# Torrefaction of pomaces and nut shells

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## HIGHLIGHTS

- Torrefied apple, grape, olive, and tomato pomaces as well as almond and walnut shells.
- Used response surface methodology (RSM) to examine mass and energy yields.
- Raw tomato pomace had the largest gross calorific value.
- RSM models showed mass and energy yields depended more on temperature than time.
- Energy yields could be predicted from mass loss.

## ARTICLE INFO

## ABSTRACT

Apple, grape, olive, and tomato pomaces as well as almond and walnut shells were torrefied at different temperatures and times in a muffle furnace. The fiber content and thermal stability of the raw byproducts were examined and the moisture and ash contents, elemental composition, and gross calorific values of the raw and torrefied samples were characterized. Response surface methodology and a central composite design were used to examine the effects of temperature and time on mass and energy yields of the torrefied byproducts. Raw apple pomace had the highest hemicellulose content, whereas raw grape pomace had the highest lignin content. Raw tomato pomace had the highest gross calorific value because of its high carbon content. Temperature had a larger effect on mass and energy yields than time. Grape pomace generally had the highest mass and energy yields. Also, energy yields of the byproducts could be predicted from mass loss values.

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## 1. Introduction

Torrefaction of biomass has recently received increased interest as a pretreatment process for gasification or as a method for producing a high density fuel as a drop-in replacement for coal. Torrefied biomass has lower oxygen to carbon (O/C) ratios and moisture contents than raw biomass, leading to higher gasification efficiency (Prins et al., 2006a). Also, torrefied biomass has an energy value comparable to low-rank coal. Many torrefaction studies had focused on different wood species (Prins et al., 2006b,c; Almeida et al., 2010; Phanphanich and Mani, 2011; Kim et al., 2012; Hill et al., 2013; Park et al., 2013) and different grass species, such as bamboo (Chen and Kuo, 2010; Wen et al., 2014), reed canary grass (Bridgeman et al., 2008), and Miscanthus (Bridgeman et al., 2010). There had also been torrefaction studies on agricultural byproducts,

such as wheat straw (Bridgeman et al., 2008; Sadaka and Negi, 2009; Shang et al., 2012), rice straw (Sadaka and Negi, 2009; Deng et al., 2009), oil palm waste (Uemura et al., 2010; Aziz et al., 2012; Sabil et al., 2013; Chin et al., 2013), sugarcane bagasse (Chen et al., 2012), and corn stover (Medic et al., 2012a,b). A previous study had also examined torrefaction of non-lignocellulose waste, such as chicken litter and sludge (Dhungana et al., 2012).

Although there had been many studies that involved torrefaction of biomass from different sources, there had been only a couple that focused on pomaces and nut shells (Pala et al., 2014; Arnsfeld et al., 2014). Pomaces are currently used in different applications, such as animal feed (tomato), pectin production (apple), or as fertilizers on crop fields (grape and olive). Also, nut shells are usually burned as fuel. In a previous study on torrefaction of pomace, Pala et al. (2014) compared hydrothermal cabonization with dry torrefaction of grape pomace. They found that hydrothermal carbonization produced samples with greater high heating values, but lower energy yields than those produced from dry torrefaction. Also, Arnsfeld et al. (2014) examined torrefaction

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of almond shells and compared their porous structures to torrefied wood. They found that shells had smaller pores than wood and these remained intact after torrefaction.

One advantage of pomaces and nut shells is that they are generated in large quantities at their processing facilities. Consequently, torrefaction of these byproducts can occur on-site, without the need to first transport them elsewhere. This should result in reduced transportation costs and lead to improved economic feasibility.

In this study, we torrefied apple pomace, almond shells, grape pomace, olive pomace, tomato pomace, and walnut shells in a muffle furnace. We used a central composite design and response surface methodology to examine the effects of torrefaction temperature and time on the mass and energy yields of the torrefied byproducts. We examined the fiber content and thermal stability of the raw byproducts using fiber analysis and TGA, respectively. We also characterized the moisture and ash contents, elemental composition, and gross calorific values of the raw and torrefied samples using TGA, elemental analysis, and bomb calorimetry, respectively.

## 2. Methods

### 2.1. Sample preparation

The apple, grape, olive, and tomato pomaces were obtained from Treetop (Oxnard, CA), Sonoma Ceuticals (Santa Rosa, CA), California Olive Ranch (Oroville, CA), and Campbell Soup (Dixon, CA), respectively. The almond and walnut shells were obtained from RPAC Almonds (Los Banos, CA) and Berkeley Bowl (Berkeley, CA), respectively. Each byproduct was dried in an oven at 55 °C for at least 24 h until it reached a steady mass value. The sample was ground and sieved (20 mesh) to produce particles less than 850 μm in size. The sample was then placed in a dessicator at room temperature (23 °C) until further use.

