ROYAL SOCIETY OF CHEMISTRY

Journal Name

ARTICLE

Production of bio- fuels and chemicals by Microwave-Assisted, Catalytic, Hydrothermal Liquefaction (MAC-HTL) of a mixture of pine and spruce biomass

Javier Remón*, James Randall, Vitaliy L. Budarin, James H. Clark*

This work firstly addresses the microwave-assisted, catalytic, hydrothermal liquefaction (MAC-HTL) of a mixture of pine and spruce biomass, examining the effects of the temperature (150-250 ºC), pressure (50-120 bar), time (0-2 h) and catalyst amount (Ni-Co/Al-Mg; 0-0.25 g catalyst/g biomass). This hydrothermal process turned out to be a very promising route for the production of a bio-oil with suitable physicochemical properties to be used as a precursor for liquid bio-fuels and/or renewable platform chemicals. The statistical analysis of the results revealed that the operating conditions exerted a significant influence on the process; the overall biomass conversion and the yields to gas and bio-oil varied by 13-77%, 7-67% and 1-29%, respectively. This liquid consisted of a complex mixture of esters (0–30%), aldehydes (4–69%), ketones (0–35%), alcohols (0–14%), phenols (0–83%), acids (0–28%), cyclic compounds (0–38%), acetates (0–11%), ethers (0–27%) and furans (0–12%). The proportions of C, H and O in the liquid shifted by 2-70 wt.%, 4-11 wt.% and 27-87 wt.%, which varied the Higher Heating Value (HHV) between 4 and 28 MJ/kg. The optimisation of the process revealed that it is possible to transform up to 27% of the original biomass into a phenol-rich (47%) bio-oil with a relatively high HHV (20 MJ/Kg) using a temperature as low as 250 ºC, at 80 bar, employing 0.25 g catalyst/g biomass for 1.9 h. The properties of the liquid produced at optimum conditions make it suitable to be used as a renewable bio-fuel precursor, a bio-based source of aromatics and/or a sustainable phenolic-rich antioxidant additive. Therefore, this process might represent a promising improvement in biomass pre-processing technologies, helping the development of novel routes for biomass valorisation.

1. Introduction

The on-going movement to replace the present fossil fuel energy sector for a bio-renewable energy market has led researches to explore the use of alternative bio-based feedstocks and to develop novel and more sustainable processes for the production of fuels and chemicals. With this in mind, lignocellulosic biomass has attracted increasing attention as a potential environmentally friendly raw material to obtain these commodities, while hydrothermal processes are gaining widespread interest for the production of energy-dense fuels and valuable chemicals from bio-based feedstocks [1].

Hydrothermal liquefaction (HTL) of biomass comprises the thermochemical conversion of a broad range of bio-based materials into a liquid product called bio-oil using water, one of the greenest solvents, as the reaction media; thus, representing a promising and sustainable option for biomass valorisation [2-4]. Bio-oil is a dark brown liquid with a higher energy density than the original biomass. It consists of a complex organic mixture with different chemical compositions depending on the biomass source and the process used for its production [5]. HTL is a thermochemical route allowing the conversion of biomass into bio-oil. This process is conducted using liquid hot compressed water at subcritical conditions; i.e. moderate temperatures (150-400 ºC) and relatively high pressures (5-25 MPa) [1, 6-10]. These conditions dispense with the need to vaporise the water and/or dry the raw material, thus helping to improve the economic aspects and energetic profitability of the process, especially when wet feedstocks are used. HTL of biomass has also several inherent benefits when compared to other thermochemical routes for bio-oil production, such as fast pyrolysis. In particular, much lower temperatures are required and the bio-oils produced have lower oxygen content and higher heating value (HHV) than those produced via biomass fast pyrolysis [1, 6-10].

Research on HTL can date back to the 1930s. Since then, a considerable amount of literature is available addressing the use of this technology for the valorisation of wet biomass [1]. However, parametric studies examining the effects of operating conditions on the product distribution and the most important properties of the bio-oil produced from lignocellulosic biomass are scarce. In this regard, several studies have been conducted with wood, agricultural wastes and waste paper. He et al. [11] investigated the HTL of swine manure into oil at 275-350 ºC, 5.5-18 MPa and 5-180 min in a 1.2 L batch reactor. They reported a maximum bio-oil yield of 61%, the liquid having a maximum HHV of 35 MJ/kg. These same

Green Chemistry Centre of Excellence, University of York, Department of Chemistry. Heslington, York, YO10 5DD, UK.
* Corresponding authors: J. Remón (javier.remonnunez@york.ac.uk) and J.H.Clark (james.clark@york.ac.uk)

authors [12] also investigated the HTL of artificial garbage, i.e. a complex solid mixture made up of vegetables, rice, bread, butter and sardines, using a 300 mL autoclave at 340 ºC and 18 MPa for 0.5 h in the presence of Na_2CO_3. Maxima for the bio-oil yield and the HHV were 21% and 36 MJ/kg, respectively. Minowa et al. [13] performed HTL of Indonesian biomass residues in a 300 mL autoclave at 300 ºC and 10 MPa for 30 min in the presence of Na_2CO_3. They reported bio-oil yields between 21 and 36%, with a maximum HHV of 30 MJ/kg. Karagöz et al. [14] addressed the HTL of sawdust and rice husk in a 200 mL autoclave reactor at 280 ºC for 15 min. Bio-oil yields of 8.3% and 8.6% for rice husk and sawdust, were respectively reported. Demirbas [15] examined the HTL of beech wood at 376 ºC using a residence time of 25 min. Under these conditions a bio-oil yield of 28% with a relatively high HHV (35 MJ/kg) was achieved.

Another important factor to bear in mind during bio-oil production is the physicochemical properties of this liquid to be used for fuel applications, either alone and/or blended with other fuels. In this regard, while HTL of biomass normally provides a viable route to liquid biofuels, a subsequent upgrading of the bio-oil might be required in some cases, in order to come up with a liquid product that could be used in the current fuel market infrastructures. A possible solution to overcome this problem is the use of a catalyst during the hydrothermal process. This is intended to improve the process efficiency by reducing char and tar formation as well as to improve the physicochemical properties of the oil [9]. The works conducted using catalytic hydrothermal liquefaction of biomass can be split into two main categories: homogeneous and heterogeneous catalysis. Homogeneous catalysts largely comprise alkali salts (Na_2CO_3, K_2CO_3 and $KHCO_3$) [9, 16]. These salts help to reduce char formation and improve the properties of the bio-oil by promoting the water-gas shift, dehydration and deoxygenation reactions [9, 16]. Heterogeneous catalysts include Pt, Ni, Ru and Pd [17], metal oxides such as MnO, MgO, NiO, ZnO, CeO_2, La_2O_3, zeolites and carbon nanotubes [18]. These heterogeneous catalysts are normally preferred over homogenous catalysts as they are normally easier to recover after the hydrothermal reaction. However, they must be carefully made in order to be resistant to deactivation and/or decomposition under hydrothermal conditions [9].

These publications reported to date provide useful information about the HTL of lignocellulosic biomass for bio-oil production. However, new insights must be gained into the development of novel processes and new reactor designs and configurations for the expansion and development of this thermochemical process. In particular, the importance of process design, control and energy efficiency in the early stage technology development is highlighted as critical to their economic and environmental viability. Having this in mind, microwave heating, i.e. converting electromagnetic radiation into heat energy within the target material is seen as one of the most promising technologies to replace conventional heating during the valorisation of biomass [19-26]. The use of microwave heating not only does allow employing lower temperatures, but also, it helps to achieve a better controllability of the process. As water is highly effective in microwave energy absorption, achieving hydrothermal conditions by means of microwave heating to

conduct hydrothermal liquefaction reactions might be a promising new technology for biomass valorisation. The use of microwave technology has recently been successfully addressed for biomass valorisation. This includes pyrolysis [19, 20, 26-32], depolymerisation [19, 20, 22-24, 30, 33-35] and solvolysis [20, 25, 36-42]. However, to the best of the authors' knowledge, microwave-assisted hydrothermal liquefaction of biomass at moderate temperatures (150-250 ºC) using pressurised reactors (50-120 bar) has never been reported.

Herein, this work firstly addresses the Microwave-Assisted, Catalytic, Hydrothermal Liquefaction (MAC-HTL) of a mixture of pine and spruce to produce bio-fuels and bio-chemicals, using a Ni-Co/Al-Mg catalyst. The effects of the temperature (150-250 ºC), pressure (50-120 bar), reaction time (0-2 h) and catalyst amount (0-0.25 g catalyst/g biomass) together with all the possible interactions between variables on the process have been thoroughly analysed on the overall conversion and product distribution (gas and bio-oil liquid yields) as well as the most important chemical and physicochemical properties of the bio-oil produced. These include the elemental and chemical compositions and Higher Heating Value (HHV). The fact that microwave-assisted, catalysed, hydrothermal liquefaction of biomass has never been reported before, together with the rigorous parametric study and process optimisation conducted, demonstrates that this work represents a novel and challenging investigation for the development of novel, quick and environmentally friendly methodologies for the production of bio-oil and bio-chemicals from biomass.

2. Experimental

2.1 Microwave experiments

A small bench scale, microwave-assisted reactor capable of achieving high temperatures and pressures was used to conduct the experiments in the presence of a co-precipitated Ni-Co/Al-Mg catalyst. This catalyst was selected having regard to its good performance during lignocellulosic bio-oil upgrading in sub and supercritical water [43]. It has 28% Ni expressed as Ni/(Ni+Co+Al+Mg) (atomic percentage), an atomic Mg/Al ratio of 0.26 and an atomic Co/Ni ratio of 0.10, with a BET surface area of about 132 m^2/g [44].

The reactor (Figure 1) is a Millestone Synth-Wave microwave designed and manufactured by Milestone, fully described in our previous publication [45]. Briefly, it consists of a 1L water-cooled high-grade stainless steel reactor completely PTFE coated, which allows running elevated temperature and pressure (up to 300 ºC and 199 bar, respectively) reactions. A magnetron connected through a waveguide to the bottom of the pressure vessel generates the microwave radiation needed to heat up the reactants. The pressure vessel is made of special stainless steel and is closed with a clamping device. The internal temperature is monitored and controlled by means of a thermo-well protected NiCr temperature sensor placed inside the reactor. The microwave power needed to achieve the temperature at reaction conditions is controlled with the aid of a PID control. The total internal pressure achieved inside the reactor is monitored by a pressure sensor. Before the experiment, the reactor was filled with the required amount of N_2 at room temperature to achieve the desired pressure at reaction
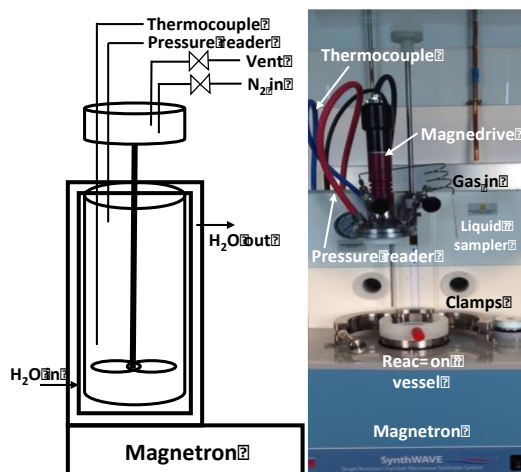
ARTICLE

Figure 1. Microwave-assisted hydrothermal reactor.

conditions using an internal calibration. For safety and security, a burst disc protects the pressure system against pressure in excess of the allowed operating pressure in case of explosions or run away reactions.

