# Optimisation of bio-oil production by hydrothermal liquefaction of agro-industrial residues: Blackcurrant pomace (Ribes nigrum L.) as an example

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# Optimisation of bio-oil production by hydrothermal liquefaction of agro-industrial residues: Blackcurrant pomace (*Ribes nigrum* L.) as an example

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A B S T R A C T

This work reports bio oil production by hydrothermal liquefaction of blackcurrant pomace (*Ribes nigrum* L.), a fruit residue obtained after berry pressing. The bio oil has a higher heating value of 35.9 MJ kg $^{1}$ and low ash content, which makes it suitable for energy applications. We report the influence of process parameters on yields and carbon distribution between products: temperature (563 608 K), holding time (0 240 min), mass fraction of dry biomass in the slurry (0.05 0.29), and initial pH (3.1 12.8) by adding sodium hydroxide (NaOH). Depending on the experiments, the bio oil accounts for at least 24% mass fraction of the initial dry biomass, while char yields ranges from 24 to 40%. A temperature of 583 K enhances the bio oil yield, up to 30%, while holding time does not have a significant influence on the results. Increasing biomass concentrations decreases bio oil yields from 29% to 24%. Adding sodium hydroxide decreases the char yield from 35% at pH = 3.1 (without NaOH) to 24% at pH = 12.8. It also increases the bio oil yield and carbon transfer to the aqueous phase. Thermogravimetric analysis shows that a 43% mass fraction of the bio oil boils in the medium naphtha petroleum fraction range. The bio oil is highly acidic and unsaturated, and its dynamic viscosity is high (1.7 Pa s at 298 K), underlining the need for further upgrading before any use for fuel applications.

## 1. Introduction

Hydrothermal processing of biomass using water in sub and supercritical conditions has been identified as a promising tech nology to convert wet resources into energy dense products in the form of solid, liquid or gaseous fuels [1 3]. Hydrothermal processes take advantage of the evolution of water properties at high tem perature and pressure [4]. In particular under subcritical condi tions, water loses its polarity, behaving similar to an organic solvent, and its ionic product $K_w$ increases up to three orders of magnitude [2]. These two modifications of water properties lead respectively to better solubility of organic compounds and increased catalytic activities to degrade the molecules contained in biomass.

In these conditions, liquid fuels can be directly produced from wet biomass by the hydrothermal liquefaction (HTL) process (T = 523 643 K, P = 10 30 MPa). The HTL process is generally seen as a sustainable and energy efficient process [3], as it converts wet biomass into four valuable streams: a crude like bio oil with higher heating values up to 35 40 MJ kg$^{-1}$, an aqueous phase containing light polar platform chemicals, a combustible solid residue called 'char' and a $CO_2$ rich gaseous phase also containing certain amounts of hydrogen and light hydrocarbons. Hydrothermal liquefaction has been applied to a wide range of resources from wood [5] to algae [6] and food processing residues [7]. The latter are of particular interest for valorisation through hydrothermal lique faction, as they contain a significant amount of valuable organic matter and are often wet resources, containing more than 50% water in weight.

Food processing residues are produced at every stage of the food supply chain, from harvesting to final consumption [8]. They currently represent more than 20% of the total mass of agricultural production in the world, but increasing urbanisation,

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industrialisation and population growth worldwide are responsible for increased generation of this type of wastes [9,10]. Dealing with the large amount of food processing residues generated each year is a critical issue, because when badly managed, they can contribute to environmental and sanitary problems. It is also necessary to consider the increasingly limited space available for disposal, which is favourable to developing alternative ways of valorisation. Food and agricultural wastes represent a widely available source for valorisation; either by recovering high value compounds from extraction or separation processes [11,12] or by producing bio based fuels. In particular, fruit processing residues are relevant for valorisation, because this industry is one of the main producers of food wastes: up to 50% mass fraction of fruits and vegetables are lost along the food supply chain [13].

Although many research papers report hydrothermal liquefac tion of various resources, a limited number of studies focuses on food processing residues, and even fewer on fruit and vegetable processing residues [14 22]. Wang et al. [18] obtained a maximum bio oil yield of 56.9% after HTL of *Litsea cubeba* seed at 563 K, 60 min. Akalın et al. [16] performed HTL of cornelian cherry stones and obtained a maximum total bio oil yield of 28%. Grape seeds were hydrothermally treated by Yedro et al. [19], resulting in 15.7% of light bio oil yield (diethyl ether soluble) and 16.2% heavy bio oil yield (acetone soluble) at 613 K. Previous studies used alkali salts as additives to improve the bio oil yields by carrying out hydrother mal liquefaction in basic medium. Karagöz et al. [23] reported an increased oil yield from 17.8% to 33.7% when using $K_2CO_3$ at increasing concentrations from 0.235 to 0.94 mol $L^{-1}$. This also led to a reduction of the char yield and higher recovery of water soluble organics. Sodium hydroxide, NaOH, was used by many au thors, e.g. Sugano et al. [24] to reduce char yield and increase the bio oil recovery. Yin et al. [25] also performed HTL of cattle manure in presence of NaOH to increase the conversion and the bio oil yield. Even though a large number of studies have been reported in the literature, the methods and resources are extremely variable. Therefore systematic studies on specific resources are required both for resource screening and comparison purposes.

We report in this paper a systematic study of HTL of black currant pomace (*Ribes nigrum* L.). This wet resource requires costly drying prior to combustion. It is also a more complex matrix than wood, making it more suitable for HTL due to the presence of lipids and proteins and a lower proportion of lignin. Under similar con ditions, beech wood produces a very viscous oil rich in phenolic compounds [26]. We chose this resource because it is representa tive of fibrous residues recovered after fruit pressing, mainly constituted by seeds, peels and pulp. The literature is quite poor regarding HTL of fruit pomace, and this study is to our knowledge the first dealing with hydrothermal conversion of blackcurrant pomace. The influence of several process parameters on HTL of blackcurrant pomace have been evaluated, with the objective of producing bio oil in high yields: reaction temperature (563 608 K), holding time (0 240 min) and mass fraction of dry biomass in the slurry (0.05 0.29). We also report observations on the impact of adding sodium hydroxide to vary the initial pH of the feed (3.1 12.8). Finally, analytical data on the molecular composi tion as well as some properties of the bio oil are reported, which are important information for further upgrading studies.

## 2. Materials and methods

First, the resource used for the experiments is presented. Sec ondly, experimental procedures for hydrothermal liquefaction are described together with recovery and analysis of products.

### 2.1. Materials

Blackcurrant (*Ribes nigrum* L.) pomace was the substrate used in the experiments. It was supplied by *Les Vergers Boiron*, a local producer of fruit purees and coulis operating in Valence, France. Blackcurrant pomace was obtained as a pressing residue of berries from mixed cultivars, namely *Noir de Bourgogne* and *Andega*. The biomass is the press cake recovered from juice production, mainly constituted by seeds, peels and pulp: it is a wet and fibre rich biomass, also containing certain amounts of proteins and lipids. Table 1 gives the composition and Higher Heating Value (HHV) of the biomass.

For hydrothermal liquefaction experiments, distilled water was used. Pellets of sodium hydroxide NaOH were purchased from Merck and used as received. Ethyl acetate used for bio oil recovery was purchased from Sigma Aldrich and used as received.

### 2.2. Hydrothermal liquefaction

In this section, we first present our experimental procedure for HTL experiments. We focus secondly on the recovery and analysis of products.

