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Modelling and Predictive Study of Hydrothermal Liquefaction: Application to Food Processing Residues

Maxime Déniel^{1,2} · Geert Haarlemmer¹ · Anne Roubaud¹ · Elsa Weiss-Hortala² · Jacques Fages²

Abstract Thermochemical processes are promising ways for energy valorization of biomass and waste, but suffer from a lack of predictability. In this work, we focus on using model molecules to model the behavior of wet organic residues during hydrothermal liquefaction (HTL), a process used to produce bio based liquid fuels from wet biomass. Monomeric and polymeric model molecules were used as modelling tools to study HTL of real resources. Experiments with model mixtures and four food processing residues (blackcurrant pomace, raspberry achenes, brewer's spent grains, grape marc) were conducted at 300 °C, 60 min holding time and a dry matter concentration of 15 wt%. To elaborate model mixtures, four model monomers (glucose, guaiacol, glutamic acid, linoleic acid) and two model polymers (microcrystalline cellulose, alkali lignin) were selected from characterization of blackcurrant pomace. HTL of model mixtures reproduced HTL of blackcurrant pomace with acceptable representativeness, but results showed that model mixtures should include polymers to represent the fiber content of the resource. Results of HTL of model compounds were used to elaborate polynomial correlations able to predict experimental yields as a function of the initial biomass composition. Calculations were within -8.0 to $+4.8$ wt% of experimental yields obtained by HTL of real food processing residues, showing a good

accuracy of the correlations. These expressions also showed good agreement with HTL results reported in the literature for other resources, and could be useful to assess the potential of various kinds of bioresources for HTL.

Keywords Hydrothermal liquefaction · Model compounds · Food processing residues · Bio oil · Polynomial regression · Mixture designs

Abbreviations

ADF	Acid detergent fibers
ADL	Acid detergent lignin
BSG	Brewer's spent grains
daf	Dry ash free
DOE	Design of experiments
HHV	Higher heating value (MJ kg ⁻¹)
HTL	Hydrothermal liquefaction
NDF	Neutral detergent fibres

Variables

b_i	Linear contribution coefficient of model compound i
b_{ij}	Binary interaction coefficient between model compound i and model compound j
F	Value of the F test
m_{BO} , m_C , m_G , m_{In} and m_R	Mass of bio oil, char, gas, initial dry ash free matter and raw organic residue (g), respectively
M_j	Molar mass of gaseous species j (g mol ⁻¹)
n	Total number of experiments
p	Number of parameters of the model ($p = 4$ for the linear model, $p = 10$ for the quadratic model)

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P_i, P_f	Initial and final pressures in the reactor (Pa), respectively
q	Number of model compounds in the DOE
R	Ideal gas constant (8.314 J K ⁻¹ mol ⁻¹)
SD_{b_i} (or b_{ij})	Standard deviation on the contribution coefficient b_i (or b_{ij})
SSO	Proportion of solvent soluble organics in the raw organic residue (wt%)
t	Value of the student test
T_i, T_f	Initial and final temperatures in the reactor (K)
V_G	Volume of gaseous phase in the reactor (m ³)
W_R	Water content of the raw organic residue (wt%)
x_i, x_j	Mass fraction of model compound i or j in the mixture or in the biomass, respectively
\bar{y}	Mean value of the experimental responses
Y	Experimental response (e.g. mass yield of bio oil)
Y_i	Experimental response of a single model compound
y_j	Molar fraction of gaseous species j
y_k	Measured experimental response for experiment k
\hat{y}_k	Calculated experimental response for experiment k
Y_A, Y_{BO}, Y_C and Y_G	Yield of organic matter in aqueous phase, yields of bio oil, char and gas (wt% of initial dry ash free matter), respectively

Introduction

Rising concerns about climate change, associated with increasing energy demand worldwide, has put the search for substitution of fossil fuels by renewable fuels on the front scene in recent years. Many biochemical and thermochemical technologies are currently under development to produce renewable fuels from biomass and organic residues [1]. The development of these technologies faces several challenges, among which is the lack of ability to predict the products of the process (e.g. bio oil, char, gas) based on the nature and characterization of the starting biomass. In this context, efforts should be made to provide predictive tools.

This work focuses on the conversion of food processing residues into bio oils through hydrothermal liquefaction, in order to study one predictive methodology. Food processing

residues contain valuable organics that could be recovered either as high value compounds or bio based fuels. They currently represent more than 20 % of the total agricultural production worldwide, generated at every stage of the food supply chain, from harvesting to final consumption. Efficient management and valorization of these waste streams are necessary to avoid environmental and sanitary consequences of their disposal [2]. To convert these resources into bio oils, the hydrothermal liquefaction (HTL) process has been selected, as it is currently receiving significant and increasing attention regarding energy valorization of wet biomass and organic residues. Hydrothermal liquefaction is a thermal process used to convert wet biomass. Under subcritical water conditions of temperature (250–400 °C) and pressure (10–30 MPa), biomass is depolymerized giving among several several products, a bio oil with high energy content. This process takes advantage of the specific properties of water properties in the subcritical region to degrade wet biomass through many reactions [3–5], converting it into renewable liquid fuels [6, 7]. Through this process, biomass is converted into four streams: a biocrude or bio oil with higher heating values up to 35–40 MJ kg⁻¹, an aqueous phase containing platform chemicals, a solid residue referred to as char and a CO₂ rich gaseous phase. Hydrothermal liquefaction has been applied to a wide range of resources from wood [8] to algae [9] and food processing residues [10] both at the laboratory and at the pilot scale.

Despite a large number of studies on various types of biomass, the HTL process lacks of predictability regarding the products distribution, which highly depends on the nature of the starting material [11]. Reaction mechanisms behind HTL are still badly understood, both because of the numerous reaction pathways and the complex composition of starting materials. One way to get insights of the fundamental mechanisms behind HTL is to simplify reaction systems by using model molecules. Reaction schemes and kinetics of single model monomers have been extensively studied, but significantly less information is reported in the literature regarding the behavior of complex model mixtures [10]. While detailed kinetic approaches are interesting to get an exhaustive understanding of the chemistry behind HTL, they do not often link the initial biomass composition (fibers, proteins, lipids...) with the mass yields of the products. This approach might be of interest in the development of HTL technologies applied to a broad range of different substrates.

To date, only few published studies have focused on linking the products distribution of HTL with the initial composition of the substrate, focusing on algal biomass. Biller and Ross [12] studied HTL of several model compounds as surrogates for algal biomass, at 350 °C and 200 bar for 60 min. Model compounds were two model proteins (albumin, soya protein) and two model

amino acids (asparagine, glutamine), one model polysaccharide (starch) and one model monosaccharide (glucose), as well as one model lipid (sunflower oil). They found that the contributions of individual species to the bio oil formation was in the order lipids > proteins > carbohydrates, and used an additive rule to model the bio oil yield as a function of the initial algae composition. This correlation showed a good agreement with experimental results from a model mixture, as well as two algae strains, but did not fit for three other strains, suggesting a more complex behavior (including interaction reactions). Valdez et al. [13] developed a kinetic model based on a reaction network using the biochemical composition of microalgae (lipid, protein and carbohydrate). They calculated the evolution of the product distribution with temperature (250–400 °C) and time (0–60 min) and obtained a good agreement with experimental values for the three tested algae strains (*Nannochloropsis* sp., *C. protothecoides* and *Scenedesmus* sp.). Their results confirmed those of Biller and Ross [12], suggesting higher contributions of lipids and proteins to bio oil formation. Teri et al. [14] used six model compounds (cornstarch, cellulose, soya protein, albumin, sunflower oil and castor oil) to investigate HTL of algal biomass at 300 and 350 °C. In this work, they used a mass averaged model and a quadratic model taking into account binary interactions and obtained a good predictability towards HTL of ternary model mixtures with both models. Yet, the authors did not test the correlations against experimental results from HTL of actual algae strains. Yang et al. [15] used pure and binary mixtures of crude extractives (polysaccharides and proteins) from algae, to investigate HTL of low lipid algae. They used a mass averaged model to correlate the mass yields to the composition of the biomass. Their results showed that polysaccharides had a small contribution to the bio oil formation compared to proteins. Results obtained with polysaccharide protein mixtures led them to conclude that the bio oil yield did not vary linearly, and that interactions between polysaccharides and proteins had a significant effect on the bio oil recovery. Finally, Leow et al. [16] developed an additivity model to predict the bio oil yield, based on HTL experiments using *Nannochloropsis oculata* with different biochemical compositions. The additivity model was more accurate than others based on model compounds. The authors also proposed an alternative model based on the contribution of the lipid content (amount and nature of fatty acids) and the non lipid contribution, allowing to predict with good accuracy the bio oil and aqueous phase yields, as well as several other properties of the bio oil (nitrogen content, elemental composition...). This approach is however more complex than a simpler

proximate analysis, as it requires full characterization of the lipids in the biomass and HTL runs with a defatted resource. Previous works have only been focused on algal biomass, and do not consider the case of organic waste which may contain lignocellulosic biomass. In addition, previous studies have mainly been focused on the bio oil phase rather than on the global products distribution. Finally, while mathematical models are confronted to model mixtures, calculated yields are rarely compared with experimental results obtained from actual resources.

The objective of the present paper is to show how the use of model compounds provides insights on the conversion of real biomass. To that end, we have studied hydrothermal conversion of model compounds alone, as well as in mixtures of two to four compounds. Representative model molecules were chosen from the molecular characterization of a reference biomass (blackcurrant pomace). Results of HTL experiments on model compounds were used to elaborate predictive correlations for mass yields, which were then tested against results of hydrothermal liquefaction of other food processing residues; namely blackcurrant pomace, raspberry achenes, brewer's spent grains (BSG) and grape marc; before being tested against literature results for a larger scope of resources.

Materials and Methods

In this section, we first present the general approach followed in this work. Characterization of the several resources tested is then reported, as well as other materials used to perform the experiments. Design of experiments and mathematical models are also explained. Finally, we give details on the experimental procedure for HTL experiments and recovery of products.

General Methodology

The aim of the work is to compare hydrothermal liquefaction of model mixtures with hydrothermal liquefaction of actual food processing residues. To that end, blackcurrant pomace was chosen as a reference biomass. The molecular characterization of this resource was used to select representative model compounds, which were hydrothermally converted alone and in mixtures. Results of the experiments on model compounds were used to elaborate predictive correlations for mass yields, which were then tested against results of hydrothermal liquefaction of other food processing residues, namely raspberry achenes, brewer's spent grains (BSG) and grape marc.

Materials

Characterization of Food Processing Residues for the Selection of Model Molecules

Table 1 reports the results of the analysis of the four food processing residues used in this study. They were all supplied by local producers operating in the south east of France.

The resources are highly fibrous, even though the nature of the fibers differs. In fact, BSG are rich in cellulosic fibers (high *NDF* content, low *ADL* content) while the other three are more lignin rich. In terms of protein content, blackcurrant pomace and BSG are richer than raspberry achenes and grape marc. Lipid contents are relatively low for all resources, varying from 5.2 to 14.8 wt%.

As explained in “[General Methodology](#)” section, the choice of model molecules was based on the characterization of blackcurrant pomace. This residue is the press cake recovered after berry pressing of two mixed cultivars (*Noir de Bourgogne* and *Andega*). It is mainly constituted by seeds, peels and pulp. As can be seen from Table 1, blackcurrant pomace is a wet and fibrous resource. Especially, the *ADF* and *ADL* contents are high, meaning that the biomass is both rich in cellulose and lignin. The first focus of the work was to study hydrothermal conversion of model monomers: glucose was therefore chosen to represent the cellulosic content in blackcurrant pomace (cellulose, xyloglucan hemicelluloses and free sugars), while guaiacol was chosen as a representative monomer for lignin. In addition to monomers, microcrystalline cellulose and lignin (alkali) were used as model compounds to represent the fibers contained in blackcurrant pomace.

