

Production of gaseous and liquid bio-fuels from the upgrading of lignocellulosic bio-oil in sub- and supercritical water: effect of operating conditions on the process

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ABSTRACT

This work analyses the influence of the temperature (310-450 °C), pressure (200-260 bar), catalyst/bio-oil mass ratio (0-0.25 g catalyst/g bio-oil), and reaction time (0-60 min) on the reforming in sub- and supercritical water of bio-oil obtained from the fast pyrolysis of pinewood. The upgrading experiments were carried out in a batch micro-bomb reactor employing a co-precipitated Ni-Co/Al-Mg catalyst. This reforming process turned out to be highly customisable for the valorisation of bio-oil for the production of either gaseous or liquid bio-fuels. Depending on the operating conditions and water regime (sub/supercritical), the yields to upgraded bio-oil (liquid), gas and solid varied as follows: 5-90%, 7-91% and 3-31%, respectively. The gas phase, having a LHV ranging from 2 to 17 MJ/m³ STP, was made up of a mixture of H₂ (9-31 vol.%), CO₂ (41-84 vol.%), CO (1-22 vol.%) and CH₄ (1-45 vol.%). The greatest H₂ production from bio-oil (76% gas yield with a relative amount of H₂ of 30 vol.%) was achieved under supercritical conditions at a temperature of 339 °C, 200 bar of pressure and using a catalyst/bio-oil ratio of 0.2 g/g for 60 minutes. The amount of C, H and O (wt.%) in the upgraded bio-oil varied from 48 to 74, 4 to 9 and 13 to 48, respectively. This represents an increase of up to 37% and 171% in the proportions of C and H, respectively, as well as a decrease of up to 69% in the proportion of O. The HHV of the

1 treated bio-oil shifted from 20 to 35 MJ/kg, which corresponds to an increase of up to
2 89% with respect to the HHV of the original bio-oil. With a temperature of around 344
3 °C, a pressure of 233 bar, a catalyst/bio-oil ratio of 0.16 g/g and a reaction time of 9
4 minutes a compromise was reached between the yield and the quality of the upgraded
5 liquid, enabling the transformation of 62% of the bio-oil into liquid with a HHV (29
6 MJ/kg) about twice as high as that of the original feedstock (17 MJ/kg).

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8 **Keywords:** bio-oil upgrading, subcritical water, supercritical water, bio-fuels
9 production

1. Introduction

Dwindling resources and the exponential growth in the demand for fossil fuels have motivated researchers to explore alternative energy supplies and technologies to produce both fuels and chemicals [1, 2]. In this context, biomass waste processing technologies are receiving increasing attention mainly because biomass is the only renewable source of carbon that can be converted into solid, liquid and gaseous products through different conversion routes [3]. Furthermore, these technologies meet the difficult challenge of producing energy and fuels through so-called environmentally friendly processes.

The thermochemical conversion of biomass is a promising route for the production of chemicals and energy from renewable resources [4-6]. Among all the possible thermochemical processes, fast pyrolysis is one of the most mature technologies used industrially for biomass conversion. This process allows the transformation of biomass into bio-oil, a combustible liquid that is easy to store and transport. Yields of 50-75% of bio-oil with a much higher volume energy density than the original feedstock can typically be obtained [7]. Bio-oils obtained from lignocellulosic biomass are dark brown organic liquids containing the degradation products of cellulose, hemicellulose and lignin [8]. They normally consist of a complex mixture of many different organic compounds such as aldehydes, ketones, sugars, carboxylic acids and phenols [9] whose specific chemical composition depends on the biomass source as well as the processing conditions under which the pyrolysis takes place [10].

The percentage of hydrogen in bio-oil (5.5-7 wt.%) makes it suitable for H₂ production

[11]. Two different thermochemical processes have normally been used for this. The first is non-catalytic steam reforming, which operates at high temperatures (1000 to 1400 °C) [12]. The second is catalytic steam reforming, which allows carrying out the process at a lower temperature (500-800 °C) but has the major drawback of the deactivation of the catalyst by coking. This motivated the implementation of a separation step in which bio-oil is split into two phases by water fractionation. The non-soluble fraction can be used for the production of high value-added chemicals, whereas the aqueous fraction is processed by catalytic steam reforming to produce H₂ [13].

With respect to the production of transportation fuels, bio-oils obtained from the pyrolysis of biomass are a possible source of biofuels [14, 15]. They offer several environmental advantages over fossil fuels. They are CO₂/GHG neutral; SO_x emission-free and release more than 50% lower NO_x than diesel during combustion [8, 16, 17]. However, the potential of these liquids for substituting petroleum fuels is limited due to their high viscosity, high water and oxygen contents, low heating value, instability and high acidity (corrosiveness) [18-21]. Consequently, the upgrading of bio-oil is essential for providing a liquid product that can be used as a fuel. There have been extensive studies on bio-oil upgrading, and various technologies have been developed: hydrotreating (HDT), hydrocracking (HDC) and the use of supercritical fluids (SCFs) [8, 16, 17].

In this context, sub- and supercritical water reforming (SWR) of bio-oil, also called supercritical water gasification (SCWG), is an interesting process for bio-oil upgrading [8, 16, 17, 22]. Cracking, reforming and hydrogenation reactions occur thanks to the generation of H₂ in the same process. In addition, the H₂ solubility limitation can be

1 reduced as H_2 and the bio-oil are brought into a single phase with the employment of
2 supercritical water [23]. The properties of water (sub/supercritical) enable the process to
3 be customised with slight changes in the process conditions towards the production of
4 liquids or gases, depending of the needs of the market. Therefore, this technology
5 represents a very challenging tailor-made alternative for bio-oil valorisation. Moreover,
6 the H_2 generated allows the in-situ hydrogenation of bio-oil to take place, which also
7 decreases the oxygen content in the bio-oil. This enables an upgraded bio-oil to be
8 obtained with better physicochemical properties than the original feedstock, which may
9 be used as a liquid fuel either alone or mixed with other petroleum-derived oils.

10
11 Studies concerning the treatment of lignocellulosic biomass and/or bio-oils in
12 sub/supercritical water can be divided into two groups. The first addresses the direct
13 conversion of biomass into H_2 using sub/supercritical water [24-26], while the second
14 examines the upgrading of bio-oils previously produced from biomass. Although the
15 former has to face several problems for the correct development of the technology, such
16 as the preparation of wet biomass in the form of a fluid that can be fed with high-
17 pressure pumps to the reformer reactor, studies in the latter group are very scarce. In
18 addition, they are more focused on H_2 and/or CH_4 production from bio-oil than on
19 producing liquid fuels, for which the only reported works concern algal bio-oils. There
20 is, therefore, little research in the field of the production of gaseous and liquid biofuels
21 from lignocellulosic bio-oil by sub- and supercritical water treatment.

22
23 Penninger and Rep [27] analysed the reforming of a bio-oil obtained from the pyrolysis
24 of biomass by its treatment in supercritical water at 650 °C for H_2 production. It was

found that the pressure of the aqueous reaction medium exerted a significant influence on the process. High pressures retarded the formation of gas and inhibited coke formation. Onwudili and Williams [28] investigated the catalytic supercritical water gasification of a heavy dewatered bio-oil in a batch reactor using a Ru/Al₂O₃ catalyst (5-20 wt.% of Ru) at a temperature between 400 to 500 °C and pressure ranging from 265 to 400 bar, varying the holding time between 0 and 60 min. They found that gas production increased with increasing the holding time and reaction temperature. Higher Ru loadings led to increased carbon gasification efficiency, high CH₄ production and a dramatic reduction in both char and oil yields.

As regards algal bio-oil upgrading, several works, most of them by Duan et al. [29-32], have been carried out with sub/supercritical water aiming to improve the properties of the original feedstock for use as a liquid fuel. These include the hydrotreatment of crude algal bio-oil in supercritical water, a parametric study examining the effect on the process of the temperature (430–530 °C), time (2–6 h), catalyst type (Pt/C, Mo₂C, HZSM-5) and catalyst loading (5–20 wt.%) as well as the use of formic acid (2-37 mmol) as a H₂ donor. This upgrading technology proved suitable for improving bio-oil properties. The temperature was always the most influential operating variable. The catalyst loading exerted the greatest effect on the higher heating value and O/C ratio in the treated oil, while the reaction time significantly affected the H/C and N/C ratios.

Given this background, the main objective of this work is to analyse the influence of the operating conditions (temperature, pressure, catalyst/bio-oil mass ratio and reaction time) during the reforming in sub- and supercritical water of a bio-oil obtained from the

fast pyrolysis of pinewood to produce gaseous and liquid biofuels. A full factorial design (DOE) with a statistical analysis of the results has been used to analyse the effect of the operating conditions. The product distribution (gas, liquid and solid) and properties of the gas and upgraded liquid obtained in the process have been addressed and fully discussed. The fact that the combined effect of the operating variables and their interactions on the valorisation of lignocellulosic bio-oil in different water regimens, i.e subcritical and supercritical water conditions, has never been reported before demonstrates, together with the results provided by the in-depth study, that this work represents a novel investigation in this field.

2. Materials and methods

2.1 Bio-oil properties

The bio-oil used in this work, supplied by BTG, was obtained during the pyrolysis of pine sawdust using a rotating cone reactor. The properties of the crude bio-oil were determined by means of elemental analysis, chemical composition, water content, density, viscosity, pH and higher heating value (HHV). These are summarised in Table 1. The elemental analysis was carried out in an elemental analyser (Leco TruSpec Micro), and the viscosity was measured in a Cannon-Fenske routine viscometer (Cannon Instrument Co., model 150 T845) at 40 °C following the standard method EN ISO 3104. The water content was determined by means of Karl Fischer titration (Mettler-Toledo V20 volumetric KF titrator), the pH was measured with a pH meter and the HHV in a Ika-Werke C2000-basic calorimeter. The empirical correlation developed by Channiwala and Parikh [33] was used for estimating the HHV of the treated liquids due to the small amount of sample obtained in each experiment. To validate this empirical correlation, the water content in the bio-oil was reduced by means of a liquid-

liquid extraction with chloroform and the HHV of this dewatered bio-oil was both determined experimentally and estimated theoretically. No statistically significant differences were found between the HHV of the dry bio-oil determined experimentally and making use of the experimental correlation with 95% confidence (p -value = 0.46). Therefore, this validates the use of this correlation for the theoretical determination of the HHV of the upgraded liquid. This comparison was not done for the original bio-oil (in raw basis) as its high water content hinders its ignition, and the experimental HHV could not be determined. The original bio-oil and the treated liquid were analysed by GC-MS using an Agilent 7890 GC-system (model G3440A) equipped with a 5975C mass spectrometer detector, and an Agilent HP-FFAP column with 0.20 mm inner diameter, 50 m length and 0.33 μ m film thickness.

Table 1. Bio-oil characterisation results. Results are presented as mean \pm standard deviation.

Composition	
Organics (wt.%)	60.95
Ashes (wt.%)	<0.001
H ₂ O (wt.%)	39.05 \pm 0.39
Ultimate Analysis (raw basis)	
C (wt.%)	32.86 \pm 0.40
H (wt.%)	6.73 \pm 0.16
O (wt.%) ^a	58.91 \pm 0.48
N (wt.%)	0.51 \pm 0.03
S (wt.%)	0.99 \pm 0.11
Physical properties	
pH	2.45 \pm 0.02
Density (g/mL)	1.16 \pm 0.01
Viscosity (mPa·s)	10.44 \pm 0.48
HHV (MJ/kg) measured	No determined
HHV (MJ/kg) estimated	13.40
HHV (MJ/kg) measured dry basis	16.52 \pm 0.48
HHV (MJ/kg) estimated dry basis	17.34 \pm 0.77
Chemical Composition (Area %)	
Ketones	18.22 \pm 0.38
Carboxylic Acids	45.52 \pm 2.42
Furans	3.71 \pm 0.32
Alcohols	2.22 \pm 0.35
Aldehydes	1.41 \pm 0.32
Phenols	21.35 \pm 1.19
Benzenes	3.86 \pm 1.93
Sugars	1.99 \pm 1.14
Nitrogen compounds	1.72 \pm 0.51

^a Determined by difference

2.2 Experimental reforming study

The influence of the temperature (310-450 °C), pressure (200-260 bar), catalyst/bio-oil mass ratio in dry basis (0-0.25 g catalyst/g bio-oil) and reaction time (0-60 min) on the catalytic bio-oil upgrading was experimentally studied using a co-precipitated Ni-Co/Al-Mg catalyst in a stainless steel micro-bomb batch reactor. The variation intervals for the reaction temperature and pressure were chosen having regard to the critical point of water ($T = 374\text{ °C}$, $P = 221\text{ bar}$). Higher and lower temperatures and pressures were used to reach sub- and supercritical conditions. The variation intervals for the catalyst/bio-oil ratio and reaction time were selected to have non-catalytic/catalytic and short/long time experiments to selectively produce gases and liquids from bio-oil. The reaction section, having a volume of 12 mL, comprised a $\frac{1}{2}$ inch Swagelok bored-through tee with two plugs and connected by means of a $\frac{1}{4}$ inch tube with a wall thickness of 0.069 inch to a high pressure-high temperature (HPT) needle valve. A detailed diagram of the reactor is shown in Figure 1. The reactor is placed inside of a heated fluidised sand bath and attached to a shaking mechanism. The HPT valve is located 10 cm above the sand level during the tests. The reactor heat-up time, i.e. the time needed to reach the desired temperature, is typically 1-2 min. The reaction time was measured from the moment when the reaction temperature was reached. The system section above the HPT valve consists of a $\frac{1}{4}$ SS tube connected to two valves and a digital pressure gauge. This configuration allows the recovery of gases for subsequent analysis as well as the quantitative determination of the gas [34]. A detailed diagram of the reactor is shown in Figure 1. The detailed preparation procedure of the catalyst and its characterisation results can be found in previous communications [35-37].

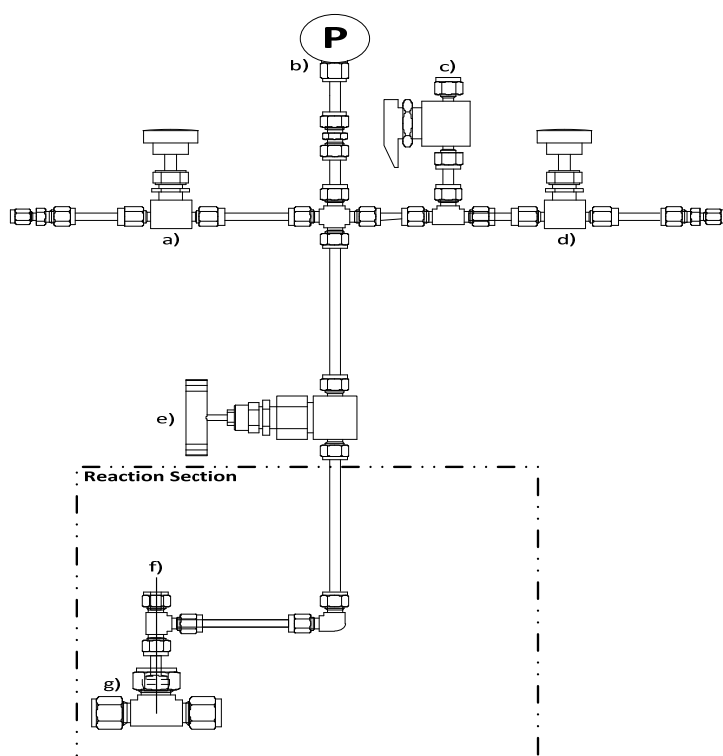


Figure 1. Schematic of the batch micro-bomb reactor. a) Purge inlet, b) Gas pressure gauge, c) Gas sampling port, d) Purge outlet, e) High pressure-temperature needle valve, f) Type K thermocouple, g) 1/2" bore-through tee.