To run the reactions, firstly, 10 g of a mixture of pine and spruce pellets, 500 mL of deionised water and different catalyst amounts were placed in the reactor. Then, it was pre-loaded with different amounts of N_2 before reaction. A ramping time of 15 min (i.e. the time the system needs to achieve the reaction temperature from room conditions) was used for all the experiments. The vessel shield remained cold all the time by means of a recirculation water cooler, which also minimises the subsequent chilling time after reaction. At the end of the reaction and once the reactor had achieved room temperature, it was opened manually, after having relieved the pressure. Subsequently, the solid phase, comprising the unreacted biomass and spent catalyst, and the liquid phase, containing the water used as the reaction media and bio-oil produced in the experiment, were recovered and separated by filtration. Then, the spent catalyst was separated from the solid biomass with the aid of a magnetic stirrer. To fully analyse and optimise the process, the bio-oil was recovered from the aqueous phase by means of a series of two liquid-liquid extractions, first with chloroform and then with ethyl acetate following the method recently developed and optimised by Ren et al. [46]. For a real application a very good

separation (>90%) can be achieved using only ethyl acetate [46]. Finally, the bio-oil was dried using Schlenk line to completely remove the water and the solvents used in the extractions.

2.2 Response variables and analytical methods

Table 1 lists the response variables and the analytical methods used for their calculation. These include the overall biomass conversion, the gas and bio-oil yields and the bio-oil elemental and chemical analyses and higher heating value (HHV). The composition of the gas phase was not determined, as the reactor system was not originally designed for gas sampling and this work primary focuses on bio-oil production. Gas formation during the hydrothermal treatment of biomass largely occurs via decarboxylation, deoxygenation and thermal decomposition, these reactions leading to CO_2 formation. At the operating conditions used in this work, H_2 and CH_4 formation are not thermodynamically favoured and CO_2 is usually the mot abundant product in the gas stream [10, 47]. Gas chromatography (GC/MS) and elemental analysis were used for the characterisation of the bio-oil. Elemental analysis was carried out using an Exeter Analytical (Warwick, UK) CE440 Elemental Analyser, calibrated against acetanilide with a S-benzyl-thiouronium chloride internal standard. A Perkin Elmer Claus 500 gas chromatograph equipped with a non-polar ZB-5HT (30m×0.25mm *id* × 0.25µm film thickness) column from Phenomenex coupled to a Perkin Elmer Claus 560s mass spectrometer was used for the analyses. Prior to the analysis, the bio-oil was dissolved in chloroform. For the analysis, the oven temperature was maintained at 60°C for 1 min, then ramped at 10°C min^{-1} until 360°C and then held for 1 min. The NIST 2008 library was used for product identification.

2.3 Experimental design and statistical analyses

The influence on the process of the temperature (150-250ºC), pressure (50-120 bar), reaction time (0-2h) and catalyst amount (0-0.25 g catalyst/g bio-oil) was experimentally analysed using a design of experiments (DOE) with statistical analysis of the results. A 2-level, 4-factor Box-Wilson Central Composite Face Centred (CCF, α: ±1) design was used to plan the experiments. This is a 2^k factorial design, where k indicates the number of factors studied (4 operating variables) and 2^k represents the number of runs (in this case 16). In addition, this design was enlarged with 8 axial

Table 1. Response variables. Definitions and analytical techniques used in their determination.

Product	Response variable	Method
Bio-oil	$\text{Bio} - \text{oil yield (\%)} = \dfrac{\text{mass of bio} - \text{oil (g)}}{\text{mass of biomass (g)}} \, 100$	Gravimetric
	$\text{Composition (Area \%)} = \dfrac{\text{Area of each compound}}{\text{total area}} 100$	GC/MS
	$\text{C, H, O (wt. \%)} = \dfrac{\text{mass of C, H, O (g)}}{\text{mass of organics (g)}} \, 100$	Elemental Analysis
	HHV (MJ/kg) = 0.3491 C (wt.%) + 1.1783 H (wt.%) − 0.1034 O (wt.%) − 0.015 N (wt.%) + 0.1005 S (wt.%)	Estimated
Solid	$\text{Solid yield (\%)} = \dfrac{\text{mass of solid (g)}}{\text{mass of biomass (g)}} \, 100$	Gravimetric
	$\text{Overall conversion (\%)} = \dfrac{\text{mass of biomass (g)} - \text{mass of solid after experiment (g)}}{\text{mass of biomass (g)}} \, 100$	Gravimetric
Gas	$\text{Gas yield (\%)} = \dfrac{\text{mass of gas (g)}}{\text{mass of biomass (g)}} \, 100$	Gravimetric
Energy Efficiency	$\text{E(\%)} = 100 \, \dfrac{m_{\text{bio}-\text{oil}} \, (\text{kg}) \cdot \text{HHV}_{\text{bio}-\text{oil}} \, (\text{MJ} \cdot \text{kg}^{-1}) + m_{\text{H2O}} \cdot (\text{Kg}) \cdot \Delta H_{\text{H2O}} (\text{MJ} \cdot \text{kg}^{-1})}{\text{E microwave (MJ)}}$	Power meter (Energenie, ENE007)

experiments to study non-linear effects and interactions, while 4 replicates in the middle of the variation interval of each factor (centre points) were carried out in order to assess the experimental error. This experimental design is very useful for studying the influence of each variable (linear and quadratic effects), and more importantly, for understanding all possible interactions between variables. This experimental strategy allows gaining a thorough insight into the process and it is tremendously useful for process optimisation as well as for a potential scale-up and commercialisation. An analysis of variance (ANOVA) was used to select the operating variables and interactions significantly influencing the process. The results of this analysis were used to develop several interactions plots to explain the effects of the operating variables on the experimental results. In the interaction plots the evolution of these variables obtained from the ANOVA analysis of all the runs conducted is represented. In addition, when possible, some experimental points were added in the interaction figures. In some cases only the upper and lower levels for one of the variables have been represented in the interaction plots; however, the whole interval of variation was considered, carefully analysed and thoroughly discussed for all the response variables.

2.4 Raw material characterisation

The feedstock used in this work consists of a palletised mixture of pine and spruce biomass. Table 2 lists the proximate and ultimate analyses, along with the ash composition and HHV of the original feedstock. Proximate analyses were performed according to standard methods (ISO-589-1981 for moisture, ISO-1171-1976 for ash and ISO-5623-1974 for volatiles). The experimental characterisation results are fairly similar to those previously reported in the literature for pine and spruce [15, 48-50].

Table 2. Feedstock characterisation

Proximate analysis (wt.%)		Ash composition (wt.%)	
Moisture	6.78 ±0.58	Ca	62.5
Ash	1.37±0.01	K	12.5
Volatiles	58.4±0.57	Mg	5.1
Fixed carbon	17.07±1.08	Mn	5.9
Fibre analysis (wt.%)		S	3.2
Cellulose	62.42	Fe	2.7
Hemicellulose	27.01	Na	1.9
Lignin	9.20	P	1.6
Ash	1.37	Others	< 5
Elemental analysis (wt.%)			
C	47.75±0.24		
H	6.20±0.05		
O	46.05±0.35		
HHV (MJ/kg)	19.21±0.15		

3. Results and discussion

The operating conditions used in the experiments and the experimental results are listed in Table 3. The results include the overall biomass conversion, the gas and bio-oil yields together with some of the most important properties of the bio-oil fraction, such as the elemental analysis, chemical composition and higher heating value (HHV). The relative importance of the operating conditions on

these response variables in accord with the statistical analyses (ANOVA and cause-effect Pareto principle) is listed in Table S2.

3.1 Overall biomass conversion and gas and bio-oil yields

The overall biomass conversion and the yields to gas and bio-oil vary by 13-77%, 7-67% and 1-29%, respectively. The statistical analysis of the results (Table S2) reveals that the temperature and, to a lesser extent, the reaction time are the operating variables exerting the greatest influence on the overall biomass conversion and the gas and bio-oil yields. The pressure does not significantly influence the overall conversion and the amount of catalyst also has a very week influence. However, these two latter variables significantly influence the gas and liquid yields. These results are in good agreement with previous work addressing the hydrothermal liquefaction of lignocellulosic biomass [7, 51-53]. In addition, several interactions between these variables also take place. The effect of the operating variables and the most important interactions on the overall conversion and gas and liquid yields obtained from the statistical analyses (Table S2) are represented in Figures 2 and 3.

3.1.1 Global biomass conversion

Figure 2 a shows the effect of the reaction time on the global biomass conversion at the lowest and highest (150 and 250 ºC) temperatures studied in this work for the whole interval of pressure considered (50-120 bar, as the conversion is not influenced by the pressure) using an intermediate amount of catalyst (0.125 g cat/g biomass). In addition, Figures 2 b and c plot the effect of the reaction time for two different amounts of catalyst (0 and 0.25 g cat/g biomass) using a reaction time of 0 and 2 h, respectively. These analyses show that regardless of the other operating conditions (temperature, pressure or amount of catalyst), an initial increase in the reaction time from 0 to around 1 h leads to an increase in the overall conversion, while a further increase up to 2 h does not significantly influence this variable and a steady value is reached (Figure 2 a).

The hydrothermal liquefaction of biomass essentially involves three steps: (i) an initial biomass depolymerisation, (ii) the decomposition of the biomass monomers by cleavage, dehydration, decarboxylation and deamination which leads to the formation reactive fragments that evolve towards bio-oil and/or gas formation and (iii) the recombination and repolymerisation of reactive fragments, resulting in the formation of more bio-oil together with solid species such as char and coke [1]. Therefore, the initial increase in the biomass conversion is accounted for by the formation of bio-oil and gaseous products due to the positive kinetic effect the reaction time has on the process. However, a further exposure of the material to microwave heating favours the formation of solid species via recombination and depolymerisation [1]; thus allowing a steady state between biomass decomposition and coke and char formation to be reached.

Journal Name   ARTICLE

Table 3. Microwave assisted experimental conditions and results.