From Table 1, we also see that blackcurrant pomace contains a non negligible amount of proteins and lipids.

From the amino acid and fatty acid profiles reported in Fig. 1, glutamic acid and linoleic acid were chosen to represent proteins and lipids, respectively. Model polymers were not considered in the case of proteins and lipids, for two different reasons. Firstly, amino acids and proteins have a very similar reactivity during HTL, as observed in previous studies [12, 20, 21]. Secondly, lipids are mainly present in the form of triglycerides in biomass: fatty acids account for up to 98 wt% in these particular structures, glycerol is therefore considered as negligible in this study.

Chemicals

Microcrystalline cellulose, lignin (alkali, low sulfonate content), glutamic acid and linoleic acid were purchased from Sigma Aldrich and used as received. HTL experiments were performed using distilled water as the reaction solvent. Ethyl acetate used for bio oil recovery was purchased from Sigma Aldrich and used as received.

Design of Experiments

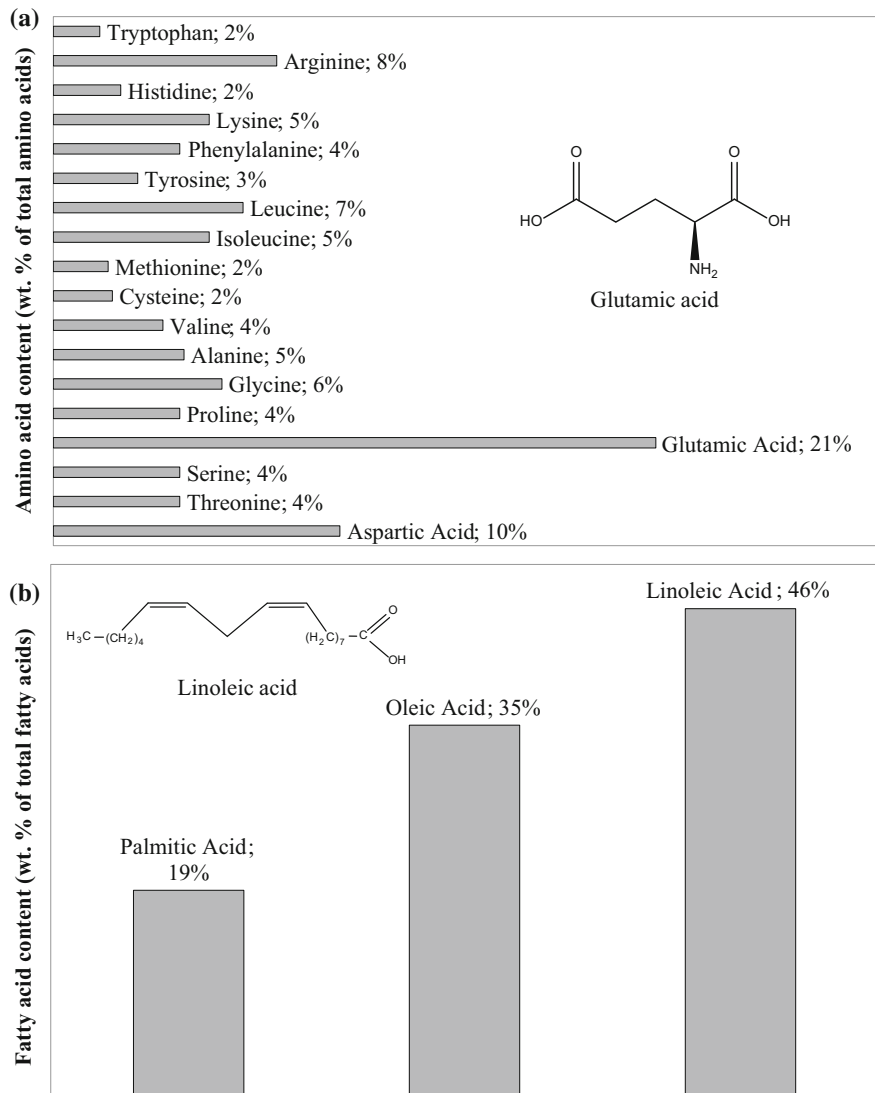
Experimental Points

Design of experiments (DOE) for hydrothermal liquefaction of model compounds was based on specific designs called *mixture designs*, in which the variables are the composition of each compound in the mixture. In a mixture DOE, variables depend on each other, as the sum of compositions must equal 100 %. In this work, two types of designs were used: Scheffe designs (4,2), also known as simplex lattice designs, and axial mixture designs. While the former only includes pure compositions and binary mixtures in equal proportions, the latter also include ternary and quaternary mixtures. The

Table 1 Characterization of blackcurrant pomace, raspberry achenes, brewer’s spent grains (BSG) and grape marc used in this work

	Blackcurrant pomace	Raspberry achenes	Brewer’s spent grains (BSG)	Grape marc (dried, ground)	Standard
Moisture content (wt%)	59.6	44.4	70.1	7.4	EN 14774 1 [17]
Fiber content (wt% of dry matter)					NF V18 122 [18]
NDF (neutral detergent fibers)	61.7	83.3	35.5	69.9	
ADF (acid detergent fibers)	52.8	74.3	11.4	63.4	
ADL (acid detergent lignin)	34.6	47.2	5.9	48.6	
Cellulose (<i>ADF ADL</i>)	18.2	27.1	5.5	14.8	
Hemicelluloses (<i>NDF ADF</i>)	8.8	9.0	24.1	6.5	
Lignin (<i>ADL</i>)	34.6	47.2	5.9	48.6	
Proteins (wt% of dry matter)	16.9 (± 0.8)	8.1 (± 0.4)	18.7 (± 0.9)	9.7 (± 0.5)	Kjeldahl method
Lipids (wt% of dry matter)	14.8	5.2 (± 0.4)	6.0 (± 0.3)	8.1 (± 0.6)	Hydrochloric acid digestion + Petroleum ether extraction
Ash content at 550 °C (wt % of dry matter)	4.3 (± 0.2)	1.2 (± 0.1)	2.9 (± 0.2)	4.8 (± 0.4)	NF EN 14775 [19]

Fig. 1 Amino acid profile (a) and fatty acid profile (b) of the proteins and lipids contained in blackcurrant pomace



variables are defined as follows: x_1 stands for the mass fraction of glucose or cellulose in a model mixture, x_2 stands for the mass fraction of glutamic acid, x_3 is the mass fraction of guaiacol or lignin, and x_4 stands for the mass fraction of linoleic acid. In Fig. 2, we show a schematic representation of the designs used to perform HTL of model compounds. Table 2 shows the experimental matrices corresponding to these designs.

Polynomial Regression Models

Results obtained following the DOEs were exploited using polynomial regression tools, to build correlations describing the mass yields as a function of the initial biomass composition. Two models were considered: a linear model and a quadratic model. General expressions of such models are given in Eqs. 1 and 2.

$$Y = \sum_{i=1}^q b_i x_i \quad (1)$$

$$Y = \sum_{i=1}^q b_i x_i + \sum_{i<j}^q b_{ij} x_i x_j \quad (2)$$

where Y is the experimental response (e.g. mass yield of bio oil); q is the number of model compounds in the DOE (here, $q = 4$); b_i is the linear contribution coefficient of model compound i ; x_i is the mass fraction of model compound i in the mixture or in the biomass; b_{ij} is the binary interaction coefficient between model compound i and model compound j ; x_j is the mass fraction of model compound j in the mixture or in the biomass.

Fitting of the model parameters was done by calculating the correlation coefficient R^2 , targeted at a value of 1. The significance of correlations was assessed by determining

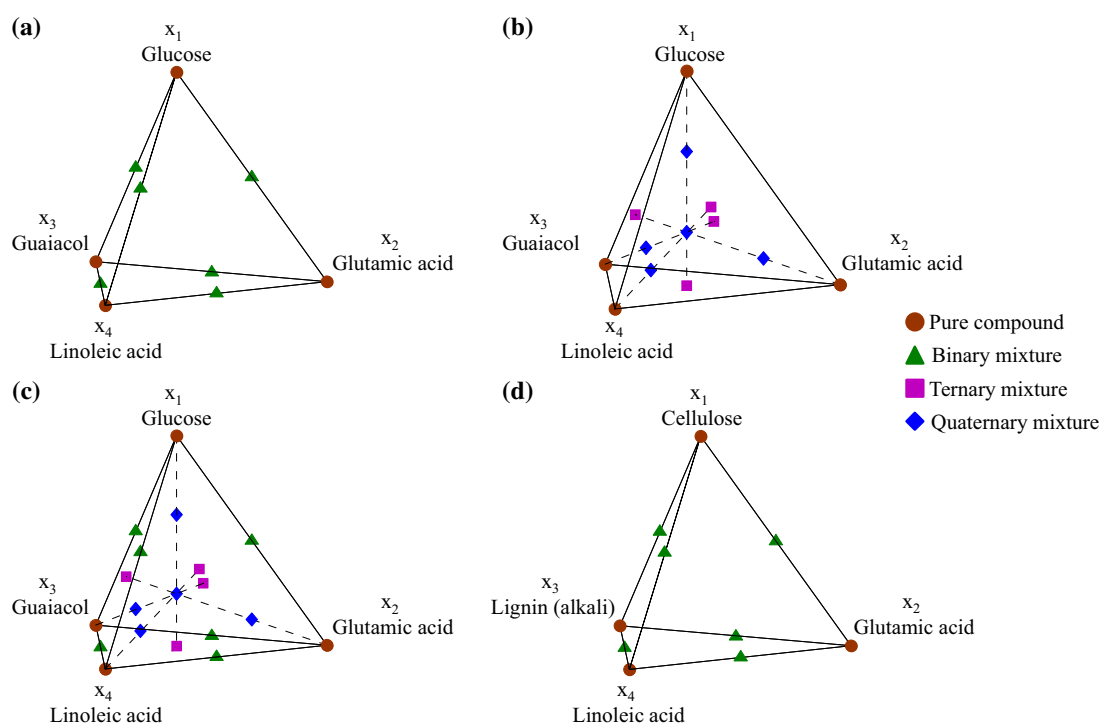


Fig. 2 DOE used in HTL of model compounds. **a** Scheffe design (4,2) with 4 model monomers, **b** axial design with 4 model monomers, **c** axial design + binary mixtures with 4 model monomers, and **d** Scheffe design (4,2) with cellulose and lignin as model compounds for fibers

Table 2 Experimental matrices for HTL of model compounds

	Run N°	x_1	x_2	x_3	x_4
Pure compounds ^{1,2}	1 (1')	1	0	0	0
	2	0	1	0	0
	3 (3')	0	0	1	0
	4	0	0	0	1
Binary mixtures ^{1,2}	5 (5')	0.5	0.5	0	0
	6 (6')	0.5	0	0.5	0
	7 (7')	0.5	0	0	0.5
	8 (8')	0	0.5	0.5	0
	9	0	0.5	0	0.5
	10 (10')	0	0	0.5	0.5
Ternary mixtures ²	11	0	1/3	1/3	1/3
	12	1/3	0	1/3	1/3
	13	1/3	1/3	0	1/3
	14	1/3	1/3	1/3	0
Quaternary mixtures ²	15	0.25	0.25	0.25	0.25
	16	0.625	0.125	0.125	0.125
	17	0.125	0.625	0.125	0.125
	18	0.125	0.125	0.625	0.125
	19	0.125	0.125	0.125	0.625

Runs between parentheses correspond to the use of cellulose and/or lignin instead of glucose and/or guaiacol

x_1 , glucose and/or cellulose; x_2 , glutamic acid; x_3 , guaiacol and/or alkali lignin; x_4 , linoleic acid

¹ Scheffe design (4,2)

² Axial mixture design + binary mixtures

the *p* value from the Fisher test (Eq. 3), and the significance of the coefficients was assessed by determining the *p* value from the Student test (Eq. 4), following the recommendations of Tinsson [22].

$$F = \frac{n - p}{p - 1} \cdot \frac{\sum_{k=1}^n (\hat{y}_k - \bar{y})^2}{\sum_{k=1}^n (y_k - \hat{y}_k)^2} \quad (3)$$

$$t = \frac{b_i \text{ (or } b_{ij})}{SD_{b_i \text{ (or } b_{ij})}} \quad (4)$$

where *F* is the value of the *F* test; *n* is the total number of experiments; *p* is the number of parameters of the model (*p* = 4 for the linear model, *p* = 10 for the quadratic model); \hat{y}_k is the calculated experimental response for experiment *k*; \bar{y} is the mean value of the experimental responses; y_k is the measured experimental response for experiment *k*; *t* is the value of the student test; b_i is the linear contribution coefficient of model compound *i*; b_{ij} is the binary interaction coefficient between model compound *i* and model compound *j*; $SD_{b_i \text{ (or } b_{ij})}$ is the standard deviation on the contribution coefficient b_i (or b_{ij}).

