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Conversion of cleaned Oltu-stone wastes (a semi-precious stone) into a valuable product using binderless agglomeration

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Abstract: Oltu-stone, a semi-precious stone found in Erzurum's Oltu area, is commonly utilized in the creation of decorative ornaments. More than 90% of the Oltu-stone mined is classified as Oltu-stone waste, consisting of poor Oltu-stone due to mineral impurities and small fragment sizes (OW). This waste is thrown or burnt, resulting in financial losses. Such losses might be reduced by using Oltu-stone waste (OW) instead of standard Oltu-stone (SO). The purpose of this study was to convert Oltu-stone waste into a useful pressed product. It was cleaned using the float-sink method with a density of 1.25 $g.cm^{-3}$ and then utilized for binderless high-pressure agglomeration to create pressed Oltu-stone. The physical, mechanical, microscopic, and spectroscopic characteristics of the material were investigated. The bulk density of pressed Oltu-stone was reported to be 1.22-1.26 $g.cm^{-3}$. However, with the same pressing time, indirect tensile strength was identical and varied when the pressing time was changed. The surface morphology of the crushed Oltu-stone revealed that it was more intact and had a less porous structure. Oltu-stone includes a lot of volatile matter and aliphatic carbon structures because of its high liptinite content. An FTIR investigation revealed that altering the pressing time affects the chemical structure but not the pressure. This effect was seen in molecules containing oxygen, namely conjugated carbonyl and carboxylic groups. It was discovered that pressed Oltu-stone has nearly identical properties to standard Oltu-stone and could be produced on a large scale commercially.

Keywords: agglomeration, cleaned Oltu-stone waste, pressed Oltu-stone, aliphatic carbon

1. Introduction

Oltu-stone is a semi-precious stone found in the Oltu region, of Erzurum, Turkey. In the literature, it is referred to as Erzurum Stone, black amber, gagat, Jayet, and Jet (Ethem, 1990; Kalkan et al., 2012; Kara-Gülbay et al., 2018). In Turkish, it is also known as Kara Kehribar, and Sengi Musa. The Oltu-stone is a geological material that is not a true mineral but rather a mineraloid formed by wood-decaying under extreme pressure (Hatipoğlu et al., 2012; Karayigit, 2007). It lacks crystallinity and has a density of nearly to coal. It is usually black, but it can also be velvet-black, blackish, gray, or greenish. The most exciting feature of Oltu-stone when excavated is its softness. When exposed to air, it begins to harden. As a result, it is easy to carve (Hatipoğlu et al., 2012; Kara-Gülbay et al., 2018; Toprak, 2013). Based on the study of Lahn (1939), only particular deposits in the Oltu district were known as Oltu-stone formation due to resin-rich content, while others were classified as coal formation due to resin-poor content. Oltu-stone colors were similar to jet (Ethem, 1990; Parlak T, 2001). Jet has organic fossil-origin characteristics similar to Oltu-stone but differs in chemical properties (Hunter et al., 1993; Smith, 2005). Oltu-stone was found to be impregnated with clay and resin components and macroscopically generated from the fossilization of tree trunks (Kara-Gülbay et al., 2018). After the latest research on the genesis of Oltu-stone, it was determined to be liptinite-rich coal (Toprak, 2013).

Oltu-stone has an important place in the economy of Erzurum in various aspects such as stone extraction, stone processing, handcraft ateliers, sales, and commerce. The small semi-precious stone sector formed around Oltu-stone, comprising small processing ateliers, shops, and activities at small

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houses, makes it the main attraction point of the economy in the Oltu district, Erzurum. Oltu-stone processing is performed in home handcraft rooms and ateliers where various machinery, including computers, is utilized. The processing yields diverse products, including jewelry, worry beads, and other types of souvenirs. The industry employs both traditional trade methods and new commerce channels, such as Internet commerce.

