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Article *in* Advanced Powder Technology · July 2017

DOI: 10.1016/j.apt.2017.07.007

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Abstract

The main objective of the present paper was to experimentally investigate the grinding kinetics of red grape seed which is the by-product of winery and juice industry. Stirred media mill was used as a high energy density mill to improve the raw grape seed fineness, i.e. mean particle size approx. 10 μm using various rotor circumferential velocities under dry condition. The effect of stress intensity and stress number on the particle size distribution of ground grape seed was investigated. Optimum conditions (rotor velocity and residence time) were determined, mean particle size close to 10 μm and 5000 cm^2/g geometric specific surface area were reached within the studied variables. Additionally, concerning the material structure, FTIR measurements of the ground grape seed samples were carried out which demonstrated that no structural changes were detected. Furthermore, the specific grinding work was measured for each test, in this way energy utilization, efficiency was determined.

Key words: red grape seed, grinding, stirred media mill, stress model, morphology.

1. Introduction

Grape pomace is the byproduct of juice industry and winery, approximately it counts for 25% of the grape weight. Various utilization possibilities of the components of this material are known worldwide – agriculture, food industry, pharmaceutical industry, cosmetics; i.e. functional foods (dietary fiber + polyphenols), food processing (biosurfactants), cosmetics (grapeseed oil +antioxidants), pharmaceutical/biomedical (pullulan) and supplements (grape pomace powder) [1].

Grape pomace was also used as raw material for biogas production experiments carried out by Hajdú [2], who found that 250-270 m^3/t biogas productivity was achieved. However, one of the most prosperous components is the grape seed which can be produced from grape pomace by different separation technologies. Grape seeds are mainly composed of lipids, proteins, carbohydrates and polyphenols. The main polyphenols isolated from grape seeds are catechins and their polymers [3].

Jayaprakasha et al. [4] established that grape seed extracts may be exploitable for the preservation of food products and for health supplements and nutraceuticals.

The study of Molva and Baysal [5] highlighted the potential use of grape seed extract of the fruit juice/beverage industry as natural antimicrobial to inhibit the growth of A. acidoterrestris bacteria.

Polyphenols from grape-derived products have been associated with the prevention of numerous diseases including cardiovascular and neurodegenerative diseases such as Alzheimer’s disease, as well as several forms of cancers [6] [7] [8].

Bagchi [9] demonstrated that grape seed powder extract provides excellent protection against oxidative stress and free radical-mediated tissue injury. The antioxidants are potent scavengers of free radicals and serve as inhibitors of neoplastic processes.

The grape seed structure can be divided into five parts: 1 - cuticle and epidermis, 2 - outer integument or soft seed coat, 3 - medium integument or hard seed coat, 4 - inner integument and 5 - endosperm and embryo. Cadot et al. [10] found that polyphenols have been observed mainly in the epidermis and in the outer integument.

Boussetta et al. [11] investigated the polyphenols extraction conditions of grape seed. Three different pre-treatments were applied on grape seeds: (1) pulsed electric fields (8-20 kV/cm, 0-20 ms), (2) high-voltage electrical discharges (10 kA/40 kV, 1 ms) and (3) grinding in a small scale cutting mill (180 W, 40 s) in order to increase the polyphenols yield. The ground samples were sieved to select particles finer than 1000 μm and were immediately used for diffusion experiments. All the pre-treatments could enhance the extraction kinetics.

Bucić-Kojić [12] studied the kinetics of a batch solid–liquid extraction of total phenolic compounds (PC) from milled grape seed using 50 % ethanol at different extraction temperatures (25-80 C). They concluded that the maximum yield of PC was 0.13 kg_{GAE}/kg_{db} after 200 min of extraction in agitated vessel at 80°C.

The above technologies are based on mainly chemical processes (i.e. extraction). However, there are numerous application in which mechanical preparation by (grinding) is appropriate to produce a valuable final product in powder form or to enhance the extraction efficiency. The grinding process has a very important role in the industry. Beside the traditional applications, such like metallurgical, chemical, cement and mineral processing industry, it is more and more widely used in the cosmetics, food, pigment and pharmaceutical industry (active materials) as well as treatment of biomass and different kinds of waste.

Smekal [13] defined the term of “mechanical activation” as processes effected by mechanical energy, which increase the chemical reactivity of the system without altering chemical composition. However, there are several states of mechanical activation and the following situations can be distinguished: i) mechanical dispersion, ii) surface activation and iii) mechano-chemical (structural) activation [14, 15, 16].

There are only limited papers reported the process of grape seed grinding. One of the known and published technology [17] using air jet milling, they reached 10 μm median particle size. Jet mills are widely used in the food industry [18, 19, 20 21]. However, the disadvantage of this kind of mill that it requires ancillary air compressors to assure high flow rates, pressure can exceed 10 bars [22].

Recently Zhao et al. [23] reported that superfine grinding decreased the bulk density and fluidity, and improved the solubility of grape seed. However, this paper is dealing only with the material properties of the ground and classified samples and not the grindability characteristics.

According to the literature the following mills are reported as micro grape seed manufacturing apparatuses: air jet mill, impact mill, cutter mill, disc mill [23, 24].

Based on the fact, that only very limited number of papers are dealing with grape seed grinding (micronization), in spite of the relevance of the size reduction process during its utilization, the goal of the research reported in this paper is to investigate the grinding kinetics of grape seed in a high energy density mill (stirred media mill) and study the particle morphology and material structure during the grinding process.

2. Material and methods

2.1. Material

The red grape seed pellet sample originated from Verimpex 2000 Co. Ltd. Hungary was generated during the grape oil manufacturing after cold pressing treatment. The maximum particle size was 15 mm andthe density of the grape seed was determined by pycnometer method using alcohol as media, it was found to be 1.52 g/cm^3. Moisture content was measured in drying oven at 105^{o}C until constant mass overnight, which was 7.47%.

Figure 1 a) and b) show the optical microscopy images of the fracture surface of a raw grape seed. The main zones of the seed structure [10] can be detected clearly in Figure 1 b, which are as follows from the left side: 1 - cuticle and epidermis, 2 - outer integument or soft seed coat, 3 - medium integument or hard seed coat, 4 - inner integument and 5 - endosperm and embryo.

The cuticle and epidermis are very thin layers on the outer surface, followed by the outer integument or soft seed coat (Fig 1.b). This latter one is dark brown, having a 100-200 μm layer thickness. The next layer is a light brown, orange colored one, with size of 200-500 μm, which is ridged, ribbed toward the center of the core. The biggest part in volume of the seed is a more or less transparent light colored material, so called endosperm and embryo consisting of rounded and spherical shaped primary particles with a median size of 20-30 μm (Fig 1.b). Between the two latter ones there is the inner integument in the size range of 10-20 μm.

2.2. Preparation methods

The raw grape seed pellet was pre-ground in a hammer mill and a Retsch centrifugal ZM 200 type impact mill prior to the systematic grinding experiments in stirred media mill. The hammer mill was used with 2 mm sieve and the Retsch ZM 200 with 0.5 mm sieve and 10.000 1/min revolutional number.

The grinding of the grape seed was carried out in a batch stirred media mill with 530 cm^3 grinding chamber volume. Stirred media mills are widely used in various fields, i. e. pharmaceutical, ceramic, mineral processing and chemical industry [25]. The chamber is filled with fine size grinding media (mostly wear resistant ceramics) which are put into relative motion by the rotating agitator, therefore high energy density can be reached compared with a conventional tumbling mill.

