m}_{syn}}{LHV_{biom} \cdot \dot{m}_{biom}} \cdot 100 \tag{7}$$

where LHV_{syn} and LHV_{biom} are the lower heating value (*LHV)* of the syngas and the raw biomass, whereas $\dot{m}_{syn}$ and $\dot{m}_{biom}$ are means the mass flow rate of the syngas and the mass flow rate of the dry biomass fed, respectively.

The carbon conversion efficiency (η_{CCE}), instead represents the capacity of the system to convert the carbon content in the raw biomass, and it was calculated from Eq. 8 [30]:

$$\eta_{CCE}(\%) = \frac{mol_{Csyngas}}{mol_{Cbiom}} \cdot 100 \tag{8}$$

where $mol_{Csyngas}$ and mol_{Cbiom} are the moles of carbon contained in the produced syngas and the moles of carbon contained in the biomass.

3. Results and Discussion

3.1. Thermogravimetric analysis

Thermal decomposition behaviors in terms of mass loss (TGA) and rate of mass loss (DTG) of White pine, Citrus peels and Posidonia Oceanica under nitrogen and steam atmosphere were reported in Fig. 2. Thermal degradation curves showed three main steps for all biomass samples. The first, between 293-425 K, attributed to moisture release, the second, between 373-748 K, corresponding to the major mass loss of the feedstock due to the volatile matter; and the third stage, between 773-1173 K, featured to a very slow decomposition rate ascribable at the carbonaceous matter stabilization (bio-char) formed by previous step. In addition, DTG analysis performed in nitrogen-steam atmosphere (Fig. 2c) highlighted (840-1135 K) a further decomposition step attributed to char gasification reaction.

All biomass samples have a lignocellulosic content, however by comparison of the biomasses thermal degradations curves a shift of the peaks corresponding to hemicellulose, cellulose and lignin compounds was recorded (Figs. 2b and 2c). According to literature, this effect was attributed to the interaction of lignocellulosic compounds with other molecules of the structure [32]. Hence, the following “ease of decomposition scale” depending on biomass chemical nature can be deduced: Citrus peels > Posidonia Oceanica > White pine. In particular, the latter showed the highest decomposition temperature (653 K) and also the highest peak intensity (Figs. 2b and 2c). This behavior was ascribed to the higher cellulose and lignin contents than other biomasses [29]. In the same way, Posidonia Oceanica showed a single major peak, nevertheless it resulted shifted to lower temperatures (596 K) than that White pine. Furthermore, a small shoulder was detected at temperature ≥ 680 K, corresponding to lignin degradation [16]. The DTG profile of the Posidonia Oceanica could be due to compounds, such as: proteins and lipids, that are thermally less stable than hemicellulose, cellulose and lignin.

Otherwise, Citrus peels thermal degradation exhibited the main decomposition step among 373-633 K. In particular, three peaks related to decomposition of holocellulose (453 K) and to the scission and depolymerization reactions (503 K and 573 K, respectively) were detected. While the peak corresponding to lignin decomposition was obtained at temperature ≥ 630 K [27].

In order to a better comprehension of the biomasses gasification behaviors TGA measurements were carried out under nitrogen-steam atmosphere (Fig. 2c). Steam thermal graphs resulted to be very close to profiles recorded in exclusively nitrogen atmosphere. Though, a further peak probably corresponding to char gasification was detected for all biomasses. In particular, gasification temperature ranges for Posidonia Oceanica, Citrus peels and White pine were 836-920 K, 848-983 K and 998-1083 K, respectively. Thus, it is clear that woody biomass required an higher temperature (1073 K) than other biomasses to gasify, this means that more reactive bio-chars coming from conversions both Posidonia Oceanica and Citrus peels can be produced. This behavior could be attributed to the high ash content into Posidonia Oceanica and Citrus peels (14 wt% and 9 wt%, respectively) compared with that of the White pine (0.9 wt%). Indeed, the inorganic components of the ash lead to higher thermal conductivity, that promote a more efficient intra-particle heating transfer at lower temperatures [25]. In this way, Posidonia Oceanica would result more reactive than Citrus peels and white pine in disagree with thermal decomposition order deduced by Fig. 2b.