The experimental procedure was as follows. The reactor was loaded with 0.82 g of bio-oil (0.5 g of bio-oil in dry basis), and the mass of catalyst and volume of deionised water were varied depending on the catalyst to bio-oil ratio and the pressure required in each experiment. The amount of water, based on a homemade calibration, allowed the operating pressure to be reached at the reaction temperature. Different water contents, from 3.28 to 6.23 g, had to be used depending on the temperature and pressure of each experiment. These different amounts of water varied the water/bio-oil ratio from 6.5 to 12.5. However, as a batch reactor was used and water was present in a greater proportion in comparison with bio-oil in all the experiments, the effect of the water/bio-oil ratio was not considered in this work. Secondly, the reactor was purged with He to remove air from the system prior to reaction. Thirdly, the micro-bomb system was placed in a Techne SBL-2D fluidised sand bath, previously heated up to the reaction

temperature. The temperatures of the sand bath and the reactor were monitored in situ with two type K thermocouples placed in the sand bath and inside the main reaction section, respectively. The reactor was kept submerged in the sand bath during the reaction steps. These include the first initial heating up (around 1-2 minutes), where the reaction temperature is reached, and the reaction itself. Finally, the reactor was quenched with cold water to drastically stop the reaction. After reaching room temperature, the gas, liquid (upgraded bio-oil) and solid products were recovered, measured and characterised.

The amount of gas produced was measured using an Omega digital pressure gauge. The gas product was analysed in a Perkin Elmer Clarus gas chromatograph equipped with a thermal conductivity detector (TCD) and a Carboxen plot 1010 capillary column. The liquid product was recovered from the system by rinsing the reactor with Sigma Aldrich 99 wt.% chloroform to recover the organic and aqueous products. This liquid phase was then filtered with Whatman 1 μm membrane filters (PTFE supported) to separate the solid fraction (spent catalyst, coke and char). The organic and aqueous phases were then separated through decantation in a 500 mL separation funnel. Afterwards, the organic fraction was dried under N_2 flow to determine the amount of bio-oil recovered. The upgraded bio-oil was then characterised by gas chromatography and elemental analysis using the apparatus already described in section 2.1. The solid fraction was dried overnight at room temperature. The catalyst particles with coke were separated from the char and both fractions were quantified and characterised by elemental analysis in a Leco TruSpec Micro elemental analyser.

2.3 Experimental plan, response variables and data analysis

The experiments were planned with a 2 level 4 factor Box-Wilson Central Composite Face Centred (CCF, $\alpha: \pm 1$) design. This corresponds to a full 2^k factorial design, where k indicates the number of factors studied (in this case 4 operating variables) and 2^k represents the number of runs (in this case 16), enlarged with 8 axial experiments to study non-linear effects and interactions according to the CCF design. In addition, four replicates at the centre point (centre of the variation interval of each factor) were carried out in order to evaluate the experimental error. This experimental design is suitable not only for studying the influence of each variable (linear and quadratic effects) but also for understanding possible interactions between variables.

The effect of the operating conditions on the reforming process has been evaluated using different response variables. These include the product distribution yields (%) to gas, liquid (upgraded bio-oil) and solid as well as the most important properties of the gas and the liquid phases. Table 2 summarises the response variables and the analytical methods used for their calculation. The results were analysed with an analysis of variance (ANOVA) with 95% confidence. The ANOVA analysis helped for the selection of the operating variables and interactions that significantly influence the response variables under consideration. In addition, the cause-effect Pareto principle was used to calculate the relative importance of the operating variables in the response variables. The higher the Pareto percentage of an operating variable, the greater is its influence on the response variable. In these analyses the lower and upper limits of all the factors (temperature, pressure, catalyst/bio-oil mass ratio and reaction time) were normalised from -1 to 1 (coded factors). This codification permits all factors to vary

within the same interval and helps to investigate their influence in comparable terms. Interaction plots have been developed from the statistical analyses conducted by means of the ANOVA test. In the interaction plots, the evolution of the response variables are plotted along with the LSD values obtained from the Fisher's least significant difference (LSD) test. To ensure significant differences between any pairs of data or the within the evolution of a response variable, the LSD bars must not overlap.

Table 2. Response variables. Definitions and analytical techniques used in their determination.

Product	Response variable	Analytical method
Gas	Gas yield (%) = $\frac{\text{mass of gas (g)}}{\text{mass of dry bio - oil (g)}} 100$	Gas Chromatograph
	Composition (vol. %) = $\frac{\text{mol of each gas}}{\text{total mol of gas}} 100$	
	LHV (MJ/m ³ STP) = 0.1079 H ₂ (vol.%) + 0.1263 CO (vol.%) + 0.3581 CH ₄ (vol.%)	Estimated
Liquid	Liquid yield (%) = $\frac{\text{mass of upgrading bio - oil (g)}}{\text{mass of dry bio - oil (g)}} 100$	GC-MS (Gas Chromatography-Mass Spectrometry). Elemental Analysis
	Composition (area %) = $\frac{\text{area of each compound}}{\text{total area}} 100$	
	C, H, O (%) = $\frac{\text{mass of C, H, O (g)}}{\text{mass of dry bio - oil (g)}} 100$	
	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	Solid yield (%) = $\frac{\text{mass of solid (g)}}{\text{mass of dry bio - oil (g)}} 100 = \text{Coke yield} + \text{Char yield}$	Elemental analysis
	Coke yield (%) = $\frac{\text{C on the catalyst (g)}}{\text{mass of dry bio - oil (g)}} 100$	
	Char yield (%) = $\frac{\text{mass of char (g)}}{\text{mass of dry bio - oil (g)}} 100$	

3. Results and discussion

Table 3 summarises the operating conditions for the experiments and the experimental results.

3.1. Yields to gas, liquid and solid products

The yields to gas, liquid and solid vary as follows: 7-91%, 5-90% and 3-31%, respectively. The relative influence of the operating variables on the global yields according to the ANOVA analysis and the cause effect Pareto principle is shown in Table 4.

1 *Table 3. Experimental conditions: temperature (T), pressure (P), reaction time (t) and catalyst/bio-oil (Wcat/Wbio) ratio and results obtained in*
2 *the experiments*
3

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
T (°C)	310	450	310	450	310	450	310	450	310	450	310	450	310	450	310	450	380	450	380	380	380	380	380	380	450
P (bar)	200	200	260	260	200	200	260	260	200	200	260	260	200	200	260	260	230	230	200	260	230	230	230	230	230
t (min)	0	0	0	0	60	60	60	60	0	60	0	0	60	60	60	60	30	30	30	30	0	60	30	30	30
Wcat/Wbio (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	0.125	0.125	0.125	0.125	0.125	0.125	0	0.25	0.125
Global results																									
Gas yield (%)	7.2	65.4	29.0	27.9	27.2	69.5	31.9	28.7	56.8	59.4	47.9	73.3	71.9	89.7	50.3	90.5	46.6±3.5	33.2	51.6	59.4	58.0	28.3	61.6	36.7	60.1
Liquid yield (%)	90.1	20.2	65.6	52.8	66.4	13.7	47.1	54.4	35.5	33.1	47.7	23.9	23.6	6.4	44.4	5.2	46.2±2.3	61.2	16.9	29.7	31.6	64.5	31.0	45.1	31.7
Solid yield (%)	2.8	14.4	5.4	19.3	6.4	16.9	21.0	16.9	7.7	7.5	4.4	2.8	4.5	3.9	5.3	4.3	7.1±2.3	5.7	31.4	10.9	10.4	7.2	7.4	18.2	8.1
Char yield (%)	2.8	14.4	5.4	19.3	6.4	16.9	21.0	16.9	4.6	5.5	0.8	1.5	1.1	1.0	1.6	3.5	5.4±2.4	2.4	29.7	7.4	7.1	3.2	4.2	18.2	4.8
Coke yield (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.1	2.0	3.6	1.3	3.4	2.9	3.7	0.8	1.8±0.1	3.2	1.7	3.5	3.3	4.0	3.1	0.0	3.3
Gas properties																									
H ₂ (vol.%)	9.37	11.43	28.03	12.94	13.42	15.19	8.63	25.15	20.28	16.38	16.69	20.10	27.79	15.43	13.50	11.50	24.6±2.4	23.44	19.66	23.21	21.40	26.93	22.64	22.78	18.75
CO ₂ (vol.%)	83.52	67.17	62.19	52.81	73.19	56.36	79.97	45.41	66.84	42.97	63.36	43.16	56.93	40.68	76.81	42.38	52.8±5.5	61.88	44.18	55.97	53.26	59.60	52.94	56.36	52.39
CO (vol.%)	6.65	11.17	5.33	22.26	11.34	13.07	9.78	11.32	2.32	3.70	2.06	3.09	0.64	1.36	5.92	1.48	2.1±0.7	2.30	2.81	1.55	2.14	3.90	2.03	13.39	1.37
CH ₄ (vol.%)	0.45	10.23	4.45	11.99	2.06	15.38	1.62	18.12	10.56	36.95	17.90	33.66	14.65	42.53	3.77	44.63	20.5±3.5	12.39	33.35	19.28	23.20	9.57	22.39	6.40	27.49
LHV (MJ/m ³ N)	2.01	6.31	5.29	8.50	3.62	8.80	2.75	10.63	6.26	15.47	8.47	14.61	8.32	17.07	3.55	17.41	10.3±1.4	7.25	14.42	9.60	10.89	6.82	10.72	6.44	12.04
Liquid properties																									
C (wt.%)	47.50	65.17	63.16	67.75	60.65	69.05	65.59	70.31	67.00	73.71	68.21	73.36	66.47	67.45	71.96	77.34	72.34±2.2	66.10	74.88	74.02	73.55	66.32	75.34	67.36	76.36
H (wt.%)	4.00	7.32	6.58	7.44	6.43	7.56	6.38	7.59	6.71	7.24	6.62	7.54	5.50	8.16	7.22	7.82	6.98±0.3	6.60	7.51	7.73	7.20	7.01	7.83	7.00	7.24
O (wt.%)	48.05	26.39	30.04	24.26	32.60	21.64	27.68	21.43	25.67	18.67	24.88	17.21	27.85	22.56	20.56	12.66	20.25±2.5	26.20	17.06	17.45	18.29	25.57	15.94	25.16	15.59
H/C	0.084	0.112	0.104	0.110	0.106	0.109	0.097	0.108	0.100	0.098	0.097	0.103	0.083	0.121	0.100	0.101	0.010±0.00	0.098	0.100	0.100	0.104	0.098	0.106	0.104	0.104
O/C	1.012	0.405	0.476	0.358	0.538	0.313	0.422	0.305	0.383	0.253	0.365	0.235	0.419	0.334	0.286	0.164	0.281±0.04	0.253	0.396	0.228	0.236	0.249	0.386	0.212	0.374
HHV (MJ/kg)	16.37	28.70	26.72	29.92	25.40	30.85	27.59	31.29	28.70	32.37	29.07	32.80	26.80	30.90	31.53	35.01	31.42±1.36	28.18	33.26	33.16	32.30	28.88	33.91	29.19	33.59
Liquid composition (% Area)																									
C.Acids	15.57	11.75	12.33	0.00	1.70	2.05	23.87	8.31	10.84	5.86	20.40	0.00	13.26	0.00	8.92	1.39	12.14±4.57	0.00	2.68	5.45	9.45	16.06	0.00	18.90	0.00
Ketones	11.35	14.84	25.35	4.28	23.73	19.99	2.80	8.18	10.91	4.34	12.16	2.53	8.41	4.07	4.86	0.00	4.76±2.32	7.45	4.71	3.49	2.43	15.45	3.49	21.95	0.00
Phenols	21.68	43.56	42.54	27.27	44.87	62.06	42.72	39.65	30.69	58.69	48.40	70.67	57.89	21.21	43.19	0.00	48.18±7.76	57.71	51.94	21.74	22.80	59.16	61.69	51.92	31.48
Cyclics	22.80	14.34	12.00	55.28	23.08	8.53	12.79	31.83	29.11	24.37	6.42	21.43	6.05	53.45	33.70	62.04	19.06±2.63	21.11	32.02	64.72	32.50	5.33	19.09	0.00	52.45
Furans	6.41	6.01	3.47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.83	0.92	3.80	0.00	1.57±2.33	1.69	0.00	0.00	7.31	0.00	2.18	6.66	4.77
Hydrocarbons	7.30	6.06	4.32	0.00	6.62	7.38	17.83	12.02	6.28	3.14	9.24	5.37	9.31	9.59	4.07	6.77	5.13±2.54	9.33	5.66	2.91	14.21	4.00	12.16	0.57	3.18
Ethers	0.00	2.02	0.00	0.00	0.00	0.00	0.00	0.00	12.17	1.66	2.29	0.00	3.26	10.76	1.47	29.80	5.45±2.68	2.72	0.00	1.69	11.29	0.00	1.39	0.00	8.12

4
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6
7

1 According to the cause-effect Pareto analysis, the temperature and the catalyst/bio-oil
2 ratio are the operating variables with the highest influence on the yields to gas, liquid
3 and solid. This finding was also reported by Duan et al. [30, 31] for crude algal bio-oil
4 upgrading in supercritical water. The relative coefficients for these two variables in the
5 models indicate that an increase in the temperature increases (positive term) the yields
6 to gas and solid and decreases (negative term) the yield to liquid. Cracking, reforming
7 [23, 27, 38, 39] and free-radical [39, 40] reactions are enlarged with temperature, which
8 favours gas formation from bio-oil. An increase in the catalyst/bio-oil ratio results in an
9 increase in the yield to gas and decreases in the yields to liquid and solid. The presence
10 of a catalyst in the process enhances gas formation, increasing the reaction rates of the
11 reforming and water gas shift reactions due to the availability of a large number of
12 active metal sites [29-32, 38, 40]. Furthermore, the catalyst might inhibit char formation
13 and/or favours char gasification, which also contributes to a decrease in the formation of
14 char, decreasing the yield to solid [29]. These developments in the yields to gas, liquid
15 and solid are in agreement with those previously reported by Onwudili and Williams
16 [28].

17
18 The reaction time and the total pressure of the system exert a significant influence on
19 the global yields, although their effect is weaker than the effects of the temperature and
20 catalyst/bio-oil ratio, as was also reported by Duan et al. [30, 31]. Interestingly, the
21 effect of the reaction time on the yield to solid is not significant. This indicates that a
22 great amount of solid (char) might have its origin in the thermal decomposition of non-
23 volatile species during the heating up of the reactor [23]. This stage occurs 1-2 minutes
24 prior to the start of the reaction when immersing the reactor in the sand bath. Significant
25 interactions between variables also take place, demonstrating that the other operating

variables influence the effect that each variable has on the global yields. To gain a better understanding of the process, Figures 2 and 3 display the effect of the operating variables and the most important interactions detected with the ANOVA analysis.

