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Torrefaction of almond shells: Effects of torrefaction conditions on properties of solid and condensate products

Bor-Sen Chiou[a,*], Diana Valenzuela-Medina[a], Cristina Bilbao-Sainz[a], Artur P. Klamczynski[a], Roberto J. Avena-Bustillos[b], Rebecca R. Milczarek[b], Wen-Xian Du[b], Greg M. Glenn[a], William J. Orts[a]

[a] Bioproducts Research Unit, U.S. Department of Agriculture, Albany, CA 94710, United States
[b] Healthy Processed Foods Research, U.S. Department of Agriculture, Albany, CA 94710, United States

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ABSTRACT

Almond shells were torrefied in a fixed bed reactor and their solid and condensate products were collected for analysis. Response surface methodology was used to examine effects of torrefaction temperature (230 °C, 260 °C, and 290 °C) and time (60, 80, and 100 min) on mass and energy yields of solid products as well as mass yields and gross calorific values (GCVs) of condensate products. This was the first study on condensates produced during torrefaction of almond shells. Also, true density, moisture sorption isotherms, thermal stability, and elemental composition of the solid products were characterized. The mass yields of solid products drastically decreased at higher temperatures, from 85.4–92.7% at 230 °C to 39.4–45.3% at 290 °C. Also, mass yields (8.79–11.71% at 230 °C to 23.13–29.39% at 290 °C) and GCVs of condensates (2.3 ± 0.3 to 4.3 ± 1.0 MJ/kg at 230 °C to 5.6 ± 1.0 to 7.1 ± 1.2 MJ/kg at 290 °C) generally increased in value at higher temperatures and longer times. Moisture sorption isotherms of torrefied shells were measured for the first time and all torrefied shells had lower equilibrium moisture contents than raw shells. In addition, equilibrium moisture contents and GCVs of the condensates were found, for the first time, to be predicted relatively well using just the sample mass loss results. The minimum moisture contents were predicted to occur at 16.4–19.9% mass loss.

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1. Introduction

The U.S. had almost doubled its production of almonds over the last seven years, with 950,000 tons of almonds produced in 2013. This accounted for more than 80% of worldwide production (Almond Almanac, 2014). The increase in production also resulted in an increase in generation of byproducts, such as almond shells. Currently, raw almond shells are primarily combusted as fuel.

Torrefaction, which involved heating biomass between 200 and 300 °C under inert conditions, offers a viable alternative for upgrade of almond shells as a fuel source. Torrefaction removes moisture and volatile components to produce a stable, high density fuel. The torrefied biomass can then serve as a drop in replacement for coal or as a feed source for gasification. Many studies of torrefaction had focused on different wood species (Prins et al., 2006; Almeida et al., 2010; Phanphanich and Mani, 2011; Kim et al., 2012; Hill et al., 2013; Pushkin et al., 2015) and energy crops, such as Miscanthus (Bridgeman et al., 2010). There had also been some studies on agricultural byproducts, such as oil palm waste (Sabil et al., 2013; Chin et al., 2013; Chen et al., 2016), corn stover (Medic et al., 2012a, 2012b), wheat straw (Bridgeman et al., 2008; Sadaka and Negi, 2009; Shang et al., 2012), rice straw (Sadaka and Negi, 2009; Deng et al., 2009; Nam and Capareda, 2015), and pomaces (Chiou et al., 2015; Benavente and Fullana, 2015; Toscano et al., 2015). However, there had been few studies on torrefaction of nut shells, such as almond shells (Chiou et al., 2015; Arnsfeld et al., 2014).

The few studies on torrefaction of almond shells had mainly focused on properties of the resulting solid products. For instance, Arnsfeld et al. (2014) torrefied almond shells at 300 °C and characterized their pore size distributions. Also, Chiou et al. (2015) examined the effects of torrefaction conditions on mass and energy yields of almond shells. They found that mass and energy yields decreased more rapidly at higher torrefaction temperatures.

Volatiles produced during torrefaction could be combusted to provide an additional energy source, but few studies had directly measured their heating values (Dhungana et al., 2012; Chen et al.,

* Corresponding author.
E-mail address: bor-sen.chiou@ars.usda.gov (B.-S. Chiou).

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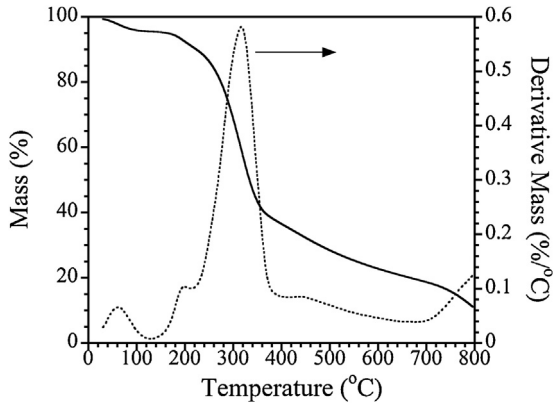

Fig. 1. TG and DTG curves of raw almond shells.

