Physicochemical Analysis of Apple and Grape Pomaces

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This study details a comprehensive analysis of apple and grape pomaces that were generated in the course of juice and wine production, respectively. An extensive physicochemical analysis of these pomaces was performed to determine the elemental composition, ash content, sugar profile, and lignocellulose content. Scanning electron microscopy (SEM) images were taken to examine the morphology of the pomaces. Thermal stability was also examined using thermogravimetric analysis (TGA). Infrared spectroscopy was performed to observe the functional groups on the surfaces of the pomace samples. Grape pomace (GP) had better thermal stability than apple pomace (AP), but washing AP improved its thermal stability. The results from this study provide crucial information for various value-added applications of both apple and grape pomaces, especially for applications which are temperature-dependent. The diversion of these materials from waste back into the economic stream can alleviate their environmental burden and promote sustainable product development.

Keywords: Apple pomace; Grape pomace; Thermal stability

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INTRODUCTION

Fruits and vegetables are the fundamental raw materials of the food processing industry. Wastes called pomaces or marc (if processed for juice or oil) are often produced in large quantities after processing and represent a huge economic and environmental burden for the industry and society. Although the exact amount of food waste produced per year is unknown, it is widely accepted that food waste is an important issue and should be reduced (Garcia *et al*. 2016). The industry is, therefore, in constant search of novel applications for these materials.

Apple pomace (AP) biomass is generated during apple cider and juice production; it is a combination of the seeds, flesh, skin, and occasionally stem material from the apple. Large quantities of AP are produced annually. It was estimated in the 2016 growing season that over 64 million tons of apples were grown world-wide (WAPA Association 2018), an amount which has since increased. Ontario, Canada produced 108,000 tonnes of apples in 2017 (OMAFRA 2018). Approximately 30% of all apples produced are used for the production of juice, apple sauce, or cider (U.S. Apple Association 2018). By weight, approximately 30% of an apple is considered a waste product, which results in large amounts of waste as a by-product (Vendruscolo *et al.*

2008). AP is composed mainly of cellulose, hemicellulose, lignin, and pectin (Guerrero *et al*. 2014). AP will begin to oxidize immediately after processing (Bhushan *et al*. 2008); therefore, the uses of AP are limited. Oxidation causes the change in color of the pomaces. Fermentation occurs by microorganisms consuming the available sugars. Thus, oxidation and fermentation are the main issues related to the reduction in quality of pomaces. Fermentation produces a pungent odour and degrades valuable compounds within the sample. The fermentation begins immediately after processing and progresses rapidly. Therefore, proper storage and/or fast transportation of the material to the processing centers are important considerations to preserve the valuable compounds or fibrous material within the sample. Drying the material or storing at sub-zero temperatures are widespread methods to delay oxidation and fermentation

Grape pomace (GP) is the biggest by product of the wine industry. Worldwide, approximately 50 to 60 million tons of grapes were used to produce wine in 2017 (70% to 75% of the total production of grapes, worldwide); and in Ontario, Canada, 89,000 tonnes of grapes were produced (Garcia-Lomillo and Gonzalez-SanJose 2017; OMAFRA 2018). Approximately 20% to 25% of all wine manufacturing results in GP (Dwyer *et al*. 2014). GP contains the skin, seeds, and stems of the wine grapes; it is composed of cellulose, hemicellulose, pectin, sugars, and low amounts of protein, lipids, and polyphenolics (Jiang *et al*. 2011). When improperly disposed, GP can cause serious and negative environmental impacts. Usually wineries have limited disposal options due to high fees and transportation costs. Although research has been done on extracting chemicals in economically viable and safe ways, alternative uses of pomaces should be explored.

In general, if the quality of the pomaces deteriorates, they will be sent to a landfill or left on site to decompose. Therefore, research aimed at the manufacturing of value-added products based on pomaces or chemical derivatization through biorefining is required to divert these materials from waste streams. Previous studies have been completed with various pomaces to produce value-added products. Apple pomace, for example, has been treated to extract pectin (Yates *et al.* 2017) and phenolic compounds (Bhushan *et al*. 2008). Apple pomace has been modified to enhance its nutritional value for use as a feedstock (Vendruscolo *et al*. 2008). Similarly, GP lacks the high amounts of nitrogen required for use as a suitable fertilizer, and it is only used is small quantities as animal feed (Dwyer *et al.* 2014). The skin of GP after pressing still contains high quantities of phenolic compounds, antioxidants, and fiber. The stem contains tannins, while the seeds are a potential source for the production of oil as well as fiber (Garcia-Lomillo and Gonzalez-SanJose 2017). Furthermore, GP can also be considered for the derivatization of energy, which can be obtained through thermo-chemical processing or pyrolysis—yielding gaseous, liquid, and solid fuels and/or novel materials including bio-based plastics (Cáceres *et al*. 2012; Toscano *et al*. 2013).

The development of sustainable composite materials has been at the forefront of polymer engineering research for the last two decades (Mohanty *et al*. 2000; Muthuraj *et al*. 2017). Composites are fabricated from bio-based plastics in combination with novel natural fillers (NFs). Natural fillers act as reinforcing agents within the matrix material to improve the mechanical properties of the composite blends. Many types of NFs have been investigated for these purposes, such as perennial grasses (Muthuraj *et al.* 2017), bamboo (Lee and Wang 2006; Chattopadhyay *et al*. 2011), hemp, and flax (Murdy *et al*. 2015). To date, however, there has been limited attention given to wastes generated by the food processing industry, such as apple, tomato, and grape pomaces. However, some research has been done on using fatty acids from tomatoes to create polymers (Benítez *et*

al. 2018; Tedeschi *et al*. 2018). Based on the chemistry of these materials and reliable/constant supplies, fruit and vegetable pomaces offer substantial potential as cellulosic materials in composites (Mohanty *et al*. 2000). The use of these post-industrial waste materials in composite applications offers a green alternative to synthetic fillers or fibers and contributes to a "circular economy" (Ellen MacArthur Foundation 2017).

