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Microwave-induced low temperature pyrolysis of macroalgae for unprecedented hydrogen-enriched syngas production

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Abstract

An efficient methodology based on low temperature microwave-induced pyrolysis has been developed for syngas production from macroalgae. The protocol provided an unprecedented hydrogen production, with switchable H_2/CO ratios depending on pyrolysis conditions which were found to remarkably improve conventional pyrolysis experiments even at significantly higher temperatures (400 vs 800ºC). Arcing effects under microwave irradiation as well as an interestingly observed *pseudo*-catalytic reforming effect of metal oxides contained in macroalgae seem to account for the improved results.

1. Introduction

Biomass research as alternative feedstock to fossil fuels is intensifying in recent years due to its important role in reducing CO_2 emissions and the promotion of environmentally acceptable practises. Many technologies are currently under investigation for biomass utilisation both for power generation, biofuels and chemical commodities production.[1]

Marine origin biomass (e.g. seaweed) has attracted considerable attention as a potential biofuel feedstock.[2] Seaweeds are important components in marine ecosystems providing essentially unique ecological functions.[3] Algae have a number of desirable features including fast growth, high biomass conversion rate, short growth cycle, ease of handling and reduced potentially-zero net CO_2 emissions.[4] The average photosynthetic efficiency of aquatic biomass (ca. 6–8%) is remarkably superior to that of terrestrial biomass (typically 1.8 - 2.2%).[5] Additional advantages for algal feedstocks also include the absence of competition with conventional agriculture for land, the possibility to utilize various unconventional water sources in their growth (e.g., seawater, brackish water and wastewater), a potential recycling of carbon dioxide as well as an interesting potential compatibility with integrated production of fuels and co-products within biorefineries. [6,7]

Seaweed production is mostly divided into two types across the globe: naturally and artificially/marine farmed produced species. Asian countries generally follow the molecular farming strategy to achieve different types of algal species while European countries obtain seaweed from natural or wild habitats. Importantly, seaweeds constitute a promising and already economically valuable resource, currently employed in a range of applications such as food additives, fodder, manure, medicine, industrial raw material and nutrient remover.[8,9]

Importantly, somewhat related types of algae species (e.g. algal blooms) originate as a consequence of euthrophication due to an increase of nutrient input, mainly nitrogen and phosphorus.[10] There are significant concerns around such algal blooms due to their potential production of toxins (e.g. microcystins) as secondary metabolites which can have significant effects in the growth and development of agricultural and biological environments.[11] The management of such algal blooms is in fact an important issue that has rarely been addressed in detail to date in a different way to disposal and/or landfilling.

In the perspective of exploiting macroalgae and particularly algal residues as biofuel feedstock, several studies have been conducted in order to convert marine biomass into biofuels via different processes including Anaerobic Digestion (AD) for biogas production,[4] bioethanol,[7, 9] and bio oil.[2] Interestingly, less attention has been devoted to thermochemical conversion of seaweeds into biofuels.[12] The different thermochemical options for macroalgae utilisation include direct combustion, gasification, pyrolysis and liquefaction. Ross *et al.* investigated thermal treatment of five macroalgae (*Fucus vesiculosus*, *Chorda filum*, *Laminaria digitata*, *Fucus serratus*, *Laminaria hyperborea*, and *Macrocystis pyrifera*) and their suitability for different thermal routes.[12] They concluded that ash content and chemistry itself restricted the use of macroalgae for direct combustion and gasification. Hydrous pyrolysis or digestion methods, more tolerant to the ash components in the fuel, were suggested as potentially appropriate for seaweed valorisation to fuels and chemicals. In a more recent study, Trinh *et al.* demonstrated that fast pyrolysis performed in a pyrolysis centrifugal reactor (PCR) at low temperatures (as compared to combustion and gasification) was not remarkably affected by slagging, fouling, and aerosol formation, problems essentially related to ash content.[13] Macroalgae pyrolysis (*Ulva lactuca* species) were eventually found to exhibit promising results in terms of bio-oil yield and energy recovery.[13]

Microwave mediated pyrolysis of seaweed has comparably been only recently tested on *Gracilaria gracilis*[14] and *Ulva prolifera*[15] aiming to maximise bio-oil yields, with no characterization performed on produced syngas. Most importantly, the oils obtained in algal pyrolysis are acidic, unstable, viscous, include chemically dissolved water and have high proportions of nitrogen compounds,[15, 16] a series of undesirable features which require additional bio-oil upgrading post-treatments. In the light of these premises, processes focused on gas generation from pyrolysis of algal biomass and residues could offer a promising alternative to direct biofuels production (e.g. syngas).