#### 2.2.1. HTL experiments

Hydrothermal liquefaction experiments were performed in a 0.6 L stainless steel (type 316) stirred batch reactor (Parr In struments). In a typical experiment, the reactor was filled with approximately 240 g of biomass slurry prepared from raw black currant pomace, distilled water and a certain amount of NaOH when needed. Before each experiment, pH was measured (Scien tific Instruments IQ170 pH meter). The initial pH of the raw slurry without additives was 3.1. The pH was measured at 5.5, 7.4, 10.8, and 12.8, when adjusting the quantity of NaOH to respectively 2, 3, 5, and 9% mass fraction of the dry biomass. The autoclave was leak tested, purged and pressurised to 1 MPa with nitrogen gas to guarantee sufficient pressure for gas analysis after the reaction. The total pressure inside the reactor was a function of the reaction temperature, the amount of water and of gas produced. The reactor was heated from room temperature to the reaction temperature in about 35 40 min. Reaction temperatures were between 563 K and 608 K. Once the reactor reached the reaction temperature, it was held during a specified holding time within ±1 K of the reaction temperature. Holding times were between 0 and 240 min. A stir ring speed of 10 Hz was set. After the holding time, the reactor was

**Table 1**
Characterisation of blackcurrant pomace
(HHV: Higher Heating Value; NDF: Neutral Detergent Fibres; ADF: Acid Detergent Fibres; ADL: Acid Detergent Lignin).

| Blackcurrant Pomace | | Standard |
|---|---|---|
| Moisture content (%) | 59.6 | EN 14774-1 |
| Fibre content (% of dry matter) | | NF V18-122 |
| NDF | 61.7 | |
| ADF | 52.8 | |
| ADL | 35.4 | |
| Proteins (% of dry matter) | 16.9 | Internal method |
| Lipids (% of dry matter) | 14.8 | Internal method |
| Ash content at 823 K (% of dry matter) | 4.3 | NF EN 14775 |
| Elemental composition | | NF EN 15104 |
| (% of dry matter) | | |
| C | 50.3 | |
| H | 6.8 | |
| O | 36.8 | (by difference) |
| N | 1.9 | |
| S | 0.2 | |
| HHV (MJ kg $^{1}$) | 18.51 | NF EN 14918 |

rapidly cooled down to room temperature in 20 min by an air quench. Experiments at the highest temperature of 608 K required the use of a different reactor capable of supporting higher pres sures, described in Huet et al. [27], having a similar operating procedure. The gas in the reactor was vented and analysed by a micro chromatograph (Varian Quad CP 4900) used on line. Per manent gases ($O_2$, $H_2$, CO and $CH_4$) were analysed 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 analysed on a Poraplot U column using helium as carrier gas. Solid and liquid products were then recovered following the recovery procedure described in paragraph 2.2.2.

*2.2.2. Product recovery procedure*

After gas analysis, the reactor was opened and the products were recovered following the procedure given in Fig. 1. 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 sticky, and removed from the reactor as best as possible. The reactor was then weighed and the weight difference with the empty reactor was counted as remaining raw organic residue (wet). As illustrated by Fig. 1, the material left in the reactor was taken into account in the calculation of the mass yields. Moisture content of the raw organic residue ($W_R$) was estimated using two methods: drying at room temperature under air circu lation 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 estima tion of the moisture content of the raw organic residue.

Depending on the proportion of bio oil and char, the aspect of the raw organic residue can vary from an oily solid to a free flowing viscous residue. When the amount of char is high, the bio oil cannot be directly valorised and solvent extraction is necessary to separate the liquid from the solid fraction. We chose ethyl acetate to recover the bio oil, because it allows good bio oil recovery, it is non toxic, and has a low miscibility with water. The raw organic residue was then extracted using a tenfold mass of ethyl acetate to separate the bio oil from the char on a Buchner filter. Bio oil was recovered after evaporation of ethyl acetate at room temperature under air circulation, until a stable weight was obtained. An esti mation of the amount of residual solvent in the bio oil was per formed by dissolving the bio oil recovered after ethyl acetate evaporation in 2 propanol, followed by GC MS analysis. The anal ysis showed that only traces of ethyl acetate were left after evap oration. It was therefore assumed that no significant amount of residual solvent was left in the bio oil. The char was also dried at room temperature under air circulation until a stable weight 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. Calcu lation of the yields is explained in detail in the supplementary material.

Mass 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. Detailed cal culations are explained in the supplementary information. Only the bio oil ($Y_{BO}$), char ($Y_C$) and gas ($Y_G$) yields are reported in this paper. In fact, the quantity of organic matter in the water phase is difficult to assess by simple drying as many compounds are volatile. In the literature, the aqueous phase yield is sometimes calculated by

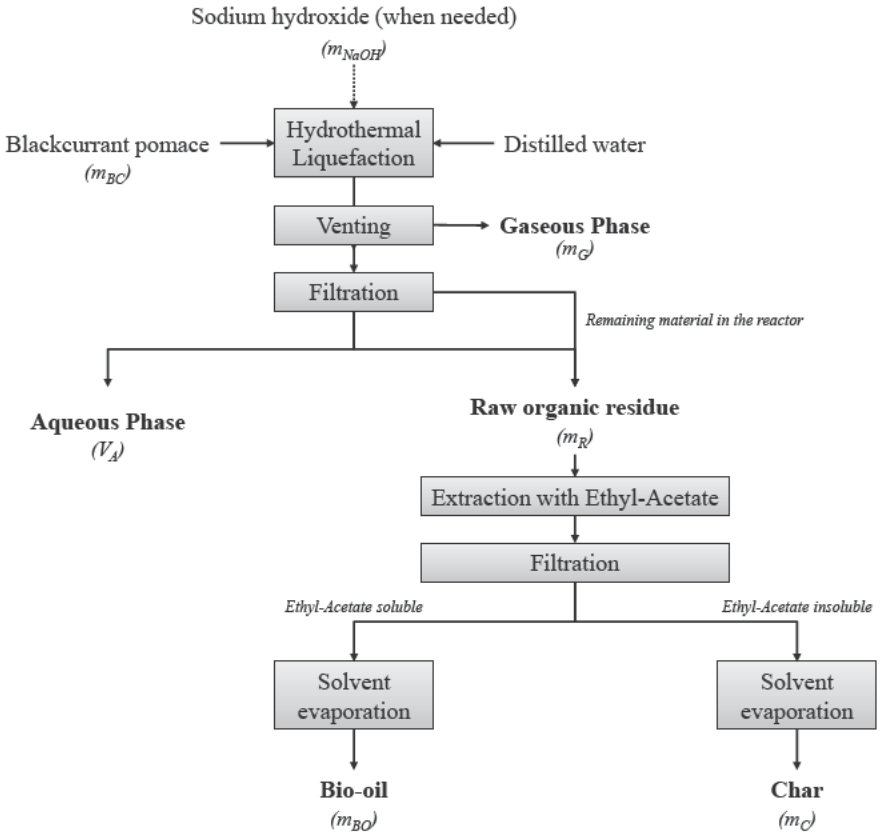


**Fig. 1.** Recovery procedure for products after hydrothermal liquefaction of blackcurrant pomace.

difference, closing the mass balance on the organic matter to 100% [28,29]. By doing so, the aqueous phase yield integrates the mass balance closure error. Due to hydration and dehydration reactions, the overall organic mass balance does not necessarily close to 100%. Therefore, we do not report the mass yield of organics in the aqueous phase together with the mass yield of the other phases, since it cannot be accurately determined. However, carbon recov ery in the aqueous phase can be determined and is reported. Car bon recoveries are defined as the ratios between the mass of carbon contained in the recovered phases and the initial mass of carbon in the biomass. Detailed calculations are explained in the supple mentary information.

In the results and discussion section, reported experimental values are the mean values of two replicates of each experiment. Error bars represent the standard deviations. Unless otherwise indicated, "%" refers to mass percentages.

*2.2.3. Analysis of products*

Total carbon of the solid and oil samples were quantified by a total carbon analyser (Shimadzu SSM 5000 A). Total carbon of the aqueous phase ($CT_A$) was quantified by a total organic carbon analyser (Shimadzu TOC L CSH/CSN). Elemental analysis of the bio oil was performed on a CHNS analyser Elementar Vario El Cube. Ash contents of the bio oil and char samples were determined by burning the samples in air at 823 K according to the EN14775 standard. Higher heating values of solid and oil samples were measured using a Parr 6200 bomb calorimeter.

For experiments involving NaOH, the sodium content of the aqueous phase was determined by ion chromatography using a Dionex ICS3000 equipped with a Dionex IonPac CS 16 column (5 × 250 mm) and a Dionex IonPac CG 16 guard column (5 × 50 mm). A 25 $mm^3$ injection volume of diluted sample was used. A 48 mmol $L^{-1}$ solution of Methanesulfonic acid (MSA) was used as eluent in isocratic conditions with a 1 $cm^3$ $min^{-1}$ flowrate. The column temperature was maintained at 303 K. The sodium content of the aqueous phase generated in the absence of NaOH was measured by the same procedure.