This study featured the physicochemical analysis of apple and grape pomaces. The physical structures of the samples were also observed *via* scanning electron microscopy (SEM). Chemical analyses performed on the pomaces include: ash content, pH, sugar profiles, and lignocellulose tests. Fourier transform infrared spectroscopy (FTIR) was used to determine the surface functionality of the samples. The thermal stability of the pomace materials was determined *via* thermogravimetric analysis (TGA). This analysis was performed to determine the viability of the samples for applications such as polymer processing. More in specific terms, this work provides fundamental information for the processability of AP and GP in thermal applications. AP and GP are abundantly available at limited to no cost, and we strongly believe that these materials would function well as a natural filler source in composites applications. Therefore, this work intends to bridge the knowledge gap on the usability of pomaces such that these fibrous materials could be used successfully in polymer processing. Furthermore, the extensive physicochemical analysis provides essential information, which is fundamental for understanding any kind of physical or chemical derivatization that the pomaces could be potentially used for. The elemental composition provides an idea of the energy stored within the material; suggesting that the pomaces could be used as low or no cost sources of energy or they could be converted to biochar/biocarbon for further industrial applications

EXPERIMENTAL

Materials

The AP used in this study was produced after the extraction of apple juice and was provided by Martin's Family Fruit Farm Ltd. based in Waterloo, Ontario, Canada. Normally, apple pomace is composed of various varieties of apples. The sample studied here included a blend of Northern Spy, MacIntosh, Empire, Gala, and Ambrosia varieties. Samples of AP were frozen after juice production to prevent oxidation. The juicing process takes fresh apples, presses then, and the remnants are discarded as biomass immediately. Oxidation of apple is commonly noted as a brown discolouration and slight acidic smell. Two different treatments of one sample of AP were used in this study. The first was used as received and the second was washed, as described below. GP was obtained from Andrew Peller Winery, Grimsby, Ontario, Canada. GP contains various amounts of different types of grapes, including: Cabernet Franc, Baco Noir, Cabernet Sauvignon, Merlot and Pinot Noir ("Andrew Peller Limited" 2018). This GP sample had a dark brown colour with a purple tinge, which is to be expected for such a material. It was generated from red wine making. This means that this sample, unlike AP, was fermented during the wine making process to extract readily available sugars and compounds. The as received material was quite dry and did not possess any odour, suggesting limited further fermentation of the sample. Both samples contained fruit skin, stem, seeds and flesh materials and were initially prepared following the same seven steps outlined below, some AP material was set aside and washed as outlined below.

Methods

Pomace preparation

Samples of both AP and GP were air dried prior to commencement of physicochemical analysis. Both AP and GP samples were stored for a short time before received. The AP had a noticeable odour and colour change, which could be indicative to fermentation taking place. This was not observed with the GP. Both pomaces were air dried at 23 °C (to save on energy and costs associated with drying). Fresh AP samples were also given to compare the sugar profiles between fresh and aged AP.

Air drying consisted of the following steps: 1) the AP and GP were spread out as evenly as possible inside a fume hood to increase the exposed surface area, to ensure maximal drying surface exposure; 2) the samples were hand tossed as frequently as possible to increase aeration within the sample and promote a more even rate of drying; 3) moisture content was recorded every day to track changes; 4) the pieces of pomace were processed in a Fritsch Universal Cutting Mill (Pittsboro, NC, USA) to reduce size of material if necessary; 5) once samples met a moisture content of 15%, they were dried in a Hotpack commercial oven (Philadelphia, PA, USA) at 80 °C to reduce the moisture further; 6) at approximately 3% moisture, AP and GP samples were ground with a Retsch GmbH ZM 200 Grinding Mill (Haan, Germany) with a 1 mm sieve at 6000 RPM; 7) finally, the sample were placed in 80 °C oven until they reached a final moisture content of about 2 %. Moisture contents of less than 10% are sufficient to preserve most of the fibrous materials. In this case, a final moisture content of ~2% was chosen as the optimal level of drying for long term storage; considering the sugars' content, and a level which did not require excessive energy for drying. Furthermore, the samples were inherently hydrophilic and complete removal of moisture is not possible, as a low percentage of water in the pomace is bound water and therefore quite difficult to remove.

The AP samples were split into two groups; washed and unwashed, which will be referred to as WAP and UAP, respectively. The AP was washed to increase its thermal stability as suggested by previous work (Zarrinbakhsh *et al.* 2011). Washing the samples removes free sugars and low molecular weight compounds that thermally degrade at lower temperatures. This is discussed further in the TGA analysis of the samples. The WAP followed the same process as the UAP until reaching step 6. Afterwards 250 g of apple pomace was immersed in 1 L warm water, stirred for 10 min, vacuum filtrated and ground, as the washing process caused agglomeration. The WAP was then dried at 80 °C in an oven.

Moisture content

Moisture contents of AP and GP were measured after oven drying using a Sartorius AG Moisture Analyzer (Gottingen, Germany). An average sample size of 5 g was placed on an aluminum tray and subjected to infrared radiation at 105 °C in the automatic mode.

Elemental analysis

Elemental analysis was performed to determine the carbon, nitrogen, hydrogen, and sulphur content of the samples. A CHNS Elemental Analyzer by Thermo Fisher Scientific (Waltham, MA, USA) was used along with 2,5-bis(5-tert-butyl-2-benzo-oxazol-2-yl) thiophene (BBOT) as a standard. An average of three 2.5 mg samples of BBOT, AP, and GP were taken. Samples were placed into tin foil wrappers, rolled

tightly, and placed in the machine under pyrolysis conditions (inert atmosphere) at 950 °C for 12 min per sample.

