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Article

A new step forward non-seasonal 5G bio-refineries: Microwave-assisted, synergistic, co-depolymerisation of Wheat Straw (2G biomass) and Laminaria Saccharina (3G biomass)

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8 Microwave-assisted, synergistic, co-
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12 depolymerisation of Wheat Straw (2G biomass) and
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16 Laminaria Saccharina (3G biomass)
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45 **KEYWORDS:** Bio-refinery, biomass, synergetic co-valorisation, value-added chemicals,
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47 autocatalysis, microwave heating.
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51 **ABSTRACT:** This investigation explores the microwave-assisted, synergistic co-
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53 depolymerisation of wheat straw (2G biomass) and Laminaria Saccharina (3G biomass) as a novel
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55 strategy for the production of sugar-rich aqueous carriers. The effects of the feedstock (each
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3 material alone and all the possible binary mixtures) were carefully analysed over a wide range of
4 reaction temperatures and times. The optimisation of the process revealed that 19 wt.% of wheat
5 straw and 46 wt.% of *Laminaria Saccharina* could individually be converted into an aqueous, high
6 purity (85-95 C-wt.%), sugar solution at 190 °C using a reaction time of 18 and 35 min,
7 respectively. The reactivity of wheat straw can be synergistically increased by co-feeding this
8 material a relative amount of seaweed varying between 36 and 57 wt.% with respect to the total
9 biomass content, at 215°C for 40 min. This allowed the transformation of 30 wt.% of the feedstock
10 mixture into a sugar-rich (90 C-wt.%) aqueous solution. The higher reactivity of seaweed than that
11 of wheat straw, as well as the synergistic effects that the former exerted on the depolymerisation
12 of the latter, were accounted for by the formation of ‘a pool of active catalytic species’. The
13 mechanism involved an ‘in-situ’ metal-biomass, microwave-promoted catalysis with marginal
14 mass transfer limitations; followed by metal leaching, leading to a greater spread of the reactions
15 occurring in the liquid phase. This resulted in the formation of new ‘in-situ catalytic species’, i.e.
16 carboxylic acids, which acted as homogeneous catalysts and ended up being transformed to gases
17 so that they did not affect sugar purity. Therefore, this novel co-valorisation strategy might
18 represent a step-change for the development of novel ‘non-seasonal, non-feedstock dependent’ 5G
19 bio-refineries and can help to render the entire bio-refinery for 2G and 3G biomasses more
20 logistically efficient and economically competitive.
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46 INTRODUCTION

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48 The development of advanced bio-refinery processes and novel strategies for the valorisation of
49 biomass into platform chemicals, value-added products and/or energy carriers is critical to
50 progressively diminish human dependence on crude oil. In this line, biomass is regarded as an
51 excellent feedstock for the production of these commodities. This is the result of biomass being
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3 the only renewable source of carbon that can be converted into gas, liquid and solid products ¹.
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5 Therefore, this emerging bio-refinery philosophy focused around the valorisation of biomass
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7 wastes and residues is directly linked to the context of circular economy and connects very well
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9 with the United Nations Sustainable Development Goals (UN SDGs), as societies currently strive
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11 towards a greener and more sustainable future ².
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15 One of the most promising routes for biomass valorisation is the exploitation of its carbohydrate
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17 content for the production of aqueous sugar-rich carriers ³⁻⁵. This approach allows the
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19 transformation of biomass into a liquid solution, containing soluble oligosaccharides and
20
21 saccharides, that can be used as a feedstock in many subsequent processes. The applications
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23 include the production of fuels, advanced materials and chemicals ⁶, while the procedures range
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25 from biological to thermochemical routes such as fermentation, hydrogenation, hydrolytic
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27 hydrogenation and aqueous phase/gas phase reforming ⁷. Among the different processes to produce
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29 saccharide-rich solutions from biomass, microwave-assisted hydrothermal depolymerisation is an
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31 up-and-coming alternative ⁸⁻¹⁰. This route allows the selective and precise depolymerisation of
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33 biomass into soluble, low molecular weight oligosaccharides and saccharides, substantially
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35 avoiding the subsequent degradation of these species into low value or unwanted products ¹¹. This
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37 is accounted for by microwave-assisted depolymerisation being an outstanding technology to
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39 strike an excellent compromise between a first biomass selective depolymerisation and the
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41 subsequent degradation of the saccharides produced. In particular, microwave heating is decidedly
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43 advantageous if used appropriately. The excellent controllability of microwave heating, combined
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45 with water, an excellent microwave absorber, at hydrothermal conditions, permit that sugar
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47 degradation does take place to a lesser extent than when acid- or alkali-hydrolysis are used ¹²⁻¹⁵,
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49 but also this process is much faster than other routes such as acid or enzymatic treatments ^{12, 16}.
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3 Another essential advantage of this microwave-assisted treatment is the conservation of the
4 biomass core carbohydrate structure in the form of water-soluble oligosaccharides ^{2, 17}. This
5 represents a conservative and smart strategy to help increase the reactivity of biomass (as the
6 entropy of the feedstock is substantially increased when being converted from a solid to a liquid
7 state) without significantly altering its chemical nature, and therefore, this step does not
8 substantially hamper its future applications. Moreover, it also facilitates the use of recoverable
9 solid catalysts in subsequent valorisation processes, thus avoiding mass transfer limitations
10 occurring when solid catalysts are used for the upgrading of solid biomass ^{18, 19}. Also, microwave-
11 assisted hydrothermal depolymerisation is extremely adaptable and can be applied efficiently for
12 the pre-treatment and/or upgrading of different biomasses, including both second (2G) and third
13 (3G) biomass generations ¹²⁻¹⁵. 2G biomass primarily comprises non-edible lignocellulosic
14 materials and wastes, which structurally consist of cellulose, hemicellulose and lignin ²⁰. 3G
15 biomass involves micro- and macroalgal matter, which is mostly made up of active compounds
16 (proteins, nucleic acids and lipids) and carbohydrates such as cellulose, hemicellulose and alginic
17 acid, among others ^{21, 22}.

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38 Despite these outstanding features, the vast majority of works addressing the use of microwave-
39 assisted processes for biomass valorisation are very ‘feedstock-dependant’, as are most of the bio-
40 refinery models/concepts reported to date which use convectional heating ²³. These models are
41 based mainly on a concatenation of operating units and/or catalytic processes for the
42 transformation of a few types of biomass into different commodities. This feedstock limitation is
43 one of the main challenges that future bio-refineries might have to face due to the greater diversity
44 of biomass in comparison to petroleum. Future bio-refineries might also have to adapt to the
45 seasonal nature of biomass, as it is difficult to collect a sufficient amount of one type of biomass
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3 for the development of an economically feasible bio-refinery unit. Therefore, for the development
4 of new and more efficient and flexible processes, it is necessary a transition from this reductionist
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8 ‘one feedstock strategy’ to a holistic, deep and more integrated concept to treat different types of
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10 biomass in the same processing unit. For these new concepts, not only is it essential to consider
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12 the most suitable combination of processing units and/or catalyst types but also it is essential to
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14 smartly combine the feedstocks to gain the most of potential and exciting synergistic effects
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17 between materials.

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19 This co-valorisation strategy has recently emerged and been tested in biomass hydrothermal
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21 liquefaction ²⁴, pyrolysis ^{25, 26} and sub/supercritical treatments ²⁷ using conventional heating.
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23 Among the different possible biomass combinations, the co-valorisation of lignocellulosic biomass
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25 (2G) and (micro/macro) algae (3G) biomass might be a fascinating approach for the development
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27 of non-seasonal, synergistic, new bio-refineries; i.e. ‘5G bio-refineries’. This idea has been only
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29 proved during the hydrothermal liquefaction of biomass using conventional heating. In particular,
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31 Gai et al. ²⁸ addressed the co-valorisation of rice husk with *Chlorella Pyrenoidosa*, analysing the
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33 effects of the temperature (200-350 °C), reaction time (10-90 min), solid loading (10-30 wt.%) and
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35 feedstock composition (0-100 *Chlorella Pyrenoidosa*/rice husk wt.%). They reported that
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37 increasing the algae content resulted in an increase in the bio-oil yield and a decrease in the solid
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39 yield. The reductions occurring in the ash and lignin contents of the feedstock when increasing the
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41 proportion of *Chlorella Pyrenoidosa* in the mixture were responsible for such variations. Chen et
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43 al. ²⁹ co-liquefied swine manure and microalgae in different ratios at 300 °C for 60 min. They
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45 found that the more significant the proportion of swine manure in the mixture, the higher was the
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47 bio-oil yield. Brilman et al. ³⁰ studied the co-valorisation of sugar belt pulp (micro-algae) with
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49 pinewood at a temperature ranging from 250 to 350 °C. They suggested that the presence of
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3 microalgae degradation intermediate products, such as organic acids, enhanced the decomposition
4 of pinewood. Feng et al.³¹ carried out the co-liquefaction of *Spartina alterniflora* (lignocellulosic)
5 and *Spirulina* (lipid-rich microalgae) using temperatures between 260 and 320 °C for 30 min. A
6 synergetic effect was observed when both feedstocks were mixed at 1:1 weight ratio, which
7 resulted in a significant increase in the bio-oil yield. Sintamarean et al.³² co-liquefied willow wood
8 with brown, red and green seaweeds. Several synergistic effects were observed. These were
9 accounted for by the presence of organic acids produced during the co-liquefaction, which
10 increased the bio-oil yield and improved its physicochemical properties.
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22 These publications provide valuable insights into the synergistic hydrothermal co-valorisation
23 of 2G and 3G biomasses using conventional heating. However, to the best of the author's
24 knowledge, microwave-assisted hydrothermal co-depolymerisation of biomass has not been yet
25 reported. Microwave heating is based on the high-frequency rotation of polar molecules, which
26 produces quicker and higher heat of the species with high polarity³³⁻⁴⁰. Carbohydrates, including
27 both cellulose and hemicellulose, are much polar than lignin. As a consequence, they are more
28 likely to interact with microwaves, which favours the solubilisation of the carbohydrate matter
29 without substantially dissolving the lignin fraction^{41,42}. Nevertheless, it is also important to note
30 that the elevated crystallinity of cellulose in combination with the strong hydrogen bonds within
31 its structure hamper the depolymerisation of this carbohydrate^{43,44}. A possible solution already
32 adopted to overcome this issue was the addition of a homogeneous catalyst such as acetic acid,
33 which allowed the solubilisation of the cellulose and hemicellulose in lignocellulosic biomass
34 without dissolving its lignin content⁴¹.
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51 Taking these features into account, new bio-refinery models should be directed towards
52 autocatalytic and more efficient processes, i.e., taking advantages of possible catalytic synergies
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3 between materials. For example, algae biomass contains a substantial amount of metals, these
4 being excellent absorbers of microwave radiation ⁴⁵. This higher metal content might result in
5 greater reactivity of algae biomass than lignocellulosic biomass when subjected to microwave
6 heating. This could be smartly used to increase the reactivity of 2G biomass and develop new bio-
7 refinery models. Besides, metals may be leached to the reaction medium during the hydrothermal
8 treatment ⁴⁶ and/or interact with lignocellulosic biomass if the stirring is appropriate. Therefore,
9 these features can contribute to increasing the reactivity of 2G biomass if both feedstocks are
10 treated in the same unit. Moreover, the higher reactivity of 3G biomass in comparison with 2G
11 biomass also results in a greater spread of hydrolysis reactions of the former than the latter
12 biomass, thus leading to the formation of carboxylic acids from 3G biomass, which might act as
13 ‘in-situ produced catalytic species’ to increase the reactivity of lignocellulosic 2G biomass ³². As
14 such, these intrinsic peculiarities of microwave heating together with the different behaviours of
15 2G and 3G biomasses under microwave radiation might potentiate synergetic effects between both
16 materials, thus opening the door for the development of advanced and more efficient processes
17 that take advantages of these features.