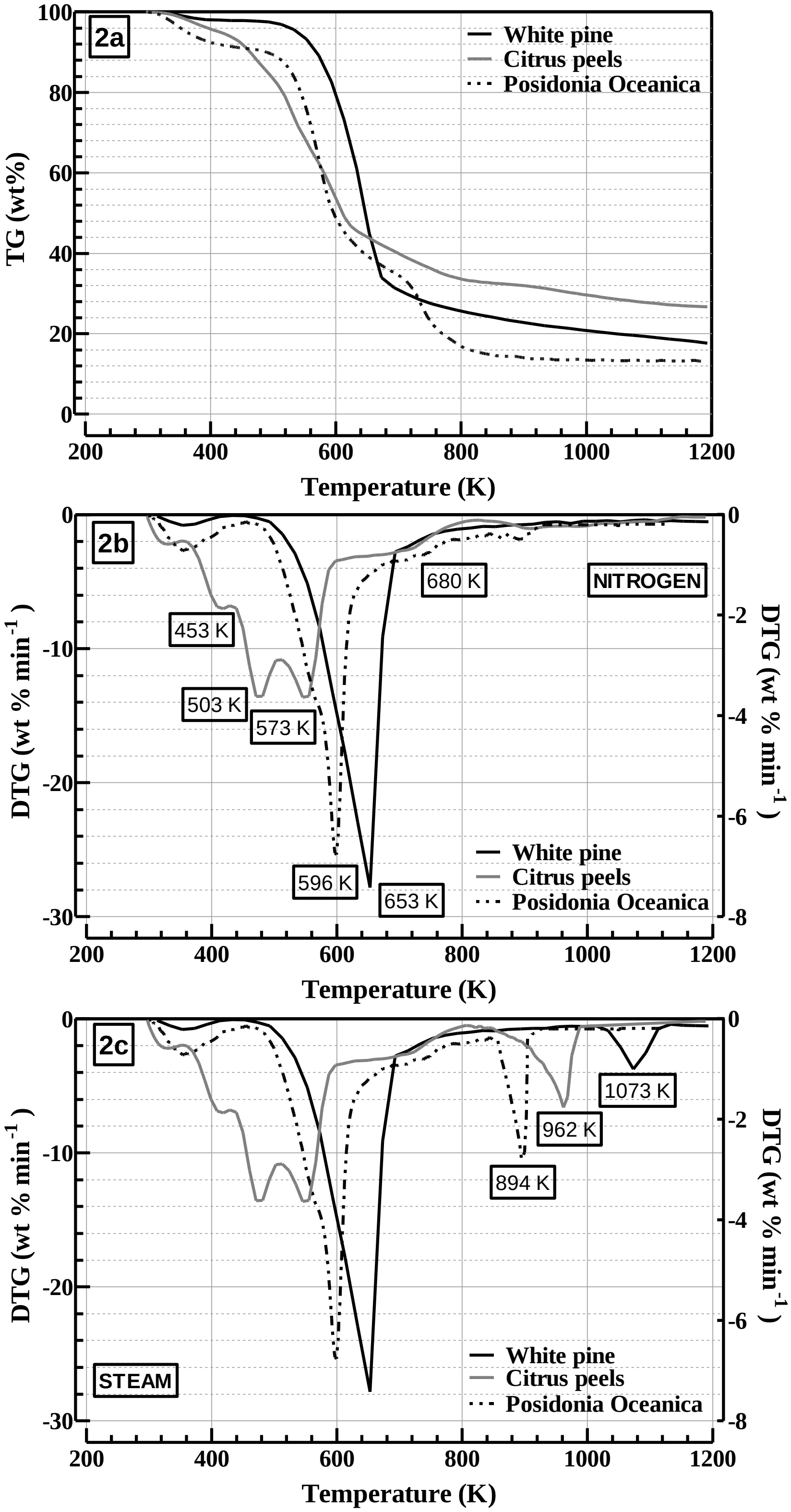

Figure 2: Thermogravimetric analysis of biomasses; a. TGA curves, b. DTG in nitrogen atmosphere, c. DTG in steam atmosphere