The material of the liners and the five stirrer discs made of high wear resistant Al_2O_3 ceramic. The perforated stirrer discs have a triangular shape. The mill was operated in horizontal position. During the grinding experiments water cooling was applied using double coated jacket, so the temperature was controlled during the grinding. Grinding media were ceramic grinding beads with the diameter range of 1.2-1.6 mm. The mill filling ratio was 0.7. Stress intensity was set by changing the circumferential speed of the rotor for 4, 5, 6 and 7 m/s. Table 1 contains the main operating parameters of the mill. The residence time of grinding tests in the stirred media mill was 1, 3, 5, 10 and 15 minutes in dry state. Prior to the grinding the raw material was dried (60^{o}C) in a drying cabinet to decrease the residual moisture content to avoid aggregation of fine particles.

2.3. Characterization methods

2.3.1.Laser Particle Size Analyzer

The particle size distribution and the calculated specific surface area (S) of the ground grape seed samples were determined using a HORIBA LA-950V2 type laser particle size analyzer. From the measured data the computer calculated the particle size distribution according to the Fraunhofer-theory. The measurement range of the analyzer is between 10 nm and 3 mm. During the measurement ultrasonic treatment was used for the dispersion of fine particles.

2.3.2. Optical Microscopy

In order to investigate the size and shape of the ground grape seed particles measurements were carried out with optical microscopy using Zeiss ImagerM2m under various magnifications (50x, 200x). Alcohol media was used in order to disperse the particles on the surface of the glass plate prior to the investigation. At least 10 images were taken after each grinding residence time to have representative number of particles, then image analysis was performed.

2.3.3. Fourier Transform Infrared Spectrometry

The material structure after grinding was detected by FT-IR method using a JASCO FT-IR 4200 type apparatus used in reflection mode equipped with diamond ATR type PRO470-H. Two spectra were made from each grape seed sample. Spectra are the average of 32 measurements with 4 cm^{-1} wavenumber resolution.

2.3.4. BET specific surface area

BET specific surface area (SSA) of the ground red grape seed (Langmuir surface area) samples were determined by a Micromeritics Tristar 3000 apparatus. The Micromeritics Tristar 3000 Analyzer uses physical adsorption and capillary condensation principles to obtain information about the surface area and porosity of a solid material. The analytical method is simple: a sample contained in an evacuated sample tube is cooled to cryogenic temperatures and then exposed to the analysis gas (nitrogen) at a series of precisely controlled pressures. With each incremental pressure increase, the number of gas molecules adsorbed on the surface increases. The equilibrated pressure (P) is compared to the saturation pressure (P_0) and their relative pressure ratio (P/P_0) is recorded along with the quantity of gas adsorbed by the sample at each equilibrated pressure. Data were measured by the use of nitrogen adsorption/desorption isotherms at liquid nitrogen temperature and relative pressures (P/P_0) ranging from 0.01-1.0.

2.4.Evaluation of the grinding process by stress model

The stress models are widely used for the description of the stirred media milling. Using the product related stress model, described by Kwade [18], the specific surface area or the particle size can be related to the operation parameters. Based on thework of Kwade and Others [25, 26, 27, 28] the grinding process can be described from two different points of view: i) based on the particles of the feed or ii) based on the mill. According to these approaches the mill related and the product (particle) related stress models can be distinguished. The basic idea or principle of the product-related stress model is that for a given feed particle, the product quality and fineness achieved in a comminution or dispersing process is determined by two facts: First, how often each feed particle and its resulting fragments are stressed, and thus by the number of stress events of a feed particle (SN_F). Second, ow high the specific energy or specific force at each stress event is, and thus by the stress intensity at each stress event (SI). The value of SN_F and SI depend on the operation parameters. For the characterization of a mill, it makes more sense to define characteristic numbers, which are independent on the size and other properties of the product particles. Therefore, instead of a product- related model, the following mill-related model should be used: the comminution behavior of a mill is determined by the number of stress events which are supplied by the mill per unit time, the so-called frequency of stress events (SFM); and the energy which can be supplied to the product particles by the mill at each stress event, the so-called stress energy (SE).

During the evaluation of the measurement result the product related stress model was applied to describe the effect of the operational parameters on the product dispersity.

The stress intensity (SI) of the grinding media (GM) was calculated by the following equation, based on [27]:

$$SI_{GM} = d_{GM}^3 \cdot \rho_{GM} \cdot v_t^2 \qquad (1)$$

where d_{GM} is the diameter of the grinding media, ρ_{GM} is the density of the grinding media and v_t is the circumferential velocity of the stirrers.

However, the above presented model was developed for wet grinding processes, therefore, the stress number was needed to be modified for dry grinding. Details about the recently developed product related stress model for dry batch grinding and its application can be seen in the work of Rácz and Csőke [21]. Based on their findings the stress number was calculated as follows:

$$SN_F^{**} = n\, t\, \frac{(1-\varepsilon_{GM})x^3}{\varepsilon_{GM}(1-\varepsilon_a)d_{GM}^2\varphi_m} \qquad (2)$$

where n is the revolution number, t is the residence time, ε_{GM} is the porosity of the grinding media and φ_m is the material filling ratio.

In case if

$$\varphi_m = \frac{V_m}{V_{P,GM}} \qquad (3)$$

the material filling ratio φ_m is the quotient of the material volume V_m and the pore volume between the grinding media $V_{P,GM}$.

The energy utilization (EU) is defined as the ratio of the new produced specific surface, ΔS, to the specific energy W_{spec} required to produce SSA difference ΔS [27, 30, 31] in the unit of cm^2/kJ.

$$EU = \frac{\Delta S}{W_{spec}} \qquad (4)$$

If a single particle is stressed once, the stress intensity corresponds to the specific energy for stressing the particle; hence, in this case, the energy utilization is equal to ΔS/SI. At the optimum stress intensity, SI_{opt}, the energy utilization has its maximum value, EU_{max}, at which a certain specific surface can be produced with a minimum of specific energy [27].

3. Results and discussion

3.1. Grinding kinetics

The grinding of the grape seed is of great importance since the active ingredients can be utilized more efficiently by the human body if the reaction surface is higher. The primary goal of our grinding investigation was to reach mean particle size close to 10 μm. This specific characteristic particle size was given in order to generate finer particles than the available red grape seed products on the market.

Figure 2 shows the relationship between the stress number of grinding and the specific surface area of the products at various stress intensity regimes. It can be seen that the highest specific surface area (5000 cm^2/g) reached using 4.81 10^{-4} Nm stress intensity at the stress number of 300. Additionally, all of the stress intensity regimes resulted in similar behavior concerning stress number (SN_F^{**}) – specific surface (S) relation, i.e. specific surface increased until a certain point and then decreased as function of SN_F^{**}. The highest stress intensity found to be the most efficient since it reached the highest specific surface area.

In order to evaluate the total specific surface area (total SSA), BET (Langmuir surface area) related to the experimental series of 7 m/s circumferential velocity values are summarized in Table 2. It can be seen clearly that the total SSA increased gradually from the initial value of 0.3613 m^2/g (at 1 min residence time) up to 0.6906 m^2/g after 10 min of grinding. Based on these results compared with the geometric specific surface area it can be established that the agglomerates are strongly bonded, furthermore it proves the presence of secondary particles.

From energetic point of view the relationship between specific grinding work and mean particle size of the ground grape seed was determined; the results are plotted in Figure 3 a. At all SI values the curves were almost linear in the first section (up to 1000 kJ/kg). Furthermore, the mean particle size decreases as a function of the specific grinding work until a given value (about 10 μm), so the curves have minimum points. Therefore, it can be concluded that the material aggregated after certain specific grinding work.

The specific grinding work is plotted as function of span of the particle size distribution of the ground red grape seed (Fig. 3 b) which was determined as follows:

$$RS = \frac{d_{90} - d_{10}}{d_{50}} \qquad (5)$$

The Figure 3 b shows the highest span values in the case of 6 m/s tip speed. It means that stirred media mill at this speed produced a ground material with the widest particle size distribution. Additionally, it can be established fluctuations in the value of span in each cases which is the result of the aggregation-desaggregation processes during grinding.

