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Original Research

Using Glycerin, a By-Product of Biodiesel, as a Grinding Aid in the Dry Grinding of Marble Dust Waste

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A B S T R A C T

Glycerin represents the primary by-product of biodiesel generation when vegetable oil is transesterified with ethanol or methanol. It is essential to study how to prevent natural resource depletion and transform waste into usable and valuable products. Using glycerin as a grinding aid can be an alternative solution for utilizing the excess glycerin resulting from biodiesel production. This paper investigated the usability of unrefined glycerin as a grinding aid in the dry grinding of marble wastes in terms of grinding efficiency while planning to reduce the adverse impacts of waste on the environment via its efficient utilization. The dry grinding experiments conducted within the study's scope researched the impacts of five dosages (0%, 0.25%, 0.5%, 1%, and 2% by weight) on the product. The current research is promising in terms of preventing the depletion of natural resources and transforming waste into usable and valuable products. Furthermore, considerable enhancements were obtained in the grinding performance with the grinding aid utilized.

Keywords: *Marble waste, Mineral filler, Dry grinding, Grinding aid, Recycling*

Introduction

Like all industrial activities, the adverse influence of marble dust wastes (MDW) on the environment constitutes a problem, and waste management is also inevitable in natural stone plants. Moreover, industries have a social responsibility to protect the environment and ensure that natural resources are used sustainably. For a sustainable economy, environmental protection must accompany industrialization and utilizing natural resources (Mymrin, 1997). Nowadays, the need to turn to alternative materials is increasing daily due to developing technology, competition from industry, and the rapid consumption of the Earth's resources. The most crucial step in achieving the said balance is to ensure the reuse of the waste generated in one area within the same area, in another industrial sector, or for another aim, e.g., as a filler instead of calcite. MDW contains a high amount of calcium carbonate (El-Sherbiny et al., 2015). The excess $CaCO_3$ ratio in the chemical composition of MDW expands its usage area and provides the opportunity for its use instead of calcite, which is highly needed in the industry. Particle size is desired from 1-2 µm to 50-100 µm according to the sector used (DPT, 2001). Alyamac and Ince (2009) and Tunc (2018) reported the reuse of waste marble in the paper, plastic, chemical, glass, and fertilizer industries and construction activities. Nayak et al. (2022) assessed the physical and mechanical properties of MDW-filled polyester composites and reported that MDW was highly compatible as a potential filler in polyester resin up to 32% by weight. To use MDW as a filler instead of calcite, it must have a high degree of hydrophobicity and be able to be ground to ultrafine sizes. The prominent properties of composites are attributed to a small particle size, thus resulting in a large interface area and high surface energy of nanoparticle fillers, leading to strong interfacial adhesion between fillers and the polymeric matrix (Zhang et al., 2010). Bringing these wastes to the desired size is one of the most energy-consuming and costly processes. Improvements, albeit small, to be made at low costs in grinding processes consuming a lot of energy will provide significant economic benefits. Size reduction processes are highly affected by the physical and chemical conditions of the grinding medium. The inefficiency of

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grinding, especially in dry grinding, is generally explained by the slowing effect caused by fine particles. This may originate from the regrowth or rebuilding of particles from smaller particles as a result of either agglomeration, including van der Waal's forces, or direct briquetting, or coating of balls for the purpose of providing soft surfaces (Austin et al., 1984; El-Shall and Somasundaran, 1984; Locher and Seebach, 1972; Orumwense and Forssberg, 1992). The use of chemical additives represents an economical alternative for industrial applications. The utilization of chemical additives does not influence the breakage of coarse material. However, it only becomes a factor when fine material is built up in the mill (Locher and Seebach, 1972). It is necessary to add chemicals under conditions that cause chemisorption on particles' surfaces and utilize a sufficient amount of additives with the objective of creating the adsorbed layer on the whole area of fine particles generated in the course of grinding. The impact of additives is reducing the van der Waal's adhesion force between fine particles, thus ensuring more effective breakage interactions between grinding media and particles through a mechanism that is not completely understood and reducing the formation of agglomerate in cases when this constitutes a problem. The adsorbed additive also provides improved powder flowability (Fuerstenau, 1995). Although grinding aids provide efficiency and reduce energy costs, they create a separate cost item since they are generally imported from abroad. In this context, as an alternative to these expensive, imported grinding chemicals, various waste/by-products are important in reducing costs and evaluating waste.