2016). The volatiles were usually cooled to form condensates and their compositions were characterized by high performance liquid chromatography (HPLC) (Prins et al., 2006), Fourier Transform Infrared (FTIR) spectroscopy (Bridgeman et al., 2008; Nocquet et al., 2014), gas chromatography (Medic et al., 2012b; Fagernas et al., 2015), or gas chromatography–mass spectrometry (Kim et al., 2012; Ren et al., 2012; Fagernas et al., 2015; Le Thanh et al., 2015). One study calculated heating values of volatiles from their elemental compositions and from mass balances during torrefaction (Peduzzi et al., 2014). However, the heating values were not directly measured in that study.

Equilibrium moisture content is also an important property for torrefied biomasses since it affects their handling conditions, combustion or gasification products, and resistance to microbial attack (Medic et al., 2012c). However, there had been few studies examining moisture contents of torrefied biomass over a wide relative humidity range. In one study, Achargee et al. (2011) examined the equilibrium moisture contents of raw and torrefied loblolly pine over a relative humidity range of 11–97% at 30 °C. They found that torrefaction did not affect the content of non-bonded water in the samples. Also, Medic et al. (2012c) measured equilibrium moisture contents of raw and torrefied corn stover over a relative humidity range of 10–98% at 10–40 °C. They found that samples torrefied at higher temperatures generally had lower equilibrium moisture contents. In addition, torrefied samples had greater resistance to microbial attack than raw samples.

In this study, we torrefied almond shells in a fixed bed reactor and characterized properties of the solid and condensate products. We used response surface methodology to examine the effects of torrefaction temperature and time on mass and energy yields of the solid products, as well as mass yields and gross calorific values (GCVs) of the condensates. We also characterized the samples' moisture sorption isotherm, true density, thermal stability, and elemental composition using dynamic vapor sorption (DVS), gas pycnometry, thermogravimetric analysis (TGA), and elemental analysis, respectively.

2. Materials and methods

2.1. Sample preparation

Almond (*Prunus dulcis*) shells from the nonpareil variety were obtained from RPAC (Ryan Parreira Almond Company) Almonds (Los Banos, CA) in March of 2012 and stored at 4 °C. For sample preparation, the shells were first dried in an oven at 55 °C for at least 24 h. They were then ground and sieved (<850 μm) before being placed in a dessicator at room temperature (23 °C).

2.2. Torrefaction of almond shells

A stainless steel fixed bed reactor (7.5 cm in diameter and 11 cm in height) and an Isotemp muffle furnace (Fisher Scientific, Philadelphia, PA) were used to torrefy the samples. First, 3 g of shells was placed in the reactor and the reactor was placed inside the furnace. The reactor was purged with nitrogen gas (140 ml/min) for 20 min prior to and during the torrefaction test. The furnace was then set to the torrefaction temperature (230 °C, 260 °C, and 290 °C). The torrefaction lasted for 60, 80, and 100 min after the sample temperature reached 200 °C. Condensable gases generated during torrefaction were collected in a condenser cooled by crushed ice.

2.3. Design of experiments

Response surface methodology (Minitab (State College, PA) version 14.12) was used to determine the effects of torrefaction temperature and time on mass yield, energy yield, and true density of the solid products as well as mass yield and gross calorific value of the condensates. The mass yield of the solid product was determined by:

$$MY_S = \frac{m_{S(daf)}}{m_{R(daf)}} x100 \quad (1)$$

where MY_S (%) is mass yield of the solid product, $m_{S(daf)}$ is mass of the solid product (dry and ash free), and $m_{R(daf)}$ is mass of the raw sample (dry and ash free). The mass yield of the condensate was determined by:

$$MY_C = \frac{m_C}{m_{R(af)}} x100 \quad (2)$$

where MY_C (%) is mass yield of condensate, m_C is mass of the condensate, and $m_{R(af)}$ is mass of the raw sample (ash free). The energy yield of the solid product was determined by:

$$EY_S = MY_S \frac{GCV_{S(daf)}}{GCV_{R(daf)}} \quad (3)$$

where EY_S (%) is energy yield of the solid product, $GCV_{S(daf)}$ is gross calorific value of the solid product (dry and ash free), and $GCV_{R(daf)}$ is gross calorific value of the raw sample (dry and ash free). A central composite design, with three levels and five center points, was used in the study. The torrefaction temperatures were 230 °C, 260 °C, and 290 °C and the torrefaction times were 60, 80, and 100 min.

2.4. Moisture and ash contents

A TA Instruments (New Castle, DE) thermogravimetric analyzer TGA 2950 was used to determine moisture and ash contents of the samples. The moisture content was determined by heating the sample at 107 °C for one hour under nitrogen flow (40 cm^3/min). The ash content was determined by heating the sample at 750 °C for 2 h without any nitrogen flow.

2.5. True density

A Micromeritics (Norcross, GA) AccuPycII 1340 gas pycnometer was used to measure the true density of the samples. The samples were first dried overnight in a vacuum oven set at 70 °C. Each 0.3–0.5 g sample was then placed in the gas pycnometer and the true density was measured at room temperature using helium displacement. The sample was first sealed in a compartment of known volume. Helium was then introduced into this compartment and then expanded into another compartment of known volume. The helium pressure before and after expansion was measured and used to calculate sample volume.