The validity of the correlations was then evaluated by comparison with the results of hydrothermal liquefaction of two model mixtures and four real food processing residues: blackcurrant pomace, raspberry achenes, brewer's spent grains and grape marc. A mass averaged model was also tested (Eq. 5), as suggested in previous studies [12, 14, 15].

$$Y = \sum_{i=1}^q Y_i x_i \quad (5)$$

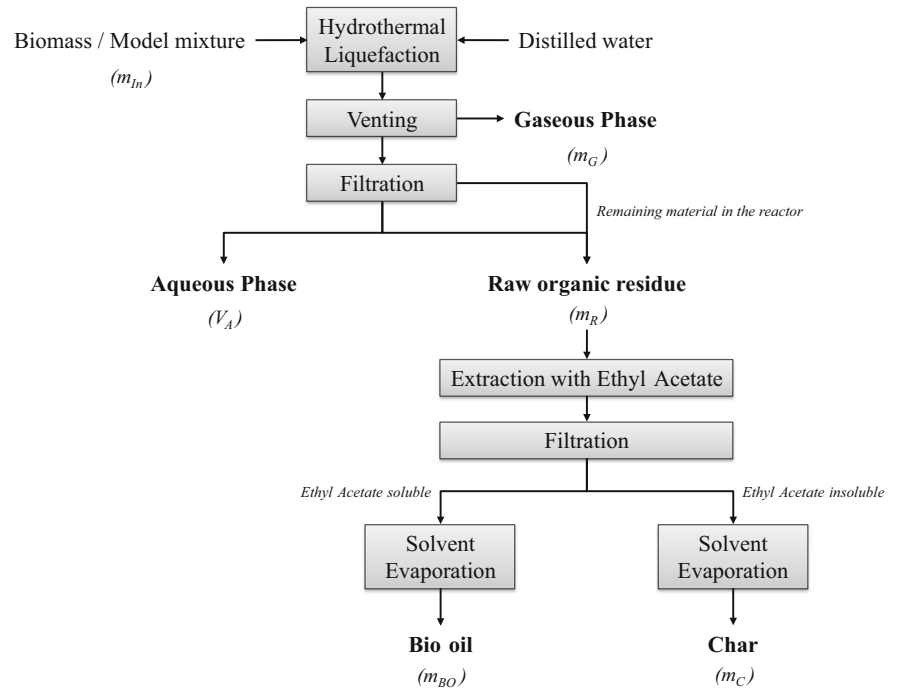
where *Y* is the experimental response (e.g. mass yield of bio oil); *q* is the number of model compounds in the DOE (here, *q* = 4); Y_i is the experimental response of a single model compound *i* (e.g. mass yield of bio oil for compound *i*); x_i is the mass fraction of model compound *i* in the mixture or in the biomass.

Hydrothermal Liquefaction

HTL Experiments

Hydrothermal liquefaction experiments were performed in a 0.6 L stainless steel (type 316) stirred batch reactor (Parr Instruments). In a typical experiment, the reactor was filled with approximately 240 g of slurry prepared from either model compounds, model mixtures or real food processing residues. A constant concentration of 15 wt% dry matter in the reaction slurry was used. Figure 3 shows the experimental procedure for HTL experiments and recovery of products. Before running an experiment, the autoclave was leak tested, purged and pressurized to 1 MPa with nitrogen gas to guarantee sufficient pressure for gas analysis after the reaction. The reactor was then heated from room temperature to the reaction temperature (300 °C) in about 30–35 min. Once the reactor reached the reaction temperature, it was

Fig. 3 Experimental procedure for HTL experiments and recovery of products



held during a 60 min holding time within ± 1 °C of the reaction temperature. The reaction was performed at a stirring speed of 600 rpm. After the holding time, the reactor was rapidly cooled down to room temperature in 20 min by an air quench. The gas in the reactor was vented and analyzed by a micro chromatograph (Varian Quad CP 4900) equipped with a thermal conductivity detector used on line. Permanent gases (O_2 , H_2 , CO and CH_4) were separated by a molecular sieve column using argon as carrier gas. Light hydrocarbons (C_2H_4 , C_2H_6 , C_2H_2 and C_3H_8), CO_2 and sulphur species (H_2S and COS) were separated on a Poraplot U column using helium as carrier gas. Solid and liquid products were then recovered and analyzed following the recovery procedure described in “[Recovery of Products](#)” section.

Recovery of Products

After gas analysis, the reactor was opened and the products were recovered following the procedure given in Fig. 3. The content of the reactor was first filtered on a Buchner filter to separate the aqueous phase from the raw organic residue. The raw organic residue was recovered as a hydrophobic solid liquid mixture containing bio oil and char. In most experiments, the raw organic residue was easily separated from the aqueous phase by filtration. The aqueous phase would pass through the filter while the raw organic residue would stay on the filter. The bio oil and the char are intimately associated and remain on the filter. In some experiments, only an aqueous phase and an organic phase (bio oil) were recovered (no char): in these specific cases, the bio oil was separated from the aqueous phase using a separatory funnel. As shown in Fig. 3, the remaining material in the reactor was counted as raw organic residue (wet). Moisture content of the raw organic residue (W_R) was estimated using two methods: drying at room temperature under air circulation until a stable mass was obtained, and Karl Fischer titration using a Schott Instruments Titroline KF. Combination of the two methods allows evaluating the experimental error due to estimation of the moisture content of the raw organic residue. The difference is partly due to the evaporation of some volatile compounds.

The raw organic residue was then extracted using a tenfold amount of ethyl acetate (w/w) to separate the bio oil from the char on a Buchner filter. Ethyl acetate was chosen because it allows good bio oil recovery [23], is non toxic, and has a low miscibility with water. Bio oil was recovered after evaporation of ethyl acetate at room temperature under air circulation until a stable mass was obtained. The char was also dried at room temperature under air circulation until a stable mass was obtained. Weight loss of the char after extraction and drying was used to determine the proportion of solvent soluble

organics in the raw organic residue (SSO), and therefore the bio oil yield (Y_{BO}). Calculation of the yields is explained in “[Calculation of the Mass Yields](#)” section.

Calculation of the Mass Yields

Yields were calculated from the obtained experimental results. They are defined as the mass ratios between the recovered phases and the dry biomass used in the experiment. The bio oil (Y_{BO}) and char (Y_C) yields were calculated using the results from solvent extraction (Eqs. 6 and 7).

$$Y_{BO} = \frac{m_{BO}}{m_{In}} = \frac{m_R \cdot (SSO - W_R)}{m_{In}} \quad (6)$$

$$Y_C = \frac{m_C}{m_{In}} = \frac{m_R \cdot (1 - SSO)}{m_{In}} \quad (7)$$

where Y_{BO} and Y_C are the bio oil and char yields (wt% of initial dry ash free matter), respectively; m_{BO} , m_C , m_{In} and m_R are the mass of bio oil, char, initial dry ash free matter and raw organic residue (g), respectively; SSO is the proportion of solvent soluble organics in the raw organic residue (wt%) and W_R is the water content of the raw organic residue (wt%).

The gas yield (Y_G) was calculated by initial and final temperatures and pressures measurements using the ideal gas law, and the composition of the gas phase obtained by micro chromatography (Eqs. 8 and 9).

$$m_G = \frac{V_G}{R} \cdot \left(\frac{P_f}{T_f} - \frac{P_i}{T_i} \right) \cdot \sum_j M_j \cdot y_j \quad (8)$$

$$Y_G = \frac{m_G}{m_{In}} \quad (9)$$

where m_G is the mass of gas formed during an experiment (g); V_G is the volume of gaseous phase in the reactor (m^3); R is the ideal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$); P_f and P_i are respectively the final and initial pressures in the reactor (Pa); T_f and T_i are respectively the final and initial temperatures in the reactor (K); M_j is the molar mass of gaseous species j (g mol^{-1}); y_j is the molar fraction of gaseous species j , Y_G is the gas yield (wt % of initial dry ash free matter) and m_{In} is the initial dry ash free matter (g).

In the results and discussion section, we report the yield of organic matter in aqueous phase (Y_A). The aqueous phase yields (Y_A) was calculated by difference (Eq. 10). These yields should be considered as indicative values, as the overall organic mass balance does not necessarily close to 100 %, because of hydration and dehydration reactions involving water as either a catalyst or a reactant.

$$Y_A = 1 - Y_{BO} - Y_C - Y_G \quad (10)$$

In the results and discussion section, experimental values are the mean values of two replicates of each experiment. Error bars are the standard deviations.

Results and Discussion

Assessment of the Representativeness of Model Mixtures Towards HTL of Blackcurrant Pomace

Composition of the Model Mixtures

Hydrothermal liquefaction of two different model mixtures was conducted to assess the representativeness of model molecules towards HTL of blackcurrant pomace, based on the comparison between mass yields of the products. Table 3 reports the composition of the two model mixtures used for the comparison, based on the composition of blackcurrant pomace shown in Table 1. Note that the carbohydrate content (*cellulose hemicelluloses sugars*, corresponding to the x_1 variable in the DOEs) is calculated as the difference between 100 % and the sum of lignin, protein and lipid contents. Although some other components may be integrated in this fraction, it gives a good estimate of the carbohydrate fraction of the biomass.

The above mixtures only differ by the model molecules used to represent the fiber content of blackcurrant pomace. Either only model monomers are used (mixture 1), or exclusively model polymers (mixture 2). We made this choice because the biopolymers constituting the fibers of biomass have been identified before as high contributors to the char yield during hydrothermal liquefaction [24].

Comparison of the Mass Yields

We show in Fig. 4 the comparison between the experimental mass yields obtained by HTL of blackcurrant pomace and HTL of the model mixtures. The results show a great variation in the products distribution. A better representativeness of mixture 2 is observed towards the real case of blackcurrant pomace.

Bio oil yields are slightly overestimated in the case of mixture 1 and mixture 2, respectively by 7 wt% and 1 wt%, compared to the experimental yields obtained with blackcurrant pomace. Char yields are at the same time underestimated by 23 wt% (mixture 1) and 12 wt% (mixture 2). In terms of char yields, the most representative model mixture is the one using polymers as model compounds for the native fiber content of blackcurrant pomace, indicating a strong contribution of these compounds to the formation of solid residue during HTL. From the results, two different contributions to the char yield can be identified: the first one corresponds to an incomplete hydrolysis of the fibers, while the second one is due to recombination of reactive intermediates (model monomers and subsequent degradation products). This is what is illustrated by the higher char yield obtained in mixture 2, compared to mixture 1. When only model monomers are used (mixture 1), the char yield is lower because it simulates an “ideal” case, in which the fibers are already totally hydrolyzed and model monomers totally available for subsequent reactions. On the other hand, incomplete hydrolysis of the fibrous polymers in the case of mixture 2 leads to a higher amount of char. Finally, the lower char yield compared to blackcurrant pomace can be explained by the fact that fibers are not linked to each other in model mixtures, contrarily to real biomass.