Run	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17 - 20	21	22	23	24	25	26	27	28
Temperature (ºC)	150	250	150	250	150	250	150	250	150	250	150	250	150	250	150	250	200	150	250	200	200	200	200	200	200
Pressure (bar)	50	50	120	120	50	50	120	120	50	50	120	120	50	50	120	120	85	85	85	50	120	85	85	85	85
time (h)	0	0	0	0	2	2	2	2	0	0	0	0	2	2	2	2	1	1	1	1	1	0	2	1	1
Catalyst/biomass (g/g)	0	0	0	0	0	0	0	0	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.125	0.125	0.125	0.125	0.125	0.125	0	0.25
Overall Results																									
Overall conversion (%)	17.04	44.1	13.02	43.95	29.75	68.2	30.11	65.59	13.07	32.89	15.31	41.21	23.63	77.26	23.31	67.62	41.38 ± 2.58	25.14	70.77	44.75	44.55	32	29.3	40.25	59.69
Bio-oil yield (%)	1.31	5.35	1.39	4.28	1.41	1.01	1.65	19.23	5.56	6.3	0.32	16.57	2.27	20.51	1.17	28.82	8.56 ± 0.92	0.87	19.5	13.62	9.71	0.97	12.91	13.69	9.77
Gas yield (%)	15.73	38.75	11.63	39.67	28.34	67.19	28.46	46.36	7.52	26.59	14.99	24.64	21.36	56.76	22.14	38.8	33.32 ± 3.40	24.27	51.28	31.12	34.84	31.04	16.39	26.56	49.92
Bio-oil elemental Analysis																									
C (wt.%)	62.65	58.61	64.67	57.64	61.61	60.83	48.53	51.82	2.1	56.03	63.81	35.96	37.83	51.68	63.3	47.16	55.04 ± 1.84	52.2	50.59	39.96	49.15	69.54	48.78	54.3	50.37
H (wt.%)	7.67	5.68	7.26	5.51	6.92	6.17	6.79	5.76	10.72	6.02	7.17	4.15	8.75	6.36	7.15	5.94	5.70 ± 0.22	8.29	5.83	4.36	5.26	5.45	5.61	5.29	5.8
O (wt.%)	29.68	35.71	28.08	36.85	31.46	33	44.69	42.42	87.18	37.95	29.02	59.89	53.43	41.97	29.55	46.91	39.65 ± 1.91	39.51	43.58	55.68	45.59	25.01	45.61	40.41	43.84
HHV (MJ/kg)	27.84	23.46	28.22	22.81	26.41	25.09	20.32	20.49	4.35	22.73	27.72	11.25	17.99	21.19	27.47	18.61	22.21 ± 1.42	23.91	20.03	13.33	18.65	28.11	18.92	21.01	19.88
Bio-oil Chemical Composition (Area %)																									
Esters	20	15.72	4.72	13.9	5.46	5.5	19.69	0	7.64	1.04	18.52	9.22	30.15	11.5	12.58	8.45	12.21 ± 2.58	8.82	1.89	26.89	7.66	6.38	14.9	4.41	0.98
Aldehydes	10.35	50.38	10.96	56.63	43.9	17.73	15.12	24.93	7.26	28.24	6.89	29.73	3.59	4.48	4.65	4.02	29.50 ± 2.28	4.18	13.88	40.51	35.04	5.16	20.48	68.95	19.08
Ketones	3.67	2.62	0	6	4.81	30.46	1.82	35.17	13.01	13.2	8.31	3.43	0	15.38	4.38	16.12	8.76 ± 1.89	0	15.68	5.96	6	0	12.72	3.85	10.09
Alcohols	4.18	0	0	0	0	9.65	1.4	1.65	0	0.85	1.91	0	0	13.89	0	14.01	4.49 ± 0.75	2	3.73	0	0	0	4.78	4.69	1.29
Phenols	29.73	0	40.19	4.03	3.2	0	57.74	0	37.08	32	41.62	26.98	44.46	12	54.9	21.83	18.66 ± 2.41	73.52	17.92	16.8	17.97	82.83	19.29	2.72	32.74
Acids	8.66	0	0	6.61	14.5	0	3.13	8.03	0	0	1.5	21.47	17.23	1.37	0	15.16	1.63 ± 1.04	2.31	19.73	2.6	0	0	0	0	26.87
Cyclic compounds	13.82	15.81	37.99	0	17.49	0	1.1	2.43	24.5	2.94	11.49	1.71	4.58	8.58	2.56	7.38	2.14 ± 2.49	5.74	8.45	7.24	4.55	0	0	0	3.57
Acetates	9.59	2.43	6.14	0	0	2.52	0	0	10.5	1.37	9.75	3.88	0	2	2.19	2.11	1.74 ± 1.01	0	2.81	0	1.9	0	2.53	0	5.37
Ethers	0	13.03	0	12.84	10.62	14.56	0	9.34	0	20.34	0	0	0	17.77	18.74	0	19.39 ± 2.62	19	15.9	0	26.88	5.63	25.31	15.38	0
Furans	0	0	0	0	0	19.58	0	18.45	0	0	0	3.59	0	13.04	0	10.9	0	5.44	0	0	0	0	0	0	0

Hence, since the overall solid (biomass) conversion was gravimetrically calculated using the solid product recovered after the experiments a steady conversion is observed. The spent solid recovered after the experiments comprise both unreacted biomass together with coke and char. Other authors [1, 7, 47] addressing the hydrothermal valorisation of biomass using conventional heating also observed this steady evolution. Besides, this steady state for the conversion could be followed by a posterior decrease (or an increase in the solid yield) with time as a result of a substantial solid formation (char and coke) if longer reaction times are used [1, 7, 47].
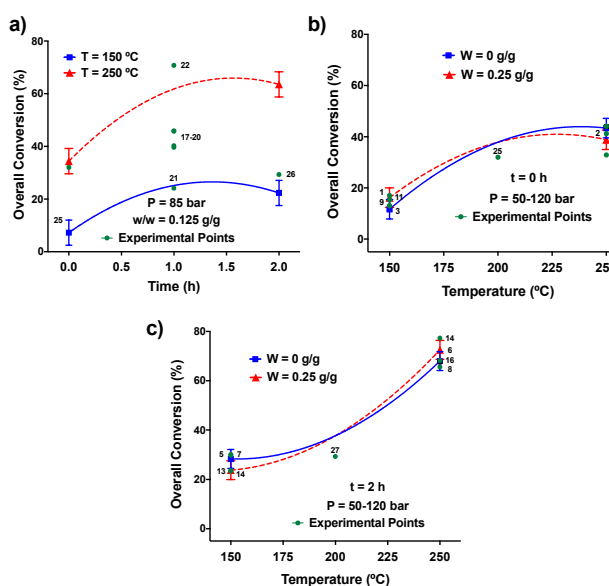
Figure 2. Interaction plots showing the effect of the temperature, reaction time and catalyst amount on the overall biomass conversion. Bars are LSD intervals with 95% confidence.

The effect of the temperature depends on the reaction time with two different outcomes occurring regardless of the amount of catalyst. For a short reaction time (0 h; i.e. only 15 min of ramping time to reach the reaction temperature), an initial increase in the temperature from 150 to 200 ºC leads to an increase in the overall biomass conversion due to the positive kinetic effect of this variable on the process, which increases the reaction rates [1, 7, 9, 47] of all reactions involved (depolymerisation, decomposition and re-polymerisation). In addition, a further increase up to 250 ºC does not influence the overall conversion and a relatively steady value is observed between 200 and 250 ºC. This development is thought to be the consequence of the steady state reached, balancing biomass decomposition and solid formation as described earlier and previously reported using conventional heating [1, 7, 9, 47]. Conversely, when a long reaction time is used (2 h) the opposite trend takes place; i.e. an initial steady evolution between 150 and 200 ºC, followed by a substantial increase from 200 to 250 ºC. This is accounted for by the positive kinetic effect that the reaction time exerts on the process, which allows us to reach the same level of conversion at low temperature and long reaction time (150-200 ºC and 2 h) than that achieved at high temperature and short reaction time (200-250 ºC, 0 h). In addition, the subsequent increase in the overall conversion from 200 to 250 ºC for a 2 h reaction is the consequence of the greater range of decarboxylation, deoxygenation and thermal decomposition reactions at high temperature and long reaction time, which allows the transformation into gases (largely CO_2 at HTL conditions) of the biomass reactive fragments as well as part of the bio-oil and solid products, such as char and coke [7, 54].

The catalyst exerts a very weak influence on the global biomass conversion (Table S2 and Figures 2 b and c). This is believed to be the consequence of the heterogeneous nature of the catalyst, hindering the intimate contact between the biomass and the catalyst, leading to mass transfer limitations between both solid species [7, 9, 47]. This prevents the catalyst from having a substantial influence on the global conversion; however the catalyst significantly influences the product distribution (i.e. the gas and bio-oil yields) along with the properties of the bio-oil produced, as will be described next.

3.1.2 Product distribution: gas and bio-oil yields

The effects of the operating conditions on the gas and liquid yields are plotted in Figure 3. Specifically, Figures 3 a and f respectively show the effect of the reaction time on the gas and bio-oil yields at 150 and 250 ºC, for an intermediate pressure (85 bar) using a medium amount of catalyst (0.125 g cat/g biomass). Figures 3 b/g and c/h plot the effects of the temperature on the gas/bio-oil yield in the absence of the catalyst (0 g catalyst/g biomass) at 50 and 120 bar using a reaction time of 0 and 2 h, respectively. Figures 3 d/i and e/j show these effects on the gas/bio-oil yield for the highest catalyst/biomass ratio (0.25 g catalyst/g biomass).

The reaction time has a significant influence on the gas and bio-oil yields. In particular and regardless of the temperature, an increase from 0 to 1 h leads to a significant increase in gas production (Figure 3 a). However, a further increase up to 2 h does not significantly increase the gas yield and a steady evolution is observed regardless of the temperature. An increase in the reaction time promotes the formation of gases via decarboxylation and pyrolysis reactions [7, 54]. However, the levelling of the gas yield is accounted for by the competition between cracking and pyrolysis reactions (leading to gas formation) and condensation, crystallisation and re-polymerisation reactions (increasing the bio-oil yield) [7, 54]. The effect of the reaction time on the bio-oil production depends on the temperature with two different outcomes taking place (Figure 3 f). At low temperature (150 ºC), the reaction time does not significantly influence the bio-oil yield and a negligible bio-oil production takes place regardless of the time (0-2 h). This suggests that while at low temperature, biomass depolymerisation and fragmentation occur to a substantial extent, leading to the formation of reactive fragments [1], the subsequent transformation of these species into bio-oil is not substantial at low temperature and gas formation is favoured over bio-oil production. Conversely, increasing the temperature significantly increases bio-oil production, probably as a consequence of the positive effect of the temperature on the recombination of these reactive fragments into bio-oil [1]. As a result, at high temperature (250 ºC), an initial

increase in bio-oil production takes place between 0 and 1 h, followed by a steady evolution with a further increase in the reaction time. This levelling-off of the bio-oil yield after longer reaction times is believed to be the result of the subsequent transformation of this liquid into gas (largely CO_2 at HTL conditions, by cracking, gasification and/or pyrolysis), and/or char (by condensation, crystallination and/or repolymerisation) [1, 7, 54].

The effects of the temperature and pressure on the gas and bio-oil yields depend on the reaction time and catalyst amount (Figures b-e and and g-j, respectively). On the one hand, for a 0 h reaction, the pressure does not have a significant influence on the gas or bio-oil yield in the absence of a catalyst. Under such conditions, an increase in the temperature from 150 to 250 ºC leads to a progressive increase in the gas yield; the bio-oil yield being very low (<5%) and unaffected by the temperature. Increasing the temperature kinetically promotes the decomposition of biomass into reactive fragments via depolymerisation, cleavage, dehydration and decarboxylation. However, in the absence of a catalyst and using short reaction times, these reactive species are more likely to evolve towards gas formation via decarboxylation and thermal cracking than bio-oil production by recombination and/or re-polymerisation [1, 7, 54]. This experimentally results in a very low bio-oil yield regardless of the temperature along with an increase in gas formation with increasing the temperature from 150 to 250 ºC.