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19 Given all the above, this work addresses the microwave-assisted, synergistic co-
20 depolymerisation of wheat straw (2G, lignocellulosic biomass) and *Laminaria Saccharina* (algae,
21 3G biomass) for the production of sugar-rich aqueous carriers. The experiments were planned
22 following a statistical design to carefully analyse the effects (additive, negative, synergistic and/or
23 antagonistic) of the feedstock composition (2G biomass, 3G biomass and all the possible binary
24 mixtures) at different reaction temperatures (80-250°C) and times (0-60 min). These include the
25 influence of these variables on the overall distribution of the reaction products (gas, liquid and
26 solid) and their key properties, such as the detailed chemical composition, pH and conductivity of
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3 the liquid product (hydrolysate) together with the elemental composition and calorific value of the
4 solid product. The fact that the co-valorisation of 2G and 3G biomass using microwave-assisted
5 hydrothermal conditions has never previously been reported, together with the results provided in
6 the in-depth study addressing the synergetic effects between materials, demonstrates that this work
7 represents a new investigation in this field and substantially contributes to the development of non-
8 seasonal 5G bio-refineries.
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19 **EXPERIMENTAL**

20 **Microwave experiments**

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22 The experiments were conducted in a Milestone Synth-Wave microwave unit previously
23 described in detail ^{18, 19, 47}. Briefly, it comprises a 1L stainless steel reactor cooled with water
24 capable of achieving high temperatures and pressures, in which microwave radiation is generated
25 by a magnetron directly connected to the bottom of the reactor. The microwave power to achieve
26 the desired temperature is controlled by a PID control with the aid of a thermowell placed inside
27 the reactor. The pressure is monitored with a pressure sensor connected to a pressure gauge. For
28 the experiments, firstly, 20 g of solid (either the individual feedstock or the binary mixtures)
29 together with 400 mL of deionised water were placed into the reactor to achieve a solid/water ratio
30 of 1/20 (g/g). Subsequently, the reactor was closed, leak tested and purged with nitrogen to remove
31 the air of the system. Before the heating step, the reactor was pressurised with 15 bar (at 25 °C) of
32 N₂, to make sure all the reactions take place in the liquid phase. For all runs, a 15 min of ramp time
33 (time to reach reaction conditions from 25 °C) was employed. After the reaction, the reactor was
34 chilled until a temperature of 60 °C was achieved using a rate of 12 °C/min. Once the reactor was
35 cooled, the mass of the reactor vessel was recorded and its content, mainly consisting of a liquid
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3 phase (hydrolysate) and a spent solid material, was transferred to a plastic centrifuge container.
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5 The liquid fraction was separated from the solid residue by low temperature, high-speed
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7 centrifugation (8 °C, 3500 rpm, 20 minutes). Subsequently, the liquid phase was stored for further
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9 analysis, whereas the solid was desiccated for 24h at 105 °C.
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14 **Experimental design and statistical analyses**

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17 The influences on the process of the feedstock composition, calculated as the relative amount of
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19 wheat straw (0-100 wt.%) with respect to the total amount of solid (wheat straw/wheat straw +
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21 Laminaria Saccharina), the reaction temperature (80-250°C) and reaction time (0-60 min) were
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23 analysed experimentally through a 2 level 3 factor (2^3) Box-Wilson Central Composite Face
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25 Centred (CCF, $\alpha: \pm 1$) design. These intervals of variation were selected based on our previous
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27 publications. Besides, a biomass/water ratio of 1/20 (g/g) was used for the experimentation as it
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29 represents an energy-efficient option to maximise liquid production based on our previous work².
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17. The experimental design includes 2^3 (8) experiments for the basic factorial design to determine
simple linear effects and first-order interactions, 4 repeats in the middle of the variables (centre
points) to determine the error variance and 6 axial experiments to study quadratic effects and non-
linear interactions. An ANOVA with 95% confidence was employed to select the operating
variables and interactions that exert a statistically significant effect on the process. Also, the
relative importance of these significant operating conditions on the response variables was
compared by using the cause-effect Pareto test. In both statistical tests, the lower and upper limits
of the factors were normalised from -1 to 1 (codec factors) so that all factors (feedstock
composition, time and temperature) vary within the same interval and, therefore, their relative
influence can be directly compared. The design, model, confidence level and unexplained variation

with 95% confidence were used to calculate the height of the LSD bars. These results were used to develop interaction figures, which were depicted from the ANOVA analysis of all the runs conducted. Besides, some experimental points were included in these plots in some cases, thus allowing a thorough examination of the experimental data.

Response variables and analytical methods

The effects of the feedstock composition, temperature and reaction time during the microwave-assisted co-depolymerisation process addressed in this work were experimentally analysed on the distribution of the global products (gas, solid and liquid yields) as well as on some essential properties of the liquid and solid fractions. These include the liquid composition in carbon basis (C-wt.%), pH and conductivity, as well as the elemental analysis, higher heating value (HHV) and fibre analysis of the spent solid material. The analytical methods and calculations are listed in Table 1.

Table 1. Response variables and analytical methods

Product	Response variable	Analytical method
Liquid	Liquid yield (%) = $\frac{\text{liquid compounds (g)}}{\text{mass of biomass (g)}} 100 = 100 - (\text{Gas yield} + \text{Solid yield})$	Balance
	Composition (C - wt.%) = $\frac{\sum \text{mass of C of each compound (g)}}{\text{total mass of C in solution (g)}} 100$	HPLC and elemental analysis
	C, H, O (wt. %) = $\frac{\text{mass of C, H, O, N (g)}}{\text{mass of liquid (g)}} 100$	Elemental Analysis
	pH Conductivity (mS)	pH-meter Conductivimeter
Solid	Solid yield (%) = $\frac{\text{mass of solid (g)}}{\text{mass of biomass (g)}} 100$	Gravimetric
	HHV (MJ/kg) = $0.3491 \text{ C (wt. \%)} + 1.1783 \text{ H (wt. \%)} - 0.1034 \text{ O (wt. \%)} - 0.015 \text{ N (wt. \%)} + 0.1005 \text{ S (wt. \%)}$	Estimated
	C, H, O, N (wt. %) = $\frac{\text{mass of C, H, O, N (g)}}{\text{mass of solid (g)}} 100$	Elemental Analysis
Gas	Gas yield (%) = $\frac{\text{mass of gas (g)}}{\text{mass of biomass (g)}} 100$	Gravimetric

The chemical composition of the liquid phase was determined by High-Performance Liquid Chromatography. The proportion of DP>6 oligosaccharides concentration in the liquid was

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3 determined as the difference between the total organic carbon (TOC) of the solution and the C
4 quantified by HPLC. More detailed information about the characteristics, experimental conditions
5 used in the analyses and separation columns can be found in the ESI and our previous publication
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17. The elemental analyses were conducted with an Exeter Analytical (Warwick, UK) CE440 Elemental Analyser. The HHV of the solid was measured in an automatic calorimeter (6400 Parr). Besides, structural data of the solid residue was provided for some experiments by FTIR using a Perkin Elmer FTIR spectrum 400 analyser. The spectra were taken between 700 and 4000 cm^{-1} with 16 scans and steps of 4 cm^{-1} .

Characterisation of the Wheat straw and *Laminaria Saccharina*

The wheat straw used in this work was provided by Agripellets Ltd (UK) and produced from British wheat straw. For the experiments, the wheat straw pellets were ground using a coffee grinder to give a light brown powder with a particle size between 150-300 μm . The alga, *Laminaria Saccharina*, was harvested from Plymouth in September 2017 and kept frozen until used. For the experiments, the frozen algae were chopped using a knife mill and dried in an oven at 55 $^{\circ}\text{C}$ for 48 hours. Subsequently, the dried algae were then milled using a coffee grinder to give a medium brown powder with a particle size of 150-300 μm .

Both materials were characterised in terms of proximate, ultimate and fibre (cellulose, hemicellulose, lignin and protein) analyses and ash content, following standard methods (ISO-589-1981, ISO-1171-1976 and ISO-5623-1974). Ultimate and proximate analyses were conducted using the same apparatus and methodologies described above, while fibre characterisation was performed by thermogravimetric (TG) analysis taking into account the decomposition temperature of cellulose, hemicellulose and lignin⁴⁸; the protein content being calculated using N content

quantified by elemental analysis⁴⁹. Table 2 lists the most important physicochemical properties of the wheat straw and brown macroalgae (*Laminaria Saccharina*) used in this work. The chemical properties of both feedstocks are reasonably similar to those already reported for wheat straw⁵⁰⁻⁵² and *Laminaria Saccharina*⁵³.

Table 2. Characterisation of the Wheat straw and *Laminaria Saccharina* used in this work.

Feedstock	Wheat Straw	<i>Laminaria Saccharina</i>
Proximate analysis (wt.%)		
Moisture	2.12	1.72
Ash	5.03	12.80
Volatiles	60.45	53.79
Fixed carbon	27.04	34.91
Fibre analysis (wt.%)		
Cellulose	33.85	55.84
Hemicellulose	41.51	14.45
Lignin	16.01	9.71
Ash	5.00	13.00
Proteins	2.63	7.00
Ultimate analysis (wt.%)		
C	42.96±0.12	36.13±0.16
H	5.42±0.08	5.60±0.10
N	0.373±0.05	1.09±0.03
O	50.99±0.26	57.19±0.29
HHV (MJ/kg)	12.12±0.11	13.31±0.14
Ash composition (wt.%)		
K	49.93	29.92
Na	0	22.56
Ca	33.11	22.00
S	7.76	17.10
Mg	3.77	3.02
P	3.20	3.81
Si	2.23	0
Sr	0	1.59

RESULTS AND DISCUSSION

Table 3 summarises the microwave operating conditions (reaction temperature and time) together with the feedstock composition, expressed as Seaweed/(Seaweed+Wheat straw) used in the experiments and the experimental results obtained. These include the yields to gas, solid and liquid products (%) together with the detailed chemical composition (C-wt.%), pH and conductivity of the liquid phase (hydrolysate), as well as the elemental composition (C, H, O, N)

and calorific value of the spent solid material. Table 4 lists the full effects of the operating conditions and interactions obtained from the statistical analysis of all the experiments conducted, derived from the ANOVA and the cause-effect Pareto analyses.