Lignocellulose test and sugar profile test

There are two major methods for determining the fiber content of a lignocellulosic material. The first is acid detergent fiber (ADF), which is used in most commercial applications and includes the determination of the cellulose and lignin fractions. Total fiber content of a biomass can also be determined through neutral detergent fiber (NDF), a method that measures all contents of the plant cell wall: the cellulose, hemicellulose and lignin. This method looks at the bulk of the biomass and its ability to act as a filling fiber in bovine feedstock (Beauchemin 1996). Chemical analysis of the AP and GP were performed by the SGS laboratories in Guelph, Ontario, Canada. The ADF test was performed in accordance with (AOAC Official Method 973.18 (2005). The NDF test was performed in accordance to ANKOM Technology Method 13 (2015) using amylase and sodium sulphite and is further described in literature (Van Soest *et al.* 1991). Likewise, the free sugars such as glucose, fructose, sucrose, maltose, and lactose were measured through sugar profile testing completed by SGS labs at a subsidiary laboratory location (Burnaby Lab, Burnaby, British Columbia, Canada) *via* (AOAC Official Method 982.14 (1983).

Ash content

The ash content of the pomace was determined using a Thermo Fisher Scientific Lindberg Blue M vacuum oven (Waltham, MA, USA). Three small ceramic crucibles were filled with approximately 3 g of sample. Testing was performed according to ASTM E1755-01 (2000). First, the moisture content was recorded from the AP and GP samples, and the samples were then heated to 525 °C and held at temperature for 3 h. Final weights were obtained and recorded (ASTM Commitee E48 2000).

pH of pomaces

The pH values of the AP and GP samples were taken using a Mettler-Toledo Automatic Titrator (Greifensee, Switzerland). Calibration before testing was performed by using known buffer solutions with pH values of 4, 7, and 10 from North Central Laboratories (Birnamwood, WI, USA). Samples of 4 g of pomace were mixed with 40 mL of distilled water and were then loaded in the titration trays. When measuring the pH, each sample was subjected to a voltage measurement with a glass probe while experiencing constant stirring for 40 s. This process is a modification to ASTM D1512-15b, Standard Test Methods for Carbon Black-pH value (2015), as there was no specific standard for pH of biomass materials (ASTM Committee D24 2016).

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed in accordance with ASTM E1131-08 (2014) using a Q500 from TA Instruments (New Castle, DE, USA). Approximately 10 mg of AP and GP were placed into a platinum pan starting at room temperature (23 °C) and heated to 800 °C at a temperature ramp rate of 10 °C/min under a nitrogen atmosphere. The tests were repeated, and results produced both thermogravimetric (TG) and derivative thermogravimetric (DTG) curves. The data were analyzed using TA Instruments Software, Version 4.5A, Universal Analysis 2000 (New Castle, DE, USA).

Fourier transform infrared spectroscopy (FTIR)

AP and GP samples were pressed flat onto the diamond crystal surface of a Fourier transform infrared-attenuated total reflectance (FTIR-ATR) Nicolet 6700 machine by Thermo Fisher Scientific (Waltham, MA, USA). The analysis was performed to investigate functional groups present within the samples by plotting transmittance *versus* wavenumber in the range of 4000 cm^{-1} to 400 cm^{-1} with 64 consecutive scans at a resolution of 4 cm^{-1}.

SEM

The Phenom-World BV ProX Scanning Electron Microscope (Eindhoven, Netherlands) collected the back-scattering electrons to generate images. The SEM images of dried and ground AP and GP pomace (after step 7) were taken at 10 kV acceleration voltages with magnification between 500 and 1000 times. The samples were uncoated, due to the charge-reduction fixture of the microscope.

RESULTS AND DISCUSSION

Elemental Analysis

The elemental compositions of unwashed apple pomace (UAP) and washed apple pomace (WAP) are displayed in Table 1. Small differences occurred between unwashed and washed samples. This result was anticipated, as the materials were roughly the same. The only difference was the removal of small molecular weight compounds and water-soluble compounds during washing. Carbon was the most abundant element, at 46.73% w/w and 48.77% w/w for UAP and WAP, respectively. The second most abundant element was oxygen at 45.69% w/w and 43.21% w/w for UAP and WAP, respectively. Hydrogen was the next most abundant element at 6.43% w/w and 6.57% w/w, followed by nitrogen and sulphur at 1.12% w/w and 1.41% w/w and 0.03% w/w and 0.04% w/w for UAP and WAP, respectively. These results are similar to those found in previous studies (Mason *et al*. 1985; Verma *et al*. 2011; Guerrero *et al*. 2014). Slight differences can be attributed to different species of apples and environmental conditions.

The elemental composition of GP is shown in Table 2. The most abundant element found in the grape pomace was carbon, 54.0% w/w, followed by oxygen 37.85 %w/w and hydrogen at 6.08% w/w. The amount of nitrogen was 1.99% w/w, and traces of sulphur were found at 0.08% w/w. The data for hydrogen and nitrogen were similar to those reported in other studies, suggesting that, despite the grape sources and various environmental conditions, these values remain almost constant (Mason *et al*. 1985; González-Vázquez *et al*. 2017; Mäkelä *et al*. 2017; Botelho *et al*. 2018; Khiari and Jeguirim 2018). However, sulphur content was slightly lower than in the other studies, and carbon was slightly greater than in the other studies.

The elemental composition of pomace samples is of importance for their potential applications. For example, upon analysis of pomace samples, farmers can tailor the use of fertilizers and the growing conditions for optimizing crop yields. As noted in previous reports, carbon, hydrogen, and oxygen are supplied from the air and water (irrigation and rain), while nitrogen and sulfur are provided from fertilizers (McKenzie 1998). Elemental composition is also important for determining the applicability of biomass/pomace material as a fuel source (Verma *et al*. 2011).