Fig 4 proves the aggregation of the fine particles, where the frequency curves can be seen. After 15 minutes grinding, the volume fraction of the 100-400 μm particles significantly increased. The higher the stress intensity, the lower the minimum point of the mean particle size in the above stress intensity regime ranges. The lowest mean particle size was found to be 13 μm at 4100 kJ/kg grinding work under 4.81 10^{-4} Nm stress intensity.

Figure 4 shows the frequency curves of the ground grape seed related to the highest stress intensity (SI = 4.81 10^{-4}) Nm. Concerning the raw feed the frequency curve is trimodal type, which remains the same type at 1 min grinding time. Only the coarsest mode (350 μm) decreased resulted in fine particles in the range of 10-20 μm probably due to the abrasion of coarse particles' surface. At 10 min residence time two characteristic mode size was found, 200 μm and 9 μm. Later at 15 min grinding time significant aggregation appeared. Namely the coarser mode size increased to 250 μm, and the amount of coarse particles increased dramatically. The frequency curve became more equalized, more symmetric like.

The multimodal frequency distribution curves show the different grindability between the various grape seed zones (epidermis, integuments, endosperm). There is a mode between 200-300 μm, which indicates a very high grindability. To compare the grinding results between the seed zones the optical microscopy images will serve important information in the next paragraph.

Figure 5 shows the energy utilization of the grinding of grape seed in relation to stress number. It was found that energy utilization decreased in all the four examined stress intensity regimes, but the slope was different as a function of stress number. At the beginning of grinding the highest energy utilization belongs to the higher $3,54.10^{-4}$ and $4.81.10^{-4}$ Nm stress intensity. At these two stress intensities the energy utilization is nearly the same as a function of the stress number. The $1.57.10^{-4}$ Nm stress intensity resulted in significantly lower energy utilization than the higher ones. However, the curve belongs to the $2.46.10^{-4}$ Nm stress intensity the initial value is a bit lower than other cases, which might be a measurement error, but after this point the trend is similar to the other ones.

3.2.Particle morphology

In order to monitor the morphology of the ground grape seed samples produced at v_t = 7 m/s circumferential speed (SI = 4.81 10^{-4} Nm), optical microscopy images were taken, the most relevant ones can be seen in Figure 6 (a-c). In the ground particles the previously detected (Figure 1 b) structural parts (epidermis, inerguments, seed coats, endosperm and embryo) can be differentiated. The characteristic color is light brown and transparent, which might belong to the medium integuments and endosperm.

Ground particles after 1 min grinding (SN_F^{**} = 29.7) can be seen in Figure 6 a) in which rounded and more or less spherical particles are found. There are several primary particles in the size range of 200-300 μm. Basically, three types of particles can be discovered in Figure 6 a, 1) the darker brown part which is the outer inerguments of the seed, 2) the light brown particles are the medium integument and 3) the transparent like ones are the endosperm. The coarsest particles are the light brown medium inergument and the finest ones are originated from the endosperm. It can be concluded that the endosperm can be ground easier than the medium inergument. Figure 6 b) shows the 10 min (SN_F^{**} = 296.9) ground particles where the above mentioned coarse fraction still exists. After 10 min grinding the difference between particle size of the sections is equalized. Significant decrease of the particle size can be seen compared with 1 min grinding. Coarse secondary particles are seen in Figure 6 c), which was resulted in due to aggregation (SN_F^{**} = 445.3). Microcracks can be detected on the surface of the aggregated particles. The size of these secondary particles is 400-800 μm. The original plant cell was broken.

Grinding of non-brittle (elastic, elastic-plastic, viscoelastic) materials is a complex and unique task [32] [33] compared with general questions of mineral processing where mainly brittle materials (ores, industrial minerals, etc…) are comminuted. Therefore, the careful selection of the appropriate apparatus and optimization of the grinding conditions is very important. However, if we take into account all of the five layers of a grape seed, it can be concluded that this is a heterogenous material consisting of easy-, as well as hard-to-grind parts. In this way, its comminution requires various grinding stresses in order to achieve effective size reduction. Based on these problems a suitable equipment, where such complex grinding stresses can be generated, is essential for efficient grinding. Therefore the stirred media mill is an appropriate device since the grinding stresses are friction, impact and pressure. Moreover, the shear stress could be useful for the comminution of fibrous materials. In the stirred media mill such stress can occur if the grinding beads collide with each other tangentially. These stresses occurred during grinding in stirred media mill are investigated via DEM simulation in some papers. According to Cleary et al. [34] the shear stresses have a very similar distribution to the normal stresses. The shear stress is limited to half the normal stress. The shear stress on the chamber wall is significantly less than the normal stress. Based on the numerical modelling Gers et al. [35] established that the tangential stress (related to attrition by friction of neighbouring layers) is at least one order of magnitude larger than the compressive force. Beinert et al [36] investigated the contacts of the grinding beads in a wet stirred media mill with disc stirrers based on CFD-DEM modelling. The model presented in this work suggests that the differentiation between four different contact types should be taken: impact, torsion, shearing and rolling. Additionally, they found that with increasing tip speed the stress energy increases and he number of contacts per time behaves differently. While the increase in tip speed from v=4 up to 6 m/s leads to an increase in contacts a further increase up to v = 9m/s reduces the number of contacts.Based on the grinding kinetics results and the optical microscopy images different grindability behavior of the various grape seed layers can be distinguished. The medium inergument is more hard to grind material than the endosperm. However, this is true only under low stress number, since at higher stress number they behave more or less similarly.

3.3.Material structure

During ultrafine grinding, the surface of ground material undergoes some changes, bringing out advantageous characteristics. Due to these favorable properties, these powders might find more applications than conventionally-ground materials in the food industry or in other fields [37]. On the other hand, based on the industrial practice temperature increase generated by grinding process may cause important losses of aroma, nutrients and flavor components, as well as considerable quality degradation of the raw material especially for heat-sensitive materials [38]. The first requirement of grape seed grinding was to not destroy the original material structure by mechanical forces or heat generated by friction of the grinding media. Therefore, the temperature control of the grinding chamber is of great importance. In order to moderate the heat generation due to friction forces a water cooling jacket was equipped to the system and used during the measurements.

Figure 7 shows the FTIR spectra of the ground grape seed for 1, 10 and 15 minutes using 7 m/s circumferential velocity. As a general observation, the chemical structure of the material did not change significantly due to the grinding effect. The peak at 3313 cm^{-1} related to -OH stretching vibration in phenolic structure. Peak at 2925 corresponds to stretching vibration of C-H band. Vibration at 1742 cm^{-1} comes from carbonyl (C=O) functional groups. Vibration at 1516 cm^{-1} attributed to aromatic CH bonds. Peak at 1442 cm^{1} corresponds to asymmetric in-plane bending of $–CH_3$. The peaks at 1237 and 1032 cm^{-1} represents the vibration of stretching mode from C-O group (at 1237 cm^{-1} it comes from esters). The band at 781 cm^{-1} is the vibration of aromatic ring breathing manner. The above peak positions are well correlated with other scientific works [23] [39]. Additionally, it can be noticed that the stirred media milling did not destroy the structure of phenolic molecules similarly to Zhao et al. [23] observations. On the other hand we did not observe the break of the intramolecular hydrogen bonds like Zhao et al [23], since the peak at 3313 cm^{-1} was more or less stable.

Future aim of our research is to fulfill bio viability tests of the ground products in order to control more accurately the application of the resulted materials.

4. Conclusions

As a result of the experimental investigation of grape seed grinding the following conclusions are drawn:

- Successful grinding (micronization) of grape seed was achieved in a high energy density stirred media mill in dry condition.
- Ideal conditions in the examined cases (residence time, stress number, rotor velocity, stress intensity) of red grape seed grinding were determined. These were as follows:

residence time t = 10 min, stress number SN = 297, tip speed v = 7 m/s and stress intensity SI =4.81 10^{-4} Nm.

