Industrial Crops and Products 101 (2017) 92–102

Contents lists available at ScienceDirect

Industrial Crops and Products

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

Overcoming the caking phenomenon in olive mill wastes

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ARTICLE INFO

Article history:
Received 19 September 2016
Received in revised form
28 November 2016
Accepted 26 February 2017

Keywords:
Orujillo
Olives
Caking
Comminution
Differential scanning calorimetry
Glass transition step

ABSTRACT

The use of olive mill wastes (*orujillo*) within coal fired power stations in the UK has led to unexpected difficulties with material caking within the fuel handling plant. This study replicated orujillo caking on a laboratory scale using a planetary ball mill and explored the impact of mill parameters (speed, volume, and duration) on the caking phenomenon. The impact of orujillo composition was examined for 4 sections of fresh and dried orujillo (whole, pulp 0–850 μm, pulp 850–3350 μm, and cluster 3350 μm+) for set milling conditions. Caking was induced by heat generation within the mill and was most prevalent in the pulp section of orujillo. Caking was brought on by a glass transition step, which was measured to be around 97–98 °C for a moisture content of 6–7% in a differential scanning calorimeter (DSC). Caking was the result of the bulk moisture content (14–18%) being higher than the standard moisture content of orujillo (<12%), and can be mitigated through drying. Thus the key to overcoming orujillo caking in fuel handling plants is through moisture content control. Additionally, as the caking issue is most prevalent in the pulp section, all fines below the required combustion particle size (typically <1 mm) should be removed prior to comminution and sent directly to the burner. This would also reduce the comminution load by nearly 50%, increase the energy potential of the fuel, and remove the most problematic section of orujillo from the fuel handling plant.

1. Introduction

Biomass co-firing and conversions offer a near term low cost solution for reducing emissions from conventional fossil fuel power plants. Agricultural residues offer a plentiful supply of material for combustion (Daioglou et al., 2015) and biodiesel (Hernández et al., 2014), and include olive mill wastes, which are often disposed of in landfill (Paraskeva and Diamadopoulos, 2006). However the agglomeration and caking of olive mill wastes in fuel handling plants of power stations is a limiting factor in its viability as a combustion fuel. This paper replicates the caking of olive mill wastes on a laboratory scale, investigates the reasons behind it, and strategies to overcome the problem.

By 2100, it has been projected that there will be an additional theoretical global bioenergy potential of 20-50 EJ/yr from agricultural residues (Daioglou et al., 2015). In Spain, 2625 ktoe/yr of primary energy could be sourced from agro-industrial residues, primarily from olive mill and wood processing residues (Gómez et al., 2010). Over 75% of global olive oil production originated from Europe in 2013–2014, with over 70% of this coming solely from Spain (International Olive Council, 2015). In Spain, the two-phase continuous centrifugal olive oil extraction system is used in approximately 90% of olive mills (Dermeche et al., 2013). In this system, the olive paste is separated into two phases; olive oil and wet pomace known as "alperujo", which is a semi-solid combination of olive husk and olive mill waste water. Alperujo is usually treated with a secondary centrifugation to extract the residual oil (Alburquerque et al., 2004), and the resulting by-product is dried and subjected to chemical extraction in order to maximise the oil yield. The resulting dry waste from this solvent extraction is known as "orujillo", is free of oil and usually contains 10–12% moisture content (Ollero et al., 2002). At present, there is no European legislation regulating the disposal of olive mill wastes (Rodrigues et al., 2015). Current disposal practices include landfill disposal, discharge into nearby rivers, lakes or seas and storage/evaporation in lagoons. However this has led to soil contamination and high phytotoxicity, water body pollution, underground seepage, and problems with offensive odours (Goula and Lazarides, 2015; Paraskeva and Diamadopoulos, 2006). Due to the respectable higher heating value of olive mill wastes (17–19 MJ/kg) (Álvarez et al., 2015; Williams et al., 2015),

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http://dx.doi.org/10.1016/j.indcrop.2017.02.036
0926-6690/

one method of reusing the waste is as a fuel for electricity generation (Oktay, 2006; Roig et al., 2006).

Caking can be defined as a deleterious transformation of low moisture, free flowing powders into an agglomerated solid, firstly as lumps, and ultimately as a solid sticky material, resulting in loss of material quality and function (Aguilera et al., 1995). Caking is a common issue in food, fertiliser, and pharmaceutical industries (Gabbott, 2008; Palzer, 2011; Roos, 2010), and is now being experienced with orujillo in power generation fuel handling systems. The caking rate of a powder will depend on the instantaneous moisture content and the ambient temperature and humidity, with the material's glass transition temperature being the most representative parameter of this transition (Boonyai et al., 2004). Moisture acts as an extremely good plasticiser in dried foods, and can reduce the glass transition temperature to room temperature, decrease viscosity, and result in caking (Lazou and Krokida, 2011; Roos, 2010). The glass transition temperature of the olive mill waste water is moisture dependent. The glass transition occurs around 56 °C for 9% moisture content, and reduces towards freezing as the moisture content increases (Goula and Adamopoulos, 2013). While the drying of orujillo has been investigated for bioenergy purposes (Casanova-Peláez et al., 2015; Christoforou and Fokaides, 2016; Goula et al., 2015), the caking and glass transition behaviour of orujillo has not been explored in literature. The present study explores the mechanisms of orujillo caking in relation to mill settings and material composition by replicating the phenomenon on a laboratory scale in a planetary ball mill. In addition, analytical techniques were used to examine the thermal properties of orujillo. This paper provides insight into the causation of orujillo caking and practical approaches to overcoming the issue in power generation fuel handling systems.

2. Materials and methods

Orujillo has routinely been co-combusted up to 10% by weight with coal at EDF Energy plc pulverised fuel coal fired power station at Cottam in Lincolnshire, UK, for several years through a semi-direct injection system. Orujillo is milled separately in a hammer mill and then pneumatically injected into the coal pulverised fuel stream, and the coal and orujillo are then co-combusted in the boiler. Orujillo caking has led to blockages in the fuel handling system, with the resultant cake proving difficult to remove, resulting in significant operational downtime for system repairs. The caking of orujillo has been replicated in two laboratory scale mills. In a preliminary study in the planetary ball mill, the caking of fresh orujillo was replicated with the severity of caking being influenced by the mill speed, fill volume, and milling duration (Williams et al., 2013). Orujillo caking was also observed in a laboratory scale ring-roller mill, which resulted in the formation of a solid cake, and subsequently in mill overload and failure of the mill bed motors (Williams et al., 2016). In order to explore the mechanisms behind the caking effect, a full study was formulated to investigate orujillo caking on a laboratory scale. The study characterised the orujillo to establish its composition and thermal behaviour, and two sets of experimental trials were conducted in a planetary ball mill to establish the influence of environment and material composition on the caking effect. The study focuses on the use of orujillo in moisture and temperature conditions experienced in industrial processing rather than on moisture treated samples.