By-products and waste products can be grinding aids for effective size reduction and minimizing energy consumption. Using grinding aids, it is possible to increase the amount of production with the wanted product fineness, and a finer product can be obtained in an identical amount of production. There are many studies in the literature on the usability of various wastes and by-products as grinding aids. Gao et al. (2011) investigated whether utilizing beet molasses as a grinding aid for blended cement with high volumes of mineral admixtures was viable. Beet molasses (0.01–0.05% by weight of cement) was added at various ratios into a blended cement. Concerning the performance of the blended cement, beet molasses led to a higher compressive strength at 3 days and 28 days. Li et al. (2016) tried waste cooking oil (WCO) as a grinding aid while grinding cement clinker and gypsum. The findings demonstrated that WCO considerably enhanced cement grinding. In another study, Li et al. (2015) used recycled beet molasses as a grinding aid in cement generation. The results revealed in detail that the recycled beet molasses contributed to clinker grinding and improved other cement properties. Leoneti et al. (2012) investigated the utilization of glycerol, a by-product of biodiesel generation in Brazil. They stated that glycerol was used as one of the grinding chemicals, especially in the form of commercial mixtures. However, the mentioned glycerin has limited use because it is accepted as an unrefined raw material, which should be refined for its utilization in the future. Generally, 10 kg of glycerol is created as a by-product of each 100 kg of biodiesel generated (Chi et al., 2007). The study by Karinen and Krause (2006) showed that biodiesel generation produced almost 10% of glycerol by volume.

Reducing environmental problems from waste generation to its irresponsible disposal is based on the adequate use of wastes in appropriate environments. Managing waste on a global scale is an essential and important strategy since it has become a critical factor for people, animals, and vegetation (Sabine, 2013). The nature, amount, and type of waste vary from country to country. Helping to preserve the quality of the environment and health requires looking for an effective way to manage waste appropriately. For these purposes, waste must be recycled, reused, and directed to a valuable and usable product. These days, the use of waste is a priority for sustainable development success. In this respect, it is necessary to investigate wastes produced in natural stone processing plants as mineral fillers in terms of both using these wastes and eliminating their negative environmental effects. The purposes of this paper are to investigate the effect of glycerin on the grinding efficiency of MDW. Experimental results were assessed based on several product properties like particle size distribution (d_{50}), size reduction (F_{90}/P_{90}), grinding media coating, and energy consumption. This study is important since, to the best of our knowledge, it is the first study in the literature that compares the usability of by-products as grinding aids on the waste calcitic and dolomitic marble in mineral filler production.

1. Materials and methods

1.1. Materials

There are two subclasses of marble, calcitic ($CaCO_3$) and dolomitic ($CaMg(CO_3)_2$). The current research utilized Afyon white (calcitic) marble and Aydın yellow (dolomitic) marble wastes (Figure 1). After drying waste samples in an oven at a temperature of 60 °C to a constant weight, the feed size (< 2 mm) required for the conventional ball mill was produced, which was crushed in two stages with a jaw and hammer crusher. Canada Acme Lab analyzed the chemical properties of the marble wastes utilized in the above-mentioned tests by employing the ICP-MS method. Table 1 presents the materials' chemical content.