Table 3. Experimental data: operating conditions and experimental results.

Run	1	2	3	4	5	6	7	8	9-12	13	14	15	16	17	18
Temperature (°C)	80	250	80	250	80	250	80	250	165	80	250	165	165	165	165
Time (min)	0	0	60	60	0	0	60	60	30	30	30	0	60	30	30
S/(S+W) (wt.%)	0	0	0	0	100	100	100	100	50	50	50	50	50	0	100
Overall product distribution															
Gas yield (%)	5.29	8.26	6.21	17.78	4.54	27.43	10.6	33.81	15.96±0.66	8.57	30.21	13.81	13.64	12.35	17.27
Solid yield (%)	84.28	85.53	90.22	38.98	40.43	45.48	49.46	35.54	63.21±3.95	83.32	34.90	60.85	59.94	83.13	48.87
Liquid yield (%)	5.49	6.22	13.35	43.23	55.02	27.09	39.93	30.65	20.83±3.91	14.04	34.9	25.34	26.42	8.56	43.64
Liquid (hydrolysate) chemical composition (C-wt.%)															
Oligosaccharides DP>6	70.94	56.7	84.9	64.38	0.00	41.05	0.00	40.24	8.35±1.84	7.72	64.99	0.00	17.15	33.48	22.01
Oligosaccharides DP3-6	7.66	6.78	0.00	6.73	92.64	29.01	94.45	19.14	73.23±1.23	87.22	6.87	81.7	65.7	48.6	56.78
Saccharides	15.37	10.69	12.94	4.01	6.26	18.43	5.03	27.07	14.87±0.49	4.59	12.46	16.68	12.6	10.94	18.24
Carboxylic Acids	5.98	10.37	2.16	11.85	1.1	4.62	0.52	6.38	2.65±0.18	0.47	7.91	1.56	2.62	5.81	1.8
Ketones	0.00	5.25	0.00	2.61	0.00	1.28	0.00	4.29	0.04±0.02	0.00	2.37	0.00	0.24	0.33	0.09
Furans	0.05	10.21	0.00	10.43	0.00	5.61	0.00	2.88	0.86±0.04	0.00	5.4	0.07	1.69	0.84	1.09
Liquid (hydrolysate) properties															
pH	6.55	3.36	6.63	3.29	5.12	3.71	5.03	4.2	4.47±0.04	5.77	3.63	5.15	4.38	4.59	4.46
Conductivity (mS)	18.16	3.41	18.89	2.41	7.37	10.06	7.44	10.3	6.12±0.05	4.52	2.99	4.84	6.27	2.26	10.03
Solid product elemental analysis and calorific value															
C (wt.%)	45.63	49.93	44.89	62.48	36.88	45.17	38.36	49.82	44.99±0.47	39.51	52.69	43.22	44.92	45.40	39.56
H (wt.%)	5.67	5.56	5.54	5.50	5.25	4.95	5.42	4.74	5.22±0.15	5.02	5.17	5.53	5.53	5.55	5.60
N (wt.%)	0.00	0.16	0.00	0.62	1.33	1.74	1.07	1.75	0.25±0.19	0.40	0.94	0.47	0.61	0.28	1.39
O (wt.%)	48.70	44.35	49.57	31.41	56.54	48.14	55.15	43.69	49.56±0.74	55.08	41.20	50.78	48.93	48.78	53.45
HHV (MJ/kg)	17.58	19.40	17.07	25.05	13.24	16.65	14.09	18.49	16.73±0.40	14.01	20.24	16.36	17.15	17.35	14.90

Overall products distribution: gas, solid and liquid yields

The yields to gas, solid and liquid (hydrolysate) products vary between 0-19%, 9-80% and 17-90%, respectively. The cause-effect Pareto analysis reveals that the gas and solid yields are mostly affected by the reaction temperature and feedstock mixture composition. In contrast, the liquid yield is substantially influenced by the feedstock mixture composition and its interaction with the reaction time. Regarding feedstock synergies, for the gas and liquid yields, the quadratic term for the feedstock mixture (F^2) is significant, which indicates the existence of synergetic or antagonistic effects. In particular, for the gas yield the term in the codec model is negative, i.e., it displays concave trend, thus denoting an antagonistic effect; while for the liquid yield is positive, i.e., a

convex trend thus exemplifying a synergistic effect. In both cases, the contribution of the synergistic/antagonistic effects accounts for 19% of the total impact of the feedstock composition ($F^2/(F+F^2)$).

Table 4. Effects of the feedstock composition and processing conditions.

	R ²	Int.	T	t	F	Tt	TF	tF	T ²	t ²	F ²	TtF	T ² t	T ² F	Tt ²	T ² t ²
Overall products distribution																
Gas yield (%)	0.98	16.30	10.81 (32)	n.s.	2.46 (17)	1.12 (4)	3.95 (14)	n.s.	2.75 (1)	-2.91 (8)	-1.82 (4)	-1.04 (4)	2.86 (10)	2.39 (3)	-3.23 (3)	n.s.
Solid yield (%)	0.95	63.21	-24.21 (17)	-4.24 (7)	-16.24 (26)	-8.93 (13)	5.14 (7)	4.96 (7)	-4.39 (5)	n.s.	n.s.	4.19 (6)	n.s.	n.s.	16.85 (12)	n.s.
Liquid yield (%)	0.97	23.12	10.43 (3)	n.s.	17.54 (26)	5.98 (11)	-8.48 (16)	-7.05 (14)	n.s.	n.s.	4.32 (6)	n.s.	4.17 (8)	-6.99 (6)	-11.26 (10)	n.s.
Liquid (hydrolysate) composition (C-wt.%)																
Oligosaccharides DP>6	0.99	88.43	28.63 (13)	8.57 (5)	-5.74 (26)	n.s.	14.51 (16)	-2.81 (3)	27.93 (25)	n.s.	19.31 (10)	n.s.	-5.97 (3)	-18.71 (9)	-22.82 (12)	-10.89 (4)
Oligosaccharides DP3-6	0.99	73.39	-40.18 (18)	-8 (3)	4.09 (19)	n.s.	-18.1 (14)	n.s.	-26.34 (18)	n.s.	-20.7 (8)	-2.41 (2)	6.03 (2)	22.67 (8)	23.54 (8)	5.7 (1)
Saccharides	0.99	14.74	3.94 (14)	-2.04 (3)	3.65 (10)	0.7 (3)	5.98 (26)	2.06 (9)	6.22 (10)	n.s.	n.s.	1.76 (8)	1.83 (4)	-1.93 (4)	-1.36 (3)	3.95 (8)
Carboxylic Acids	0.99	2.49	3.72 (31)	n.s.	2.18 (13)	0.95 (22)	0.44 (9)	1.64 (5)	1.64 (4)	n.s.	1.26 (7)	-0.37 (3)	n.s.	n.s.	-0.79 (3)	n.s.
Ketones	0.98	0.04	1.18 (31)	0.12 (1)	-0.12 (5)	0.046 (1)	-0.29 (5)	0.71 (12)	1.15 (19)	0.085 (3)	0.17 (3)	0.71 (12)	-0.074 (1)	-0.17 (1)	0.49 (4)	0.23 (1)
Furans	0.96	0.87	2.7 (32)	0.81 (1)	0.13 (11)	-0.31 (3)	-1.51 (13)	-0.36 (3)	1.83 (16)	n.s.	0.097 (3)	-0.37 (3)	-1.13 (4)	-1.65 (6)	0.93 (3)	0.85 (2)
Liquid (hydrolysate) properties																
pH	0.99	4.49	-1.09 (45)	-0.39 (1)	n.s.	0.054 (2)	0.54 (20)	0.049 (2)	0.21 (5)	0.28 (4)	n.s.	0.091 (3)	0.44 (7)	-0.22 (8)	n.s.	-0.24 (3)
Conductivity (mS)	1	6.13	-0.76 (6)	0.71 (6)	3.89 (6)	-0.2 (9)	4.6 (7)	0.072 (16)	-2.37 (6)	-0.57 (2)	n.s.	0.24 (8)	-0.71 (1)	-4.85 (6)	-2.45 (10)	6.57 (17)
Spent solid properties																
C (wt.%)	0.97	45.04	5.48 (7)	n.s.	-3.85 (10)	2.06 (4)	n.s.	n.s.	n.s.	n.s.	-2.56 (30)	-1.27 (21)	2.24 (19)	n.s.	n.s.	4.17 (9)
H (wt.%)	0.92	5.17	n.s.	n.s.	n.s.	n.s.	-0.10 (18)	n.s.	n.s.	0.40 (43)	0.45 (12)	n.s.	n.s.	-0.24 (15)	-0.14 (9)	-0.65 (2)
N (wt.%)	0.90	0.42	0.24 (8)	n.s.	0.62 (41)	n.s.	n.s.	n.s.	n.s.	n.s.	0.41 (51)	n.s.	n.s.	n.s.	n.s.	n.s.
O (wt.%)	0.96	50.02	-5.63 (9)	-1.98 (24)	3.42 (15)	-2.11 (5)	n.s.	n.s.	-2.64 (24)	n.s.	n.s.	1.34 (23)	n.s.	n.s.	n.s.	n.s.
HHV (MJ/kg)	0.95	16.59	2.38 (11)	0.86 (29)	-1.91 (11)	0.89 (3)	n.s.	n.s.	0.99 (19)	n.s.	n.s.	-0.65 (27)	n.s.	n.s.	n.s.	n.s.

n.s. = Non significant term with 95% confidence. T = temperature, t = time, F = seaweed/(seaweed+wheat straw).

Response = Int + coefficient T · T + coefficient t · t + coefficient F · F + coefficient Tt · T · t + coefficient TF · T · F + coefficient tF · t · F + coefficient T² · T² + coefficient t² · t² + coefficient F² · F² + coefficient TtF · T · t · F + coefficient T²t · T² · t + coefficient T²F · T² · F + coefficient Tt² · T · t² + coefficient T²t² · T² · t².

Standardised codec formula: all operating variables vary between -1 and +1. Numbers in brackets show the relative influence (%) of each factor on the response variable. These values indicate the orthogonal estimated total value (%). The higher the Pareto value is, the greater the influence of the parameter in the response.