3.2. Gasification results

To analyze the potential use of residual biomasses (Citrus peels and Posidonia Oceanica) as alternative fuels through gasification technology, a comparison was carried out with a typical lignocellulosic material (White pine) working under air and air-steam gasification conditions at E/R=0.3, 1023 K and 1 bar of pressure. Table 2 depicts the variation of the outlet syngas streams (N_2, CO, CO_2, CH_4 and H_2) with S/B ratio. Results showed that by adding of steam in the inlet stream an increasing both hydrogen and carbon dioxide concentration is promoted for all biomasses, while a reduction of N_2, CO and CH_4 concentration was recorded. In particular, at S/B=1 very close rates both hydrogen and carbon dioxide were obtained by air-steam gasification of Citrus peels and Posidonia Oc. (about 24.8 mol% and 20 mol%, respectively), while marked lower rate of H_2 was detected by White pine in all range of S/B ratio investigated.

These data resulted in according with information provided in literature [33-35]; it can be justified taking into account the mass action promoted by steam (as gasify agent) on steam reforming reactions of methane, coke (eqs. 9 and 10) and the Boudouard reaction (eq. 11). This can also turn in an increase of H_2 production via water gas shift reaction (reaction 13) [35-37].

$$CH_4 + H_2O\ (g) \rightleftharpoons CO + 3H_2 \qquad \Delta H_{298K} = +201.9\ \text{kJ/mol} \qquad (9)$$

$$C + H_2O\ (g) \rightleftharpoons CO + H_2 \qquad \Delta H_{298K} = +131.4\ \text{kJ/mo} \qquad (10)$$

$$C + CO_2 \rightleftharpoons 2CO \qquad \Delta H_{298K} = +172.6\ \text{kJ/mol} \qquad (11)$$

$$C + 2H_2 \rightleftharpoons CH_4 \qquad \Delta H_{298K} = -74.91\ \text{kJ/mol} \qquad (12)$$

$$CO + H_2O\ (g) \rightleftharpoons CO_2 + H_2 \qquad \Delta H_{298K} = -412.6\ \text{kJ/mol} \qquad (13)$$

Furthermore, data reported in Table 2 highlighted how all biomasses gasified in air-steam atmosphere lead to a reduction of the nitrogen concentration than experiments performed exclusively in air. This means that in presence of steam the syngas production is promoted than secondary gasification products (tar and char) in according to the nitrogen mass balance as expressed by eq. 4 [30]. Indeed, Fig. 3, clearly shows how the syngas yield rate obtained by gasification exclusively with air (S/B=0) was almost the same for all biomasses (about 2 $Nm^3/Kg_{biomass}$); while operating with air-steam oxidant atmosphere syngas yields increased for all feedstocks, nevertheless with different increasing rates. In particular, Posidonia oceanica recorded an increasing of syngas yield from 2.1 $Nm^3/Kg_{biomass}$ at S/B=0 to 2.7 $Nm^3/Kg_{biomass}$ at S/B=1. Otherwise, White pine performances resulted to be very poorly improved by steam presence (from 2.0 $Nm^3/Kg_{biomass}$ at S/B=0 to 2.2 $Nm^3/Kg_{biomass}$ at S/B=1).

Table 2: Biomasses outlet stream composition (mol%)

	S/B	N_2	CO	CO_2	CH_4	H_2
White pine	0.00	61.09	10.36	15.13	2.37	8.13
	0.50	60.75	6.45	17.70	1.92	12.18
	0.75	59.34	5.19	19.06	2.01	13.41
	1.00	59.22	3.66	19.98	1.87	14.27
Citrus peels	0.00	52.60	12.40	18.30	3.70	10.50
	0.50	44.00	11.40	19.40	3.40	20.00
	0.75	42.40	9.90	19.60	2.70	23.80
	1.00	42.00	8.70	20.60	2.40	24.80
Posidonia Oceanica	0.00	55.00	16.67	14.47	3.04	8.49
	0.50	51.45	11.18	16.04	2.78	16.35
	0.75	49.08	6.20	18.06	2.33	22.57
	1.00	47.46	4.14	20.02	1.99	24.87