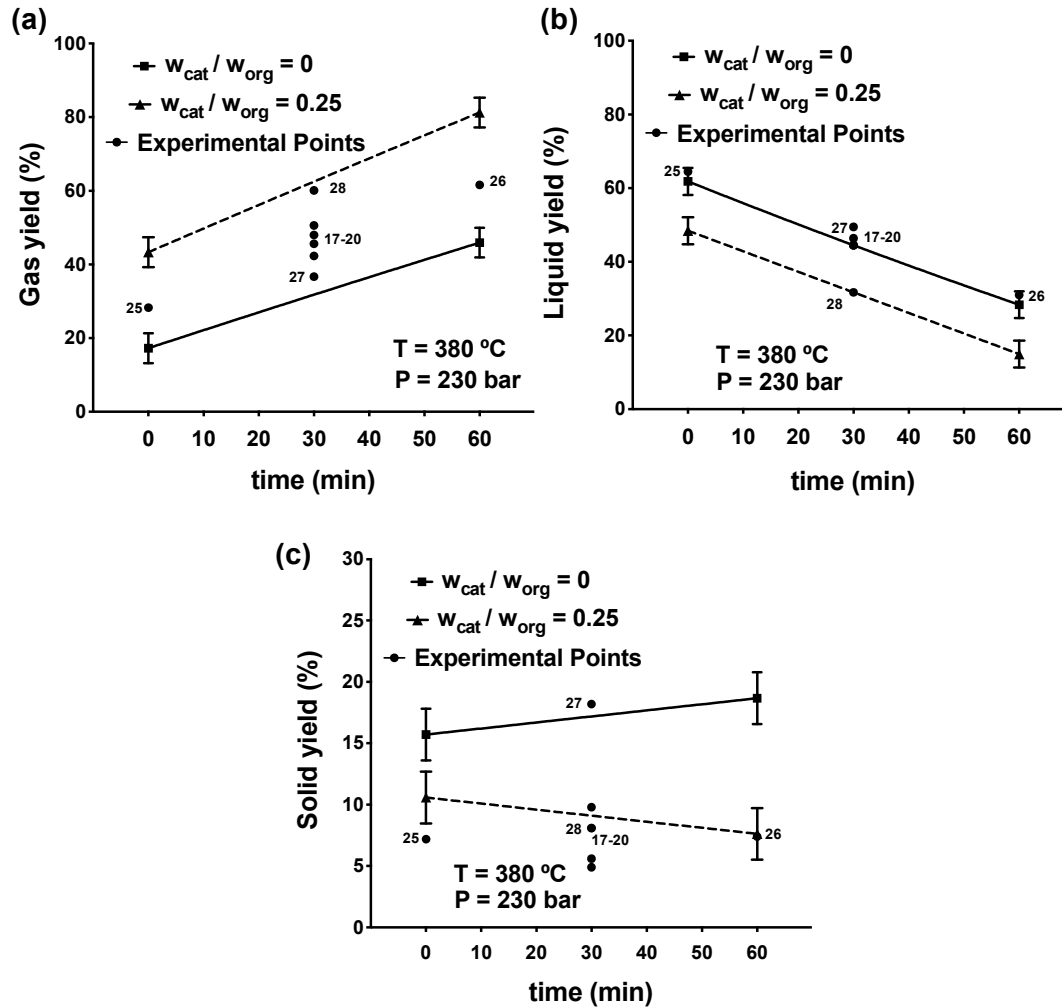


Figure 2. Influence of the reaction time on the yields to gas, liquid and solid at 380 °C and 230 bar for catalyst/bio-oil (W_{cat}/W_{org}) ratios of 0 and 0.25. Bars are LSD intervals with 95% confidence.

1
2 Table 4. Relative influence of the operating conditions on yields to gas, liquid and solid according to the ANOVA analysis

	R ²	Indep.	T	P	t	W	TP	Tt	TW	Pt	PW	tW	T ²	P ²	t ²	W ²	TPt	TPW	TtW	$\frac{Pt}{W}$	T ² P	T ² t	T ² W	TP ²	T ² P ²	$\frac{TPt}{W}$
Gas yield (%)	0.99	46.94	17.29 (18)	n.s	16.65 (9)	15.36 (25)	-3.72 (5)	n.s	9.62 (14)	-2.89 (1)	2.25 (5)	2.33 (1)	-5.72 (1)	10.58 (7)	n.s	n.s	n.s	9.37 (17)	-2.25 (2)	n.s	-4.23 (4)	-10.85 (6)	n.s	n.s	ns	n.s
Liquid yield (%)	1	46.73	-22.15 (20)	n.s	-16.75 (8)	-6.70 (16)	4.61 (5)	n.s	2.84 (5)	1.87 (1)	n.s	n.s	-7.68 (2)	-16.08 (4)	n.s	-8.33 (1)	n.s	-10.03 (1)	-4.22 (2)	n.s	-3.26 (3)	10.02 (6)	-5.21 (2)	8.98 (5)	24.75 (6)	-0.94 (1)
Solid yield (%)	0.98	7.18	12.85 (10)	n.s	n.s	-4.05 (14)	-0.88 (3)	-1.18 (5)	-2.21 (7)	1.02 (3)	-1.81 (6)	-1.48 (6)	11.4 (4)	3.47 (5)	ns	5.97 (1)	-0.99 (1)	n.s	1.21 (2)	n.s	0.96 (2)	0.93 (2)	n.s (21)	-11.07 (12)	-19.01 (10)	1.12 (4)

3

n.s: Non significant with 95% confidence

Response = Indep. + Coefficient T·T + Coefficient P·P + Coefficient t·t + Coefficient W·W + Coefficient Tt·T·t + Coefficient TW·T·W + Coefficient Pt·P·t + Coefficient PW·P·W + Coefficient tW·t·W + Coefficient T²·T² + Coefficient P²·P² + Coefficient t²·t² + Coefficient W²·W² + Coefficient TPt·T·P·t + Coefficient TPW·T·P·W + Coefficient TtW·T·t·W + Coefficient PtW·P·t·W + Coefficient T²P·T²·P + Coefficient T²t·T²·t + Coefficient T²W·T²·W + Coefficient TP²·T·P² + Coefficient TPtW·T·P·t·W.

4

5

Numbers in brackets indicate the percentage Pareto influence of each factor on the response variable. Pareto values represent the percentage of the orthogonal estimated total value.

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T = temperature, P = pressure, t = reaction time and W = catalyst/bio-oil ratio

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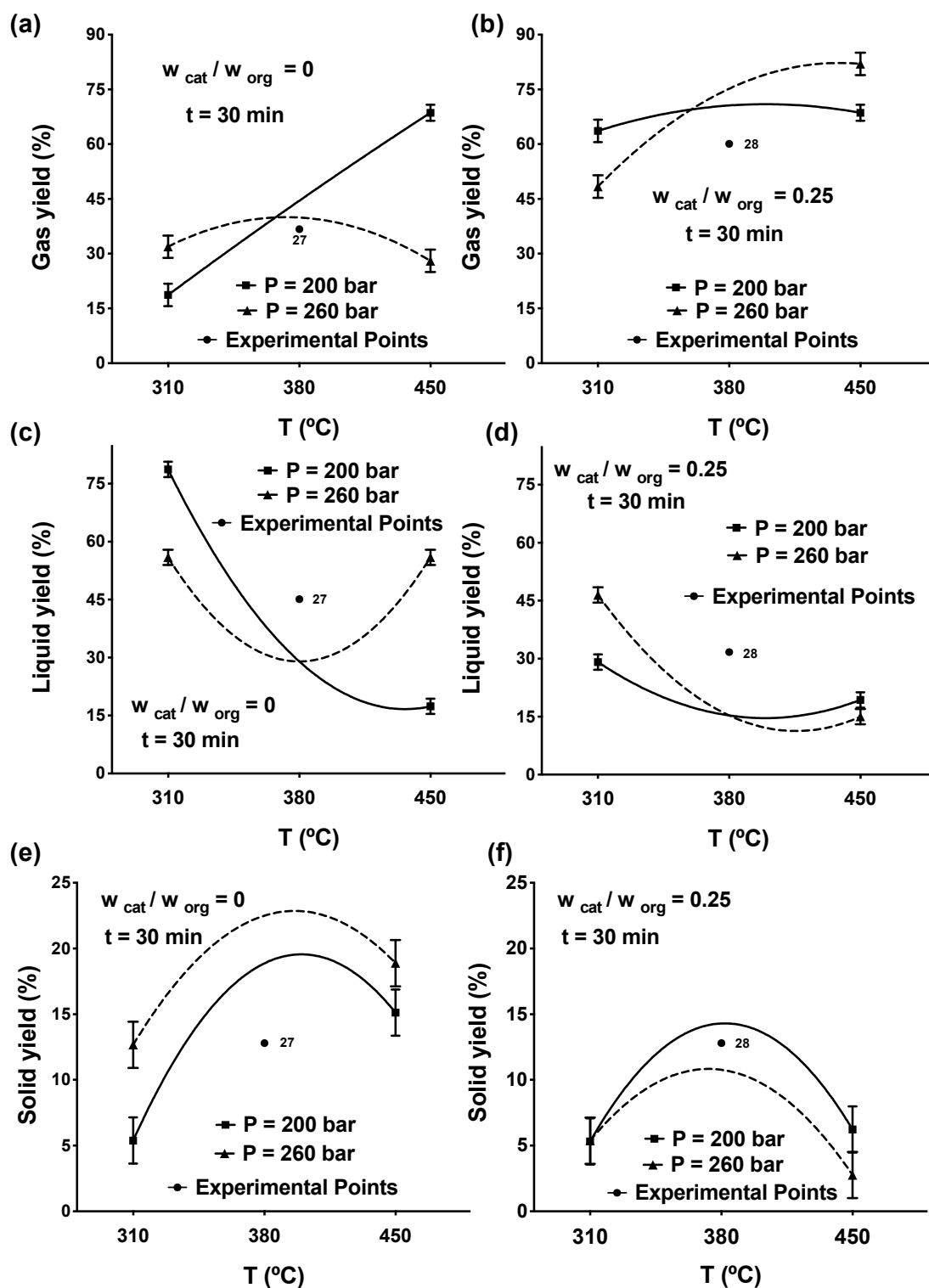


Figure 3. Effect of the temperature and pressure for 30 min reaction time using catalyst/bio-oil (w_{cat}/w_{org}) ratios of 0 and 0.25 on the yields to gas, liquid and solid. Bars are LSD intervals with 95% confidence.

3.1.2 Effect of the reaction temperature and pressure on the yields to gas, liquid and solid

The effect of the temperature and the pressure on the global yields is shown and discussed for a reaction time of 30 minutes. Specifically, Figures 3 a, c and e illustrate the effect of the temperature and the pressure on the global yields in the absence of catalyst for a reaction time of 30 min. These effects are shown for a catalyst/bio-oil ratio of 0.25 g/g in Figures 3 b, d and f.

The effect of the temperature on the global yields depends on both the pressure and the catalyst/bio-oil ratio. In the absence of catalyst, an increase in the temperature from 310 to 450 °C at 200 bar increases the gas yield and reduces the liquid yield. Between 310 and 380 °C, the yield to solid increases with the temperature, reaching a maximum. A further increase in the temperature up to 450 °C slightly decreases the yield to solid. The temperature exerts a kinetic effect on cracking and reforming reactions [23, 27, 38, 39], thus increasing the formation of gas from bio-oil. In addition, under this pressure, an increase in temperature changes the state of water from subcritical water to vapour at 366 °C. This enlarges the thermal cracking and steam reforming reactions, thus dramatically increasing the gas formation. Steam can help the gasification of char, which explains the reduction in the yield to solid observed.

Conversely, at 260 bar an increase in the temperature between 310 and 380 °C slightly augments the yield to gas and dramatically reduces the liquid yield. A further increase in the temperature up to 450 °C leads to a mild decrease in the gas yield and a sharp increase in the yield to liquid. At this pressure, the increase in temperature causes the water to change from the subcritical to the supercritical state. At subcritical conditions

1 an increase in temperature results in an increase in gas production from bio-oil. Once
2 supercritical conditions are reached, the reaction pathway, rates and equilibrium are
3 modified [29]. The ion reactions rate increases and free-radical reactions occur to a
4 lesser extent [41], thus decreasing and increasing the yields to gas and liquid,
5 respectively. In addition, water as a solvent can act as a physical barrier that retards the
6 process of a chemical reaction [27, 41], which also helps to reduce gas formation.

7
8 The yield to solid follows the same trend as described for 200 bar, indicating that the
9 presence of supercritical water can partially reduce solid formation and/or favour its
10 removal [27, 29]. One possible explanation for the coke control in SCW is attributed to
11 the good solubility of potential coke precursors in SCW, so that they are extracted and
12 transported from the catalyst pores, thus retarding coke formation [29]. In addition, the
13 formation of coke precursors is also diminished in SCW due to the reduction in water
14 diffusivity, a phenomenon commonly known as the “cage effect” [27, 41].

15
16 The effect of the pressure depends on the temperature. While an increase in the pressure
17 from 200 to 260 bar increases gas formation, decreasing the yield to liquid between 310
18 and 380 °C; it exerts the opposite effect from 380 to 450 °C. Between 310 and 367 °C
19 water remains under subcritical conditions between 200 to 260 bar, and the pressure
20 exerts a positive effect on the process, increasing the cracking and reforming reaction
21 rates. Conversely, between 367 and 450 °C the same increment in the pressure changes
22 the state of water from steam, where reforming and cracking reactions are favoured, to
23 supercritical water, reducing the gas formation and thus increasing the yield to liquid.
24 The rate of reaction of bio-oil in water depends on the density and viscosity of water,
25 which are functions of temperature and pressure. In SCW, diffusion of high molecular

weight organic radicals is hindered by the formation of a solvent cage around the solute molecules, commonly known as the supercritical “cage effect”. The cage effect hinders fission-type reactions by detaining the nascent product within the cage. If the products cannot escape from the cage, they are more likely to recombine and regenerate the reactants, decreasing the gas formation and thus increasing the yield to upgraded liquid product [27, 41]. The cage effect increases when increasing the pressure [27, 41], which accounts for the experimental observations of this work.

The effect of the pressure on the solid yield is relatively low. In general, an increase in pressure slightly increases the yield to solid, especially between 310 and 380 °C. The highest increase in the solid yield (from 7 to 14%) occurs at 310 °C. This increase is reduced as the temperature increases from 310 to 380 °C. At temperatures higher than 380 °C, the pressure negligibly influences the solid yield. The physicochemical properties of water change at temperatures higher than 300 °C, and the solubility of the bio-oil in water can be enhanced with pressure, thus decreasing char formation. Other authors have observed a decrease in the solid yield with pressure, which has been attributed to an increase in the cage effect with increasing pressure due to the increase in the density of water [27, 41]. In the present work, the pressure exerts a negligible effect on the yield to solid, probably due to the fact that solid formation is principally char being formed during the heating up of the reactor.

The effect of the presence of a catalyst on the yields to gas, liquid and solid can be gathered comparing Figures 3 a and b, 3 c and d, and 3 e and f, respectively. It is observed that an increase in the catalyst/bio-oil ratio from 0 to 0.25 g/g increases gas formation, reducing the yields to liquid and solid. Increasing the amount of catalyst

enhances the reforming and cracking reactions from bio-oil due to the availability of a large number of active metal particles [29-32, 38, 40]. In addition, it decreases the solid yield, inhibiting solid formation and/or helping its elimination.