Table 3 Composition of the model mixtures used for comparison with HTL of blackcurrant pomace (wt% daf)

Model compound	Blackcurrant pomace	Mixture 1 (monomers only)	Mixture 2 (monomers and polymers)
Cellulose hemicelluloses sugars	30.6 ^a		
Glucose		30.7	
Microcrystalline cellulose			30.6
Lignin	36.2		
Guaiacol		36.3	
Lignin (alkali)			36.3
Proteins	17.7		
Glutamic acid		17.6	17.8
Lipids	15.5		
Linoleic acid		15.4	15.4

^a Calculated by difference from the data presented in Table 1

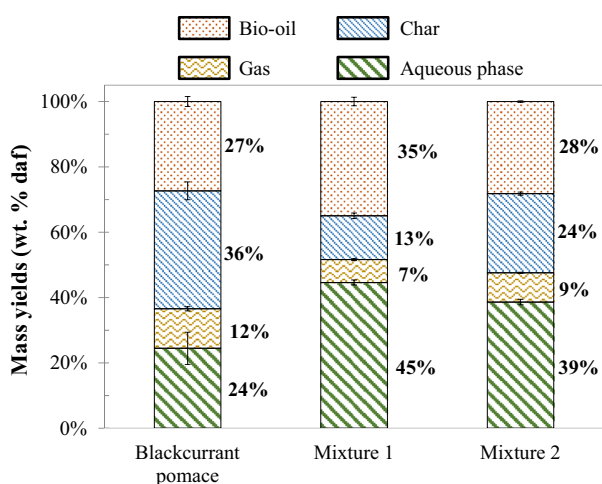


Fig. 4 Comparison of experimental mass yields from HTL of blackcurrant pomace and two model mixtures

Higher gas yield and closer estimation of the real case is obtained when using polymers (mixture 2) instead of monomers (mixture 1) as model molecules for the fibers. This indicates the occurrence of direct gas formation from polymer degradation, leading to a higher amount of gas. Yet, gas yields are still underestimated in the case of model mixtures, which could result from the absence of inorganics in the model mixtures: inorganic salts have been identified before as influencing the gas formation pathways [25].

Finally HTL of model mixtures leads to a higher aqueous phase yield, mainly because of the lower yields of other products. Therefore, the overall comparison of the results shows that the most representative model mixture is the one using model polymers as representatives for fibers. Mixture 2, using exclusively model polymers for the fiber content of blackcurrant pomace, seems to be the most representative when compared with the real case. Some differences are still observed, as discussed above, mainly because of the nature of the model molecules. In the next section, we present the experimental results obtained by hydrothermal conversion of the model compounds, following the DOEs presented in “Design of Experiments” section.

Hydrothermal Conversion of Model Monomers

Results of HTL Experiments

Hydrothermal conversion of model monomers was conducted for pure model compounds, as well as model mixtures of two to four compounds, following the mixtures designs described in Table 2. We report in Table 4 the results of the experiments.

Experiments on pure model compounds show that the smallest contributors to the bio oil yield are glucose (run 1) and glutamic acid (run 2). While glucose degrades to form mainly char and water soluble organics, glutamic acid reacts to produce mainly water soluble organics and a

Table 4 Experimental yields from HTL of model monomers (wt% of initial dry ash free matter)

Run N°	Model compounds	Bio oil	Char	Gas	Aqueous phase
1	Glucose	6.4 (± 2.4)	40.0 (± 0.1)	8.3 (± 0.7)	45.3 (± 2.0)
2	Glutamic acid	0.0 (± 0.0)	0.0 (± 0.0)	4.9 (± 0.4)	95.1 (± 0.4)
3	Guaiacol	71.1 (± 11.3)	0.0 (± 0.0)	0.0 (± 0.0)	28.9 (± 11.2)
4	Linoleic acid	95.0 (± 2.5)	0.0 (± 0.0)	0.2 (± 0.2)	4.8 (± 2.3)
5	Glucose glutamic acid	12.7 (± 1.2)	24.6 (± 6.6)	12.8 (± 0.2)	49.9 (± 5.2)
6	Glucose guaiacol	27.3 (± 0.0)	35.4 (± 0.0)	3.8 (± 0.0)	33.6 (± 0.0)
7	Glucose linoleic acid	62.7 (± 0.0)	9.9 (± 0.0)	3.8 (± 0.0)	23.6 (± 0.0)
8	Glutamic acid guaiacol	21.4 (± 0.0)	0.0 (± 0.0)	1.3 (± 0.0)	77.3 (± 0.0)
9	Glutamic acid linoleic acid	58.6 (± 2.7)	0.0 (± 0.0)	1.9 (± 0.1)	39.5 (± 2.8)
10	Guaiacol linoleic acid	76.0 (± 7.6)	0.0 (± 0.0)	0.0 (± 0.0)	24.0 (± 7.6)
11	Glucose glutamic acid guaiacol	29.0 (± 2.0)	10.2 (± 0.0)	8.2 (± 0.0)	52.6 (± 2.0)
12	Glucose glutamic acid linoleic acid	43.5 (± 1.8)	13.5 (± 0.0)	8.7 (± 0.0)	34.3 (± 1.8)
13	Glucose guaiacol linoleic acid	51.9 (± 0.0)	0.0 (± 0.0)	2.6 (± 0.0)	45.5 (± 0.0)
14	Glutamic acid guaiacol linoleic acid	59.7 (± 0.0)	0.0 (± 0.0)	0.6 (± 0.0)	39.7 (± 0.0)
15	Quaternary mixture (25 % each)	44.8 (± 3.8)	7.9 (± 0.0)	7.1 (± 0.0)	40.2 (± 3.8)
16	62.5 % Glucose 12.5 % others	24.6 (± 5.7)	32.0 (± 0.0)	7.1 (± 0.0)	36.2 (± 5.7)
17	62.5 % Glutamic acid 12.5 % others	25.8 (± 0.0)	4.1 (± 0.0)	7.6 (± 0.0)	62.5 (± 0.0)
18	62.5 % Guaiacol 12.5 % others	85.7 (± 0.0)	0.6 (± 0.0)	3.7 (± 0.0)	10.0 (± 0.0)
19	62.5 % Linoleic acid 12.5 % others	70.2 (± 0.0)	0.9 (± 0.0)	0.5 (± 0.0)	28.5 (± 0.0)

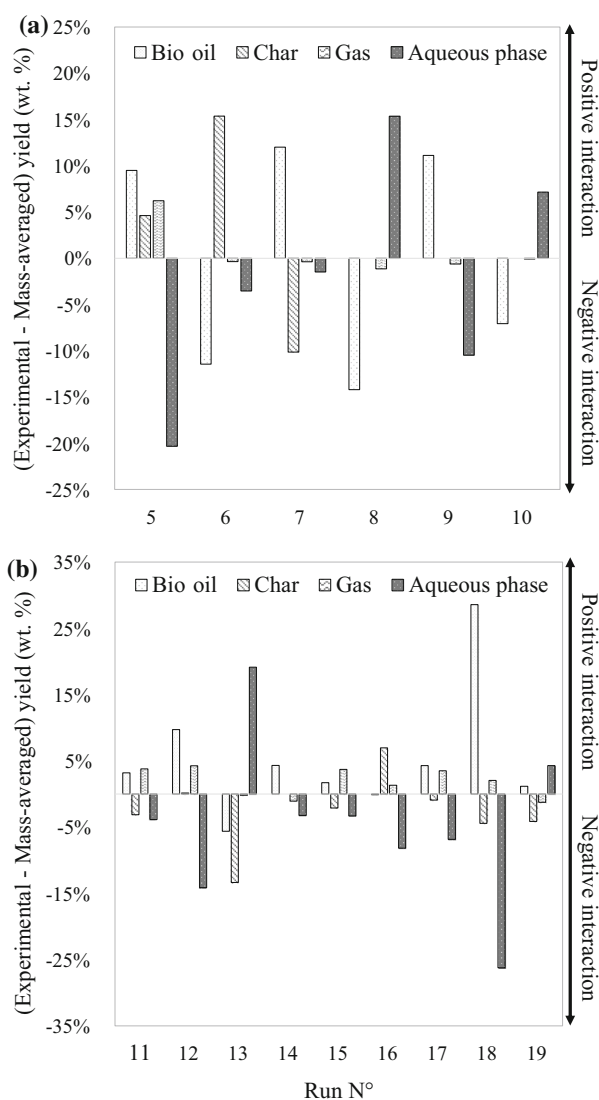


Fig. 5 Comparison between experimental and mass averaged calculated yields from HTL of **a** binary mixtures, and **b** ternary and quaternary mixtures of model monomers

small amount of gas. On the other hand, guaiacol and linoleic acid contribute significantly to the bio oil yield. These results are in line with previous works from the literature, which identified lipids to be the main contributors to the bio oil yield [12, 13]. Contrarily to what has been observed with model proteins (polymers) in previous works, the conversion of a single amino acid alone (monomer) does not lead to bio oil in this work. In the case of model monomers, char formation is mainly the results of repolymerization reactions from the intermediates produced by glucose degradation, as evidenced by the fact that solid residue was only recovered when glucose was initially present in the reaction medium.

In Fig. 5, potential positive or negative interactions in model mixtures are identified by comparing experimental yields with mass averaged yields, calculated from the mass yields obtained with individual model compounds (Eq. 5). When the experimental yield is higher than the mass averaged one, a positive interaction is identified.

In the case of binary mixtures, the comparison between mass averaged yields and experimental results allows identifying positive interactions for formation of some products. This is especially the case for the glucose glutamic acid binary mixture (run 5), which produces higher bio oil, char and gas yields than their respective individual model monomers. This means that model monomers and their degradation products take part in interaction reactions, increasing the formation of some products. In particular, the increase of the bio oil yields can be explained by Maillard type reactions, producing nitrogen heterocycles [15]. Yang et al. [15] also reported a strong beneficial effect of carbohydrate protein interaction for the bio oil formation at 300 °C. Maillard type reactions produce polymeric melanoidins that decompose to generate nitrogenous heterocycles. Another positive interaction towards bio oil formation seem to arise from the glucose linoleic acid binary mixture (run 7). When compared to the case of pure glucose, hydrothermal conversion of this mixture results in a 4 fold reduction of the char amount. In addition, the bio oil yield is higher than 50 wt% in the case of the binary mixture, suggesting a positive interaction for bio oil formation. Therefore, the bio oil yield seems to benefit from the interaction between glucose and linoleic acid, because of the inhibition of char formation from bio oil repolymerization. Similarly, the glutamic acid linoleic acid binary mixture (run 9) produces a bio oil yield higher than the mass averaged yield calculated from individual model compounds, indicating that certain interactions occur, probably through formation of long chain amides [26].

Experimental yields suggest that positive interactions for char formation occur during hydrothermal conversion of the glucose guaiacol binary mixture (run 6). In fact, using twice less glucose in the initial mixture does not result in a twofold reduction of the char yield, but in a comparable char yield to the case of glucose converted alone. The bio oil yield is at the same time reduced 3 fold compared to the case of pure guaiacol. This indicates that glucose, guaiacol and their respective degradation compounds may interact via condensation pathways to form char. Finally, another observable interaction is an increased solubilization of organic matter in the aqueous phase in the case of the glutamic acid guaiacol (run 8) and guaiacol linoleic acid binary mixtures (run 10), at the expense of the bio oil yields.

The results of hydrothermal conversion of ternary and quaternary mixtures are in good agreement with the results from the individual model compounds and binary mixtures.