The molecular composition of the bio oil was analysed by a Gas Chromatograph coupled with a Mass Spectrometer, GC MS (Clarus 500/Clarus 600 S, Perkin Elmer, USA) equipped with a DB 1701 capillary column 60 m × 0.25 mm, 0.25 μm film thickness. A 1 $mm^3$ sample was injected into the instrument with a split ratio of 10:1. Helium was used as carrier gas. The GC oven temperature was programmed from 318 K (10 min) to 503 K at a rate of 6 K $min^{-1}$, and held at 503 K during 9.17 min. It was then raised to 523 K at a rate of 10 K $min^{-1}$, and held at 523 K during 20 min. The NIST mass spectral database was used to identify the peaks. For GC/MS anal ysis, a mass ratio of raw organic residue to ethyl acetate of 1:1 was used to minimise the effect of potential solvent pollution on the chromatograms.

Thermogravimetric analysis (TGA) of the bio oil was performed to evaluate the boiling point distribution of the bio oil and the fraction of bio oil analysed by GC MS, using a Setaram Setsys Evolution apparatus. A bio oil sample of 5 6 mg in a platinum crucible was heated from 333 K to 1173 K at a rate of 10 K $min^{-1}$ to let it evaporate under a 50 $cm^3$ $min^{-1}$ nitrogen flow at atmospheric pressure. The boiling point distribution was evaluated according to the classification proposed by Speight for petroleum products [30].

Total Acid Number (TAN), iodine value, density and dynamic viscosity of the bio oil were determined according to the methods described in Anouti et al. [31].

## 3. Results and discussion

We report in this section the effect of several process parameters, as well as the influence of adding sodium hydroxide NaOH to increase the initial pH of the feed. Some properties of the bio oil relative to molecular composition and fuel specifications are also reported in section 3.3.

### *3.1. Effect of operating conditions*

In this sub section we report the effect of several operating conditions on HTL of blackcurrant pomace: reaction temperature between 563 K and 608 K, holding time between 0 min and 240 min and mass fraction of dry biomass in the reaction slurry between 0.05 and 0.29.

#### *3.1.1. Effect of reaction temperature*

The effect of the reaction temperature on HTL of blackcurrant pomace was evaluated between 563 K and 608 K, with a fixed 60 min holding time and a fixed mass fraction of dry biomass in the slurry of 0.14. Fig. 2 shows the effect of the reaction temperature on the products and carbon distribution. Global mass balances and carbon balances vary from 103% to 111%, which is relatively good considering the experimental error for this set of experiments.

The results show that increasing the temperature from 563 K to 583 K tends to enhance the bio oil yield and carbon recovery in the bio oil, associated with lower char yields. Higher temperatures lead to a slight decrease of the bio oil yield and to a slight increase of gas formation. This is consistent with most published studies in the

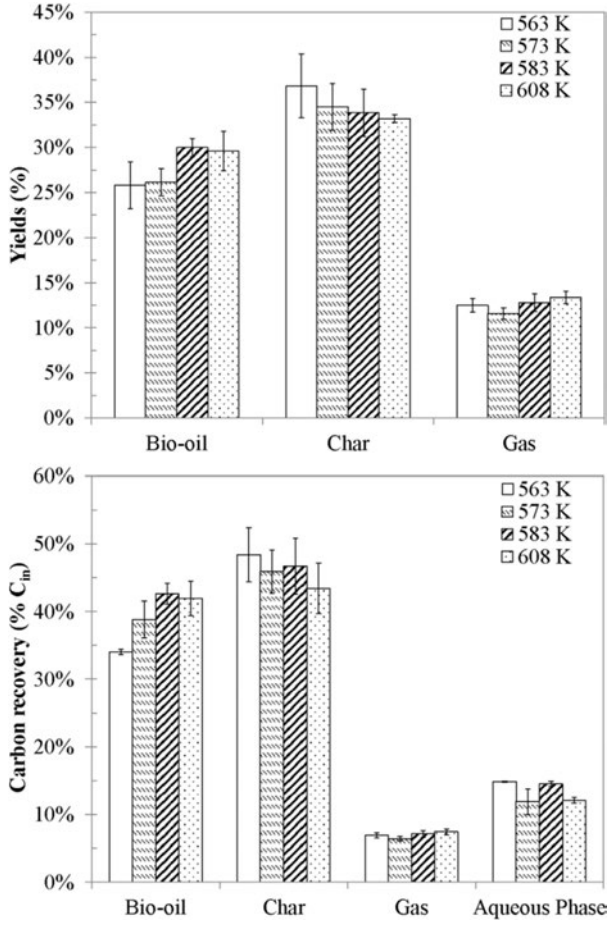


**Fig. 2.** Effect of reaction temperature on products distribution and carbon recovery (holding time 60 min).

literature [32]. In addition, these experimental observations can be linked to the pathway of bio oil formation.

In subcritical water, biomass is first hydrolysed and releases reactive monomers in the reaction medium. Depending on the resource composition, hydrolysis of biopolymers requires different levels of temperatures. Amorphous hemicelluloses are hydrolysed at lower temperatures than cellulose, while lignin conversion re quires higher temperatures than cellulose. This is for instance the observation made by Karagöz et al. [33], who reported that cellu lose was converted at 70.1% at 553 K, while lignin was only con verted at 40.0% and produced more solid residue. The characterisation of blackcurrant pomace showed that it is a particularly fibrous biomass, with high cellulose and lignin con tents (Table 1). This might explain that a better conversion is ob tained at temperatures above 310 °C.

Hydrolysis of biopolymers releases reactive monomers in the reaction medium, which degrade subsequently to give light polar molecules found in the aqueous phase, as well as bio oil and char through condensation and polymerisation reactions. Gaseous products originate either from degradation of water soluble prod ucts (decarboxylation, decarbonylation) or from bio oil decompo sition by steam reforming reactions [25,34]. Gas formation pathways are favoured with increasing temperatures, due to frag mentation reactions. In the temperature range that we considered, the gaseous phase is mainly formed by $CO_2$ (>95%), because of decarboxylation, decarbonylation and Water Gas Shift reactions. Fig. 2 also shows that a non negligible amount of char is produced. This is probably due to the highly fibrous nature of the resource, particularly the high lignin content, and to repolymerisation of reactive intermediates both in the aqueous phase and in the bio oil. For instance, self condensation of the bio oil fraction formed by lignin depolymerisation can occur, leading to polymeric structures found in the char. As well, operating in batch mode might lead to more char than what could be expected because of long heating and cooling periods, as we discuss in section 3.1.2.

From the data presented in Fig. 2, we see that a temperature near 583 K appears to be adapted to increase the bio oil recovery, while higher temperatures might lead to more gas. The results illustrate the synergetic effect between high dissociation of water and thermal activation of bond cleavage. The temperature has to be high enough to ensure that biopolymers such as cellulose and lignin are hydrolysed and participate in bio oil formation. For the following experiments, we chose a fixed temperature of 573 K, which allows a good bio oil recovery and a safer operation of our experimental device.

### 3.1.2. *Effect of holding time*

The effect of holding time on HTL of blackcurrant pomace was evaluated at a fixed temperature of 573 K and a fixed mass fraction of dry biomass in the slurry of 0.14. Holding times were varied from 0 min (immediate cooling after heating to the reaction tempera ture) to 240 min. A holding time of 0 min allows determining the impact of the heating time associated with using a batch reactor. Fig. 3 shows the effect of holding time on the products and carbon distribution. Global mass balances and carbon balances are gener ally good as they vary from 101% to 112% for this set of experiments.