Figure 1. *The appearance of Afyon white (calcitic) marble and Aydin yellow (dolomitic) marble dust*

Table 1. *ICP-MS elemental analysis of the calcitic and dolomitic marble wastes (in wt%)*

Sample	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	MnO	Na_2O	K_2O	Cr_2O_3
Afyon white	55.86	0.36	0.29	0.05	<0.04	<0.01	0.02	0.02	<0.002
Aydın yellow	30.56	21.21	0.09	0.03	0.24	0.01	0.01	<0.01	<0.002

Test samples with an average particle size of d_{50}=16.9 μm for calcitic marble and d_{50}=17.8 μm for dolomitic marble were used in grinding studies (Figure 2). The unit weights of calcitic marble powder (ɣs = 2.68 g/cm^3) and dolomitic marble powder (ɣs = 2.78 g/cm^3) were determined with a pycnometer (ASTM D 854-02). High-density (6000 kg/m^3) yttria-stabilized zirconia (ZrO_2) grinding media purchased from Cenotec Co., Ltd., Korea, were used in the ultrafine grinding experiments.

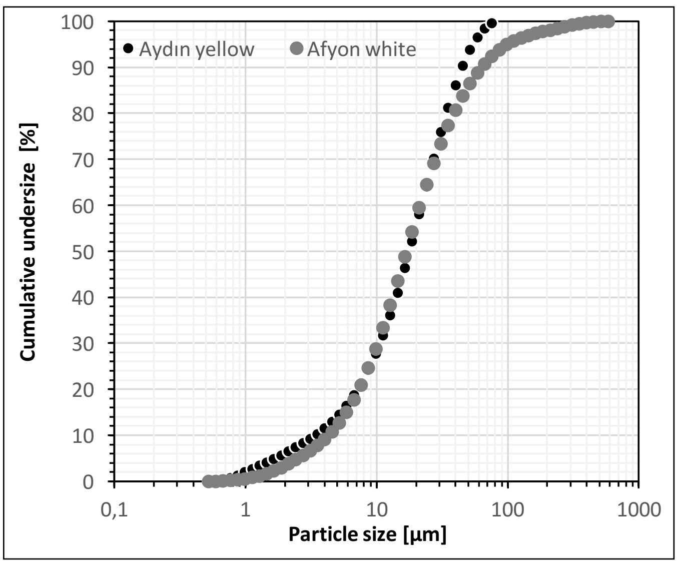

Figure 2. *Particle size analysis of the samples used in the experiments*

Unrefined glycerin, a light yellow transparent liquid, is obtained while producing biodiesel. Glycerin was provided by the Kolza Biodizel Fuel and Petrol Products Inc. A Bruker Vertex 70 Fourier-Transform Infrared Spectrometer (FTIR) was used to characterize the grinding aid in the range of 4000–400 cm^{-1}.

Figure 3 shows the FT-IR spectrum of the grinding aid. Glycerin is a complex organic material with different types of polar groups. There are evident O-H stretching vibration peaks at 3600-3200 cm^{-1} and the contribution of the broadband of -OH with absorption varying between 3000 and 3500 cm^{-1} was also detected. These polar hydroxyl groups in its structure provide good grinding performance. C-H stretching vibrations are observed at a wave number of 2925 cm^{-1}. A shoulder at 2853 cm^{-1} is attributed to the C–H symmetrical stretching vibration of the aliphatic CH_2 group (Zhang et al., 2016), the band observed at 1740–1653 cm^{-1} stands for C=O stretching vibrations found in aromatic groups, and the obvious stretching vibration of the free fatty acid carbonyl group is observed at 1030-1200 cm^{-1}.