Increasing the reaction time from 0 to 2 h modifies the effects of the temperature and pressure. For a 2 h reaction, an initial increase in temperature between 150 and 200 ºC decreases the gas and increases the bio-oil yield. In addition, within this temperature interval, the pressure does not significantly influence the gas or bio-oil yield. A further increase up to 250 ºC produces a significant increase in the gas yield regardless of the pressure. In addition, an increase in the pressure from 50 to 120 bar leads to decrease in the gas yield with different outcomes occurring for bio-oil yield depending on the pressure. At low pressure (50 bar) an increase in the temperature between 200 and 250 ºC leads to a substantial decrease in the bio-oil yield, while at high pressure (120 bar), bio-oil production increases between 200 and 225 ºC and remains high and steady with a further increase in the temperature up to 250 ºC. Biomass liquefaction is usually endothermic at low temperatures and becomes exothermic at high temperatures [9, 55]. As a result, the bio-oil yield increases with temperature and reaches a point at which a further increase in temperature supresses liquefaction. In addition, the decrease in the bio-oil yield observed at low pressure (50 bar) when the temperature increases between 200 and 250 ºC might be the result of the dominating secondary decomposition and Bourdard gas reactions, which promote CO_2 formation [1, 7, 54]. In addition, part of the bio-oil can also be transformed into gas (mainly CO_2 at the conditions used in this work) at high temperature when using long reaction times [7]. An increase in the pressure decreases the density of the water which also diminishes its dielectric loss factor [56], leading to a decrease in the effectiveness of microwave heating [45]. This lower efficiency might hinder the transformation of bio-oil into gas and provides evidence for the lower gas yield at high temperature and low pressure as well as the steady evolution observed for the bio-oil yield at high temperature (200-250 ºC) and pressure (120 bar).
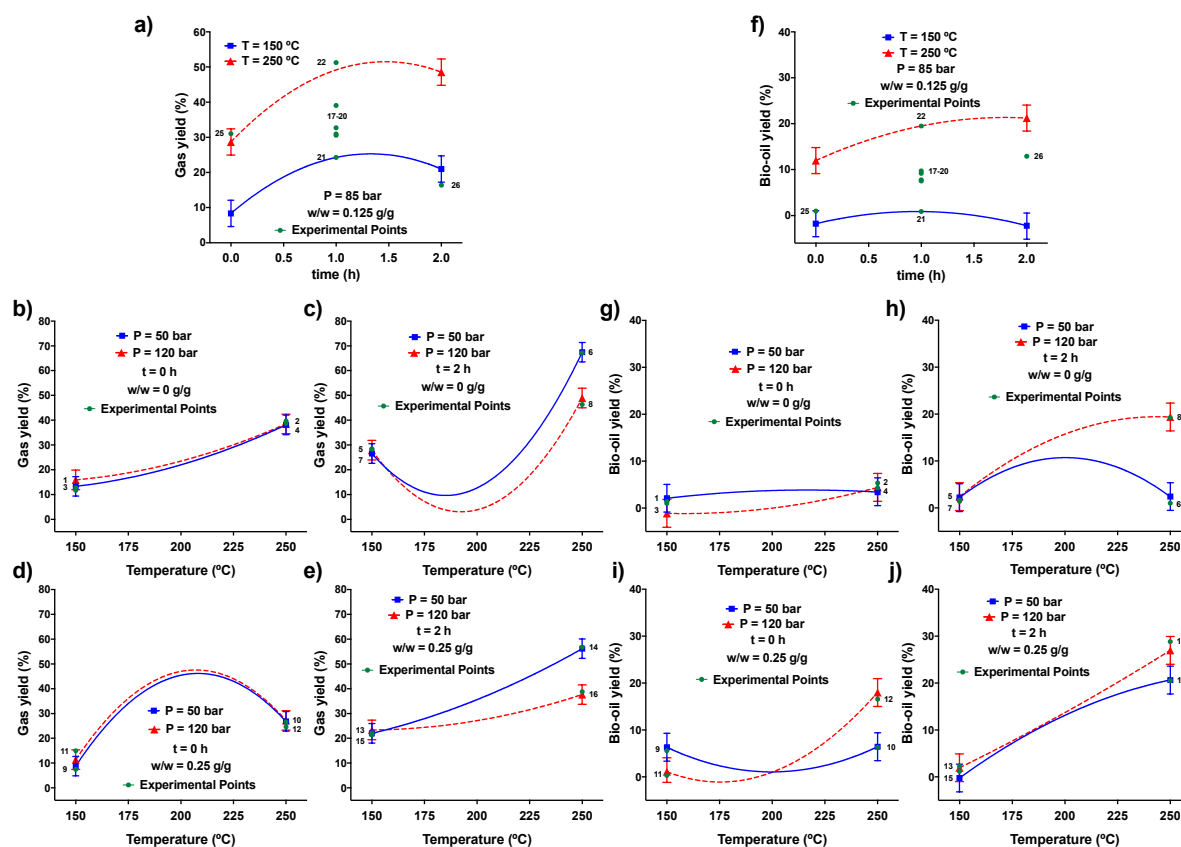

Figure 3. Interaction plots showing the effect of the temperature, reaction time, pressure and catalyst amount on the gas and bio-oil yields. Bars are LSD intervals with 95% confidence.

The catalyst amount also exerts a significant influence on gas and bio-oil production (Figures 3 b, c, g and h vs. d, e, i and j, respectively); its influence depending on the operating conditions. For a 0 h reaction, the catalyst plays an important role between 160 and 210 ºC. Within this temperature interval, an increase in the catalyst/biomass ratio from 0 to 0.25 g cat/g biomass significantly increases the gas yield regardless of the pressure, while the bio-oil yield is unaffected. At described earlier, when short reaction times are used at low temperature, bio-oil formation from the reactive intermediates produced from biomass decomposition is not favoured and gas formation prevails. In addition, the presence of the catalyst kinetically promotes the transformation of these intermediates into gas via pyrolysis and decarboxylation [7, 9, 54], thus increasing gas (CO_2) production. Between 220 and 250 ºC the same increase in the catalyst amount slightly decreases the gas yield, while two outcomes take place for the bio-oil yield. At low pressure, the effect of the catalyst is negligible, while at high pressure (120 bar), augmenting the catalyst/biomass ratio leads to an increase in the bio-oil yield. Augmenting the total pressure increases the partial pressure of the reactive species produced from the decomposition of the biomass. This kinetically promotes the condensation and re-polymerisation reaction, increasing the bio-oil yield. In addition, the very short reaction time used (0 h) might prevent the transformation of the bio-oil into gaseous products.

For a 2 h reaction, an increase in the catalyst amount does not greatly influence the gas and bio-oil yields when a reaction temperature between 150 and 200 ºC is used. As an exception, a small increase in the gas yield occurs between 180 and 200 ºC when the catalyst amount increases from 0 to 0.25 g cat/g biomass. Conversely, this same increase in the amount of catalyst substantially decreases the gas yield and increases the bio-oil yield between 200 and 250 ºC due to the positive catalytic effect of the catalyst on bio-oil production during the hydrothermal liquefaction of biomass [1, 7, 54]. In addition, these variations in the gas and bio-oil yields are notably more marked at low (50 bar) than at high pressure (120 bar). The lower dielectric loss factor of water, decreasing the microwave efficiency [56], helps prevent gas formation, and therefore can mask the positive effect of the catalyst. As a result, when the highest catalyst/biomass (0.25 g cat/g biomass) ratio is used for a long reaction time (2 h), increasing the temperature from 150 to 250 ºC increases the bio-oil and gas yields due to the higher biomass conversion together with the inhibitory effect of the catalyst on char formation [1, 7, 54].
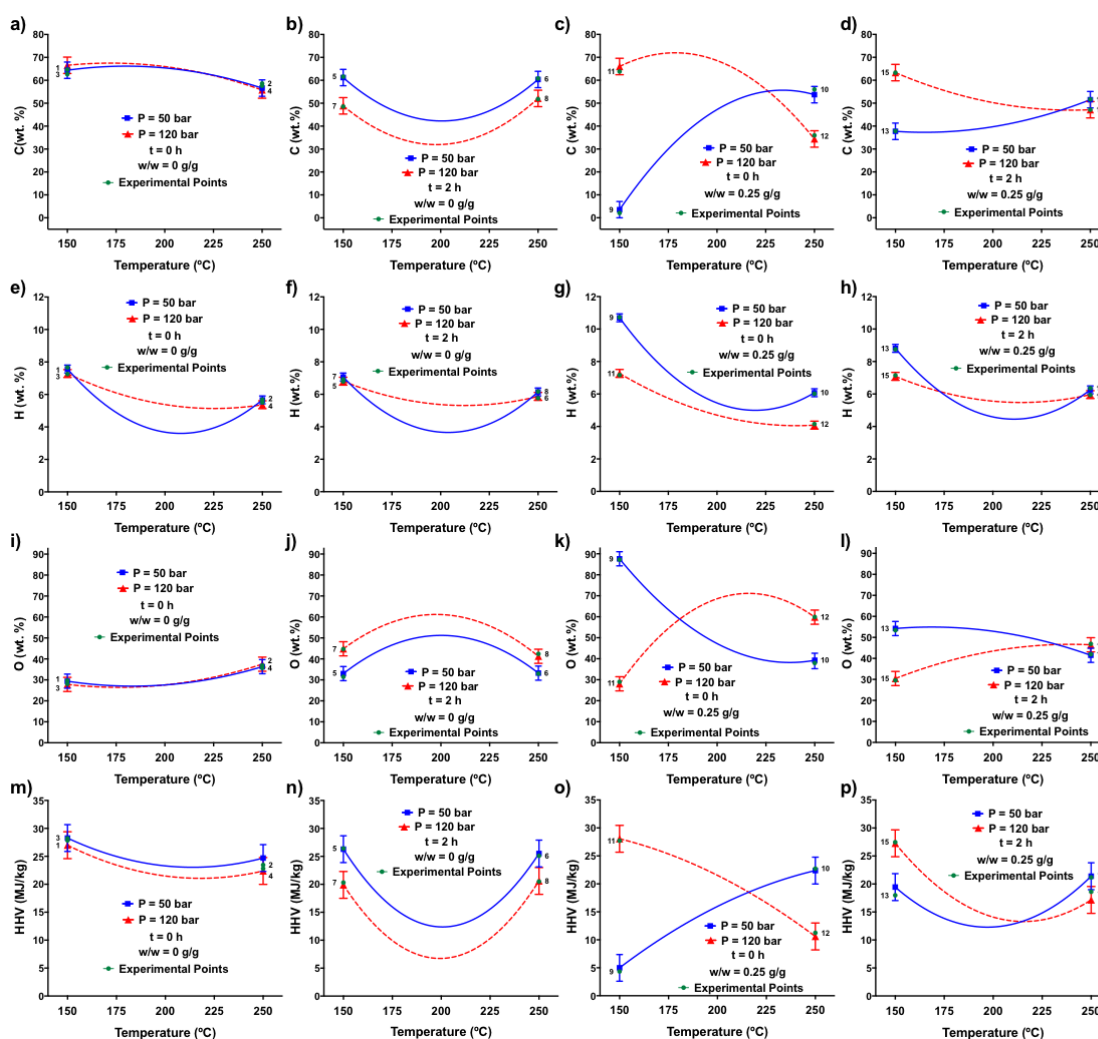

Figure 4. Interaction plots showing the effect of the temperature, reaction time, pressure and catalyst amount on the proportions of C, H and O and HHV of the bio-oil. Bars are LSD intervals with 95% confidence.