The results show that the holding time has no significant in fluence on the yields. This observation suggests that the majority of reactions occurred in the early stages of the process, possibly dur ing the relatively long heating period of the batch autoclave. In fact, it is well agreed that hydrothermal liquefaction is a fast process: hydrolysis of biopolymers and degradation of monomers generally occur within seconds to a few minutes [35]. It is therefore likely that hydrothermal conversion of blackcurrant pomace also occurs rapidly. Fig. 4 shows a typical heating and cooling profile at a

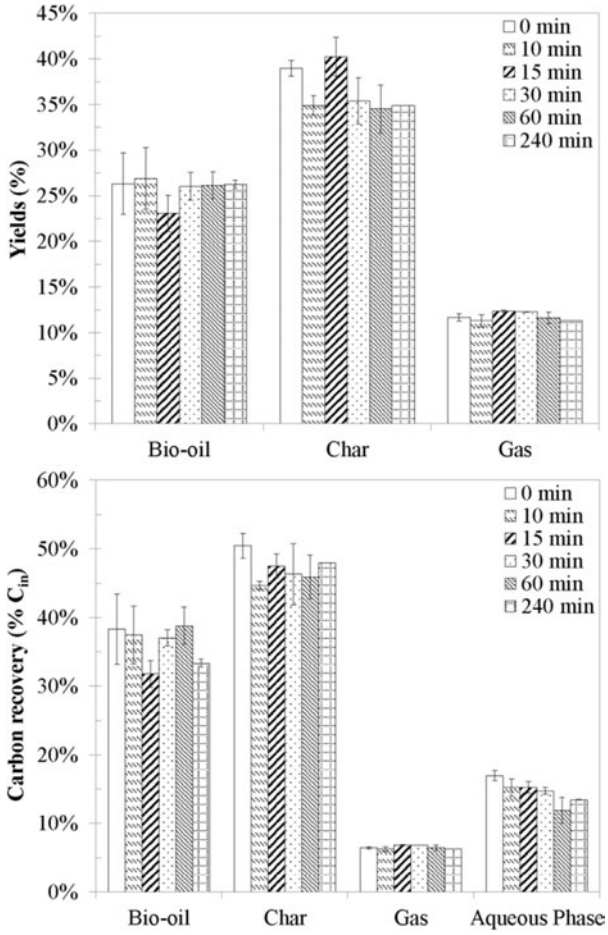


**Fig. 3.** Effect of holding time on products distribution and carbon recovery (reaction temperature 573 K).

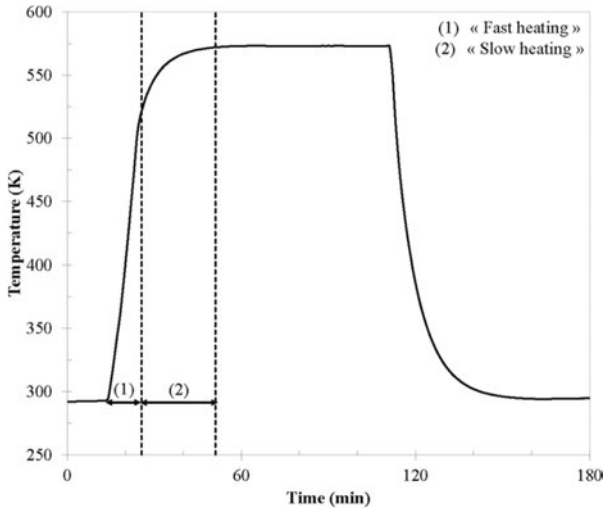


**Fig. 4.** Temperature profile recorded during HTL of blackcurrant pomace (reaction temperature 573 K, holding time 60 min).

reaction temperature of 573 K. Two distinct periods can be iden tified: a “fast heating” period in which the reactor temperature increases from room temperature to 523 K in about 10 15 min,

followed by a “slow heating” period in which the temperature steadily increases towards the reaction temperature in about 25 30 min. Therefore, blackcurrant pomace spends the major part of the heating time at relatively high temperature in subcritical conditions before reaching the reaction temperature, which might explain why the yields seem little affected by the holding time. In addition, the long heating period of the batch reactor might be detrimental to the bio oil yield, as it would allow more secondary polymerisation reactions to occur and produce more char. In batch mode, the char amount is therefore probably higher than what could be obtained using a continuous unit with shorter heating periods. It has been shown before that longer heating times lead to higher char yields [29].

In this set of experiments, the yields seem little affected by the holding time, due to the rapidity of the reactions in the conditions of the study. This directs further studies towards the use of continuous conversion units with shorter heating times and reduced residence times. Achieving high bio oil yields in short residence times is particularly important when considering development of a continuous process, because it would decrease the size of the conversion units and therefore capital costs.

*3.1.3. Effect of biomass concentration*

The solids loading at the inlet of the conversion unit is a crucial process variable for hydrothermal liquefaction, since it directly impacts the energy consumption of the process. To date, mass ra tios between dry biomass and water around 0.15 are achievable for continuous feeding of HTL units [3], although pre treatment methods could increase this ratio to 0.2 [36]. Solid loadings around 15 20% mass fraction are generally needed to ensure the economic benefits of the process, while lower concentrations might reduce its economic advantages because of high capital costs and high energy consumption [2]. The amount of water in the slurry is important as it is as much a reactant (e.g. hydrolysis of bio polymers) as a solvent in HTL. Therefore we decided to evaluate the influence of the biomass loading on HTL of blackcurrant pomace, at a fixed temperature of 573 K and a fixed holding time of 60 min. Three mass fractions of dry biomass in the reaction slurry were used: 0.05, 0.14 and 0.29. Fig. 5 shows the results of the experi ments on the products and carbon distribution. Global mass bal ances and carbon balances are relatively good for this set of experiments, as they vary from 91% to 109%.

Results of the experiments show that the bio oil yield decreases from 29% to 24% of the initial dry mass of biomass with increasing biomass loadings from 0.05 to 0.29, while the char amount in creases from 35% to 37% of the initial mass of dry matter. These results are consistent with results from the literature, which generally report a decrease of the bio oil yield with increasing biomass concentrations [37,38]. At high biomass concentrations, reactive intermediates in the aqueous phase and the bio oil are present in higher amounts in the reaction medium. The probability of repolymerisation reactions between reactive fragments leading to char formation might be consequently increased compared to more diluted cases.

Secondly, the availability of liquid water might be playing an important role. In batch mode, the pressure is self generated and can be described as a function of the reaction temperature, the amount of water and of gas produced. The amount of water introduced in the reactor determines whether it is in the liquid state, the gaseous state or at liquid vapour equilibrium when the reaction temperature is reached. Liquid vapour equilibrium calcu lations reported in the supplementary information show that the fraction of evaporated water increases with increasing dry biomass concentration. This means that less water is available in the liquid phase at higher biomass concentrations. At low biomass

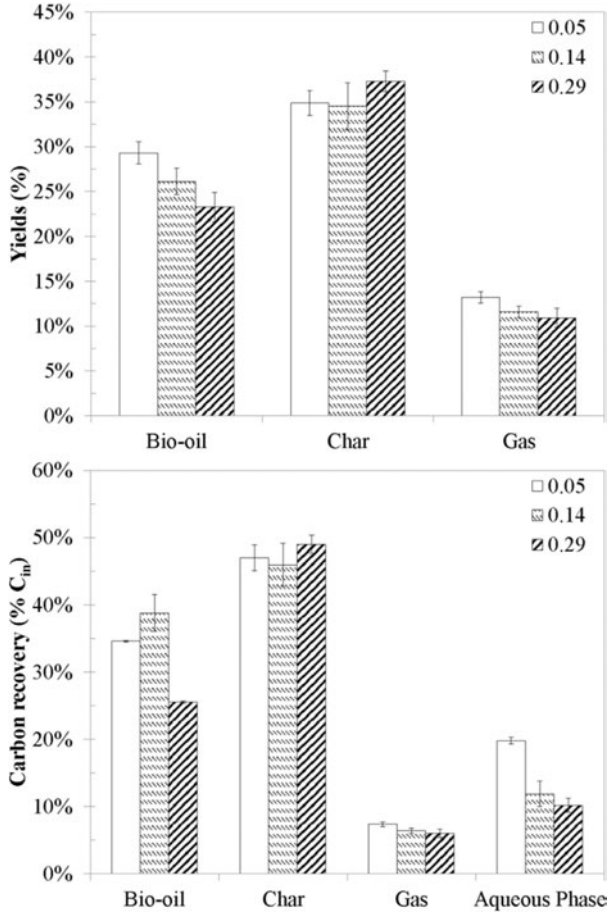


**Fig. 5.** Effect of the mass fraction of dry biomass in the slurry on products distribution and carbon recovery (reaction temperature 573 K; holding time 60 min).

concentrations, more water molecules per unit molecules of biomass are therefore available; increasing both the extraction and solvation powers, as well as it favours degradation of the biomass in liquid phase. This could be one explanation of higher bio oil for mation at low biomass concentrations.

