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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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KEYWORDS: Bio-refinery, biomass, synergetic co-valorisation, value-added chemicals, autocatalysis, microwave heating.

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

INTRODUCTION

The development of advanced bio-refinery processes and novel strategies for the valorisation of biomass into platform chemicals, value-added products and/or energy carriers is critical to progressively diminish human dependence on crude oil. In this line, biomass is regarded as an excellent feedstock for the production of these commodities. This is the result of biomass being the only renewable source of carbon that can be converted into gas, liquid and solid products [1]. Therefore, this emerging bio-refinery philosophy focused around the valorisation of biomass wastes and residues is directly linked to the context of circular economy and connects very well with the United Nations Sustainable Development Goals (UN SDGs), as societies currently strive towards a greener and more sustainable future [2].

One of the most promising routes for biomass valorisation is the exploitation of its carbohydrate content for the production of aqueous sugar-rich carriers [3-5]. This approach allows the transformation of biomass into a liquid solution, containing soluble oligosaccharides and saccharides, that can be used as a feedstock in many subsequent processes. The applications include the production of fuels, advanced materials and chemicals [6], while the procedures range from biological to thermochemical routes such as fermentation, hydrogenation, hydrolytic hydrogenation and aqueous phase/gas phase reforming [7]. Among the different processes to produce saccharide-rich solutions from biomass, microwave-assisted hydrothermal depolymerisation is an up-and-coming alternative [8-10]. This route allows the selective and precise depolymerisation of biomass into soluble, low molecular weight oligosaccharides and saccharides, substantially avoiding the subsequent degradation of these species into low value or unwanted products [11]. This is accounted for by microwave-assisted depolymerisation being an outstanding technology to strike an excellent compromise between a first biomass selective depolymerisation and the subsequent degradation of the saccharides produced. In particular, microwave heating is decidedly advantageous if used appropriately. The excellent controllability of microwave heating, combined with water, an excellent microwave absorber, at hydrothermal conditions, permit that sugar degradation does take place to a lesser extent than when acid- or alkali-hydrolysis are used [12-15], but also this process is much faster than other routes such as acid or enzymatic treatments [12, 16].

Another essential advantage of this microwave-assisted treatment is the conservation of the biomass core carbohydrate structure in the form of water-soluble oligosaccharides [2, 17]. This represents a conservative and smart strategy to help increase the reactivity of biomass (as the entropy of the feedstock is substantially increased when being converted from a solid to a liquid state) without significantly altering its chemical nature, and therefore, this step does not substantially hamper its future applications. Moreover, it also facilitates the use of recoverable solid catalysts in subsequent valorisation processes, thus avoiding mass transfer limitations occurring when solid catalysts are used for the upgrading of solid biomass [18, 19]. Also, microwave-assisted hydrothermal depolymerisation is extremely adaptable and can be applied efficiently for the pre-treatment and/or upgrading of different biomasses, including both second (2G) and third (3G) biomass generations [12-15]. 2G biomass primarily comprises non-edible lignocellulosic materials and wastes, which structurally consist of cellulose, hemicellulose and lignin [20]. 3G biomass involves micro- and macroalgal matter, which is mostly made up of active compounds (proteins, nucleic acids and lipids) and carbohydrates such as cellulose, hemicellulose and alginic acid, among others [21, 22].

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

This co-valorisation strategy has recently emerged and been tested in biomass hydrothermal liquefaction [24], pyrolysis [25, 26] and sub/supercritical treatments [27] using conventional heating. Among the different possible biomass combinations, the co-valorisation of lignocellulosic biomass (2G) and (micro/macro) algae (3G) biomass might be a fascinating approach for the development of non-seasonal, synergistic, new bio-refineries; i.e. '5G bio-refineries'. This idea has been only proved during the hydrothermal liquefaction of biomass using conventional heating. In particular, Gai et al. [28] addressed the co-valorisation of rice husk with *Chlorella Pyrenoidosa*, analysing the effects of the temperature (200-350 ºC), reaction time (10-90 min), solid loading (10-30 wt.%) and feedstock composition (0-100 *Chlorella Pyrenoidosa*/rice husk wt.%). They reported that increasing the algae content resulted in an increase in the bio-oil yield and a decrease in the solid yield. The reductions occurring in the ash and lignin contents of the feedstock when increasing the proportion of *Chlorella Pyrenoidosa* in the mixture were responsible for such variations. Chen et al. [29] co-liquefied swine manure and microalgae in different ratios at 300 ºC for 60 min. They found that the more significant the proportion of swine manure in the mixture, the higher was the bio-oil yield. Brilman et al. [30] studied the co-valorisation of sugar belt pulp (micro-algae) with pinewood at a temperature ranging from 250 to 350 ºC. They suggested that the presence of microalgae degradation intermediate products, such as organic acids, enhanced the decomposition of pinewood. Feng et al. [31] carried out the co-liquefaction of Spartina alterniflora (lignocellulosic) and *Spiritulina* (lipid-rich microalgae) using temperatures between 260 and 320 ºC for 30 min. A synergetic effect was observed when both feedstocks were mixed at 1:1 weight ratio, which resulted in a significant increase in the bio-oil yield. Sintamarean et al. [32] co-liquefied willow wood with brown, red and green seaweeds. Several synergistic effects were observed. These were accounted for by the presence of organic acids produced during the co-liquefaction, which increased the bio-oil yield and improved its physicochemical properties.

These publications provide valuable insights into the synergistic hydrothermal co-valorisation of 2G and 3G biomasses using conventional heating. However, to the best of the author's knowledge, microwave-assisted hydrothermal co-depolymerisation of biomass has not been yet reported. Microwave heating is based on the high-frequency rotation of polar molecules, which produces quicker and higher heat of the species with high polarity [33-40]. Carbohydrates, including both cellulose and hemicellulose, are much polar than lignin. As a consequence, they are more likely to interact with microwaves, which favours the solubilisation of the carbohydrate matter without substantially dissolving the lignin fraction [41, 42]. Nevertheless, it is also important to note that the elevated crystallinity of cellulose in combination with the strong hydrogen bonds within its structure hamper the depolymerisation of this carbohydrate [43, 44]. A possible solution already adopted to overcome this issue was the addition of a homogeneous catalyst such as acetic acid, which allowed the solubilisation of the cellulose and hemicellulose in lignocellulosic biomass without dissolving its lignin content [41].