Conversely, the quadratic term of the feedstock mixture is not significant for the solid yield, which indicates the absence of synergistic/antagonistic effects, thus denoting a linear evolution for

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3 this variable, which accounts for a mere dilution effect. Figure 1 shows the full effects of the
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5 feedstock mixture, reaction conditions and all the interactions between these variables detected
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7 according to the ANOVA analysis. In particular, Figure 1 a/b/c shows the effect of the feedstock
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9 composition (seaweed, wheat straw and all possible binary combinations) at the lowest (80 °C)
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11 and highest (250°C) temperature for a 0/30/60 min reaction time. These effects are shown in
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13 Figures 1 (d-f) and Figure 1 (g-i) for the liquid and solid yield, respectively.
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17 The effect of the feedstock mixture on the gas yield depends on the temperature and reaction
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19 time. On the one hand, at low temperature (80 °C), the effect of the feedstock composition is
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21 negligible, and irrespectively of the solid mixture (seaweed, wheat straw or any binary mixture),
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23 the gas yield is meagre. This suggests that hydrolysis and depolymerisation reactions are the
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25 essential routes responsible for depolymerisation, whereas pyrolysis and decarboxylation reactions
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27 ⁵⁴⁻⁵⁶, which promotes gas formation ^{57,58}, are not favoured at low temperature. However, increasing
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29 the reaction time increases gas formation when the reaction mixture is enriched in seaweed, which
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31 indicates that seaweed is more reactive than wheat straw at these reaction conditions, especially
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33 using long reaction times. This development can be the consequence of the lower lignin content
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35 and the higher protein and ash contents of *Laminaria Saccharina* in comparison to wheat straw.
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37 The gas formation can increase due to proteins decomposition into gaseous products via
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39 decarboxylation and deamination reactions ^{57,58}. Besides, the more significant proportion of ashes
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41 in *Laminaria Saccharina* can facilitate the gas formation, as these species exert a positive catalytic
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43 effect on pyrolysis and gasification reactions ⁵⁹⁻⁶³. The evolution depicted by the gas yield is not
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45 linear, showing an initial increase from a feedstock mixture consisting of pure wheat straw up to a
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47 mixture containing half of each biomass, which indicates a positive synergistic effect of seaweed
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49 on wheat straw decomposition towards the gas formation. An increase in the reaction temperature
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3 increases the gas yield irrespectively of the feedstock composition or reaction time. This is
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5 accounted for by a more significant development of pyrolysis and decarboxylation reactions when
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7 increasing the reaction time at high temperature ⁵⁴⁻⁵⁶, thus leading to gas formation ^{57,58}. However,
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9 the increases observed are more pronounced as the proportion of seaweed in the feedstock
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11 increases.
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15 On the other hand, at high temperature (250 °C), an increase in the proportion of seaweed leads
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17 to a pronounced increase in the gas yield, thus indicating that seaweed is more likely to produce
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19 gaseous products than wheat straw due to its higher reactivity as described above. Besides, the
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21 increase observed is not linear, which suggests that seaweed exerts a positive synergetic effect on
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23 wheat straw conversion to gaseous products. The greater reactivity of seaweed in comparison to
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25 wheat straw leads to an increase in the proportion of secondary products, such as organic acids.
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27 These acids might exert a positive catalytic effect of wheat straw depolymerisation ³⁰, as they can
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29 act as a form of auto-catalysis ³². The impact of the reaction time depends on the temperature
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31 (Figure 1 a vs. b and c). While at low temperature, increasing the reaction time from 0 to 60 min
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33 does not substantially increase gas production regardless of the feedstock mixture, at high
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35 temperature, this same increase in the reaction time leads at first to a rise in the gas yield between
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37 0 and 30 min, followed by a steady evolution when the reaction time increases up to 60 min. The
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39 combination of high temperatures and long reaction time promotes a higher spread of pyrolysis,
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41 decarboxylation and deamination reactions ¹⁷⁻¹⁹, thus increasing gas formation.
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48 The effects of the feedstock mixture on the liquid and solid yields substantially depend on the
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50 reaction time. For a short reaction time, higher liquid yields are obtained with pure seaweed than
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52 with pure wheat straw regardless of the reaction temperature. An increase in the proportion of
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54 seaweed in the feedstock mixture leads to a rise in the liquid yield. The convex increase depicted
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3 by this variable indicates an antagonistic effect on liquid production, as the addition of seaweed
4 favours gas formation over the liquid produced. This can be accounted for by a positive effect of
5 seaweed on depolymerisation reactions accounted for the positive impact of metal particles under
6 microwave heating ^{64, 65} together with their catalytic behaviour ⁶¹⁻⁶³. This leads to a greater spread
7 of hydrolysis reactions, favouring the formation of small oxygenates in the liquid product that can
8 be more easily converted to gas ^{2, 17}. The effect of the temperature depends on the feedstock
9 composition. On the one hand, for pure wheat straw, increasing the temperature from 80 to 250 °C
10 does not increase the liquid yield. On the other side, as the reaction mixture is enriched in seaweed,
11 this same increase in the temperature rises the liquid yield; the higher the proportion of seaweed
12 in the mix, the sharper is the increment observed in the liquid yield due to the greater reactivity of
13 seaweed than that of wheat straw as described earlier. Besides, increasing the temperature shifts
14 hydrolysis reactions towards the production of carboxylic acids, these species being capable of
15 assisting biomass depolymerisation, thus increasing the liquid yield. Besides, the effect of the
16 feedstock composition on the solid yield does not depend on the temperature for a very short
17 reaction time (0 min). Irrespectively of the temperature, higher solid yields are obtained with pure
18 wheat straw than with pure seaweed due to the lower reactivity of the former than the latter, which
19 hinders its transformation into gas and liquid products. An increase in the proportion of seaweed
20 in the feedstock mixture linearly diminishes the solid yield, due to the absence of
21 synergistic/antagonistic effects. This suggests that the positive impact of the addition of seaweed
22 to wheat straw assist in the transformation of already solubilised liquid species, via enhancement
23 of the chemical reactions occurring in the liquid phase. This can be the consequence of mass
24 transfer limitations, which hampers their intimate contact ^{54, 55, 66}, and thus avoiding possible
25 synergistic effects to take place.
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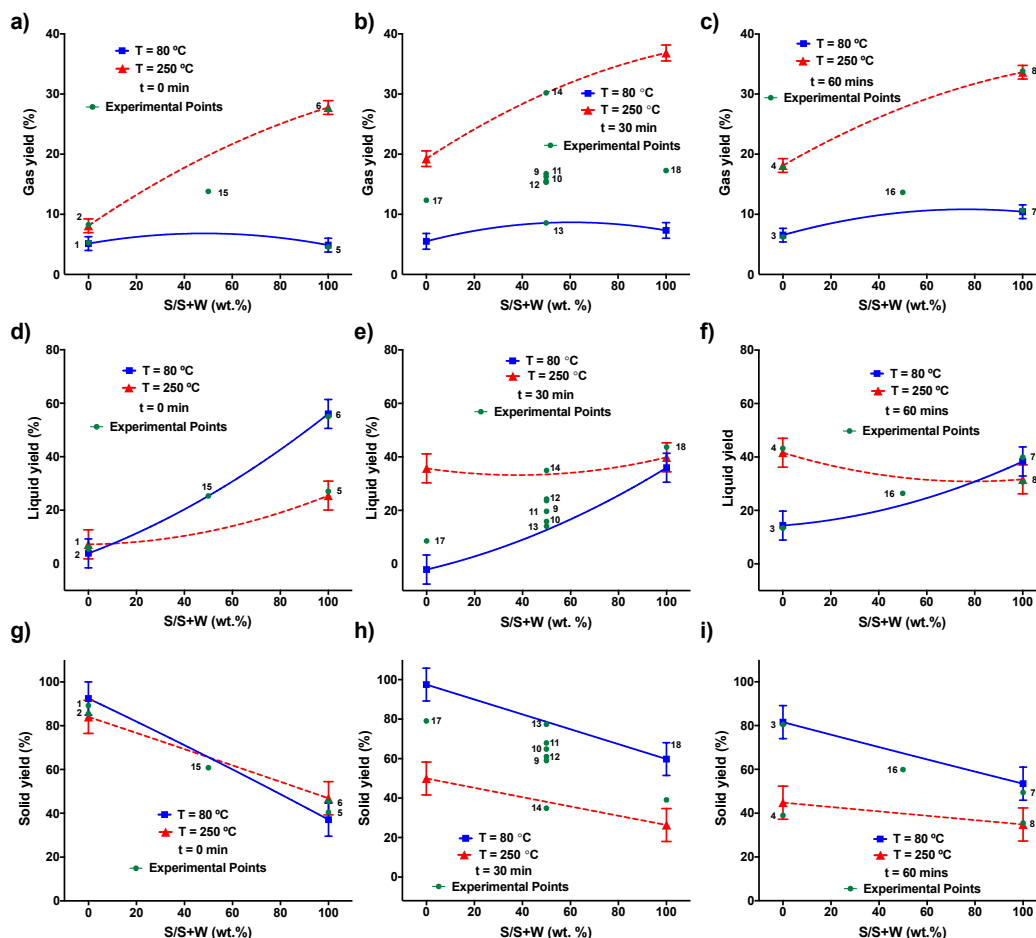


Fig. 1. Interaction plots between the feedstock composition (Seaweed/Seaweed+Wheat Straw) and the temperature using different reaction times for the yields to (a-c) gas, (d-f) liquid and (g-i) solid at 0, 30 and 60 min, respectively.

The effect of the reaction time on the liquid and solid yields depends on the reaction temperature. At low temperature (80 °C), the effect of the reaction time depends on the feedstock mixture composition. In particular, for a feedstock consisting of pure wheat straw, an initial increase in the reaction time from 0 to 30 min does not substantially modify the liquid (Figure 1 d vs. e) or solid yields (Figure 1 g vs. h). In comparison, a subsequent increase up to 60 min leads to a small increase in the liquid yield (Figure 1 e vs. f), together with a slight decrease in the solid yield (Figure 1 h vs. i) due to the positive kinetic effect of the reaction time on hydrolysis and depolymerisation reactions. Conversely, when pure seaweed is used, a different evolution is

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3 observed. The same increase in the reaction time leads to a progressive decrease in the liquid yield,
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5 together with an increase in the solid yield between 0 and 60 min due to the formation of gas and
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7 solid species. Gaseous products formation takes place to a greater extent due to the higher tendency
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9 of this material to produce gases. Besides, long reaction times at low temperatures favours the
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11 development of hydrothermal carbonisation reactions from seaweed, thus leading to an increase in
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13 the solid yield. Therefore, in these cases, the solid product accounts for both un-reacted material,
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15 along with new solid species formed. At high temperature (250 °C), not only the effect of the
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17 reaction time is more important, but also the variations observed do not depend on the feedstock
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19 composition. Regardless of the feedstock mixture composition, an initial increase between 0 and
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21 30 min leads to a raise and a decrease in the liquid and solid yield, respectively due to the positive
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23 kinetic effect of the reaction time on the process. A subsequent increase from 30 to 60 min results
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25 in a steady evolution for the liquid yield, this plateau being also accompanied by a small decrease
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27 in the solid yield. These developments modify the effects of the temperature when reaction times
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29 between 30 and 60 min are used. In these cases, an increase in the reaction temperature between
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31 80 and 250 °C leads to an increase in the liquid yield and a decrease in the solid yield, as hydrolysis
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33 and depolymerisation reactions are favoured with increasing the temperature, thus helping the
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35 transformation of the biomass into liquid products. These variations are more marked for shorter
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37 reaction time (30 min vs. 60 min), and a feedstock consisting of pure wheat straw and diminish
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39 progressively as the content of seaweed in the feedstock mixture increases. Higher reaction times
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41 and greater proportions of seaweed in the feedstock mixture might mask the positive effect of the
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43 temperature due to their positive kinetic effects on liquid production via biomass depolymerisation.
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51 **Chemical composition of the liquid phase**