Yet, the majority of water remains in the liquid state in the conditions of the experiments. An additional factor that could explain our experimental results might be the reduced contact between the solid biomass and water at high biomass concentra tions. When the mass fraction of dry biomass in the slurry increases from 0.05 to 0.29, we estimate that the volume ratio between dry biomass and water increases from 0.1 to 0.4. It is therefore likely that a certain fraction of the biomass is poorly in contact with liquid water. Thus, at (very) high biomass to water ratios, different reac tion mechanisms might be driven. In these conditions, interactions between biomass and water molecules in liquid phase are less important, and the reactivity between blackcurrant pomace and the vapour phase might be more important. Especially, organic molecules can be formed in the gaseous phase. Even though it is mainly composed by $CO_2$ and low amounts of CO, $H_2$ and $C_1$ $C_3$ hydrocarbons, Madsen et al. [39] recently reported that organic compounds such as thiols, olefins and aromatic compounds can account for up to 4% of the volume of the gas phase produced during HTL of dried distillers grains with solubles. In our experi ments, we observed a lower mass balance closure for the experi ments at the highest biomass concentration, which can be partially

explained by this behaviour. However, we could not analyse all possible organic species in the gaseous phase, due to lack of adapted equipment. Measured species are limited to $N_2$, $H_2$, CO, $CO_2$, and $C_1$ $C_3$ hydrocarbons.

Therefore, combined effects might explain the decrease of bio oil yield at high biomass concentrations: increased repolymerisation reactions leading to char formation because of higher concentrations of reactive intermediates, lower availability of liquid water in the reactor, and reduced contact between biomass and liquid water in the reactor, driving different reaction mechanisms.

We observed in this section that low biomass concentrations lead to higher oil yields. In addition, from a process development perspective, continuous feeding of the biomass slurry requires sufficient dilution of biomass so that it can be pumped properly into the reactor without causing any plugging issues. Using diluted feed slurries leads however to higher energy consumption: it would cost around 34% more energy to heat water from 293 K to 573 K in the more diluted case considered (0.05), compared to the more concentrated case (0.29). It seems therefore preferable to use biomass loadings as high as possible, to reduce the energy input needed to heat water to the desired reaction temperature. Using concentrated feed slurries would also reduce the overall dimensions of the equipment and the wastewater treatment requirements, leading to reduction of the capital costs. A compromise has therefore to be found between high bio oil recovery (favoured in diluted conditions) and process development considerations. From our test points, we consider the intermediate concentration (0.14) to be a good compromise between process development considerations and bio oil recovery. In addition, this intermediate concentration is close to what is technologically achievable today [3]. A thorough study of processing costs might however be necessary to identify the optimal concentration from an economic point of view.

### 3.2. Effect of addition of sodium hydroxide

As discussed in the introduction, alkali catalysts are often used in the HTL process. In this section we evaluate the effect of adding sodium hydroxide (NaOH) to the reaction medium. Then, we focus briefly on the sodium distribution between phases.

#### 3.2.1. Evolution of yields and carbon distributions

The effect of using NaOH to vary the initial pH of the feed was evaluated at a fixed temperature of 573 K and a fixed holding time of 60 min. Initial pH ranged from 3.1 (natural acidity of the mixture, without NaOH addition) to 12.8 (corresponding to a NaOH to dry matter mass ratio of 9%). Fig. 6 shows the effect of adding sodium hydroxide on the products and carbon distribution. Global mass balances and carbon balance closures vary from 99% to 111%, which is relatively good considering the experimental error for this set of experiments.

The results show that using NaOH leads to a reduction of the char yield, corresponding to a higher solubilisation of the organic matter in the aqueous phase. The reduction of the char yield is especially important at higher NaOH to dry matter ratios (e.g. 9%). Carbon recovery in the aqueous phase increases from 12% of the initial mass of carbon at $pH_{in} = 3.1$ (case without NaOH), to 25% of the initial mass of carbon at $pH_{in} = 12.8$ (corresponding to a NaOH to dry matter mass ratio of 9%). This observation means that more water soluble molecules are formed when the initial pH of the feed increases, and is consistent with results reported elsewhere in the literature [40 42]. As well, using NaOH as additive increases the bio oil yield from 26% of the initial dry mass of blackcurrant pomace at $pH_{in} = 3.1$ to 31% of the initial dry mass of biomass at $pH_{in} = 12.8$. The relative decrease observed at NaOH mass loadings

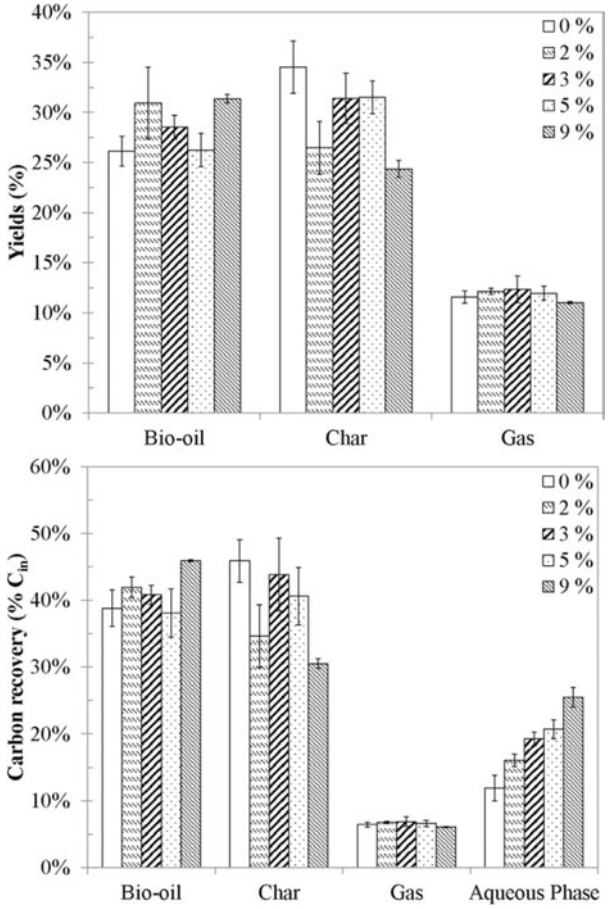


**Fig. 6.** Effect of NaOH to dry matter ratio on products distribution and carbon recovery (reaction temperature 573 K, holding time 60 min).

of 3% and 5% could be partially explained by the aspect of the raw organic residue recovered in these experiments: it was a tarry and extremely sticky material. Solvent extraction was therefore quite hard to perform on this raw organic residue. Globally, using NaOH impacts the distribution between bio oil and char, and the proportion of organic molecules in aqueous phase.

The decrease of the amount of char in favour of the organic content of the aqueous phase is mainly due to two beneficial effects of NaOH for HTL. Firstly, hydroxide ions can neutralise connecting molecules acting as polymerisation intermediates in the formation of char. For instance, hydroxide ions neutralise the carboxylic acids formed during hydrothermal conversion of biomass. It has been observed that polymerisation reactions can occur between carboxylic groups in the aqueous phase and hydroxyl groups at the surface of the residue, forming ester bonds and yielding more char [24]. By reacting with hydroxide ions, carboxylic acids remain in the aqueous phase as carboxylate ions, as shown in Equation (1). This is illustrated by the decrease of the pH of the aqueous phase after the reaction, which was measured at 5.3 when no NaOH was added (Fig. 7). Therefore, using NaOH avoids polymerisation because carboxylic acids are neutralised and cannot participate in condensation reactions [24,43].

$$RCO_2H + NaOH \rightarrow RCO_2^- + Na^+ + H_2O \quad (1)$$

The use of NaOH influences the reaction pathways occurring in subcritical water, depending on the biomass composition. As