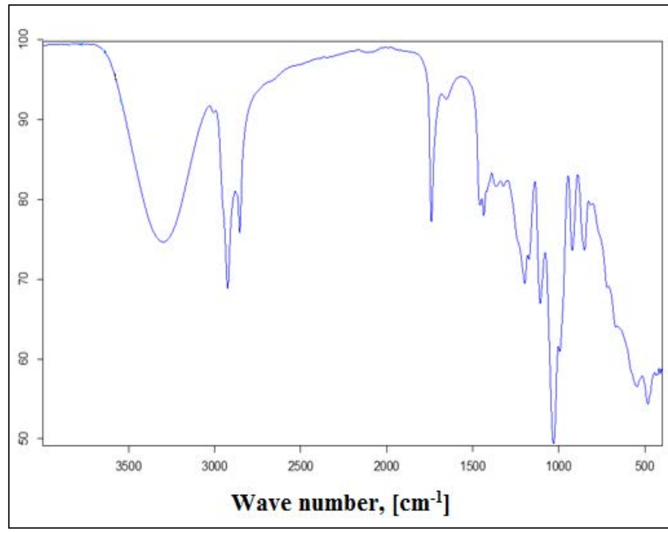

Figure 3. *FT-IR spectrum of the grinding aid*

1.2. Methods

Marble wastes were ground in a type of a Standard-01 laboratory batch mill produced by Union Process (USA) (Figure 4). Table 2 summarizes the technical specifications of the stirred ball mill. The grinding tank is equipped with a water jacket to ensure cooling. It is necessary to eliminate the heat produced in the course of grinding with circulating cooling water via the grinding container jacket. A Rev 2580 voltomat-meter (Rev Ritter GmbH, Deutschland) was utilized to measure the energy the mill consumed. Table 3 summarizes the experimental conditions.

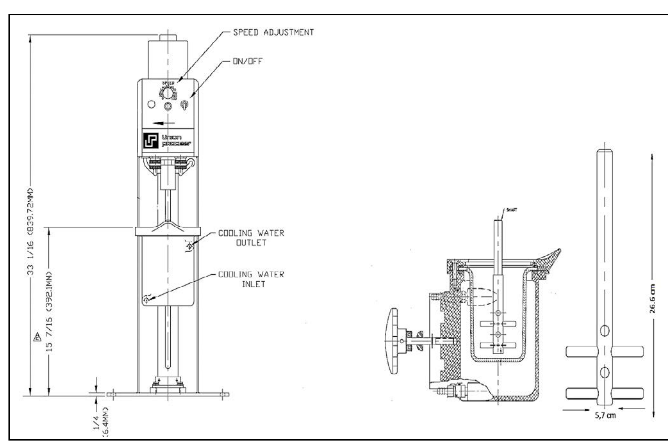

Figure 4. *Laboratory-scale vertical stirred ball mill*

Table 2. *Technical specifications of the vertical stirred ball mill*

Property	Value
Motor speed (max.)	600 rpm
Tank height	12.3 cm
Tank diameter	8.04 cm
Shaft type	Pin
Shaft length	26.6 cm
Number of pins	4

Table 3. *Experimental conditions used in the dry grinding of marble wastes*

Parameter	Value
Ball filling ratio, (J)	65
Powder filling ratio, (fc)	0.125
Grinding time, (min)	75
Mill speed, (rpm)	600
Ball size distribution	3 mm (50%) and 5 mm (50%)
Grinding aid dosage, (by weight %)	0, 0.25, 0.5, 1, and 2

Equation 1 is used to calculate the ball filling ratio (J). This parameter indicates how much of the volume is filled with media using a bed porosity of 0.4 (Austin et al., 1984); the value equals 100%.

$$J = \frac{\text{Mass of media (gr)/Density}(gr/cm^3)}{\text{Mill volume }(cm^3)} \times \frac{1.0}{0.6} \quad (1)$$

Likewise, the ratio of the mill volume filled with solids ratio (fc) is explained by Equation 2.

$$fc = \frac{\text{Mass of powder (gr)/Powder density}(gr/cm^3)}{\text{Mill volume }(cm^3)} \times \frac{1.0}{0,6} \quad (2)$$

The measurement of the energy consumption in the course of the dry grinding process was performed for the purpose of assessing the efficiency of the grinding process.

$$E_m(kWh/t) = \frac{E - E_0}{m_p} \quad (3)$$

Where denotes the product mass of marble wastes, E is the energy used at the time t, and is the no-load energy.