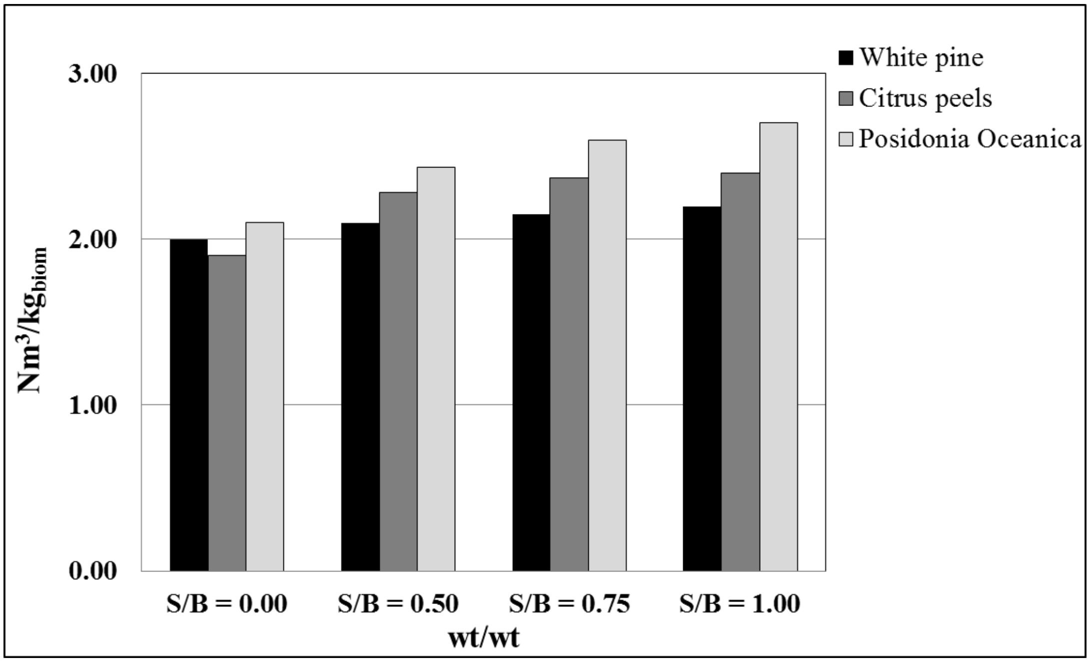

Figure 3: Syngas yield at different S/B ratios

In terms of hydrogen yield (Fig. 4), the White pine showed the lowest H_2 yield rates in all testing performed (0.17-0.30 Nm^3/kg_{biom} at $0<S/B<1.0$), while this parameter was the highest obtained by conversion of Posidonia Oceanica and Citrus peels at S/B=1.0 (0.60 Nm^3/kg_{biom} and 0.66 Nm^3/kg_{biom}, respectively).

The lower yield rates both syngas and hydrogen recorded by gasification of White pine (mainly using air-steam as gasifying agent) than other biomasses at the temperature investigated (1023 K) could be due to the woody material properties in terms of lignin, cellulose and hemicellulose composition. In particular, as highlighted by Fig. 2c, White pine has an higher lignin content than Citrus peels and Posidonia Oceanica; this means that probably it needs temperature higher than 1073 K for a complete decomposition [32]. Hence, the heterogeneous secondary reactions (eqs. 10,11 and 12) involving on primary char (coming from pyrolysis step) are probably so slow that are not able to contrast the steam effect introduced in the inlet gas stream at relative low temperature [11,38].