- No structural changes of the ground material were detected by FTIR due to the grinding process.
- The micronization of the grape seed might have the advantage on the extraction process of the active ingredients in a further step of the technology.

Acknowledgements

The research work was performed in the framework of the Centre of Excellence in Sustainable Natural Resource Management at the Faculty of Earth Science and Engineering, University of Miskolc. The authors greatly appreciate the help in the experimental work for Zoltán Molnár (PhD student) and Diána Tamás (MSc student).

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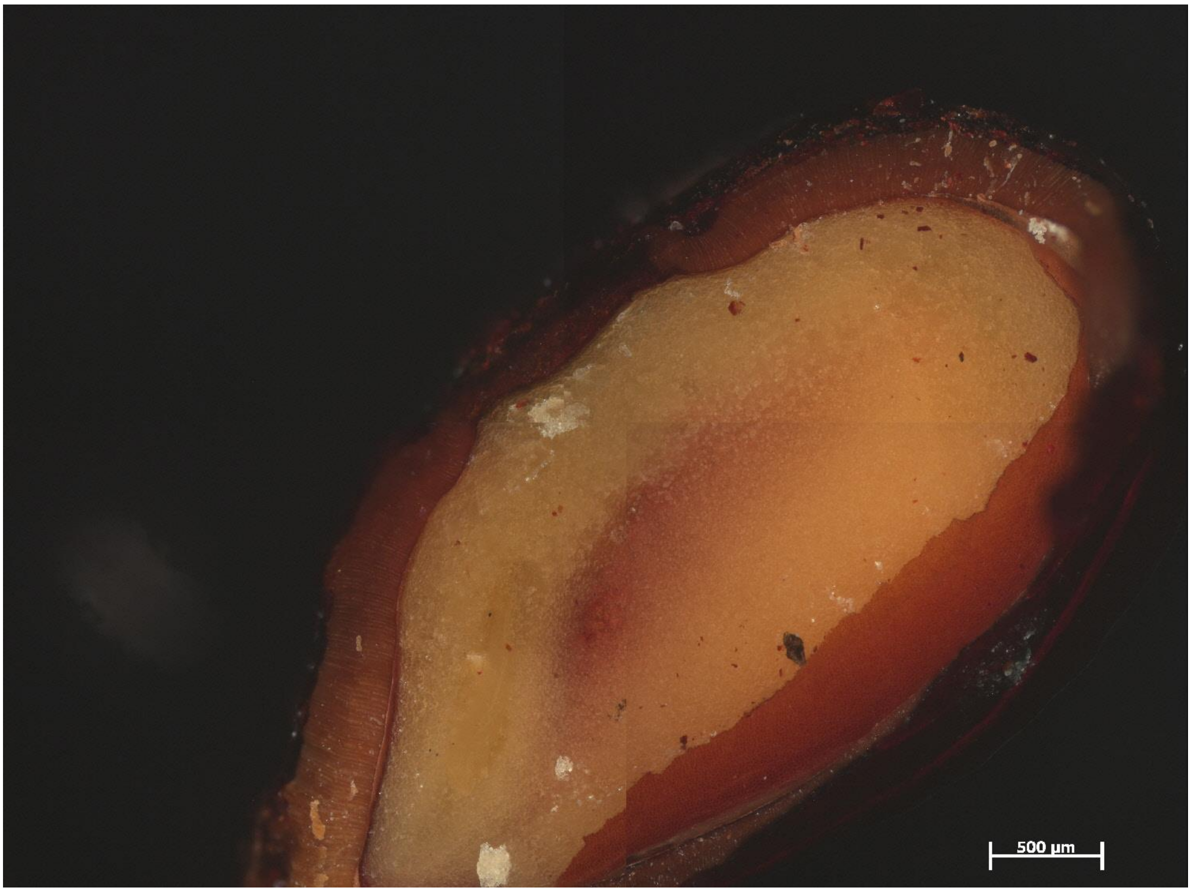
Figures



(a)

(b)

Figure 1. Optical microscopy images of raw grape seed, a – cross section, b – detail of cross section

1 - cuticle and epidermis, 2 - outer integument or soft seed coat, 3 - medium integument or hard seed coat, 4 - inner integument and 5 - endosperm and embryo