Taking these features into account, new bio-refinery models should be directed towards autocatalytic and more efficient processes, i.e., taking advantages of possible catalytic synergies between materials. For example, algae biomass contains a substantial amount of metals, these being excellent absorbers of microwave radiation [45]. This higher metal content might result in greater reactivity of algae biomass than lignocellulosic biomass when subjected to microwave heating. This could be smartly used to increase the reactivity of 2G biomass and develop new bio-refinery models. Besides, metals may be leached to the reaction medium during the hydrothermal treatment [46] and/or interact with lignocellulosic biomass if the stirring is appropriate. Therefore, these features can contribute to increasing the reactivity of 2G biomass if both feedstocks are treated in the same unit. Moreover, the higher reactivity of 3G biomass in comparison with 2G biomass also results in a greater spread of hydrolysis reactions of the former than the latter biomass, thus leading to the formation of carboxylic acids from 3G biomass, which might act as 'in-situ produced catalytic species' to increase the reactivity of lignocellulosic 2G biomass [32]. As such, these intrinsic peculiarities of microwave heating together with the different behaviours of 2G and 3G biomasses under microwave radiation might potentiate synergetic effects between both materials, thus opening the door for the development of advanced and more efficient processes that take advantages of these features.

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

EXPERIMENTAL

Microwave experiments

The experiments were conducted in a Milestone Synth-Wave microwave unit previously described in detail [18, 19, 47]. Briefly, it comprises a 1L stainless steel reactor cooled with water capable of achieving high temperatures and pressures, in which microwave radiation is generated by a magnetron directly connected to the bottom of the reactor. The microwave power to achieve the desired temperature is controlled by a PID control with the aid of a thermowell placed inside the reactor. The pressure is monitored with a pressure sensor connected to a pressure gauge. For the experiments, firstly, 20 g of solid (either the individual feedstock or the binary mixtures) together with 400 mL of deionised water were placed into the reactor to achieve a solid/water ratio of 1/20 (g/g). Subsequently, the reactor was closed, leak tested and purged with nitrogen to remove the air of the system. Before the heating step, the reactor was pressurised with 15 bar (at 25 ºC) of N_2, to make sure all the reactions take place in the liquid phase. For all runs, a 15 min of ramp time (time to reach reaction conditions from 25 ºC) was employed. After the reaction, the reactor was chilled until a temperature of 60 ºC was achieved using a rate of 12 ºC/min. Once the reactor was cooled, the mass of the reactor vessel was recorded and its content, mainly consisting of a liquid phase (hydrolysate) and a spent solid material, was transferred to a plastic centrifuge container. The liquid fraction was separated from the solid residue by low temperature, high-speed centrifugation (8 °C, 3500 rpm, 20 minutes). Subsequently, the liquid phase was stored for further analysis, whereas the solid was desiccated for 24h at 105 ºC.

Experimental design and statistical analyses

The influences on the process of the feedstock composition, calculated as the relative amount of wheat straw (0-100 wt.%) with respect to the total amount of solid (wheat straw/wheat straw + Laminaria Saccharina), the reaction temperature (80-250ºC) and reaction time (0-60 min) were analysed experimentally through a 2 level 3 factor (2^3) Box-Wilson Central Composite Face Centred (CCF, α: ±1) design. These intervals of variation were selected based on our previous publications. Besides, a biomass/water ratio of 1/20 (g/g) was used for the experimentation as it represents an energy-efficient option to maximise liquid production based on our previous work [2, 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	$\text{Liquid yield (\%)} = \frac{\text{liquid compounds (g)}}{\text{mass of biomass (g)}} 100 = 100 - (\text{Gas yield} + \text{Solid yield})$	Balance
	$\text{Composition (C} - \text{wt.\%)} = \frac{\sum \text{mass of C of each compound(g)}}{\text{total mass of C in solution (g)}} 100$	HPLC and elemental analysis
	$\text{C, H, O (wt. \%)} = \frac{\text{mass of C, H, O,N (g)}}{\text{mass of liquid(g)}} 100$	Elemental Analysis
	pH	pH-meter
	Conductivity (mS)	Conductivimeter
Solid	$\text{Solid yield (\%)} = \frac{\text{mass of solid (g)}}{\text{mass of biomass (g)}} 100$	Gravimetric
	HHV (MJ/kg) = 0.3491 C (wt.%) + 1.1783 H (wt.%) – 0.1034 O (wt.%) – 0.015 N (wt.%) + 0.1005 S (wt.%)	Estimated
	$\text{C, H, O, N (wt. \%)} = \frac{\text{mass of C, H, O,N (g)}}{\text{mass of solid (g)}} 100$	Elemental Analysis
Gas	$\text{Gas yield (\%)} = \frac{\text{mass of gas (g)}}{\text{mass of biomass (g)}} 100$	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 determined as the difference between the total organic carbon (TOC) of the solution and the C quantified by HPLC. More detailed information about the characteristics, experimental conditions used in the analyses and separation columns can be found in the ESI and our previous publication [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 °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 lignin [48]; the protein content being calculated using N content quantified by elemental analysis [49]. 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 straw [50-52] and Laminaria Saccharina [53].

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

Feedstock	**Wheat Straw**	***Laminaria Saccharina***
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 (ºC)	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^2t	T^2F	Tt^2	T^2t^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 (13)	2.18 (22)	0.95 (9)	-0.59 (5)	0.44 (4)	1.64 (16)	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 T^2 · T^2 + coefficient t^2 · t^2 + coefficient F^2 · F^2 + coefficient TtF · T·t·F + coefficient T^2t · T^2·t + coefficient T^2F · T^2·F + coefficient Tt^2 · T·t^2 + coefficient T^2t^2 · T^2·t^2.

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 this variable, which accounts for a mere dilution effect. Figure 1 shows the full effects of the feedstock mixture, reaction conditions and all the interactions between these variables detected according to the ANOVA analysis. In particular, Figure 1 a/b/c shows the effect of the feedstock composition (seaweed, wheat straw and all possible binary combinations) at the lowest (80 ºC) and highest (250ºC) temperature for a 0/30/60 min reaction time. These effects are shown in Figures 1 (d-f) and Figure 1 (g-i) for the liquid and solid yield, respectively.