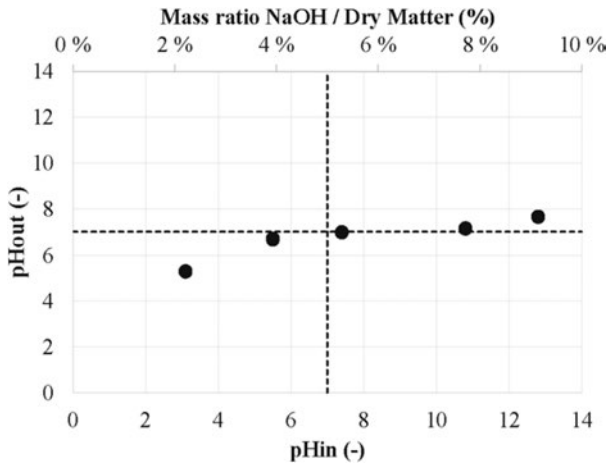


**Fig. 7.** Comparison of initial ($pH_{in}$) and final ($pH_{out}$) pH of aqueous phases at various NaOH loadings.

shown in Table 1, blackcurrant pomace is mainly composed of fibres, with a total fibre (*NDF*) content representing 61.7% of the total mass of dry matter. Especially, the *ADF* and *ADL* contents are high, meaning that the fibres are both rich in cellulose and lignin. Hydrothermal liquefaction of cellulosic polymers produces sugar degradation products: furans, aldehydes, ketones and carboxylic acids [44,45]. Particularly, acidic conditions drive the reaction mechanism towards dehydration of sugars, forming mainly furan derivatives such as 5 (hydroxymethyl) furfural and furfural which can polymerise and increase char formation [40,46]. With increasing pH, reaction mechanisms shift to fragmentations such as retro aldol condensations, leading to the formation of short chain polar compounds, mainly found in the aqueous phase: aldehydes, ketones, and ultimately carboxylic acids [40]. This could partially explain the increased solubilisation of organic matter in the aqueous phase.

While lignin is poorly reactive in acidic conditions, base catalysed hydrolysis with sodium hydroxide is an efficient way to achieve depolymerisation and yield phenol monomers and dimers in the aqueous phase [41]. Base catalysed depolymerisation of the high amount of lignin contained in blackcurrant pomace through hydrolysis could help understanding the better degradability of biomass and the increased solubilisation of organic matter in the aqueous phase. The seeds are lignin rich, and using NaOH allows good degradation of these particular structures, as shown in Fig. 8. In presence of NaOH, the seeds develop a porous surface: the formation of pores could enhance the liberation of reserve molecules such as proteins and fatty acids contained in the endosperm of the seed, which are important contributors to the bio oil yield.

Inhibition of char formation can also be explained by the fact that using NaOH provides a more reductive environment than in acidic conditions. In fact, alkali salts (here NaOH) have been identified before as promoters of the Water Gas shift reaction [47]. Hydroxide ions $OH^-$ react with $CO_2$, which is solubilised in the form of carbonates (Equation (3)). We observed in our experiments an increase of the concentration of inorganic carbon in the aqueous phase, corresponding to higher $CO_2$ solubilisation. The reaction between $CO_2$ and $OH^-$ moves forward the equilibrium towards $H_2$ formation (Equations (2) (4)). $H_2$ can act as a reducing agent, limiting condensation reactions between polymerisation intermediates, therefore reducing char formation. We observed in our experiments an increase of the amount of $H_2$ produced in the gas phase, which shows the positive effect of NaOH on the Water Gas Shift reaction.

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2)$$

$$2Na^+ + 2OH^- + CO_2 \rightarrow 2Na^+ + CO_3^{2-} + H_2O \quad (3)$$

$$CO + 2Na^+ + 2OH^- \rightarrow H_2 + 2Na^+ + CO_3^{2-} \quad (4)$$

### 3.2.2. Sodium recovery after the conversion

Adding sodium hydroxide to the reaction medium has an important positive effect on the degradability and bio oil production by hydrothermal liquefaction of blackcurrant pomace. As discussed in the previous paragraph, hydroxide ions $OH^-$ take part in reactions that avoid char formation. According to equations (2) and (4), the majority of sodium ions $Na^+$ should remain in the aqueous phase. However, adding sodium hydroxide to the reaction medium could also lead to favouring saponification reactions with fatty acids contained in the biomass and to a decrease of the bio oil quality. We therefore decided to evaluate the sodium distribution after HTL of blackcurrant pomace, to determine whether the bio oil is affected by saponification reactions.

Table 2 shows the sodium recovery in the aqueous phase (determined by ion chromatography), and the ash contents of the bio oil and char samples. Between 58% at $pH_{in} = 5.5$ and 72% at $pH_{in} = 12.8$ of the initial mass of sodium in the reactor is recovered in the aqueous phase. Ash contents of the bio oil are low, compared to ash contents of the char. This indicates that the remaining fraction of sodium is mainly distributed in the char. Yet, ash contents of both char and bio oil increase with increasing NaOH concentrations, indicating a certain transfer. A small saponification effect is observed in the bio oil fraction when adding NaOH to the reaction medium. This transfer could be detrimental to the oil quality at higher NaOH concentrations. Direct combustion of bio oils with non negligible ash contents may lead to problems such as corrosion and deposit in the equipment.

## 3.3. Characterisation of the bio oil

In this section, we focus on characterisation of the bio oil produced by HTL of blackcurrant pomace. We first report the results of thermogravimetric analysis (TGA), which was proven before as an effective and useful method to analyse the boiling point distribution of bio oils produced by hydrothermal liquefaction [48,49]. TGA can be considered as a small scale distillation that can be used to estimate the boiling fractions of bio oils. Then, we report the results of GC MS analysis of the volatile fraction of the bio oil, as well as some physical and chemical properties. Characterisation of the bio oil gives useful information for further upgrading.

### 3.3.1. Thermogravimetric analysis of the bio oil

Thermogravimetric analysis of the bio oil obtained at 573 K and 60 min holding time in the absence of NaOH was performed to evaluate its volatility. We reported in a previous paper that using NaOH has a limited influence on the volatility of HTL bio oils [31]. The results of the TG analysis are shown in Fig. 9. The boiling point distribution was described according to the terminology and classification proposed by Speight for petroleum products [30]. For our samples, the gas fraction (boiling points < 288 K) is not applicable.

The evaporation behaviour of the bio oil shows that it is mainly constituted of a medium naphtha fraction, and of high boiling constituents. High boiling point fractions (b.p. > 505 K) represent 53% mass fraction of the total bio oil. On the other hand, the bio oil