Microwave induced pyrolysis has shown an exceptional ability to maximise gas production in the pyrolysis of various feedstocks including sewage sludge, glycerol or coffee hulls, even at low temperatures.[17, 18] In addition, the outstanding quality of the gas produced in microwave induced pyrolysis (featuring high proportions of H_2 and syngas as compared to conventional pyrolysis) as well as the possibility to conduct the process at significantly reduced temperatures make this process even more attractive. Moreover, it has been recently reported a mechanistic study of the interaction between microwave irradiation and cellulose (one of the main components of *Gracilaria* cell wall) which explains, among other findings, different experimental observations such as high efficiency of microwave treatment.[19]

Herein, we report an unprecedented production of hydrogen-enriched syngas with tuneable H_2/CO ratios from *Gracilaria gracilis,* a macroalgae grown in the Lessina lake in Italy to remove the previously mentioned eutrophication problem. Syngas production could be simply achievable from *Gracilaria* via low temperature microwave induced pyrolysis (MIP). Gas production and composition using the MIP methodology was compared to those obtained under conventional thermal pyrolysis (CP). To the best of our knowledge, this is the first example of a comparison between microwaves and conventional heating for algal pyrolysis focusing on syngas production as well as the first technology able to provide a sustainable direct solution to the valorisation of algal blooms different from photocatalytic degradation or removal of cyanotoxins generated by such algae.[20]

2. Materials and Methods

2.1 Gracilaria sampling

The red seaweed *Gracilaria gracilis* was collected from the western area of the Lesina lagoon, where a stable assemblage of this seaweed grown to remove the significant eutrophication issue of the lake was found (41.866470° N, 15.363350° E). About 1 Kg of wet biomass was sampled in July 2011. Algal biomass was washed with distilled water and their epiphytes removed. The fresh seaweed was placed in a freezer (-20°C) immediately after collection. The cleaned seaweed was freeze-dried at -110°C to preserve the algae for future analysis and then ground to fine powder and stored in airtight containers at -20°C. The biochemical composition of macroalgae is summarised in Table 1.

Table 1. Biochemical composition (% d.w.) of *Gracilaria gracilis* sampled in the Lesina lagoon (Italy).

Total Lipids	1.98
Fatty Acids Methyl Esters	0.47
Proteins	30.93
Carbohydrates	27.54
Ashes	27.89

Figure 1. Mechanical harvesting process of *Gracilaria gracilis* in the Lesina lagoon (Italy).

2.2. Experimental procedure

Seaweed pyrolysis was conducted in two different heating devices: a conventional electrical furnace for CP and a single mode microwave oven for MIP. The microwave oven uses a magnetron of a maximum power of 2 kW to generate the microwave radiation. Three different pyrolysis temperatures (400, 600 and 800 ºC) were screened in both CP and MIP (Table 2).

Experiments were performed as follows: 4 g of macroalgae sample were introduced into a quartz reactor and degassed under a helium flow (100 mL STP min^{-1}) for about 30 minutes, when flow rate was reduced to 20mL STP min^{-1} in order to perform the pyrolysis experiments. In the case of MIP, a mass of ca. 1.2 g of microwave absorber was also added to the feedstock prior to commencing the pyrolysis. Biomass is in fact a poor microwave absorber.[18] Moreover, a blank experiment without any microwave absorber was performed, finding that the macroalgae were not heated to more than 120ºC by microwave irradiation. Therefore, a material able to absorb the initial microwave radiation in order to reach the temperature required to perform the pyrolysis experiments was added. The char obtained in the process of algae CP (pyrolysis temperature: 800 ºC) was originally added as microwave captor in MIP to avoid the use of a material with very different properties to those of algae. Initially, microwaves start to pass through the sample and absorbed by the captor, increasing its temperature. This allows the heat to be conducted to the macroalgae until a high enough temperature is reached to start the pyrolysis. As the pyrolysis proceeds, the waste is carbonized and is then able to absorb microwaves, so that from that point on it can be directly heated by microwave radiation. A 30 wt% of microwave absorber captor (mw captor/biomass sample: 30/70, 1.2 g) was selected as optimum for MIP experiments based on experimental data and previous experience of the group. Quantities of microwave absorber lower than 30 wt% were unable to provide reproducible results due to issues related to homogeneous heating in microwave-assisted pyrolysis experiments (see ESI for full details). Additionally, powdered graphite was used as mw absorber in a comparative experiment under otherwise identical conditions to those detailed before.