The effect of the feedstock mixture on the gas yield depends on the temperature and reaction time. On the one hand, at low temperature (80 ºC), the effect of the feedstock composition is negligible, and irrespectively of the solid mixture (seaweed, wheat straw or any binary mixture), the gas yield is meagre. This suggests that hydrolysis and depolymerisation reactions are the essential routes responsible for depolymerisation, whereas pyrolysis and decarboxylation reactions [54-56], which promotes gas formation [57, 58], are not favoured at low temperature. However, increasing the reaction time increases gas formation when the reaction mixture is enriched in seaweed, which indicates that seaweed is more reactive than wheat straw at these reaction conditions, especially using long reaction times. This development can be the consequence of the lower lignin content and the higher protein and ash contents of Laminaria Saccharina in comparison to wheat straw. The gas formation can increase due to proteins decomposition into gaseous products via decarboxylation and deamination reactions [57, 58]. Besides, the more significant proportion of ashes in Laminaria Saccharina can facilitate the gas formation, as these species exert a positive catalytic effect on pyrolysis and gasification reactions [59-63]. The evolution depicted by the gas yield is not linear, showing an initial increase from a feedstock mixture consisting of pure wheat straw up to a mixture containing half of each biomass, which indicates a positive synergistic effect of seaweed on wheat straw decomposition towards the gas formation. An increase in the reaction temperature increases the gas yield irrespectively of the feedstock composition or reaction time. This is accounted for by a more significant development of pyrolysis and decarboxylation reactions when increasing the reaction time at high temperature [54-56], thus leading to gas formation [57, 58]. However, the increases observed are more pronounced as the proportion of seaweed in the feedstock increases.

On the other hand, at high temperature (250 ºC), an increase in the proportion of seaweed leads to a pronounced increase in the gas yield, thus indicating that seaweed is more likely to produce gaseous products than wheat straw due to its higher reactivity as described above. Besides, the increase observed in not linear, which suggests that seaweed exerts a positive synergetic effect on wheat straw conversion to gaseous products. The greater reactivity of seaweed in comparison to wheat straw leads to an increase in the proportion of secondary products, such as organic acids. These acids might exert a positive catalytic effect of wheat straw depolymerisation [30], as they can act as a form of auto-catalysis [32]. The impact of the reaction time depends on the temperature (Figure 1 a vs. b and c). While at low temperature, increasing the reaction time from 0 to 60 min does not substantially increase gas production regardless of the feedstock mixture, at high temperature, this same increase in the reaction time leads at first to a rise in the gas yield between 0 and 30 min, followed by a steady evolution when the reaction time increases up to 60 min. The combination of high temperatures and long reaction time promotes a higher spread of pyrolysis, decarboxylation and deamination reactions [17-19], thus increasing gas formation.

The effects of the feedstock mixture on the liquid and solid yields substantially depend on the reaction time. For a short reaction time, higher liquid yields are obtained with pure seaweed than with pure wheat straw regardless of the reaction temperature. An increase in the proportion of seaweed in the feedstock mixture leads to a rise in the liquid yield. The convex increase depicted by this variable indicates an antagonistic effect on liquid production, as the addition of seaweed favours gas formation over the liquid produced. This can be accounted for by a positive effect of seaweed on depolymerisation reactions accounted for the positive impact of metal particles under microwave heating [64, 65] together with their catalytic behaviour [61-63]. This leads to a greater spread of hydrolysis reactions, favouring the formation of small oxygenates in the liquid product that can be more easily converted to gas [2, 17]. The effect of the temperature depends on the feedstock composition. On the one hand, for pure wheat straw, increasing the temperature from 80 to 250 ºC does not increase the liquid yield. On the other side, as the reaction mixture is enriched in seaweed, this same increase in the temperature rises the liquid yield; the higher the proportion of seaweed in the mix, the sharper is the increment observed in the liquid yield due to the greater reactivity of seaweed than that of wheat straw as described earlier. Besides, increasing the temperature shifts hydrolysis reactions towards the production of carboxylic acids, these species being capable of assisting biomass depolymerisation, thus increasing the liquid yield. Besides, the effect of the feedstock composition on the solid yield does not depend on the temperature for a very short reaction time (0 min). Irrespectively of the temperature, higher solid yields are obtained with pure wheat straw than with pure seaweed due to the lower reactivity of the former than the latter, which hinders its transformation into gas and liquid products. An increase in the proportion of seaweed in the feedstock mixture linearly diminishes the solid yield, due to the absence of synergistic/antagonistic effects. This suggests that the positive impact of the addition of seaweed to wheat straw assist in the transformation of already solubilised liquid species, via enhancement of the chemical reactions occurring in the liquid phase. This can be the consequence of mass transfer limitations, which hampers their intimate contact [54, 55, 66], and thus avoiding possible synergistic effects to take place.