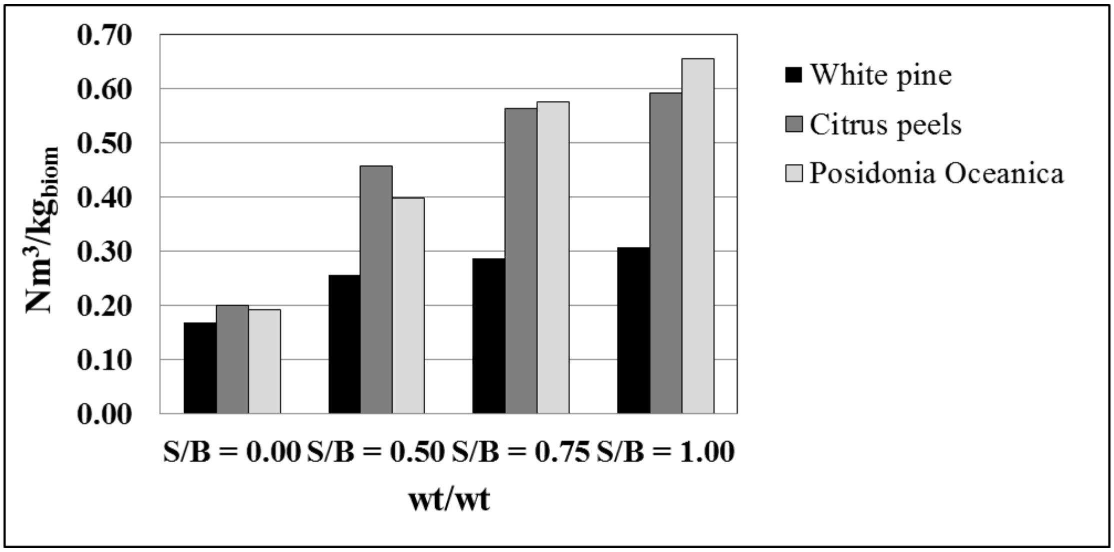

Figure 4: Hydrogen yield at different S/B ratios

From energetic point of view, Fig. 5 shows the variation of LHV of the gasification outlet stream gas with S/B ratio. In particular, significant difference among biomasses behaviors can be observed: Citrus peels increased the LHV rate from 4.0 MJ/Nm^3 to 4.8 MJ/Nm^3 when the operative conditions were changed from air gasification to air-steam gasification (S/B=0.5). nevertheless, a further increase of steam in the reactant mixture (S/B=0.75) did not show an increase of LHV. In fact, a slight decreasing trend was recorded.

On the other side, both Posidonia Oceanica and White pine no significant difference highlighted by adding of steam in the gasification reactor, rather minor LHV declines were obtained working with S/B ratio ≥ 0.5 (mainly with White pine). These behaviors are consistent with the higher “quality” in terms mainly of methane and carbon monoxide of the Citrus peels outlet stream gas than Posidonia Oc. and White pine (see Table 2).