Table 1. Organic Elemental Analysis of AP and Comparison with Literature (Nitrogen, Carbon, Hydrogen, Sulphur, and Oxygen Content of AP in %w/w)

Element (% w/w)	UAP	WAP	(Guerrero *et al*. 2014)	(Mason *et al*. 1985)	(Verma *et al*. 2011)
C	46.73	48.77	47.98	44.56	48.80
H	6.43	6.57	6.65	6.18	6.50
O*	45.72	43.25	37.44	44.78	43.0
N	1.12	1.41	0.78	0.42	1.70
S	0.03	0.04	ND*	0.05	ND*
* O (% w/w) = 100 – [H (%w/w) + C(%w/w) + N(%w/w)] (Verma *et al*. 2011)					

Table 2. Organic Elemental Analysis of GP and Comparison with Literature (Nitrogen, Carbon, Hydrogen, Sulphur and Oxygen Content of GP in % w/w)

Element (% w/w)	GP	(Mason *et al*. 1985)	(González-Vázquez *et al*. 2017)	(Mäkelä *et al*. 2017)	(Botelho *et al*. 2018)	(Khiari and Jeguirim 2018)
C	54.0	52.74	45.5	48.7	51.1	42.2
H	6.08	7.21	5.1	5.57	6.7	3.5
O*	37.93	35.59	34.7	35.9	40.1	37.7
N	1.99	1.51	1.8	1.66	1.9	3
S	0.08	0.23	0.17	ND*	0.2	0.3
* O (% w/w) = 100 – [H (%w/w) + C(%w/w) + N(%w/w)] (Verma *et al*. 2011)						

Lignocellulose Content

Acid detergent fiber is used to measure the majority components of a plant cell wall, in this case composed of cellulose and lignin. Neutral detergent fiber measures all components of a plant cell wall: cellulose, lignin, and hemicellulose (Beauchemin 1996).

Apple pomace had ADF values of 30.5% and 43.4% for UAP and WAP, respectively (Table 3). The NDF values were 40.5% and 54.8% for UAP and WAP, respectively. Unwashed apple pomace had lignin, cellulose, and hemicellulose contents of 18.9%, 11.6%, and 10.0%, and WAP had lignin, cellulose, and hemicellulose contents of 29.2%, 14.3%, and 11.4%. Overall, the lignocellulose results of AP samples were quite variable among the results from previously completed work and from this study. There was a relative higher fiber content in the WAP samples because of the removal of impurities, removing the non-cellulosic components during the washing process as well as a relatively large proportion of the ash (Dinand *et al.* 1996). Therefore, a higher weight percent of the remaining material was fiber for the washed samples. Coherently, the UAP contained more free constituents, which reduced the overall weight percentage of fiber in the samples as there was more material present to compare to. For GP, the ADF content was 42.4%, and the NDF content was 48.5%. Individual measurements showed a lignin content of 31.9%, while the cellulose content was 10.5%, and hemicellulose was 6.1% (Table 4). Other researchers found lignin contents of 32.5% ± 2.1% w/w and cellulose contents of 20.8% w/w (no distinction made between hemicellulose and cellulose) for Cabernet Sauvignon pomace (Corbin *et al.* 2015). The cellulose content of the grape pomace was lower when compared to other raw plant materials such as grasses or trees, which had cellulose values around 35% to 40% (Ververis *et al*. 2004). However, the AP in this study was more within the ranges reported in studies of other biomasses. In contrast, the lignin amounts in both samples were on the higher limit of what is typically

found in raw plant materials, with values ranging from 14% to 30% (Ververis *et al*. 2004).

Table 3. Lignin, Cellulose, and Hemicellulose Contents of AP Compared to Previous Studies

Material (%)	UAP	WAP	(Wang and Thomas 1989)	(Nawirska and Kwaśniewska 2005)	(Guerrero *et al*. 2014)	(Gullón *et al*. 2007)
Acid Detergent Fiber (ADF)	30.48	43.42	25.31	64.0	72.21	34.0-43.5
Natural Detergent Fiber (NDF)	40.50	54.80	29.20	88.4	99.98	54.0-73.4
Lignin	18.92	29.16	8.87	20.4	24.72	13.8-17.1
Cellulose	11.56*	14.27*	16.44	43.6	47.49	20.2-26.4
Hemicellulose	10.00**	11.37**	4.09	24.4	27.77	20.0-29.9
*Calculated as (ADF – lignin); **Calculated as (NDF – ADF)						

Table 4. Lignin, Cellulose, and Hemicellulose Contents of GP Compared to Literature

Material (%)	GP	(Moldes *et al*. 2007)	(Gómez-Brandón *et al*. 2011)	(Corbin *et al*. 2015)	(Vaccarino *et al*. 1987)
Acid Detergent Fiber (ADF)	42.38	74.9	69.2	ND	63.2
Natural Detergent Fiber (NDF)	48.5	82.9	76.1	ND	ND
Lignin	31.9	56.7	51.7	32.5	37.9
Cellulose	10.5*	18.2	17.5	20.8***	25.3
Hemicellulose	6.1**	8.0	6.9		ND
* Calculated as (ADF – lignin), **Calculated as (NDF – ADF), ***No distinction between cellulose and hemicellulose					

The amount of lignocellulosic material in biomass samples, determined through ADF and NDF test methods, was very important to quantify. For example, the content of these fibrous materials needs to be quantified to determine the validity of the pomace as a feedstock source based on the amount of usable energy available (Beauchemin 1996). Furthermore, the amount of fibrous material present in the samples is important to know when developing polymer composites. The fibrous content of biomass material is very important in polymer engineering when choosing sustainable natural filler, because fiber content impacts the mechanical properties of composites (Muthuraj *et al*. 2015). The filler not only reduces the cost of the polymer, but it improves mechanical performance and increases the bio-content/sustainability of polymer blends (Nagarajan *et al*. 2013; Muthuraj *et al*. 2015). For example, the impact strength of composites is often improved with the presence of fiber since this reinforcing phase is used to transfer the impact force more evenly throughout the matrix in the final composite material (Gowman *et al*. 2018).

