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# Hydrothermal treatment of grape marc for solid fuel applications

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ABSTRACT

The treatment and disposal of grape marc, a residue from grape processing, represents a significant economic and environmental challenge for the winemaking industry. Hydrothermal treatment of grape marc could be an efficient way for producing solid fuels on-site at the wineries. In this work the effects of treatment temperature and liquid pH on grape marc char and liquid properties were determined based on laboratory experiments and the combustion characteristics of char were assessed through thermogravimetric analysis and fuel ash classification. The results showed that hydrothermal treatment increased the energy and carbon contents and decreased the ash content of grape marc. The effect of liquid pH was statistically significant ($p < 0.05$) only for the determined carbon yield of liquid samples. The energy yield from grape marc was maximized at lower treatment temperatures, which also decreased the content of less thermally stable compounds in the attained char. Higher treatment temperatures decreased grape marc solid, carbon and energy yields and led to an increase in thermally labile compounds compared to lower temperatures likely due to the condensation of liquid compounds or volatiles trapped in the pores of char particles. The alkali metal contents of char ash were reduced coupled with an increase in respective phosphorus. Overall the results support the use of hydrothermally treated grape marc in solid fuel applications, if elevated levels of ash phosphorus can be tolerated.



## 1. Introduction

Winemaking is based on converting sugars into alcohol through fermentation. Grapes, the main raw material, can contain up to 25% of skins, seeds and stems [1] that remain unutilized after they have been pressed for wine production. This remaining material is commonly known as grape marc, or grape pomace, and is generated in significant quantities in wine producing countries. A global grape production of 67 Mt leads to the generation of 5 Mt of fresh grape marc every year [2]. The exact composition of grape marc depends on the grape variety, the relative proportions of its constituents, and the used pressing method [2].

The treatment and disposal of grape marc represents a significant economic and environmental challenge for the winemaking industry. In Australia alone the industry produces approximately 230,000 tons of fresh grape marc each year, which is generally disposed of at a cost to the winery [2,3]. Some of the generated marc is used for the production of grape spirit and tartaric acid for use in the beverage and food industries [3], but the rest could be used for generating energy on-site. Grape marc normally contains over 60% moisture [4], which significantly increases the costs of handling and transport and decreases the efficiency of energy recovery through incineration. Recent research on the treatment of grape marc for energy applications has included potential fermentation into bioethanol [2], anaerobic digestion for biogas production [5] and hydrothermal liquefaction for bio-oil production [6].

Hydrothermal treatment, also known as hydrothermal carbonization or wet torrefaction, can also be used for upgrading a variety of wet feedstock to solid fuels suitable for use in existing combustion or gasification units. Thermochemical treatment under elevated temperature and self-generated pressure offers relatively high solid yields and can be used for upgrading low-value wet feedstocks such as agricultural or industrial wastes [7–10]. The process is robust and is generally not affected by potential shutdowns, biological disruptors or changes in feed quality. It is also well-known that hydrothermal treatment affects the ash content and composition of the feedstock [11,12], which can be beneficial for subsequent combustion by decreasing potential slagging, deposition and corrosion problems. Although the principle of artificial

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coalification or carbonization was already reported in the beginning of the 20th century [13], research activity within the field has increased significantly within the last 5–10 years [14]. Several pilot-scale investigations and continuous process alternatives have recently been reported [15–17], suggesting that the practical experience on operating under hydrothermal conditions is also increasing.

Hydrothermal treatment of grape marc has previously been reported. Pala et al. [18] compared properties of grape marc after hydrothermal treatment and torrefaction. The authors showed that hydrothermal treatment provided lower char ash contents and higher energy densification and energy yield than torrefaction. In addition, Petrović et al. [19] characterized the char and attained liquid from hydrothermal treatment of grape marc and concluded that grape marc can have valuable fuel properties. Catalkopru et al. [20] also reported that liquid recirculation during hydrothermal treatment of grape marc led to minor increases in char mass and energy yields. This work was aimed at determining the effects of treatment temperature and liquid pH on the properties of hydrothermally treated grape marc and evaluating its potential for subsequent combustion. Although temperature generally governs char properties during hydrothermal treatment, changes in liquid pH can be used for controlling reaction mechanisms. The decomposition of biomass under hydrothermal conditions generally proceeds through hydrolysis and decomposition of polysaccharides into simple sugars and organic acids, which lower liquid pH [21,22]. Changes in liquid pH affect hydrolysis of polysaccharides and lignin and can thus help to catalyze further decomposition and transformation reactions and enhance char properties. Although the recovery of additional acid or alkali after hydrothermal treatment is difficult [23], changes in liquid pH have previously been found to control ash dissolution during hydrothermal treatment and have led to increased carbon content of char [12,24]. Laboratory experiments were thus performed according to an experimental design and correlations between experimental conditions and char properties were determined through multivariate data analysis and individual regression models. In addition, potential combustion behavior was assessed through thermogravimetric analysis and fuel ash classification. The attained results enable evaluating the potential of hydrothermal treatment of grape marc for solid fuel applications.