3.2 Effects of the operating conditions on bio-oil properties

3.2.1 Elemental composition and higher heating value (HHV)

The relative amounts of C, H and O in the bio-oil vary as follows: 2-70 wt.%, 4-11 wt.% and 27-87 wt.%, respectively. These variations shift the HHV between 4 and 28 MJ/kg. The statistical analysis of the results (Table S2) reveals that the proportions of C and O and the HHV of the bio-oil are strongly affected by the interactions of the temperature with the pressure and catalyst, while the proportion of H in the liquid is strongly affected by the temperature. Figure 4 shows the effects of these variables and the most important interactions on the bio-oil elemental composition and HHV. Specifically, Figures 4 a/b and c/d plot the effects of the temperature for the highest and lowest (50 and 120 bar) pressure considered using a catalyst/biomass ratio of 0 and 0.25 g cat/g biomass for a reaction time of 0/2 h. Figures 4 e-h, i-l and m-p plot the same effects for the proportions of H and O and the HHV, respectively.

In the absence of a catalyst, the elemental composition and the HHV strongly depend on the reaction time; the temperature and pressure exerting a very weak influence. In particular, for a 0 h reaction and regardless of the pressure, an increase in the temperature from 150 to 250 ºC leads to a small decrease in the proportions of C and H in the bio-oil along with an increase in the relative amount of O, which leads to a moderate decrease in the HHV of the bio-oil. The pressure does not significantly influence the elemental analysis or HHV of the bio-oil. As an exception, the proportion of H increases very slightly when the pressure increases from 50 to 120 bar, however this variation is not very important from a practical point of view. As described earlier, in the absence of a catalyst and using a very short reaction time (0 h), the bio-oil yield is very low (<5%) regardless of the temperature and the pressure since bio-oil formation is not favoured when using very short reaction times. This potentially leads to small variations in the elemental analysis and HHV, probably because the chemical reactions substantially modifying the bio-oil elemental composition such as dehydration, decarboxylation and thermal cracking do not take place to a substantial extend to observe differences when very short reaction times are used.

Conversely, increasing the reaction time from 0 to 2 h (for non-catalytic experiments) not only does slightly modify the bio-oil elemental composition and HHV of the bio-oil, but also changes the effect of the temperature and pressure. The reaction time exerts the greatest influence between 175 and 225 ºC, interval at which increasing the reaction time from 0 to 2 h decreases and increases the relative amounts of C and O, respectively, without significantly modifying the proportion of H; these variations leading to a decrease in the HHV. As described before, within this temperature interval, an increase in the reaction time upsurges the bio-oil yield as the recombination and/or repolymerisation of the reactive fragments produced during the solvolysis and depolymerisation of biomass [1, 7, 54] occurs to a greater extent. This spread also decreases gas formation via decarboxylation, as bio-oil formation is favoured over gas production at low temperature; thus decreasing and increasing the proportions of C and O in the bio-oil. In addition, for

a long reaction time (2 h), an increase in the temperature between 150 and 200 ºC decreases the proportion of C and the HHV and increases the proportion of O of the bio-oil regardless of the pressure. A further increase from 200 to 250 leads to the opposite effect; i.e. the proportion of C and the HHV increase, while the relative amount of O in the bio-oil decreases. At low temperature (150-200 ºC) gas formation decreases at the expense of bio-oil production due to the greater extension of re-polymerisation and recombination reactions, and the lower spread of deoxygenation and thermal cracking reactions. This leads to a decrease and an increase in the proportions of C and O in the bio-oil, respectively. On the contrary, between 200 and 250 ºC bio-oil transformation into gas via decarboxylation and thermal cracking occurs to a substantial extent, which leads to an increase in the C content and HHV along with a decrease in the concentration of O in the bio-oil.

An increase in the catalyst/bio-oil ratio from 0 to 0.25 g cat/g bio-oil substantially modifies the bio-oil elemental analysis and HHV. For a short reaction time (0 h), the effect of the catalyst depends on the pressure and temperature (Figures 4 a, e, i, m vs. c, g, k, o). On the one hand, at low pressure (50 bar) two different outcomes are observed depending on the temperature. Between 150 and 225 ºC, an increase from 0 to 0.25 g cat/g biomass leads to a pronounced decrease in the proportion of C and HHV of the bio-oil together with a substantial increase in the O and H contents of the liquid. Conversely, this same increase has a negligible effect between 225 and 250 ºC. On the other, at high pressure (120 bar) the catalyst has the opposite influence; i.e. a weak effect between 150 and 225 ºC together with a significant impact between 225 and 250 ºC. Within this latter temperature interval, an increase in the catalyst/biomass ratio from 0 to 0.25 g cat/g biomass decreases and increases the proportion of C and O in the bio-oil, respectively, without substantially modifying the concentration of H, which lead to a decrease in the HHV. These variations in the proportions of C and O occur along with decreases in the gas yield and/or increases in the bio-oil yield and they are accounted for by the lesser extent of the dehydrogenation and deoxygenation, decarboxylation and decarbonylation reactions under such conditions, which lead to a decrease in the amount of C together with an increase in the proportion of O in the bio-oil [57-60]. This suggests that when a short reaction time is used, the catalyst might also have a positive kinetic influence on the recombination and/or repolymerisation of the reactive fragments produced during the solvolysis and depolymerisation of biomass promoting bio-oil production [1, 7, 54] and preventing char formation.

In addition, the effects of the temperature and pressure are also modified with the addition of a catalyst. As a result, for a catalyst/biomass ratio of 0.25 g cat/g biomass the effect of the temperature depends on the pressure. At low pressure (50 bar), the bio-oil has a high proportion of O and a very low HHV at low temperature. Increasing the temperature between 150 and 210 ºC leads to a considerable increase in the amount of C along with a substantial decrease in the relative amounts of H and O, which leads to significant increase in the bio-oil HHV. These variations are accounted for by the positive effect of the catalyst promoting the

deoxygenation, decarboxylation, decarbonylation and hydrodeoxygenation reactions occurring under hydrothermal conditions. This is in good agreement with the results reported by other authors using heterogeneous catalysts based on Ni [61] or on other metals [57, 58, 60, 62] during bio-oil upgrading in sub-critical water. A further increase up to 250 ºC does not significantly modify the proportions of C or O in the bio-oil, however, the relative amount of H and the HHV increase slightly. Conversely, at high pressure (120 bar), the bio-oil produced at low temperature (150 ºC) is rich in C and H and has a low O content along with a high HHV. Increasing the temperature increases the proportion of O and decreases the relative amount of H and the HHV of the bio-oil between 150 and 200 ºC, without substantially modifying the concentration of C. A further increase up to 250 ºC decreases the concentration of C and HHV of the bio-oil, the proportions of H and O decreasing very slightly. This might be the result of two counteracting effects. On the one hand, an increase in the total pressure increases the partial pressure of the reactive species produced from the decomposition of the biomass, which kinetically promotes their condensation and re-polymerisation, consequently leading to an increase in the bio-oil yield. On the other, increasing the pressure also diminishes the dielectric loss factor of water, thus decreasing the microwave efficiency of the process. This hinders the deoxygenation and dehydrogenation reactions, which reduces the O content and increases the bio-oil C and H proportions and HHV.

For a long reaction time (2 h) the catalyst exerts the most important influence at low temperature (150-210 ºC) with different outcomes taking place depending on the pressure. While at low pressure (50 bar), an increase from 0 to 0.25 g cat/g biomass decreases the proportion of C and HHV and increases the relative amounts of O and H of the bio-oil; at high pressure (120 bar), the proportions of C and O increases and decreases, respectively, without significantly influencing the proportion of H, leading to an increase in the HHV. The catalyst exerts a positive effect on both bio-oil formation from biomass reactive fragments, thus increasing the biomass conversion, and bio-oil decomposition, leading to an increase in the gas yield; the bio-oil yield remaining constant. At low pressure the proportions of C and O and the bio-oil HHV increases due to the decrease in the gas yield. However, the pressure kinetically promotes bio-oil decomposition and biomass conversion, which increases the initial amount of bio-oil produced as well as the amount of bio-oil converted into gas. As a result of this balanced production/decomposition, the bio-oil yield is not substantially modified but some increases in the proportion of C and HHV and decreases the relative amount of O in the bio-oil are observed.

The kinetic effect of the catalyst also modifies the effect of the temperature and pressure when a long reaction time (2 h) is used, however, the effects of these two latter variables on the bio-oil chemical composition and HHV are not very important. In particular, at low pressure (50 bar), an increase in the temperature slightly increases and decreases the amounts of C and O (especially between 200 and 250 ºC), respectively and decreases the

proportion of O (largely between 200 and 250 ºC). These variations lead to a small decrease in the HHV between 150 and 200 ºC, followed by a subsequent increase between 200 and 250 ºC. At high pressure (120 bar), an increase in the temperature decreases the amounts of C and H and increases the proportion of O of the bio-oil, especially between 150 and 200 ºC; these variations decreasing the HHV of the liquid. At low pressure (50 bar) increasing the temperature produces a greater spread of the deoxygenation and dehydrogenation reactions only at high temperature. Conversely, at high pressure (120 bar), the positive kinetic effect of the pressure allows reaching the same elemental composition at lower temperatures. However, it must be borne in mind that the pressure also has a thermodynamic inhibitory effect due to the decrease in the water dielectric loss factor when the pressure increases. This increases the bio-oil yield, but also increases the proportions of C and O and decreases the HHV of bio-oil as the deoxygenation and dehydrogenation reactions occur to a lesser extent.