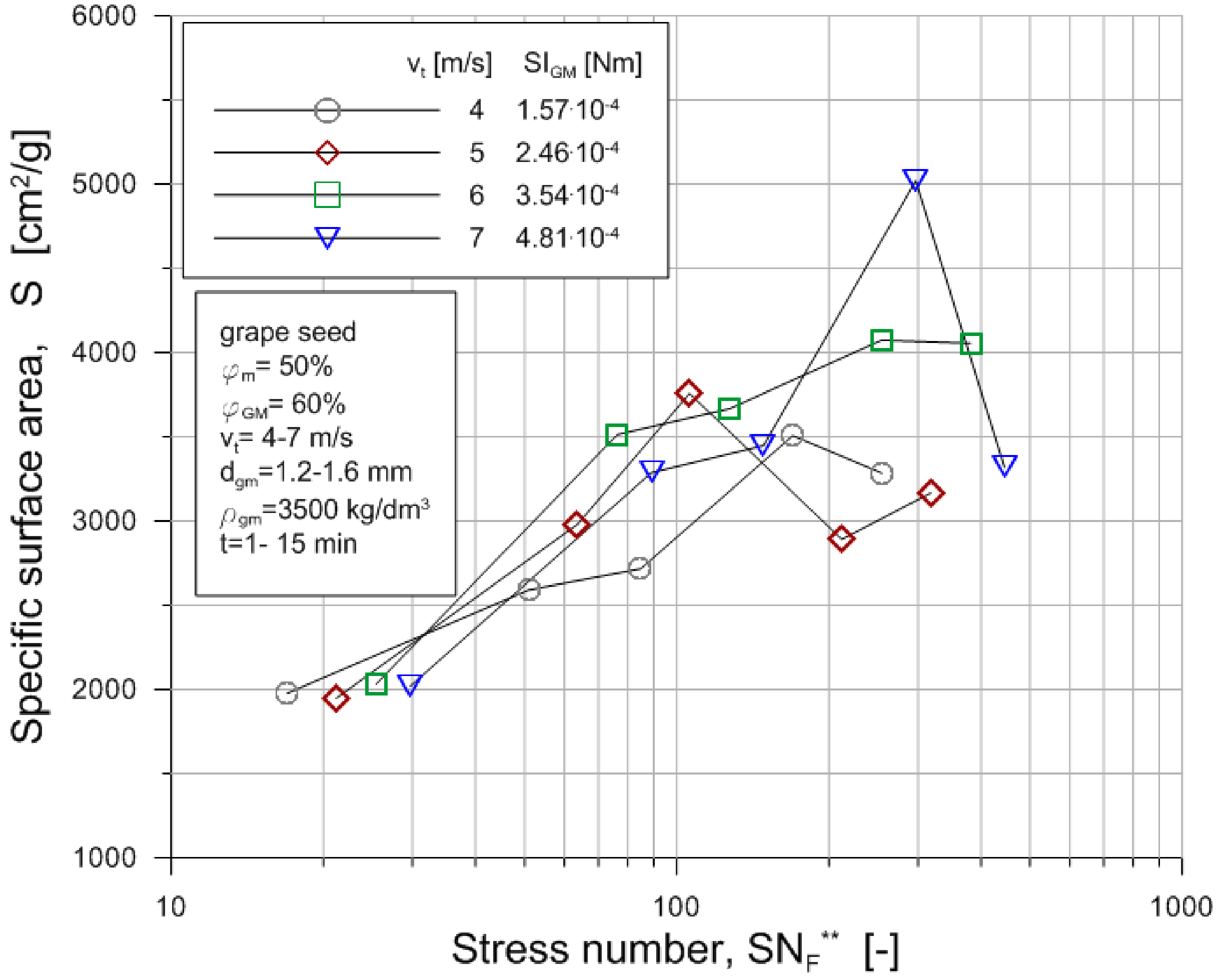
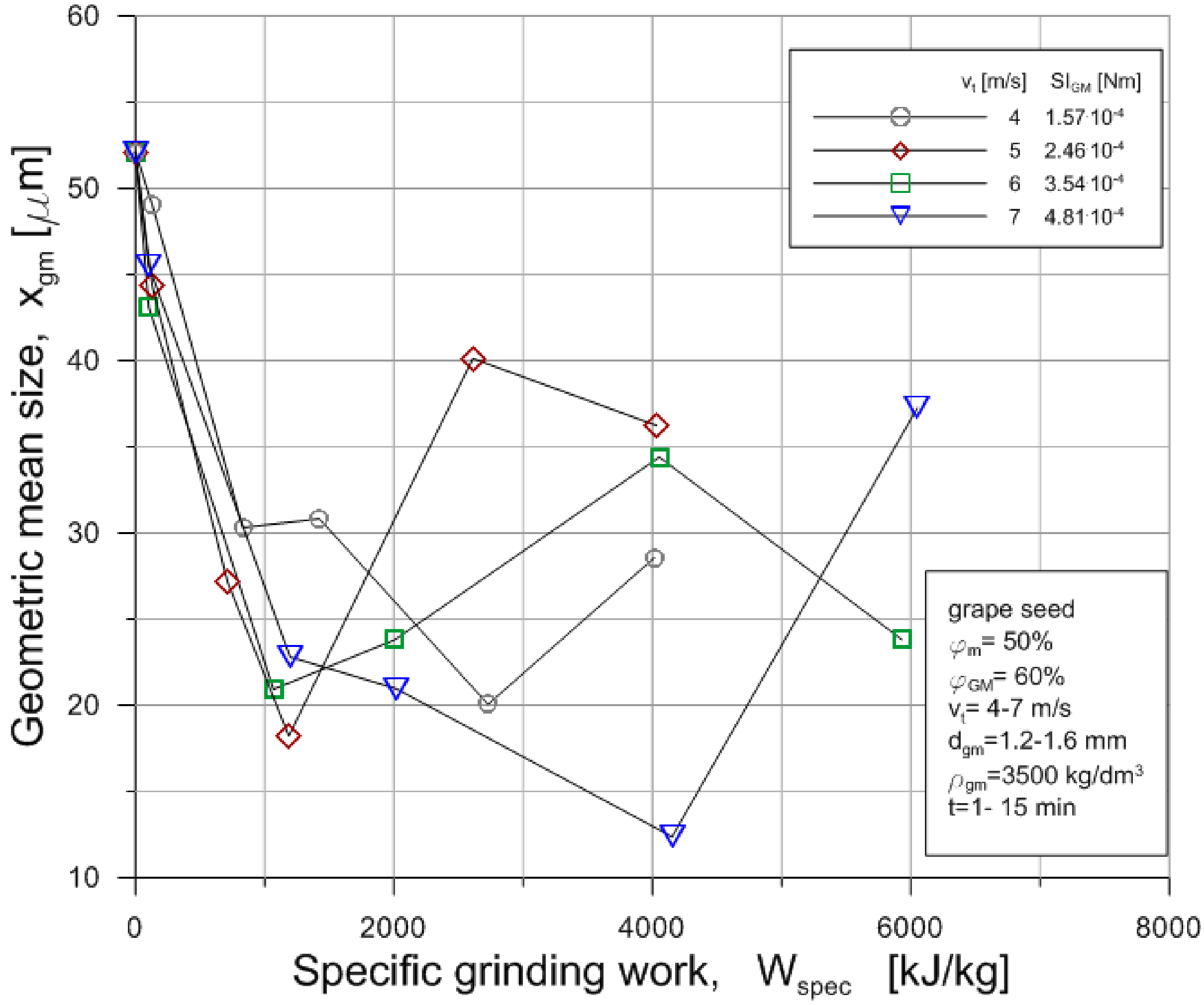
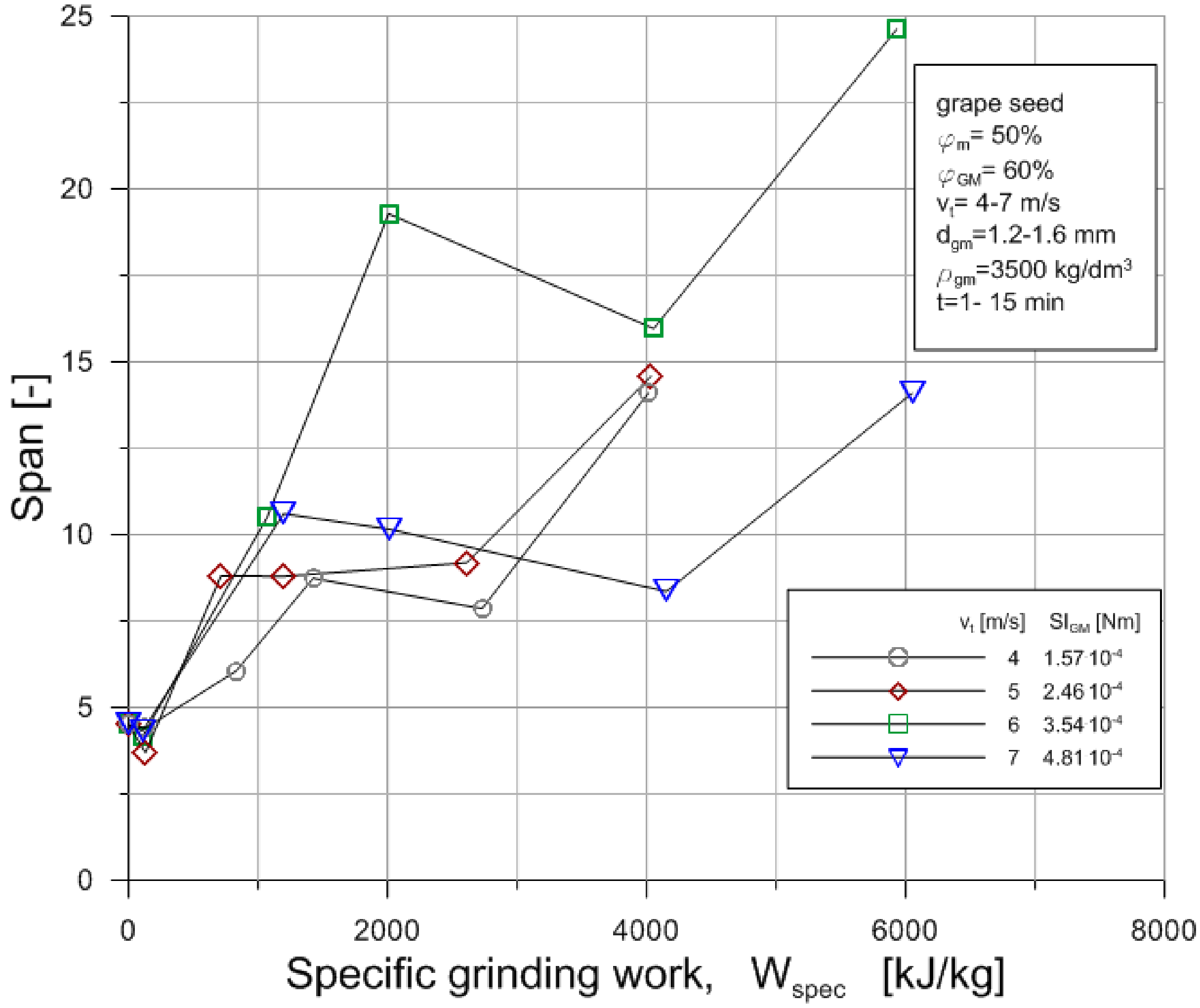