Sugar Profile

The sugar content of AP is shown in Table 5. A comparison of WAP and UAP was made to determine the effects of fermentation (digestion of sugars within the samples) as well as the effects washing of both. Washing samples removed water-soluble

compounds as expected (Zarrinbakhsh *et al.* 2013). The sugar profile validated the stage of fermentation of the samples, which was responsible for the acidic pH and odour. It was noted from this study and confirmed in literature that fructose was the most prevalent sugar in apple pomace sample as compared to glucose, sucrose, maltose, and lactose (Wang and Thomas 1989; Zupan *et al.* 2016; Persic *et al.* 2017).

The sugar content of GP is less investigated than that of AP. The sugar content of GP is highly variable (Table 6). The variability in sugar content of GP samples resulted from use of the sugars within the wine-making process. Many red wine samples require fermentation of GP such that the sugars are digested in the process. The length of the fermentation would also affect the residual sugar content in the samples. Furthermore, different cultivars would impact the remaining sugar content in the samples. It was also likely that oxidation took place for GP samples during improper storage.

The amount of free sugars in the sample is important for applications in polymer fabrication. As noted in the thermogravimetric analysis below, the free sugars of the samples decrease the thermal stability during processing (Zarrinbakhsh *et al.* 2013). However, synthesis of other value-added products from pomace benefit from increased sugar content. For example, GP was used a substrate for enzymatic degradation of sugars by various fungi to produce bulk chemicals. The free sugars in the samples act as a food source for the microorganisms (Botella *et al.* 2005).

Table 5. Free Sugar Content of AP Compared with Previous Studies

Sugar (%)	Aged UAP	Aged WAP	Fresh UAP	Fresh WAP	AP (Wang and Thomas 1989)	AP (Zupan *et al.* 2016)	AP (Persic *et al.* 2017)
Fructose	3.9	1.4	31.3	17.9	21.85	6.06	3.25
Glucose	2.7	0.9	12.6	8.6	10.55	1.98	0.76
Sucrose	<0.2	<0.2	11.3	6.1	4.39	2.41	1.26
Maltose	<0.2	<0.2	<0.2	<0.2	ND	ND	ND
Lactose	<0.2	<0.2	<0.2	<0.2	ND	ND	ND
Total Sugars	6.6	2.2	55.2	32.6	36.71	10.44	5.27

ND = not determined

Table 6. Free Sugar Content of GP Compared to Previous Studies

Sugar (%)	GP	(Corbin *et al.* 2015)	(Valiente *et al.* 1995)	(Korkie *et al.* 2002)
Fructose	<0.2	2.5 ± 0.8	ND	2.4
Glucose	<0.2	2.1 ± 0.7	14.01 ± 0.58	0.26
Sucrose	<0.2	ND	ND	ND
Maltose	<0.2	ND	ND	ND
Lactose	<0.2	ND	ND	ND
Total Sugars	<0.2	ND	ND	ND

ND = not determined

Ash Content

Ash content measures the amount of inorganic compounds present in a material, the remainder will be mostly minerals. The pomace ash was white grey and uniform in colour and composition for both AP and GP samples. The ash content of AP was 3.57% ± 0.51% for UAP and 1.26% ± 0.27% for WAP. Table 7 shows ash content for other samples of AP. The ash content obtained in this study was within the range of 1.5% to

4.01% as noted from previous studies (Mason *et al*. 1985; Gullón *et al*. 2007; Guerrero *et al*. 2014). The ash content of the GP, also found in Table 7, was 4.65% ± 0.43%. Previous works determined an ash content for wine-derived grape pomace of 4% at a moisture content of approximately 7% (Botelho *et al*. 2018). Cabernet Sauvignon pomace possessed an ash content of 3.0% ± 0.8% w/w (Corbin *et al*. 2015). Another study found an ash content of GP of 6.1% (Park *et al*. 2010). The AP and GP used in this study had similar ash contents to those of previous studies and to each other, as expected. Although environmental conditions and cultivar of apple or grape may differ, the species remains the same, so the values should be similar (Campbell and Sederoff 1996). Furthermore, the ash contents obtained for both GP and AP in this work were within the range of other raw plant materials such as miscanthus, switchgrass, kenaf, and olive tree, with a range of 1.5% to 5% ash (Ververis *et al*. 2004).

Table 7. Ash Content of AP and GP

Sample	Source	Ash (%)
AP	UAP	3.57 ± 0.51
AP	WAP	1.26 ± 0.27
AP	Guerrero *et al*. (2014)	3.40
AP	Gullón *et al*. (2007)	1.5-1.7
AP	Mason *et al*. (1985)	4.01
GP	GP	4.65 ± 0.43
GP	Vaccarino *et al*. (1987)	6.4 ± 0.07
GP	Miranda *et al*. (2011)	7.47
GP	Tseng and Zhao (2012)	5.57
GP	Mason *et al*. (1985)	2.72

Ash content is important to study for composite processing and fuel sourcing. In work by Park *et al*. (2010), high ash content in grape pomace composites decreased the flexural properties of composite blends due to processing difficulties and binding adherence problems. Ash content of pomace/biomass samples for fuel sources is important to investigate, as the production of ash can cause problems in boilers or other equipment and raise environmental concerns (Vamvuka and Kakaras 2011).