2. Results and discussion

2.1. Product fineness

First, the influence of glycerin dosage on grinding was investigated under constant mill parameters, as shown in Figure 5, using the particle sizes d_{50} for calcitic marble (left side) and dolomitic marble (right side).

Figure 5 obviously shows that with the addition of glycerin, the d_{50} size becomes narrower in comparison with the no-aid condition. Glycerin consists of a chain of three carbon atoms where each carbon atom is bonded to a hydrogen atom (+H) and a hydroxyl group (-OH). Furthermore, it is all highly adsorbed by polar -OH groups. However, the d_{50} size increased beyond the dosage of 0.5% for calcitic marble and dolomitic marble. Generally, this is not surprising since this phenomenon is called "negative grinding," known as the re-agglomeration of fine particles (Hasegawa et al., 2001). Similar results to this study were obtained in the studies by Katircioglu-Bayel and Toghan (2022) on waste eggshell, Toraman (2012) and Çayirli (2018) on calcite, and Oksuzoglu and Ucurum (2016) on gypsum.

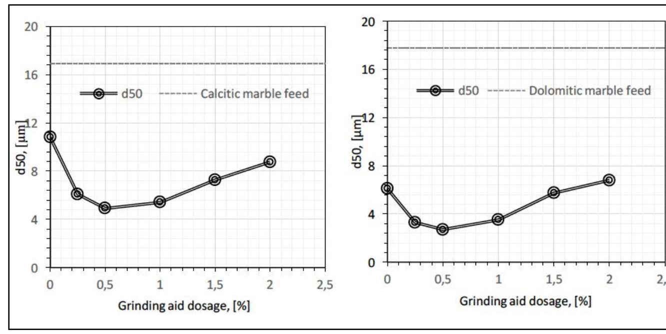

Figure 5. *Influence of the grinding aid concentration on the d_{50} size*

Except for the d_{50} size, Figure 6 shows the influence of the grinding aid dosage on size reduction (F_{90}/P_{90}) for calcitic marble (left side) and dolomitic marble (right side). Glycerin had higher size reduction ratios than the no-aid condition. The size reduction ratio increases with an increasing dosage up to 0.5% for calcitic and dolomitic marble and then decreases. As the grinding aid dosage increases (after optimal dosage), the distance between particles changes with the contribution of repulsive and attractive forces and the thickening of the adsorption layer (Prziwara et al., 2018).

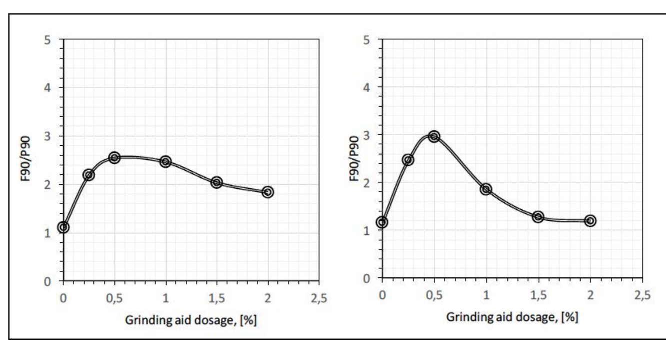

Figure 6. *Influence of the grinding aid concentration on the d_{50} size*

2.2. Grinding media coating

The coating of grinding media with waste products was detected by weighing it after 30 s of dry sieving. Figure 7 shows the coating values according to the decrease and increase of coating on grinding media.

The grinding media coating without any additives was 83 and 15 g/m^2 for calcitic and dolomitic marbles, respectively. The results for all dosages show that the coating of grinding media with the product decreased dramatically.