3.2.2 Chemical composition

The total amount of compounds present in bio-oils obtained from lignocellulosic biomass that can be analysed by Gas Chromatography normally represents about 25 wt.% of the crude bio-oil [5], due to the presence of high molecular weight lignin-derived compounds. Despite this fact, useful trends can be retrieved and a reliable comparison can be established between the chemical compositions of the bio-oils obtained using different operating conditions in order to address the effect of these operating variables on the chemical composition of the bio-oil. The bio-oil produced in this work (Table 2) is made up of esters (0–30%), aldehydes (4–69%), ketones (0–35%), alcohols (0–14%), phenols (0–83%), acids (0–28%), cyclic compounds (0–38%), acetates (0–11%), ethers (0–27%) and furans (0–12%). Table S1 shows the precise chemical composition of the bio-oil. Some of the most abundant esters are butyl octyl ester 1,2-benzenedicarboxylic acid and 9,12,15-Octadecatrienoic acid, 2,3-bis[(trimethylsilyl)oxy]propyl ester. Aldehydes include phenolic aldehydes such as vanillin, 3-hydroxy-4-methoxy- benzaldehyde and 2-Propenal, 3-(4-hydroxy-3-methoxyphenyl). Ketones comprise, 1-(2,3,4-trihydroxyphenyl)-ethanone and 3-methoxyacetophenone. Alcohols are made up of homovanillyl alcohol, 1,2,3-benzenetriol and 3-methyl-1,2-benzenediol. Phenols include 4-ethyl-2-methoxy-phenol and 2-methoxy-4-(1-propenyl)-phenol, while carboxylic acids comprise homovanillic acid and gibberellic acid were found. Cyclic compounds largely comprise olean-12-ene-3,15,16,21,22,28-hexol and 1-methyl-trans-decahydroquinol-5(equat)-ol. Ethers comprise methyl-(2-hydoxy-3-ethoxy-benzyl) ether, 2,3-epoxypropyl 3,5-xylyl ether and 1-monolinoleoylglycerol trimethylsilyl ether, while furans are largely made up of 2-acetyl-5-methylfuran and 1-(4-methoxy-2-nitroanilino)-1-deoxy-a-d-arabinofuranose. These compound have been found in other forms of chemically characterised bio-oil produced by hydrothermal liquefaction of biomass [1, 7, 9, 47].
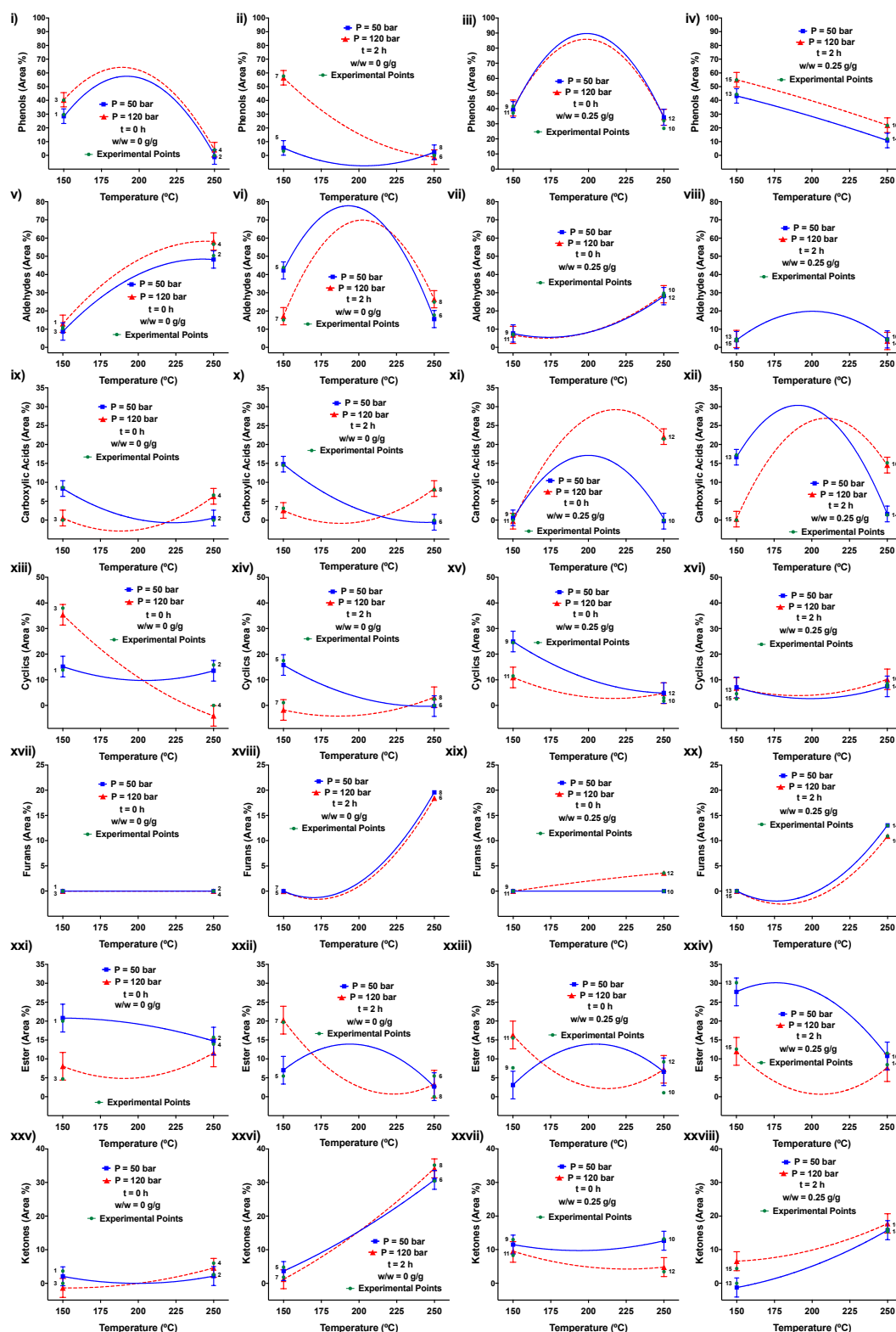
Figure 5. Interaction plots showing the effect of the operating conditions on the bio-oil chemical composition. Bars are LSD intervals with 95% confidence.

The statistical analysis of the results (Table S2) reveals that the temperature strongly affects the chemical composition of the bio-oil. In addition, the reaction time plays a very important role on the proportions of ketones, alcohols, and cyclic compounds, while the relative amounts of aldehydes and esters are significantly influenced by the amount of catalyst used in the process. In addition, some interactions between the operating variables also have a key influence on the chemical composition of the liquid. For

example, the interactions between the temperature and reaction time have a significant influence on the proportions of aldehydes, furans, alcohols, phenols and cyclic compounds, while the interaction between the reaction time and catalyst along with the interaction between the temperature and pressure largely influence the proportions of esters and ketones in the bio-oil. Figure 5 plots the effects of the operating variables and the most important interaction on the relative amount of the most abundant chemical families of compounds found in the bio-oil.

In the absence of a catalyst, phenols and aldehydes, closely followed by cyclic compounds, esters and furans are the most abundant compounds in the bio-oil. The presence of these compounds is in good agreement with previous pathways addressing biomass decomposition under hydrothermal conditions. The process mechanism involves the hydrolysis of biomass biopolymers into water soluble oligomers followed by their breakup into reactive fragments comprising a mixture of sugars, aldehydes, furans and phenols [9, 63]. For these non-catalytic experiments (0 g catalyst/g biomass), the bio-oil chemical composition and the effects of the temperature and pressure depend on the reaction time and two developments are observed. On one hand, for a short reaction time (0 min), the chemical composition is strongly influenced by the reaction temperature. In particular, and regardless of the pressure, an initial increase in the temperature between 150 and 200 ºC leads to a sharp increase in the proportions of phenols and aldehydes. During the hydrothermal liquefaction of biomass, the polysaccharide content (cellulose and hemicellulose) evolves towards the formation of phenols via isomerisation, cyclisation and dehydration reactions, while the lignin content depolymerises to give alkyl-substituted phenols [9, 64]. An increase in the temperature kinetically promotes these reactions, which explains the increase observed in the proportions of phenols and aldehydes. At low pressure (50 bar) these variations lead to a decrease in the relative amount of esters and carboxylic acids, while at high pressure (120 bar), the proportion of cyclic compounds decreases, as depolymerisation reactions are promoted with increasing the temperature. A further increase in the temperature from 200 to 250 ºC substantially decreases the proportion of phenols and slightly increases the proportions of aldehydes, due to the higher transformation of the lignin fraction of the biomass, which increases the relative amount of these aromatic aldehydes in the bio-oil. In addition, acid-catalytic reactions of phenols yielding phenolic aldehydes are likely to occur at high temperature even in the absence of a catalyst due to the acidic nature of the bio-oil [60, 65]. Carboxylic acids, furans and esters are less influenced by the temperature when a short reaction time is used in the absence of a catalyst. The proportions of carboxylic acids, ketones and furans are very low regardless of the pressure, while the proportion of esters is quite high a low pressure (50 bar) and progressively decreases with increasing the pressure up to 120 bar.

On the other hand, for a 2 h reaction, both the temperature and the pressure significantly influence the chemical composition of the bio-oil. At a low pressure (50 bar), the proportion of aldehydes initially increases between 150 and 200 ºC, where a maximum is reached, and subsequently decreases when the temperature is increased up to 250 ºC. In addition, reductions in the proportions of carboxylic acids and cyclic compounds (specially between 150 and 200) and esters (between 200 and 250 ºC) with increasing the temperature are also observed. The relative amount of phenols is unaffected by the temperature; remaining lower than 10% in all the cases, while the proportions of ketones and furans display a sharply increase. An increase in the reaction time helps lignin depolymerisation, thus increasing the proportion of phenolic aldehydes in the liquid when a long reaction time (2 h) is used. This latter fraction upsurges when the temperature is increased between 150 and 200 ºC due to the positive effect of the temperature on lignin depolymerisation. These variations are in good agreement with the results reported by other authors, who suggested that the formation of phenolic derivatives occurs via Diels-Alder and/or retro-Diels-Alder reactions between furanic compounds and aldehydes [66, 67], thus proving evidence for the decrease observed in the proportions of phenols and aldehydes and the increase in the relative amount of furans.

Increasing the pressure significantly modifies the chemical composition of the bio-oil; the most important variations occurring between 150 and 200 ºC. In particular, an increase in the pressure between 50 and 120 bar leads to a substantial increase in the proportion of phenols, along with a significant decrease in the relative amounts of aldehydes, carboxylic acids and cyclic compounds. An increase in pressure augments the partial pressure of the reactive species inside the reactor, which kinetically produces a greater development of the hydrolysis, isomerisation and cyclisation reactions. This promotes the formation of phenols and decreases the concentration of the species produced at early reaction stages, such as carboxylic acids [9]. Besides, increasing the pressure also modifies the effect of the temperature on the bio-oil chemical composition. Specifically, at 120 bar, increasing the temperature from 150 to 250 ºC leads to a substantial decrease in the proportions of phenols and esters along with an increase in the relative amounts of ketones and furans, while the proportions of carboxylic acids and cyclic compounds in the bio-oil are negligible regardless of the reaction temperature. At high pressure (120 bar), the thermodynamic inhibitory effect of the pressure decreasing the microwave efficiency might hinder the Diels-Alder and/or retro-Diels-Alder reactions between furanic compounds and aldehydes. As a result, the concentration of phenols is very low at 50 bar regardless on the temperature, while at 120 bar the relative amount of phenols decreses with increasing the temperature due to the positive kinetic influence of this variable. On the contrary, the effect of the temperature on the proportion of aldehydes does not depend on the pressure and the same evolution occurs within the whole pressure interval analysed in this work (50-120 bar).

An increase in the catalyst/bio-oil ratio from 0 to 0.25 g cat/g biomass substantially modifies the chemical composition of the bio-oil with the changes depending on the reaction time. For a short reaction time (0 h), increasing the amount of catalyst leads to an increase in the proportions of phenols, carboxylic acids and, to a

lesser extent, the amount of ketones. This also reduces the proportions of aldehydes and esters. At short reaction times, the hydrolysis of the biomass carbohydrate content (cellulose and hemicellulose) is favoured over lignin depolymerisation due to the higher reactivity of the former than the latter fraction [68]. In this regard, the catalyst might significantly promote the hydrolysis, isomerisation and dehydration reactions of cellulose and hemicellulose, which leads to the formation of phenolic compounds [9] as described earlier, thus increasing the amount of phenols in the liquid.

When the highest catalyst/biomass ratio is used (0.25 g cat/g biomass), the temperature has a very important influence on the proportions of phenols and carboxylic acids regardless of the pressure. In particular, their concentrations increase between 150 and 200 ºC. A further increase in the temperature up to 250 ºC decreases the relative amount of both families of compounds. The temperature kinetically promotes the decomposition of cellulose and hemicellulose fractions, which experimentally leads to an increase in the proportion of phenols and carboxylic acids between 150 and 200 ºC. A further increase in the temperature up to 250 ºC results in a substantial increase in the bio-oil yield, as lignin depolymerisation increases with increasing the temperature, which also leads to an increase in the proportion of aldehydes in the liquid. The influence of the temperature on the other families of compounds is less important; the principal variations occurring for aldehydes and cyclic compounds. In particular, regardless of the pressure, increasing the temperature from 150 to 250 ºC leads to an increase and a decrease in the concentration of the former and the latter compound, respectively. These variations are accounted for by the positive effect of the temperature on the process, which increases lignin depolymerisation. This leads to an increase in the proportions of aldehydes and produces a greater spread of the hydrolysis reactions, decreasing the proportions of cyclic compounds produced at early reaction stages.