pH of Pomaces

pH is the measure of acidity or basicity of an aqueous solution. The pH of the WAP and UAP were similar with values of 3.81 and 3.69, respectively (Table 8). In general, the samples exhibit an acidic pH. The slightly lower pH obtained for UAP was attributed to the fermentation process. It is well known that weak acid-like compounds are produced during the fermentation process; thus the washed samples were less acidic due to the removal of free acidic compounds during the washing. However, the concentration of acidic compounds depends on the stages of ripening of the fruit and on the possible fermentation. Hang *et al*. (1982) fermented AP and found no change in the pH after fermentation; therefore, it is reasonable that the pH values of UAP and WAP remained similar. In other words, the pH in the apple pomace can also be related to the ripening effect of the fruit at the moment of processing, which is a reflection of the concentration of sugars as well as acidic natural compounds present in the remnants of the fruit.

The pH of the grape pomace was 4.24, which again is very close to those reported in the literature. These slight differences could be attributed to the stage of ripening of the fruit, or even environmental differences (climate, sunshine, soil, growing conditions, water availability, *etc.*), which could make the grapes less acidic resulting in variations of sugars and acidic compounds contents.

The pH is important to study for various applications if the pomace is used as a value-added material. For example, the pH of pomace samples is less important for polymer processing, but it would be important for applications such as baking (Masoodi and Chauhan 1998; Masoodi *et al.* 2002), solid state fermentation (Albuquerque *et al.* 2006), and fertilizer (Moldes *et al.* 2007), to give a few examples.

Table 8. pH Content of AP and GP Samples

Sample	Source	pH
AP	WAP	3.81 ± 0.01
AP	UAP	3.69 ± 0.02
AP	Albuquerque *et al*. (2006)	4.0
AP	Joshi and Sandhu (1996)	4.2
AP	Dhillon *et al*. (2013)	3.5 ± 0.1
GP	GP	4.24 ± 0.01
GP	Moldes *et al*. (2007)	3.8
GP	Deng and Zhao (2011)	3.65
GP	Licciardello *et al*. (2015)	3.4 ± 0.05

Thermogravimetric Analysis

Depending on the intended application of either pomace material, thermal stability could be an important property. For example, if either pomace is to be used as NF within a plastic matrix, it is important to ensure the pomace is thermally stable to withstand processing temperatures and to avoid degradation of the NF (Zarrinbakhsh *et al*. 2013). Typical polymer processing temperatures range from 160 °C to 250 °C for commodity plastics and engineering plastics, so it is important to determine if the filler can be included if processed at these temperatures (Zarrinbakhsh *et al*. 2016). The thermal stability of the pomaces can be seen in the figures below. Figure 1 shows the TG graph, which shows the mass loss of the pomace as temperature increases, while Fig. 2 shows the DTG graph, showing the rate at which mass loss occurs. The first mass loss, noted by a mild slope of the TG curve, can be attributed to water evaporation, as the moisture contents of the AP and GP were both at approximately 2%.

All samples showed a smooth curve, indicating that the samples experienced decomposition while forming gaseous products (Widmann 2001). The GP showed the best thermal stability compared to both apple samples. The temperature at 5% weight loss was 171 °C for GP and 113 °C for unwashed pomace. Once the AP was washed, this temperature increased to 209 °C. The UAP started degrading at low temperatures due to the presence of low molecular weight components. The WAP sample showed improved thermal stability compared to the unwashed sample (Fig. 1). The temperature at 50% weight loss was 396 °C for GP, 321 °C for UAP, and 341 °C for WAP.

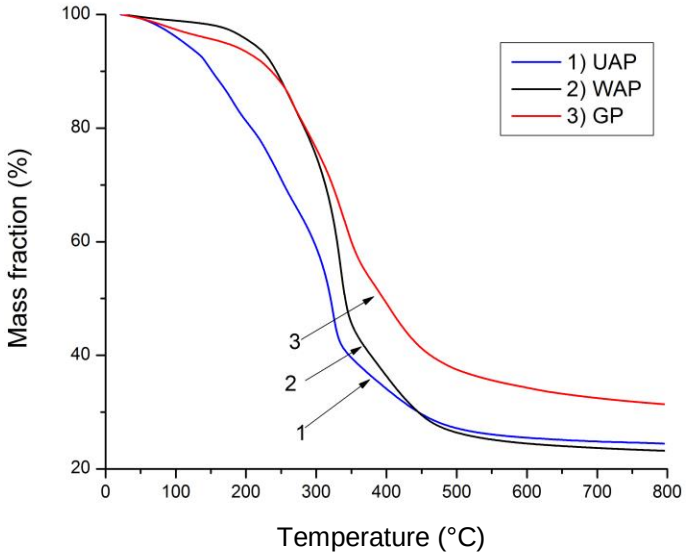

Fig. 1. Thermogravimetric analysis curve (TG) displaying the mass fraction remaining for samples of WAP, UAP, and GP

The onset degradation temperatures are best seen in Fig. 2. There are three distinct peaks characteristic to the degradation of hemicellulose, cellulose, and lignin, which are present in all pomace samples. The UAP had some additional peaks present, which may be attributed to the presence of lower molecular weight oxidative products (such as glucans and xylans) that were removed after washing (Zarrinbakhsh *et al*. 2013, 2016). The first peak present was due to the hemicellulose component degrading; it was seen at 267 °C for GP, 147 °C to 248 °C for UAP, and 260 °C for WAP. The cellulose component degraded at 340 °C, 324 °C, and 335 °C for AP, UAP, and WAP, respectively.