The insertion of the quartz reactor with the sample was different depending on the heating device used. In the case of CP, the pyrolysis temperature is firstly set and the reactor with the seaweed is placed inside the furnace once the furnace starts to heat to the desired temperature (monitored by means of a type K thermocouple). Comparatively, the reactor was placed in the centre of the microwave guide prior to starting microwave radiation in MIP as in this case the needed time to reach the pyrolysis temperature is very short (about 2-5 minutes). Unlike electric furnaces, there are limitations when a thermocouple type K is used in microwave devices.[21] Therefore, the temperature is monitored by an infrared optimal pyrometer for microwave-induced pyrolysis (MIP).

Macroalgae pyrolysis results in three different fractions: solid, liquid and gas. The liquid fraction is recovered from a condensation system cooled down with a cryogenic solution formed by a mixture of water and sodium chloride. The residue content in the condensation system is dissolved in dichloromethane and the liquid fraction is obtained upon evaporation of the solvent at 40 ºC. The composition of the oil fraction has not been analysed in this work. The non-condensable gases are collected in Tedlar® bags (at 10 minutes intervals) with a propylene fitting for sampling and subsequently analysed in a Varian CP-3800 gas chromatograph. In order to determine pyrolysis yields, the solid and bio-oil fraction yields were calculated from the weight of each fraction whereas the gas fraction was determined by difference. The composition of the gaseous fraction was determined from the composition of each Tedlar® bag and the He flowrate (which is constant throughout the experiment at the inlet and the outlet of the reactor because He cannot be produced or consumed in the pyrolysis process). With this composition and the weight of gas, the total gas production can be calculated._In the case of the solid fraction, the microwave receptor mass was not accounted for the yield calculation. The total time required to complete the pyrolysis experiments was selected according to the outlet flow rate of the pyrolysis gases. The pyrolysis is finished when the flow rate of the pyrolysis gases was less than the 3 % of the helium flow (0.6 mL STP min^{-1}).

Table 2. Summary of pyrolysis experimental conditions tested in this work.

Reference	Heating device	Temperature (ºC)	MW absorber
400CP	Electric furnace	400	None
400MIP	Microwave oven	400	Pyrolysis residue 70:30 wt.%
400MIP-G	Microwave oven	400	Graphite 70:30 wt.%
400MIP-50C	Microwave oven	400	Pyrolysis residue 50:50 wt.%
600MIP	Microwave oven	600	Pyrolysis residue 70:30 wt.%
800CP	Electric furnace	800	None
800MIP	Microwave oven	800	Pyrolysis residue 70:30 wt.%

3. Results and Discussion

The present work was aimed to maximise syngas and particularly hydrogen production as compared to bio-oil from the microwave-induced low temperature pyrolysis of macroalgae residues. Figure 2 shows the yields (expressed in mass percentage) of the different fractions obtained in the pyrolysis experiments. MIP maximises the gaseous fraction, both at high and low temperatures, with a maximum gas production of 63-65%. The solid fraction was comparatively maximised at low temperatures in CP experiments (35-48%), while larger quantities of bio-oil were obtained at high pyrolysis temperatures. In contrast, larger quantities of both liquid and solid phases were produced under CP.