For instance, a glucose rich mixture (run 16) leads to more char formation, while a linoleic acid rich mixture (run 19) produces more bio oil. Overall, when comparing experimental data to calculated mass averaged yields from individual model compounds, results show that the products result both from individual model compounds degradation and interactions.

Correlating the Mass Yields by Polynomial Regression

From the above results, polynomial regression models were used to establish correlations describing the mass yields as a function of the starting composition of the biomass. Three different designs of experiments (simplex lattice, axial and axial + binary mixtures) and two different models (linear and quadratic) led to the building of 6 correlations for each mass yield. We report in Table S1 of the electronic supplementary material the calculated coefficients for each correlation, as well as the corresponding correlation coefficients. The correlations are named according to the used DOE (1 for Scheffe design, 2 for axial design and 3 for axial + binary mixtures design), the product phase (*b* for bio oil, *c* for char, *g* for gas, and *a* for aqueous phase) and the regression model used (*l* for linear, *q* for quadratic).

Linear coefficients corresponding to the contribution of individual model compounds only differ slightly from one correlation to the other. They confirm the observations made in “Results of HTL Experiments” section on the contribution of individual model compounds on the formation of products. For instance, guaiacol and linoleic acid are the major contributors to the bio oil yield. Especially, the linear coefficients corresponding to the lipid contribution are very close to those previously determined in the literature, over 0.95. This confirms the high contribution of lipids to the bio oil, and the advantage of using subcritical water to separate the lipid content from the biomass [14, 16]. Higher variability is observed in the calculated coefficients for the binary interaction terms. Especially,

most binary coefficients calculated using the axial design and the quadratic regression model (correlations $2b,q$, $2c,q$, $2g,q$ and $2a,q$) are not in agreement with the observations made in Fig. 5 about binary interactions between model monomers. For instance, the coefficient b_{14} (glucose linoleic acid binary interaction) is negative in correlation $2b,q$, while a positive interaction was identified in Fig. 5. This is most likely due to the fact that binary mixtures are excluded from this particular DOE, leading to bad estimation of binary interactions. Evaluating the significance of the coefficients for these correlations confirms this observation, as no quadratic coefficient is considered as significant by the Student test (Table S2 of the electronic supplementary material). Other coefficients are generally in agreement with observations made in “Results of HTL Experiments” section. Correlation coefficients R^2 are relatively good (0.78–0.996), meaning that the correlations fit the experimental results. In addition, *F tests* result in very low *p values*, showing a good significance of the models (Table S2 and S3 of the electronic supplementary material). As shown in the electronic supplementary material, correlation coefficients are generally better for the quadratic correlations, which is in agreement with product formation pathways both from individual compound degradation and interaction phenomena. In “Tests and Validation of Correlations” section, the validity of the correlations is tested against experimental results of model mixtures and real resources.

Hydrothermal Conversion of Model Monomers and Polymers

Results of HTL Experiments

In this set of experiments, microcrystalline cellulose and alkali lignin were used as model compounds for fibers, respectively instead of glucose and guaiacol. Hydrothermal conversion experiments were conducted following the

Table 5 Experimental yields from HTL of model monomers and polymers for fibers (wt% of initial dry ash free matter)

Run N°	Model compounds	Bio oil	Char	Gas	Aqueous phase
1'	Cellulose	5.6 (± 1.9)	40.9 (± 0.6)	10.3 (± 0.2)	43.3 (± 1.6)
2	Glutamic acid	0.0 (± 0.0)	0.0 (± 0.0)	4.9 (± 0.4)	95.1 (± 0.4)
3'	Lignin (alkali)	0.1 (± 0.1)	61.6 (± 2.3)	4.1 (± 0.3)	34.2 (± 2.3)
4	Linoleic acid	95.0 (± 2.5)	0.0 (± 0.0)	0.2 (± 0.2)	4.8 (± 2.3)
5'	Cellulose glutamic acid	7.3 (± 3.1)	22.9 (± 3.8)	15.5 (± 0.3)	54.3 (± 0.8)
6'	Cellulose lignin (alkali)	22.5 (± 1.5)	24.2 (± 0.7)	11.1 (± 0.1)	42.2 (± 2.2)
7'	Cellulose linoleic acid	61.6 (± 1.6)	10.2 (± 1.3)	4.5 (± 0.2)	23.7 (± 1.8)
8'	Glutamic acid lignin (alkali)	5.7 (± 1.8)	31.3 (± 0.2)	8.6 (± 0.1)	54.4 (± 1.8)
9	Glutamic acid linoleic acid	58.6 (± 2.7)	0.0 (± 0.0)	1.9 (± 0.1)	39.5 (± 2.8)
10'	Lignin (alkali) linoleic acid	40.2 (± 2.8)	38.9 (± 3.3)	2.4 (± 0.3)	18.5 (± 6.1)

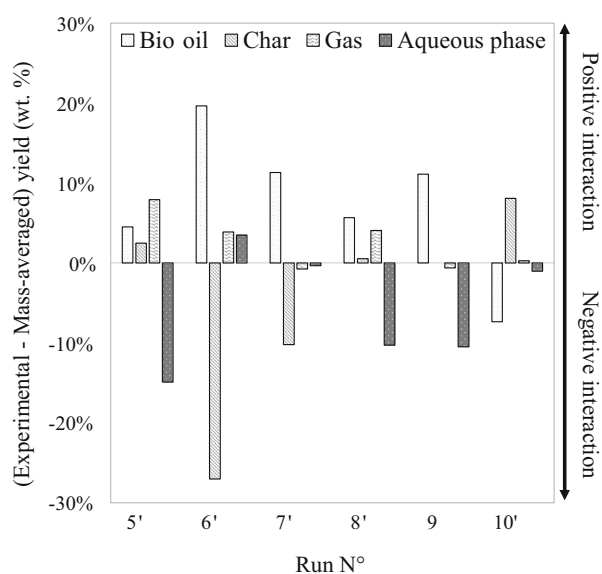


Fig. 6 Comparison between experimental and mass averaged calculated yields from HTL of binary mixtures of model monomers and polymers

Scheffe design (4,2) described in Table 2. In Table 5, we report the results of the experiments.

From the results, it can be seen that cellulose behaves in a very similar way to glucose in hydrothermal conditions, while producing higher gas yield. This was also observed by Biller and Ross [12] when comparing HTL of glucose and starch at 350 °C. The higher amount of gas in the case of cellulose indicates that direct gas formation from cellulose decomposition occurred in the experiments. On the contrary, lignin shows a very different behavior compared to guaiacol. Nearly no bio oil is recovered from HTL of lignin, while it produces a great amount of char, some gas and water soluble organics. These observations underline the resistance of lignin to hydrolysis in the conditions of the study, as well as it shows the occurrence of direct gas formation from lignin.

In Fig. 6, experimental yields obtained from HTL of binary mixtures are compared with calculated mass averaged yields. From the comparison, it is observed that most interactions benefit to the bio oil phase, at the expense of the char and aqueous phase. Especially, the bio oil yield seem to be highly favored in the case of a cellulose lignin binary mixture (run 6'), contrarily to what was observed in the case of a glucose guaiacol binary mixture (run 6). This could be the result of the basic nature of the lignin used in this study (alkali lignin): in fact, HTL of cellulose in basic medium highly benefits to the bio oil yield, at the expense of char formation [27]. Compared to the observations made on model monomers (Fig. 5), differences only arise in the case of the mixtures involving lignin (runs 6', 8' and 10').

Correlating the Mass Yields by Polynomial Regression

From the above results presented in Table 5, polynomial regression models were used to establish correlations describing the mass yields starting from the initial biochemical content of the biomass. In this case, only one DOE was used (simplex lattice design: Scheffe (4,2)), and two different regression models (linear and quadratic). This led to the building of 2 correlations for each mass yield. We report in Table S2 of the electronic supplementary material the calculated coefficients for each correlation, as well as the corresponding correlation coefficients. Correlations are named in the same way as previously described in “Correlating the Mass Yields by Polynomial Regression” section. As it was the case with model monomers, the calculated coefficients for linear contributions of individual model compounds are very similar for a given yield. Interaction coefficients also show a good agreement with the interactions that arise from Fig. 6. Correlation coefficients R^2 are relatively good (0.75–0.998), showing a good fit of the correlations to the experimental results. In addition, F tests result in very low p values, showing a good significance of the models (Table S5 and S6 of the electronic supplementary material). In the next section (Tests and Validation of Correlations), the validity of the correlations is tested against experimental results of model mixtures and real resources.

Tests and Validation of Correlations

Results of HTL Experiments of the Test Points

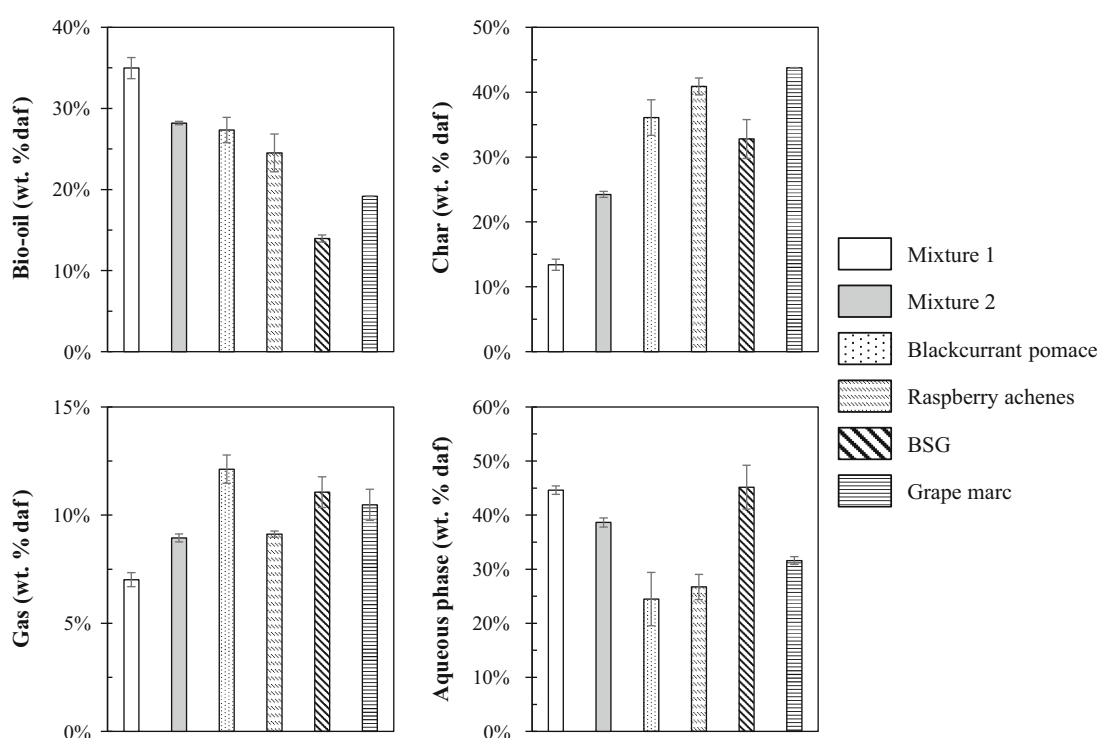
The use of different DOEs and several regression models led to the elaboration of 8 correlations for each mass yield. Yet, all correlations might not represent accurately experimental results obtained with different model mixtures and real food processing residues. Therefore, we tested the validity of the correlations by comparing them with results obtained from the two model mixtures, as well as four real food processing residues. Table 6 recalls the composition of the chosen test points, and Fig. 7 shows the experimental yields of the products for the six test points.