Figure 2: Relationship between stress number and specific surface area of the ground grape seed



Geometric mean size, x_gm [μm]
Specific grinding work, W_spec [kJ/kg]
v_t [m/s] SI_GM [Nm]
4 1.57·10^-4
5 2.46·10^-4
6 3.54·10^-4
7 4.81·10^-4
grape seed
φ_m= 50%
φ_GM= 60%
v_t= 4-7 m/s
d_gm=1.2-1.6 mm
ρ_gm=3500 kg/dm^3
t=1- 15 min

(a)



(b)

Figure 3: a) Relationship between specific grinding work and mean particle size of the ground grape seed, b) Relationship between specific grinding work and span of particle size distribution of the ground grape seed

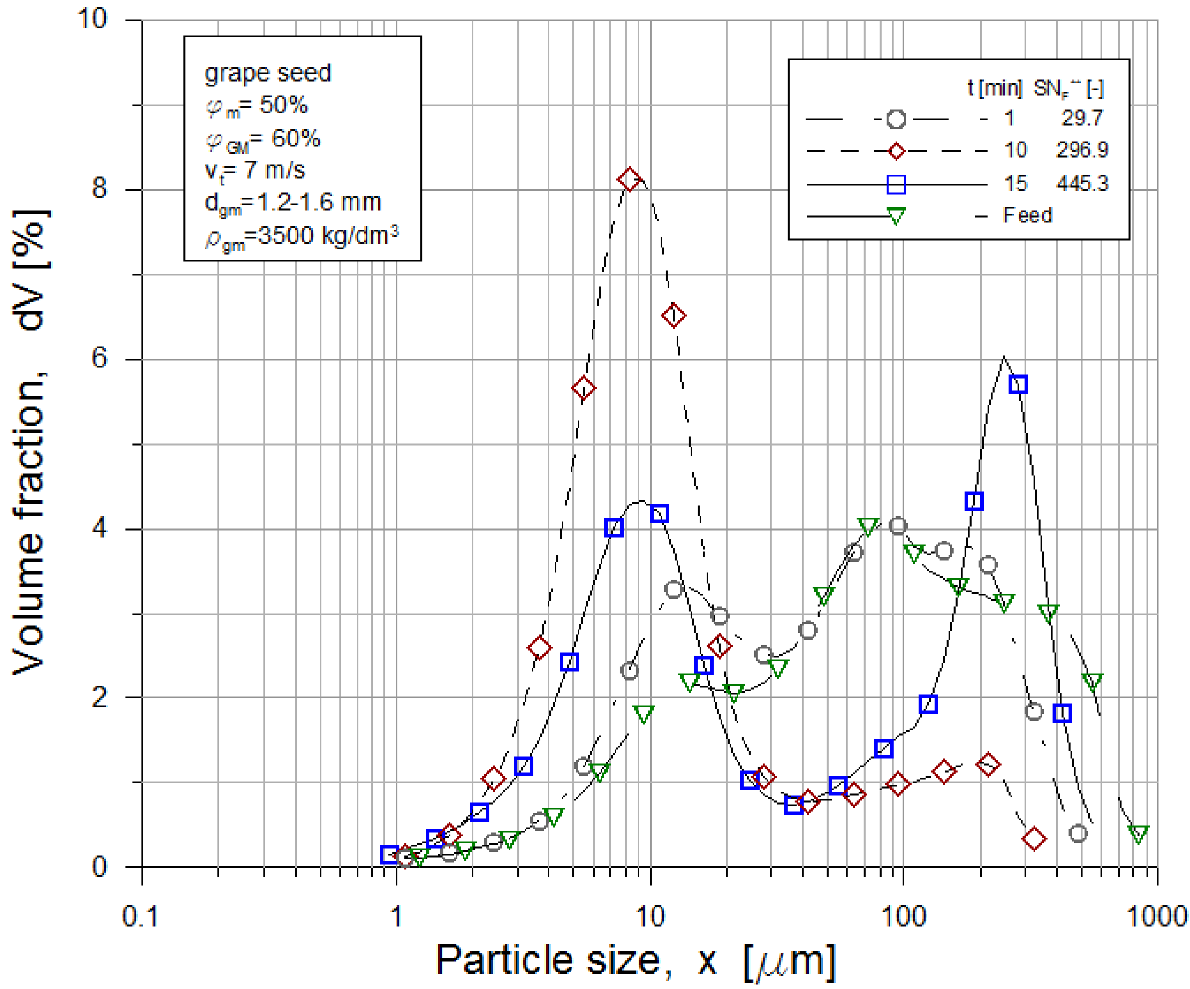


Figure 4: Frequency curves of the ground grape seed at 7 m/s speed after various residence time

