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Utilization of wastes/by-products as grinding additives

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ABSTRACT

In this work, the use of water (W) as a grinding additive in addition to waste/by-products such as olive black water (BW) and residue of olive black water (RBW) in calcite dry grinding to be sized in microns was investigated at a laboratory scale. The test results were evaluated in terms of particle size and powder flowability as a function of liquid material dosage and grinding time. The study revealed that the use of any kind of liquid materials tested improved the grinding process compared to the without-aid condition. Removing the water content (RBW) in BW resulted in further improvements in both particle size and powder flowability. The findings from both the BW and W data revealed that the dose increase does not yield favorable outcomes in relation to the ffp index. Nevertheless, there was a noticeable enhancement in particle fineness.

Keywords: *Grinding additive, Waste/by-product, Dry calcite grinding, Powder flowability*

Introduction

With the improvement of technology, micronized calcite (<10 µm) is used as a filler raw material, particularly in sectors such as plastic, paper, and paint. In our country, calcite in micron sizes is manufactured and marketed to the aforementioned industries using dry techniques. In addition to situations where dry processes are mandatory and advantageous (cement, calcite, etc.), the importance of dry processes is increasing with the increasing use of water day by day. It is also important to use dry processes and to increase the studies on this subject, especially in countries where water is limited and in regions where environmental sensitivity is important. Dry grinding additives are one of the subjects on which important studies have been carried out recently in dry grinding. With the increase in the surface area of the material in dry grinding processes (especially in micronized grinding), intermolecular attraction forces and regional forces and particle-particle interaction increase, and this leads to a change in the flow properties of the material. In dry grinding, this situation is tried to be kept under control with grinding additive chemicals. In the reported studies, the use of pure and commercial chemicals was carried out and their positive influences were presented (Paramasivam and Vedaraman, 1992; Katsioti et al., 2009; Zhang et al., 2015; Gökçen et al., 2015; Toprak et al., 2018; Çayırlı, 2018; Çayırlı, 2022). Also employed as grinding additives were several waste materials and by-products (Gao et al., 2011; Leoneti et al., 2012; Li et al., 2015; Akar and Canbaz, 2016; Li et al., 2016; Zhang et al., 2016; Li et al., 2017; Li et al., 2018; Çayırlı et al., 2020).[1]

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In particular, these chemicals create an extra cost as they are used extensively in grinding processes. Accordingly, the utilization of waste materials or by-products as a grinding additive can be considered as an alternative. Starting from this, the possibility of using olive black water (BW) as a grinding additive in the dry micronized grinding of calcite was investigated. In addition, distilled water (W) and residue of olive black water (RBW) were tested in order to better demonstrate the effectiveness of BW, and comparisons were performed with W and RBW. The grinding experiments were evaluated in terms of particle size and powder flowability as a function of liquid material dosage and grinding time.

1. Meterials and Metods

1.1. Materials

For the dry grinding experiments, a calcite sample (98.838% $CaCO_3$) by Mikron'S Inc., Türkiye with a median particle size of x_{50}: 83.77 µm was used. Its specific gravity was found to be 2.71 using a helium pycnometer.

In the previously reported study (Çayırlı et al., 2023), the effect of BW on calcite grinding was investigated along with various grinding additives. In order to reveal the effect of BW in more detail, the research was continued, and the distilled water and residue of olive black water were added to the agenda and constituted the main subject of this study. In this context, three liquid materials (BW, W and RBW) were used as grinding additives. Distilled water was preferred in terms of representing the water part of BW. The BW sample was collected from Dalan Oil Industry Inc. in Türkiye. The values of free fatty acids, specifically in terms of oleic acid, in BW, were determined by the analyses made in the Food Engineering Laboratory of Niğde Ömer Halisdemir University. In this context, free fatty acidity values were found to be 2-3%. In order to increase the fatty acid concentration in BW and to observe the influences of the water in it on the experimental results, RBW was obtained by evaporating 84% of the water in the BW content at 100°C.