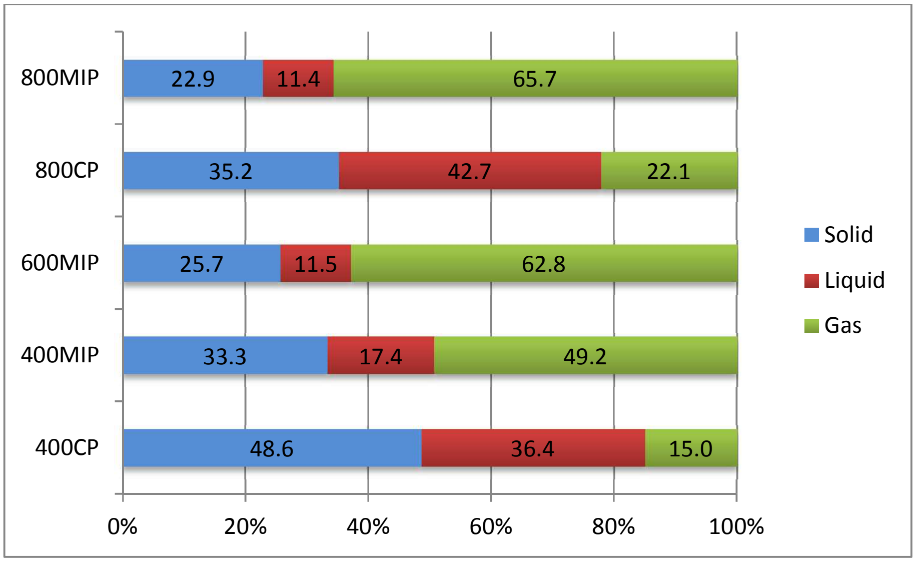

Figure 2. Yields of the different fractions obtained in the pyrolysis of macroalgae

Figure 3 depicts the cumulative gas production in the various conducted experiments. Remarkable differences were observed between CP and MIP, being interestingly more significant at low temperatures. MIP produces ca. 8 times more gaseous products as compared to CP at 400ºC; Figure 3, solid vs discontinuous lines). Increasing pyrolysis temperature to 600ºC or 800ºC reduces such differences (e.g. gas production is 4 times higher under MIP at 800ºC, Figure 3). Experiments also pointed out that there is no need to extend the pyrolysis process for a long time as gaseous production normally levels off at relatively short times of reaction (only low amounts of gas- <5% extra- are produced at extended pyrolysis times, Figure 3). Optimum pyrolysis times range from 35-50 min under CP to ca. 70 min for microwave-assisted pyrolysis (see Figure 1S and Table 1S in ESI for full details). This could be seen as contradictory, since microwave heating is known to accelerate chemical processes[17] while requiring longer times in this case. The explanation is that microwave heating increases reactions rates, but this does not precisely leads to shorter reaction times. As can be seen in Figure 3, reactions are quicker in the case of MIP since gas production is faster. For example, the use of CP to achieve 0.24 L/g at 800ºC can take more than 50 minutes, whereas it takes just around 10 minutes under MIP conditions. However, there is a higher amount of volatiles produced under MIP and thus involved in the process (as can be seen from the yields data shown in the Fig 2). In spite of having improved reaction rates, the whole reaction time needed to treat all these volatiles increases. The carbonization of the material surely finishes more rapidly under MIP as compared to CP. Comparatively, the whole pyrolysis process including tar cracking and gas phase reactions needs larger processing times under microwave iradiation. The observed differences between CP and MIP were also reflected in the gas composition as clearly visible in Tables 3 and 4.