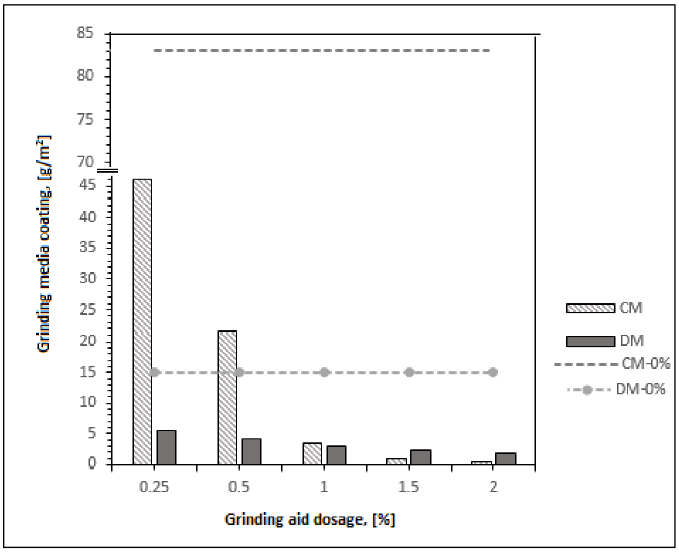

Figure 7. *Grinding media coating of calcitic and dolomitic marble*

2.3. Energy consumption

It is known that the fineness of the product obtained as a result of grinding is proportional to the energy consumed. One way to increase the grinding energy efficiency in ultrafine grinding is to use grinding additives. Tuunila (1997), Wang and Forssberg (1995), Zheng et al. (1997), Choi et al. (2010), and Choi and Wang (2007) planned to increase the grinding and energy efficiency with the addition of appropriate chemicals. The results obtained in this study are in agreement with previous studies in the literature.

The influence of the grinding aid dosage on energy consumption was investigated, as shown in Figure 8, for calcitic marble (left side) and dolomitic marble (right side).

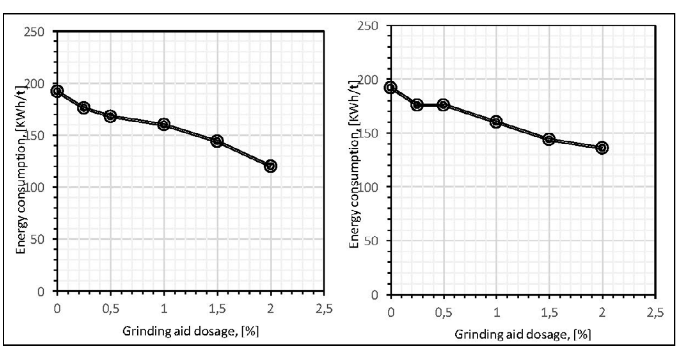

Figure 8. *Energy consumption of calcitic and dolomitic marble*

Concerning the experimental results, energy consumption for calcitic marble, which was 192 kWh/t without additives, decreased to 120 kWh/t with the use of glycerin. Thus, 72 kWh/t energy savings were achieved. The energy consumption for dolomitic marble, which was 192 kWh/t without additives, decreased to 136 kWh/t. Thus, 56 kWh/t energy savings were achieved in dolomitic marble. The specific energy consumption improved with grinding additives (Katırcıoğlu-Bayel, 2018).

Conclusions

This study identified the effects of glycerin on product fineness, energy consumption, and grinding media coating. Based on the results, the following conclusions can be drawn:

(1) Adding glycerin improved the product fineness compared to the no-aid condition. The increase in grinding aid dosage from 0 to 0.5% decreased the d_{50} particle size from 10.3 to 4.9 µm for calcitic marble and from 6.1 to 2.7µm for dolomitic marble. However, the re-agglomeration phenomenon was observed again, and the d_{50} particle size was increased. The same results were obtained for the size reduction ratio.

(2) The grinding media coating without any additives was 83 and 15 g/m^2 for calcitic and dolomitic marbles, respectively. The results for all concentrations show that the coating of grinding media with the product decreased dramatically.

(3) The specific energy consumption improved with grinding additives. Moreover, as the amount of grinding aids increased, energy consumption decreased. This positive impact of grinding aids on energy consumption could be attributed to the ease of powder flow.