2.1. Materials

Spanish *orujillo* (olive cake) was provided by EDF Energy plc. Orujillo exhibits a seasonable variance of up to 8% in moisture content due to its external storage in Spain prior to shipping to the UK. Orujillo is classed as "chemically untreated fruit residues, crude olive cake (class 3.2.1.4)" according to BS EN 17225-1:2014 (The British Standards Institution, 2014).

2.2. Moisture content

Moisture content was measured in accordance with BS EN 14774-1:2009 (The British Standards Institution, 2009). 300 ± 1 g of orujillo was dried in a Thermo Scientific Heraeus UT 6 forced-air oven at 105 ± 2 °C for 24 h. After drying the weight of the sample was recorded and used to calculate the moisture content of the sample; each sample was tested in triplicate. The dried orujillo used in the milling tests were dried under the same conditions, and then placed in zip-lock sealed bags until use. To analyse the moisture re-adsorption of orujillo in atmosphere, 100 g ± 1 g of orujillo was dried according to BS EN 14774-1:2009 and then placed on a Ohaus Pioneer PA4102c balance for 24 h. The weight was logged via a laptop using the Ohaus Data Acquisition Software at 10 s intervals over a 24 h period in an air conditioned laboratory. To analyse the moisture re-adsorption of orujillo in sealed storage, 100 ± 1 g of orujillo was dried to BS EN 14774-1:2009 and then stored in zip-locked bags and weighed. After 6 days the moisture increase was found by weighing the samples and zip-lock bags again and noting the increase in mass.

2.3. Sieving

Particle size distributions were determined by sieving for the pre-milled and milled product in accordance with BS EN 15149-2:2010 (The British Standards Institution, 2010). The samples were sieved into 16 size fractions (4750, 3350, 2360, 1700, 1180, 1000, 850, 600, 425, 300, 212, 150, 75, 53, 45, 38 μm sieves). Sieving was conducted on a Retsch AS200 Control vibratory sieve shaker in two stages. In the first stage, 8 coarse sized sieves (4750–600 μm) were used, and in the second stage, 8 finer sieves (450–38 μm) were used. Each sieving stage was conducted for 15 min at a 3 mm amplitude.

2.4. Rosin-Rammler distribution analysis

The Rosin-Rammler distribution equation was originally developed to describe the distributions of coal fines from coal mills (Rosin and Rammler, 1933), and it is often used to describe the particle size distribution of comminuted biomass (Bitra et al., 2009a; Gil et al., 2012). The Rosin-Rammler equation is defined as:

$$R(d) = 100\left(1 - e^{-\left(\frac{d}{d'}\right)^{n}}\right) \quad (1)$$

where R is cumulative percentage mass undersize (%), d is particle diameter (μm), d' is the characteristic particle size (μm) and corresponds to the 63.2% cumulative distribution particle undersize value ($1 - 1/e = 0.632$), and n is the Rosin-Rammler size distribution parameter (dimensionless). A lower value of n means a lower slope and thus a wider distribution and higher diversity of the particles sizes. The Rosin-Rammler parameters were obtained with the Matlab® GUI Tool developed by Brezáni and Zelenak (Brezáni and Zelenak, 2010) using a non-linear curve fitting technique.

2.5. Thermogravimetric analysis

The thermal composition of orujillo was obtained by using a TA Instruments Q500 Thermogravimetric Analyser (TGA). TGA runs used 10–15 mg of milled sample with a particle size range of 75–300 μm, and used the method developed by Lester et al. (Lester et al., 2007) for analysing the composition of biomass. The sample was heated in a Nitrogen atmosphere with a flow rate 100 ml/min, a heating rate of 5 °C/min from room temperature to 900 °C, after which the gas was switched to air and held isothermally at 900 °C. The composition of the samples is given by moisture, dry ash free volatile, fixed carbon, and dry ash contents.

2.6. Differential scanning calorimetry

Heat flow analysis was conducted on a TA Instruments Q10 Differential Scanning Calorimeter (DSC). DSC is an established method of analysing the glass transition temperature of materials (Perinović et al., 2010), and is an indicator of a material's stickiness (Boonyai et al., 2004). 10-15 mg of fresh sample with a particle size range of 75–300 μm was placed in an aluminium pan and equilibrated at −50 °C. It is then heated at 10 °C/min to 150 °C in Nitrogen flowing at 50 ml/min. The results were analysed in the Universal Analysis Software (Version 4.5A, TA Instruments) and the glass transition temperature (T_g) was taken as the inflection point of the specific heat decrement at the glass transition on the second heating scan.

2.7. Replicating the caking phenomena in laboratory conditions

A Retch PM100 planetary ball mill was used to explore the role of environment and material composition on orujillo caking. The planetary ball mill has a 500 ml stainless steel milling bowl and eight 30 mm diameter stainless steel balls, and a 0.75 kW drive unit, with total power draw of 1.25 kW. The input energy consumed was measured directly by the planetary ball mill unit (Retsch Gmbh, 2012). The specific effective energy consumption (E_e) was obtained by taking the energy input value measured by the mill (E_I), and dividing by the sample mass, m, and is expressed as:

$$E_e = \frac{E_I}{m} \tag{2}$$

A FLIR T400 thermal imaging camera was used to qualitatively investigate the impact of the heat generated during the milling process. A temperature scale of 18.5–50 ± 0.1 °C was used for all images, and the images were taken immediately after the milling process completed. All milling trials were repeated in triplicate and all samples were split using a riffle box prior to testing to ensure that a representative sample was used.

2.7.1. Impact of mill settings on the caking phenomena

The impact of changing 3 mill parameters on fresh orujillo was examined in the planetary ball mill. The mill was operated at 200 RPM for 100 ml (70 g) of orujillo for 10, 20, 30, 40, and 50 min. Immediately after milling, thermal images of the milling bowl, milling balls and comminuted sample were taken to ascertain the temperature rise during the milling process. The impact of speed on temperature was examined for a set time and volume. The mill was operated for 60 s for 100 ml of orujillo at 100, 200, 300, 400, 500, and 600 RPM and in the same fashion as described previously, thermal images again were taken. Finally the impact of volume was analysed for a fixed time of 60 s over a speed range of 200, 300, 400, 500, and 600 RPM for 100 ml (70 g) and 200 ml (140 g) of sample. The initial sample mass (m_a), and the loose mass (m_b) in the milling bowl after milling, were recorded for each test. The caking effect was quantified through the percentage loose mass (m_l) available after milling, defined as:

$$m_l = 100 \cdot \left(\frac{m_b}{m_a}\right) \tag{3}$$

The loose material contained some partially caked material, and the percentage loose mass available provides an indication of the severity of the caking effect. A low percentage of loose mass indicates that the majority of the sample had caked and stuck to the milling bowl, while a high percentage of loose mass indicates that most of the sample had not experienced severe caking.