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3 The liquid phase consists of a mixture of DP>6 oligosaccharides (0-85 C-wt.%), DP 2-6
4 oligosaccharides (0-95 C-wt.%), saccharides (4-27 C-wt.%), ketones (0-5 C-wt.%), carboxylic
5 acids (0-12 C-wt.%) and furans (0-10 C-wt.%). The detailed chemical composition of the liquid
6 phase is provided as supplementary material in Table S1. These results show that the proportions
7 of oligosaccharides and saccharides account for more than 75 C-wt.% in all the cases, thus
8 highlighting the selectivity of this microwave process for biomass transformation into sugar-rich
9 aqueous carriers. The cause-effect Pareto analysis reveals that the temperature (including both
10 linear and quadratic contributions) is the operating variable exerting the greatest influence,
11 followed by the feedstock mixture, on the chemical composition of the liquid phase.
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24 The significant influence of the quadratic coefficient of the feedstock mixture (F^2) reveals the
25 existence of significant synergistic/antagonistic effects. In particular, the contribution of the
26 quadratic value of the feedstock in comparison to the total feedstock influence $F^2/(F^2+F)$ is as
27 follows: 28% for DP>6 oligosaccharides, 29% for PD2-6 oligosaccharides, 38% for ketones, 24%
28 for carboxylic acids and 21% for furans. This indicates the existence of significant interactions
29 between both feedstocks (wheat straw and seaweed) substantially affecting the chemical
30 composition of the liquid phase. Figure 2 a/b/c shows the effects on the relative amount of DP>6
31 oligosaccharides of the feedstock composition (seaweed, wheat straw and all possible binary
32 combinations at the lowest (80 °C) and highest (250°C) temperature for a 0/30/60 min reaction
33 time. These effects are shown in Figures 2 d-f, g-i, j-l, m-o, p-r for DP2-6 oligosaccharides,
34 saccharides, carboxylic acids, ketones and furans, respectively.
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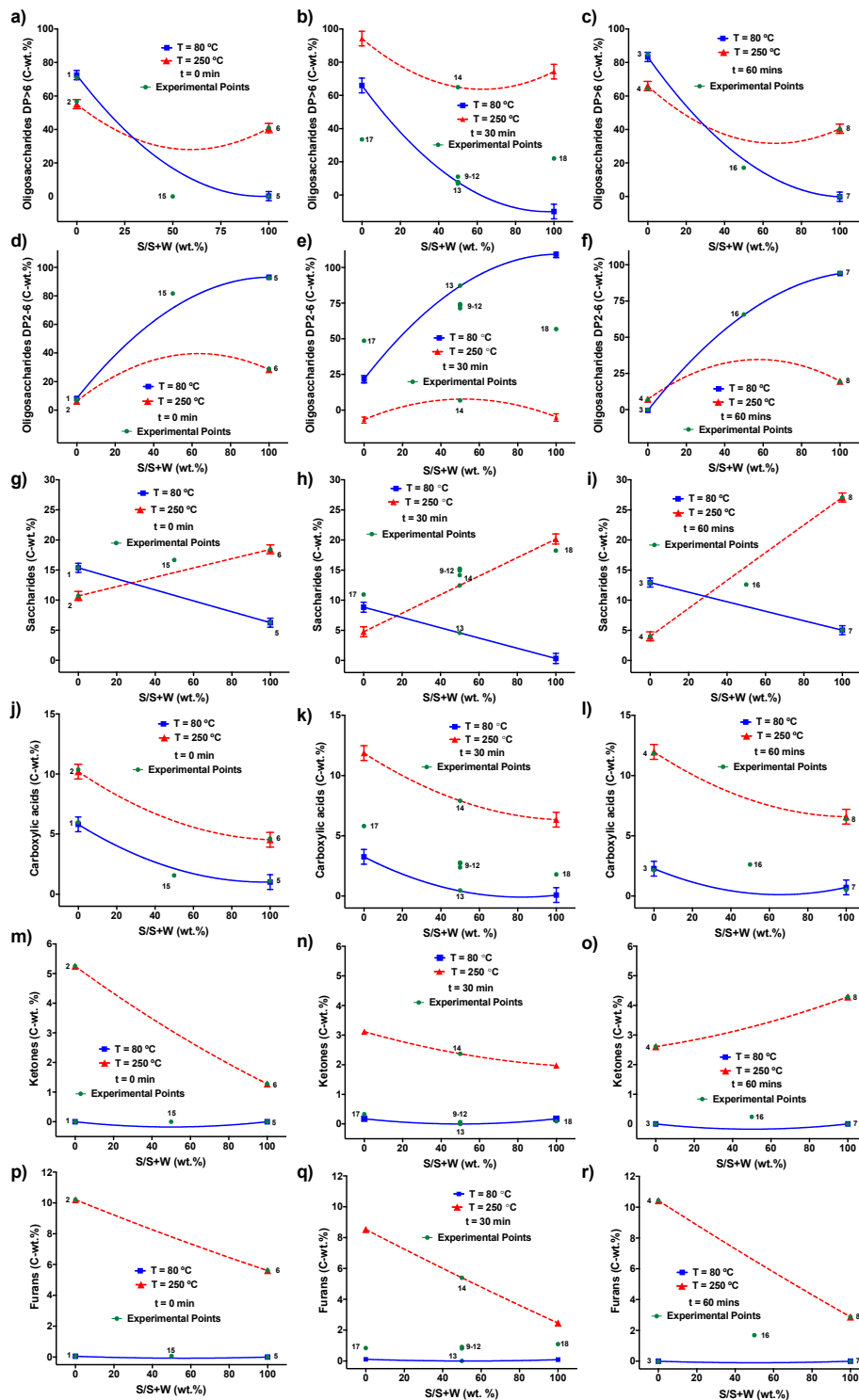


Fig. 2. Interaction plots between the feedstock composition (Seaweed/Seaweed+Wheat Straw) and the temperature using different reaction times for the chemical composition of the liquid phase: oligosaccharides DP>6 (a-c), oligosaccharides DP 2-6 (d-f), saccharides (g-i), carboxylic acids (j-l), ketones (m-o) and furans (p-r) at 0, 30 and 60 min, respectively.

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3 The effect of the feedstock mixture composition on the liquid composition primary depends on
4 the temperature, the effects of the reaction time being less critical. When a low temperature (80
5 °C) is used, the liquid phase mostly consists of oligosaccharides regardless of the reaction time or
6 the feedstock mixture composition. In particular, for pure wheat straw, the liquid phase is made up
7 of DP>6 oligosaccharides; however, as the feedstock mixture is enriched in seaweed, the
8 proportion of DP>6 oligosaccharides decreases at the expenses of the relative amount of DP 2-6
9 oligosaccharides, due to the progressive transformation of the former into the latter species via
10 hydrolysis ^{2, 17, 41}. This is thought to be a consequence of the greater reactivity of Laminaria
11 Saccharina than that of wheat straw and could be accounted for by its greater contents in cellulose
12 and hemicellulose as well as its more significant proportion of ashes. Ashes not only are sound
13 microwave absorbers ^{64, 65}, but also they have catalytic properties ⁶¹⁻⁶³, which lead to a greater
14 spread of hydrolysis and depolymerisation reactions. As a result, for pure seaweed, the liquid phase
15 primary consists of DP 2-6 oligosaccharides.
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33 In addition, the decreases and increases depicted by DP>6 and DP 2-6 oligosaccharides do not
34 follow a linear trend. This denotes the existence of synergistic effects, and very interestingly, it
35 allows achieving a complete DP>6 oligosaccharides depolymerisation into DP 2-6
36 oligosaccharides using a feedstock mixture having up to 30 wt.% of wheat straw; thus highlighting
37 the importance of co-valorisation as a new bio-refinery strategy. Besides, at low temperature
38 (80°C), the proportions of saccharides and carboxylic acids are meagre. At the same time, the
39 relative amounts of ketones and furans are negligible since low temperatures might hinder the
40 extension of secondary reactions leading to the formation of these species ^{2, 17}. However, as the
41 feedstock contains more seaweed, the relative amounts of saccharides and carboxylic acids in the
42 liquid phase decrease down to negligible levels. This might be the result of two different
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3 developments. On the one hand, the higher reactivity of *Laminaria Saccharina* leads to a more
4 significant extension of hydrolysis reactions towards the formation of carboxylic acids. These
5 acids can be easily transformed into gaseous products ^{2,17}, thus decreasing their relative proportion
6 in the liquid phase. On the other hand, wheat straw contains more hemicellulose and less cellulose
7 than *Laminaria Saccharina*, which might favour carboxylic acids production as hemicellulose is
8 more reactive under microwave heating ¹⁷. Therefore, as the feedstock mixture is enriched in
9 seaweed, the liquid product has a lower proportion of carboxylic acids.