Figure 7 shows variations of the product yields depending on the starting biomass or model mixture. For instance, brewer's spent grains (BSG) produce the lower bio oil yield, as well as the higher proportion of organic matter recovered in the aqueous phase. A similar amount of char is obtained, when compared to other resources. The results obtained by HTL of BSG might be linked to the higher carbohydrate content of BSG compared to other resources which are richer in lignin (Table 6). In fact, we identified in previous sections that cellulosic fibers and sugars mainly produce char and water soluble organics

Table 6 Composition of the model mixtures and food processing residues used for testing the correlations

Composition (wt% daf)	Model mixture/biomass					
	Mixture 1	Mixture 2	Blackcurrant pomace	Raspberry achenes	BSG	Grape marc
x ₁ : cellulose hemicellulose sugars ^a	30.7 (glucose)	30.6 (cellulose)	30.6	38.7	68.5	30.3
x ₂ : proteins	17.6 (glutamic acid)	17.8 (glutamic acid)	17.7	8.2	19.3	10.2
x ₃ : lignin	36.3 (guaiacol)	36.3 (alkali lignin)	36.2	47.8	6.0	51.0
x ₄ : lipids	15.4 (linoleic acid)	15.4 (linoleic acid)	15.5	5.3	6.2	8.5

^a Calculated by difference using the data from Table 1

**Fig. 7** Experimental yields produced by HTL of two model mixtures and four food processing residues (daf: dry ash free)

during HTL. As well, grape marc produces a relatively low bio oil yield and the highest char yield, which might result from the high fiber content in this biomass. Grape marc is especially rich in lignin, which leads to low bio oil and high char recovery, as observed in “Results of HTL Experiments” section from HTL of alkali lignin. In the next section, experimental results shown in Fig. 7 are compared with calculated yields obtained using the correlations, with the objective of selecting appropriate equations to describe the mass yields as a function of the initial biochemical content of the biomass.

Selection of the Correlations

To select adequate correlations describing the mass yields from the initial biomass composition, experimental yields are compared with calculated yields in Fig. 8. To assess in a visual way the representativeness of correlations, we considered an interval of ± 5 wt% around each experimental yield (dashed lines in Fig. 8).

The results presented in Fig. 8 show that few correlations are able to predict the bio oil yields within ± 5 wt% of experimental yields. In the case of mixture 1, only

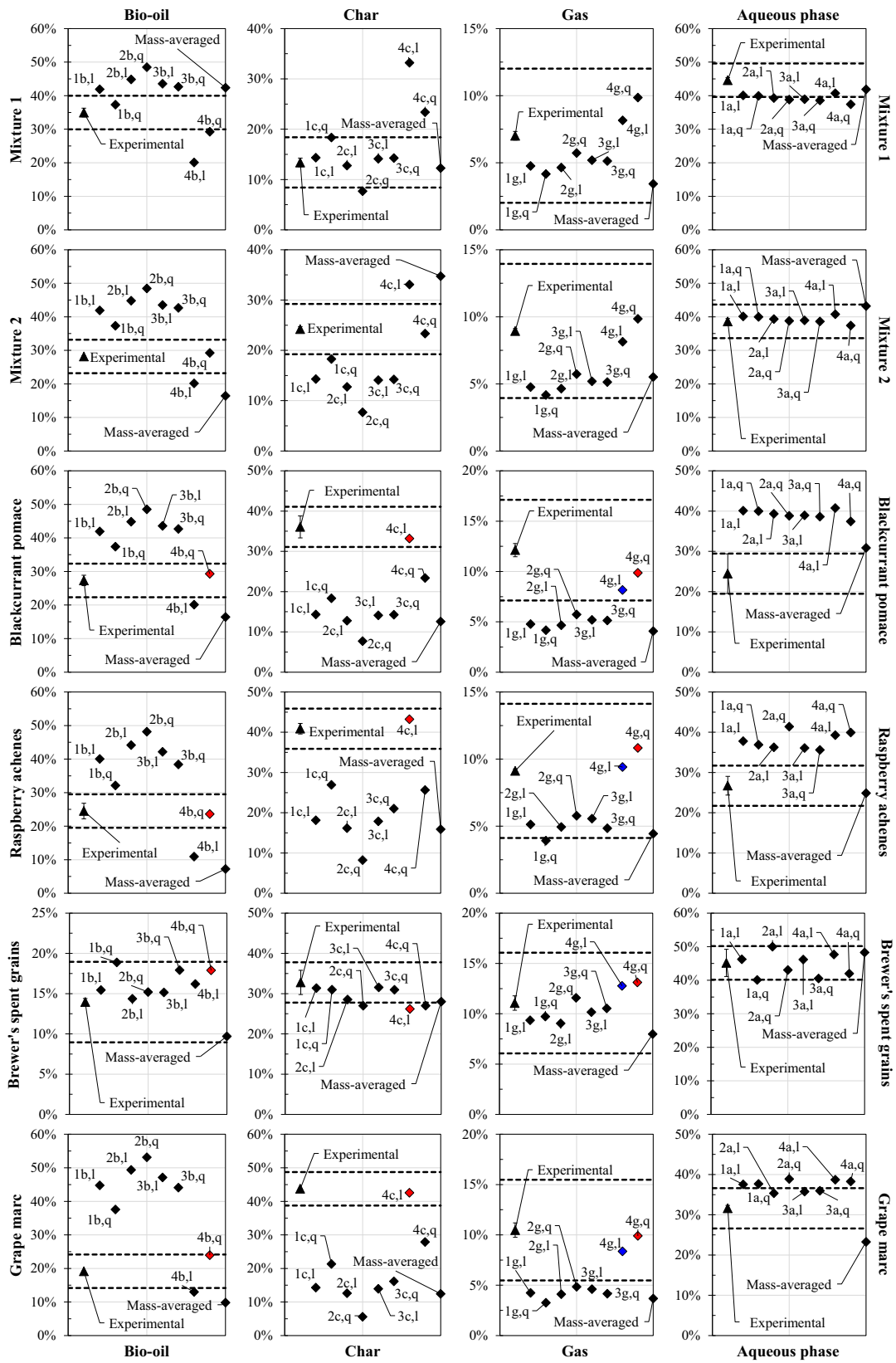


Fig. 8 Comparison between experimental and calculated yields using correlations

correlation $1b,q$ predicts with good accuracy the bio oil yield, with a slight overestimation of 2.4 wt%. The second best correlation in this case is $4b,q$, which underestimates the bio oil yield by 5.7 wt%. This same correlation ($4b,q$) predicts well the bio oil yield in the case of mixture 2, with a slight overestimation of 1.1 wt%. Experimental char yields for mixtures 1 and 2 are generally predicted with good accuracy by the correlations, even though correlations elaborated from model monomers ($1b,l$ to $3b,q$) systematically underestimate the char yield in the case of mixture 2. This results from the polymeric nature of fibers used in mixture 2, as discussed before in “[Comparison of the Mass Yields](#)” section. The same observation applies for the prediction of gas yields by most correlations. Finally, aqueous phase yields are overall well predicted by the correlations. Aqueous phase yields are systematically underestimated in the case of mixture 1, which may be linked to an overestimation of the bio oil yield. From the results, it is possible to say that correlations obtained from model monomers cannot be applied to experimental results from HTL of model polymers, especially regarding the formation of bio oil and char. Several correlations can however be used to calculate the mass yields from the starting composition of the model mixture.

The comparison of the calculations with experimental yields for real resources show that some correlations are able to predict accurately the behavior of biomass during HTL. When considering the results for bio oil, it is observed that the correlation $4b,q$ might be able to predict the mass yields within ± 5 wt% of experimental results for most resources. Other correlations might be more accurate for specific resources, but cannot be applied to the whole range of resources that we considered. For instance, correlations obtained from HTL of model monomers ($1b,l$ to $3b,q$) seem to be more accurate for BSG, but they overestimate greatly the bio oil yields for the other three food processing residues. This is probably due to the different nature of fibers in BSG, which would be responsible for different reactivity. In fact, contrarily to the other three studied food processing residues, BSG are rich in carbohydrate and poor in lignin (Table 6). Despite these

differences, we chose correlation $4b,q$ to model the bio oil yield, because it allows a good prediction of bio oil yields, between -0.9 and $+4.8$ wt% of experimental yields.

The comparison of experimental results and calculations for char yields shows that correlation $4c,l$ seems to be the most representative for most food processing residues. Using correlation $4c,l$, char yields for blackcurrant pomace, raspberry achenes and grape marc are predicted with a maximum underestimation of 2.9 wt% and a maximum overestimation of 2.3 wt%. However, the correlation $4c,l$ seems less adapted to predict the char yield from HTL of BSG, which is underestimated by 6.6 wt%. The different nature of fibers contained in BSG might explain this observation. Contrarily to the other three food processing residues, BSG are poor in lignin and especially rich in carbohydrate, which are more readily converted in sub critical water [24]. It is therefore likely that char formation pathways differ between BSG and the three other resources: while char is mainly due to bad hydrolysis for the three most lignin rich resources, it might result from recombination of reactive intermediates in the case of BSG. This could explain why the correlations based on the results from model monomers predict in a better way the char yield for BSG.

From the gas yields, the correlations $4g,l$ and $4g,q$ seem to be the most representative of HTL of real food processing residues. In fact, the correlations obtained from HTL of model monomers only seem to be adapted in the case of BSG, but they underestimate the gas yields for the other three food processing residues. From a chemical point of view, this could mean that the gas formation pathways differ between BSG and the other resources: while gas is mainly produced from monomer degradations in the case of BSG, the main gas formation pathways for the three other resources could also result from the degradation of polymeric fibers. Nonetheless, we chose correlation $4g,q$ which predicts the gas yields with a maximum underestimation of -2.3 wt% and a maximum overestimation of 2.0 wt%.

Finally, we see from the results that no correlation predicts accurately the aqueous phase yields for

Table 7 Coefficients of the predictive correlations chosen to calculate mass yields in HTL of food processing residues

Product	Correlation N°	b ₁	b ₂	b ₃	b ₄	b ₁₂	b ₁₃	b ₁₄	b ₂₃	b ₂₄	b ₃₄	R ²
Bio oil	4b,q	0.05	0.00	0.00	0.95	0.18	0.79	0.45	0.23	0.44	0.30	0.998
Char	4c,l	0.33	0.00	0.64	0.00							0.86
Gas	4g,q	0.10	0.05	0.04	0.00	0.32	0.16	0.03	0.16	0.02	0.01	0.998
Aqueous phase ^a	1 (4b,q + 4c,l + 4g,q)	0.48	0.05	0.68	0.95	0.50	0.94	0.42	0.39	0.42	0.28	0.91 ^b

^a Coefficients correspond to (1 Y_A)

^b Tested against HTL experimental results from Table 5

blackcurrant pomace and raspberry achenes. In the case of BSG, most correlations predict the mass yields within the ± 5 wt% interval, as well as some correlations in the case of grape marc (2a,l, 3a,l and 3a,q). Contrarily to other products, it is therefore not possible to select one existing correlation. We chose therefore to determine the correlation for the aqueous phase by difference, as a linear combination of correlations for bio oil, char and gas.

Validation of the Correlations

The previous section showed that some correlations are adequate to predict product yields from the initial biochemical content of food processing residues. The chosen correlations are summarized in Table 7. Correlation coefficients are good (0.86–0.998), indicating a good fit of the models to the experimental data.

The low *p* values obtained from the *F* tests (see Table S7 of the electronic supplementary material) show that the significance of the models is good (*p* values $< 5.2 \times 10^{-5}$). In addition, observations made in the previous sections on contributions of biochemical compounds to the various products are confirmed, when assessing the significance of the parameters (Table S7 of the electronic supplementary material)

- Bio oil yield: all parameters are significant at a level over 97 %, except x_2 (proteins) and x_3 (lignin).