2.7.2. Impact of material on the caking phenomena

In order to investigate if any specific section of orujillo showed a greater propensity to caking, a riffled sample was split into the constituent sections, and the tendency to cake in individual or combined sections was investigated. 100 ml (70 g) of each of the four sets of orujillo (whole, pulp, pip, and clusters) were milled at 300 RPM, for 3 min to ascertain the impact on specific effective energy consumption, particle size, heat generation and caking for each section. In order to investigate the impact moisture played in the tendency to cake, the same test was conducted on dried orujillo sections. The Von Rittinger relationship was used to relate the specific effective energy consumption with particle size reduction, and to assess how drying affected the caking and grindability of each section. Milling theories relate the energy consumption and product particle size obtained from a given feed size. Rittinger's first theory of comminution states that "*The energy required for size reduction is proportional to the new surface area generated*" (von Rittinger, 1867), and is expressed as:

$$E_e = K\left(\frac{1}{d_2} - \frac{1}{d_1}\right) \tag{4}$$

where E_e is the specific effective energy (kWh/t), K is the constant characteristic for the material and is obtained by the ratio of the specific effective energy and the particle size change, d_1 is the 80th percentile feed passing size (μm), and d_2 is the 80th percentile product passing size (μm).

3. Results

3.1. Composition of orujillo

The pre-milled particle size distributions of fresh and dried orujillo are shown in Fig. 1. Both the fresh and dried orujillo were found to be a composite material composed of three distinct sections: a 0–850 μm pulp section, an 850–3350 μm pip section, and a 3350+ μm pellet and self-formed clusters section. This can be traced back to the original composition of the olive fruit. Olive fruits are made of two components (Kailis and Harris, 2007); a stone where the lignin is concentrated and correlates with the pips section of the orujillo (850–3350 μm in Fig. 1), and the outer pulp or flesh where the hemicellulose and cellulose is concentrated and correlates to the pulp section (0–850 μm in Fig. 1). This is distinctly different to woody biomasses that have a low density, cellular polymeric composite of hemicellulose, cellulose, and lignin (Dinwoodie, 2000), giving it a single mode distribution commonly seen in milling studies (Bitra et al., 2009b; Gil et al., 2012). The presence of the self-formed lumps in the orujillo, which were between 3 mm and 40 mm in diameter, indicates that the first stages of caking are being initiated during storage (Aguilera et al., 1995). Clusters which were too large to pass through the riffle box (12 mm gap) were not included in testing.

The moisture content of the fresh orujillo was found to be 17.9 ± 0.04% for the whole section, with the constituent parts having 17.1 ± 0.07% for the pulp section, 14.6 ± 1.31% for the pip section, and 16.6 ± 0.06% for the cluster section. The moisture contents were higher than the typical moisture contents of orujillo of 10–12% (Ollero et al., 2002). Moisture and oil are concentrated in the pulp section of olive fruits (Kailis and Harris, 2007), and thus the moisture content of the pulp section is expected to be higher than the pip section. In the moisture reabsorption tests, orujillo gained 2.1% increase in mass when left exposed in average atmospheric conditions of 21 °C and 50% relative humidity over 24 h. In contrast, the dried orujillo stored in zip-locked bags showed a mass increase

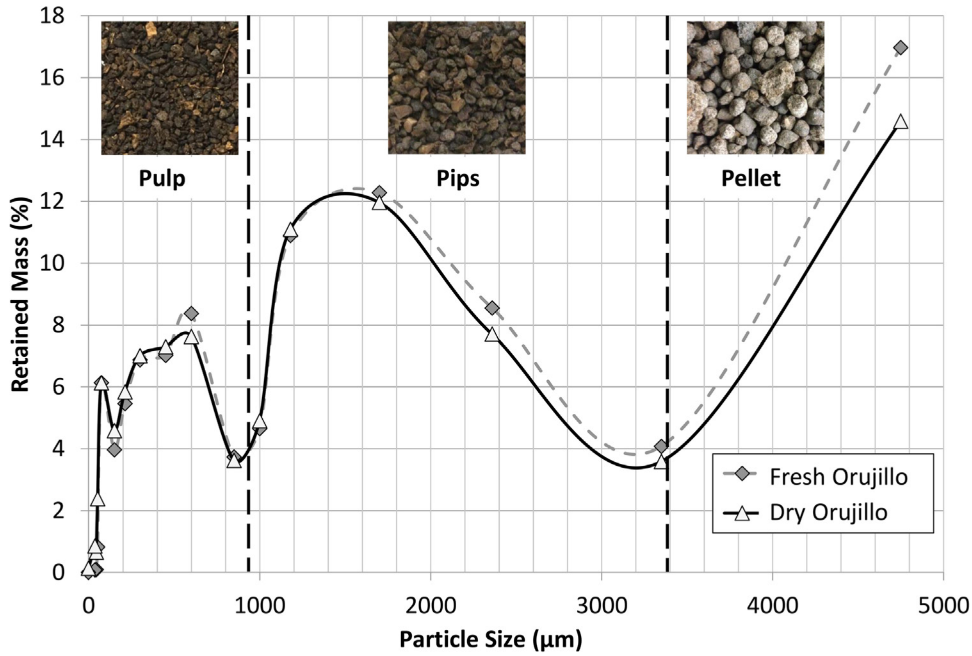

Fig. 1. Tri-modal structure of fresh and dried orujillo obtained by sieving.

of 0.3% over 6 days. Thus for the dried milling trials, the dried samples were stored in zip locked bags and were taken as dry at the point of use. This method of storing samples to maintain moisture content prior to testing has been used in several other studies (Castellano et al., 2015; Larsson et al., 2013; Rudolfsson et al., 2015). Prior to drying, the overall mass composition of orujillo was: 42.6% pulp, 40.5% pip and 16.9% cluster; after drying it was: 46.1% pulp, 39.3% pip, and 14.6% clusters. Drying did not substantially change the mass composition of the orujillo.

The dry higher heating value of the orujillo was previously found to be 19.3 MJ/kg (Williams et al., 2015), which corresponded to similar values for olive cake in literature (Demirbas, 2004). Table 1 shows that the thermal composition of orujillo is similar for all sections. The pulp section has the highest ash (9.52%) and volatile (71.69%) content, and lowest fixed carbon content (18.79%). In contrast the pip section had the lowest ash (8.20%) and volatile (70.78%) content, and highest fixed carbon content (21.02%). The whole and cluster sections were between the values obtained for the pip and pulp sections, which is to be expected as they are composites of the pulp and pip sections.

3.2. Glass transition in orujillo

Fig. 2 shows the DSC heat flow characteristics of the fresh whole, pulp, and pip orujillo sections. The heating scans illustrate how moisture impacts the heat flow characteristics of the orujillo sections. There is a large endothermic dip (negative direction) at around 60 °C for all the fresh samples, which is related to moisture release, after which it rises exothermically (positive direction) and starts to level out around 120 °C. The fresh pulp section exhibits a strong exothermic-endothermic shift on the first heating scan between 85 and 100 °C. A comparable but less pronounced inflection is also present for the whole and pip sections at similar temperatures. On the second heating scan, the glass transition was observed at 97.6 °C for the pulp section, 97.8 °C for the pip section, and 97.4 °C for the whole section. The moisture content of the samples tested in the DSC was between 6.5% and 7.7% for all three samples (Table 1), indicating that the glass transition occurs at almost identical temperatures for all sections for a similar moisture content.