19 An increase in the temperature modifies the chemical composition of the liquid phase. In
20 general, an increase in the temperature leads to a decrease in the proportion of DP 2-6
21 oligosaccharides together with increases in the relative amounts of carboxylic acids, ketones and
22 furans irrespectively of the feedstock composition. These variations are accounted for by the
23 positive effect of the temperature on hydrolysis and depolymerisation reactions, which promotes
24 sugars decomposition into secondary products ^{21, 22, 67}. Conversely, the effects of the temperature
25 on the proportions of DP>6 oligosaccharides and saccharides depend on the reaction time and
26 feedstock mixture composition. For a feedstock consisting of pure wheat straw and/or any mixture
27 comprising less than 30 wt.% of seaweed, an increase in the temperature from 80 to 250 °C
28 decreases the relative amount of DP>6 oligosaccharides and saccharides, while for pure seaweed
29 and/or any feedstock mixture having more than 30 wt.% of seaweed, this same increase in the
30 temperature leads to improvements in the proportions of DP>6 oligosaccharides and saccharides.
31 This might indicate that for pure seaweed and enriched-seaweed solids, the first
32 depolymerisation/liquefaction reaction step, comprising the formation of water-soluble DP>6
33 oligosaccharides, is quicker than the subsequent transformation of these species into DP 2-6
34 oligosaccharides. As a result, increasing the temperature favours the conversion of DP 2-6 into
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3 saccharides as well as the subsequent transformation of these species into small oxygenates
4 (carboxylic acids, ketones and furans). However, these transformations do not compensate for the
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6 more considerable amount of DP>6 oligosaccharides solubilised in the liquid product, and as a
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8 result, the proportion of DP>6 oligosaccharides increases. An exception to this occurs for a 30 min
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10 reaction, time at which increasing the temperature leads to an increase in the proportion of DP>6
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12 oligosaccharides irrespectively of the feedstock mixture composition. As a result of these
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14 developments, at high temperature (250 °C), although the liquid phase is primarily made up of
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16 oligosaccharides and saccharides, the presence of secondary products such as carboxylic acids,
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18 ketones and furans increases. The positive kinetic effect of the temperature on the process, leading
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20 to a greater spread of hydrolysis and depolymerisation reactions, might be responsible for such
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22 variations.
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29 Regardless of the reaction time, the chemical composition of the liquid phase depends on the
30
31 feedstock mixture. A higher proportion of DP>6 oligosaccharides and lower portions of DP 2-4
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33 oligosaccharides and saccharides are obtained for pure wheat straw than for a feedstock consisting
34
35 of pure seaweed. In addition, increasing the relative amount of seaweed in the feedstock mixture
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37 up 70 wt.% leads to a decrease in the relative amount of DP>6 oligosaccharides together with an
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39 increase in the relative amount of DP 2-6 oligosaccharides due to the progressive transformation
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41 of the former into the latter via hydrolysis reactions. A subsequent increase in the proportion of
42
43 seaweed slightly increases the percentage of DP>6 oligosaccharides and decreases the proportion
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45 of DP 2-6 saccharides in the liquid product, as the first solubilisation step into DP>6
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47 oligosaccharides could be faster than the subsequent transformation into lower molecular weight
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49 species, as described earlier. This suggests that microwaves might activate metals present in
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51 seaweed and, due to their catalytic properties, these metals could promote the first
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3 depolymerisation step aiding to the solubilisation of biomass into water-soluble species. The
4 intimate contact between these metallic species and the biomass facilitates the catalytic
5 transformation of biomass into soluble oligosaccharides, while the effect of metals in the
6 subsequent hydrolysis reactions might be less effective due to mass transfer limitations. The liquid
7 phase contains a lower proportion of saccharides and higher proportions of carboxylic acids,
8 ketones and furans with a feedstock consisting of wheat straw than with feeding pure seaweed.
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10 The presence of seaweed in the feedstock leads to a linear increase in the relative amount of
11 saccharides together with linear decreases in the relative amount of ketones and furans. The
12 relative amount of carboxylic acids decreases as the feedstock is enriched in seaweed, this drop
13 displaying a concave decay, which denotes a synergetic effect between feedstocks. This decrease
14 is accompanied by a concave increase in the proportion of gas, thus suggesting the possible
15 transformation of these species into gases, denoting synergistically positive catalysis.
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31 The effect of the reaction time depends on the temperature and feedstock composition. At low
32 temperature (80 °C), the effect of the reaction time does not depend on the feedstock composition,
33 and similar evolutions are observed. An initial increase in the reaction time from 0 to 30 min leads
34 to a small decrease in the proportion of DP>6 oligosaccharides and saccharides together with an
35 increase in the relative amount of DP 2-6 oligosaccharides due to the transformation of DP>6
36 oligosaccharides into DP 2-6 oligosaccharides, along with sugars decomposition into small
37 oxygenates. A further increase up to 60 min results in improvements in the proportions of DP>6
38 oligosaccharides and saccharides accompanied by a decrease in the concentration of DP 2-6
39 oligosaccharides. The relative amount of carboxylic acids decreases progressively as the reaction
40 time increases from 0 to 60 min, while the proportions of ketones and furans are negligible at low
41 temperature. At high temperature (250 °C) increasing the reaction time leads to a first increase (0-
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3 30 min) in the proportion of DP>6 oligosaccharides and a decrease in the concentration of DP 2-6
4 oligosaccharides due to the positive kinetic effect of the reaction time on biomass solubilisation
5 into soluble oligosaccharides as well as the transformation of DP 2-6 oligosaccharides into
6 saccharides and small oxygenates. A subsequent increase in time (30-60 min) decreases and
7 increases in the proportions of DP 2-6 and DP>6 oligosaccharides, respectively. Increasing the
8 reaction time facilitates the extension of hydrolysis reactions in the liquid phase, thus promoting
9 oligosaccharides and saccharides decomposition into small oxygenates, such as carboxylic acids,
10 furans and ketones. However, gas formation from small oxygenates is also favoured at high
11 temperature and using long reaction times. As a result of the different reaction rates of the reactions
12 involved, the liquid product is enriched in DP>6 oligosaccharides due to transformation of small
13 oxygenates into gas. Besides, while, the proportion of carboxylic acids does not much depend on
14 the reaction time and significant variations are not observed, the effect of the reaction time on the
15 proportions of saccharides, ketones and furans depends on the feedstock mixture composition. For
16 pure wheat straw, an increase in the reaction time leads to small decreases in the proportions of
17 saccharides and ketones, the relative amount of furans being unaffected. Conversely, when the
18 amount of seaweed in the feedstock increases, this same increase in the reaction time leads to a
19 small increase in the proportion of saccharides and ketones along with a decrease in the relative
20 amount of furans; though, these variations are not very important from a practical point of view.
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47 **Properties the liquid phase: pH and conductivity**

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49 The pH of the liquid phase varies from 3.29 to 6.67, while the conductivity shifts between 2.26
50 and 18.89 mS. According to the cause-effect Pareto principle, the reaction temperature and its
51 interaction with the feedstock composition mixture are the operating variables exerting the most
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substantial influence on the pH of the hydrolysates. The interaction between the reaction time and the feedstock mixture along with the interaction between the temperature and reaction time are the variables with the most considerable importance on the conductivity of the liquid phase. For both responses, feedstock synergetic or antagonistic effects are not statistically significant, and linear evolutions (additive mixing effects) are observed for the pH and conductivity. Figures 3 a/b/c and 3 d/e/f show the influence of the feedstock composition (seaweed, wheat straw and all possible binary combinations at the lowest (80 °C) and highest (250 °C) temperature for a 0/30/60 min reaction time on the pH and conductivity, respectively.

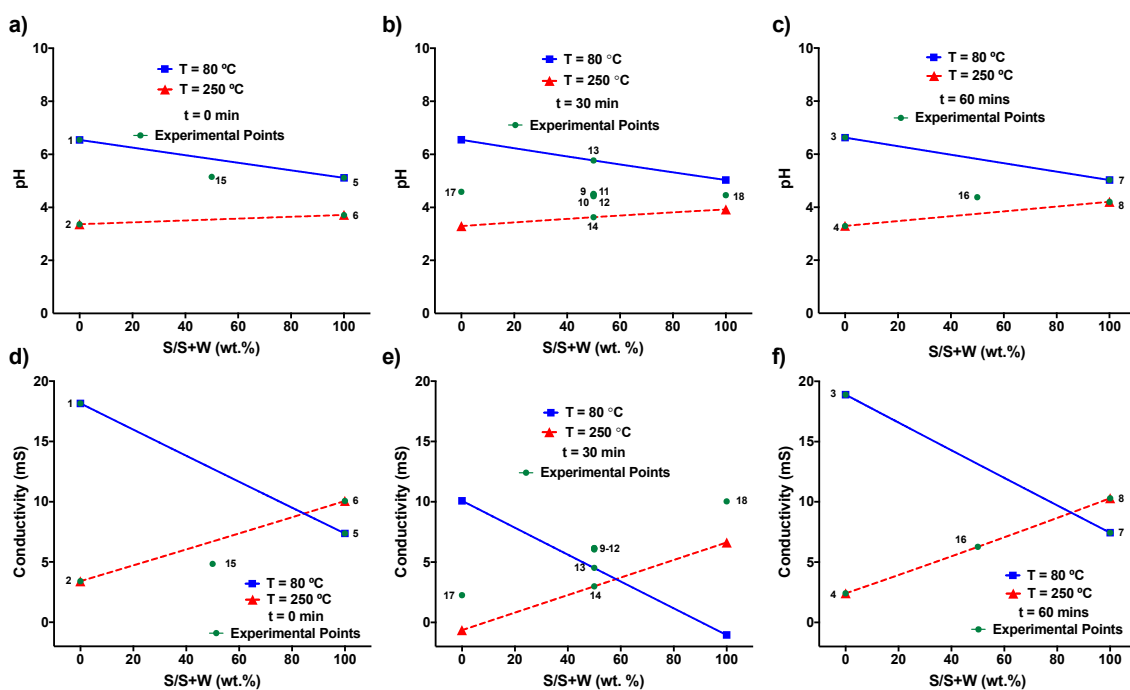


Fig. 3. Interaction plots between the feedstock composition (Seaweed/Seaweed+Wheat Straw) and the temperature using different reaction times for the pH (a-c) and conductivity (d-f) of the liquid phase at 0, 30 and 60 min, respectively.

The pH of the liquid phase depends on the feedstock mixture composition and the temperature used in the microwave process. At low temperature (80 °C), when wheat straw is used as a

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3 feedstock, the liquid phase has a neutral pH (ca. 7) irrespectively of the reaction time. However,
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5 as the mixture is enriched in seaweed, the pH decreases linearly, probably due to the more
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7 considerable amount of alkaline salts in wheat straw in comparison to *Laminaria Saccharina*
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9 which neutralise acids formed. An increase in the temperature from 80 to 250 °C decreases the pH
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11 of the liquid phase regardless of the reaction time or feedstock mixture composition; the effect of
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13 this latter variable being less and less significant as the temperature increases. As a consequence,
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15 at 250 °C, the pH of the solution is around 3.8 – 4.0 regardless of the other variables.
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20 The conductivity of the solution depends on the feedstock composition, temperature and
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22 reaction time. Two different developments occur for the conductivity of the solution when the
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24 composition of the feedstock mixture is altered. At low temperature (80°C), irrespectively of the
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26 reaction time, a liquid phase with a higher conductivity is produced with pure wheat straw than
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28 with pure seaweed; the conductivity progressively decreasing as the solution is enriched in
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30 seaweed. This suggests that at low-temperature ash leaching is more likely to take place with
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32 feeding wheat straw than when seaweed is used as the feedstock. This might indicate that metals
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34 could be more integrated into the solid structure in seaweed than in wheat straw, thus being less
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36 accessible to water at low temperature. Besides, this supports the positive catalytic effect of metals
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38 in *Laminaria Saccharina*, as they are well distributed into the core structure of the solid, thus aiding
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40 to the first depolymerisation step to produce soluble oligosaccharides, without being leached to
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42 the solution.
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47 Increasing the temperature has different consequences for the conductivity of the solution
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49 depending on the feedstock mixture composition and reaction time. For a feedstock mixture
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51 consisting of pure wheat straw, increasing the temperature leads to a decrease in the conductivity,
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53 while for a feedstock mixture composed of pure seaweed this same temperature increase results in
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3 an increase in the conductivity. As a consequence of these developments, when a temperature of
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5 250 °C is used, increasing the proportion of seaweed in the reaction mixture leads to an increase
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7 in the conductivity of the solution. The use of high temperatures leads to an increase in seaweed
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9 conversion into gas and liquid products, thus decreasing the solid yield. As such, ashes, primarily
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11 alkali metals, are more accessible to water and could be more easily leached to the liquid phase.
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13 The effect of the reaction time does not depend on the feedstock mixture composition or the
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15 reaction temperature. In particular, the conductivity decreases between 0 and 30 min and increases
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17 with a subsequent increase in the reaction time up to 60 min, for all feedstock mixture
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19 combinations and reaction temperatures. This increase might be accounted for by the positive
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21 effect of the reaction time on biomass conversion, which makes the ash content of the biomass
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23 more accessible to water, following the un-reacted core shrinking model, thus increasing metal
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25 leaching into the hydrolysate as solid depolymerises.
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32 **Elemental composition and calorific value of the solid phase**