With this study, it was understood that calcitic and dolomitic marble samples could be dry ground to ultrafine sizes in a laboratory-scale vertical stirred mill. As a result, unrefined glycerin was identified as an excellent quality additive improving the grinding performance of marble waste. A study was carried out to shed light on the fact that it could be used in alternative products in grinding processes where imported grinding chemicals were generally used.

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References

Alyamac, K.E., Ince, R. 2009. A preliminary concrete mix design for SCC with marble powders. Construction and Building Materials. 23(3), 1201-1210.

https://doi.org/10.1016/j.conbuildmat.2008.08.012

Austin, L.G., Klimpel, R.R., Luckie, P.T. 1984. Process engineering of size reduction: Ball milling. SME, New York, 561 p.

Cayirli, S. 2018. Influences of operating parameters on dry ball mill performance. Physicochemical Problems of Mineral Processing. 54(3), 751–762. https://doi.org/10.5277/ppmp1876

Chi, Z., Pyle, D., Wen, Z., Frear, C., Chen, S.A. 2007. Laboratory study of producing doco-sahexaenoic acid from biodiesel-waste glycerol by microalgal fermentation. Process Biochemistry. 42(11):1537-45. https://doi.org/10.1016/j.procbio.2007.08.008

Choi, H.K., Wang, L. 2007. A quantitative study of grinding characteristics on particle size and grinding consumption energy by stirred ball mill. Korean Journal of Materials Research. 17(10), 532–537. https://doi.org/10.3740/MRSK.2007.17.10.532

Choi, H.K., Lee, W., Kim, D.U., Kumar, S., Kim, S.S., Chung, H.S., Kim, J.H., Ahn, Y.C., 2010. Effect of grinding aids on the grinding energy consumed during grinding of calcite in a stirred ball mill. Minerals Engineering. 23, 54-57. https://doi.org/10.1016/j.mineng.2009.09.011

DPT, 2001. Madencilik Özel İhtisas Komisyonu Raporu, Endüstriyel Hammaddeler Alt Komisyonu Genel Endüstri Mineralleri I, Çalışma Grubu

Raporu. DPT:2618- ÖİK:629, 99sf.

El-Shall, H., Somasundaran, P. 1984. Physico-chemical aspects of grinding: a review of use of additives. Powder Technology. 38, 275-293. https://doi.org/10.1016/0032-5910(84)85009-3

El-Sherbiny, S., El-Sheikh, S. M., Barhoum, A. 2015. Preparation and modification of nano calcium carbonate filler from waste marble dust and commercial limestone for papermaking wet end application. Powder Technology. 279, 290-300. https://doi.org/10.1016/j.powtec.2015.04.006

Fuerstenau, D.W. 1995. Grinding aids. Kona. 13, 5-18.

Gao, X., Yang, Y., Deng, H. 2011. Utilization of beet molasses as a grinding aid in blended cements. Construction and Building Materials. 25(9), 3782-3789.

https://doi.org/10.1016/j.conbuildmat.2011.04.041

Hasegawa, M., Kimata, M., Shimane, M., Shoji, M., Tsuruta, M. 2001. The effect of liquid additives on dry ultrafine grinding of quartz. Powder Technology. 114, 145–151. https://doi.org/10.1016/S0032-5910(00)00290-4

Karinen, R.S., Krause, A.O.I. 2006. New biocomponents from glycerol. Applied Catalysis A: General. 306, 128-133. https://doi.org/10.1016/j.apcata.2006.03.047

Katırcıoglu-Bayel, D. 2018. The Effect of Grinding Additives on Stirred Media Milling of Talc. International Journal of Innovative Science, Engineering & Technology. 5(7), 36-39.

Katırcıoglu-Bayel, D., Toghan E.W. 2022. Karıştırmalı Bilyalı Değirmende Biyo-Dolgu Malzemesi Üretiminde Öğütme Yardımcılarının Etkisi. Konya Mühendislik Bilimleri Dergisi. 10(1), 61-71.