3.3. Impact of mill settings on orujillo caking

A typical example of caking within the mill is illustrated in Fig. 3. The olive cake starts as a loose powder of varying particle sizes (Fig. 1), and planetary ball milling involves a sample being comminuted via high impact centrifugal compression fracture mechanisms induced by rotating the milling bowl and balls at high speeds. For orujillo however, this process results in the formation of a solid hard cake within the milling bowl that is stuck to the sides of the bowl and balls (Fig. 3), which was not observed for other biomasses tested within this mill (Williams et al., 2016).

The post-test temperature profiles in the milling duration tests show that for varying milling durations, moderate escalation in heat was observed. With increased duration this was exacerbated (Fig. 4). However the severity of caking was found to be significantly more sensitive to varying mill speed than milling duration. A significant temperature increase was observed with higher speeds (Fig. 5), particularly for speeds over 400 RPM. When comparing the impact of each variable, a milling duration of 50 min at 200 RPM produced similar temperature profile to that obtained by operating the mill for 60 s at 500 RPM. Thus the thermal images in Fig. 4 and 5 illustrate that speed has a greater impact on heat generation within the mill than milling duration.

The mill bowl fill volume was also found to influence the caking effect. Fig. 6 shows how the specific effective energy increases in a similar power relationship with mill speed for 100 ml and 200 ml fill volumes. Greater energy consumption is observed for the 100 ml fill volume compared to the 200 ml fill volume. The energy recorded by the mill is a function of the current drawn by the motor to maintain the set speed of the mill, and higher fill volumes result in less space for the milling balls to gain momentum, and thus there will be less resistance on the motor drive and less current will be drawn. There is a dramatic increase in caking for speeds over 300 RPM for 100 ml, and at 200 RPM for 200 ml, as the percentage loose mass drops off significantly (Fig. 6). Once speeds exceed 400 RPM, less than 10% loose mass was recovered for both volumes. Fig. 6 indicates

Table 1
Thermal composition by percentage mass of fresh orujillo sections.

Section	Moisture%	Dry Ash%	Fixed Carbon%	Dry Ash Free Volatiles%
Fresh Whole Milled	6.64	9.43	19.63	70.94
Fresh Pulp Milled	7.22	9.52	18.79	71.69
Fresh Pips Milled	7.73	8.20	21.02	70.78
Fresh Clusters Milled	7.86	8.93	20.07	71.00

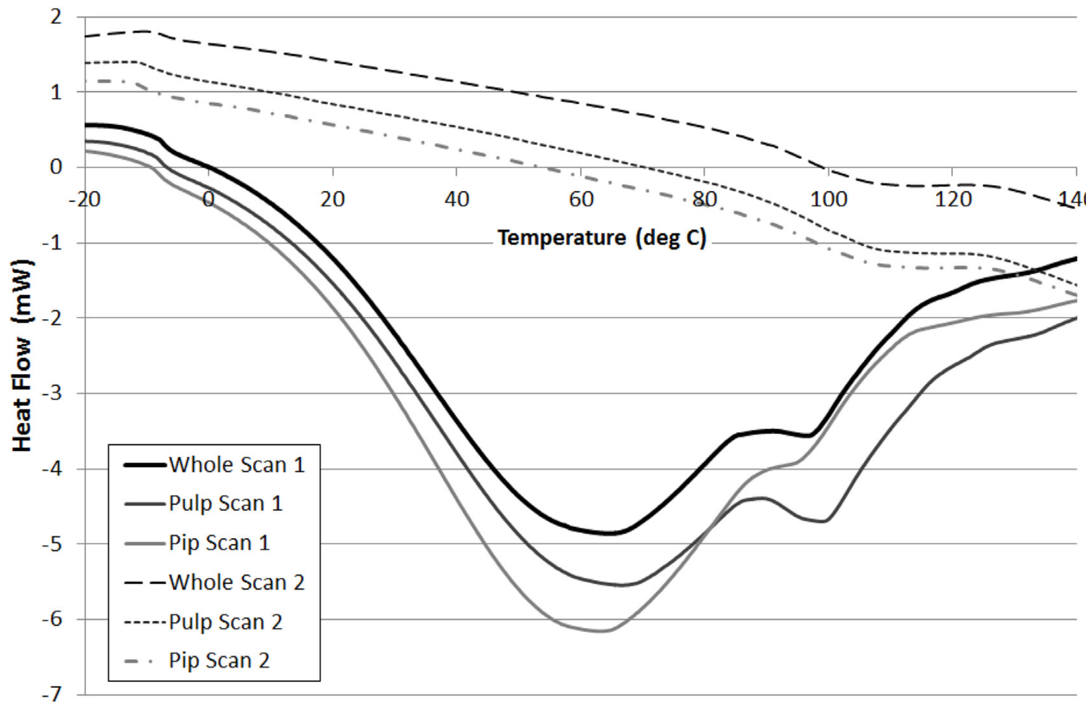

Fig. 2. First and second heat flow DSC curves for fresh orujillo.

Fig. 3. Caking phenomena replicated in planetary ball mill with orujillo caking on mill balls and bowl (left) and enlarged image section showing caking of orujillo (right).

that although higher fill volumes result in lower specific effective energy consumption, they also result in a reduction in the loose mass available after milling. When larger volumes were tested, the resultant cake comprised of a solid hard top layer, with a loosely compacted softer layer beneath. This indicates that the material which was in contact with the milling balls caked, and trapped the rest of the material beneath it, resulting in a compacted layer at the base of mill bowl, and hence the lower percentage loose mass for the higher fill volumes. Thus caking is more pronounced for higher fill volumes and speeds, while lower speeds and fill volumes result in reduced compaction and caking.

3.4. Impact of orujillo composition on the caking phenomena

While heat generation and the associated temperature rise within the planetary ball mill has been demonstrated to induce