Increasing the reaction time when using a 0.25 g cat/g biomass ratio has different consequences for the chemical composition of the bio-oil. The most important variations take place between 175 and 225 ºC. Within this interval and regardless of the pressure, an increase in the reaction time from 0 to 2 h decreases the proportion of phenols. This variation is accompanied by an increase in the proportion of both carboxylic acids and esters when a low pressure is used (50 bar), or by an increase in the proportion of carboxylic acids at high pressure (120 bar). These results seems to indicate that for long reaction times, the catalyst promotes dehydration reactions over isomerisation and cyclisation reactions; thus increasing the proportion of carboxylic acids and decreasing the formation of phenols. As a result, when the highest amount of catalyst (0.25 g cat/g biomass) is used for a long reaction time (2 h), and regardless of the pressure, increasing the temperature leads to a decrease in the relative amount of phenols within the whole temperature interval and an increase in the proportions of ketones and furans, specially between 200 and 250 ºC for these latter compounds. The proportion of carboxylic acids increases between 150 and 200 ºC and the decreases with a further increase up to 250

ºC, probably due to the thermal cracking of this compounds leading to gas formation. The effect of the temperature on the proportion of esters depends on the pressure: at 50 bar, a substantial decrease is observed at high temperature (between 200 and 250), while at 120 bar this decrease occurs at low temperature (between 150 and 200 ºC).

The effect of the pressure when using a high catalyst/biomass (0.25 g cat/biomass) ratio is relatively weak. For a short reaction time (0 h), an increase in the pressure from 50 to 120 bar leads to an increase in the proportion of esters and a decrease in the cyclics, between 150 and 175 ºC as well as an increase in the proportions of carboxylic acids and a decrease in the relative amount of esters between 175 and 250 ºC. For a long reaction time (2h), the pressure exerts a substantial influence at low temperature (150-200 ºC). Within this temperature interval, increasing the pressure from 50 to 120 bar decreases the proportion of esters and carboxylic acids and increases the relative amount of phenols and ketones. This can be accounted for by the lower microwave efficiency at high pressure, which hinders lignin depolymerisation, and therefore, the liquid contains a higher proportion of carbohydrate-derived species.

3.3 Theoretical optimisation and energy assessment

Optimum conditions were sought for the production of liquid biofuels and platform chemicals making use of the empirical models developed during the statistical analysis of the results. In particular, three options were considered. The first and the second scenarios are directed towards the production of a liquid bio-fuel. The first is aimed at maximising the bio-oil yield and HHV, while the second also includes the minimisation of the relative amount of carboxylic acids in the bio-oil. These acids increase the acidity of the bio-oil, which can cause corrosion problems in the combustor and increase the instability of the liquid. The third comprises the production of a bio-oil containing a high amount of phenolic compounds. A bio-oil containing a high proportion of aromatics could be used as a starting material to produce a wide spread range of chemicals as well as green and sustainable fuel additives to improve the oxidation stability of other liquid bio-fuels. In the optimisations, a relative importance (1-5) has been given to each objective to come up with a solution that satisfies all the criteria. Table 4 lists the objectives, the relative importance assigned to each objective together with the optimum values obtained for each optimisation.

Taking these restrictions into account, the three optima were found at high temperature (250 ºC) and long reaction time (112-116 min) employing a large amount of catalyst (0.17-0.25 g catalyst/g biomass). A good compromise between bio-oil yield (27%) and HHV (20 MJ/kg) (Opt. 1) takes place at medium pressure (80 bar). Increasing the pressure up to 120 bar helps minimise the relative amount of carboxylic acids (Opt. 2) in the bio-oil (2%) maintaining a relatively high bio-oil yield (25%) and HHV (19 MJ/kg). The maximum production of phenolic compounds (Opt. 3) occurs at 98 bar. However, this increase in the pressure (from 80 to 98 bar) does not translate into a significant increase in the proportion of phenolic compounds in comparison to those produced in Opt. 1. This indicates that a phenol-rich and energetic bio-oil could be

Table 4. Optimisations: objectives, relative importance and optimum values.

Optimisation	1		2		3	
	Objective	Solution	Objective	Solution	Objective	Solution
Temperature (ºC)		250		250		250
Pressure (ºC)		80		120		98
time (h)		1.86		1.93		1.88
Catalyst/biomass (g/g)		0.25		0.17		0.25
Global results						
Conversion (%)		73.4±4.72		65.9±4.72		73.4±4.72
Gas yield (%)		49.4±3.30		38.9±3.30		46.5±3.30
Bio-oil yield (%)	Maximise (5)	27.1±2.25	Maximise (4)	24.5±2.25	Maximise (5)	28.1±2.25
Bio-oil chemical Composition (Area %)						
Esters		1.4±3.76		12.1±3.76		1.1±3.76
Ketones		16.1±2.42		22.3±2.42		16.4±2.42
Alcohols		13.3±1.39		10.8±1.39		13.6±1.39
Phenols		46.4±3.48		9.8±3.48	Maximise (5)	47.2±3.48
Carboxylic acids		32.3±1.39	Maximise (5)	2.1±1.39		34.1±1.39
Cyclics		9.7±3.25		7.7±3.25		10.1±3.25
Acetates		5.1±0.83		0.1±0.83		5.1±0.83
Ethers		11.4±7.07		14.2±7.07		9.0±7.07
Furans		3.4±0.10		12.9±0.10		3.3±0.10
Aldehydes		0±3.10		0±3.10		0±3.10
Bio-oil elemental analysis and HHV						
C (wt.%)		55.8±2.59		47.5±2.59		54.7±2.59
H (wt.%)		6.4±0.18		5.9±0.18		6.3±0.18
O (wt.%)		37.8±2.44		46.2±		39.1±2.44
HHV (MJ/kg)	Maximise (5)	20.0±1.82	Maximise (4)	18.1±1.82		19.1±1.82

produced from biomass using this microwave-assisted hydrothermal process.

An energetic assessment was conducted to analyse the energy requirements of this process. The Energy consumption of the microwave was measured using a power meter (Energenie, model ENE007) directly connected to the microwave unit. At optimum conditions (250 ºC and 115-120 min, 10 g of a mixture of pine and spruce biomass and 500 mL H_2O), the total electric energy required for running the microwave reaction (including electricity to microwaves and microwaves to thermal conversions) is 0.164 kWh (0.59 MJ), which corresponds to 59 MJ/kg of biomass. The theoretical total energy required to heat up the feedstock (biomass and water) is around 0.47 MJ, which gives a microwave energy efficiency of around 80%. The energy efficiency for bio-oil production in this work can be estimated as the output energy, which includes the calorific value of the bio-oil and the energy that can be recovered from water cooling (from 250 ºC to 40 ºC, 0.44 MJ), divided by the total microwave energy (input energy) required to heat up the original bio-mass, catalyst and water used as the solvent (Table 1).

Taking this information into account, energy efficiencies between 82% (opt 2) and 84% (Op 1 and 3) are achieved at optimum conditions. However, it must be borne in mind that lab scale microwaves operate at a frequency of 2.45 GHz, thus having a low electrical efficiency, while industrial large-scale microwaves work at much lower frequency (in the region between 896 and 922 MHz) and electrical efficiencies higher than 85% can be attained [69, 70]. This could potentially increase the overall energy efficiency of this process. In addition, new catalysts can be developed and tested to increase both the bio-oil yield and its HHV and the biomass/water ratio could also be increased during the scale up;

these two strategies would help increase the overall energy efficiency of this developing technology. In addition, the microwave reactor could be modified to allow the sampling and analysis of the gas phase in order to gain more insights into the process for future applications. Therefore, the promising results of this preliminary study open the door for the use of microwave heating during the hydrothermal liquefaction of biomass for real future applications. In particular, this microwave-assisted hydrothermal process allows converting biomass into a high-energy, phenol-rich bio-oil at much lower temperatures (250 ºC) than those commonly used during hydrothermal liquefaction (300-350 ºC) [1, 7-10, 47]. This bio-oil could be used for the production of aromatic compounds, used as a bio-fuel precursor and/or as a renewable liquid additive to improve the oxidation stability of other fuels ought to its high aromaticity. Hence, this emerging technology might represent a step-change in the future energy and chemical production, helping to the development of novel and more energy efficient routes for biomass valorisation.

4. Conclusions

This work firstly addresses the Microwave-Assisted, Catalytic, Hydrothermal Liquefaction (MAC-HTL) of a mixture of pine and spruce biomass. The most important conclusions are summarised as follows.

1. The overall biomass conversion and the yields to gas and bio-oil varied by 13-77%, 7-67% and 1-29%, respectively. The temperature and the reaction time exerted the greatest influence on the global results. While an initial increase in these variables increased the conversion, a levelling-off was observed for the bio-oil yield when using high temperatures and long reaction times. The pressure and

the amount of catalyst also played an important role. An increase in the pressure drops the dielectric loss factor of water, decreasing the effectiveness of microwave heating. An increase in the catalyst amount promoted gas formation at low temperature/short reaction times and bio-oil production at high temperature/long reaction times.

2. The proportions of C, H and O in the bio-oil varied by 2-70 wt.%, 4-11 wt.% and 27-87 wt.%, which shifted the bio-oil HHV between 4 and 28 MJ/kg. In the absence of a catalyst, the bio-oil elemental analysis was not greatly influenced by the other conditions. Conversely, an increase in the catalyst amount significantly modified the elemental composition and HHV of the bio-oil due to the positive effect of the catalyst on depolymerisation, re-polymerisation, decarboxylation and deoxygenation reactions.

3. The bio-oil consisted of a mixture of esters, aldehydes, ketones, alcohols, phenols, carboxylic acids, cyclic compounds, acetates, ethers and furans. Increasing the temperature, reaction time and catalyst amount led to more isomerisation, cyclisation and dehydration reactions, promoting the formation of phenols and decreasing the concentration of species produced at early reaction stages, such as aldehydes and carboxylic acids. The pressure had both a kinetic positive influence along with an inhibitory thermodynamic effect due to the lower dielectric loss factor of water at high pressure.