Lignin degrades over a range of temperatures, and this was seen starting at 378 °C, 365 °C, and 383 °C onwards for GP, UAP, and WAP, respectively. Yang *et al*. (2007) showed similar results with hemicellulose degrading at 268 °C and cellulose at 233 °C, with lignin degrading over a range of temperatures starting at ambient temperature and up to 900 °C. The values Yang *et al*. (2007) reported are similar to the values obtained for AP and GP.

Other researchers have found hemicellulose and cellulose degrading from approximately 160 °C to 500 °C, while lignin degraded over a range of 362 °C to 500 °C for GP (Khiari and Jeguirim 2018). Furthermore, the last peak of the DTG curve in the range of 375 °C to 500 °C was found in GP and AP samples and in other biomass samples such as distiller's grains (Zarrinbakhsh *et al*. 2011). According to previous studies, this peak is a result of the degradation of protein. Finally, the rightmost portions of the TG and DTG curves occur due to the slow loss of mass of higher molecular weight constituents (Kumar *et al*. 2008; Zarrinbakhsh *et al*. 2013).

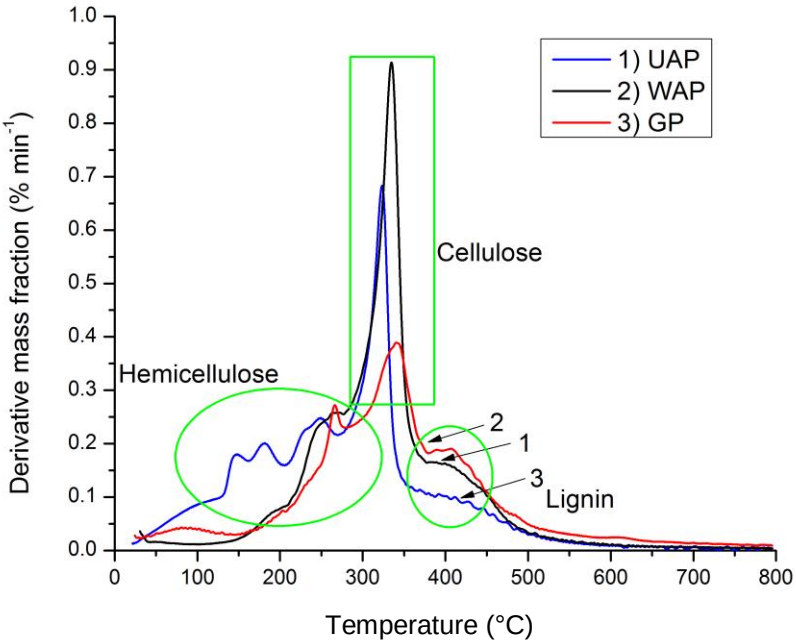

Fig. 2. Thermogravimetric analysis curve for derivative weight (DTG) of WAP, UAP, and GP

Fourier Transform Infrared Spectroscopy

The FTIR spectra of WAP, UAP, and GP are shown in Fig. 3. All samples show a broad peak from around 3000 cm^{-1} to 3600 cm^{-1}, which relates to the O-H and N-H bonds stretching, present in lignocellulose components of both pomace materials (Zarrinbakhsh *et al*. 2016). The peaks present around 2850 cm^{-1} and 2920 cm^{-1} in all the samples are attributed to both symmetric and asymmetric stretching of C-H bonds.

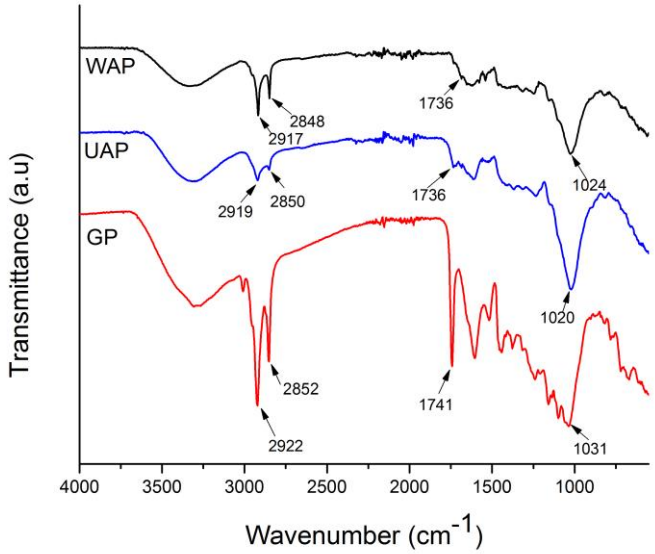

Fig. 3. FTIR spectra for samples of Washed Apple Pomace (WAP), Unwashed Apple Pomace (UAP), and Grape Pomace (GP)

Similar peaks have been reported in previous studies around 2920 cm^{-1} and are attributed specifically to the C-H in the lignin components (Xu *et al*. 2009). The peak around 1740 cm^{-1} is associated with the stretching absorption of carbonyl (C=O) along with the two previously mentioned peaks, relating to the ester group of a triglyceride in fat (Gordon *et al*. 1997; Cremer and Kaletunç 2003). Triglycerides are present in biomass/food samples (Guillén and Cabo 1997; Zarrinbakhsh *et al*. 2013). These bands have also been attributed to cutin, a material present in the plant cuticle (Heredia-Guerrero *et al*. 2014). As mentioned above, C=O peaks in the range of 1700 cm^{-1} to 1800 cm^{-1} and can also be a result from the C=O in hemicellulose and lignin (Zarrinbakhsh *et al*. 2013). The peaks in the range from 1200 cm^{-1} to 800 cm^{-1} were from the vibrations between C-O in the water-soluble components. Furthermore, the peaks at 1024 cm^{-1}, 1020 cm^{-1}, and 1031 cm^{-1} for WAP, UAP, and GP, respectively, may be a result of the vibrations of C-6 of cellulose (Pastorova *et al*. 1994; Zarrinbakhsh *et al*. 2013).