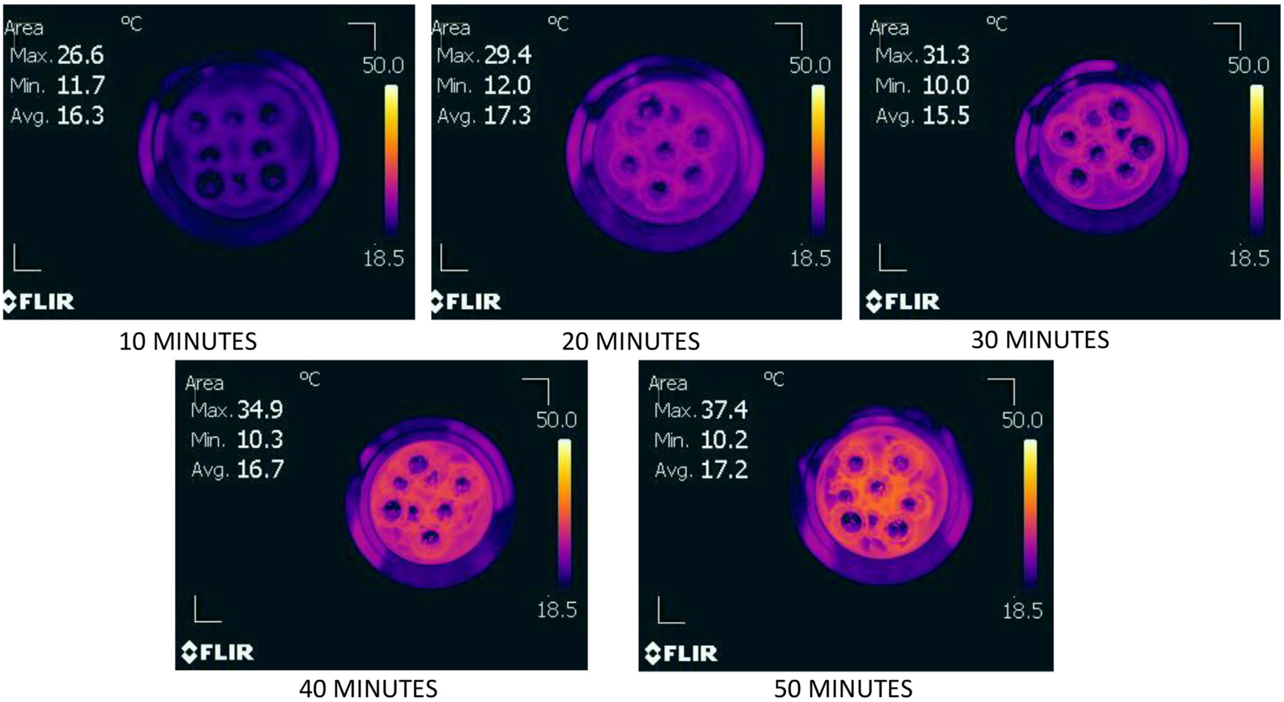

Fig. 4. Thermal imaging of temperature profile in orujillo milled in a planetary ball milling at 200 RPM for 10–50 min.

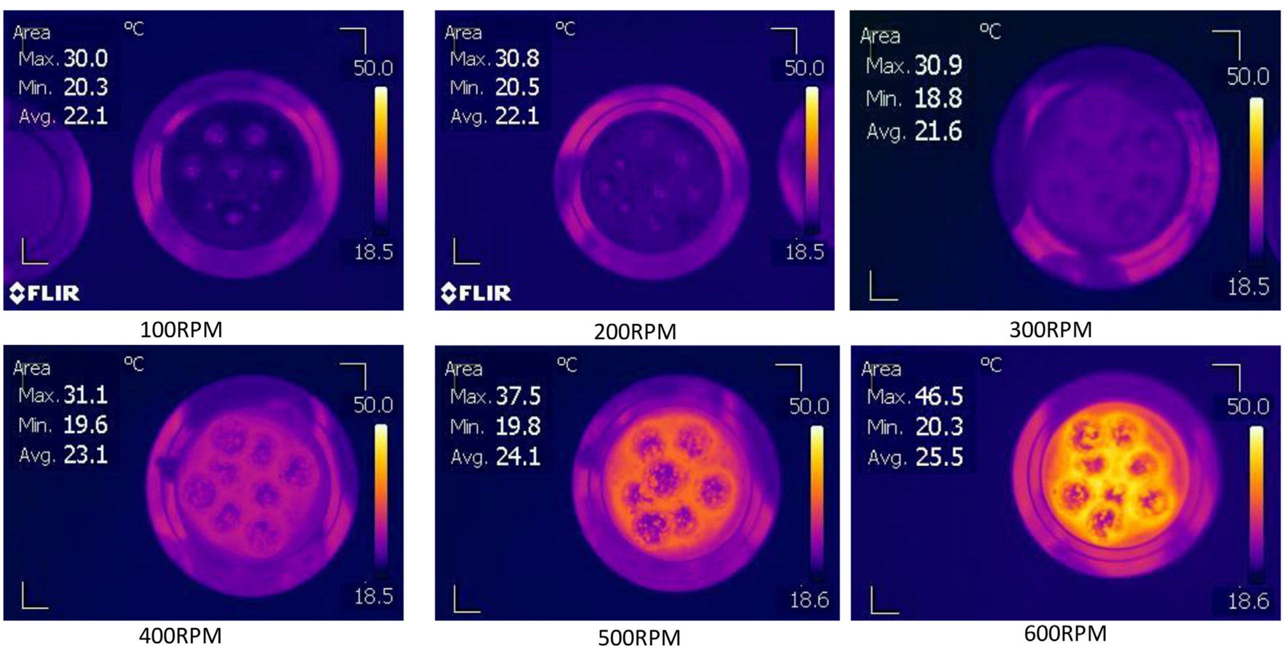

Fig. 5. Thermal imaging of temperature profile in orujillo milled in a planetary ball milling for 60 s at 100–600 RPM.

the caking of orujillo, the influence of the material composition was not established. The mill specific effective energy consumption (E_e) was found to vary by orujillo section, and was dependent on moisture content (Table 2). For the fresh trials, the lowest E_e was recorded in the pulp section (19 ± 0.79 kWh/t), and the highest in the pip section (29 ± 0 kWh/t). The cluster and whole sections E_e lay in between the pulp and pip, which was expected as they are a mix of the pulp and pip sections. When the pulp was dried, it had the highest E_e of all the sections (39 ± 1.39 kWh/t), over double its fresh value. The dried whole portion had the lowest energy consumption (33 ± 1.37 kWh/t), but its variance was within the values of E_e for the dried pip (34 ± 1.15 kWh/t) and cluster sections (35 ± 1.96 kWh/t).

The tendency to cake also affected the milled particle size distribution of the orujillo. Fig. 7 shows the pre-milled and milled fresh and dried whole orujillo section particle size distributions. There is a large difference in the milled particle size distributions for the fresh and dried orujillo despite the similarity in the fresh and dried pre-milled distributions. The dried orujillo produces a much finer particle size, with the 80th percentile particle size (d_{80}) being over three times larger for the fresh sample (d_{80} 1812 μm) compared to the dried (d_{80} 539 μm). No caking was observed for