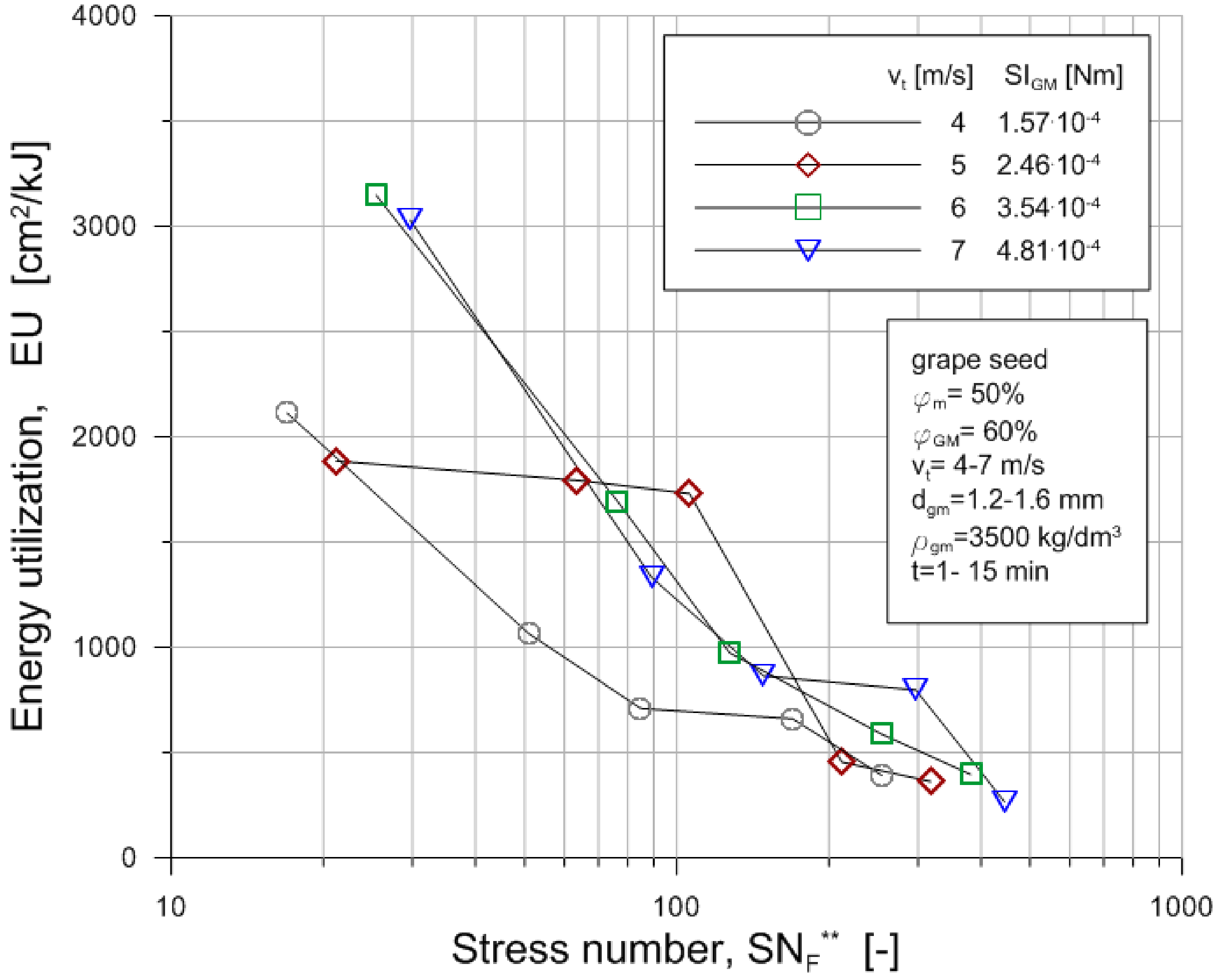
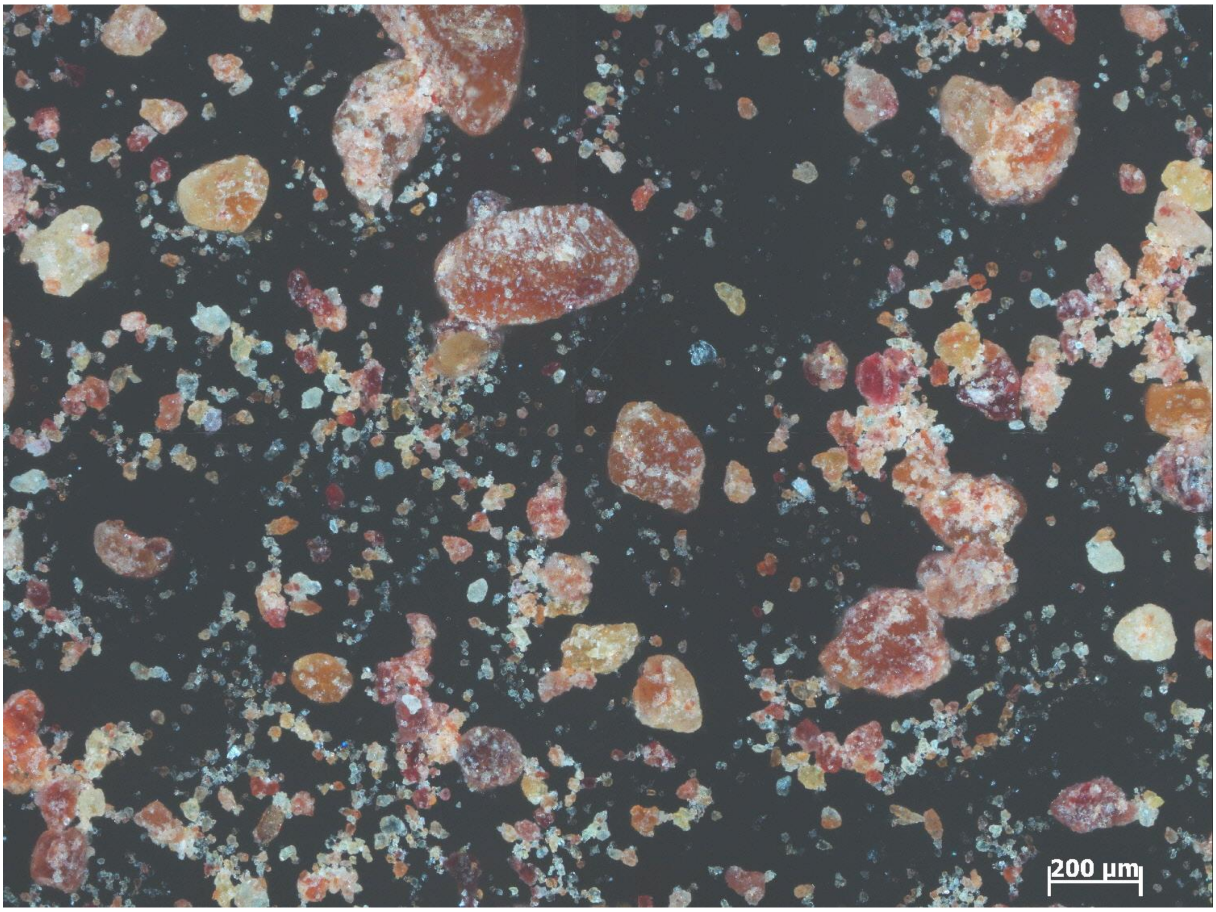
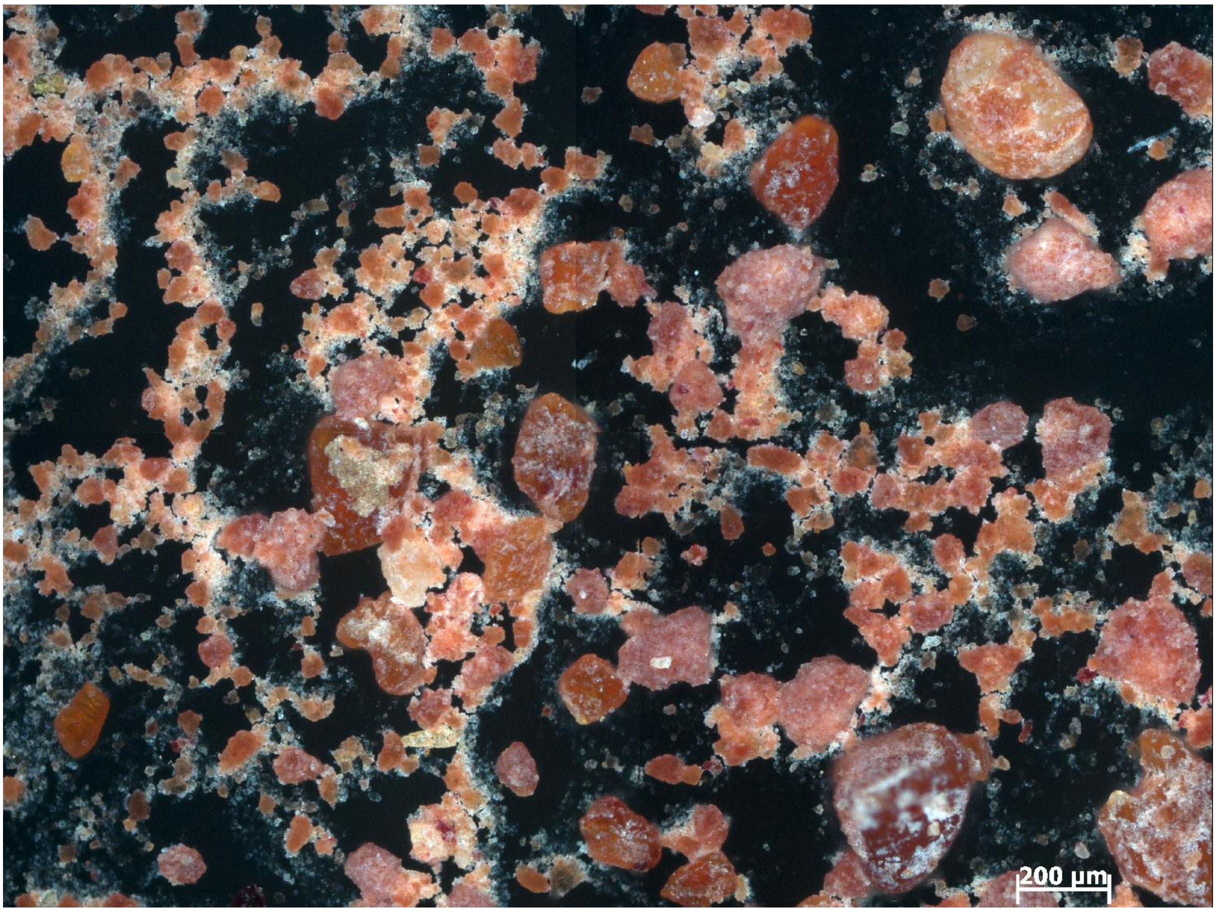


