Waste Management 47 (2016) 114–121

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Agro-industrial waste to solid biofuel through hydrothermal carbonization

Daniele Basso [a], Francesco Patuzzi [b], Daniele Castello [a], Marco Baratieri [b], Elena Cristina Rada [a], Elsa Weiss-Hortala [c], Luca Fiori [a,*]

[a] University of Trento, Department of Civil, Environmental and Mechanical Engineering, Italy
[b] Free University of Bolzano, Faculty of Science and Technology, Italy
[c] Université de Toulouse, Mines Albi, CNRS, Centre RAPSODEE, France

ARTICLE INFO

Article history:
Available online 29 May 2015

Keywords:
Biochar
Biofuel
Grape marc
Hydrochar
Hydrothermal carbonization
Thermochemical conversion

ABSTRACT

In this paper, the use of grape marc for energy purposes was investigated. Grape marc is a residual lignocellulosic by-product from the winery industry, which is present in every world region where vine-making is addressed. Among the others, hydrothermal carbonization was chosen as a promising alternative thermochemical process, suitable for the treatment of this high moisture substrate. Through a 50 mL experimental apparatus, hydrothermal carbonization tests were performed at several temperatures (namely: 180, 220 and 250 °C) and residence times (1, 3, 8 h). Analyses on both the solid and the gaseous phases obtained downstream of the process were performed. In particular, solid and gas yields *versus* the process operational conditions were studied and the obtained hydrochar was evaluated in terms of calorific value, elemental analysis, and thermal stability. Data testify that hydrochar form grape marc presents interesting values of HHV (in the range 19.8–24.1 MJ/kg) and physical–chemical characteristics which make hydrochar exploitable as a solid biofuel. In the meanwhile, the amount of gases produced is very small, if compared to other thermochemical processes. This represents an interesting result when considering environmental issues. Statistical analysis of data allows to affirm that, in the chosen range of operational conditions, the process is influenced more by temperature than residence time. These preliminary results support the option of upgrading grape marc toward its energetic valorisation through hydrothermal carbonization.

1. Introduction

Nowadays, the need for energy is a strong and relevant issue worldwide. The international community agrees that a strong effort should be made looking for alternative energy resources, capable to lower as much as possible the amount of fossil fuels from the energy portfolio and to develop a sustainable supply chain. At the same time, another important issue concerns waste management. As a matter of fact, proper waste management and treatment may allow both greenhouse gases (GHGs) mitigation and possibilities for bioenergy production (Pyo et al., 2014; Rada, 2014). These constraints are a strong driving force for the investigation on new and affordable technologies, able to combine proper and sustainable waste management with the production of clean and renewable energy.

During the last decades, many processes have been proposed which could successfully address such issues. Such technologies can be classified as biological or thermochemical. In the general case, biological processes are quite sensitive with respect to the inlet feedstock as, potentially, microorganisms could be easily inhibited by toxic substances present in the substrate. Additionally, they need very long residence times (*i.e.* from one day to several weeks). Therefore, besides being slower, these processes entail bigger volumes, which cause higher design and manufacturing costs. On the contrary, the time scale of thermochemical processes generally ranges from a few minutes to some hours. Moreover, since such processes do not rely on microorganisms, they can overcome the limitations due to chemical lag and the possible inhibition by toxic agents, as described above. This is a noticeable advantage for the treatment of heterogeneous feedstock or substrates with a low degree of purity (e.g. organic wastes, sewage sludges, etc.). Several thermochemical processes have been

* Corresponding author at: University of Trento, Department of Civil, Environmental and Mechanical Engineering, via Mesiano 77, I-38123 Trento, Italy. Tel.: +39 0461282692, +39 0461282672.

E-mail address: luca.fiori@unitn.it (L. Fiori).

http://dx.doi.org/10.1016/j.wasman.2015.05.013
0956-053X/

proposed and discussed for the treatment of different kind of biowaste (Khoo, 2009; Iakovou et al., 2010; Devesa-Rey et al., 2011).

Referring to the type of feedstock, thermochemical processes can be divided into two main groups: dry and wet processes. The former, such as combustion or pyrolysis, are suitable when the feedstock has low water content. For example, several authors have discussed the application of these processes to woody agricultural biomass waste (Barbieri et al., 2013) or municipal solid wastes (Ragazzi and Rada, 2012; Abnisa and Wan Daud, 2014; Chen et al., 2014). When the feedstock presents high water content (*i.e.* moisture higher than 60%), hydrothermal processes become more appropriate. These processes make use of hot pressurized water to convert wet substrates. Pressure is always held high enough to keep water in its liquid or, possibly, supercritical state. Among them, a classification on the basis of the process temperature and the type of obtained products can be done. When the temperature values range between 180 °C and 250 °C, the main product is a solid material (referred to as hydrochar) and the process is called hydrothermal carbonization (HTC) (Castello et al., 2014). If the temperatures are increased from 250 °C to about 373 °C, hydrothermal liquefaction (HTL) is performed, with the main production of a liquid phase (Elliott et al., 2015). Finally, rising the temperature and the pressure above the critical values for water (373.95 °C and 22.06 MPa), the process is called hydrothermal gasification (HTG) or supercritical water gasification (SCWG), which allows for a combustible gas as main product (Castello et al., 2014). The application of these hydrothermal processes to several typologies of biomass has been discussed by many authors (Fiori et al., 2012a; Lu et al., 2012; Pala et al., 2014; Xiao et al., 2012; Subagyono et al., 2014; Yedro et al., 2014).

