



## Hydrothermal conversion of grape pomace: Detailed characterization of obtained hydrochar and liquid phase



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### ABSTRACT

In this study, carbonization products of grape pomace (hydrochar and process water) have been thoroughly characterized in order to assess its fuel properties, physico-chemical composition and to optimize its production. The obtained detailed insight into transformations of the biomass during hydrothermal conversion between 180–220 °C revealed that the hydrochar obtained at 220 °C exhibits a considerable energetic potential, increased porosity and re-adsorption ability. Hydrothermally induced structural changes in the obtained hydrochars were unveiled by thermal and morphology analysis, FTIR and NIR spectroscopy. Temperature increment caused a decrease in antioxidative capacity, anthocyanin and organic acid content in process water and simultaneous increase in total phenolic and individual organic components content. The overall effect of the reaction temperature on products characteristics was assessed by multivariate data analysis. Obtained results substantiated the suitability of hydrothermal conversion of grape pomace into highly valuable fuels and versatile products.

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### 1. Introduction

Hydrothermal carbonization (HTC) is a promising technology for conversion of wet lignocellulosic biomass into highly functional materials [1]. HTC process is carried out in a suspension of biomass and water at saturated pressure, whereby subcritical water reacts with fibrous components of lignocellulosic biomass, leading to its degradation and reconstruction [2].

HTC treatment of biomass (associated with hydrolysis, dehydration, decarboxylation, condensation, polymerization and aromatization) [3], generates two main products: (i) insoluble carbon-rich hydrochar (HC) and (ii) process water (PW), whereas only small amounts of gases are formed [4]. Hydrochar is a homogeneous, hydrophobic, energy-dense solid, which contains micro- to nano-sized carbon spheres, oxygen-containing functional groups and has a porous structure [2]. Due to its physico-chemical characteristics, HC has great potential for numerous practical applications. So far this material has been tested for use as solid fuel [1,4], soil supplement [5], as feedstock for pellets [6] etc. On the other side, the PW

from HTC process is comprised mostly of source-related organic acids and other intermediate products such as furfurals, phenols and monomeric sugars [7]. Various nutrients from biomass may also be present. However, subsequent usage of PW is questionable because it may as well contain potentially genotoxic and/or cytotoxic substances [5].

Until now, HTC has been employed on a wide range of different biomass feedstock [3,6,8] and it has been shown that the characteristics of HTC products are strongly dependent on reaction conditions and feedstock type.

One of raw materials that is highly suitable for HTC processing is grape pomace (GP), which is a wet biomass (>60% water) that is composed of seeds, skins, and stems remaining after grape processing. GP is produced in significant amounts by wine industry globally as a 20–25% feedstock waste [9]. Regardless of its reputation as environment-friendly, current inadequate waste management practice within the wine industry induces a large number of environmental issues such as production and handling of solid waste stream, energy usage, generation of greenhouse gas emissions etc. [10]. In order to reduce these negative environmental impacts, appropriate utilization of GP is indispensable. There are several potential applications of untreated GP, such as animal feed [11] and soil fertilizer [12], while several studies have examined its antiox-

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ident activity [13] and its suitability for biofuel production [14]. However, they all require drying and storage of pomace, which makes its utilization costly and complex, thus hindering the motivation for its reuse. This is where the HTC has the biggest advantage compared to other carbonization processes such as torrefaction and pyrolysis [9]: application of wet biomass, relatively low operating temperatures, the absence of CO<sub>2</sub> emission and high conversion efficiency. Besides the emphasis on the energetic potential of the GP-HC [9,15], literature regarding comprehensive characterisation and potential utilization of HTC-GP process streams is scarce. For economically beneficial GP-HTC process and efficient treatment methods of PW, a detailed characterization of compounds obtained along the HTC process streams is highly needed. In this way an appropriate and more sustainable reuse of this vastly available waste material could be more effectively outlined.

The aim of this study was to provide a detailed insight into the physico-chemical and fuel properties of HTC products streams of GP in relation to different HTC temperatures. The novelty of this study is reflected in the holistic multi-method approach, where the raw material (GP), solid products (GP-HC) and liquid products (GP-PW) are characterised. Detailed characterization of GP-HCs was performed by Atomic Absorption Spectrometry (AAS), Thermal gravimetric analysis/differential thermal analysis (TGA/DTA), Scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR) and Near-infrared spectroscopy (NIR). Detailed characterization of GP-PWs was performed by using High-performance liquid chromatography (HPLC, LC-MS), FTIR and UV-Vis spectroscopy. Since the literature on the spectroscopic characterisation of the biomass materials is still in the developing phase, multivariate data analysis methods such as Principal Component Analysis (PCA) and Partial Least Square Regression (PLSR) were applied. This was done in order to better understand the HTC process and correlate spectroscopic data with structural and chemical changes in GP-HTC product streams, as well as to provide additional interpretation of the obtained spectroscopic data.