The waste statistics were collected by interviews and field observations. Based on waste statistics, The market consumes about 1.6 tons of material which is triaged from an approximately 8 tons of excaved material from the galleries. However, the 0.32-0.8 tons of material is transformed in a final jewelry product. The wastes are coming either from mines or ateliers after finishing the stone. Three types of waste are generated from mining to final polishing i.e., rock wastes, Oltu-stone wastes chips, and Oltu-stone wastes powder. Rock wastes include sandstone and claystone fragments which are the primary rocks of the formation where Oltu-stone is extracted. Surfaces where the wall rocks touch with Oltu Stone lenses and fragments of Oltu Stone. During the extraction of Oltu-stone large blocks, the rock wastes are generated inside the mines. After extraction of Oltu-stone from mines, the large blocks of Oltu-stones are transported to the surface. The hammer is used to break those blocks, and hand sorting is done to get a standard Oltu-stone. This breaking generates lots of elongated chips containing minerals and an underdeveloped Oltu-stone. Some chips exhibit good quality stone but are not used due to size limitation (<3 cm) and are discarded as waste. The Oltu-stone waste chips, the second type of waste, combine standard Oltu-stone (<3 mm), and Oltu-stone chips contain mineral impurities. After hand sorting of standard Oltu-stone, it was processed at Oltu ateliers, including cutting, crushing, grinding, and polishing. This process generates powder wastes in a small amount. Based on literature, the number of studies on Oltu-stone were conducted for characterization. However, to the best of author knowledge, no study has been reported in the literature yet on the bindlerless high pressure agglomeration. The aim of this study is to convert the Oltu-stone wastes into valuable product.

2. Materials and methods

2.1. Materials

The Oltu-stone wastes produced during hand sorting comprise more than 90% of extracted material based on atelier data. For that reason, it was used in this study and termed Oltu-stone waste (OW). The Oltu-stone wastes produced during hand sorting comprises standard Oltu-stone (<3 cm in size) and Oltu-stone containing mineral impurities. After hand sorting, the samples were collected from the vicinity of mines at Dutlu mountains.

2.2. Sample preparation

Based on a previous study (Bawani et al., 2019), it was revealed that the cleaned Oltu-stone wastes obtained at below 1.25 g.cm^{-3} density using dense medium separation, had similar characteristics compared to standard Oltu-stone. Therefore, the Oltu-stone wastes were first crushed below 1 mm and then cleaned at 1.25 g.cm^{-3} density using a $ZnCl_2$ solution by the float-sink method. In order to convert a grain size particle into a solid piece or disc, this type of waste is mostly treated by binderless high-pressure agglomeration methods as documented previously (Vikhareva et al., 2016). Han et al. (2013), stated that the conditions such as pressure, temperature, and pressing time are essential variables to consider in the binderless agglomeration.

2.3. Agglomeration method

For binderless high-pressure agglomeration, a hydraulic press with a capacity of 1000 Mpa was used. This machine uses thermocouples to control the temperature of the molds at the same time. The particle size of the cleaned Oltu-stone was still coarser, i.e., less than 1 mm. As a reason, it was reduced to a particle size of less than 30 µm before being used for binderless high-pressure agglomeration. 2 g powder samples were placed in a mold (diameter 20 mm, length 100 mm) and pressed. Preheating, pressing, and cooling are all phases in this agglomeration process. It was first preheated to 100°C for 30 minutes then elevated the temperature of the mould to 200°C for the next 30 minutes. After preheating, it was pressed at various pressures and periods before being cooled to 50°C.

2.4. Characterization of pressed Oltu-stone

The physical, mechanical and chemical properties of Pressed Oltu-stones were analyzed to compare with standard Oltu-stone. The bulk density of pressed Oltu-stone was determined by direct measurement of length and diameter using a vernier caliper (±0.02 mm). Disc surfaces were leveled with sandpaper. Electronic balance laboratory scales determined the mass of the individual disc. Determination of density was done 7 days after pressing. The following formula calculated bulk density:

$$\rho = \frac{4m}{\pi d^2 h}$$

where is a ρ bulk density (g.cm^{-3}), m is a mass of cylindrical disc (g), d is a diameter of cylindrical disc (cm) and h is a thickness of cylindrical disc (cm).

The Load control testing equipment for laboratory scale was used in this work, which is manufactured by KONTROL-TEST equipment, Ankara. This machine is usually used to produce coal briquettes by applying a variable load. This machine has the capacity of applying a 50 KN load maximum with a variable loading rate. In this study, the disc specimen (pressed Oltu-stone) was loaded radially at a 1mm/min rate during indirect strength testing. The maximum load at fracture was measured. The indirect tensile strength was calculated using the following formula mentioned below:

$$\delta t = \frac{2P}{\pi \mathrm{DT}}$$

where δt is an indirect tensile strength (MPa), P is a failure load (N), D is a diameter of cylindrical disc (mm) and T is a thickness (mm)

SEM-EDS analyses were carried out to examine the morphology and mineral content on two machines. (i) JEOL instrument couples with EDS, at METU central laboratory, and (ii) inspect 50 (FEI company), coupled with an EDAX OCTANE (AMETEK Inc.), at General Directorate of Mineral and Exploration, Ankara (MTA).