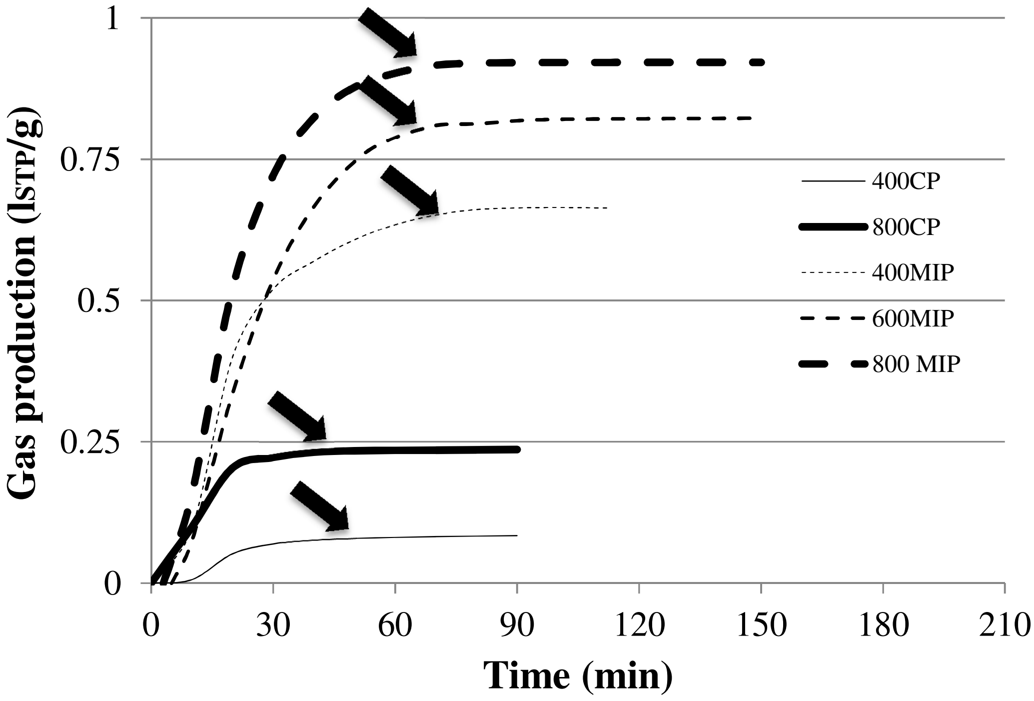

Figure 3. Cumulative gas production in the pyrolysis experiments at 400ºC and 800ºC degrees in conventional pyrolysis (400CP, 800CP) and at 400ºC, 600ºC and 800ºC in the microwave oven (400MIP, 600MIP, 800MIP). The arrows indicate the point at which the pyrolysis can be considered to be finished.

Table 3 summarises compositions of the gaseous fraction of the different pyrolysis experiments (see Figure 2S in the ESI). Results demonstrate that the percentage of syngas (H_2 + CO) generated under MIP also is remarkably larger with respect to conventional (only CO was produced). Importantly, an interesting H_2/CO ratio (3.01) was obtained at low MIP temperature (400ºC), with H_2/CO ratios of ca. 1-1.2 at increased temperatures (Table 3). Furthermore, an additional advantage of MIP relates to the superior hydrogen production as compared to CP, particularly at low pyrolysis temperatures (Table 3, 400 MIP vs 400 CP).

Table 3. Gas compositions (vol.%) of the gaseous fractions obtained in macroalgae pyrolysis

	400CP	400MIP	600MIP	800CP	800MIP
H_2	-	57	48	33	49
CH_4	4	2	2	11	1
CO_2	78	22	9	18	6
C_2H_4	1	1	0	1	1
C_2H_6	2	0	0	1	0
CO	15	19	41	36	43
Syngas (H_2+CO)	15*	76	89	69	92
H_2/CO	0	3.0	1.2	0.9	1.1

*only CO was produced

Hydrogen and syngas production from macroalgal waste obtained under MIP conditions (Table 4) are unprecedently large as compared to any CP or MIP reports, particularly at 400ºC, but generally regardless of the pyrolysis temperature. To support this statement, a careful and comprehensive literature search was conducted to further compare results with literature results. Table 5 summarises H_2 and syngas productions obtained in microwave-induced pyrolysis of a series of different feedstocks that can be found in the literature. As clearly evidenced from this table, results reported here are remarkably superior to most previously reported cases and only marginally comparable in the cases of rice straw (forcing conditions) and high temperature MIP of glycerol. Even the reported syngas production at 400ºC under the investigated conditions was significantly larger as compared to many of the literature examples.