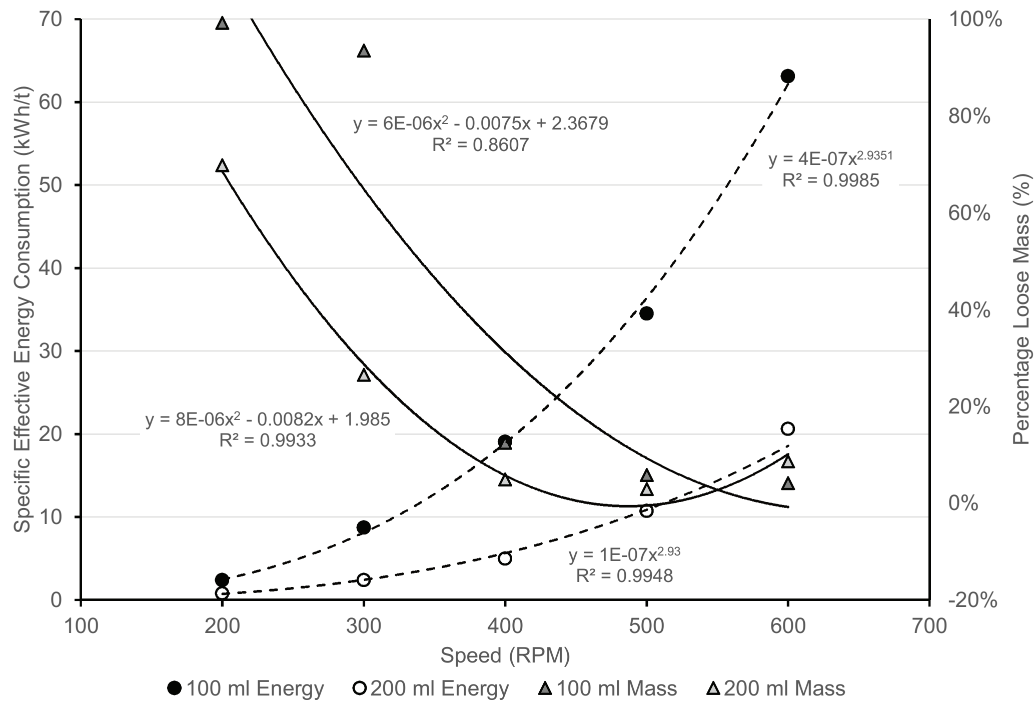

Fig. 6. Impact of varying speed and volume on specific effective energy consumption and percentage loose mass of orujillo milled in a planetary ball mill for 60 s.

Table 2
Particle size characteristics, specific effective energy E_e, and Von Rittinger constant for fresh and dried orujillo sections.

Sample	Percentage Loose Mass Available After Milling (%)	Rosin-Rammler			d_{80} (μm)	Specific Effective Energy E_e (kWh/t)	Von Rittinger's Constant (K)
		d' (μm)	n	R^2			
Fresh Whole	–	2105	0.89	0.998	4093	–	–
Dried Whole	–	1760	0.86	0.998	3020	–	–
Fresh Whole Milled	5.1	1048	1.02	0.998	1812	22.21	6.1
Dried Whole Milled	100	369	1.18	0.997	539	32.56	54.4
Fresh Pulp Milled	1.3	998	0.96	0.994	1969	19.09	−21.5
Dried Pulp Milled	100	138	1.79	0.993	188	38.79	138.6
Fresh Pips Milled	99.38	625	1.03	0.996	1012	29.23	18.8
Dried Pips Milled	100	799	1.13	0.999	1223	34.42	15.5
Fresh Clusters Milled	89.0	654	1.13	0.995	1055	22.43	16.0
Dried Clusters Milled	100	329	1.30	0.995	478	35.14	62.4

the dried sample, and all the dried samples had 100% loose mass after milling (Table 2). However as Fig. 8B illustrates, the heat generation in the dried sample was significantly higher. The specific heat capacity of biomasses is known to be temperature and moisture dependent, and generally increases linearly with moisture and temperature, thus higher moisture contents in biomass will result in a lower temperature rise (Dupont et al., 2014). While dried olive pomace has a specific heat capacity of 1.345 kJ/kg K, the stainless steel milling balls have a specific heat capacity of approximately 0.502 kJ/kg K. Thus the thermal mass of the biomass is small compared to mill balls, and the milling ball temperature rise represents the heat generated in the system uniformly across all tests. Thus Fig. 8 indicates that there is a higher heat generated for the dried samples compared to the fresh samples.

When the analysis of the particle size distributions of all the sections are compared (Table 2), the pulp section shows the most dramatic change in behaviour through drying. Its fresh d_{80} was 1969 μm, but drying reduces d_{80} by an order of magnitude to 188 μm. After milling, 37.89% of the milled fresh pulp section was above the pre-milled top size of 850 μm and only 1.3% of the mass was loose after milling (Table 2). This increase in particle size is indicative of extreme caking in the pulp section, which is evident in Fig. 8C. The pulp has completely caked and has formed a compressed layer on the sides of the bowl and stuck to the milling balls. However when dried, the caking disappeared and all the comminuted material was available as loose mass (Table 2). Furthermore, the milled pulp section had the finest particle size distribution (d_{80} 188 μm) and the highest transfer of energy to heat as indicated by the elevated temperature of all the sections (Fig. 8D). The pip section showed a different trend to the pulp section as the particle size distribution was slightly coarser after drying (fresh d_{80} 1012 μm, dried d_{80} 1223 μm). Caking was observed for the fresh sample (Fig. 8E) and only 5.1% of the mass was loose after milling, but as with the other sections, drying eliminated the caking effect (Fig. 8F). Higher heat generation was also noted in the dried state, which suggests that pips become harder with drying and thus harder to mill, resulting in the coarser particle size distribution. The cluster section showed the same trend as the pulp and whole sections, with much finer particle size distributions after milling (Fresh d_{80} 1055 μm, dried d_{80} 478 μm). Thus along with heat generation, moisture can be seen to be a key factor in the caking of olive in a planetary ball mill, and the caking effect is most prominent in the pulp section of

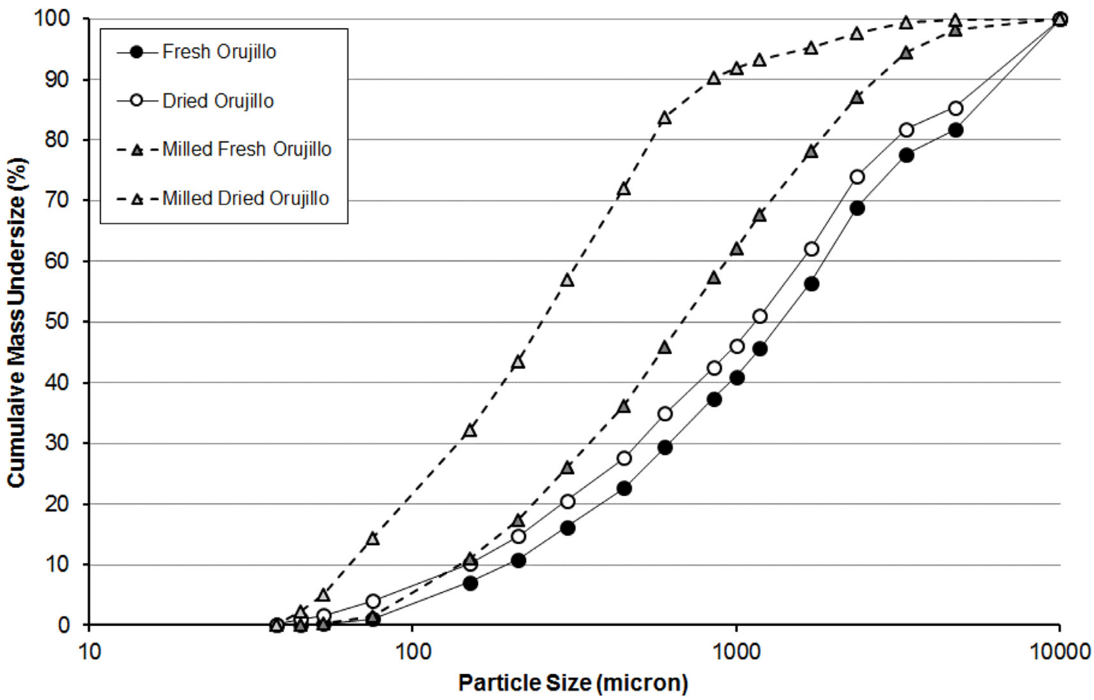

Fig. 7. Cumulative particle size distribution for pre-milled and milled fresh and dried orujillo.