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35 The relative amounts of C, H, O and N in the solid product vary by 37-62 wt.%, 5-6wt.%, 31-
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37 57 wt.% and 0-2 wt.%, these variations shifting the HHV of the material between 13 and 25 MJ/kg.
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39 The cause-effect Pareto analysis reveals that the relative amounts of C and N are primarily affected
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41 by the feedstock composition. At the same time, the proportion of H is substantially influenced by
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43 the reaction time, the proportion of O and HHV mainly depending on the reaction time and
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45 temperature. Besides, feedstock synergistic/antagonistic effects take place for the proportions of
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47 C, H and N. The contribution of the quadratic value of the feedstock in comparison to the total
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49 feedstock influence $F^2/(F^2+F)$ is as follows 75, 100 and 55%. Figure 4 shows the effects of the
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51 operating conditions and feedstock mixture on the elemental composition and HHV of the liquid
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53 phase. In particular, Figure 4 a/b/c shows the effects on the proportion of C in the solid phase of
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3 the feedstock composition (seaweed, wheat straw and all possible binary combinations at the
4 lowest (80 °C) and highest (250°C) temperature for a 0/30/60 min reaction time. These effects are
5 shown in Figures 4 d-f, g-i, j-l, m-o, for the relative amounts of H, O N and the HHV of the solid
6 product.
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12 The elemental analysis and HHV of the solid product depend on the feedstock composition. In
13 particular, irrespectively of the temperature or reaction time, the solid derived from the treatment
14 of pure wheat straw contains more significant proportions of C and H as well as lower amounts of
15 O and N than the solid produced during the treatment of seaweed. A material with a higher HHV
16 is produced with pure wheat straw compared to seaweed. These variations are in good agreement
17 with the elemental analysis of the original feedstocks. The progressive addition of seaweed into
18 the feedstock mixture leads to decreases in the proportions of C and H and the HHV together with
19 increases in the relative amount of O and N. The variations in the proportions of C, H and N depend
20 on the composition of the reaction mixture due to the existence of synergistic and antagonistic
21 effects as described earlier. In particular, an initial increase from 0 to 60 wt.% in the proportion of
22 seaweed in the reaction mixture does not significantly modify the relative amounts of C or N, while
23 a further increase up to 100 wt.% decreases the C and increases the N. Conversely, the proportion
24 of H decreases as the relative amount of seaweed in the feedstock mixture rises up to 60 wt.%. In
25 contrast, the increase and the decrease respectively observed for the proportion of O and HHV
26 depict a linear evolution. These developments might be the result of two opposing effects. On the
27 one hand, *Laminaria Saccharina* has lower C content and higher O content. Therefore, the
28 proportion of C and O in the feedstock mixture decreases and increases, respectively, when the
29 amount of this material increases. On the other, the solubilisation of cellulose and hemicellulose
30 into the liquid phase results in a solid product with higher C and lower O due to the increase in the
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3 proportion of lignin in the spent solid material ⁶⁸ . Lignin has higher C, lower O and similar H
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5 content than the biomasses used in the present work, which logically results in a solid product with
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7 a higher C content and a lower O content. Therefore, the compensatory influence of both
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9 developments (one increases and the other decreases the amount of C) can be responsible for the
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11 steady evolution observed for the C content when small amounts of *Laminaria Saccharina* are
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13 introduced in the feedstock mixture.
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17 The effect of the temperature does not depend on the reaction time or feedstock composition.
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19 Increasing the temperature between 80 and 250 °C leads to an increase in the proportions of C and
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21 N along with a decrease in the proportion of O, which increase the HHV of the solid. These
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23 variations are thought to be the consequence of the positive kinetic effect of the temperature on
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25 the process, which lead to a greater spread of decarboxylation and deoxygenation reactions ^{18, 19}.
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27 Furthermore, they also depend on the feedstock mixture composition; the greater the proportion of
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29 seaweed in the feedstock mixture, the more pronounced are the variations observed for the
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31 elemental composition and the HHV of the solid product due to the greater reactivity of this
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33 biomass as well as the lower solid yield obtained with this feedstock as commented earlier. The
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35 effect of the reaction time mostly depends on the temperature. At low temperature, the reaction
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37 time does not exert a high impact on the elemental composition or the HHV of the solid.
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39 Conversely, as the temperature increases, the effect of the reaction time becomes more and more
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41 important. This mostly affects the relative amounts of C and O as well as the HHV. As such, at
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43 high temperature (250 °C) and regardless of the feedstock composition, an increase in the reaction
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45 time leads to a rise in the proportion of C together with a decrease in the relative amount of O, thus
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47 leading to an increase in the HHV of the solid product. These variations are accounted for by the
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more prolonged exposure of the material to microwave heating, which results in a more significant extension of decarboxylation and deoxygenation reactions^{18,19}.

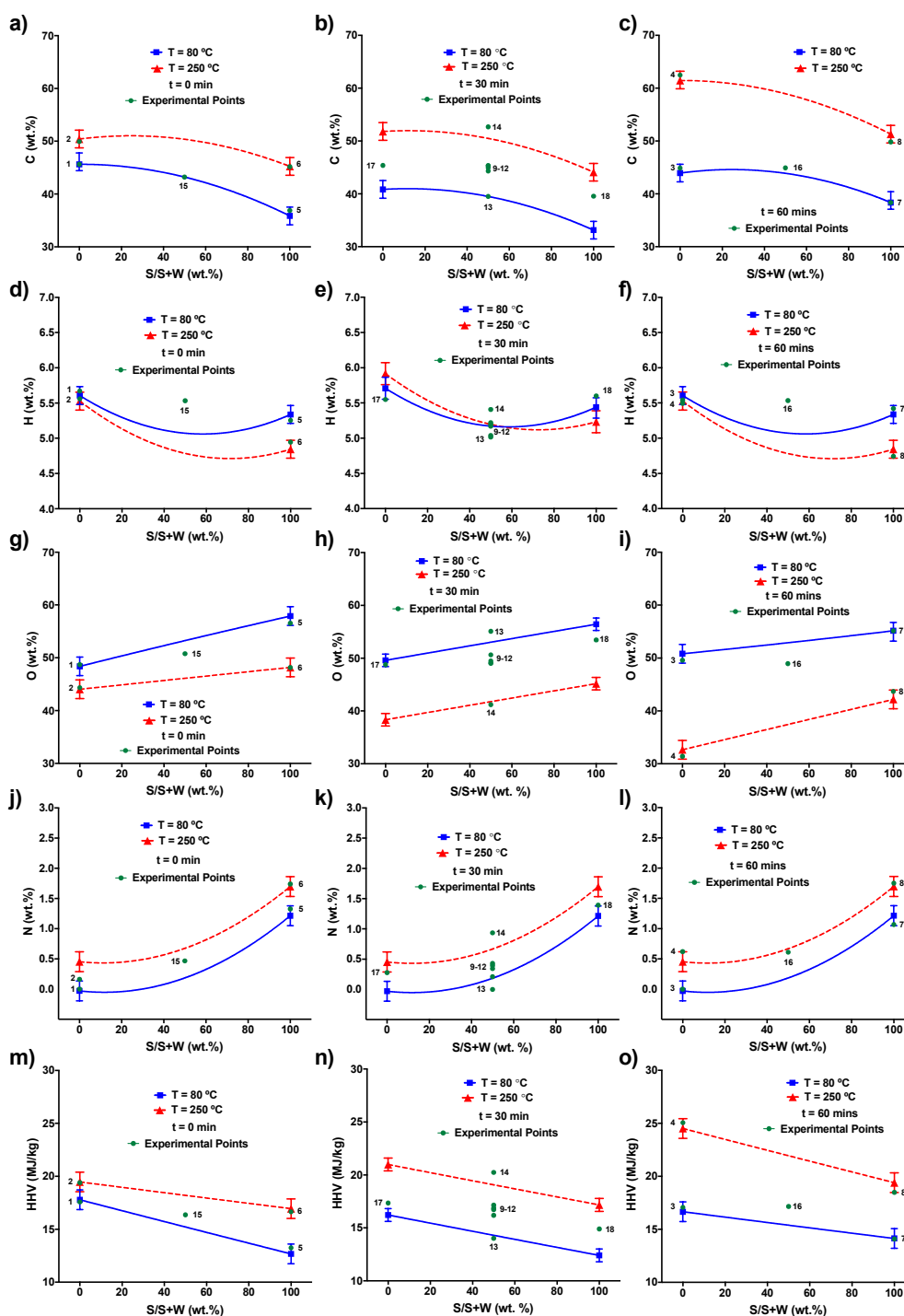


Fig. 4. Interaction plots between the feedstock composition (Seaweed/Seaweed+Wheat Straw) and the temperature using different reaction times for the elemental composition: C (a-c), H (d-f), O (g-i) and N (j-l) and the HHV of the solid product at 0, 30 and 60 min, respectively.

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3 To gain a more in-depth insight into the synergistic effects within feedstocks, the solids
4 produced in Runs 17, 10 and 18 were characterised by means of proximate analysis. Besides, an
5 ash balance was conducted considering the products (gas, liquid and solid) yields. These
6 experiments were conducted at intermediate conditions (165 °C and 30 min) using a feedstock
7 mixture comprising: pure wheat straw, a 50/50 wheat straw/seaweed mixture and pure seaweed,
8 respectively. The results of these analyses are summarised in Table 5. These results show that
9 metal leaching does not occur to a substantial extent when wheat straw is used as the feedstock at
10 intermediate operating conditions (around 92 wt.% of the initial ash content remains in the spent
11 solid material). Conversely, leaching becomes very important when seaweed is used in the process.
12 In this case, the spent solid contains only around 32 wt.% of the initial ash content of the feedstock.
13 In addition, the ash recovery from a feedstock mixture containing half of each biomass (Run 10)
14 is lower than the average individual value obtained with each biomass, thus denoting a positive
15 synergetic effect, as described earlier. This provides evidence for the higher conductivity and lower
16 pH of the liquids obtained with seaweed than those produced during the treatment of wheat straw.
17 Besides, the solubilisation of metals into the liquid phase together with the positive catalytic effect
18 of these species in hydrolysis, cracking and decarboxylation reactions are in line with these
19 observations. These metals also aid to polarise water, thus increasing the concentration of protons
20 in the liquid medium, which promotes acid catalysed reactions to take place. These developments
21 can explain the higher gas formation occurring with seaweed than with wheat straw, as well as the
22 higher reactivity of the former. The presence of metals also helps shift the reactions occurring in
23 the liquid phase towards the formation of small oxygenates, such as carboxylic acids. The presence
24 of these acids, together with a higher concentration of metals in the liquid might result in the
25 formation of ‘a pool of active catalytic species’ which might be responsible for most of the
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synergistic effects resulting from the addition of seaweed in the depolymerisation of wheat straw and open the door for the development of new bio-refinery processes.