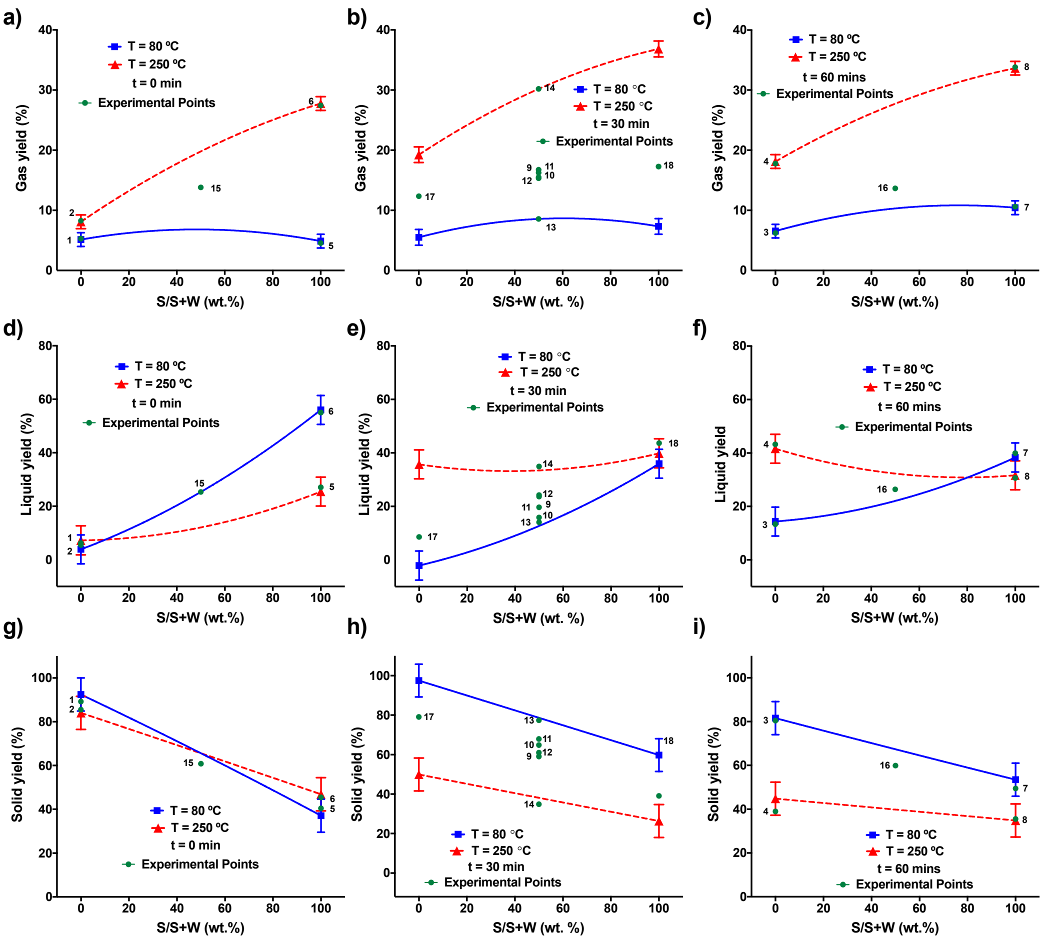

Fig. 1. Interaction plots between the feedstock composition (Seaweed/Seaweed+Wheat Straw) and the temperature using different reaction times for the yields to (a-c) gas, (d-f) liquid and (g-i) solid at 0, 30 and 60 min, respectively.

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

Chemical composition of the liquid phase

The liquid phase consists of a mixture of DP>6 oligosaccharides (0-85 C-wt.%), DP 2-6 oligosaccharides (0-95 C-wt.%), saccharides (4-27 C-wt.%), ketones (0-5 C-wt.%), carboxylic acids (0-12 C-wt.%) and furans (0-10 C-wt.%). The detailed chemical composition of the liquid phase is provided as supplementary material in Table S1. These results show that the proportions of oligosaccharides and saccharides account for more than 75 C-wt.% in all the cases, thus highlighting the selectivity of this microwave process for biomass transformation into sugar-rich aqueous carriers. The cause-effect Pareto analysis reveals that the temperature (including both linear and quadratic contributions) is the operating variable exerting the greatest influence, followed by the feedstock mixture, on the chemical composition of the liquid phase.

The significant influence of the quadratic coefficient of the feedstock mixture (F^2) reveals the existence of significant synergistic/antagonistic effects. In particular, the contribution of the quadratic value of the feedstock in comparison to the total feedstock influence $F^2/(F^2+F)$ is as follows: 28% for DP>6 oligosaccharides, 29% for PD2-6 oligosaccharides, 38% for ketones, 24% for carboxylic acids and 21% for furans. This indicates the existence of significant interactions between both feedstocks (wheat straw and seaweed) substantially affecting the chemical composition of the liquid phase. Figure 2 a/b/c shows the effects on the relative amount of DP>6 oligosaccharides of the feedstock composition (seaweed, wheat straw and all possible binary combinations at the lowest (80 ºC) and highest (250ºC) temperature for a 0/30/60 min reaction time. These effects are shown in Figures 2 d-f, g-i, j-l, m-o, p-r for DP2-6 oligosaccharides, saccharides, carboxylic acids, ketones and furans, respectively.

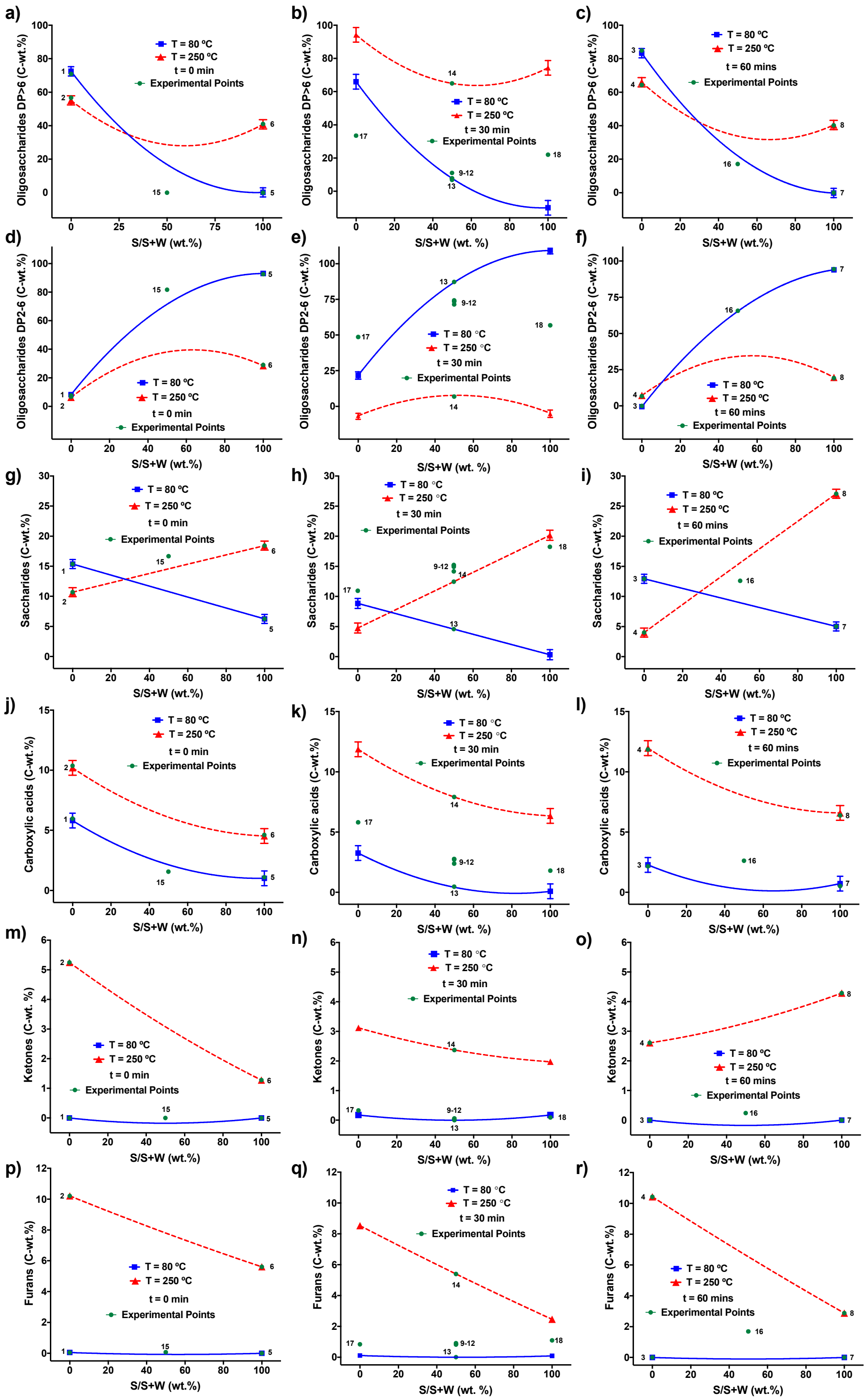

Fig. 2. Interaction plots between the feedstock composition (Seaweed/Seaweed+Wheat Straw) and the temperature using different reaction times for the chemical composition of the liquid phase: oligosaccharides DP>6 (a-c), oligosaccharides DP 2-6 (d-f), saccharides (g-i), carboxylic acids (j-l), ketones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