The thermal analyses include proximate and elemental analyses. For proximate analysis, Perkin Elmer STA6000 was used. This equipment is micro-TGA and requires a small sample of 15-20 mg. Czajka (2018) studied the comparative study between mico-TGA and macro-TGA (ASTM standard) for coal and proposed a methodology which was adopted in this work.

Drift spectroscopy was performed on an FTIR spectrometer (spectrum-II, PerkinElmer) for functional group analysis. The scanning region ranged from 4000 cm^{-1} to 450 cm^{-1} (Mid-infrared region), with 32 scans at 4.0 cm^{-1} resolution. A powder sample (below 30 µm) was used to get FTIR spectra. Specific regions were then evaluated by a curve-fitting tool using peak-fit software for low absorption bands and overlapping bands. Peak positions were determined by the second derivative of the experimental curve, and the shape of the fitted peak was produced using the Gaussian method.

3. Results and discussion

Regardless of different pressure and pressing times, the bulk density remains between 1.22-1.26 g.cm^{-3}. The increase in pressing time and pressure results in variation in bulk density, likely due to the readjustment of the particles or variation in liptinite content (which has low density). These differences are approximate 2-3%, which is come under error deviation. Therefore, it is assumed that the change in pressure (Fig. 1a) and pressing time (Fig. 1b) has little or no effect on bulk density. Maceral are the smallest components of coal recognizable on the microscopic scale, even when opticiallity homogenous might have variable elemental and molecular chemistry not only across different coal ranks but also in iso-rank coals. These variations in maceral chemistry may have significant impact on the behavior of the material during processing and might complicate conversion behavior (Holuszko and Mastalerz., 2015).

In indirect tensile strength, three distinct behaviors were observed at different pressures with constant time. Compaction, breaking, and re-compaction were among the behaviors observed (Fig. 2a). The fine reactive particles (<15 µm) are pushed closer together and react with one another and the edges of coarse particles when the pressure is at 250 MPa. Compared to standard Oltu-stone, it has a higher indirect tensile strength of 8 MPa, which is good enough. The space between coal particles reduces when pressure rises to 300 MPa, increasing contact forces such as capillary forces, van der Waal forces, and chemical bridges between reactive macerals (Olugbade & Ojo, 2021), increasing strength to 9.5 MPa. At 350 MPa, a significant decrease in strength was observed due to excessive pressure, suggesting bond breaking and elongated particle fragmentation, causing fractures inside the agglomerates. Meanwhile, the liptinite content (particularly resinite) inside the coarse particles (15-35 µm) softens but cannot move towards pores, fractures, or fissures due to a lack of pressure.

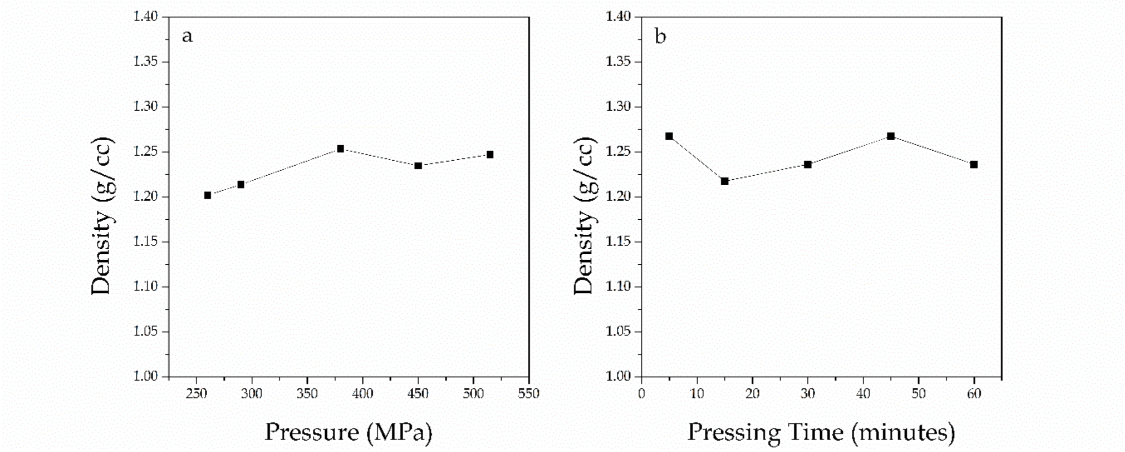

Fig. 1. Bulk density of pressed Oltu-stone a) different pressure with a constant time of one hour and b) different pressing time at 450 MPa