1.2. Methods

The grinding experiments were conducted using a vertical batch-type laboratory stirred ball mill (Figure 1). As introduced in a former study (Çayırlı et al., 2023), the mill is equipped with a cylindrical 1200 ml grinding chamber made of steel and equipped with a water jacket. Both, shaft and stirrers (pin type) are also made of stainless steel. After weighing the samples and balls in accordance with the test conditions, the balls were fed first into the grinding chamber, and then the sample was placed second. The liquid material was added to the calcite sample. The shaft was placed into the chamber by adjusting the speed of the agitator to ~100 rpm. After all the settings of the mill were made, the cap was sealed, the planning speed was set, and the milling operation began. The mill was stopped at the determined grinding time. Experimental conditions are summarized in Table 1 and related calculations are given in Equation (1), (2) and (3). At the end of the experiment, the mill cap was opened first and the material and balls were removed from the grinding chamber and their separation was made by sieving. According to sample division techniques, representative samples from the obtained products were taken for size and flowability measurements.

Figure 1. *Vertical batch-type laboratory stirred ball mill, pin-type stirrer and grinding tank*

Table 1. *Test conditions for dry grinding (Çayırlı, et al., 2023)*

Parameter	Value
Stirrer velocity (m/s)	4
Ball loading (J*)	0.60
Powder-ball loading (U*)	0.80
Liquid material dosage (g/t)	0, 500, 1000, 2000, 4000
Ball diameter (mm)	2.8-3.2 (average 3)
Density of ball (g/cm3)	~3.7
Milling time (min)	5.5, 7.5, 9.5

$$*J=\frac{\text{mass of balls/ball density}}{\text{mill volume}}\times\frac{1.0}{0.60} \quad (1)$$

$$*fc=\frac{\text{mass of powder/powder density}}{\text{mill volume}}\times\frac{1.0}{0.60} \quad (2)$$

$$*U=\frac{fc}{0.40J} \quad (3)$$

The particle size distributions of the product samples were measured by laser diffraction using Malvern 2000 Ver. 2.00 with Hydro 2000 MU attachment (Malvern Co., Ltd., UK). The device repeats the measurement of each sample at certain intervals and measures three times and gives the average of these three measurements.

The powder flowability was analyzed using a ring shear tester (230VAC-Brookfield, UK) (Figure 2). The sample cell of the device (230 cm^3, 6in diameter) consists of a movable upper disc and a still lower chamber. In the upper disc, there are 18 chambers in order to create shear stress in the powder whose flowability is desired to be measured. The lower chamber is designed as a perforated plate to prevent the sliding movement of the powder material on the surface. While the lower chamber is stationary, the upper disc applies consolidation stress (σ_1) at varying rates with downward linear movement and at the same time causes unconfined yield strength in the powder sample with its rotational movement. The basic measurement principle of the powder flow tester is based on measuring the powder material's necessary shear stress (σc) to begin to flow or deform after the compression stress is applied (Slettengren et al., 2015; Çayırlı et al., 2023). At this point, the flowability index ff_p, which is defined as the ratio between consolidation stress σ_1 and unconfined yield strength σc (see Equation 4), is used to qualify the powder flowability:

$$ffp=\frac{\sigma_1}{\sigma c} \qquad (4)$$

Powder flowability can be categorized using the ff_p value, according to Jenike (1964). In the range $ff_p<1$, $1<ff_p<2$, $2 < ff_p < 4$ and $4 < ff_p < 10$, $10<ff_p$ a powder is non-flowing, very cohesive, cohesive, easy-flowing and free-flowing, respectively.

Figure 2. *Powder flow tester*

2. Results and Discussion

2.1. Comparison in terms of product fineness

The influence of the liquid material type and its level of concentration on the fineness of the product was examined by wet particle size measurements, as depicted in Figure 3. Without aid conditions, particle sizes of 8.05, 7.49, and 6.18 µm were obtained at grinding times of 5.5, 7.5, and 9.5 min, respectively. Regarding BW, there is a lack of significant impact on the d_{50} value when the additive concentration is low and the time to grind is 5.5 min, compared to when there are no additives. In contrast, it has been noticed that the use of BW results in a significant enhancement in the d_{50} size at concentrations of 1000 and 2000 g/t. Higher BW dosing (4000 g/t) resulted in poor grinding performance. This result can be explained by the fact that as the amount of BW increases, the amount of water in the sample concentrate also increases. Because there is a high amount of water in BW. Additional water dosing (liquid bridging) generates forces of adhesion that are relatively strong, which in turn raises powder cohesion (Rumpf, 1974). Moreover, for each evaluated grinding time, the positive impact of BW at concentrations of up to 4000 g/t was seen. The results also showed that the d_{50} sizes decreased from 7.92 to 6.31 µm when BW was increasing at dosages ranging from 500 g/t to 2000 g/t at a shorter milling period as opposed to the without-aid condition, which had an 8.05 µm d_{50} value at a 5.5 min grinding time as already shown in the former study (Çayırlı et al., 2023).