The type of feedstock is another important aspect to be considered in order to guarantee an appropriate degree of both sustainability and profitability. In particular, the ready availability of the biomass on the territory around the treatment plant, as well as its cost, is crucial. As a matter of fact, when a substrate is produced as a by-product of agricultural and industrial activities established nearby the conversion plant, its supply and transportation costs are lowered, which is beneficial to the overall economic balance of the energy production process. Additionally, such choice improves the sustainability of the process by reducing the polluting emissions due to biomass transportation over long distances. Moreover, if the company that produced that by-product is also in charge of its disposal, the possibility to collect this by-product as a feedstock for energy purposes can represent an interesting, viable and advantageous alternative.

In the region in which the present research group is operating (*i.e.* the North-East of Italy), grape marc is widely available, as it is an important by-product of the wine making industries. Grape marc already has a utilization for the production of spirits through distillation. However, downstream of such process, most residual grape marc is still found as a wet ligno-cellulosic residue, which must be properly disposed of. HTC could be an effective technology to achieve both the disposal and valorisation of such feedstock.

Considering that HTC is performed at milder operational conditions than the other hydrothermal processes, this process has been investigated in the present paper as a suitable way to energetically valorise the grape marc by-product which is affordable also at the SME (Small and Medium Enterprise) level.

In this paper, the results of HTC of grape marc performed in a lab scale batch reactor are presented. Several reaction conditions were explored, including different reaction temperatures and residence times. Both solid and gaseous products were sampled and analyzed. The energy content, the elemental analysis and the thermal stability of the solid was determined, showing the great potentiality of hydrochar as a fuel. Analyses on the gaseous phase were performed both to try to understand the chemical processes occurring during HTC and to get information on the gaseous emissions on the environment.

2. Materials and methods

2.1. The feedstock

Grape marc collected after wine production consists of seeds, skins and, possibly, stalks. Actually, stalks are collected together with seeds and skins or, vice versa, separately according to the different wine-making procedures. Usually, when grape marc originates from the wine-making process, it is referred to as "fresh grape marc", while after it has been used for spirits production, it is referred to as "exhausted grape marc". In the case of fresh grape marc, the moisture content ranges between 60% and 70% (Fiori and Florio, 2010). Thus, after a drying pre-treatment, which could be addressed also through innovative technologies such as bio-drying (Rada et al., 2009), grape marc can be exploited for energy purposes through conventional thermochemical processes such as combustion or pyrolysis (Fiori et al., 2012b). Alternatively, it can undergo hydrothermal treatments, like the HTC here investigated.

For the present research, fresh grape marc was collected at a wine-production site located in Trentino (North-East of Italy). The raw feedstock was dried in a ventilated oven at 65 °C for about 48 h. Subsequently, grape marc was let cooling down to room temperature and finally stored into plastic bags, until use. The final average moisture was measured to be about 5%. This kind of pre-treatment was performed in order to collect data regardless of the degree of moisture of the incoming feedstock, which could be variable. Furthermore, this drying pre-treatment was necessary to prevent the degradation of the feedstock during the period between its collection and its actual utilization for the experiments (up to some weeks). The presence of water would have caused undesired degradation reactions, as well as mould formation, which would have altered the quality and composition of the substrate in a significant way. Nevertheless, when applying HTC to grape marc in a real industrial process, wet grape marc would most likely be used as received and possibly applying additional quantities of water, in order to reach the optimal biomass to water (B/W) ratio.

2.2. The HTC experimental apparatus

As explained above, the hydrothermal carbonization is usually performed in a temperature range of 180–250 °C. Since water has to be maintained in its liquid state, pressures reach values of 40–50 bar. Therefore, a 50 mL stainless steel (AISI 316) batch reactor was designed and built, with a design temperature and pressure of 300 °C and 140 bar, respectively. For further technical information, the reader can refer to Basso et al. (2015). The experimental apparatus was equipped with a thermocouple embedded inside the reactor. For the measurement of the pressure, both a pressure gauge and a pressure recorder were used.

2.3. Experimental procedure

The reactor was filled with 5.4 ± 0.1 g of feedstock and 27.0 ± 0.1 g of distilled water, obtaining a biomass to water ratio of about 0.19 (dry basis). The reactor was sealed with a copper gasket and then it was closed. Before each test, nitrogen was flushed within the reactor to purge it from the presence of air. The reactor was warmed up through a band heater. At the end of each test, the reactor was quenched with the help of a stainless steel block kept at −26 °C which was put underneath the reactor itself, while fresh