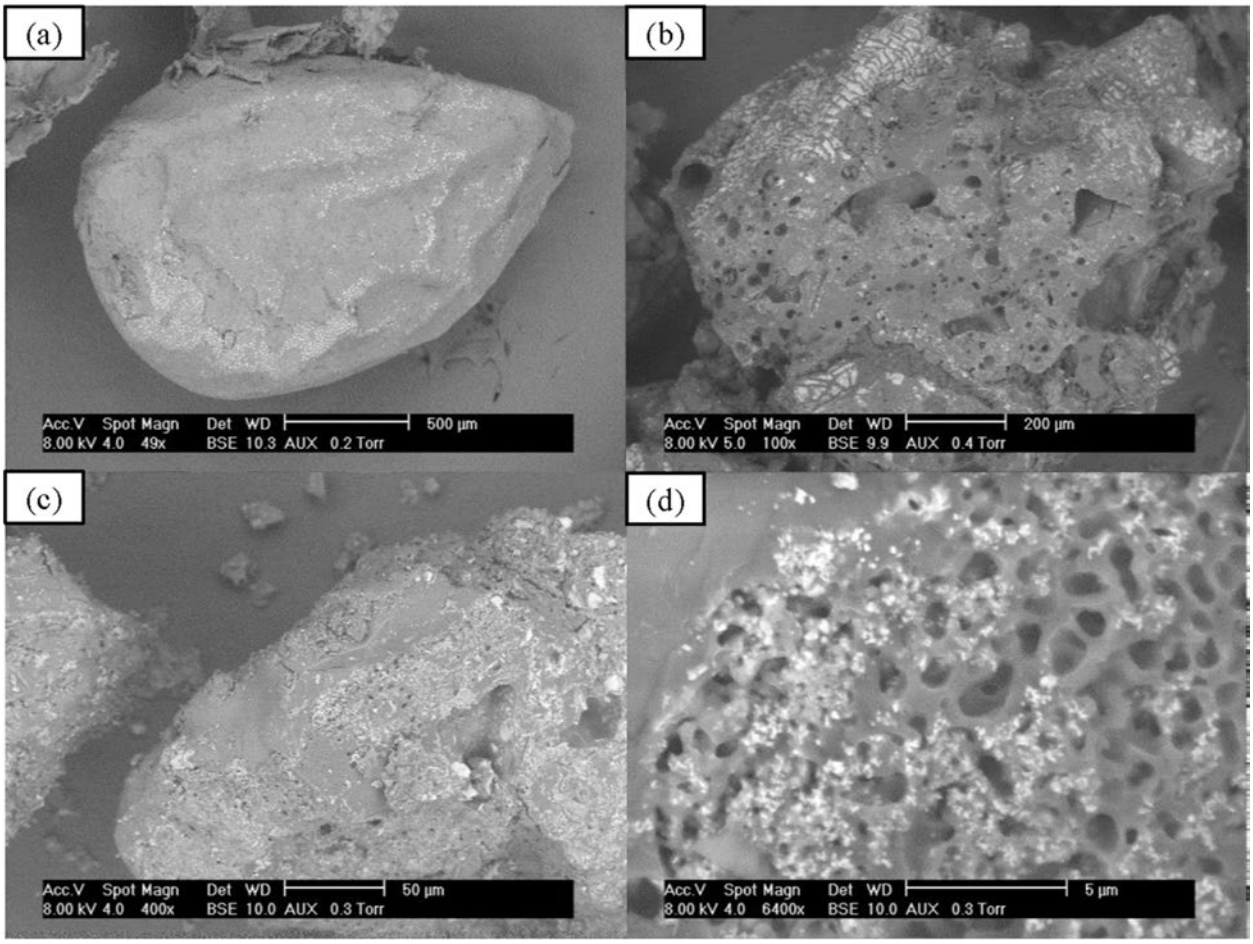


**Fig. 8.** SEM images of (a) raw blackcurrant seed, (b) char after HTL at $pH_{in}$ 5.5 (NaOH to dry matter mass ratio 2%), (c,d) char after HTL at $pH_{in}$ 12.8 (NaOH to dry matter mass ratio 9%).

**Table 2**
Sodium recovery in aqueous phase ($NaR_A$) and ash contents of bio-oil and char samples for HTL of blackcurrant pomace at various initial pH of the feed (reaction temperature 573 K; holding time 60 min).

| $pH_{in}$ (−) | NaOH to dry matter ratio (%) | $NaR_A$ (%) | Ash content in bio-oil (%) | Ash content in char (%) |
|---|---|---|---|---|
| 3.1 | 0% | 5 ± 1 | <0.1 | 7.0 ± 0.3 |
| 5.5 | 2% | 58 ± 12 | <0.1 | 9.3 ± 0.8 |
| 7.4 | 3% | 73 ± 12 | 0.2 | 8.8 ± 0.5 |
| 10.8 | 5% | 76 ± 16 | 1.0 | 9.7 |
| 12.8 | 9% | 72 ± 1 | 5.3 | 13.1 |

has a small fraction of low boiling point constituents. This observation might be explained by the bio oil recovery procedure: low boiling point molecules are evaporated along with ethyl acetate, which is observed by GC MS analysis of the bio oil before and after evaporation [31].

While TG analysis is a useful tool to get insights on the distillation potential of the bio oil, it should be kept in mind that not only the boiling points but also the chemical nature of the molecules is important for further upgrading steps. In the following section, we present the molecular composition of the bio oil obtained by GC MS analysis.

### 3.3.2. Molecular composition by GC MS analysis

The molecular composition of the volatile fraction of the bio oil obtained after HTL of blackcurrant pomace was analysed using GC MS. A typical chromatogram of the bio oil (before evaporation of ethyl acetate) is shown in Fig. 10.

As illustrated by the chromatogram, the bio oil is a very complex mixture formed by more than 300 different compounds. The complexity of the mixtures makes the exhaustive identification of the bio oil composition difficult, due to many co eluting peaks and many similar structures leading to similar identifications by the mass spectral database for different retention times. Even though GC MS analysis is limited by the complex composition of the mixture, it is possible to identify the main molecules. We provide in the supplementary information a list of the 50 first compounds in terms of relative peak areas, which can be used as an indication about the chemical composition of the bio oil. These compounds

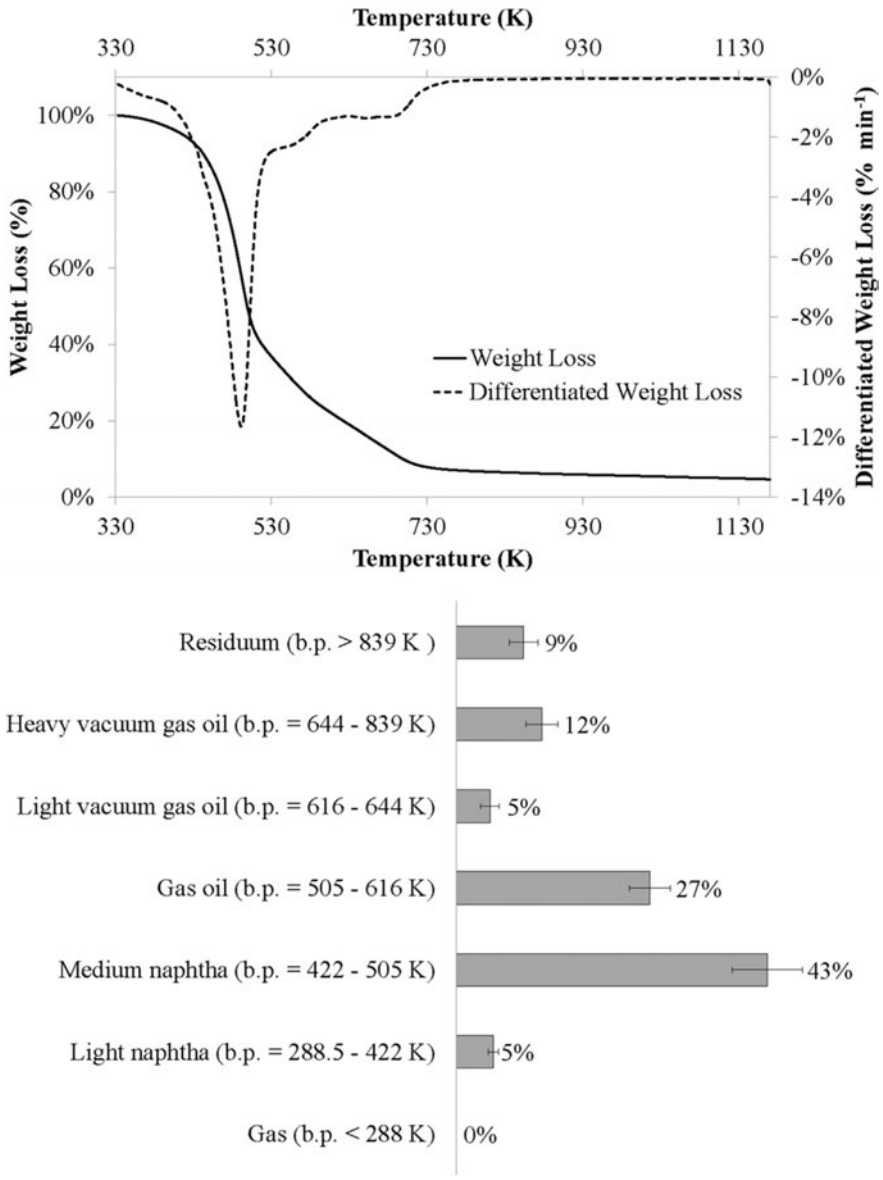


**Fig. 9.** TG analysis (a) and boiling-point distribution (b) of the bio-oil produced by HTL of blackcurrant pomace (reaction temperature 573 K, holding time 60 min).

are lumped as several chemical families in Fig. 11, and represent 76.2% of the total area in the chromatogram.

The volatile fraction of the bio oil is mainly formed by heavy compounds such as fatty acids and their derivatives which repre sent more than 30% of the total peak area, eluting at retention times higher than 45 min. These compounds are fatty acid alkyl esters, long chain amides and fatty acids originating from the lipid content of blackcurrant pomace, mainly found in the seeds. Lipids in the form of triglycerides are hydrolysed in subcritical water and react subsequently with alcohols to form esters and with amino acids originating from the protein content of blackcurrant pomace to form amides.