In comparison to the without-aid condition, the d_{50} size was reduced with increasing RBW dosage for each milling period of time. In addition, as the grinding time increased, the use of more RBW resulted in finer particle size. In other words, at each grinding time, the effect of the RBW dosage was observed.

In the case of using water, the d_{50} size did not change (compared to the without-aid condition) for the short grinding time (5.5 min) as its dosage increased. As the grinding time increased, the d_{50} size decreased, particularly at a 1000 g/t dosage. Further dozing (2000 g/t) adversely affected the milling performance. It was also determined by Toraman et al. (2016) that the increasing concentration of water has a negative effect on grinding. In their work, they investigated how water affects particle fineness and surface area, indicated that it had a positive effect on grinding performance up to a certain amount and observed that the administration of higher dosages resulted in a negative impact.

Consequently, in 5.5 min grinding experiments using BW, the finest particle size, d_{50}: 6.31 µm, was obtained by using 2000 g/t BW. Similarly, a particle size of d_{50}:5.94 µm was attained using a dosage of 2000 g/t RBW, also within a 5.5 min grinding duration. Additionally, W achieved a particle size of d_{50}:7.71 µm at 1000 g/t in 5.5 min experiments. At the end of the grinding process lasting 7.5 min, the most refined particle sizes were achieved with d_{50} values of 5.79 and 5.75 when utilizing 2000 g/t in BW and RBW, respectively. However, a d_{50} value of 6.61 was obtained at a concentration of 1000 g/t when employing W. Within the experiments, the longest grinding time utilized was 9.5 min, resulting in the acquisition of the finest particle sizes when employing a dosage of 2000 g/t for both BW and RBW. The particle sizes acquired are 5.34 and 4.82 µm, respectively. The utilization of W resulted in the attainment of the particle size d_{50}:5.42 µm at a concentration of 1000 g/t.

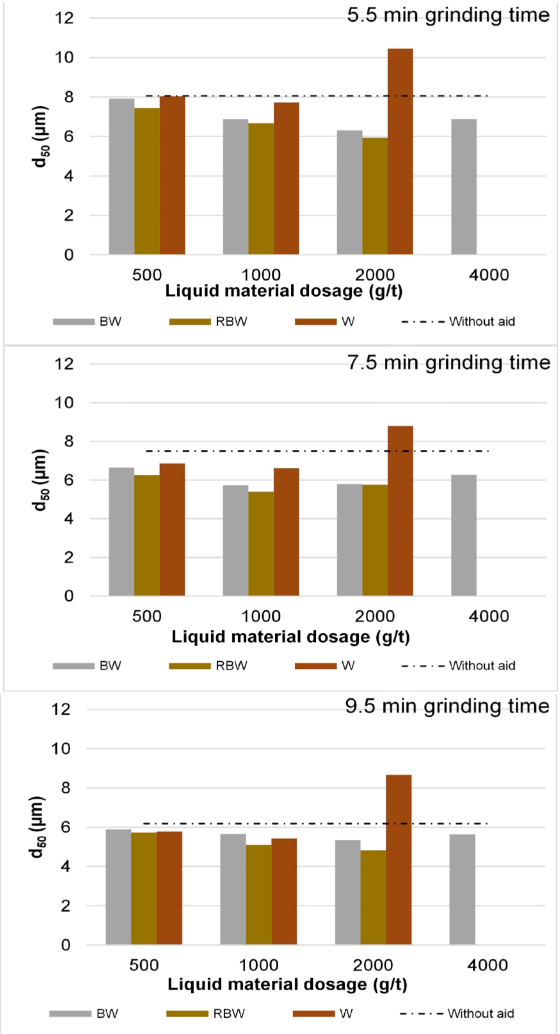

Figure 3. *The influence of all tested liquid materials on particle size*

2.2. Comparison in terms of powder flowability

The impact of liquid materials on the flowability of powders is depicted in Figure 4, which presents the ff_p indices of the product powders. Among the all investigated liquid materials, only RBW affected the powder flowability compared to the without-aid condition. As the grinding time increased, the use of more RBW resulted in finer particle size. It can be said that the influence of RBW dosage is demonstrated at every milling time. Surprisingly, the BW and W powder flowabilities were lower than the results from the without-aid condition. To put it another way, the data from BW and W indicated that the ff_p index would not benefit from the dosage increase.