The effect of the catalyst depends on the temperature and pressure. At 200 bar an increase in the catalyst/bio-oil ratio between 310 and 380 °C produces a higher increase in the yield to gas and a lower decrease in the yield to liquid than between 380 and 450 °C. The temperature exerts a positive kinetic effect on gas production; therefore the positive catalytic effect of the catalyst could be masked as the temperature increases, especially at high temperatures where gas production is favoured due to the presence of steam. Under such conditions the effect of the catalyst turns out to be insignificant.

Conversely, as the pressure increases the catalyst exerts a greater influence on the yields to gas and liquid. A higher increase and decrease in the yields to gas and solid, respectively, occur at temperatures higher than 380 °C. Under these conditions, water is in the supercritical state and gas formation is not as favoured in the absence of catalyst as it is in subcritical conditions. Therefore, the effect of the catalyst is more evident. At 450 °C an increase in the catalyst/bio-oil ratio from 0 to 0.25 increases the gas yield from 30 to 80%, which corresponds to an increase of 167% in gas production due to the presence of a catalyst. In addition, SCW as a reaction medium can influence bio-oil decomposition towards gases. Water can participate as a collision partner in intermolecular energy-transfer steps, which are required for nominally unimolecular reactions, increasing the gas formation due to the presence of a catalyst. Solid formation also decreases when increasing the catalyst/bio-oil ratio. This suggests that the catalyst is capable of suppressing char formation by breaking C-C bonds in the bio-oil

components [28, 42, 43]. This reduction depends on the pressure and the temperature. At 260 bar a decrease in solid formation takes place for the whole temperature range, while at 200 bar it takes place at temperatures higher than 380 °C. At low pressure, steam is needed for the gasification of coke, while high pressure helps to decrease solid formation in the presence of a catalyst.

3.2 Gas composition

As can be seen from the results listed in Table 3, the gas phase consists of a mixture of H₂ (9-28 vol.%), CO₂ (41-84 vol.%), CO (1-22 vol.%) and CH₄ (1-45 vol.%) and has a Lower Heating Value (LHV) varying from 2 to 18 MJ/m³ STP. The temperature and the catalyst/bio-oil ratio are the operating variables with the greatest influence on the volumetric composition and the LHV of the gas (Table 5). The temperature was also identified by Duan et al. [30, 31] as the most influential parameter on the gas composition during algal bio-oil upgrading in SCW. In addition, significant interactions between the operating variables occur, which makes the effect of each operating variable different depending on the other operating conditions.

1 *Table 5. Relative influence of the operating conditions on the composition of the gas phase and the LHV according to the ANOVA analysis*
2

	R ²	Indep.	T	P	t	W	TP	Tt	TW	Pt	P·W	tW	T ²	P ²	t ²	W ²	TPt	TPW	TtW	PtW	T ² P	T ² t	T ² W	TP ²	TPtW
H ₂ (vol.%)	0.90	25.35	n.s	n.s	n.s	n.s	n.s	n.s	-1.32 (6)	2.14 (11)	-2.65 (12)	n.s	-3.99 (9)	n.s	n.s	-4.78 (23)	2.12 (12)	1.31 (4)	-2.77 (15)	n.s	n.s	n.s	n.s	n.s	-1.86 (7)
CO ₂ (vol.%)	0.93	53.33	-10.66 (34)	n.s	n.s	n.s	n.s	-1.87 (7)	n.s	3.38 (12)	3.78 (11)	n.s	n.s	n.s	5.78 (13)	n.s	-3.05 (11)	n.s	n.s	n.s	n.s	n.s	-5.61 (14)	n.s	n.s
CO (vol.%)	0.99	2.48	n.s	n.s	n.s	-6.01 (26)	0.57 (3)	-1.37 (7)	-1.77 (9)	-0.57 (4)	n.s	n.s	n.s	n.s	n.s	4.41 (15)	-1.23 (7)	-0.96 (6)	0.90 (5)	1.06 (6)	0.83 (5)	n.s	1.47 (3)	1.32 (6)	n.s
CH ₄ (vol.%)	0.96	19.77	10.25 (31)	n.s	6.41 (6)	9.28 (28)	n.s	2.09 (7)	4.33 (12)	n.s	n.s	n.s	n.s	n.s	-2.74 (6)	n.s	2.16 (5)	n.s	n.s	n.s	n.s	-5.72 (5)	n.s	n.s	n.s
LHV (MJ/m ³ STP)	0.97	10.03	3.74 (31)	n.s	1.95 (5)	2.80 (23)	n.s	0.70 (6)	1.19 (9)	-0.54 (5)	-0.69 (4)	n.s	n.s	n.s	-1.24 (7)	n.s	0.85 (6)	n.s	n.s	n.s	n.s	-1.72 (4)	n.s	n.s	n.s

n.s: Non significant with 95% confidence

Response = Indep. + Coefficient T·T + Coefficient P·P + Coefficient t·t + Coefficient W·W + Coefficient Tt·T·t + Coefficient TW·T·W + Coefficient Pt·P·t + Coefficient PW·P·W + Coefficient tW·t·W + Coefficient T²·T² + Coefficient P²·P² + Coefficient t²·t² + Coefficient W²·W² + Coefficient TPt·T·P·t + Coefficient TPW·T·P·W + Coefficient TtW·T·t·W + Coefficient PtW·P·t·W + Coefficient T²P·T²·P + Coefficient T²t·T²·t + Coefficient T²W·T²·W + Coefficient TP²·T·P² + Coefficient TPtW·T·P·t·W

Numbers in brackets indicate the percentage Pareto influence of each factor on the response variable. Pareto values represent the percentage of the orthogonal estimated total value.

T = temperature, P = pressure, t = reaction time and W = catalyst/bio-oil ratio

3.2.1 Influence of the reaction time on the gas phase

3.2.1.1 Concentrations of H_2 and CO

The effect of the reaction time on the proportions of H_2 and CO is shown in Figures 4. Specifically, Figures 4 a and b, and 4 e and f display the effect of the time on the concentrations of H_2 and CO as a function of the catalyst/bio-oil ratio at 200 bar for the lowest (310 °C) and the highest (450 °C) temperature, respectively. Figures 4 c and d, and g and h illustrate these effects for a pressure of 260 bar.

At 200 bar there are different trends for the proportion of H_2 in the gas depending on the temperature and catalyst/bio-oil ratio. At 310 °C, the proportion of H_2 increases when increasing the holding time or the catalyst/bio-oil ratio. Conversely, at 450 °C there is a steady evolution of the proportion of H_2 regardless of the catalyst/bio-oil ratio. At low temperatures, high reaction times are needed for gas production. In addition, at 310 °C hydrogenation reactions of the bio-oil might not be kinetically favoured, which leads to a progressive increase in the proportion of H_2 in the gas with time. Conversely, an increase in the temperature up to 450 °C enhances both the production of H_2 by cracking and reforming reactions and H_2 consumption by bio-oil hydrogenation. Therefore, H_2 production and elimination can compensate each other, resulting in a steady concentration of H_2 with time. Isa et al. [39] found that around 0.48% of the H_2 produced was donated to the liquid phase during the treatment of miscanthus in SCW at 460 °C. In addition, these trends are also consistent with the evolution over time of the concentration of H in the liquid product.

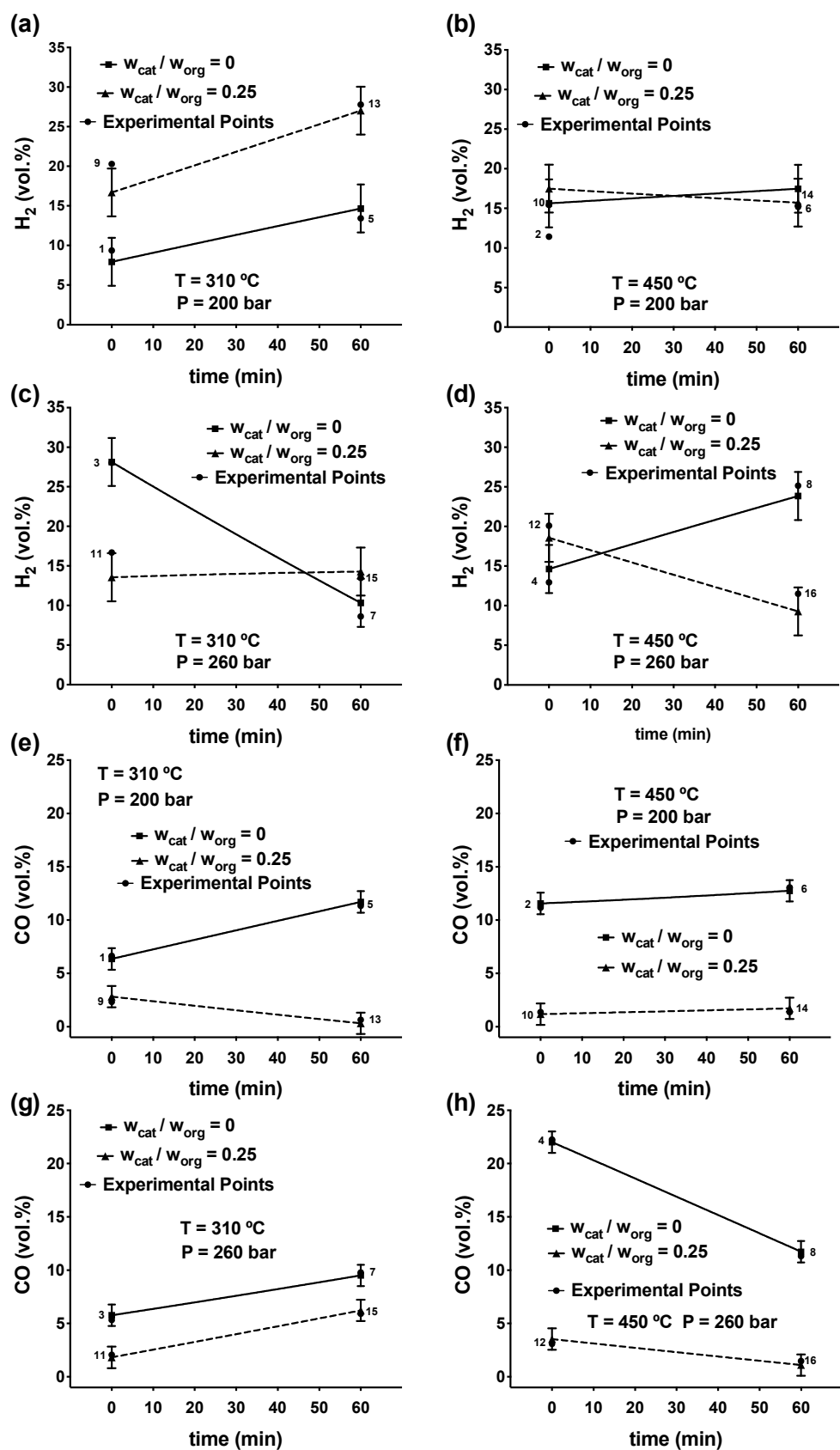


Figure 4. Effect of the reaction time on the volumetric composition of H_2 and CO at 200 and 260 bar for temperatures of 310 and 450 °C using catalyst/bio-oil (w_{cat}/w_{org}) ratios of 0 and 0.25. Bars are LSD intervals with 95% confidence.

At 260 bar a different evolution of the proportion of H_2 with time takes place. On the one hand, at 310 °C, the proportion of H_2 in the gas decreases with time in the absence of catalyst. An increase in the catalyst/bio-oil ratio decreases the proportion of H_2 in the gas and a steady evolution takes place. In the absence of catalyst, an increase in pressure from 200 to 260 bar increases gas production, as previously explained, which leads to an initial increase in the proportion of H_2 at the beginning of the reaction. However, when increasing the holding time, the H_2 produced could be progressively consumed during the hydrogenation of the bio-oil [39]. These two developments produce a decrease in the proportion of H_2 in the gas together with an increase in the concentration of H in the liquid phase. In addition, H_2 can also be consumed during methanation reactions, as the proportion of CH_4 in the gas increases when increasing the holding time in SCW [40, 41]. An increase in the total pressure increases the partial pressure of H_2 , thus producing a greater spread of hydrogenation reactions. This sharply reduces the proportion of H_2 in the gas. Reforming and hydrogenation reactions might account for the different evolution with time of the proportion of H_2 at 200 and 260 bar. At 200 bar, an increase in the holding time increases H_2 production as reforming reactions might be prevalent over hydrogenations. Conversely, at 260 bar hydrogenation reactions are intensified due to the higher partial pressure of H_2 , which reduces the proportion of H_2 in the gas.

An increase in the catalyst/bio-oil ratio promotes bio-oil hydrogenation reactions, thus decreasing the proportion of H_2 in the gas. This increase in pressure leads to an increase in the proportion of H in the liquid, providing evidence for this hypothesis. At 260 bar a further increase in temperature up to 450 °C changes the state of the water from subcritical to supercritical, which results in a different evolution over time for the

1 proportion of H_2 in the gas. In the absence of catalyst, an increase in the proportion of
2 H_2 over time takes place, while increasing the catalyst/bio-oil ratio up to 0.25 g/g results
3 in a decrease in the proportion of H_2 with time. In addition, a decrease in the proportion
4 of CO together with an increase in the concentration of CO_2 in the gas suggests a
5 progressive shift of the water gas shift reaction with time. Methane formation is
6 favoured under these operating conditions and the presence of the catalyst also favours a
7 greater spread of the methanation reaction [40, 41], explaining the decrease in the
8 concentration of H_2 .

9
10 The effect of the reaction time on the proportions of CO is dependent on the
11 temperature, pressure and catalyst/bio-oil ratio. At 200 bar and 310°C an increase in the
12 reaction time slightly varies the concentration of CO in the gas. This variation is directly
13 linked with the catalyst/bio-oil ratio. In the absence of catalyst, the proportion of CO
14 increases, while in the presence of a catalyst the proportion of CO in the gas drops with
15 time. In contrast, a steady evolution is observed at 450 °C. It is believed that the positive
16 kinetic effect that the temperature exerts on gas production accounts for these
17 differences. A high temperature allows a steady gas composition to be achieved from
18 the beginning of the reaction, which makes the effect of the reaction time insignificant.
19 As previously explained, the statistical analysis performed in this work reveals that
20 temperature exerts a greater effect than reaction time on the gas composition, as also
21 reported in the literature [30, 31], providing evidence for this hypothesis.

22
23 In contrast, at 260 bar the effect of the reaction time (which also depends on the
24 temperature) on the proportion of CO in the gas turns out to be different. At 310 °C the
25 proportion of CO in the gas slightly increases with time regardless of the catalyst/bio-oil

ratio. Other authors have also reported small variations in the proportion of CO in the gas when using water in subcritical conditions [44]. Conversely, at 450 °C, water is in a supercritical state, and a drop in the proportion of CO in the gas occurs over time. Short reaction times and low catalyst loadings lead to a relatively high initial proportion of CO in the gas when employing SCW, which is progressively reduced when increasing the holding time [30]. The catalyst/bio-oil ratio exerts the same effect on the proportion of CO in the gas regardless of the pressure and temperature. Figures 4 e-h show how an increase in the catalyst loading from 0 to 0.25 g catalyst/g bio-oil decreases the proportion of CO in the gas as the water gas shift reaction occurs to a greater extent [23, 30].

