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Research paper

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

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ABSTRACT

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 technology 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 temperature and pressure [4]. In particular under subcritical conditions, 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 liquefaction, 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 liquefaction 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 hydrothermal 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 authors, 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 blackcurrant 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 conditions, beech wood produces a very viscous oil rich in phenolic compounds [26]. We chose this resource because it is representative 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 composition 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. Secondly, 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 Instruments). In a typical experiment, the reactor was filled with approximately 240 g of biomass slurry prepared from raw blackcurrant pomace, distilled water and a certain amount of NaOH when needed. Before each experiment, pH was measured (Scientific 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 stirring 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 (% of dry matter)		NF EN 15104
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