Bioresource Technology 196 (2015) 35–42

Contents lists available at ScienceDirect

Bioresource Technology

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

# Characterization of products from hydrothermal carbonization of orange pomace including anaerobic digestibility of process liquor

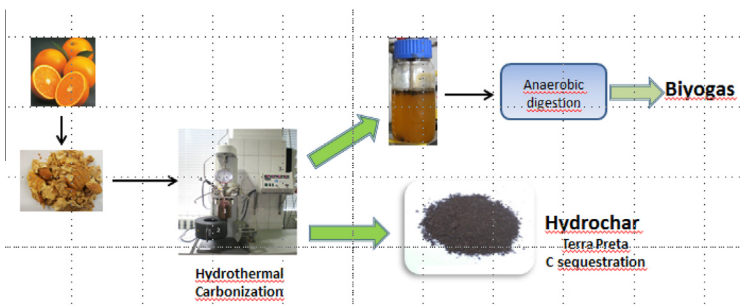
Ezgi Erdogan [a], Buse Atila [a], Jan Mumme [b,c], M. Toufiq Reza [b,d], Asli Toptas [e], Murat Elibol [f], Jale Yanik [e,*]

[a] Center for Environmental Studies, Ege University, 35100 Bornova, Izmir, Turkey
[b] Leibniz Institute for Agricultural Engineering Potsdam-Bornim, Max-Eyth-Allee 100, 14469 Potsdam, Germany
[c] UK Biochar Research Center, School of GeoSciences, University of Edinburgh, Crew Building, King's Buildings, Edinburgh EH9 3JN, UK
[d] Department of Chemical and Materials Engineering, University of Nevada Reno, 1664 North Virginia Street, Reno, NV 89557, USA
[e] Faculty of Science, Department of Chemistry, Ege University, 35100 Bornova, Izmir, Turkey
[f] Faculty of Engineering, Department of Bioengineering, Ege University, 35100 Bornova, Izmir, Turkey

## HIGHLIGHTS

- HTC is a promising process for production of hydrochar from orange pomace.
- Spent liquor was used as feedstocks for biogas production.
- No PAHs were detected in the hydrochars.
- Heavy metal contents in hydrochars were found below limits.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 22 May 2015
Received in revised form 22 June 2015
Accepted 23 June 2015
Available online 29 June 2015

*Keywords:*
Hydrothermal carbonization
Orange pomace
Anaerobic digestion
Hydrochar
Biogas

## ABSTRACT

In this study, the effect of the temperature and reaction time on hydrothermal carbonization (HTC) of orange pomace was investigated. In addition, a set of anaerobic batch tests were performed to determine the resulting biogas and methane potential of the spent liquor. Hydrochar yields followed a decreasing trend with the increasing temperature, whereas reaction time had no considerably effect on the yield. The evolution of the H/C and O/C atomic ratios from the raw material to the hydrochars suggested that dehydration reactions prevail during HTC. The hydrochars tended to become enriched in Ca, Mg and P minerals by increasing HTC temperature. The heavy metal contents in hydrochars were found below limits and no PAH compound was detected. Anaerobic digestion tests showed that the aqueous phase from HTC can be used as feedstocks for biogas production.



## 1. Introduction

Recently biochar, a charcoal-like substance, has been gained importance: It is mainly produced from municipal, agriculture and forest wastes and can be used as fuel and soil enhancer to increase fertility, prevent soil degradation and to sequester carbon in the soil. Numerous studies on biochar production can be found in literature. From these studies, it can be understood that both production method and biomass feedstock type are important factors in determining the suitable application for biochars. Biochar is among others produced by pyrolysis and hydrothermal carbonization. Pyrolysis is a dry conversion method and can only work with high energetic efficiency when dry feedstock is used. However,

* Corresponding author. Tel./fax: +90 232 3888264.
*E-mail address:* jale.yanik@ege.edu.tr (J. Yanik).

http://dx.doi.org/10.1016/j.biortech.2015.06.115
0960-8524/© 2015 Elsevier Ltd. All rights reserved.

hydrothermal carbonization (HTC) is an especially promising technology for feedstocks having high water content (up to 80%). HTC process occurs in aqueous medium at low temperatures ranging from 160 to 270 °C. Because of this, the HTC offers the advantage of converting wet biomass into carbonaceous solids, which are called hydrochar, without energy intensive drying process. In addition, some degradation products and inorganics in biomass are dissolved in the aqueous phase. Since the aqueous phase from HTC contains dissolved organics (e.g. sugars and fatty acids) and minerals (e.g. N, P, K), it can be used as fertilizer or feedstock in anaerobic reactors (Becker et al., 2014; Wirth and Mumme, 2013). The HTC process takes place via a series of hydrolysis, polymerization, condensation, and dehydration reactions (Titirici et al., 2008), showing that hydrochar is a potential carbon sequestration agent. Hydrochars, in comparison to torrefaction, show unique characteristics and can be used in various applications, such as supercapacitor (Kruse et al., 2013), metal/carbon nanoarchitectures, carbon nanofibers, and soil improver (Cao et al., 2011) etc.