## 2. Materials and methods

### 2.1. Grape marc

Grape marc was obtained after the pressing of red fruit (Caubernet Sauvignon) sourced from the Waite campus vineyards at the University of Adelaide, Australia. The moisture content of the fresh marc was approximately 75% and it was dried at 105 °C overnight and stored at room temperature and humidity in a sealed container before the experiments. The dried untreated grape marc was analyzed as described in Section 2.3 after homogenization with a Fritsch pulverisette ball mill (Fritsch GmbH). The results are given in Table 1.

**Table 1**
Grape marc properties.

| Parameter | Unit | Value |
|---|---|---|
| Dry solids content (105 °C) | % | 98.6 |
| Ash content | % (db) | 8.23 |
| Higher heating value | MJ $kg^{-1}$ (db) | 19.6 |
| C | % (db) | 48.7 |
| H | % (db) | 5.57 |
| N | % (db) | 1.66 |
| O | % (db) | 35.9 |

db = dry basis.

### 2.2. Hydrothermal treatment

The hydrothermal experiments were performed in a glass tube with a 0.5 L MMJ-500 (OM Lab-tech Co., Ltd.) pressure reactor having a final working volume of approximately 0.4 L. A constant 30 g of dry grape marc was mixed with 90 g of liquid to attain a reactor load of 25% of dry solids. The reactor was closed, purged with argon, and heated to 180–260 °C with a PID controlled 0.95 kW electrical heater. Reactor pressure was observed from a pressure gauge and was approximately equal to saturated vapour pressure of water at the respective reactor temperatures. After an isothermal holding time of 30 min the reactor was cooled with the help of a fan and the gases were vented to a fume hood. Reactor solid and liquid phases were separated by vacuum filtration through a Whatman 1.6 μm filter paper. Reactor heating and cool-down profiles for different treatment temperatures are given in Fig. A.1 (Supplementary material).

The individual experiments were organized according to an experimental design in which treatment temperature and liquid pH were varied on three different levels (Table 2). The final design was composed of 11 individual experiments including three repetitive experiments in the design center. Liquid pH was adjusted by using distilled water or AcOH (99%, Wako Chemical Industries, Ltd.) or KOH (85%, Wako Chemical Industries, Ltd.) diluted to respective pH values of 2.5 (0.57 M) and 11.6 (3.2 mM). The diluted solutions were prepared prior to the experiments.

### 2.3. Analyses

After solid and liquid separation, the char samples were dried overnight at 105 °C and ground in a mortar. The respective ash contents were determined through loss on ignition at 550 °C for 2 h. Ash compositions were determined with an X-ray fluorescence spectrometer (XRF, S2 Ranger, Bruker Corp.) from the ignited samples. The spectrometer was operated with a 10–50 kV voltage coupled with a current of 0.98–1.35 mA depending on the individual element. CHN contents of the char samples were determined with a JM10 microanalyzer (J-Science Lab Co., Ltd.) equipped with a thermal conductivity detector. Oxygen contents were calculated by subtraction. Char heating values were estimated based on the formula of Channiwala and Parikh discussed by Kieseler et al. [25]. Hydrochar ash (%), solid (%, daf) and carbon yields (%), O/C ratio (daf), energy densification (daf) and energy yield (%) were calculated as previously described [26]. In addition, char H/C ratios (daf) were calculated based on the fuel and ash analyses and respective molecular weights of the elements. Thermal decomposition was determined using a thermogravimetric analyser (TGA, Q5000IR, TA Instruments). Approximately 5 mg samples were

**Table 2**
Hydrothermal experiments.

| Experiment no. | Treatment temperature (°C) | Initial liquid pH |
|---|---|---|
| 1 | 180 | 2.5 |
| 2 | 260 | 2.5 |
| 3 | 180 | 11.6 |
| 4 | 260 | 11.6 |
| 5 | 180 | 7 |
| 6 | 260 | 7 |
| 7 | 220 | 2.5 |
| 8 | 220 | 11.6 |
| 9 | 220 | 7 |
| 10 | 220 | 7 |
| 11 | 220 | 7 |