orujillo. The particle size distributions show good agreement with the Rosin-Rammler equation ($R^2 > 0.995$), apart from the pulp section, which showed a poorer fit (Table 2). For the fresh sample this is due to the caking of the pulp section skewing the results, while for the dried sample the poor fit is due to the majority of the sample being very fine (*d*' 138 μm) with a high distribution parameter (1.79) resulting in a very steep curve slope and very narrow distribution. For the fresh and dried whole sections, the distribution parameters increased through milling. In general, the milled dried samples showed higher distribution parameters than milled fresh samples. Thus drying the samples resulted in narrower particle size distributions with less diversity in particle sizes.

By using Von Rittinger's theory, the combined impact of specific energy consumption and particle size reduction can be analysed for fresh and dried orujillo sections (Fig. 9). The analysis shows that the whole and cluster sections show similar results to each other in the fresh and dried tests. This is to be expected due to the similarity of the samples. The pip section shows an increase in energy consumption, but decrease in particle size through drying, illustrating the hardening of the pips through drying. However the clearest impact of caking on milling behaviour is in the pulp section. There was a negative particle size reduction in the fresh state, due to the increase in particle size after milling due to caking. When the pulp section was dried, and the caking effect is removed, the pulp section has the highest energy consumption and largest reduction in particle size of all the samples. This reinforces the finding that the caking issue is most prevalent in the pulp section of the orujillo.

A comparison of the Von Rittinger's constant further illustrates the impact of caking on the pulp section (Table 2). There is little change in the constant for the pips, indicating that there is little change in the milling behaviour of the pips through drying. However there is a dramatic change for the pulp section through drying, indicating a completely different milling behaviour in the two states, which is due to the caking phenomenon. The whole and separated portions show an increase in constant through drying, indicating that the pulp section is influencing the overall behaviour of the orujillo.

4. Discussion

The mechanism of orujillo caking can be linked to the material composition and the process conditions in which the caking is experienced. In this study, moderate heat generation within a planetary ball mill was able to replicate orujillo caking which has been observed in the fuel handling plants. Caking was most prevalent in the pulp section of orujillo, and drying the sample prior to comminution eliminated this issue. The pronounced glass transition step for the pulp section shows there is a significant change in behaviour at temperatures just below 100 °C. While the overall bulk surface temperature profile within the mill was lower than the glass transition temperature (Figs. 4, 5, and 8), the local instantaneous heat generated from the milling ball and sample interactions will be higher before dissipating into the bulk. The heat generated within the mill can be related back to the fracture mechanism induced within the planetary ball mill. During any planetary ball milling operation the contact area during collisions in a ball mill will be relatively small, but results in high average stresses in the contact areas (Venkataraman and Narayanan, 1998). As contact times are short, there is little time for heat dissipation and stress relaxation, leading to high stress gradients in the particles caught between the colliding bodies, with high energy densities in the contact areas and resulting in localised and transient hotspots. As the mill speed rises, the forces involved in the ball-particle collisions increase, resulting in higher levels of heat generation within the milled material (Fig. 5).

There are two key factors related to the material composition of orujillo which influence its caking; namely moisture and sugar content. No olive oil is present in orujillo due to the removal of all residual oil through chemical extraction (Alburquerque et al., 2004) and thus olive oil plays no role in orujillo caking. The bulk moisture content of orujillo was found to be between 14.6% and 17.9%, compared to the 6–7% for the small samples tested in the DSC. The moisture content of orujillo is usually between 10 and 12% (Ollero et al., 2002), and as higher moisture contents are known to lower the glass transition temperature of olive mill waste water (Goula and Adamopoulos, 2013), this elevated moisture content is likely