- Char yield: all parameters are significant at a level over 99 %, except x_2 (proteins) and x_4 (lipids).
- Gas yield: all parameters are significant at a level over 98 %, except x_4 (lipids) and x_3x_4 (binary interaction between lignin and lipids).
- Aqueous phase yield: all parameters are significant at a level over 99 %, as a result of the mathematical construction of this correlation. It is also consistent with the reaction network proposed by Valdez et al. [13], who suggest contributions of the biomolecules to both the aqueous phase and the bio oil prior to further degradation.

As can be seen from Table 7, quadratic models were chosen to represent the bio oil and gas yields, taking into account binary interactions between biomass components. Important binary interactions have for example been observed between carbohydrate and proteins, via Maillard reactions, confirming previous results from the literature [15]. On the contrary, a linear correlation was chosen to predict char yields from the carbohydrate and lignin contents of the biomass. This indicates that the main char formation is due to the fiber content in the initial material, and that interaction pathways have less influence. Figure 9 shows the comparison between calculated yields and experimental results.

The correlations allow to predict with good accuracy experimental results for HTL of real food processing residues. Calculated yields vary from -0.9 to 4.8 wt% of

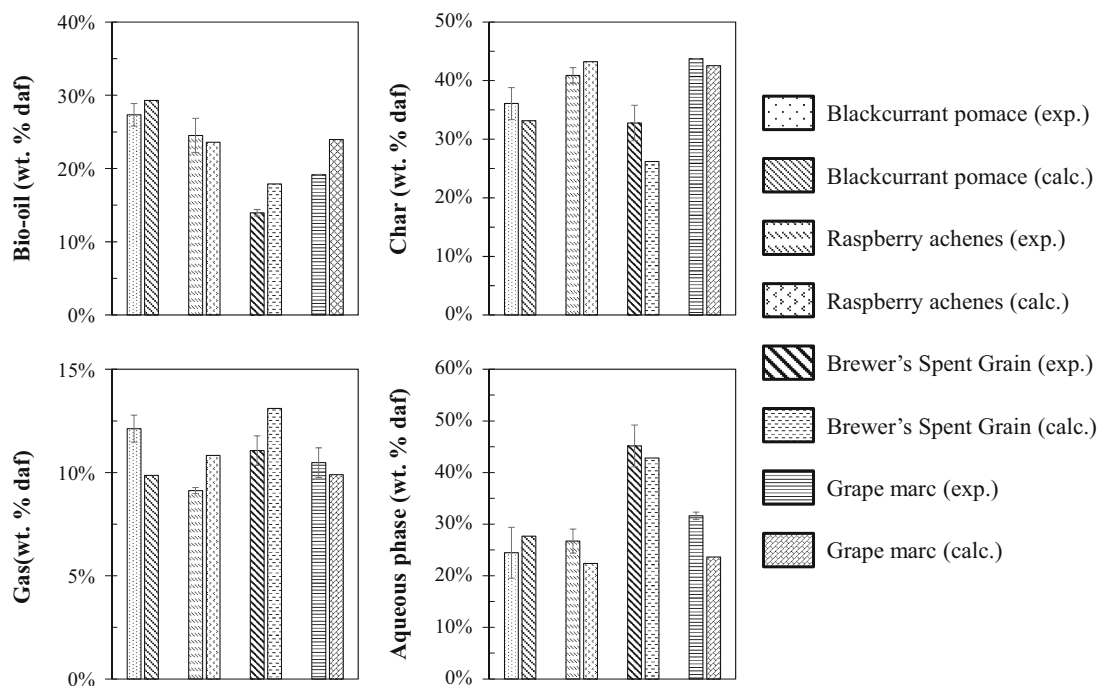


Fig. 9 Comparison between calculated mass yields and experimental results from HTL of real food processing residues

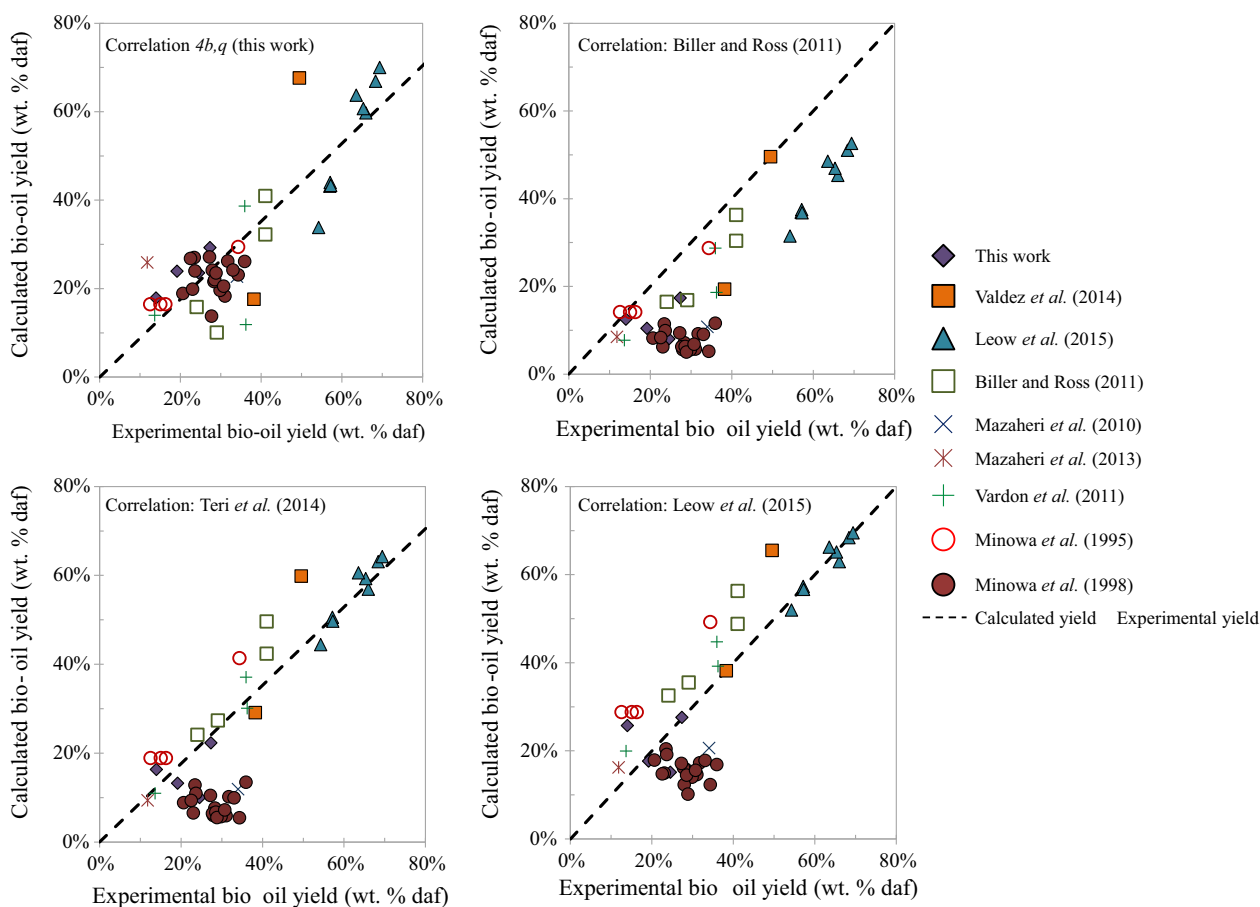


Fig. 10 Comparison of the correlations for calculating bio oil yields from the initial biomass composition (this work, [12 14, 16, 28 33])

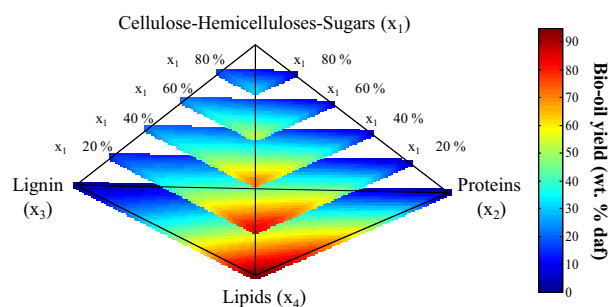
experimental bio oil yields, -6.6 to 2.3 wt% of experimental char yields, -2.3 to 2.0 wt% of gas yields and -8.0 to 3.2 wt% of aqueous phase yields. Considering experimental errors, the chosen correlations are in good agreement with HTL of real food processing residues.

In Fig. 10, we compare the prediction capability of our correlations with previously published correlations based on additivity laws [12, 14, 16]. To do so, we used studies from the literature reporting both the biochemical composition of their starting biomass and the bio oil yields, at close operating conditions to ours (300 °C). The objective was to diversify the scope of resources. Therefore, we included in the comparison algae [12, 13, 16, 28, 29], as well as lignocellulosic biomass and organic residues (this work, [28, 30 33]). The presented comparison was performed exclusively for the bio oil yield, as other yields were not discussed by all previous studies. Yet, the correlation for the char yield is able to accurately predict results from HTL of microalgae obtained by Valdez et al. [13] and Leow et al. [16]. Gas and aqueous phase yields are somewhat predicted with less accuracy (results not shown).

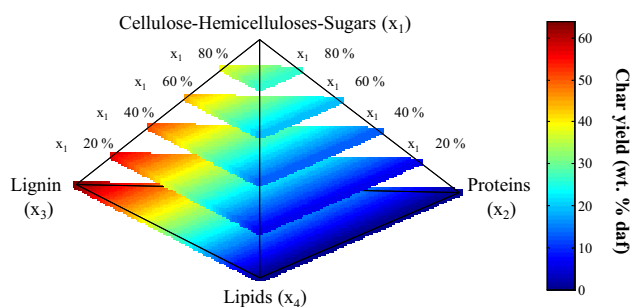
The results shown in Fig. 10 illustrate the good accuracy of our correlation to calculate the bio oil yields from HTL of several resources of different natures. The correlation developed in the present paper allows a good prediction of a large scope of bioresources, in comparison with correlations developed specifically for microalgae. The largest discrepancies arise in the case of protein rich and lipid poor resources. In fact, in these cases, our correlation underestimates the bio oil yields reported in other studies (Biller and Ross [12], Vardon et al. [28], Valdez et al. [13], Leow et al. [16]). This is most likely due to the fact that we did not include a model polymer in our study to represent the protein content of the biomass, leading to discrepancies at high protein contents. Future work should be done to correct the correlations using a model protein instead of a model amino acid.

A better accuracy is obtained when comparing our calculations to experimental results for lignocellulosic biomass (Minowa et al. [30]) and organic residues such as manure, sewage sludge or municipal solid waste (Minowa et al. [31], Vardon et al. [28]), which have a lower protein

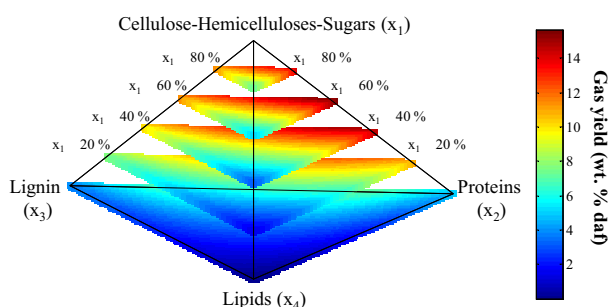
Bio oil



Char



Gas



Aqueous phase

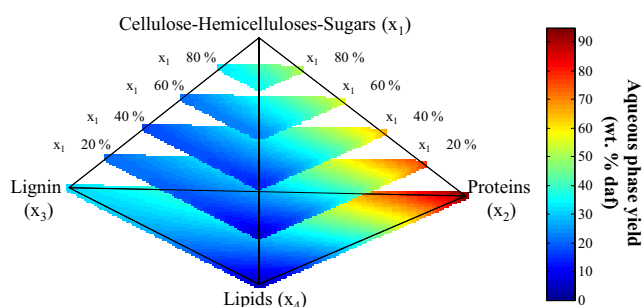


Fig. 11 Evolution of mass yields (wt% of initial dry ash free matter) for HTL of food processing residues as a function of the initial biomass composition (fixed carbohydrate content: 0, 20, 40, 60 and 80 wt% daf)

content. In particular, a better accuracy towards lignocellulosic resources is achieved by the fact that our model includes a variable for lignin. Note that discrepancies between calculations and experiments may also arise from the biomass characterization methods, which often differ between authors, as well as the product workup procedures. Bio oil yields can be influenced for instance by the nature of organic solvents used to perform the extraction [23, 34], and by the steps followed for bio oil recovery [35]. Despite the observed discrepancies, we conclude from Figs. 9, Fig. 10 that the correlations can be used to describe the evolution of mass yields from the initial biomass composition. This is what is illustrated in Fig. 11.