A number of studies have been performed on hydrothermal carbonization covering a wide range of lignocellulosic wastes, such as wood chip (Hoekman et al., 2011; Reza et al., 2014a; Sun et al., 2014), peanut shell and bamboo (Huff et al., 2014), digestate (Mumme et al., 2011), coconut fiber and dead eucalyptus leaves (Liu et al., 2013), bagasse (Sun et al., 2014), olive residues (Wiedner et al., 2013), wheat straw (Becker et al., 2014), and manure (Cao et al., 2011; Mumme et al., 2011; Oliveira et al., 2013), sewage sludge (He et al., 2013). All these studies show that hydrochar properties mainly depend on feedstock type and temperature. For each feedstock, it is necessary to optimize the reaction conditions to better satisfy their applications. In addition, a treatment option of spent liquor, which was obtained as by-product, is needed to make the overall process environmentally friendly. There are a few studies on recycling of spent liquor, anaerobic digestion for methane production (Wirth and Mumme, 2013), use as further feedstock in HTC process (Stemann et al., 2013; Uddin et al., 2014).

Citrus fruits are processed into juice and often preferred to vinegar as an ingredient in sauces and salad dressing for its special flavor. Most food processing residues are disposed without being recycled. These residues are mainly composed of the part of peel, juice sack and seed. Pectins which are widely used in the food and pharmaceutical industries are major components of peel. Lemon and grape peels are considered the best sources of citrus pectin. Unfortunately, pectin from orange peels is considered to have the poorest structure/function properties among citrus pectins (Fishman et al., 2003). Unlike the lignocellulosic biomasses, which were widely studied in literature, orange pomace is rich in pectin and may be available in large quantities (Figuerola et al., 2005). Pectin consists of a complex set of polysaccharides and there is little information on pyrolysis and hydrothermal processing mechanisms of pectin (Ge et al., 2015; Hoshino et al., 2009). Hoshino et al. studied the sub-critical water extraction (at the temperature range of 110–160 °C) of the citrus junos residue for the separation of pectin (Hoshino et al., 2009). They observed that pectin molecules begin to be decomposed at the temperature higher than 140 °C. Besides pectin, orange pomace may contain polyphenols as bioactive compounds. On the other, orange pomace might be suitable feedstock for HTC process due to its acidic nature and high moisture content (~80 wt%).

In the present study, hydrochar production from orange pomace was studied for the first time. The effects of temperature and time on the yield and properties of hydrochar were investigated. Additionally, biogas and biomethane potential determination of the spent liquor from HTC was performed.

## 2. Methods

### 2.1. Material

Orange pomace was provided by Anadolu Etap, Mersin. It was dried first in the air environment and then in oven at 60 °C for 24 hours to a moisture content of 41 wt%. Then all of the materials were stored in plastic bags at refrigerator (at +5 °C). Before experiments, pomace (−2 cm) was dried at 105 °C for overnight and used without grinding. Some properties and inorganic contents of orange pomace are given in Table 1.

### 2.2. Hydrothermal carbonization

Hydrothermal carbonization (HTC) experiments were carried out using a 1 L Parr 4520 Series stirred pressure reactor. In a typical run, 50 g of pomace was mixed with distillated water in a 1:8 biomass/water ratio (w/w). Prior to reaction, residual air was removed from the sealed reactor by repeatedly pressurizing with nitrogen and venting to atmosphere. The reactor and contents were then heated at a heating rate of 3 K/min while stirring (90 rpm). HTC were carried out at the reaction temperatures between 175 and 260 °C for 30, 60, 90, and 120 min.

After HTC of the pomace at the desired temperature and holding time, the reactor vessel was removed from the heated well and placed in an ice bath to cool the contents. When the inner reactor temperature reached approximately 50 °C, the non-condensable gases were released to atmosphere. The aqueous solution was filtered and the solid product (hydrochar) was washed with distillated water and then dried at 105 °C for overnight.

The yield of hydrochar was calculated using equation: hydrochar yield, % = (mass of hydrochar, g/oven dry mass of pomace, g) × 100. Dried hydrochar was placed into a zip-lock bag and stored for further use. The aqueous solution was stored in a 4 °C refrigerator for further analyses.

### 2.3. Anaerobic digestion test

The anaerobic digestion tests were conducted based on the biochemical methane potential (BMP) according the VDI 4630 guideline. In detail, the biogas yield of aqueous solutions from HTC was determined according to the Hohenheimer Biogas Yield Test (HBT) (Helffrich and Oechsner, 2003). HBT is a batch fermentation test in which the reactor is a 100 mL glass syringe with a capillary extension for feeding and sampling. The aqueous solutions from HTC experiments at 190 °C, 225 °C and 260 °C for 120 min (donated as A190, A225 and A260, respectively) were chosen as substrate. The inoculum was obtained from a local on-farm biogas plant (Groß Kreutz, Germany). More detail on the biogas plant is given in reference (Mumme et al., 2014). In a typical run, the aqueous solution with an organic load of 100 mg COD and 50 mL inoculum was filled into each syringe. No additional substrate was fed.

**Table 1**
Some properties of orange pomace, (dry basis).

| | | | | | |
|---|---|---|---|---|---|
| Ash (wt%) | | | 5.5 ± 0.1 | *Component analysis (wt%)* | |
| HHV* (MJ/kg) | | | 20.3 | Cellulose | 14.3 ± 2.5 |
| *Ultimate analysis (wt%)* | | | | Hemicellulose | 6.3 ± 1.6 |
| C | 45.4 ± 0.1 | Na (mg/kg) | 24.39 | Lignin | 3.3 ± 2.3 |
| H | 6.3 ± 0.2 | K (mg/kg) | 6250.86 | Crude fiber | 14.7 ± 0.4 |
| N | 1.59 ± 0.02 | Ca (mg/kg) | 6918.58 | | |
| S | 0.15 ± 0.01 | Mg (mg/kg) | 809.89 | | |
| O | 41.1 | P (mg/kg) | 1002.31 | | |
| | | S (mg/kg) | 922.61 | | |

* High heating value.