Leoneti, A.B., Aragão-Leoneti, V., De Oliveira, S.V.W.B. 2012. Glycerol as a by-product of biodiesel production in Brazil: alternatives for the use of unrefined glycerol. Renewable Energy. 45, 138-145. https://doi.org/10.1016/j.renene.2012.02.032

Li, H., Jiang, Z., Yang, X., Yu, L., Zhang, G., Wu, J., ve Liu, X. 2015. Sustainable resource opportunity for cane molasses: Use of cane molasses as a grinding aid in the production of portland cement. Journal of Cleaner Production. 93, 56-64. doi: https://doi.org/10.1016/j.jclepro.2015.01.027

Li, H., Zhao, J., Huang, Y., Jiang, Z., Yang, X., Yang, Z., Chen, Q., 2016. Investigation on the potential of waste cooking oil as a grinding aid in Portland cement. Journal of environmental management. 184, 545-551. https://doi.org/10.1016/j.jenvman.2016.10.027

Locher, F.W., Seebach, H.M. 1972. Influence of adsorption on industrial grinding. Ind. & Eng. Chem. Des. Develop. 11(2), 190-197.

Mymrin, V.A. 1997. Environment protection by industrial wastes utilization for engineering geology goals. Engineering Geology and the Environment. 2027-2031.

Nayak, S. K., Satapathy, A., Mantry, S. 2022. Use of waste marble and granite dust in structural applications: A review. Journal of Building Engineering. 46, 103742. https://doi.org/10.1016/j.jobe.2021.103742

Oksuzoglu, B., Ucurum, M. 2016. An experimental study on the ultra-fine grinding of gypsum ore in a dry ball mill. Powder Technology. 291, 186–192. https://doi.org/10.1016/j.powtec.2015.12.027

Orumwense, O.A., Forssberg, E. 1992. Superfine and ultrafine grinding-a literature survey. Mineral Processing and Extractive Metallurgy Review. 11, 107-127.

https://doi.org/10.1080/08827509208914216

Prziwara, P., Breitung-Faes, S., Kwade, A. 2018. Impact of grinding aids on dry grinding performance, bulk properties and surface energy. Advanced Powder Technology. 29(2), 416-425. https://doi.org/10.1016/j.apt.2017.11.029

Sabine, S., 2013. The role of universities in fostering sustainable development at the regional level. J. Clean. Prod. 48, 74-84. https://doi.org/10.1016/j.jclepro.2013.01.029

Toraman, O.Y. 2012. Effect of chemical additive on stirred bead milling of calcite powder. Powder Technology. 221, 189-191. https://doi.org/10.1016/j.powtec.2011.12.067

Tunc, E.T. 2018. Investigation of the abrasion resistance of the quartzitic natural aggregate for different test parameters. Qualitative Studies. 13(2), 57-67.

Tuunila, R., 1997. Ultrafine grinding of FGD and phosphogypsum with an attrition bead mill and a jet mill: optimisation and modelling of grinding and mill comparison. Thesis (PhD). Lappeenranta University of Technology.

Wang, Y. and Forssberg, E. 1995. Dispersants in stirred ball mill grinding. KONA Powder and Particle Journal. 13, 67-77. https://doi.org/10.14356/kona.1995011

Zhang, L., Luo, M., Sun, S., Ma, J., & Li, C. 2010. Effect of surface structure of nano-CaCO3 particles on mechanical and rheological properties of PVC composites. Journal of Macromolecular Science, Part B. 49(5), 970-982. https://doi.org/10.1080/00222341003609336

Zhang, Y., Fei, A., Li, D. 2016. Utilization of waste glycerin, industry lignin and cane molasses as grinding aids in blended cement. Construction and Building Materials. 123, 785-791. https://doi.org/10.1016/j.conbuildmat.2016.07.034

Zheng, J., Harris, C.C., Somasundaran, P. 1997. The effect of additives on stirred media milling of limestone. Powder Technology. 91(3), 173–179. https://doi.org/10.1016/S0032-5910(96)03236-6