Figure 11 recalls the main observations made in this study, and show the main contributing species for each product:

- Lipids are the main contributors to the bio oil yield, but interaction phenomena have also been observed, such as between carbohydrate and proteins, or between proteins and lipids. Interactions between degradation products of carbohydrate and lignin correspond to condensation reactions that can benefit to bio oil formation, but also to char through polymerization.
- Fibers contribute the most to the char yield, either individually or through interaction reactions between monomers and reactive intermediates.

- As for the char yield, gas formation is driven by the fiber content of the biomass, as well as by Maillard reactions between carbohydrates and protein.
- Formation of water soluble organics is mostly the results of carbohydrate and protein degradation, and to a lesser extent of lignin depolymerization by hydrolysis.

Conclusion

This paper has presented a modelling study of hydrothermal liquefaction (HTL) of food processing residues using model compounds, selected from the characterization of blackcurrant pomace. By selecting appropriate model molecules, HTL of blackcurrant pomace could be reproduced with acceptable representativeness, especially when model polymers were used to represent the fiber content of the biomass. In this case, the bio oil was slightly overestimated by 1 wt%, while char and gas yields were respectively underestimated by 8 and 3 wt%. Using exclusively model monomers results in a lower representativeness towards HTL of blackcurrant pomace, evidencing the strong influence of the nature of model molecules (monomers or polymers) on HTL results.

Studying hydrothermal conversion of model compounds alone, and in mixture of 2 to 4 compounds, allowed the identification of the main contributing species to product formation, as well as interaction phenomena. Lipids are the main contributors to the bio oil yield, while interaction reactions can also increase bio oil formation (e.g. carbohydrate protein, carbohydrate lipid, protein lipid). As shown by the comparison between model mixtures and HTL of blackcurrant pomace, fibers contribute the most to the char yield, either individually or through interaction reactions between monomers and reactive intermediates (e.g. carbohydrate lignin monomers interaction). Gas formation is also driven by the fiber content of the biomass, as well as some interactions (e.g. carbohydrate protein). Finally, formation of water soluble organics mostly results from carbohydrate and protein individual degradation, and to a lesser extent from lignin depolymerization by hydrolysis.

The hydrothermal conversion of model compounds, following several designs of experiments, led to the elaboration of correlations able to predict HTL results with good accuracy for the four studied real food processing residues. Quadratic correlations were chosen to predict the bio oil and gas yields, taking into account binary interactions, while a linear correlation was chosen to calculate the char yield. This is the mathematical translation of the main contribution of fibers to char formation, with less influence of interaction pathways. Finally, the calculation of the aqueous phase yield was elaborated as a linear combination of other correlations. Overall, calculations are within -8.0 to $+4.8$ wt% of experimental yields of the products, indicating the good agreement between models and experimental data. The obtained correlations were then validated on a larger scope of resources based on results from the literature, showing some limitations (e.g. protein rich lipid poor algae strains). Future work should focus on further validation of the correlations, for instance by including a model protein in the DOEs or by using native extracts of the biomass as model molecules to gain better representativeness. The expressions established in this work could nevertheless be useful tools to evaluate potential resources for the HTL process from straight forward information (biochemical composition), therefore avoiding the need for multiple scouting tests. The correlations could also be used to design biomass blends able to produce a standard quality oil in high yield, opening the way to co processing of different resources.

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References

1. van Swaaij, W., Kersten, S., Palz, W.: Biomass power for the world: transformations to effective use. Biomass power for the world: transformations to effective use, pp. 1 734 (2015)
2. FAO: Food Wastage Footprint: Impacts on Natural Resources. FAO (2013)
3. Akiya, N., Savage, P.E.: Roles of water for chemical reactions in high temperature water. Chem. Rev. **102**, 2725 2750 (2002)
4. Weing artner, H., Franck, E.U.F.: Supercritical water as a solvent. Angew. Chem. Int. Ed. **44**, 2672 2692 (2005)
5. Ruiz, H.A., Rodr iguez Jasso, R.M., Fernandes, B.D., Vicente, A.A., Teixeira, J.A.: Hydrothermal processing, as an alternative for upgrading agriculture residues and marine biomass according to the biorefinery concept: a review. Renew. Sustain. Energy Rev. **21**, 35 51 (2013)
6. Toor, S.S., Rosendahl, L., Rudolf, A.: Hydrothermal liquefaction of biomass: a review of subcritical water technologies. Energy **36**, 2328 2342 (2011)
7. Elliott, D.C., Biller, P., Ross, A.B., Schmidt, A.J., Jones, S.B.: Hydrothermal liquefaction of biomass: developments from batch to continuous process. Bioresour. Technol. **178**, 147 156 (2015)
8. Pedersen, T.H., Grigoros, I.F., Hoffmann, J., Toor, S.S., Daraban, I.M., Jensen, C.U., Iversen, S.B., Madsen, R.B., Glasius, M., Arturi, K.R., Nielsen, R.P., S ogaard, E.G., Rosendahl, L.A.: Continuous hydrothermal co liquefaction of aspen wood and glycerol with water phase recirculation. Appl. Energy **162**, 1034 1041 (2016)
9. Barreiro, D.L., Prins, W., Ronsse, F., Brilman, W.: Hydrothermal liquefaction (HTL) of microalgae for biofuel production: state of the art review and future prospects. Biomass Bioenergy **53**, 113 127 (2013)
10. D eniel, M., Haarlemmer, G., Roubaud, A., Weiss Hortala, E., Fages, J.: Energy valorisation of food processing residues and model compounds by hydrothermal liquefaction. Renew. Sustain. Energy Rev. **54**, 1632 1652 (2016)
11. Arturi, K.R., Kucheryavskiy, S., S ogaard, E.G.: Performance of hydrothermal liquefaction (HTL) of biomass by multivariate data analysis. Fuel Process. Technol. **150**, 94 103 (2016)
12. Biller, P., Ross, A.B.: Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content. Bioresour. Technol. **102**, 215 225 (2011)
13. Valdez, P.J., Tocco, V.J., Savage, P.E.: A general kinetic model for the hydrothermal liquefaction of microalgae. Bioresour. Technol. **163**, 123 127 (2014)
14. Teri, G., Luo, L., Savage, P.E.: Hydrothermal treatment of protein, polysaccharide, and lipids alone and in mixtures. Energy Fuels **28**, 7501 7509 (2014)
15. Yang, W., Li, X., Li, Z., Tong, C., Feng, L.: Understanding low lipid algae hydrothermal liquefaction characteristics and pathways through hydrothermal liquefaction of algal major components: crude polysaccharides, crude proteins and their binary mixtures. Bioresour. Technol. **196**, 99 108 (2015)
16. Leow, S., Witter, J.R., Vardon, D.R., Sharma, B.K., Guest, J.S., Strathmann, T.J.: Prediction of microalgae hydrothermal liquefaction products from feedstock biochemical composition. Green Chem. **17**, 3584 3599 (2015)
17. AFNOR, NF EN 14774 1 Biocombustibles solides D etermination de la teneur en humidit e M ethode par s echage   l' tuve Partie 1: humidit e totale M ethode de r ef erence (2010)
18. AFNOR, NF V18 122 Aliments des animaux D etermination s equentielle des constituants pari etaux M ethode par traitement aux d etergents neutre et acide et   l'acide sulfurique (2013)
19. AFNOR, NF EN 14775 Biocombustibles solides M ethode de d etermination de la teneur en cendres (2010)

20. Dote, Y., Inoue, S., Ogi, T., Yokoyama, S.: Distribution of nitrogen to oil products from liquefaction of amino acids. *Bioresour. Technol.* **64**, 157 160 (1998)
21. Dote, Y., Inoue, S., Ogi, T., Yokoyama, S.: Studies on the direct liquefaction of protein contained biomass: the distribution of nitrogen in the products. *Biomass Bioenergy* **11**, 491 498 (1996)
22. Tinsson, W.: *Plans d'expérience: constructions et analyses statistiques. Mathématiques et Applications*, vol. 67, 1st edn. Springer, Berlin (2010). doi:10.1007/978 3 642 11472 4
23. Anouti, S., Haarlemmer, G., Déniel, M., Roubaud, A.: Analysis of physico chemical properties of bio oil from hydrothermal liquefaction of blackcurrant pomace. *Energy Fuels* **30**, 398 406 (2015)
24. Karagöz, S., Bhaskar, T., Muto, A., Sakata, Y.: Comparative studies of oil compositions produced from sawdust, rice husk, lignin and cellulose by hydrothermal treatment. *Fuel* **84**, 875 884 (2005)
25. Akgül, G., Kruse, A.: Influence of salts on the subcritical water gas shift reaction. *J. Supercrit. Fluids* **66**, 207 214 (2012)
26. Changi, S., Zhu, M., Savage, P.E.: Hydrothermal reaction kinetics and pathways of phenylalanine alone and in binary mixtures. *ChemSusChem* **5**, 1743 1757 (2012)
27. Yin, S., Tan, Z.: Hydrothermal liquefaction of cellulose to bio oil under acidic, neutral and alkaline conditions. *Appl. Energy* **92**, 234 239 (2012)
28. Vardon, D.R., Sharma, B.K., Scott, J., Yu, G., Wang, Z., Schideman, L., Zhang, Y., Strathmann, T.J.: Chemical properties of biocrude oil from the hydrothermal liquefaction of *Spirulina* algae, swine manure, and digested anaerobic sludge. *Bioresour. Technol.* **102**, 8295 8303 (2011)
29. Minowa, T., Yokoyama, S., Kishimoto, M., Okakura, T.: Oil production from algal cells of *Dunaliella tertiolecta* by direct thermochemical liquefaction. *Fuel* **74**, 1735 1738 (1995)
30. Minowa, T., Kondo, T., Sudirjo, S.T.: Thermochemical liquefaction of Indonesian biomass residues. *Biomass Bioenergy* **14**, 517 524 (1998)
31. Minowa, T., Murakami, M., Dote, Y., Ogi, T., Yokoyama, S.: Oil production from garbage by thermochemical liquefaction. *Biomass Bioenergy* **8**, 117 120 (1995)
32. Mazaheri, H., Lee, K.T., Bhatia, S., Mohamed, A.R.: Subcritical water liquefaction of oil palm fruit press fiber for the production of bio oil: effect of catalysts. *Bioresour. Technol.* **101**, 745 751 (2010)
33. Mazaheri, H., Lee, K.T., Mohamed, A.R.: Influence of temperature on liquid products yield of oil palm shell via subcritical water liquefaction in the presence of alkali catalyst. *Fuel Process. Technol.* **110**, 197 205 (2013)
34. Valdez, P.J., Dickinson, J.G., Savage, P.E.: Characterization of product fractions from hydrothermal liquefaction of *nanochloropsis* sp. and the influence of solvents. *Energy Fuels* **25**, 3235 3243 (2011)
35. Barreiro, D.L., Riede, S., Hornung, U., Kruse, A., Prins, W.: Hydrothermal liquefaction of microalgae: effect on the product yields of the addition of an organic solvent to separate the aqueous phase and the biocrude oil. *Algal Res.* **12**, 206 212 (2015)