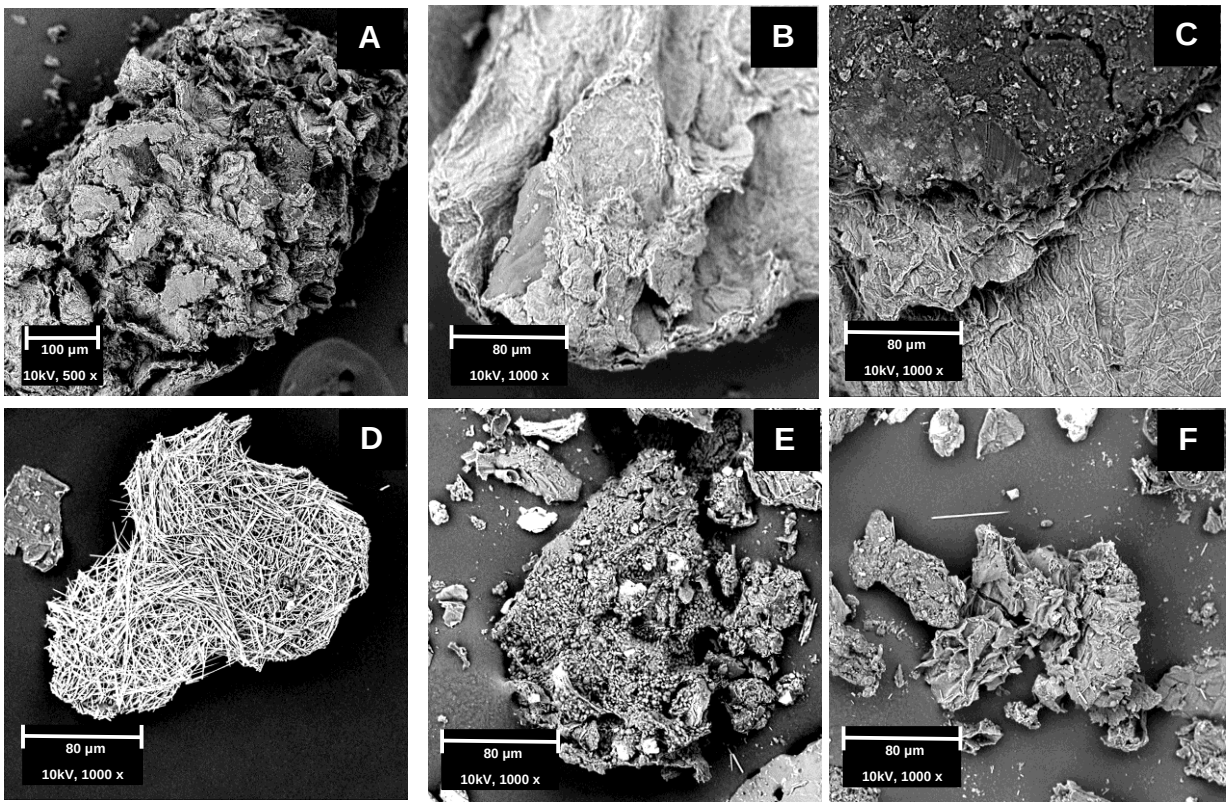

Fig. 4. Various geometries of particles found in UAP (A to C) and GP (D to F) samples

SEM

Scanning electron microscope images were taken to observe surface morphology and relative geometry of the particles present in AP and GP samples. WAP images were not included because they had the same visual appearance as UAP. The AP and GP each contained three distinct surface morphologies. Apple pomace surface morphologies and geometries are noted in Fig. 4: The structure was more porous and circular (A), the sample was flatter with noticeable gaps between (B), and there were tight distinctive layers of fibrous material (C). Likewise, GP also contained different structures, as shown

in Fig. 4: straw-like fibrous materials (D), round globular materials in combination with fibrous structures (E), and small fibrous and compact samples (F).

As noted in previous studies, the porous structure found in AP samples may be attributed to the hemicellulose structures. Furthermore, the tightly packed fibrous structures of the AP can be attributed to the strong internal bonds in the fibers (Gouw *et al*. 2017). The pomace consisted of flesh, apple skin, and seeds. The three different images below of the AP may be attributed to the different components. For example, the skin on an apple is flat and fibrous in nature, whereas the flesh is far more porous. The seeds are also fibrous but are much harder and irregular. Therefore, there are various surface geometries present in the AP samples prior to drying and milling, and the major structures are displayed below.

The image of GP in Fig. 4F is similar to that found in previous studies. According to Pala *et al*. (2014), the flat surface of the sample is attributable to the lignocellulose fibrous materials. Again, the grape consisted of seeds, flesh, and some stem material. The stem material is assumed to be very fibrous in nature. The skin of the grape is much flatter but became quite irregular upon drying of the materials. The seeds of the grapes were also quite irregular and much harder than that of the skin material. The large surface morphologies result in different fibrous or porous structures, as shown in the SEM images. Examination by SEM is helpful for various applications, including use of the pomace materials as NF in polymeric materials.

CONCLUSIONS

1. Food waste is an economic and environmental burden and must be repurposed. Apple pomace (AP) and grape pomace (GP) offer significant potential in the development of value-added and sustainable products.
2. Based upon physicochemical analysis, AP and GP contain significant amounts of lignocellulosic materials that can serve as viable materials in value-added products. Based upon ADF, NDF, and lignocellulose analysis, the fiber present in pomace samples may support applications such as natural fillers in polymeric composites.
3. Overall, GP is thermally stable for most applications; however, AP requires washing to enhance thermal stability for temperature-dependent applications. For all other applications of AP and GP, it is important to be aware that the samples will ferment until the drying process is completed, and this must be considered.

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