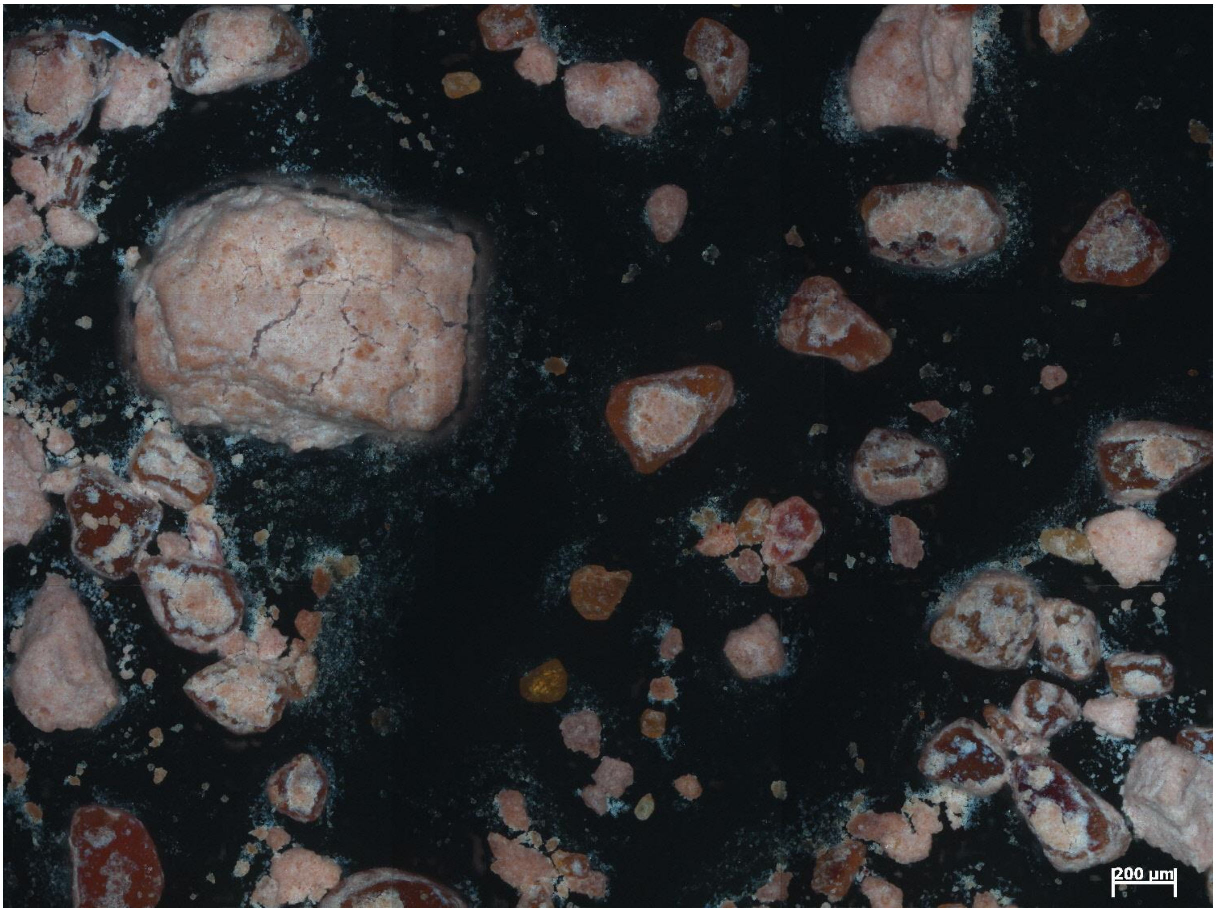
Figure 5: Relationship between stress number and energy utilization of grape seed grinding



(a)



(b)



(c)

Figure 6. Optical microscopy images of ground grape seed, a – 1 min, b – 10 min, c – 15 min

(SI= 4.81 10^{-4} Nm, 50 x magnification)

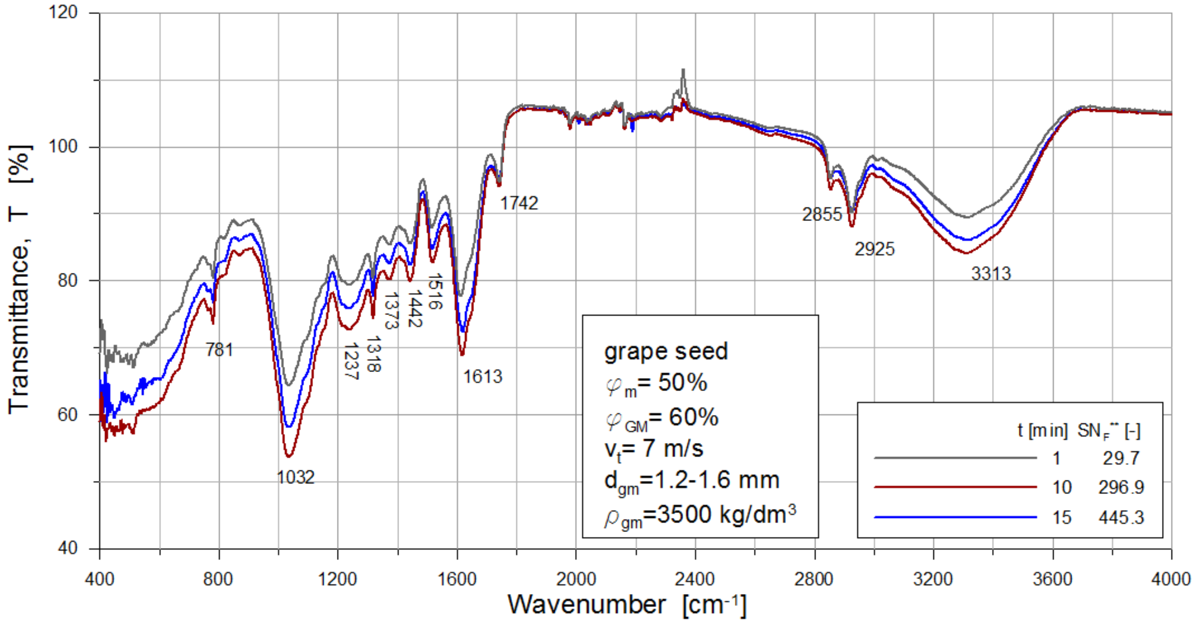


Figure 7: FTIR spectra of the ground grape seed for various residence time at 7 m/s rotor velocity (1, 10 and 15 min)

Tables

Table 1. Operating and machine parameters of the laboratory batch stirred media mill

Parameter, unit	
Grinding bead size, mm	1.2 – 1.6
Stirrer diameter, mm	153
Diamater of grinding chamber, mm	174
Length of grinding chamber, mm	250
L/D ratio	1,44
Density of grinding beads (GM), kg/m^3	3.50
Tip speed of stirrer, m/s	4, 5, 6 and 7
Residence time, min	1, 3, 5, 10 and 15

Table 2. BET total specific surface area of the ground red grape seed at 7 m/s tip speed

Grinding time, v=7 m/s	1 min	5 min	10 min	15 min
BET specific surface area (Langmuir)	0.3613 m²/g	0.4148 m²/g	0.4620 m²/g	0,6906 m²/g