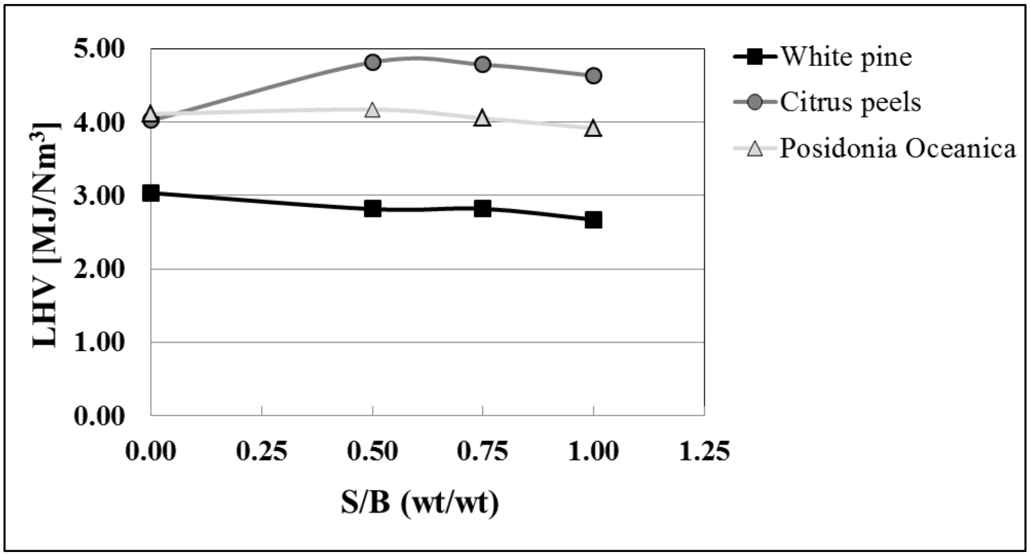

Figure 5: Syngas Low Heating Value (LHV) at different S/B ratios

Figs. 6 and 7 show the efficiency rates in terms both cold gas (CGE) and carbon conversion (CCE), respectively. In Fig. 6, is depicted that a sensibly positive changing in terms of CGE can be produced through use of air-steam as gasying agent mainly for Citrus peels gasification, that reached an efficiency of 68% at S/B=0.75; however at higher S/B ratio (0.75<S/B<1) the CGE value remained practically constant. In the same way, Posidonia Oceanica showed a slight increase of the CGE in the range 0<S/B<0.75 from 47% to 52%. Otherwise, no evident changing trend was found for White pine, that showed a CGE rate of 34% under air gasification condition and a rate of about 32% in the S/B ratio range 0.5-1.

The biomasses behaviors showed in Fig. 6 are in according to results reported in Fig. 7, where experimental results were elaborated to obtain the carbon conversion efficiency (see eq. 8). Results confirmed data obtained in terms of CGE, or rather that Citrus peels reaches the highest efficiency (CCE=98.4% at S/B=0.5) rate under air-steam gasification conditions than other biomasses. While independently by S/B ratio the white pine gasification performances resulted limited with a CCE rate of about 60%.

Data reported in Figs. 6 and 7, suggest that during air-steam gasification probably an higher reactivity between steam and biomass is promoted than gasification exclusively with air. This means that gasifying agent significantly affects the quality of the product gas from the hydrogen content point of view.

In this context, Posidonia Oceanica showed the best performances increasing: i) syngas yield from 2.1 $Nm^3/kg_{biomass}$ at S/B=0 to 2.7 $Nm^3/kg_{biomass}$ at S/B=1 and ii) hydrogen yield from 0.2 $Nm^3/kg_{biomass}$ at S/B=0 to 0.66 $Nm^3/kg_{biomass}$ at S/B=1.

On the other side, Citrus peels resulted the most suitable biomass for thermal applications taking into account that its performances recorded the highest LHV (4.81 MJ/Nm^3), CGE (66%) and CCE (98.4%) rates under air-steam atmosphere (S/B≥0.5).