3.2.1.2 Concentrations of CO₂ and CH₄

The effect of the reaction time on the proportion of CO₂ depends on the pressure and the catalyst/bio-oil ratio. The same evolution over time for this gas occurs within the whole temperature range studied in this work (310-450 °C). As an example, the effect of the reaction time is shown in Figure 5 for a temperature of 380 °C and pressures of 200 and 260 bar, in the absence of catalyst and employing a catalyst/bio-oil ratio of 0.25 g/g.

At 200 bar an increase in the reaction time or in the catalyst/bio-oil ratio slightly decreases the proportion of CO₂ in the gas during the first 30 min of reaction, reaching a steady evolution during the final 30 min of the experiment. Gas formation increases when increasing the holding time. This evolution might indicate that thermal cracking leading to the formation of CO₂ is one of the fastest steps to gas formation. With the increase in the holding time, other reactions such as reforming and methanation occur, leading to a drop in the amount of CO₂ in the gas. This is consistent with the work of

Wawrzetz et al. [45], which demonstrated that the formation of CO₂ via decarbonylation is one of the fastest reactions in the treatment of organic compounds in subcritical water.

In contrast, an increase in the pressure up to 260 bar produces the opposite effect of the reaction time and the catalyst/bio-oil ratio. Specifically, the proportion of CO₂ shows a steady evolution during the first 30 min of reaction, progressively increasing for the last 30 min. Slight increases have been reported in other works using subcritical and supercritical water due to the higher spread of cracking and reforming reactions from light oxygenated compounds present in bio-oil as well as the water gas shift (WGS) reaction when increasing the holding time [23, 38]. In addition, an increase in the catalyst/bio-oil ratio increases the proportion of CO₂ in the gas.

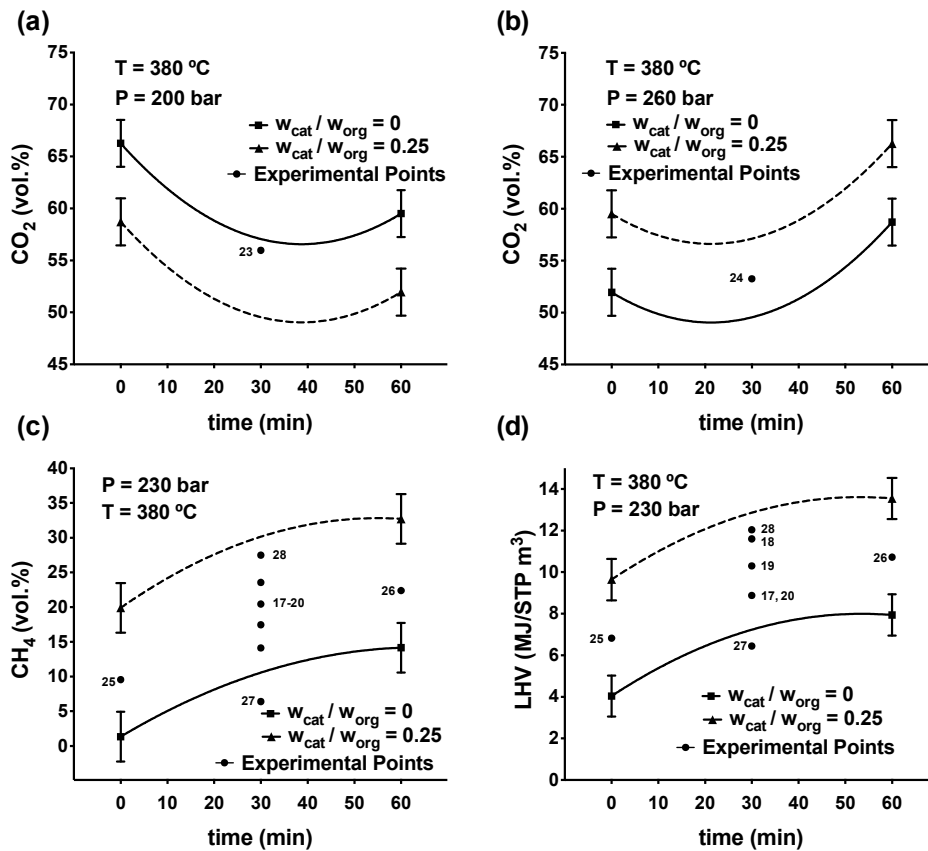


Figure 5. Effect of the reaction time on the volumetric composition of CO₂ and CH₄ and on the LHV of the gas. Bars are LSD intervals with 95% confidence.

The effect of the reaction time on the proportion of CH₄ in the gas is the same regardless of the other operating variables. As an example, Figure 5c shows the evolution over time for this gas at 380 °C and 230 bar. An increase in either the reaction time or in the catalyst/bio-oil ratio increases the proportion of CH₄ in the gas under all the experimental conditions tested in this work. The methanation reaction is favoured under sub- and supercritical water [40, 41], leading to an increase with time in the relative amount of CH₄ in the gas product, which is in agreement with the results of other authors studying bio-oil upgrading in supercritical water [28].

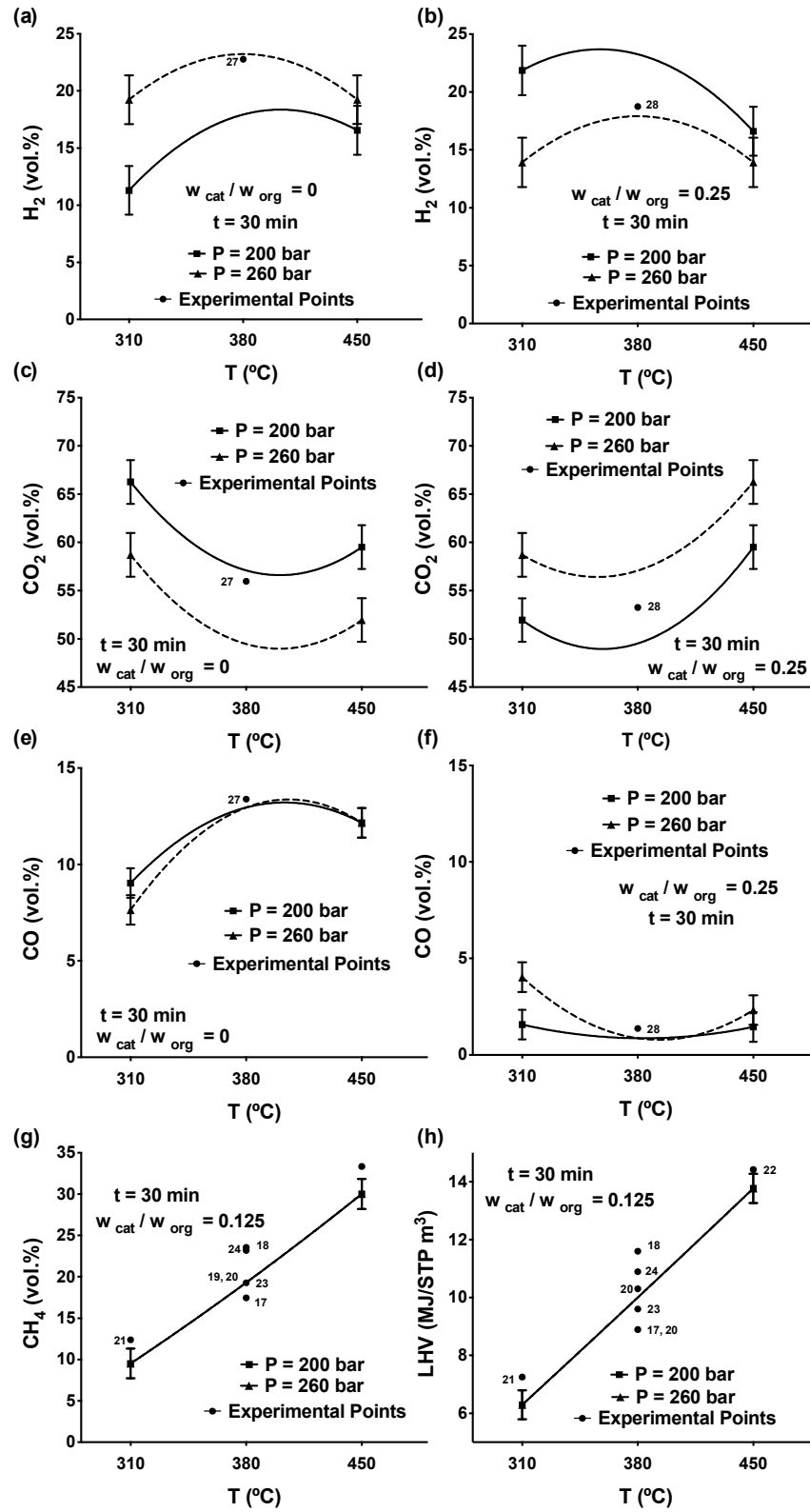
3.2.1.3 Lower Heating Value (LHV) of the gas

The evolution over time of the LHV of the gas is not affected by the other operating variables. As an example, Figure 5 d shows the evolution of the LHV at 380 °C and 230 bar. An increase in either the reaction time or in the catalyst/bio-oil ratio increases the LHV of the gas regardless of the temperature and pressure. This increase is strongly related to the increase in the proportion of CH₄ in the gas over time. A multivariate analysis by means of Spearman's test confirmed significant relationship between the concentration of CH₄ and the LHV of the gas (p-value < 0.0001; R²=0.98).

3.2.2 Effect of the temperature, pressure and catalyst/bio-oil ratio

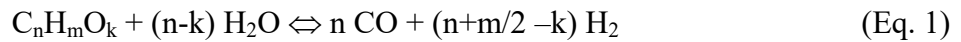
Figure 6 displays the influence of the temperature, pressure and catalyst/bio-oil ratio on the gas composition and LHV at 30 min of reaction. Specifically, Figures 6 a, c and e show the effect of the temperature and pressure in the absence of catalyst for the proportions of H₂, CO₂ and CO. Figures 6 b, d and f display these effects when the highest catalyst/bio-oil ratio (0.25 g/g) was used. Figures 6 g and h show the effect of

- 1 the temperature and pressure on the proportion of CH₄ and the LHV of the gas when a
- 2 catalyst/bio-oil ratio of 0.125 g/g was used.



- 3
- 4 Figure 6. Effect of the temperature, pressure and catalyst/bio-oil ratio on the
- 5 composition and LHV of the gas. Bars are LSD intervals with 95% confidence.

In the absence of catalyst, an increase in the reaction temperature between 310 and 380 °C increases the proportions of H₂ and CO in the gas and reduces the concentration of CO₂ regardless of the pressure. A further increase in temperature up to 450 °C slightly decreases the proportion of H₂ at 260 bar, without significantly modifying the proportions of CO₂ and CO in the gas. Fisk et al. [23] proposed that oxygenated compounds present in the bio-oil could be converted to gases via two main pathways: reforming and C-O bond cleavage. The reforming reaction rejects oxygen as CO₂, producing H₂, while the C-O bond scission yields hydrocarbons with H₂O as the co-product. Reforming is the main route for the conversion of light oxygenated compounds while C-O cleavage is more likely to occur for aromatic compounds due to the stronger C-C bonds involved. The reforming reaction of bio-oil (Eq. 1) is highly endothermic and the water gas shift reaction (Eq. 2) is moderately exothermic [46], giving an overall endothermic process. Thus, an increase in temperature increases the equilibrium concentration of H₂ and CO in the gas. The proportion of CO₂ in the gas decreases due to the exothermic character of the WGS reaction. In addition, under this temperature range the solid yield increases dramatically with temperature, thus lowering the proportion of C in the gas. This also accounts for the increase in the proportion of H₂ and the decrease in the concentration of CO₂ in the gas.



These variations observed with increasing the temperature depend on the pressure. The increase in the proportion of H₂ when increasing the temperature is higher at 200 than at 260 bar. At low pressure, this increase in temperature changes the state of water from subcritical liquid to steam, which favours H₂ production through reforming and cracking reactions, as discussed above. Conversely, at 260 bar the temperature has a

1 slight influence on the proportion of H_2 in the gas. At this pressure, water changes from
2 subcritical to supercritical. The increase in temperature increases cracking, reforming
3 and free-radical reactions, but the H_2 consumption increases in supercritical water due
4 to the greater extension of hydrogenation reactions. Isa et al. [39] reported that H_2
5 consumption via hydrogenation increases as water changes from subcritical to
6 supercritical conditions. Duan et al. [31] upgraded algal bio-oil in SCW with H_2
7 reporting a H_2 consumption of around 60% with respect to the initial H_2 charged in the
8 batch reactor. In addition, gas production is lowered in supercritical water due to the
9 aforementioned “cage effect”.

10
11 An increase in the pressure from 200 to 260 bar increases the proportion of H_2 and
12 decreases the proportion of CO_2 . This increase in the pressure favours the extension of
13 reforming and cracking reactions, as the partial pressure of the organics inside the
14 reactor increases, augmenting the proportion of H_2 in the gas. In addition, the solid yield
15 increases with pressure, lowering the amount of C in the gas and liquid phases, thus
16 increasing the concentration of H_2 and decreasing the relative amount of CO_2 in the gas.
17 Duan et al. [30] also reported a drop in the proportion of C in the liquid phase due to
18 char formation during the hydrotreatment of algal bio-oil in SCW. Interestingly, the
19 proportion of CO in the gas does not depend on the pressure, probably because the
20 thermodynamics of the water gas shift equilibrium is not dependent on the pressure.

21
22 The effect of the catalyst/bio-oil ratio on the proportions of H_2 , CO_2 and CO can be
23 gathered comparing Figures 6 a, c and e with b, d and f, respectively. An increase in the
24 catalyst/bio-oil ratio from 0 to 0.25 g/g between 310 and 380 °C at 200 bar increases the
25 proportion of H_2 and decreases that of CO_2 . Conversely, at 260 bar, this increase in the

1 catalyst/bio-oil ratio reduces the proportions of H_2 and CO in the gas for the whole
2 range of temperature and increases the concentration of CO_2 at temperatures higher than
3 350 °C. This indicates that the concentration of H_2 in the gas decreases when water is in
4 the sub- or supercritical state, probably due to the positive effect of the catalyst on
5 hydrogenation reactions of the bio-oil [23, 30, 39]. In addition, the catalyst exerts a
6 positive effect on the water gas shift reaction, which accounts for the decrease in the
7 proportion of CO. A greater spread of the water gas shift reaction should also increase
8 the proportion of H_2 in the gas; however, the presence of a catalyst can favour the
9 development of hydrogenation reactions, thus decreasing the concentration of H_2 [23,
10 30, 39].

11
12 The temperature and the catalyst/bio-oil ratio are the operating variables with the
13 greatest influence on the concentration of CH_4 and the LHV of the gas. The coefficients
14 in the ANOVA analysis for these two variables shown in Table 5 reveal that an increase
15 in the temperature or the catalyst/bio-oil ratio results in an increase in the proportion of
16 CH_4 and the LHV of the gas. This increase with temperature is the same for the whole
17 range of pressure and catalyst/bio-oil ratios considered in this work. As an example,
18 Figures 6 g and h show the effect of the temperature for a medium value of catalyst/bio-
19 oil ratio (0.125 g/g) at 200 and 260 bar. The results reveal the negligible effect of the
20 pressure and show that an increase in temperature increases the proportion of CH_4 and
21 the LHV of the gas. These results indicate that CH_4 formation is favoured at near
22 critical and SCW conditions as methanation and Fisher-Trops reactions are favoured at
23 high pressure [27, 40, 41]. In addition, the positive kinetic effect of the temperature and
24 catalyst/bio-oil ratio might also promote CH_4 formation [40].