### 2.2. Torrefaction of byproducts

An Isotemp muffle furnace (Fisher Scientific, Philadelphia, PA) was used to perform the torrefaction tests. In each test, 3 g of byproduct was placed in an aluminum pan and the pan was placed in the furnace. The furnace was purged with nitrogen gas at a flow rate of 140 ml/min for 20 min prior to and during the torrefaction test. The furnace was then set to the torrefaction temperature. The sample temperature was monitored using a thermocouple positioned next to the sample. The torrefaction start time began once the sample temperature reached 200 °C. After the test, the sample was placed in a desiccator at room temperature for 60 min prior to the measurement of its weight.

### 2.3. Design of experiments

Response surface methodology using Minitab (State College, PA) software (version 14.12) was used to determine the effects of two factors, torrefaction temperature and torrefaction time, on mass and energy yields of the samples. The mass yield of the sample was determined by:

$$MY\ (\%) = \frac{m_{T(daf)}}{m_{R(daf)}} \times 100 \qquad (1)$$

where MY is mass yield, $m_{T(daf)}$ is mass of torrefied sample (dry and ash free), and $m_{R(daf)}$ is mass of raw sample (dry and ash free). The energy yield of the sample was determined by:

$$EY\ (\%) = MY \frac{GCV_{T(daf)}}{GCV_{R(daf)}} \qquad (2)$$

where EY is energy yield, $GCV_{T(daf)}$ is gross calorific value of torrefied sample (dry and ash free), and $GCV_{R(daf)}$ is gross calorific value of raw sample (dry and ash free). A central composite design, with three levels and five center points for a total of 13 runs, was used in the study. The torrefaction temperatures were 200 °C, 230 °C, and 260 °C for apple pomace, due to its lower thermal stability, and 230 °C, 260 °C, and 290 °C for the other byproducts. The torrefaction times were 20, 40, and 60 min for all samples. A second order model was used to fit the response surface. All possible regressions were tried and used to obtain the best fit. The response surface models were hierarchical, with all models containing the first order terms of torrefaction temperature and torrefaction time.

### 2.4. Moisture and ash contents

A TA Instruments 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 1 h under a nitrogen flow rate of 40 cm³/min. The ash content was determined by heating the sample at 750 °C for 2 h without any nitrogen flow.

### 2.5. Fiber analysis

Fiber analysis was performed according to Goering and Van Soest (1970). In summary, the sample (1 g) was refluxed in a neutral detergent solution consisting of 30.0 g dodecyl sulfate, sodium salt (Sigma–Aldrich, St. Louis, MO), 18.61 g ethylenediaminetetraacetic acid disodium dehydrate (Sigma–Aldrich), 6.81 g sodium borate decahydrate (Sigma–Aldrich), 4.56 g disodium hydrogen phosphate, anhydrous (Sigma–Aldrich), and 10.0 ml of 2-ethoxy ethanol (Sigma–Aldrich) in 1 L deionized water at 115 °C for 60 min. Two milliliter decahydronaphthalene (Sigma–Aldrich) and 0.5 g sodium sulfite, anhydrous (Sigma–Aldrich) were also added before the reflux. The sample was then poured onto a #44 filter paper (Whatman, Piscataway, NJ) placed in a filter funnel. The sample was filtered by vacuum and rinsed with hot water and acetone. The sample, filter paper, and filter were placed in an oven at 100 °C to dry overnight. The remaining residue was the neutral detergent fiber and contained hemicellulose, cellulose, and lignin. The hemicellulose component was removed from the neutral detergent fiber by reflux heating a new sample (1 g) at 115 °C for 60 min in 1 L of sulfuric acid and 20 g of hexadecyltrimethylammonium bromide (Sigma–Aldrich). The sample was then poured onto a fritted filter funnel (60 ml, 40 F) and rinsed with boiling water and then with acetone. The sample and funnel were placed in an oven at 100 °C to dry overnight. The remaining residue was the acid detergent fiber and contained cellulose and lignin. The hemicellulose content in the sample was determined by subtracting the acid detergent fiber content from the neutral detergent fiber content. The cellulose component in the acid detergent fiber was removed by washing the previous acid detergent fiber sample left in the funnel with a 72% (w/w) aqueous sulfuric acid solution. This was done 3 times over 3 h. The sample was then rinsed with hot water. The sample and funnel were placed in an oven at 100 °C to dry overnight. The remaining residue was the acid detergent lignin and contained lignin. The cellulose content in the sample was determined by subtracting the acid detergent lignin content from the acid detergent fiber content.

### 2.6. Thermogravimetric analysis

A TA Instruments (New Castle, DE) thermogravimetric analyzer (TGA) 2950 was used to characterize the thermal stability of the samples. The samples were conditioned in a 50% relative humidity chamber for at least 48 h prior to each test. Each 9–11 mg sample was heated from 30 °C to 800 °C at a rate of 10 °C/min. The sample