Table 4. Gas production (l_{STP}/g of algae) of the different components of the gaseous fractions obtained in macroalgae pyrolysis

	400CP	400MIP	600MIP	800CP	800MIP
H_2	0.00	0.38	0.39	0.08	0.45
CH_4	0.00	0.01	0.01	0.03	0.01
CO_2	0.07	0.15	0.08	0.04	0.05
C_2H_4	0.00	0.01	0.00	0.00	0.01
C_2H_6	0.00	0.00	0.00	0.00	0.00
CO	0.01	0.13	0.34	0.08	0.40
Syngas	0.01	0.51	0.73	0.16	0.85

Importantly, MIP results at low temperatures (400ºC) clearly predate those obtained at high temperature conventional pyrolysis (800ºC) in terms of both H_2 proportion and production (Table 3, 400MIP vs 800CP), which illustrates the potential of MIP. In any case, a larger gas quantity was obviously produced at increasing temperatures.

Table 5. Comparison of H_2 and syngas production (l_{STP}/g of pyrolysed material) as well as H_2 proportion (vol.%) obtained in literature reports for MIP of different feedstocks.

Feedstock	Temperature (ºC)	Syngas production	H_2 production	H_2 proportion	H_2/CO ratio	Ref.
Macroalgae	400	0.51	0.38	57-19	3.0	this work
Sewage Sludge	600-1200	0.21-0.53	0.07-0.34	22-50	0.9-2.6	17,25,26,27,28
Coffe Hulls	500-1000	0.40-0.61	0.24-0.34	36-40	1.2-1.7	17,25,29
Waste Tires	350-600	0.14-0.16 [(a)]	-	-	-	30
Rice straw	400-550	0.19-0.53	0.06-0.40	18-55	0.5-4.2	31
Glycerol	800	0.88-0.90	0.36-0.40	33-35	0.7-0.8	18,25
Pine sawdust	400-800	-	-	17-30	0.4-1.6	32
Corn-Wheat stalk	600-700	0.25-0.27	0.13-0.17	35-37	1.8-2.1	33
Microalgae	400-1250	0.09-0.74	0.06-0.40	22-50	1.1-2.3	34
Macroalgae	130	0.32 [(a)]	-	-	-	14
Douglas fir sawdust	330	0.07-0.15	-	-	-	35
Automotive engine oil	400-800	0.02-0.14	0.01-0.07	12-18	1.1-1.2	36

[(a)] Total gas production including syngas

Figure 4 shows a comparison in gas evolution during CP and MIP at 800 ºC. An important production of CH_4 and CO_2 is generated under CP, which is dramatically reduced under MIP. These findings indicate that CH_4 decomposition and gasification of the carbonaceous matter by CO_2 are important factors that give rise to an increase in H_2 and CO produced under MIP conditions. However, there is still an important production of H_2 and CO after CH_4 and CO have completely disappeared under CP. Therefore, additional sources for these gases are present in the systems (i.e. tars) which can keep cracking for a longer time to explain such behaviour.

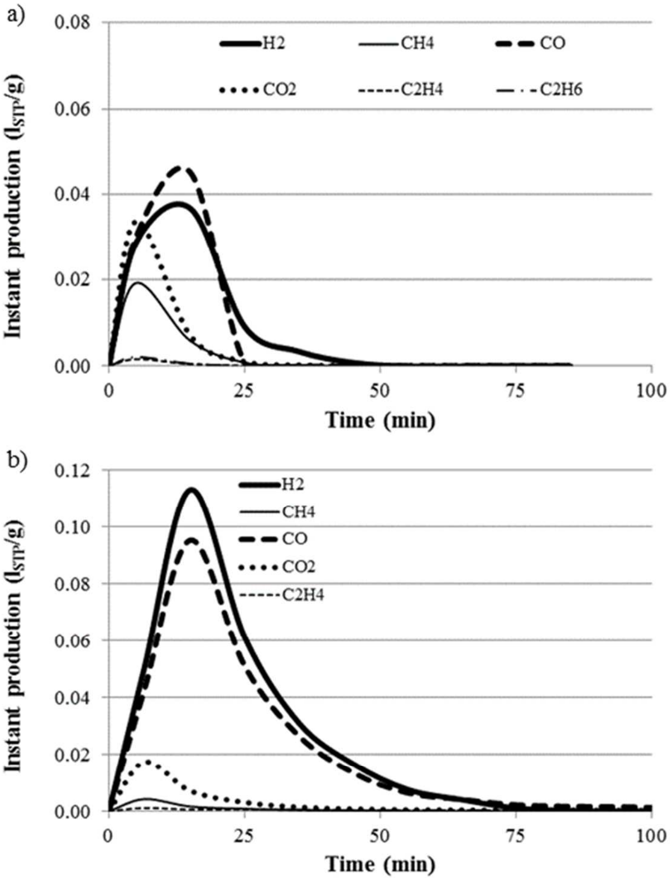

Figure 4. Evolution of the different gaseous species in the: a) CP; and b) MIP at 800 ºC.