3.3 Properties of the liquid phase

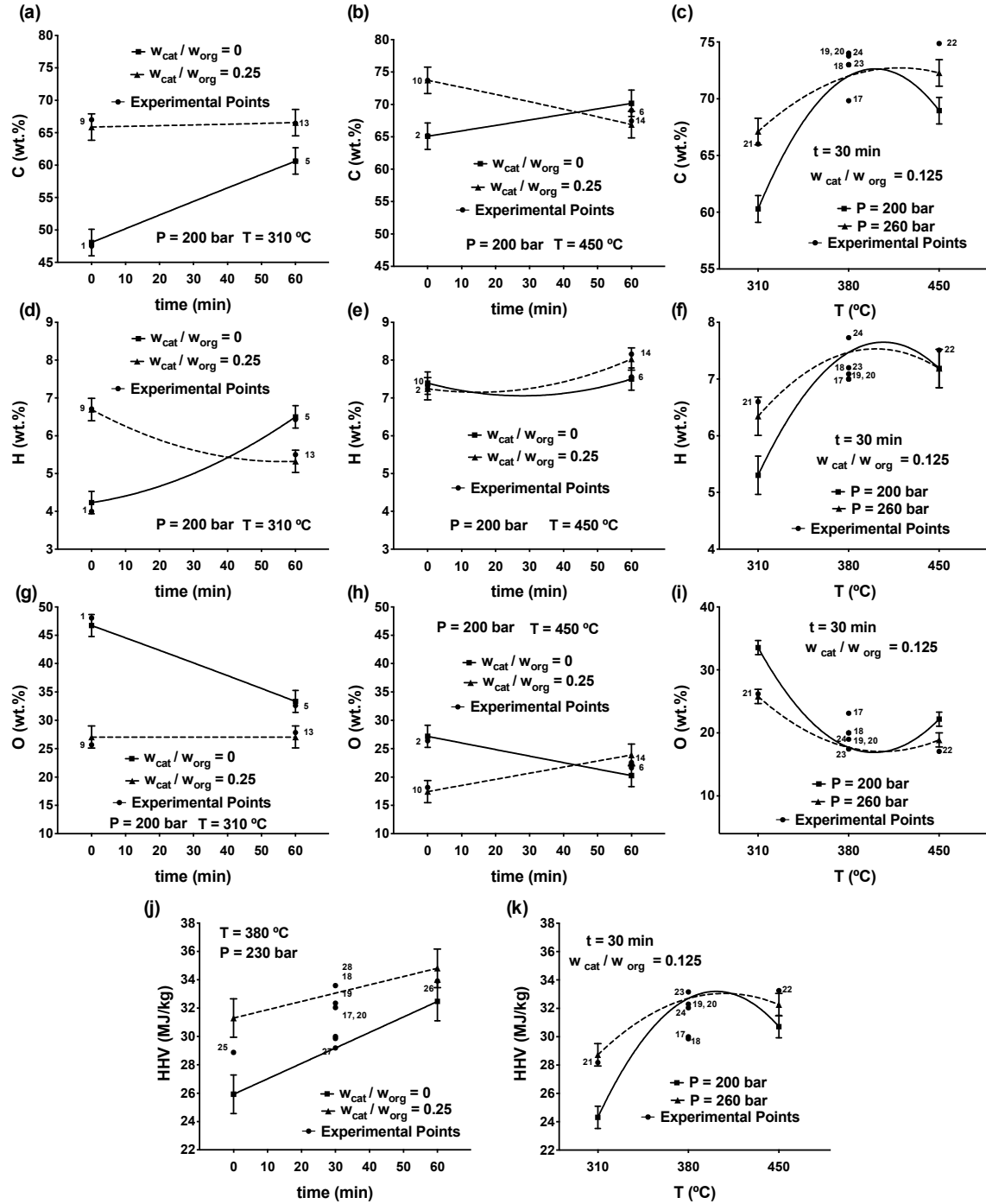
3.3.1 Elemental composition of the upgraded bio-oil

Table 3 shows that the concentrations of C, H and O in the upgraded bio-oils vary as follows: 48-77 wt.%, 4-8 wt.% and 13-48 wt.%. It also shows that the HHV of the treated liquid shifts from 16 to 35 MJ/kg. No sulphur was detected in any of the treated oils because sub- and supercritical water treatment alone (without catalyst) would also provide complete desulphurisation of the crude bio-oil [30-32]. These results represent a considerable increase in the proportions of C and H and a decrease in the concentration of O together with a substantial increase in the HHV with respect to the original bio-oil (in dry basis: 53.91 wt.% C, 3.32 wt.% H and 41.31 wt.% O; HHV = 18.51 MJ/kg). The influence of the operating conditions on the elemental composition and HHV of the treated liquids according to the ANOVA analysis is shown in Table 6.

The Pareto analysis indicates that the temperature and the catalyst/bio-oil ratio are the operating variables exerting the greatest influence on the elemental composition and HHV of the upgraded bio-oils. The relative coefficients for the temperature and catalyst/bio-oil ratio indicate that in general an increase in the temperature or the catalyst/bio-oil ratio increases the concentrations of C and H and decreases the proportion of O in the liquid. These results are in agreement with those reported by Duan et al. [30, 31]. The effects of the reaction time and the pressure are significant, although they have a lower influence. In addition, significant interactions between the operating variables were observed.

The effect of the operating conditions and the most important interactions are displayed in Figure 7. Specifically, Figures 7 a, d and g show the effect of the reaction time for

1 catalyst/bio-oil ratios of 0 and 0.25 g/g at a pressure of 200 bar and a temperature of 310
2 °C. Figures 7 b, e and h display these effects at 450 °C. Figures 7 c f and i show the
3 effect of temperature and the pressure for a catalyst/bio-oil ratio of 0.125 g/g and a
4 reaction time of 30 minutes.



5
6 Figure 7. Interaction plots for the elemental composition and HHV of the treated liquid.
7 Bars are LSD intervals with 95% confidence.

1 Table 6. Relative influence of the operating conditions on the liquid properties according to the ANOVA analysis
2

	R ²	Indep.	T	P	t	W	TP	Tt	TW	Pt	PW	tW	T ²	P ²	t ²	W ²	TPt	TP W	TtW	PtW	T ² P	T ² t	T ² W	TP ²	T ² P ²	TPt W
Elemental composition																										
C (wt.%)	0.95	72.00	3.46 (15)	n.s	4.51 (7)	3.63 (16)	-0.88 (3)	-0.91 (5)	-1.07 (5)	n.s	n.s	-1.32 (5)	n.s	n.s	n.s	n.s	0.97 (7)	1.23 (4)	n.s	1.65 (9)	2.54 (8)	-3.07 (3)	n.s	n.s	-4.83 (12)	n.s
H (wt.%)	0.95	7.04	0.67 (23)	n.s	0.22 (5)	0.21 (7)	-0.25 (8)	-0.11 (7)	-0.11 (4)	n.s	n.s	-0.13 (7)	n.s	0.43 (4)	0.38 (2)	n.s	n.s	n.s	0.23 (6)	0.24 (10)	0.27 (8)	n.s	n.s	n.s	-0.97 (7)	-0.31 (9)
O (wt%)	0.98	20.63	-4.56 (17)	n.s	-4.82 (6)	-4.01 (15)	1.11 (3)	0.76 (4)	1.02 (4)	n.s	n.s	1.44 (6)	n.s	-2.76 (9)	n.s	n.s	-0.85 (2)	-1.46 (5)	n.s	-1.90 (7)	-2.76 (10)	3.08 (3)	n.s	n.s	7.23 (8)	n.s
HHV (MJ/kg)	0.96	31.13	2.49 (18)	n.s	2.51 (6)	1.93 (14)	-0.71 (4)	n.s	-0.61 (5)	n.s	n.s	-0.76 (6)	n.s	1.60 (8)	n.s	n.s	n.s	0.64 (5)	n.s	1.06 (7)	1.49 (10)	-1.60 (3)	n.s	n.s	-3.73 (9)	-0.50 (3)
Chemical composition																										
Hydroc arbons (%)	0.80	5.84	-1.02 (10)	5.65 (9)	2.22 (15)	n.s	n.s	n.s	n.s	n.s	n.s	-1.28 (12)	n.s	2.84 (4)	2.36 (7)	-3.85 (13)	n.s	n.s	n.s	-2.38 (17)	-5.40 (13)	n.s	n.s	n.s	n.s	n.s
Acids (%)	0.87	9.84	n.s	n.s	-8.03 (8)	-9.45 (7)	-2.13 (9)	n.s	n.s	2.30 (10)	n.s	n.s	-8.50 (5)	n.s	n.s	n.s	n.s	n.s	n.s	-3.13 (6)	n.s (3)	6.95 (8)	8.52 (11)	-4.85 (18)	7.18 (9)	1.78 (6)
Ketones (%)	0.96	5.67	-2.45 (8)	n.s	-5.98 (4)	-10.98 (15)	-1.19 (4)	1.64 (6)	n.s	-2.70 (9)	1.32 (4)	n.s	n.s	-3.41 (3)	3.10 (4)	4.60 (9)	2.26 (6)	n.s	n.s	1.82 (4)	-2.34 (9)	5.12 (5)	7.02 (7)	n.s	n.s	-1.95 (5)
Phenols (%)	0.93	46.70	n.s	n.s	n.s	-10.22 (1)	-4.35 (7)	-7.66 (8)	-3.15 (5)	-5.92 (14)	n.s	-8.78 (11)	7.11 (9)	-25.5 (4)	12.7 (9)	n.s	2.82 (2)	n.s	-8.60 (3)	n.s	n.s	n.s	10.62 (7)	n.s	n.s	n.s
Cyclics (%)	0.86	20.63	7.57 (12)	-16.1 (2)	n.s	26.23 (9)	5.38 (9)	n.s	n.s	n.s	n.s	6.38 (7)	n.s	28.0 (7)	n.s	n.s	n.s	-5.29 (6)	5.99 (8)	4.94 (8)	19.5 (10)	n.s	-22.73 (11)	n.s	-22.5 (11)	n.s

3 n.s: Non significant with 95% confidence

4
5 Response = Indep. + Coefficient T·T + Coefficient P·P + Coefficient t·t + Coefficient W·W + Coefficient Tt·T·t + Coefficient TW·T·W + Coefficient Pt·P·t + Coefficient PW·P·W + Coefficient tW·t·W + Coefficient
6 T²·T² + Coefficient P²·P² + Coefficient t²·t² + Coefficient W²·W² + Coefficient TPt·T·P·t + Coefficient TPW·T·P·W + Coefficient TtW·T·t·W + Coefficient PtW·P·t·W + Coefficient T²·P
7 T²·P + Coefficient T²·t·T²·t +
8 Coefficient T²·W·T²·W + Coefficient TP²·T·P² + Coefficient TPtW·T·P·t·W.

9 Numbers in brackets indicate the percentage Pareto influence of each factor on the response variable. Pareto values represent the percentage of the orthogonal estimated total value.

10 T = temperature, P = pressure, t = reaction time and W = catalyst/bio-oil ratio

1 The effect of the reaction time on the elemental composition of the treated liquids is
2 only significant at pressures lower than 230 bar. At these pressures the composition of
3 the liquid varies with time, showing different evolutions depending on the temperature
4 and the catalyst/bio-oil ratio. When pressures higher than 230 bar are used, the
5 composition of the liquid develops a steady evolution over time. As an example, these
6 evolutions over time are represented in Figure 7 for a pressure of 200 bar. Different
7 trends are found depending on the catalyst/bio-oil ratio and the temperature. In the
8 absence of catalyst, the proportions of C and H in the liquid increases with time, while
9 the proportion of O decreases.

11 The addition of a catalyst promotes deoxygenation (decarboxylation and
12 decarbonylation) and hydrogenation (hydrodeoxygenation and hydrodesulphurisation)
13 reactions in near critical and supercritical water [29-31]. Therefore, a longer reaction
14 time is needed to achieve the same level of conversion in the absence of a catalyst; i.e.
15 to increase the proportions of H and C and to decrease the amount of O in the liquid. An
16 increase in temperature increases the proportions of C and H and decreases the
17 concentration of O in the liquid, as the rates of deoxygenation, hydrogenation and
18 thermal cracking are enhanced [23, 29-31]. In general, an increase in the catalyst/bio-oil
19 ratio increases the proportions of C and H and reduces the concentration of O in the
20 upgraded bio-oil. This indicates that the catalyst exerts a positive effect on
21 deoxygenation and hydrogenation reactions under the experimental conditions tested.
22 Other authors have reported the positive effect of using different catalysts based on Ni
23 [44] or on other metals [23, 29, 30, 47] for upgrading bio-oil in sub/supercritical water.
24 When a catalyst/bio-oil ratio of 0.25 g/g is used, the variation in the elemental
25 composition of the liquid with time shows two different trends depending on the

1 temperature. At low temperatures (310 °C) the proportion of H decreases with time
2 while the concentrations of C and O remain steady. Conversely, at high temperatures
3 the proportion of H remains steady but the concentration of C is reduced and that of O is
4 increased with time. These evolutions can be explained considering the evolution over
5 time of the gas phase. At 310 °C the evolution of the liquid phase might account for the
6 decrease over time observed for the yield to solid and the increase in the proportion of
7 H₂ in the gas phase, while at 450 °C it might be the consequence of the increases over
8 time observed for the proportions of CO₂ and CH₄ in the gas.

10 These variations in the chemical composition of the upgraded bio-oil cause the HHV of
11 the liquid to vary. An increase in the reaction time increases the HHV of the liquid over
12 the whole range of temperature, pressure and catalyst/bio-oil ratios considered in this
13 work. As an example, the evolution of the HHV over time is plotted in Figure 7 j for a
14 temperature of 380 °C and a pressure of 230 bar, using catalyst/bio-oil ratios of 0 and
15 0.25 g/g. In general, an increase in the catalyst/bio-oil ratio has similar effects for the
16 whole range of temperature and pressure considered. An increase in this ratio increases
17 the proportions of C and H and reduces the concentration of O in the liquid, leading to
18 an increase in the HHV of the liquid [23, 29-31].

20 Figures 7 c, f, i and k show the effect of the reforming temperature for pressures of 200
21 and 260 bar employing a catalyst/bio-oil ratio of 0.125 g/g and a reaction time of 30
22 min. An increase in the reaction temperature from 310 to 450 °C increases the
23 concentrations of C and H, and diminishes the proportion of O in the liquid, which leads
24 to a decrease in the HHV of the upgraded bio-oil. Deoxygenation, hydrogenation,
25 thermal cracking and reforming reactions of light oxygenates present in the bio-oil are

enhanced with the temperature [23, 29-31]. An increase in the pressure from 200 to 260 bar increases the proportions of C and H and reduces the concentration of O. It has previously been pointed out that this increase in pressure increases and decreases the proportions of H₂ and CO₂, respectively, which produces a greater spread of reforming and cracking reactions as the partial pressure of the organics inside the reactor increases, thus augmenting the proportion of H₂ in the gas which can favour hydrogenation reactions. In addition, the solid yield increases with pressure, lowering the amount of C in the gas and liquid phases. These developments can produce the experimental variations observed in the elemental composition of the treated oil with pressure and are in agreement with those reported in the work of Duan et al. [30].