Other detected molecules are phenol derivatives at retention times between 26 and 35 min: they are mainly produced by hy drolysis of lignin and subsequent degradation of its monomers, and are relatively stable in the conditions of the study. A large number of nitrogenous compounds were also detected at retention times between 30 and 61 min. Structures vary from long chain amides to simple aromatic rings such as pyridine, pyrazine, pyridinol or indole derivatives. These molecules obviously originate from the protein content of blackcurrant pomace: amino acids degrade in subcritical water to form carboxylic acids and amines which can participate to interaction reactions to form bigger nitrogenous structures, for instance via the Maillard reactions with sugars [50,51], or condensation with fatty acids to form amides [52,53]. Finally, a certain number of light structures were also detected at small retention times: they are mainly linear ketones, aldehydes, cyclopentenones, pyridines and pyrazines. Such molecules mainly derive from hydrothermal degradation of cellulosic polymers, and to a certain extent from hydrothermal conversion of proteins. In subcritical water, cellulose and hemicelluloses release mono saccharides by hydrolysis, which then degrade to give mainly light polar molecules, as well as polymeric char [54].

It is important to notice that GC MS analysis of the bio oil only

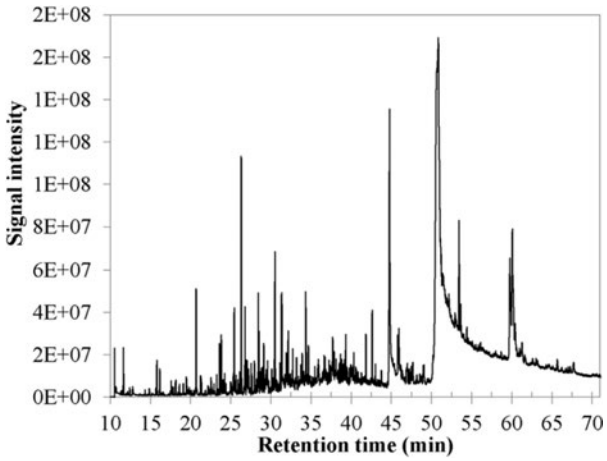


**Fig. 10.** Chromatogram of the bio-oil produced by HTL of blackcurrant pomace (reaction temperature 573 K, holding time 60 min).

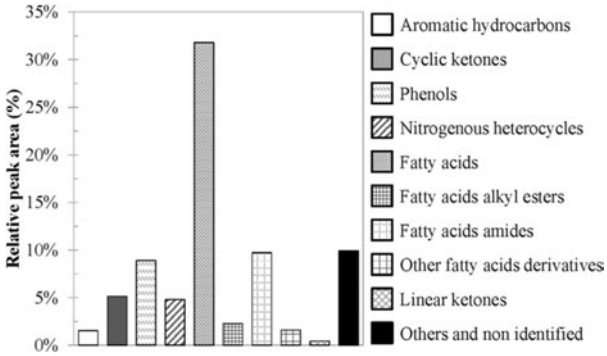


**Fig. 11.** Main chemical families found by GC-MS analysis of the bio-oil.

provides partial information, because it often cannot identify molecules with high boiling points. The TG analysis of the bio oil showed that it contains many high boiling point molecules. From the TG analysis, it is evaluated that only 57% mass fraction of the total bio oil is analysed by GC MS (boiling points < 523 K). The remaining fraction corresponds to high boiling point molecules, and should be analysed by other techniques adapted to non volatile compounds.

### 3.3.3. *Physico chemical properties of the bio oil*

Table 3 shows the physico chemical properties of the bio oil produced at 573 K, 60 min holding time in the absence of NaOH.

From the results, it can be concluded that the produced bio oil is interesting for energy applications. It has low moisture content along with a higher heating value of 35.9 MJ $kg^{-1}$. From the corresponding mass yield, the energy recovery in the bio oil is estimated at 49% of the initial energy contained in the feedstock. Elemental analysis of the bio oil shows that it contains certain amounts of nitrogen and oxygen, which would direct the upgrading process towards hydrodeoxygenation and hydrodenitrogenation steps. The high Total Acid Number (TAN) can be linked to the large proportion of fatty acids detected in the GC MS analysis, and to the presence of a non negligible amount of acidic groups such as hydroxyl groups in phenols. The relatively high iodine value measured in the bio oil shows that it contains insaturations that could be detrimental to the stability and storage potential of the bio oil. The high viscosity can be linked with the results of TG analysis, which showed that the bio oil contained a majority of high boiling point constituents, therefore high molecular weight structures. The high acidity and viscosity values underline the need for upgrading before any use as fuel in a boiler or an engine. Comparison with standard commercial fuels is an interesting way to evaluate the need for upgrading, as we recently reported [31].

**Table 3**
Properties of the bio-oil obtained by HTL of blackcurrant pomace (reaction temperature 573 K, holding time 60 min).

| | Bio-oil |
|---|---|
| Moisture content (%) | <5 |
| Elemental composition (% of dry matter) | |
| C | 73.3 |
| H | 9.6 |
| N | 3.4 |
| S | 0.1 |
| O (by difference) | 13.6 |
| HHV (MJ $kg^{1}$) | 35.9 |
| Ash content at 823 K (% of dry matter) | <0.1 |
| Total Acid Number (mg of KOH per gram of bio-oil) | 134 |
| Iodine value (g of $I_2$ per 100 g of bio-oil) | 150 |
| Dynamic viscosity at 298 K (Pa s) | 1.7 |
| Density at 288 K (kg $m^{3}$) | 960 990 |

## 4. Conclusion

This study demonstrates the feasibility of applying hydrothermal liquefaction (HTL) to process wet lignocellulosic residues generated by the agricultural and food processing industries, through the example of blackcurrant pressing residues. Bio oils mass yields of 24 31% were obtained, higher than the initial lipid content of the biomass. This means that HTL is an efficient process to produce oils in high yields from wet blackcurrant pomace.

The relatively high amount of char and the low influence of holding times on the results suggests that a reactor with shorter heating and reaction times might be adapted, i.e. with continuous operation. It would both reduce the volume of installations and char formation, in favour of better bio oil yields by avoiding repolymerisation. Low biomass concentrations enhance bio oil production, which underlines the need for a compromise between bio oil recovery and process development considerations.

Distribution of the products is significantly affected by the use of sodium hydroxide as additive. The bio oil yield is enhanced and the char amount is reduced, both due to a better degradability of blackcurrant pomace in alkaline conditions through hydrolysis of fibres, and to the inhibition of char formation by stabilisation of reactive intermediates.

The analysis of the bio oil by several complementary techniques gives a detailed knowledge of this product. HTL of blackcurrant pomace produces heavy oils with interesting properties for fuel applications. The bio oil has simultaneously high energy content (HHV = 35.9 MJ $kg^{-1}$), low ash content, and falls in the right boiling point range for upgrading to fungible fuels. Yet, some of its properties (e.g. acidity, viscosity) indicates that the bio oil must be upgraded before any use for fuel applications.

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products.

## Nomenclature

| | |
|---|---|
| ADF | Acid Detergent Fibres |
| ADL | Acid Detergent Lignin |
| $CT_A$ | Concentration of total carbon in aqueous phase (g $L^{-1}$) |
| GC MS | Gas Chromatography Mass Spectrometry |
| HHV | Higher Heating Value (MJ $kg^{-1}$) |
| HTL | Hydrothermal Liquefaction |
| $m_{BC}$ | Mass of dry blackcurrant pomace (g) |
| $m_{BO}$ | Mass of bio oil (g) |
| $m_C$ | Mass of char (g) |
| $m_G$ | Mass of gas (g) |
| $m_{NaOH}$ | Mass of sodium hydroxide (g) |
| $m_R$ | Mass of raw organic residue (g) |
| $NaR_A$ | Sodium recovery in the aqueous phase (% of initial mass of sodium in the reactor) |
| NDF | Neutral Detergent Fibres |
| SEM | Scanning Electron Microscope |
| SSO | Proportion of solvent soluble organics in the raw organic residue (% mass) |
| TAN | Total Acid Number (mg of KOH per gram of bio oil) |
| TGA | Thermogravimetric Analysis |
| $V_A$ | Volume of aqueous phase (L) |
| $W_R$ | Water content of raw organic residue (% mass) |
| $Y_{BO}$ | Bio oil yield (% of dry mass of blackcurrant pomace) |
| $Y_C$ | Char yield (% of dry mass of blackcurrant pomace) |
| $Y_G$ | Gas yield (% of dry mass of blackcurrant pomace) |

## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.biombioe.2016.10.012.

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