The effect of the feedstock mixture composition on the liquid composition primary depends on the temperature, the effects of the reaction time being less critical. When a low temperature (80 ºC) is used, the liquid phase mostly consists of oligosaccharides regardless of the reaction time or the feedstock mixture composition. In particular, for pure wheat straw, the liquid phase is made up of DP>6 oligosaccharides; however, as the feedstock mixture is enriched in seaweed, the proportion of DP>6 oligosaccharides decreases at the expenses of the relative amount of DP 2-6 oligosaccharides, due to the progressive transformation of the former into the latter species via hydrolysis [2, 17, 41]. This is thought to be a consequence of the greater reactivity of Laminaria Saccharina than that of wheat straw and could be accounted for by its greater contents in cellulose and hemicellulose as well as its more significant proportion of ashes. Ashes not only are sound microwave absorbers [64, 65], but also they have catalytic properties [61-63], which lead to a greater spread of hydrolysis and depolymerisation reactions. As a result, for pure seaweed, the liquid phase primary consists of DP 2-6 oligosaccharides.

In addition, the decreases and increases depicted by DP>6 and DP 2-6 oligosaccharides do not follow a linear trend. This denotes the existence of synergistic effects, and very interestingly, it allows achieving a complete DP>6 oligosaccharides depolymerisation into DP 2-6 oligosaccharides using a feedstock mixture having up to 30 wt.% of wheat straw; thus highlighting the importance of co-valorisation as a new bio-refinery strategy. Besides, at low temperature (80ºC), the proportions of saccharides and carboxylic acids are meagre. At the same time, the relative amounts of ketones and furans are negligible since low temperatures might hinder the extension of secondary reactions leading to the formation of these species [2, 17]. However, as the feedstock contains more seaweed, the relative amounts of saccharides and carboxylic acids in the liquid phase decrease down to negligible levels. This might be the result of two different developments. On the one hand, the higher reactivity of Laminaria Saccharina leads to a more significant extension of hydrolysis reactions towards the formation of carboxylic acids. These acids can be easily transformed into gaseous products [2, 17], thus decreasing their relative proportion in the liquid phase. On the other hand, wheat straw contains more hemicellulose and less cellulose than Laminaria Saccharina, which might favour carboxylic acids production as hemicellulose is more reactive under microwave heating [17]. Therefore, as the feedstock mixture is enriched in seaweed, the liquid product has a lower proportion of carboxylic acids.

An increase in the temperature modifies the chemical composition of the liquid phase. In general, an increase in the temperature leads to a decrease in the proportion of DP 2-6 oligosaccharides together with increases in the relative amounts of carboxylic acids, ketones and furans irrespectively of the feedstock composition. These variations are accounted for by the positive effect of the temperature on hydrolysis and depolymerisation reactions, which promotes sugars decomposition into secondary products [21, 22, 67]. Conversely, the effects of the temperature on the proportions of DP>6 oligosaccharides and saccharides depend on the reaction time and feedstock mixture composition. For a feedstock consisting of pure wheat straw and/or any mixture comprising less than 30 wt.% of seaweed, an increase in the temperature from 80 to 250 ºC decreases the relative amount of DP>6 oligosaccharides and saccharides, while for pure seaweed and/or any feedstock mixture having more than 30 wt.% of seaweed, this same increase in the temperature leads to improvements in the proportions of DP>6 oligosaccharides and saccharides. This might indicate that for pure seaweed and enriched-seaweed solids, the first depolymerisation/liquefaction reaction step, comprising the formation of water-soluble DP>6 oligosaccharides, is quicker than the subsequent transformation of these species into DP 2-6 oligosaccharides. As a result, increasing the temperature favours the conversion of DP 2-6 into saccharides as well as the subsequent transformation of these species into small oxygenates (carboxylic acids, ketones and furans). However, these transformations do not compensate for the more considerable amount of DP>6 oligosaccharides solubilised in the liquid product, and as a result, the proportion of DP>6 oligosaccharides increases. An exception to this occurs for a 30 min reaction, time at which increasing the temperature leads to an increase in the proportion of DP>6 oligosaccharides irrespectively of the feedstock mixture composition. As a result of these developments, at high temperature (250 ºC), although the liquid phase is primarily made up of oligosaccharides and saccharides, the presence of secondary products such as carboxylic acids, ketones and furans increases. The positive kinetic effect of the temperature on the process, leading to a greater spread of hydrolysis and depolymerisation reactions, might be responsible for such variations.

Regardless of the reaction time, the chemical composition of the liquid phase depends on the feedstock mixture. A higher proportion of DP>6 oligosaccharides and lower portions of DP 2-4 oligosaccharides and saccharides are obtained for pure wheat straw than for a feedstock consisting of pure seaweed. In addition, increasing the relative amount of seaweed in the feedstock mixture up 70 wt.% leads to a decrease in the relative amount of DP>6 oligosaccharides together with an increase in the relative amount of DP 2-6 oligosaccharides due to the progressive transformation of the former into the latter via hydrolysis reactions. A subsequent increase in the proportion of seaweed slightly increases the percentage of DP>6 oligosaccharides and decreases the proportion of DP 2-6 saccharides in the liquid product, as the first solubilisation step into DP>6 oligosaccharides could be faster than the subsequent transformation into lower molecular weight species, as described earlier. This suggests that microwaves might activate metals present in seaweed and, due to their catalytic properties, these metals could promote the first depolymerisation step aiding to the solubilisation of biomass into water-soluble species. The intimate contact between these metallic species and the biomass facilities the catalytic transformation of biomass into soluble oligosaccharides, while the effect of metals in the subsequent hydrolysis reactions might be less effective due to mass transfer limitations. The liquid phase contains a lower proportion of saccharides and higher proportions of carboxylic acids, ketones and furans with a feedstock consisting of wheat straw than with feeding pure seaweed. The presence of seaweed in the feedstock leads to a linear increase in the relative amount of saccharides together with linear decreases in the relative amount of ketones and furans. The relative amount of carboxylic acids decreases as the feedstock is enriched in seaweed, this drop displaying a concave decay, which denotes a synergetic effect between feedstocks. This decrease is accompanied by a concave increase in the proportion of gas, thus suggesting the possible transformation of these species into gases, denoting synergistically positive catalysis.