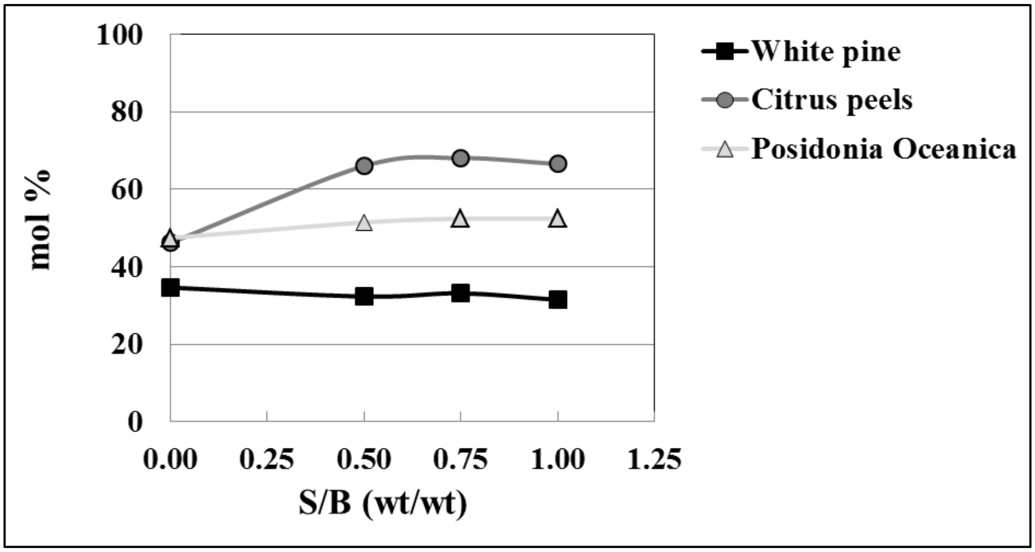

Figure 6: Cold Gas Efficiencies at different S/B ratios

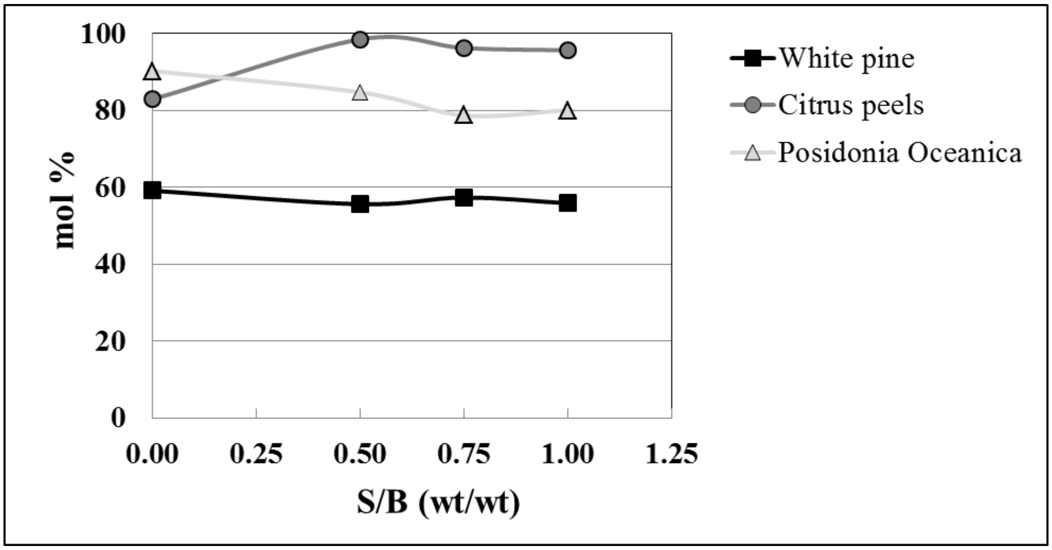

Figure 7: Carbon conversion at different S/B ratios

4. Conclusions

Thermo-chemical behaviors of waste feedstocks (Citrus peels and Posidonia Oceanica) as fuels for energy recovery through gasification in a BFB reactor were analyzed and compared with a traditional woody biomass (White pine). Hence, chemical-physical characterization showed that all biomasses have a relative high values in terms of carbon content (42.5-52.7 wt%) and HHV (16.6-18.3 MJ/kg) that make these suitable for biofuels production through thermochemical processes.

Thermal decomposition measurements in terms of mass loss (TGA) and rate of mass loss (DTG) of White pine, Citrus peels and Posidonia Oceanica under nitrogen and steam atmosphere were carried out. Therefore, by nitrogen TG/DTG analysis have led to the following “ease of decomposition scale”: Citrus peels > Posidonia oceanica > White pine, depending on biomass chemical nature was deduced. Where, Citrus peels showed the lower decomposition temperature range (453-473 K). However, further DTG analysis performed in steam atmosphere highlighted a more Posidonia oceanica bio-char reactivity due to an higher ash (14 wt%) content than other biomasses.

Experiments conducted by BFB reactor evidenced that during air-steam gasification probably an higher reactivity between steam and biomass is promoted than gasification exclusively with air. This means that gasifying agent significantly affects the quality of the product gas from the hydrogen content point of view. In particular, Posidonia Oceanica showed the best performances increasing: i) syngas yield from 2.1 $Nm^3/kg_{biomass}$ at S/B=0 to 2.7 $Nm^3/kg_{biomass}$ at S/B=1 and ii) hydrogen yield from 0.2 $Nm^3/kg_{biomass}$ at S/B=0 to 0.66 $Nm^3/kg_{biomass}$ at S/B=1. On the other side, Citrus peels resulted the most suitable biomass for thermal applications taking into account that its performances recorded the highest LHV (4.81 MJ/Nm^3), CGE (66%) and CCE (98.4%) rates under air-steam atmosphere ($S/B \geq 0.5$).

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