3.3.2 Chemical composition of the upgraded bio-oil

The upgraded liquid is made up of a mixture of hydrocarbons (0-18%), ketones (0-25%), carboxylic acids (0-24%), phenols (0-71%), cyclic compounds (0-65%) and ethers (0-30). Hydrocarbons include hexadecane, heptane and 2-methyl-2-butene. Ketones include phenyl ketones such as 1-(4-hydroxy-3,5-dimethoxy phenyl)-ethanone and 1-(4-hydroxy-3-methenyl)-ethanone, and cyclic ketones such as 2-methyl-2-cyclopenten-1-one, 2,3-dimethyl-2-cyclopenten-1-one and 2-hydroxy-2-cyclopenten-1-one. Carboxylic acids comprise linear acids such as acetic, butanoic and pentanoic acids and cyclic acids such as 3-hydroxy-4-methoxy-benzoic acid. Phenols include phenol and methoxy phenolic (2,6-dimethoxy phenol, 2-methoxyphenol and 2,6-dimethoxy-4-(2-propenyl)-phenol) and alkyl phenolic (2-methyl-phenol, 3-methyl-phenol, 2-ethyl-phenol, 3-ethyl-phenol and 4-ethyl-phenol) compounds. Cyclic compounds mainly comprise 15-crown-5 and 18-crown-6, while ethers include hexa/hepta/octa ethylenglycol-monododecyl ethers. The presence of these compounds in the treated bio-

oil is consistent with the results reported by Onwudili and Williams [28]. The comparison between the chemical compositions of the original bio-oil with the treated liquids reveals that the proportions of carboxylic acids and ketones in the liquid decrease and the concentrations of phenolic and cyclic compounds increase during the upgrading process, which is consistent with the reaction pathway proposed by Fisk et al. [23].

The influence of the operating conditions on the chemical composition of the most important families of compounds present in the liquid according to the ANOVA analysis is shown in Table 6. The temperature, pressure and time are the operating variables with the greatest influence on the proportion of hydrocarbons in the liquid. The interactions of the temperature with the catalyst/bio-oil ratio (T^2W) and with pressure (TP^2) exert the greatest influence on the proportion of carboxylic acids. Ketones are strongly affected by the catalyst/bio-oil ratio. The interactions of the reaction time with the pressure (Pt) and catalyst/bio-oil ratio (tW) greatly influence the relative amount of phenols in the liquid. The proportion of cyclic compounds depends on the temperature and its interactions with the pressure. The effects of the operating conditions and the most important interactions on the proportions of ketones, carboxylic acids, hydrocarbons, phenols and cyclic compounds are displayed in Figures 8 and 9, in which the evolution over time and the effect of the temperature, pressure and catalyst/bio-oil ratio for a reaction time of 30 min are represented, respectively.

3.3.2.1 Evolution over time of the liquid product composition

It was observed that the reaction time develops important interactions with the other operating variables for the relative amounts of some families of compounds in the

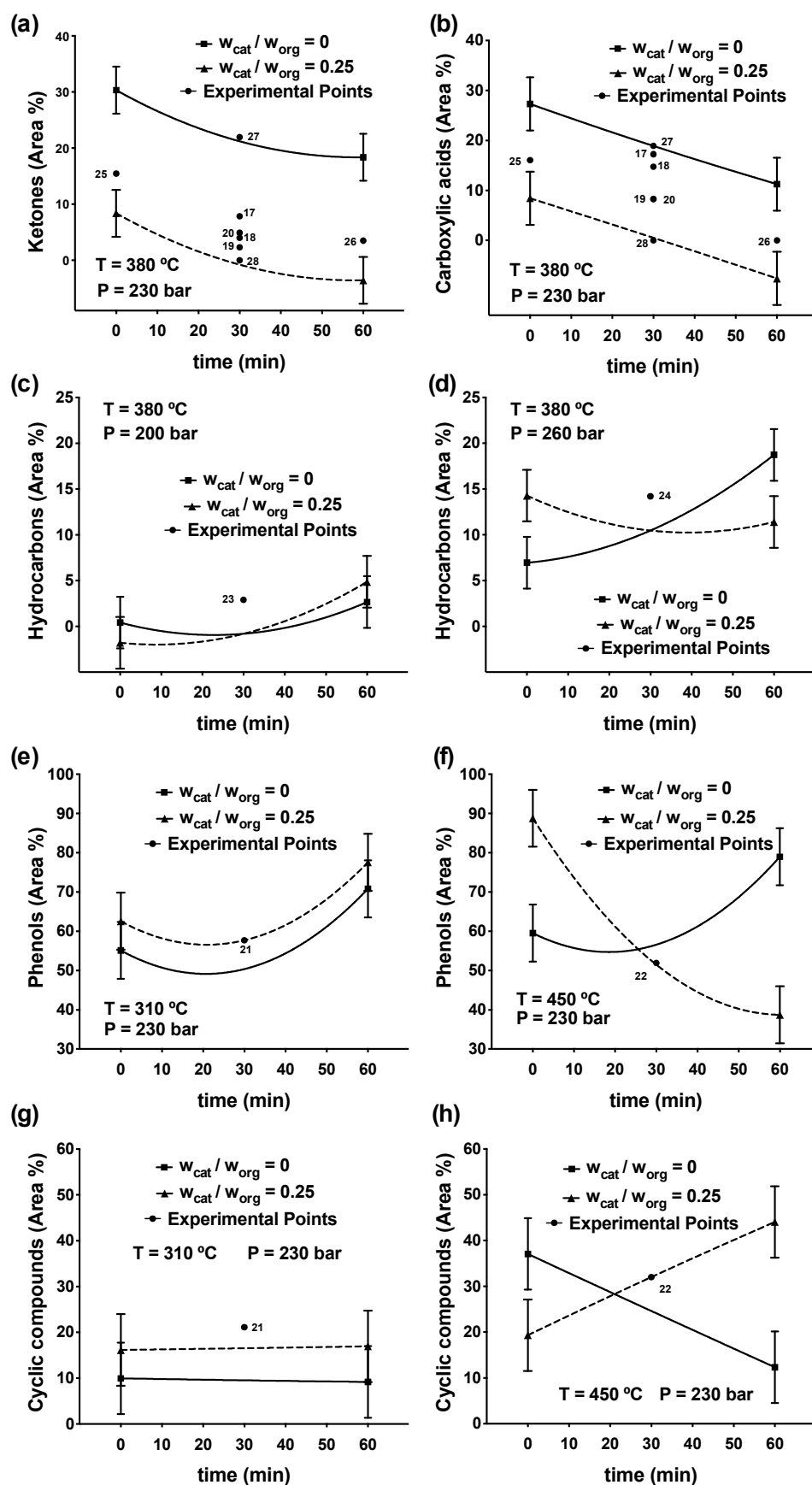
liquid. While a similar trend over time is observed for the proportions of ketones and carboxylic acids, the proportions of hydrocarbons, phenols and cyclic compounds show different evolutions over time depending on the temperature and pressure.

In general, the proportions of ketones and carboxylic acids in the upgraded liquid decrease with an increase in the reaction time or in the catalyst/bio-oil ratio, regardless of the temperature and pressure used in this work. As an example, these evolutions over time are plotted in Figures 8 a and b at the centre of variation for the temperature and pressure (380 °C and 230 bar) in the absence of catalyst and with a catalyst/bio-oil ratio of 0.25 g/g. An increase in the temperature and catalyst/bio-oil ratio promotes the reforming of these two families towards gas formation. This hypothesis was confirmed using Spearman's multivariate test. Statistically significant relationships were found between the gas yield and the proportions of ketones ($p\text{-value} = 0.0164$ $R^2 = 0.45$) and carboxylic acids ($p\text{-value} = 0.036$ $R^2 = 0.40$) in the liquid. The results of this test indicate that an increase in the yield to gas takes place along with a decrease in the proportions of ketones and carboxylic acids in the liquid. The low R^2 indicates that the evolution observed does not follow a linear trend, even though a significant relationship can be assured with 95% confidence. Fisk et al. [23] also reported that the light oxygenated compounds present in the bio-oil are likely to evolve towards gases by reforming and water gas shift reactions.

The evolution over time of the proportion of hydrocarbons in the upgraded liquid depends on the pressure and the catalyst/bio-oil ratio. Figures 8 c and d show the effect of the reaction time at 380 °C as a function of the catalyst/bio-oil ratio at 200 and 260 bar, respectively. At low pressure, the upgraded liquid has a low concentration of

hydrocarbons regardless of the catalyst/bio-oil ratio. Conversely, an increase in the pressure up to 260 bar leads to an increase in the proportions of hydrocarbons. At this pressure, the proportion of hydrocarbons increases with time in the absence of catalyst and remains constant at the highest catalyst/bio-oil ratio (0.25 g/g). The formation of hydrocarbons from bio-oil requires oxygen removal by deoxygenating reactions such as decarboxylation, decarbonylation and hydrodeoxygenation [48-50], which are enhanced by an increase in pressure and reaction time [49].

The evolution over time for the proportions of phenols and cyclic compounds depends on the temperature and the catalyst/bio-oil ratio. As an example, Figures 8 e and f and 8 g and h plot the evolution over time of the proportions of phenols and cyclic compounds, respectively, as a function of the catalyst/bio-oil ratio at 230 bar using reaction temperatures of 310 and 450 °C. At low temperatures the reaction time exerts a weak effect on the proportion of phenols, which experience a mild increase over time, and a negligible effect on the relative amount of cyclic compounds in the upgraded bio-oil. Interestingly, under these conditions the catalyst/bio-oil ratio does not significantly influence the proportions of these two families of compounds in the liquid. Moreover, the proportion of dimethyl-phenols accounts for the increase observed in the relative amount of this family of compounds. Owing to the acidity of the bio-oil, acid-catalytic and transalkylation reactions of phenols yielding alkyl phenols are likely to occur in the absence of catalyst [23, 51], thus masking the effect of the catalyst.



1

2 Figure 8. Effect of the reaction time on the chemical composition of the treated liquid.
 3 Bars are LSD intervals with 95% confidence.

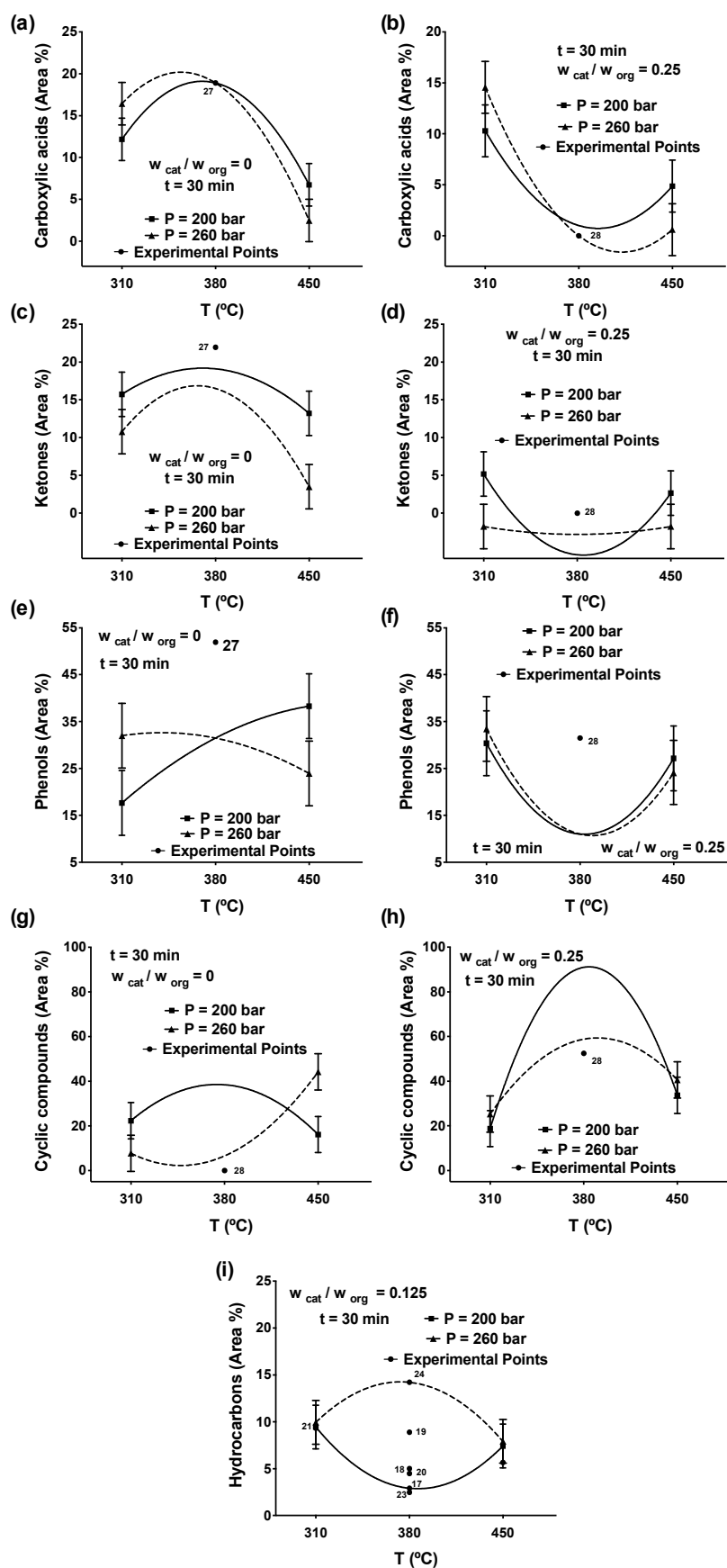
Conversely, an increase in temperature up to 450 °C increases the effect of the reaction time on the proportions of these two families. In the absence of catalyst, the proportion of phenols increases while that of cyclic compounds decreases over time. The temperature significantly potentiates gas production from the light oxygenated compounds present in the bio-oil. However, given that reforming of the aromatic compounds in the bio-oil is thermodynamically less favoured than that of the light oxygenated compounds due to the stronger C-C bonds involved [23], the upgraded liquid has a greater concentration of phenolic compounds. The addition of a catalyst has the opposite effect; i.e. the proportion of phenols decreases, while cyclic compounds increase over time. The hydrogenation activity of the catalyst together with the H₂ generated in situ might result in the hydrogenation over time of the aromatic rings [23]. This development has also been reported by other authors studying lignocellulosic bio-oil upgrading in supercritical water [28] who have suggested that aromatics are formed from phenols.

3.3.2.2 Effect of the temperature, pressure and catalyst/bio-oil ratio on the chemical composition

Figure 9 displays the influence of the temperature, pressure and catalyst/bio-oil ratio on the chemical composition of the upgraded liquid for 30 min of reaction. Specifically, Figures 9 a, c, e and g plot the effect of the temperature and pressure in the absence of catalyst on the proportions of carboxylic acids, ketones, phenols and cyclic compounds. Figures 9 b, d, f and h display these effects when the highest catalyst/bio-oil ratio (0.25 g/g) was used. Figure 9 i plots the effect of the temperature and pressure on the proportion of hydrocarbons when a catalyst/bio-oil ratio of 0.125 g/g was used.