Table 5. Proximate analysis and ash recovery balance of solid produced after reaction.

Run	S/S+W (wt.%)	Moisture (wt.%)	Volatiles (wt.%)	Fixed Carbon (wt.%)	Ash (wt.%)	Remaining ash (wt.%)
17	0	2.89	62.16	21.27	5.84	92.38
10	50	3.94	51.95	5.67	5.15	37.51
18	100	3.78	57.41	24.62	10.35	31.60

Process optimisation: towards a non-seasonal bio-refinery

Five possible different optima were sought using the empirical correlations developed from the ANOVA analysis of the results. A relative importance (from 1, the least important to 5, the most important) has been assigned to each constraint to come up with operating conditions meeting all the restrictions. Optimisations 1-4 are directed towards the production of aqueous sugar-rich solutions from wheat straw and/or *Laminaria Saccharina* (seaweed). For these optimisations, the liquid yield is maximised, while the gas and solid yields are also minimised to ensure the selective transformation of the feedstock into liquid products. In addition, the relative amounts of oligosaccharides and saccharides in the liquid have been maximised, and the proportions of carboxylic acids, ketones and furans minimised to make sure the liquid phase contains a high amount of sugars. For Opts. 1 and 2, the S/S+W ratio has been fixed to 0 and 100 wt.%, to find optimum conditions for the valorisation of wheat straw and seaweed, respectively. Conversely, for Opts. 3 and 4 the amount of seaweed in the feedstock mixture has been minimised (with different restriction criteria, i.e., relative importances of 3 and 5 respectively) to calculate the minimum amount of seaweed required to improve the reactivity of wheat straw. Opt. 5 considers the production of a solid bio-fuel from the co-valorisation of seaweed and wheat straw, thus maximising the solid yield and the HHV of the solid product. Table 6 list the optimisation

restrictions and the optimisation results, including both theoretical and experimental values for each optimum.

Table 6. Theoretical optimisation: constraints and predicted experimental values attained.

Optimisation	1			2			3			4			5		
	Obj.	Pred.	Exp.	Obj.	Pred.	Exp.	Obj.	Pred.	Exp.	Obj.	Pred.	Exp.	Obj.	Pred.	Exp.
T (°C)		197			193			215			214		Min (3)	250	
t (min)		35			18			37			41		Max (3)	60	
S/S+W (wt.%)	Fixed	0		Fixed	100		Min (3)	57		Min (5)	36		Min (3)	72	
Overall Product distribution															
Gas yield (%)	Min (3)	14.8±0.8	14.05	Min (3)	21.6±0.8	19.25	Min (3)	24.7±0.8	23.05	Min (3)	21.7±0.8	21.20	Min (3)	30.7±1.37	31
Liquid yield (%)	Max (3)	19.2±3.6	21.80	Max (3)	46.1±3.6	40.65	Max (3)	31.3±3.6	30.75	Max (3)	28.0±3.6	26.19	Min (3)	31.0±3.97	32
Solid yield (%)	Min (3)	63.9±5.4	64.15	Min (3)	38.8±5.4	40.10	Min (3)	43.1±5.4	46.20	Min (3)	48.0±5.4	52.61	Max (3)	37.6±4.89	37
Liquid composition (C-wt.%)															
Oligo. DP>6	Max (4)	46.9±1.8	50.59	Max (5)	33.8±1.8	35.52	Max (5)	36.5±1.8	37.00	Max (5)	37.4±1.8	38.54		32.1±0.78	31.51
Oligo. DP3-6	Max (4)	32.3±1.1	21.58	Max (5)	41.8±1.1	49.25	Max (5)	38.5±1.1	27.86	Max (5)	39.4±1.1	25.90		32.9±0.62	31.13
Saccharides	Max (5)	9.1±0.4	13.32	Max (5)	20.4±0.4	10.08	Max (5)	15.6±0.4	21.53	Max (5)	12.4±0.4	21.40		20.6±0.01	21.30
C. Acids	Min (5)	7.8±0.4	8.37	Max (5)	2.5±0.4	2.56	Max (5)	5.1±0.4	7.65	Max (5)	6.1±0.4	12.81		7.1±0.03	7.34
Ketones	Min (5)	0.9±0.02	0.49	Max (5)	0.1±0.02	0.00	Max (5)	1.2±0.02	0.38	Max (5)	1.2±0.02	0.00		3.7±0.62	4.23
Furans	Min (5)	3.1±0.03	5.64	Max (5)	1.5±0.03	2.59	Max (5)	3.1±0.03	5.57	Max (5)	3.7±0.03	1.35		4.9±0.88	4.49
Liquid properties															
pH		3.9±0.05	3.94		4.4±0.05	4.47		3.9±0.05	3.84		3.8±0.05	3.50		4.0±0.05	3.95
Conduct. (mS)		0.6±0.05	0.70		10.1±0.05	10.50		5.5±0.05	5.70		3.6±0.05	3.55		8.1±0.05	8.23
Solid composition and calorific value															
C (wt.%)		48.7±1.3	47.95		40.3±1.3	40.10		48.3±1.3	48.45		50.0±1.3	49.73		56.2±1.3	55.10
H (wt.%)		5.7±0.1	5.85		5.6±0.1	5.56		5.1±0.1	5.05		5.2±0.1	5.14		4.7±0.1	4.95
O (wt.%)		43.6±0.7	45.75		52.2±0.7	52.78		45.4±0.7	45.77		43.7±0.7	44.8		39.8±0.7	39.05
N (wt.%)		0.4±0.1	0.45		1.6±0.1	1.56		0.7±0.1	0.73		0.4±0.1	0.33		0.9±0.1	0.90
HHV (MJ/kg)		19.8±0.7	18.91		15.2±0.7	15.12		18.4±0.7	18.14		19.4±0.7	18.79	Max (5)	20.6±0.7	21.04

Opts. 1 and 2 show that a temperature of around 190 °C is required for the transformation of wheat straw or Laminaria Saccharina into an aqueous, sugar-rich solution. However, a slower reaction time is necessary for the alga (18 min) than for the lignocellulosic biomass (35 min) due to the higher reactivity of the former than that of the latter. At these conditions, it is possible to convert up to 19 wt.% of wheat straw and 46 wt.% of Laminaria Saccharina into a sugar-rich aqueous solution with a purity (oligosaccharides and saccharides) of 85 and 95 C-wt.%, respectively. This highlights the high selectivity and excellent controllability of this microwave-assisted process for the selective transformation of 2G and 3G biomasses into sugar-rich carriers. Besides, Opts. 3 and 4 show that using a temperature of 215 °C for around 40 min, it is possible to synergistically increase the liquid yield produced with wheat straw by introducing a proportion of

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3 seaweed (between 36 and 57 wt.%) in the feedstock mixture. Under these conditions, it is possible
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5 to transform around 30 wt.% of the solid material into a sugar-rich aqueous solution with a purity
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7 of approximately 90 C-wt.%. Besides, the spent solid material has a HHV of around 19 MJ/kg,
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9 which is much higher than those of the individual feedstocks. This is the result of the synergistic
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11 effect of seaweed on wheat straw depolymerisation, which allows increasing the liquid yield
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13 obtained with wheat straw, without compromising the oligosaccharide purity of the liquid solution.
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15 Regarding solid biofuels production, Opt. 5 shows that it is possible to transform up to 38 wt.% of
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17 the initial solid material into a solid product with a HHV of 21 MJ/kg by co-feeding 72/28 wt.%
18
19 seaweed/wheat straw. Therefore, these promising results might represent a step-change towards
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21 the development of new and environmentally friendly, 5G bio-refineries for the simultaneous co-
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23 valorisation of algae and lignocellulose biomass. This is a landmark achievement to render the
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25 entire bio-refinery concept for biomass valorisation economically competitive, aiding to decrease
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27 the feedstock dependency of current bio-refinery models.
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35 CONCLUSIONS

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37 This investigation has explored the synergistic co-valorisation of wheat straw (2G, lignocellulosic
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39 biomass) and *Laminaria Saccharina* (3G, alga biomass) for the production of sugar-rich aqueous
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41 solutions by microwave-assisted hydrothermal depolymerisation. Under the conditions tested, not
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43 only was seaweed more reactive than wheat straw but also it exerted a positive effect on wheat
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45 straw depolymerisation, hydrolysis, decarboxylation, dehydration and thermal carbonisation
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47 reactions. The optimisation of the process revealed that operating at a temperature of 190 °C, it
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49 was possible to individually convert up to 19 wt.% of pure wheat straw and 46 wt.% of pure
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51 *Laminaria Saccharina* into an aqueous sugar-rich solution (purity >85 C-wt.%) using a reaction
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3 time of 18 and 35 min, respectively. Besides, increasing the temperature up to 215 °C for around
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5 40 min, it was possible to synergistically enhance the liquid yield produced with wheat straw by
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7 introducing a proportion of seaweed (from 36 to 57 wt.% with respect to the total solid content) in
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9 the feedstock mixture. These conditions allowed transforming around 30 wt.% of the solid material
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11 into a high purity (90 C-wt.%) aqueous sugar solution. Besides, 38 wt.% of the initial solid material
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13 can be converted into an energy-rich solid product (HHV of 21 MJ/kg) by co-feeding 72/28 wt.%
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15 seaweed/wheat straw at 250 °C for 60 min. The greater reactivity of seaweed than that of wheat
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17 straw, as well as the synergistic effects of the former on the depolymerisation of the latter, were
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19 accounted for by the formation of ‘a pool of active catalytic species’. Metals in seaweed were
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21 activated by microwaves and kinetically promoted the catalytic decomposition of this material
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23 with negligible mass transfer limitations, due to their excellent integration into the biomass core
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25 structure. As seaweed depolymerised, these metals were more accessible to water and leached into
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27 the solution. These species aided to polarise water, thus increasing the concentration of protons in
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29 the liquid medium, which promoted acid catalysed reactions to take place. This represents an
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31 exciting area of research, and future work should be directed towards the investigation of which
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33 metal/s, or interactions between metals are responsible for the catalytic effects using real biomass.
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35 Therefore, these synergistic effects represent a step-change for the development of novel ‘non-
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37 seasonal, non-feedstock dependent’ 5G bio-refineries.
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46 47 **ACKNOWLEDGEMENTS**

48
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Supporting Information

Chemical composition of the liquid phase showing the species belonging to each chemical family.

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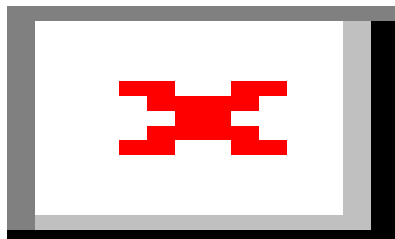
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A novel 'non-seasonal, non-feedstock dependent' 5G bio-refinery by Microwave-assisted, synergistic, co-depolymerisation