The effect of the reaction time depends on the temperature and feedstock composition. At low temperature (80 ºC), the effect of the reaction time does not depend on the feedstock composition, and similar evolutions are observed. An initial increase in the reaction time from 0 to 30 min leads to a small decrease in the proportion of DP>6 oligosaccharides and saccharides together with an increase in the relative amount of DP 2-6 oligosaccharides due to the transformation of DP>6 oligosaccharides into DP 2-6 oligosaccharides, along with sugars decomposition into small oxygenates. A further increase up to 60 min results in improvements in the proportions of DP>6 oligosaccharides and saccharides accompanied by a decrease in the concentration of DP 2-6 oligosaccharides. The relative amount of carboxylic acids decreases progressively as the reaction time increases from 0 to 60 min, while the proportions of ketones and furans are negligible at low temperature. At high temperature (250 ºC) increasing the reaction time leads to a first increase (0-

30 min) in the proportion of DP>6 oligosaccharides and a decrease in the concentration of DP 2-6 oligosaccharides due to the positive kinetic effect of the reaction time on biomass solubilisation into soluble oligosaccharides as well as the transformation of DP 2-6 oligosaccharides into saccharides and small oxygenates. A subsequent increase in time (30-60 min) decreases and increases in the proportions of DP 2-6 and DP>6 oligosaccharides, respectively. Increasing the reaction time facilitates the extension of hydrolysis reactions in the liquid phase, thus promoting oligosaccharides and saccharides decomposition into small oxygenates, such as carboxylic acids, furans and ketones. However, gas formation from small oxygenates is also favoured at high temperature and using long reaction times. As a result of the different reaction rates of the reactions involved, the liquid product is enriched in DP>6 oligosaccharides due to transformation of small oxygenates into gas. Besides, while, the proportion of carboxylic acids does not much depend on the reaction time and significant variations are not observed, the effect of the reaction time on the proportions of saccharides, ketones and furans depends on the feedstock mixture composition. For pure wheat straw, an increase in the reaction time leads to small decreases in the proportions of saccharides and ketones, the relative amount of furans being unaffected. Conversely, when the amount of seaweed in the feedstock increases, this same increase in the reaction time leads to a small increase in the proportion of saccharides and ketones along with a decrease in the relative amount of furans; though, these variations are not very important from a practical point of view.

Properties the liquid phase: pH and conductivity

The pH of the liquid phase varies from 3.29 to 6.67, while the conductivity shifts between 2.26 and 18.89 mS. According to the cause-effect Pareto principle, the reaction temperature and its interaction with the feedstock composition mixture are the operating variables exerting the most 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 ºC) and highest (250 ºC) temperature for a 0/30/60 min reaction time on the pH and conductivity, respectively.

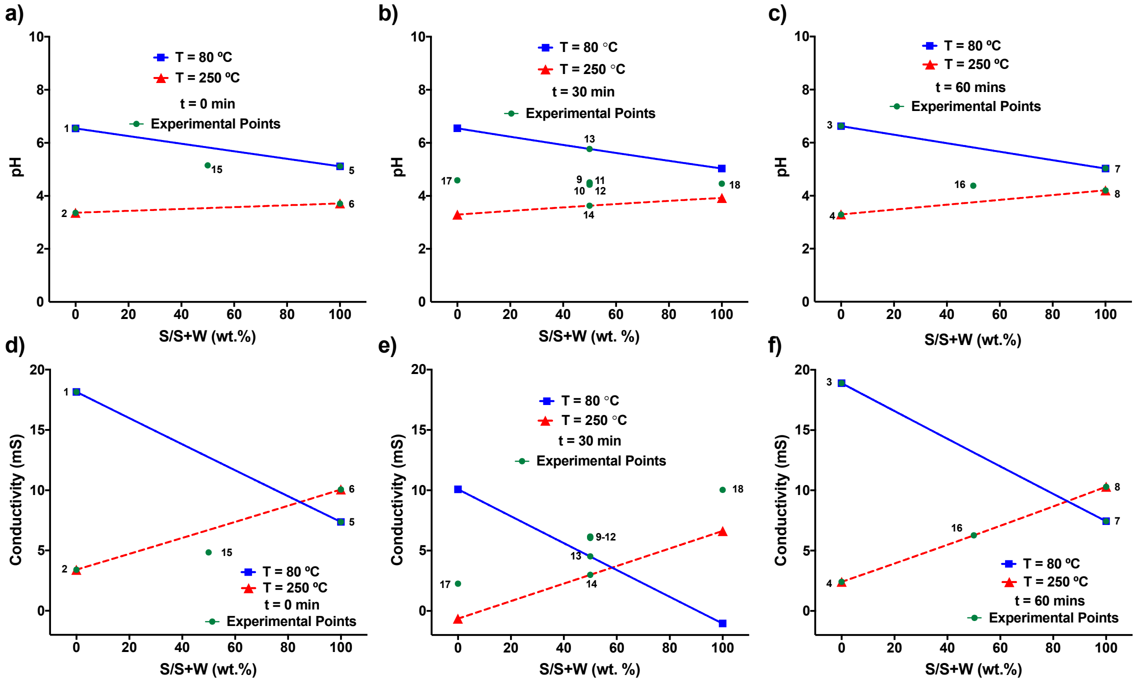

Fig. 3. Interaction plots between the feedstock composition (Seaweed/Seaweed+Wheat Straw) and the temperature using different reaction times for the pH (a-c) and conductivity (d-f) of the liquid phase at 0, 30 and 60 min, respectively.

The pH of the liquid phase depends on the feedstock mixture composition and the temperature used in the microwave process. At low temperature (80 ºC), when wheat straw is used as a feedstock, the liquid phase has a neutral pH (ca. 7) irrespectively of the reaction time. However, as the mixture is enriched in seaweed, the pH decreases linearly, probably due to the more considerable amount of alkaline salts in wheat straw in comparison to *Laminaria Saccharina* which neutralise acids formed. An increase in the temperature from 80 to 250 ºC decreases the pH of the liquid phase regardless of the reaction time or feedstock mixture composition; the effect of this latter variable being less and less significant as the temperature increases. As a consequence, at 250 ºC, the pH of the solution is around 3.8 – 4.0 regardless of the other variables.