However, the most important feature of the proposed methodology relates to its high versatility and applicability to fine tune syngas composition (H_2/CO ratio) for various types of chemistries depending on needs and demands (e.g. Fischer-Tropsch, methanol and/or oxygenates production and even as feed for bacterial fermentation)[22] Such versatility is comparably difficult to achieve under CP conditions.

Reasons behind the reported unprecedented hydrogen evolution in MIP systems are believed to be related to two different contributions. Firstly, a *pseudo*-catalytic effect is likely to be present due to plasma and arcing phenomena observed in the course of the experiments under microwave irradiation. These effects, which do not take place at processing temperatures under CP conditions, have been previously reported in related pyrolysis chemistries as well as in metal-microwave interactions.[23, 24] These plasmas appear during microwave heating and create hot spots. In these points temperature can achieve values considerable higher than the means temperature of the bed. It resembles what happens during a lightning storm, where the temperature of the rays can achieve several thousands of Celsius degrees without affecting the mean temperature of the atmosphere. As a consequence, the molecules that cross these plasmas or electric arcs are ionized, giving rise to a completely different chemistry. For these reason, processes that are not thermodynamically favored, can take place when the microwave heating is used.

Nevertheless, an additional catalytic effect of the microwave absorber (pyrolysis residue) in MIP experiments cannot be ruled out as metals contained in such material could be not only responsible of the observed arcing and plasmas but also of related reforming reactions of the gaseous mixture. An experiment using pure graphite powder as microwave captor (in comparison to the pyrolysis biochar) was consequently designed in order to address this potential catalytic effect (see Figure 3S).

Data summarised in Table 6 clearly demonstrated that larger syngas volumes (ca. 76%) were produced in the biochar experiment as compared to 60% syngas using graphite powder as microwave captor (in which more CO_2 was observed, see also ESI). Different amounts of microwave absorber were also investigated to further ascertain any catalytic effects in the systems. The increase in quantity of microwave captor (from 30 wt.% to 50 wt.%) caused no significant variation in syngas yield (from 0.51 ln.c./g of algae to 0.48 ln.c./g, see ESI).

Table 6. Gas composition of MIP experiments conducted at 400ºC using different microwave captors and proportions.[a]

	400MIP	400MIP-G	400MIP-50
H_2	57	50	58
CH_4	2	5	2
CO_2	22	34	25
C_2H_4	1	1	0
C_2H_6	0	1	0
CO	19	10	16
Syngas (H_2+CO)	76	60	74
H_2/CO	3.0	4.8	3.7

[a] 400MIP: 30 wt% biochar as mw captor; 400MIP-G: 30 wt% commercial graphite as mw captor; 400MIP-50: 50 wt% biochar as mw captor.

These findings therefore support a contribution of *in-situ* catalytic reforming of the produced gaseous products using biochar pyrolysis residues (as microwave receptor) under MIP. Elemental analysis of such MIP macroalgae derived biochar (Table 7) further confirmed the presence of important concentrations of certain transition metals including Al, Fe and Mn (see also Table 2S in ESI for full details). These metals can certainly promote reforming and cracking reactions during pyrolysis. Important amounts of some alkali metals and alkali earths (K, Na, Mg) can also promote the water gas shift reaction. However, the low content of such metals (except for K) under the operating temperatures can be expected to have a relatively low influence in this reaction.