Although the use of water and BW has an influence on the size, they do not cause any change in the powder flowability, an indication that the positive influence on grinding cannot only be explained by the powder flowability. Prziwara et al. (2018) also examined the effects of different types of grinding aids on grinding performance and powder flowability and determined that some of them had positive effects on particle size, although they did not have a positive effect on agglomeration and powder flowability.

In terms of powder flowability values, 2.08, 1.92 and 1.81 ff_p values were obtained in the 5.5, 7.5 and 9.5 grinding time experiments, respectively, in the condition where without grinding aid was used. In 5.5 min, grinding time experiments, the highest fluidity values for BW, RBW and W were achieved when 2000 g/t was used, and 1.81, 2.43 and 1.78 ff_p values were obtained at this amount, respectively. During the experiments with a grinding time of 7.5 minutes, it was observed that the maximum ff_p value in BW was 1.61 at a concentration of 500 g/t. Similarly, the highest ff_p value in RBW was 2.22 at a concentration of 1000 g/t. Additionally, the highest ff_p value in W was recorded as 1.75 at a concentration of 2000 g/t. Finally, during the experiments with a grinding time of 9.5 min, it was observed that the maximum ff_p value in BW was 1.78 at a concentration of 4000 g/t. Similarly, the highest ff_p value in RBW was 2.00 at a concentration of 2000 g/t. Additionally, the highest ff_p value in W was recorded as 1.72 at a concentration of 2000 g/t.