The conductivity of the solution depends on the feedstock composition, temperature and reaction time. Two different developments occur for the conductivity of the solution when the composition of the feedstock mixture is altered. At low temperature (80ºC), irrespectively of the reaction time, a liquid phase with a higher conductivity is produced with pure wheat straw than with pure seaweed; the conductivity progressively decreasing as the solution is enriched in seaweed. This suggests that at low-temperature ash leaching is more likely to take place with feeding wheat straw than when seaweed is used as the feedstock. This might indicate that metals could be more integrated into the solid structure in seaweed than in wheat straw, thus being less accessible to water at low temperature. Besides, this supports the positive catalytic effect of metals in Laminaria Saccharina, as they are well distributed into the core structure of the solid, thus aiding to the first depolymerisation step to produce soluble oligosaccharides, without being leached to the solution.

Increasing the temperature has different consequences for the conductivity of the solution depending on the feedstock mixture composition and reaction time. For a feedstock mixture consisting of pure wheat straw, increasing the temperature leads to a decrease in the conductivity, while for a feedstock mixture composed of pure seaweed this same temperature increase results in an increase in the conductivity. As a consequence of these developments, when a temperature of 250 ºC is used, increasing the proportion of seaweed in the reaction mixture leads to an increase in the conductivity of the solution. The use of high temperatures leads to an increase in seaweed conversion into gas and liquid products, thus decreasing the solid yield. As such, ashes, primarily alkali metals, are more accessible to water and could be more easily leached to the liquid phase. The effect of the reaction time does not depend on the feedstock mixture composition or the reaction temperature. In particular, the conductivity decreases between 0 and 30 min and increases with a subsequent increase in the reaction time up to 60 min, for all feedstock mixture combinations and reaction temperatures. This increase might be accounted for by the positive effect of the reaction time on biomass conversion, which makes the ash content of the biomass more accessible to water, following the un-reacted core shrinking model, thus increasing metal leaching into the hydrolysate as solid depolymerises.

Elemental composition and calorific value of the solid phase

The relative amounts of C, H, O and N in the solid product vary by 37-62 wt.%, 5-6wt.%, 31-57 wt.% and 0-2 wt.%, these variations shifting the HHV of the material between 13 and 25 MJ/kg. The cause-effect Pareto analysis reveals that the relative amounts of C and N are primarily affected by the feedstock composition. At the same time, the proportion of H is substantially influenced by the reaction time, the proportion of O and HHV mainly depending on the reaction time and temperature. Besides, feedstock synergistic/antagonistic effects take place for the proportions of C, H and N. The contribution of the quadratic value of the feedstock in comparison to the total feedstock influence $F^2/(F^2+F)$ is as follows 75, 100 and 55%. Figure 4 shows the effects of the operating conditions and feedstock mixture on the elemental composition and HHV of the liquid phase. In particular, Figure 4 a/b/c shows the effects on the proportion of C in the solid phase of the feedstock composition (seaweed, wheat straw and all possible binary combinations at the lowest (80 ºC) and highest (250ºC) temperature for a 0/30/60 min reaction time. These effects are 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 product.

The elemental analysis and HHV of the solid product depend on the feedstock composition. In particular, irrespectively of the temperature or reaction time, the solid derived from the treatment of pure wheat straw contains more significant proportions of C and H as well as lower amounts of O and N than the solid produced during the treatment of seaweed. A material with a higher HHV is produced with pure wheat straw compared to seaweed. These variations are in good agreement with the elemental analysis of the original feedstocks. The progressive addition of seaweed into the feedstock mixture leads to decreases in the proportions of C and H and the HHV together with increases in the relative amount of O and N. The variations in the proportions of C, H and N depend on the composition of the reaction mixture due to the existence of synergistic and antagonistic effects as described earlier. In particular, an initial increase from 0 to 60 wt.% in the proportion of seaweed in the reaction mixture does not significantly modify the relative amounts of C or N, while a further increase up to 100 wt.% decreases the C and increases the N. Conversely, the proportion of H decreases as the relative amount of seaweed in the feedstock mixture rises up to 60 wt.%. In contrast, the increase and the decrease respectively observed for the proportion of O and HHV depict a linear evolution. These developments might be the result of two opposing effects. On the one hand, Laminaria Saccharina has lower C content and higher O content. Therefore, the proportion of C and O in the feedstock mixture decreases and increases, respectively, when the amount of this material increases. On the other, the solubilisation of cellulose and hemicellulose into the liquid phase results in a solid product with higher C and lower O due to the increase in the proportion of lignin in the spent solid material [68] . Lignin has higher C, lower O and similar H content than the biomasses used in the present work, which logically results in a solid product with a higher C content and a lower O content. Therefore, the compensatory influence of both developments (one increases and the other decreases the amount of C) can be responsible for the steady evolution observed for the C content when small amounts of Laminaria Saccharina are introduced in the feedstock mixture.

The effect of the temperature does not depend on the reaction time or feedstock composition. Increasing the temperature between 80 and 250 ºC leads to an increase in the proportions of C and N along with a decrease in the proportion of O, which increase the HHV of the solid. These variations are thought to be the consequence of the positive kinetic effect of the temperature on the process, which lead to a greater spread of decarboxylation and deoxygenation reactions [18, 19]. Furthermore, they also depend on the feedstock mixture composition; the greater the proportion of seaweed in the feedstock mixture, the more pronounced are the variations observed for the elemental composition and the HHV of the solid product due to the greater reactivity of this biomass as well as the lower solid yield obtained with this feedstock as commented earlier. The effect of the reaction time mostly depends on the temperature. At low temperature, the reaction time does not exert a high impact on the elemental composition or the HHV of the solid. Conversely, as the temperature increases, the effect of the reaction time becomes more and more important. This mostly affects the relative amounts of C and O as well as the HHV. As such, at high temperature (250 ºC) and regardless of the feedstock composition, an increase in the reaction time leads to a rise in the proportion of C together with a decrease in the relative amount of O, thus leading to an increase in the HHV of the solid product. These variations are accounted for by the more prolonged exposure of the material to microwave heating, which results in a more significant extension of decarboxylation and deoxygenation reactions [18, 19].