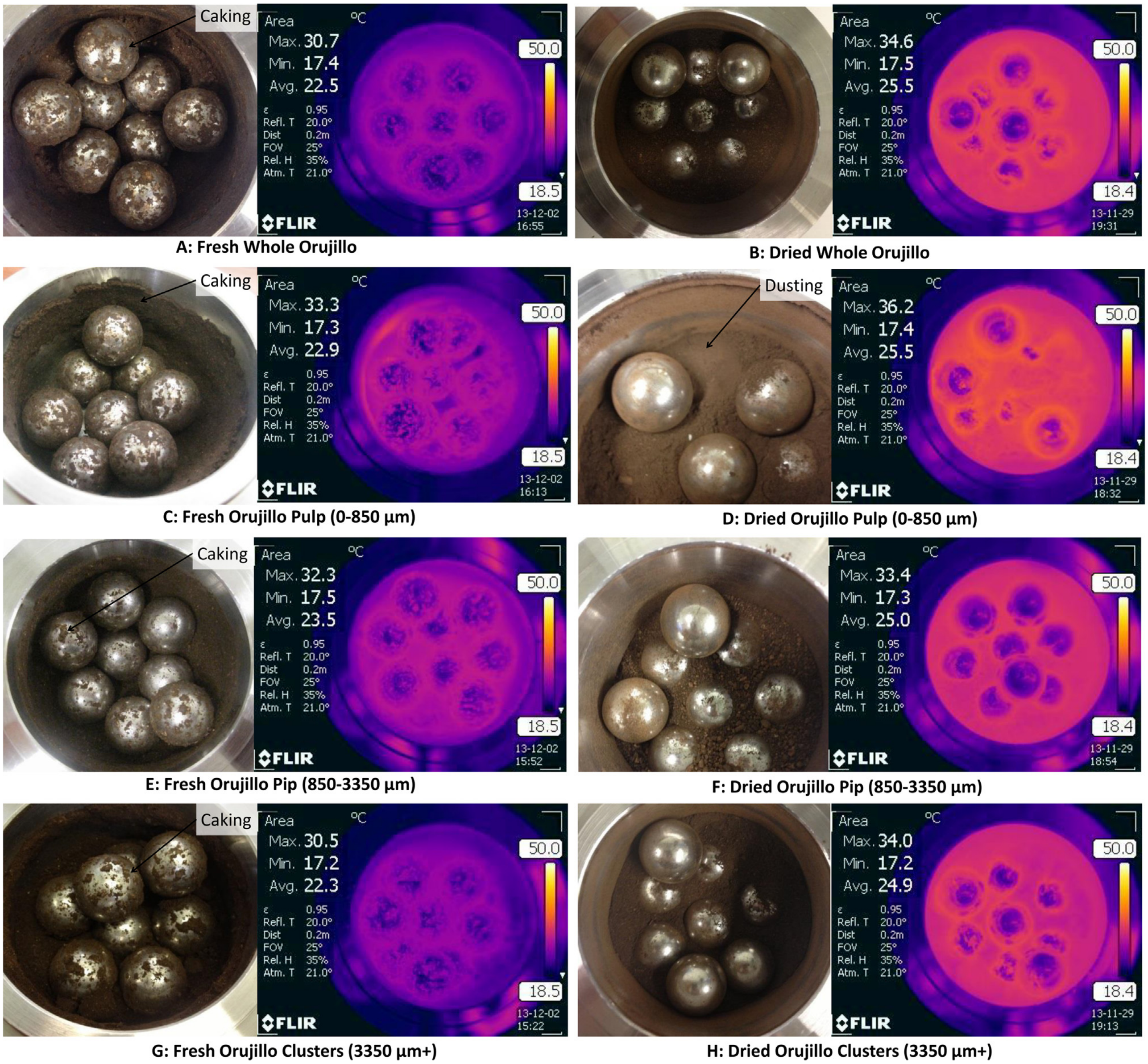

Fig. 8. Caking and temperature profiles for milled fresh and dried orujillo in whole (A-B), pulp (C-D), pip (E-F), and cluster (G-H) sections.

to be the main cause of orujillo caking. This study has identified that further research is required to characterise the glass transition and caking properties of orujillo for bioenergy purposes, as currently there is no literature available on this topic. In particular, the impact of temperature and moisture content on the glass transition temperature will provide the basis for moisture control system regulation in industrial processes using orujillo.

In addition to the moisture content of the orujillo, caking is also related to the sugar content of the orujillo sections. Sugar levels are inversely related to the oil content, and concentrations are also dependent on the moisture content of the olive flesh (Kailis and Harris, 2007). Soluble sugars decrease as the olive fruit develops and oil synthesis begins, with Spanish green-ripe olives, as used in this study, having around 4% fermentable substrates, while untreated black-ripe olives have a fermentable substrate level of typically 2-2.5%. The moisture and sugar content of olives varies seasonally, thus explaining why the caking phenomena is not experienced in some harvests of olives.

The industrial implications of this study are that moisture content control is key to overcoming orujillo caking in fuel handling plants. The use of materials such as orujillo in pulverised fuel combustion systems may also require drying as part of the fuel handling system to aid its material management and ensure caking does not occur. Drying olive mill waste water with dehumidified air has been shown to enhance its material handling management (Goula and Adamopoulos, 2013), and orujillo drying is a current topic of research for reducing transport costs for bioenergy (Casanova-Peláez et al., 2015; Gómez-De La Cruz et al., 2015). However these systems often aim to reduce moisture contents from as high as 69% to 15% of olive mill waste water mixed with olive husk, with a cost of 6.6 €/t (Caputo et al., 2003). In coal fired power stations, coal is dried during the milling process through heat recovery from the boiler to remove moisture and improve its grindability (Scott, 1995). Despite the additional energy and cost associated with drying coal during milling, it has been shown to improve coal grindability and decrease mill load, with a moisture reduction of 10% improving boiler efficiency by 4–12% (Akkoyunlu et al., 2016). This in turn reduces maintenance and repair requirements for the mill, and thus the economic cost of drying must be assessed in terms of the whole plant. Coal mills have been converted to comminute biomass, and oper-

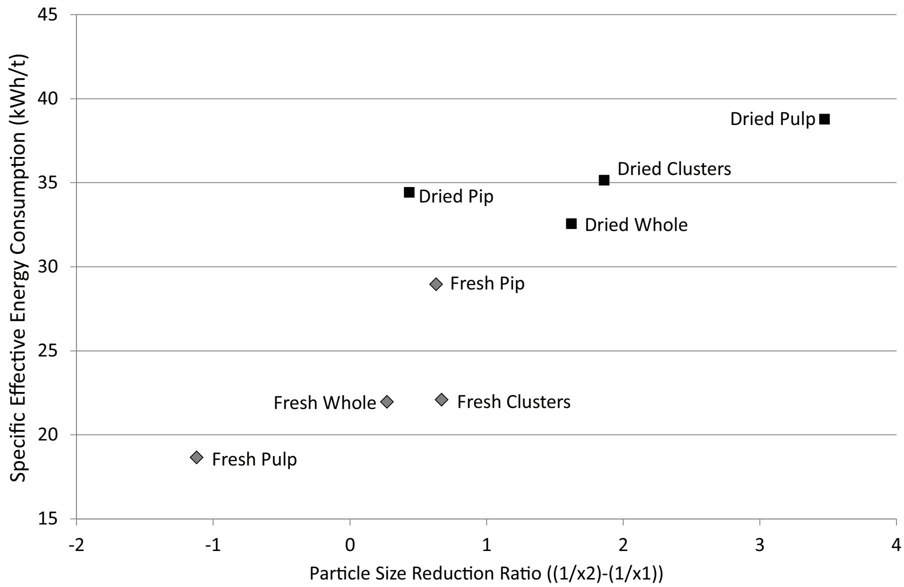

Fig. 9. Specific effective energy consumption against particle size reduction ratio for milled and dried orujillo.

ate at lower inlet and outlet temperatures than for coal (Livingston, 2012). In this study, dusting was exhibited for the dried orujillo samples (Fig. 8D), and thus drying may increase the risk of dust explosions in the fuel handling plant, which have occurred in wood pellet processing plants (Hedlund et al., 2014). Given that the caking issue is most prevalent in the pulp section, a simple solution to avoid caking in the comminution section of the fuel handling plant would be to remove all fines below the required combustion particle size, which is typically 1 mm (Esteban and Carrasco, 2006; Tamura and Van de Kamp, 2001), prior to comminution and send these fines directly to the burner. This would also reduce the comminution load by nearly 50%, increase the energy potential of the fuel, and remove the most problematic section of orujillo from the fuel handling plant.

5. Conclusions

This study replicated the orujillo caking phenomenon experienced in power generation fuel handling plants on a laboratory scale within a planetary ball mill. The study explored the impact of mill parameters and material composition on orujillo caking. Caking was induced by heat generation within the mill and was most prevalent in the pulp section of orujillo. Caking was brought on by a glass transition step, which was measured to be around 97–98 °C for a moisture content of 6–7% in a DSC. It was demonstrated that by drying the orujillo, caking could be mitigated. The moisture content control is key to overcoming the caking of orujillo in industrial plants, which would aid material management and ensure caking does not occur, but dust control will also be required to avoid dust explosion issues. By understanding the causation of orujillo caking in the pulp section, mitigation of caking can be achieved by the removal of fines below the required combustion particle size prior to milling and send these fines directly to the burner. This would also have the beneficial effect of increasing operational efficiencies and significantly enhance the energy potential of the fuel.

Acknowledgments

This work was supported by the Engineering and Physical Sciences Research Council [grant number EP/G037345/1] (EPSRC). This research is also funded and supported by the Biomass & Fossil Fuel Research Alliance (BF2RA) and EDF Energy plc. The study was part of an Engineering Doctorate at the Efficient Fossil Energy Technology Centre in the Faculty of Engineering at The University of Nottingham. The authors would like to thank all those involved for their support and cooperation during the course of the research.

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