4. The optimisation of the process revealed that it is possible to transform up to 27% of the biomass into a rich phenolic (47%) bio-oil with a relatively high HHV (20 MJ/Kg) when a temperature of 250 ºC, a pressure of 80 bar and 0.25 g catalyst/g biomass are used for 1.9 h. This liquid product could be used as a precursor for the production of aromatic compounds, liquid bio-fuels and/or phenolic-rich liquid additives.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

References

1. A. R. K. Gollakota, N. Kishore and S. Gu, *Renewable and Sustainable Energy Reviews*, 2018, **81**, 1378-1392.
2. S. Leow, J. R. Witter, D. R. Vardon, B. K. Sharma, J. S. Guest and T. J. Strathmann, *Green Chemistry*, 2015, **17**, 3584-3599.
3. Y. Li, S. Leow, A. C. Fedders, B. K. Sharma, J. S. Guest and T. J. Strathmann, *Green Chemistry*, 2017, **19**, 1163-1174.
4. C. Zhang, X. Tang, L. Sheng and X. Yang, *Green Chemistry*, 2016, **18**, 2542-2553.
5. K. Sipillä, E. Kuoppala, L. Fagernas and A. Oasmaa, *Biomass Bioenerg.*, 1998, **14**, 103-113.
6. K. R. Arturi, S. Kucheryavskiy and E. G. Søgaard, *Fuel Processing Technology*, 2016, **150**, 94-103.
7. A. Dimitriadis and S. Bezergianni, *Renewable and Sustainable Energy Reviews*, 2017, **68**, 113-125.
8. D. C. Elliott, P. Biller, A. B. Ross, A. J. Schmidt and S. B. Jones, *Bioresource technology*, 2015, **178**, 147-156.
9. M. Kumar, A. Olajire Oyedun and A. Kumar, *Renewable and Sustainable Energy Reviews*, 2018, **81**, 1742-1770.
10. S. S. Toor, L. Rosendahl and A. Rudolf, *Energy*, 2011, **36**, 2328-2342.
11. B. J. He, Y. Zhang, T. L. Funk, G. L. Riskowski and Y. Yin, *Transactions of the American Society of Agricultural Engineers*, 2000, **43**, 1827-1833.
12. T. Minowa, M. Murakami, Y. Dote, T. Ogi and S. y. Yokoyama, *Biomass and Bioenergy*, 1995, **8**, 117-120.
13. T. Minowa, T. Kondo and S. T. Sudirjo, *Biomass and Bioenergy*, 1998, **14**, 517-524.
14. S. Karagöz, T. Bhaskar, A. Muto and Y. Sakata, *Fuel*, 2005, **84**, 875-884.
15. A. Demirbaş, *Energy Sources*, 2005, **27**, 1235-1243.
16. A. Demirbaş, *Energy Conversion and Management*, 2000, **41**, 633-646.
17. A. J. Duan, Z. Y. Liu and J. Xu, *Rare Metal Materials and Engineering*, 2010, **39**, 52-55.
18. M. Saber, A. Golzary, M. Hosseinpour, F. Takahashi and K. Yoshikawa, *Applied Energy*, 2016, **183**, 566-576.
19. V. L. Budarin, J. H. Clark, B. A. Lanigan, P. Shuttleworth and D. J. Macquarrie, *Bioresource technology*, 2010, **101**, 3776-3779.
20. V. L. Budarin, P. S. Shuttleworth, J. R. Dodson, A. J. Hunt, B. Lanigan, R. Marriott, K. J. Milkowski, A. J. Wilson, S. W. Breeden, J. Fan, E. H. K. Sin and J. H. Clark, *Energy Environ. Sci.*, 2011, **4**, 471-479.
21. M. De bruyn, J. Fan, V. L. Budarin, D. J. Macquarrie, L. D. Gomez, R. Simister, T. J. Farmer, W. D. Raverty, S. J. McQueen-Mason and J. H. Clark, *Energy Environ. Sci.*, 2016, **9**, 2571-2574.
22. E. M. de Melo, J. H. Clark and A. S. Matharu, *Green Chem.*, 2017, **19**, 3408-3417.
23. J. Fan, M. De bruyn, V. L. Budarin, M. J. Gronnow, P. S. Shuttleworth, S. Breeden, D. J. Macquarrie and J. H. Clark, *J Am Chem Soc*, 2013, **135**, 11728-11731.
24. J. Fan, M. De bruyn, Z. Zhu, V. Budarin, M. Gronnow, L. D. Gomez, D. Macquarrie and J. Clark, *Chemical Engineering and Processing: Process Intensification*, 2013, **71**, 37-42.
25. T. Li, J. Remón, Z. Jiang, V. L. Budarin and J. H. Clark, *Energy Conversion and Management*, 2018, **155**, 147-160.
26. T. Li, J. Remón, P. S. Shuttleworth, Z. Jiang, J. Fan, J. H. Clark and V. L. Budarin, *Energy Conversion and Management*, 2017, **144**, 104-113.
27. Y.-F. Huang, P.-T. Chiueh and S.-L. Lo, *Sustainable Environment Research*, 2016, **26**, 103-109.
28. A. Mamaeva, A. Tahmasebi, L. Tian and J. Yu, *Bioresource technology*, 2016, **211**, 382-389.
29. R. Omar and J. P. Robinson, *Journal of Analytical and Applied Pyrolysis*, 2014, **105**, 131-142.
30. D. Rosso, J. Fan, E. Montoneri, M. Negre, J. Clark and D. Mainero, *Green Chem.*, 2015, **17**, 3424-3435.

31. Y. Q. Wan, P. Chen, B. Zhang, C. Y. Yang, Y. H. Liu, X. Y. Lin and R. Ruan, *Journal of Analytical and Applied Pyrolysis*, 2009, **86**, 161-167.
32. Z. Zhang, D. J. Macquarrie, M. De bruyn, V. L. Budarin, A. J. Hunt, M. J. Gronnow, J. Fan, P. S. Shuttleworth, J. H. Clark and A. S. Matharu, *Green Chem.*, 2015, **17**, 260-270.
33. F. Li, L. Liu, Y. An, W. He, N. J. Themelis and G. Li, *Journal of Cleaner Production*, 2016, **112**, 1049-1054.
34. N. Mahmood, Z. Yuan, J. Schmidt and C. Xu, *Renewable and Sustainable Energy Reviews*, 2016, **60**, 317-329.
35. R. Singh, B. B. Krishna, G. Mishra, J. Kumar and T. Bhaskar, *Renewable Energy*, 2016, **98**, 226-237.
36. M. F. Li, S. N. Sun, F. Xu and R. C. Sun, *Food chemistry*, 2012, **134**, 1392-1398.
37. M. F. Li, S. N. Sun, F. Xu and R. C. Sun, *Food chemistry*, 2012, **134**, 1392-1398.
38. F. Monteil-Rivera, G. H. Huang, L. Paquet, S. Deschamps, C. Beaulieu and J. Hawari, *Bioresource technology*, 2012, **104**, 775-782.
39. L. Zhou, V. Budarin, J. Fan, R. Sloan and D. Macquarrie, *ACS Sustainable Chemistry & Engineering*, 2017, **5**, 3768-3774.
40. L. Zhou, F. Santomauro, J. Fan, D. Macquarrie, J. Clark, C. J. Chuck and V. Budarin, *Faraday Discuss*, 2017, **202**, 351-370.
41. S. Zhou, L. Liu, B. Wang, F. Xu and R. Sun, *Process Biochemistry*, 2012, **47**, 1799-1806.
42. L. Zoia, M. Orlandi and D. S. Argyropoulos, *Journal of Agricultural and Food Chemistry*, 2008, **56**, 10115-10122.
43. J. Remón, P. Arcelus-Arrillaga, L. García and J. Arauzo, *Energy Conversion and Management*, 2016, **119**, 14-36.
44. J. Remón, J. A. Medrano, F. Bimbela, L. García and J. Arauzo, *Applied Catalysis B: Environmental*, 2013, **132-133**, 433-444.
45. J. Remón, G. Zhu, V. L. Budarin and J. H. Clark, *Green Chemistry*, 2018, **20**, 2624-2636.
46. S. Ren, X. P. Ye and A. P. Borole, *Journal of Analytical and Applied Pyrolysis*, 2017, **123**, 30-39.
47. S. Thiruvenkadam, S. Izhar, H. Yoshida, M. K. Danquah and R. Harun, *Applied Energy*, 2015, **154**, 815-828.
48. E. Peduzzi, G. Boissonnet and F. Maréchal, *Fuel*, 2016, **181**, 207-217.
49. J. Shen, S. Zhu, X. Liu, H. Zhang and J. Tan, *Energy Conversion and Management*, 2010, **51**, 983-987.
50. G. Yildiz, F. Ronsse, R. Venderbosch, R. v. Duren, S. R. A. Kersten and W. Prins, *Applied Catalysis B: Environmental*, 2015, **168-169**, 203-211.
51. P. Sun, M. Heng, S. Sun and J. Chen, *Energy*, 2010, **35**, 5421-5429.
52. L. Ye, J. Zhang, J. Zhao and S. Tu, *Bioresource technology*, 2014, **153**, 147-153.
53. C. Zhong and X. Wei, *Energy*, 2004, **29**, 1731-1741.
54. C. Xu and J. Lancaster, *Water Res*, 2008, **42**, 1571-1582.
55. T. Muppaneni, H. K. Reddy, T. Selvaratnam, K. P. R. Dandamudi, B. Dungan, N. Nirmalakhandan, T. Schaub, F. Omar Holguin, W. Voorhies, P. Lammers and S. Deng, *Bioresource technology*, 2017, **223**, 91-97.
56. D. I. Karpov and D. A. Medvedev, *Journal of Physics: Conference Series*, 2016, **754**, 102004.
57. P. Duan, X. Bai, Y. Xu, A. Zhang, F. Wang, L. Zhang and J. Miao, *Fuel*, 2013, **109**, 225-233.
58. P. Duan and P. E. Savage, *Applied Catalysis B: Environmental*, 2011, **104**, 136-143.
59. P. Duan and P. E. Savage, *Energy & Environmental Science*, 2011, **4**, 1447.
60. C. A. Fisk, T. Morgan, Y. Ji, M. Crocker, C. Crofcheck and S. A. Lewis, *Applied Catalysis A: General*, 2009, **358**, 150-156.
61. J. Chaminand, L. a. Djakovitch, P. Gallezot, P. Marion, C. Pinel and C. c. Rosier, *Green Chemistry*, 2004, **6**, 359.
62. W. B. Widayatno, G. Guan, J. Rizkiana, J. Yang, X. Hao, A. Tsutsumi and A. Abudula, *Applied Catalysis B: Environmental*, 2016, **186**, 166-172.
63. J. Yang, Q. He, H. Niu, K. Corscadden and T. Astatkie, *Applied Energy*, 2018, **228**, 1618-1628.
64. W. Yang, X. Li, Z. Li, C. Tong and L. Feng, *Bioresource technology*, 2015, **196**, 99-108.
65. M. Guisnet, in *Studies in Surface Science and Catalysis*, eds. C. N. G. C. Y. B. T. B. Imelik and J. C. Vedrine, Elsevier, 1985, vol. Volume 20, pp. 283-297.
66. C. Michailof, T. Sfetsas, S. Stefanidis, K. Kalogiannis, G. Theodoridis and A. Lappas, *J Chromatogr A*, 2014, **1369**, 147-160.
67. S. D. Stefanidis, K. G. Kalogiannis, E. F. Iliopoulou, C. M. Michailof, P. A. Pilavachi and A. A. Lappas, *Journal of Analytical and Applied Pyrolysis*, 2014, **105**, 143-150.
68. J. Remón, A. S. Matharu and J. H. Clark, *Energy Conversion and Management*, 2018, **165**, 634-648.
69. D. Beneroso, T. Monti, E. T. Kostas and J. Robinson, *Chemical Engineering Journal*, 2017, **316**, 481-498.
70. E. T. Kostas, D. Beneroso and J. P. Robinson, *Renewable and Sustainable Energy Reviews*, 2017, **77**, 12-27.