## 2. Materials and methods

### 2.1. Biomass

The red grape was grown on a test plot Radmilovac near Belgrade, Serbia (property of the Faculty of Agriculture, University of Belgrade). The used GP (skin, stalk and seeds) was sampled randomly from landfill sites. The biomass was air-dried until constant weight and extensively grinded in order to obtain homogenous samples. Sieved fraction of 0.5 mm was used in HTC experiments.

### 2.2. HTC experiment

HTC process was carried out in 2000 mL autoclave (Deutsch & Neumann, model 10253, Germany) equipped with external and internal thermometers, analogue manometer and a cooling system. Reaction load was composed of 250 g of raw biomass mixed with 1250 mL of distilled water (5:1 mass ratio) [15], which ensures an adequate HC yield and effective stirring of the mixture. A heating rate of 2 °C min<sup>-1</sup> was applied to reach reaction temperatures of 180, 200 and 220 °C (with starting temperature of 20 °C). The set temperatures were maintained constant for 60 min. During the whole experiment, the stirrer was operated at 60 rpm. Afterwards, the reactor was cooled to room temperature, remaining gas was vented and solid and liquid products were collected. The HC was separated from liquid by filtration, rinsed three times with distilled water and dried at 105 °C for 24 h. After weighing, samples were

placed in a sealed container. The PWs were collected in glass bottles and stored at 4 °C.

### 2.3. Physico-chemical characterization of GP and HCs

**Proximate analysis** of moisture (wt%), volatile matter (VM), and ash were determined in three replicates per sample by standard procedure ASTM D1762-84 (2007). Fixed carbon (FC) was calculated as difference from 100% [6]. Mass yield was defined as mass ratio of dried HCs and dried GP, multiplied by 100% [3].

**Inorganic analysis** (K, Mg, Ca, Na, Fe, Si, Pb, Cu, and Ni) was carried out using AAS (Perkin Elmer, AAS Analyst 300). Samples (in three replicates) were previously dissolved using the nitric-perchloric acid digestion method [16] and inorganics were determined directly from the solution. A part of undissolved Si was subsequently determined by the hydrochloric acid dehydration (gravimetric) technique [17]. Phosphorus and highly soluble phosphorus were determined from acid digested samples solutions using UV-vis spectroscopy (Jena Analytic, Spekol 1300) [18].

**Elemental analysis** (C, H, N and S) of solid samples was performed in three replicates using Vario EL III; C, H, N, S/O Elemental Analyzer equipped with a thermal conductivity detector (TCD). Operating ranges varied between the elements: 0.03–20 mg for C, 0.03–3 mg for H, 0.03–2 mg for N and 0.03–6 mg for S. Oxygen content was obtained by subtracting the sum of the obtained elemental values from 100%. Higher heating values (HHV), energy densification (ED) and energy yield (EY) of the samples were also calculated [9,19].

**Thermal analysis (TGA-DTA)** was performed on a Netzsch STA 409 EP (Selb, Germany). Samples were heated from 20 °C to 1000 °C in an air atmosphere at a heating rate of 10 °C min<sup>-1</sup> and kept in a desiccator at relative humidity of 23%, prior to analysis.

**Morphological studies** were carried out on JSM-6610 JEOL scanning electron microscope. All samples were coated with gold, and placed on the adhesive carbon disc. After coating with gold, samples were placed under vacuum conditions and scanned.

**Spectroscopic analysis:** FTIR analysis of the GP and HCs was performed using a Thermo Scientific Nicolet iS50 FTIR spectrometer in transmission mode by producing KBr pastilles with 0.8 mg sample and 80 mg KBr. The spectra were obtained in three replicates per sample in the spectral range of 4000–400 cm<sup>-1</sup>. NIR analysis of the GP and HCs was performed using a Bruker Optics TANGO FT-NIR spectrometer, equipped with an integrating sphere. The samples were analysed in a reflection mode without any pre-treatment. The spectra were obtained in three replicates per sample in the spectral range of 11540–3950 cm<sup>-1</sup>.

### 2.4. Physico-chemical characterization of PWs

**Inorganic analysis** (K, Mg, Ca, Na, Fe, and Si) of each PWs was performed in triplicates by AAS (PerkinElmer, AAS Analyst 300). Phosphorus was determined by using UV-vis spectroscopy method (Jena Analytic, Spekol 1300) [18].

**Spectroscopic analysis** was performed by FTIR on the same instrument as for GP and HCs, by using the ATR technique, with diamond. Each PW sample was recorder in three replicates, with using distilled water as background, in order to emphasize the signals of relevant components.

**Antioxidant assays:** Total antioxidant capacity (TAC) of PWs was quantified by using UV-Vis spectrometer 2501 PC Shimadzu, Japan, at 730 nm following the ABTS method [20] and results were expressed as milligrams of ascorbic acid equivalent per millilitre (mg AsA eq mL<sup>-1</sup>). Total anthocyanin content (TACY) was measured by using UV-Vis spectrometer Multiscan Spectrum, Thermo electron corporation, Finland, at 510 and 700 nm, following the modified pH differential absorbance method [21] and results were

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