The proportions of carboxylic acids and ketones in the upgraded liquid depend on the temperature, pressure and catalyst/bio-oil ratio. In the absence of a catalyst, neither the temperature nor the pressure exerts a significant influence on the proportions of carboxylic acids and ketones between 310 and 380 °C. Conversely, a further increase in the temperature up to 450 °C decreases the proportions of carboxylic acids and ketones in the upgraded bio-oil. This increase in temperature enhances gas production from the liquid oxygenated products present in the bio-oil [23], thus decreasing the proportions of these two families of compounds. Under this temperature range (380-450 °C) the pressure does not significantly influence the relative amount of carboxylic acids; however, the proportion of ketones decreases when increasing the pressure from 200 to 260 bar. H₂ solubility in water decreases when increasing the temperature, while high pressures increase the solubility of H₂ in the liquid. Therefore, ketone hydrogenation reactions might be more favoured at 260 than at 200 bar.

In general, an increase in the catalyst/bio-oil ratio from 0 to 0.25 g/g decreases the relative amounts of carboxylic acids and ketones. Specifically, the proportion of carboxylic acids decreases sharply regardless of the pressure when increasing the temperature from 310 to 450 °C. The upgraded bio-oil has a negligible concentration of carboxylic acids at temperatures higher than 380 °C. In addition, the proportion of ketones is very low under the whole range of temperature and pressure considered. A small decrease in the proportions of ketones takes place when increasing the temperature from 310 to 380 °C at 200 bar, while the liquid has a negligible concentration of ketones for the whole temperature range at 260 bar. This is consistent with the reaction pathway proposed by Fisk et al. [23].



1

2 Figure 9. Effect of the temperature, pressure and catalyst/bio-oil ratio on the chemical
3 composition of the treated liquid. Bars are LSD intervals with 95% confidence.

1 The relative amounts of phenolic and cyclic compounds in the upgraded bio-oil depend
2 on the temperature, pressure and catalyst/bio-oil ratio. In the absence of catalyst, the
3 evolution of these two families with the temperature depends on the pressure. On the
4 one hand, at 200 bar the proportion of phenols increases as the temperature increases
5 between 310 and 450 °C, while the relative amount of cyclic compounds displays an
6 increase between 310 and 380 °C, followed by a posterior decrease when further
7 increasing the temperature up to 450 °C. As described above, an increase in
8 temperature favours the reforming of light oxygenated compounds, thus producing a
9 liquid with a high concentration of phenolic and cyclic compounds. The proportions of
10 cyclic compounds in the liquid drop with a further increase in the temperature between
11 380 and 450 °C probably due to the transformation into gases, which produces an
12 upgraded liquid with a higher concentration of phenolic compounds.

13
14 On the other hand, at 260 bar the proportion of phenols remains steady when increasing
15 the temperature between 310 and 450 °C, while the proportion of cyclic compounds in
16 the treated liquid increases from 380 to 450 °C. Under this pressure an increase in the
17 temperature changes the state of water from subcritical to supercritical, where gas
18 production is less favoured than under near critical water or steam. This can make it
19 possible that the proportion of phenols does not increase with temperature. In addition,
20 the use of SCW favours hydrogenation reactions to take place, as the liquid and gas are
21 brought into a single phase. This can produce a greater spread of the hydrogenation
22 reactions of the phenolic compounds in the bio-oil [23], thus increasing the proportion
23 of cyclic compounds in the upgraded liquid.

When the highest amount of catalyst is used (catalyst/bio-oil ratio = 0.25 g/g), an increase in the temperature from 310 to 380 leads to a decrease in the proportion of phenolic compounds and an increase in that of cyclic compounds. The pressure does not significantly influence the proportion of phenols, while a greater increase with temperature takes place for the relative amount of cyclic compounds at 200 than at 260 bar. A subsequent increase in temperature between 380 to 450 °C results in an increase and a decrease in the relative amounts of phenols and cyclic compounds, respectively. The presence of catalyst favours phenol transformation into gases and cyclic compounds by reforming and acid catalysed hydrogenation reactions, respectively. These two developments are likely to occur due to the presence of the H₂ generated by reforming in situ in the process [23]. Onwudili and Williams [28] also reported a decrease in the amount of phenols when increasing the catalyst loading, due to the formation of aromatic compounds from phenol by deoxygenation and decarboxylation of the bio-oil.

The temperature and pressure exert the same effect on the proportion of hydrocarbons in the liquid regardless of the catalyst/bio-oil ratio. As an example, Figure 9 i shows the effect of these two variables for an intermediate catalyst/bio-oil ratio (0.125 g/g). The statistical analysis shown in Table 6 indicates that an increase in the catalyst/bio-oil ratio increases the proportion of hydrocarbons in the liquid product. At 200 bar the proportion of hydrocarbons decreases between 310 and 380 °C and increases from 380 to 450 °C. In contrast, the opposite takes place at 260 bar where an initial increase (310 to 380 °C) followed by a posterior decrease (380-450 °C) is observed. Alkenes can be produced via dehydration reactions on the Ni-catalyst or dehydration reactions on the alumina support, as well as C-O bond scission of the light oxygenated compounds of the

bio-oil [23]. The experimental results indicate that increasing the pressure favours C-O bond scission of light oxygenated products instead of reforming towards gas production.

3.4 Theoretical prediction of optimal operating conditions within the range of study for gas and liquid production from bio-oil

Optimal conditions for gas and liquid production were sought for this process making use of the experimental models developed. The predicted R^2 of all the models is higher than 0.90, allowing their use for prediction purposes. Specifically, three different optimisations were carried out. The first aims at the production of a gas with a high H_2 content, and therefore comprises the maximisation of the gas yield and the relative amount of H_2 in the gas. The second is directed towards energy production from bio-oil, thus maximising the gas yield and the LHV of the gas. The third considers the production of a liquid fuel from bio-oil, and consequently includes the maximisation of the liquid yield and the HHV of the liquid. In addition, the solid yield is minimised for the three optimisations.

To meet these objectives, a solution that strikes a compromise between the optimum values for all the response variables was sought for each optimisation. To do this, a relative importance (from 1 to 5) was given to each one of the objectives in order to come up with a solution that satisfies all the criteria. To globally maximise gas and liquid production, a relative importance of 5 was assigned to the global yields, while a relative importance of 3 was given to the properties of the gas or liquid (vol. H_2 , LHV of the gas and HHV of the liquid) and to the minimisation of the solid yield in all cases. Table 7 lists the optimums for the operating variables and the values for the response

variables considered.

Table 7. Optimisations

Optimisation	1	2	3
Temperature (°C)	339	450	344
Pressure (bar)	200	260	233
time (min)	60	54	9
catalyst/bio-oil (g/g)	0.2	0.24	0.16
Global results			
Gas yield (%)	75.7±3.1	88.5±1.5	34.5±3.1
Liquid yield (%)	19.2±1.9	7.79±2.1	61.9±1.9
Solid yield (%)	6.2±2.1	3.3±1.7	3.1±1.7
Gas composition and Lower Heating Value			
H ₂ (vol.%)	28.5±2.0	10.2±2.9	23.9±2.9
CO ₂ (vol.%)	57.8±3.8	43.2±3.6	60.4±3.6
CO (vol.%)	0.01±0.7	1.35±0.76	1.03±0.8
CH ₄ (vol.%)	19.6±2.8	45.8±3.1	12.6±3.1
LHV (MJ/m ³ STP)	10.3±0.9	17.3±0.85	7.4±0.9
Liquid elemental analysis and Higher Heating Value			
C (wt.%)	72.7±1.6	77.5±1.6	72.7±1.6
H (wt.%)	6.9±0.2	7.7±0.2	6.9±0.2
O (wt.%)	18.6±1.5	12.6±1.5	18.6±1.5
HHV (MJ/kg)	31.4±0.8	34.8±1.5	29.2±1.1
Liquid chemical composition (Area %)			
Hydrocarbons	9.3±2.2	4.4±2.2	6.3±2.2
Carboxylic Acids	1.6±3.4	0.5±3.3	9.9±3.4
Ketones	0±2.1	0.4±2.3	10.3±2.3
Phenols	40.1±5.8	39.1±5.8	51.7±5.8
Cyclic compounds	57.09±8.8	54.2±8.9	21.1±8.9

Taking these restrictions into account, optimisation 1 predicts a possible optimum for H₂ production at a temperature of 339 °C, a pressure of 200 bar, and a catalyst/bio-oil ratio of 0.2 g/g for a reaction time of 60 minutes. Under these conditions water is in a subcritical state and a gas yield of around 76% with a relative amount of H₂ close to 30 vol.% can be obtained from bio-oil. A gas with a similar H₂ content (30-40 vol.%) was reported by Chakinala et al. [38] during the gasification in supercritical water (T=580 °C and P=300 bar) of an aqueous fraction of bio-oil. In addition, Penniger et al. [27] obtained a similar H₂ rich gas (30 vol.%) during the reforming in supercritical water (T=650 °C and P=280 bar) of an aqueous bio-oil condensate obtained from the pyrolysis of wood. The parametric study of the present work demonstrates that the use of water in

the sub-critical state is suitable for H₂ production, increasing the efficiency of the process since lower temperatures and pressure are required.

The maximisation of the LHV of the gas (Optimisation 2) occurs at a temperature of 450 °C and 260 bar of pressure, using a catalyst/bio-oil ratio of 0.24 g/g for 54 minutes. Under these conditions, where water is in a supercritical state, a gas yield close to 90% together with a high LHV for the gas (17 MJ/m³ STP) could be produced from bio-oil. These two optimisations involve using high reaction times and catalyst/bio-oil ratios to promote gas formation, which is in agreement with the results previously discussed in the parametric study. Onwudili and Williams [28] also reported the highest LHV for the gas (25 MJ/m³ STP) in bio-oil upgrading in supercritical water employing high temperature and pressure (T=500 °C, P= 400 bar) with a Ru/Al₂O₃ catalyst.

To produce a liquid product to be used as a fuel, optimisation 3 indicates that a temperature of around 344 °C, a pressure of 233 bar and a catalyst/bio-oil ratio of 0.16 g/g for 9 minutes should be used. These conditions provide an upgraded liquid with a high HHV (29 MJ/kg), corresponding to an increase of 57 % with respect to the HHV of the original bio-oil. For liquid production, short holding times are needed to minimise gas production. In addition, a temperature and a pressure close to the critical point of water are needed to reach a compromise between the yield and the HHV of the treated liquid. Duan et al. addressed the treatment of algal bio-oil in sub/supercritical water aiming to improve the properties of the original feedstock for use as a liquid fuel. They reported an increase in the HHV of the liquid of 19% at 400 °C and 340 bar using a Pd/C catalyst for 4h [30]. In an optimisation study, Duan et al [31] analysed the upgrading of an algal bio-oil with a HHV of 39 MJ/kg. The upgrading process increased

the HHV of the treated liquid, achieving a maximum value for the HHV of the upgraded liquid of 43.5 MJ/kg. This corresponds to an increase of up to 11% with respect to the original bio-oil. The chemical composition of the upgraded liquid in optimisation 3 reveals a significant decrease in the proportions of carboxylic acids and ketones together with an increase in the relative amounts of phenols. This depletion in the proportion of carboxylic acids in the treated liquid is beneficial for using the bio-oil as a liquid fuel, as it helps to reduce the corrosion and instability of this feedstock. This result indicates that sub- and supercritical water treatment is a promising technology for bio-oil upgrading. A similar reduction in the proportion of carboxylic acids in the bio-oil can also be achieved with the use of sub- and supercritical ethanol technology, as reported by Peng et al. [52] and Zhang et al. [53]. However, two different developments account for the reduction of carboxylic acids in the original bio-oil depending on the technology. While in supercritical water such depletion is the consequence of the transformation of carboxylic acids into gases via reforming [23], carboxylic acid esterification yielding ethyl acetates accounts for the decrease achieved in the proportion of carboxylic acids in the upgraded liquid [52, 53] with the use of supercritical ethanol.

Experiment 16 was conducted using operating conditions ($T = 450\text{ }^{\circ}\text{C}$, $P = 260\text{ bar}$, $t = 60\text{ min}$ and catalyst/bio-oil ratio 0.25) very close to the optimum predicted in optimisation 2. Very similar results (Table 3) were obtained experimentally for the global yields, the composition of the gas and the liquid, the LHV of the gas and the HHV of the liquid. The chemical composition of the liquid predicted by the model was significantly different to that experimentally obtained, probably because of the low amount of upgraded liquid recovered (low yield to liquid). This can provide validation

of the theoretical prediction obtained making use of the experimental models developed with the ANOVA analysis in the optimisation process. It should be born in mind that the optimised values for the operating conditions proposed in this work provide a good approximation of optimum values for lignocellulosic bio-oil valorisation in SCW. However, the optimum values must be checked experimentally for each reactor and feedstock under consideration.

4. Conclusions

The upgrading of a lignocellulosic bio-oil in sub- and supercritical water has been investigated for the production of gaseous and liquid bio-fuels. The most important conclusions obtained from this work are summarised as follows.

1. The operating conditions and water regime (sub/supercritical) exert a significant influence on the process. The temperature, reaction time and catalyst/bio-oil ratio are the operating variables with the greatest influence on the product distribution. High temperatures, long reaction times and high catalyst loadings favour gas production, while short reaction times are needed for producing an upgraded liquid product. This indicates that bio-oil valorisation using sub- and supercritical water treatment is highly customisable for the production of either gaseous or liquid bio-fuels in the same reactor.
2. The gas phase, having a LHV ranging from 2 to 17 MJ/m³ STP, is composed of a mixture of H₂ (9-31 vol.%), CO₂ (41-84 vol.%), CO (1-22 vol.%) and CH₄ (1-45 vol.%) and is strongly influenced by the temperature and catalyst/bio-oil ratio. A possible optimum for H₂ production from bio-oil takes place at a temperature of 339 °C, 200 bar of pressure and using a catalyst/bio-oil ratio of 0.2 g/g for a reaction time of 60 minutes. Under these conditions water is in a subcritical state and a gas yield of around 76% with a relative amount of H₂ of 30 vol.% can be obtained from bio-oil. Maxima for the yield

to gas (90%) and LHV (17 MJ/m³ STP) could be achieved using water in supercritical conditions: a temperature of 450 °C and 260 bar of pressure with a catalyst/bio-oil ratio of 0.24 g/g for 54 minutes. Therefore, the operating conditions can be customised for the production of a H₂ rich gas or a gas with a high LHV for energy production to suit the different needs of the market.

3. The amount of C, H and O (wt.%) in the upgraded bio-oil varies by 48-74, 4-9 and 13-48, respectively. This represents an increase of up to 37% and 171% in the proportions of C and H, respectively, as well as a decrease of up to 69% in the proportion of O with respect to the original bio-oil. The HHV of the treated bio-oil varies from 20 to 35 MJ/kg, corresponding to an increase of about 89% with respect to the HHV of the original feedstock, which is of paramount importance for the production of renewable bio-fuels from biomass.

4. The treated liquid is made up of a mixture of hydrocarbons (0-18%), ketones (0-25%), carboxylic acids (0-24%), phenols (0-71%) and cyclic compounds (0-65%). In general, during the upgrading process carboxylic acids and ketones are transformed into gas and the treated liquid has a higher concentration of phenolic and cyclic compounds. This is beneficial for using this treated bio-oil as a liquid fuel, either alone or mixed with petroleum derived fuels. A liquid product to be used as fuel (29 MJ/kg) can be produced at a temperature of around 344 °C, a pressure of 233 bar and a catalyst/bio-oil ratio of 0.16 g/g using a reaction time of 9 minutes. This liquid bio-fuel has a HHV in the same range as conventional petroleum diesel fuel.

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