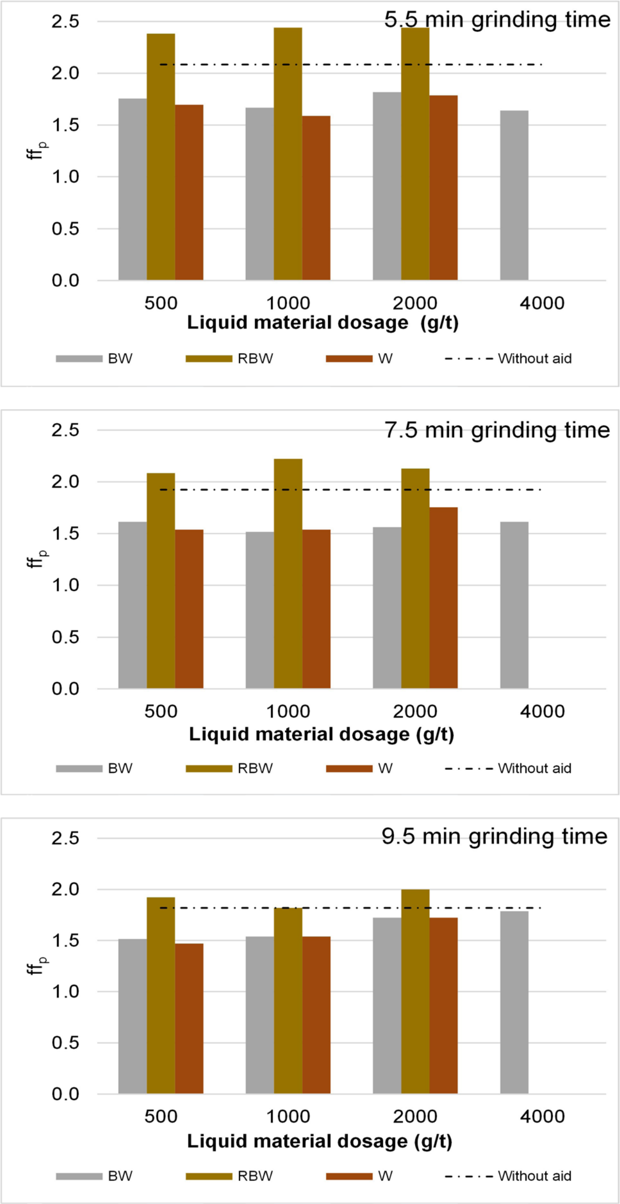

***Figure 4.** The influence of all tested liquid materials on ffp index*

To better determine the effectiveness of BW, distilled water experiments to represent the water part of the olive black water and residue experiments to represent the main substance group were carried out. According to these results, it has been revealed that RBW is more effective than W and BW in terms of particle size. According to these results, it has been revealed that the RBW is more effective than W and BW in terms of product fineness. In addition, it was found that the ff_p values overlapped with the particle size results. In other words, BW is worse than RBW and better than W in terms of flowability/grinding performance. However, BW having high water content, reduced the fluidity of the product (according to the without-aid condition), unlike RBW. It is thought that this finding is caused by the substance group increasing the powder flowability (residue-free fatty acidity 2-3%). Studies from the scientific literature can be presented as evidence for this comment. Paramasivam and Vedaraman (1993) investigated the effect of six types of fatty acids (stearic acid, lauric acid, palmitic acid, sodium lauryl sulfate, calcium stearate, and magnesium stearate) on the dry grinding of calcite. According to the findings of this study, it was determined that the fineness, bulk density and packaged bulk density of the milled product increased with the use of any tested fatty acid, while the compressibility and tensile strength of the powder bed of the milled product decreased. The reason for the change in these flow characteristics inside the mill was the adsorption of the tested long-chain fatty acid molecules on the particle surfaces, reducing the friction forces and adhesion interactions between them. In another study, the grinding performance of fatty acids (capric acid, lauric acid, myristic acid, palmitic acid, and stearic acid) used in grinding chitosan powder in a vibrating mill was examined according to fatty acid length. According to the results, it was determined that all fatty acids tested improved the grinding performance compared to the condition without grinding aid, and the best performance was obtained with stearic acid (having the longest carbon chain) (Fukumori et al., 1998). BadJena and Mishra (2011), in their study, found that stearic acid is a better grinding aid than paraffin wax and oxalic acid in grinding brass powder. Ma et al. (2013) also examined the effect of oleic acid in grinding cement. The results showed that the use of oleic acid improved the surface area and especially the rheological properties of the cement.

On the other hand, some sources from the literature confirm that water can indeed increase grinding efficiencies (Parks, 1984; Sohoni et al., 1991; Sverak et al., 2013; Çayırlı, 2014; Toraman et al., 2016; Prziwara and Kwade, 2020). As is commonly known, water molecules have a significant polar attraction, which results in relatively strong affinities for polar regions on the solid surface, similar to the polar functional groups found in conventional grinding additive molecules, hence lowering intergranular adhesion forces (Prziwara et al., 2018; Prziwara and Kwade, 2020). Parks (1984) observed in his research that it reduces the surface energy between quartz particles. In parallel with these comments, in the current investigation, it may be assumed that BW (with the existing water content) created a grinding environment by reducing the flowability in the grinding chamber which will enable the particles to be stressed more effectively by the balls. Thus, in light of the findings and comments obtained with BW in the current study, it is thought that both the residue part and the water part contribute to the grinding separately.

3. Conclusion

Experimental studies on grinding performance using calcite in a stirred ball mill have been carried out. The influences of liquid materials used as a grinding additive (olive black water, distilled water and residue of olive black water) on the particle size and powder flowability were examined. The dry grinding experiments and analyses showed that:

- The study revealed that using any of the liquid materials evaluated enhanced the grinding process versus the without-aid condition.

- In other words, at the longest grinding time tested, d_{50} values of 5.42, 5.34, and 4.82 μm were reached at certain concentrations W, BW, and RBW, respectively, whereas a product with a d_{50} size of 6.18 μm was obtained at the without-aid condition.

- Considering RBW, powder flowability improved as liquid material concentration increased. Namely, while ff_p values varied between 1.81 and 2.08 in the without-aid condition, the flowability index of the products obtained with the use of RBW increased from 1.81 to 2.43. Surprisingly, the BW and W findings showed that the rise in concentration was not advantageous regarding the ff_p values; however, the improvement in particle fineness was clear.

-Removing the water content (RBW) in BW resulted in further improvements in both particle size and powder flowability.

- Finally, it can be concluded that both the residue part and the water part of BW contribute to the grinding separately.

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