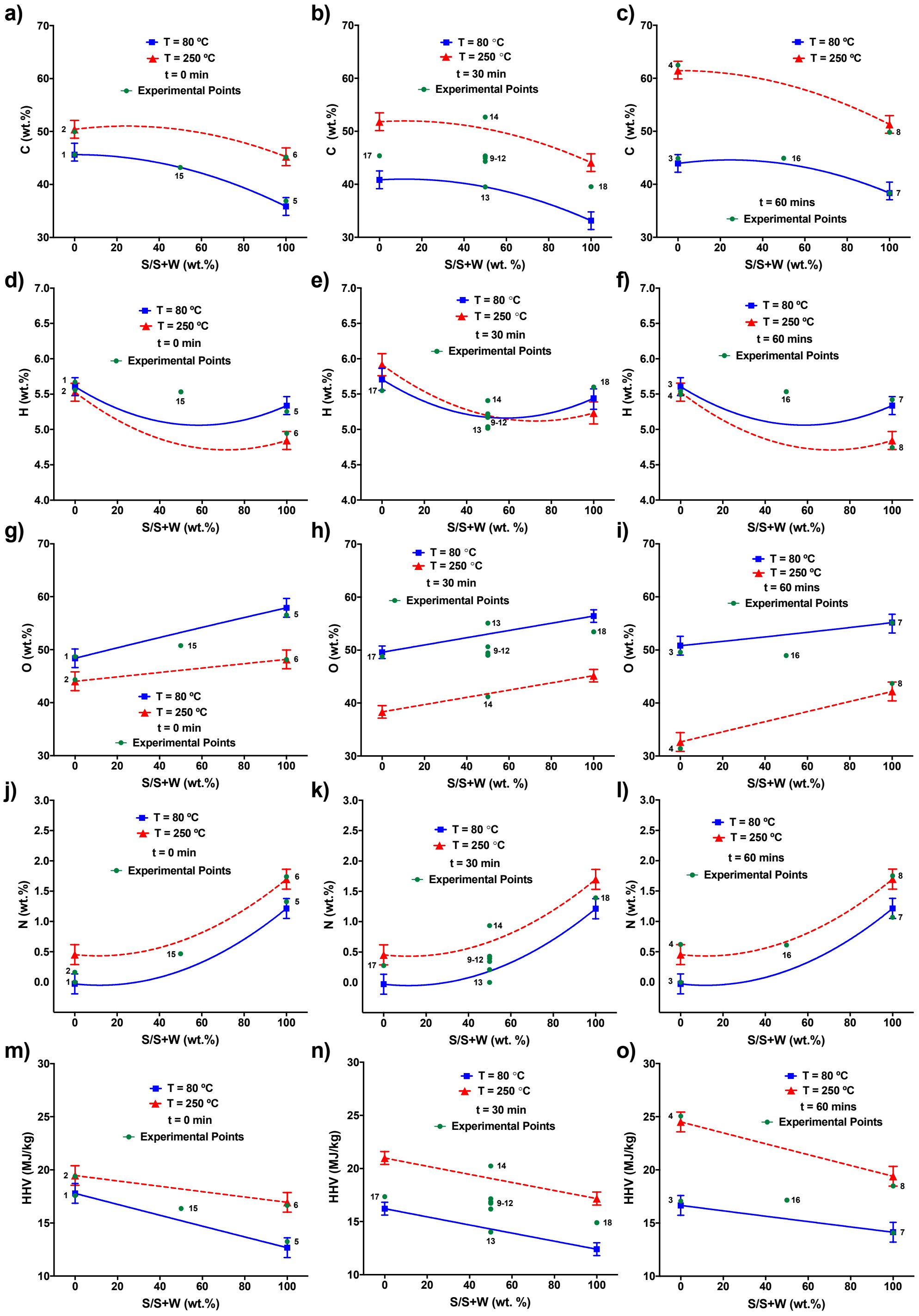

Fig. 4. Interaction plots between the feedstock composition (Seaweed/Seaweed+Wheat Straw) and the temperature using different reaction times for the elemental composition: C (a-c), H (d-f), O (g-i) and N (j-l) and the HHV of the solid product at 0, 30 and 60 min, respectively.

To gain a more in-depth insight into the synergistic effects within feedstocks, the solids produced in Runs 17, 10 and 18 were characterised by means of proximate analysis. Besides, an ash balance was conducted considering the products (gas, liquid and solid) yields. These experiments were conducted at intermediate conditions (165 ºC and 30 min) using a feedstock mixture comprising: pure wheat straw, a 50/50 wheat straw/seaweed mixture and pure seaweed, respectively. The results of these analyses are summarised in Table 5. These results show that metal leaching does not occur to a substantial extent when wheat straw is used as the feedstock at intermediate operating conditions (around 92 wt.% of the initial ash content remains in the spent solid material). Conversely, leaching becomes very important when seaweed is used in the process. In this case, the spent solid contains only around 32 wt.% of the initial ash content of the feedstock. In addition, the ash recovery from a feedstock mixture containing half of each biomass (Run 10) is lower than the average individual value obtained with each biomass, thus denoting a positive synergetic effect, as described earlier. This provides evidence for the higher conductivity and lower pH of the liquids obtained with seaweed than those produced during the treatment of wheat straw. Besides, the solubilisation of metals into the liquid phase together with the positive catalytic effect of these species in hydrolysis, cracking and decarboxylation reactions are in line with these observations. These metals also aid to polarise water, thus increasing the concentration of protons in the liquid medium, which promotes acid catalysed reactions to take place. These developments can explain the higher gas formation occurring with seaweed than with wheat straw, as well as the higher reactivity of the former. The presence of metals also helps shift the reactions occurring in the liquid phase towards the formation of small oxygenates, such as carboxylic acids. The presence of these acids, together with a higher concentration of metals in the liquid might result in the formation of 'a pool of active catalytic species' which might be responsible for most of the 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 (ºC)		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 ºC 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 ºC for around 40 min, it is possible to synergistically increase the liquid yield produced with wheat straw by introducing a proportion of seaweed (between 36 and 57 wt.%) in the feedstock mixture. Under these conditions, it is possible to transform around 30 wt.% of the solid material into a sugar-rich aqueous solution with a purity of approximately 90 C-wt.%. Besides, the spent solid material has a HHV of around 19 MJ/kg, which is much higher than those of the individual feedstocks. This is the result of the synergistic effect of seaweed on wheat straw depolymerisation, which allows increasing the liquid yield obtained with wheat straw, without compromising the oligosaccharide purity of the liquid solution. Regarding solid biofuels production, Opt. 5 shows that it is possible to transform up to 38 wt.% of the initial solid material into a solid product with a HHV of 21 MJ/kg by co-feeding 72/28 wt.% seaweed/wheat straw. Therefore, these promising results might represent a step-change towards the development of new and environmentally friendly, 5G bio-refineries for the simultaneous co-valorisation of algae and lignocellulose biomass. This is a landmark achievement to render the entire bio-refinery concept for biomass valorisation economically competitive, aiding to decrease the feedstock dependency of current bio-refinery models.

CONCLUSIONS

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

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Supporting Information

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

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