Table 7. Elemental analysis of the biochar residue after CP at 800ºC of *Gracilaria gracilis*

Metal	Concentration (wt.%)
Al	0.30
Si	1.49
Mn	0.15
Fe	0.21
Na	2
Mg	0.5
K	12

XRD patterns of the residue also confirmed a relatively high crystallinity of the residue in which a combination of mixed metal oxide species of Mn, Si and Al were found to be present (Figure 5). This biochar was also found to be porous when the pyrolysis process is carried out using microwave heating. The surface areas are in the range of 40 to 110 m^2 g^{-1} depending on the MIP temperature and essentially microporous in nature (see also Table 3S in ESI for full details). In this sense, microwave heating also favours the development of the porous structure of the char, when it is compared with the conventional heating. In the case of conventional heating, no porous development take place at 400ºC whereas extremely low BET surface was found at 800ºC. This improvement in the porosity development should be also due to the *pseudo*-catalytic effect of the microplasmas. Further in-depth investigations are currently ongoing to ascertain the crystalline phases present in the biochar and potential applications of this material in catalytic processes (e.g. oxidation, reforming, etc.) that will be reported in due course.

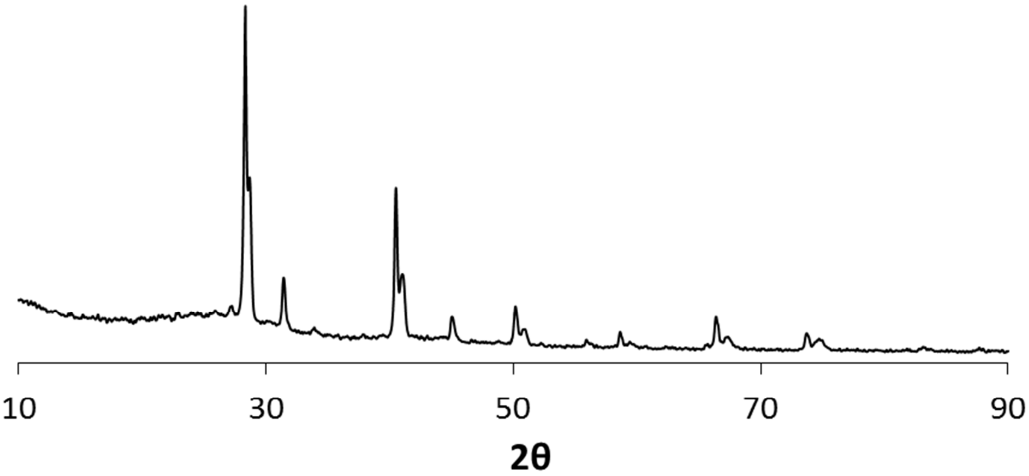

Figure 5. XRD pattern of the CP residue at 800ºC used as microwave absorber

Conclusions

We have reported for the first time an innovative alternative low temperature microwave induced pyrolysis from an algal residue able to provide high syngas yields with remarkably improved hydrogen content and tunable H_2/CO ratios from 3 to 1 depending on the investigated conditions. The use of the pyrolysis biochar residue (after CP) as microwave absorber was found to exert and unprecedented (*pseudo*)-catalytic effect able to provide an optimum hydrogen production with respect to a pure graphite material employed as comparison. The proposed methodology clearly highlights the potential of MIP as compared to CP in terms of flexibility, versatility, applicability and the possibility to work at significantly lower pyrolysis temperatures with improved performance. Further studies are currently ongoing to investigate the possibility to provide an additional versatility to the protocol by macroalgae sampling in different seasons with the aim to also demonstrate the remarkable potential of algae-derived residues as a resource for the production of high added-value compounds.

Acknowledgments

Financial support from the European Union Seventh Framework Programme (FP7/2007-2013) under agreement nº 311815 is acknowledged. JMB acknowledges the support received from the CSIC JAE Program. EGC also acknowledges a predoctoral research Grant from FICYT. RL gratefully acknowledges Ministerio de Ciencia e Innovación, Gobierno de España for the concession of a Ramon y Cajal contract (ref. RYC-2009-04199) and funding under project CTQ2011-28954-C02-02 as well as Consejeria de Ciencia e Innovación, Junta de Andalucía for funding under project P10-FQM-6711. Matteo Francavilla gratefully acknowledges the European Commission, Directorate-General for Research & Innovation, for funding the project "STAR*AgroEnergy" (FP7 Regpot 2011-1, Grant Agreement N° 286269).

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