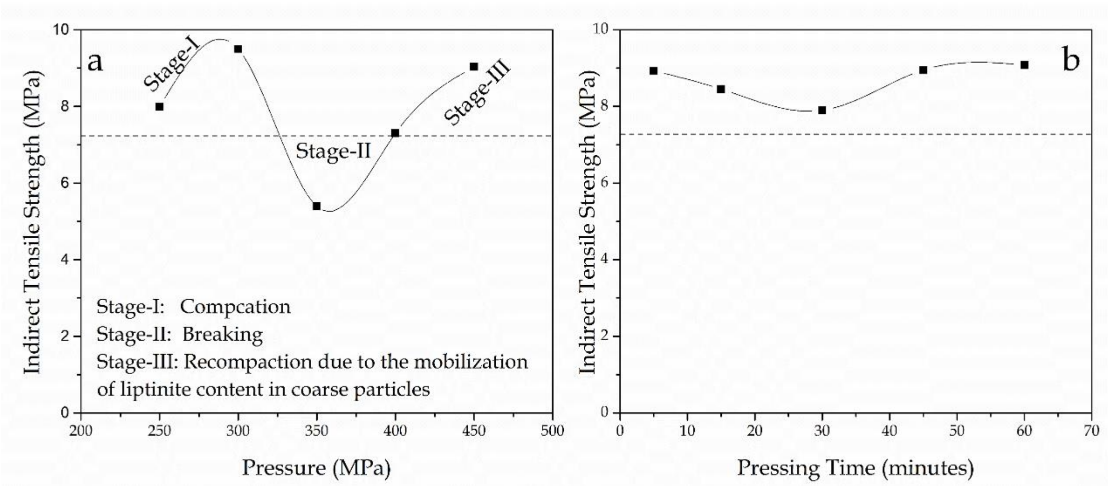

Fig. 2. Indirect tensile strength of pressed Oltustone at a) different pressure (MPa), with constant pressing time (1 hour) Indirect tensile strength of pressed Oltustone at pressing time (minute), with constant pressure (450Mpa)

In the following processing stages, the 400-450 MPa pressure mobilized the softened liptinite content towards fractures produced at 350 MPa pressure, filled the gap, and chemically bound them together, resulting in increased indirect tensile strength. Change in time at a constant pressure, on the other hand, has little effect on the strength values (Fig. 2b). The high indirect tensile strength results show that this impact is limited to the disc surface or area studied, not the complete sample. These results were also observed in the literature on the bulk density and indirect tensile strength. Apart from heat and pressure, the physical strength of Oltu-stone is most likely to come from the silicate content of the cell cavities, as reported previously (Toprak., 2013). Silicate precipitation makes the material much more physically resistant. That is why the stone is so tough and durable. Another advantage of silicate filling in Oltu-stone is that it softens when wet (Bawani., 2021).

The surface of pressed Oltu-stone shows very small pores and cavities (Fig. 3a), but the cross-sectional part shows an intact structure (Fig. 3b). The area was observed at high magnification, revealing the nanopore (Fig. 3c), mesopores (Fig. 3d), and macropores (Fig. 3e). Due to the chemical changes upon heat treatment, it was challenging to distinguish macerals. However, a brighter area is huminite or degraded liptinite, and a dark area shows the concentration of unaffected/ less affected liptinite content. The transition of liptinite macerals towards huminite owing to agglomeration can be seen in a change in color from darker to lighter (Fig. 3b). It may increase the rank of coal (Han et al., 2013). Apart from macerals, the framboidal pyrites were filled with liptinite mobilized material (Fig. 3f), and the plasticity is linked to this mobile phase (Jiménez et al., 1998). These morphological results are in agreement with the results of the previous study of the Oltu-stone (Bilgin., 2019; Toprak., 2013).

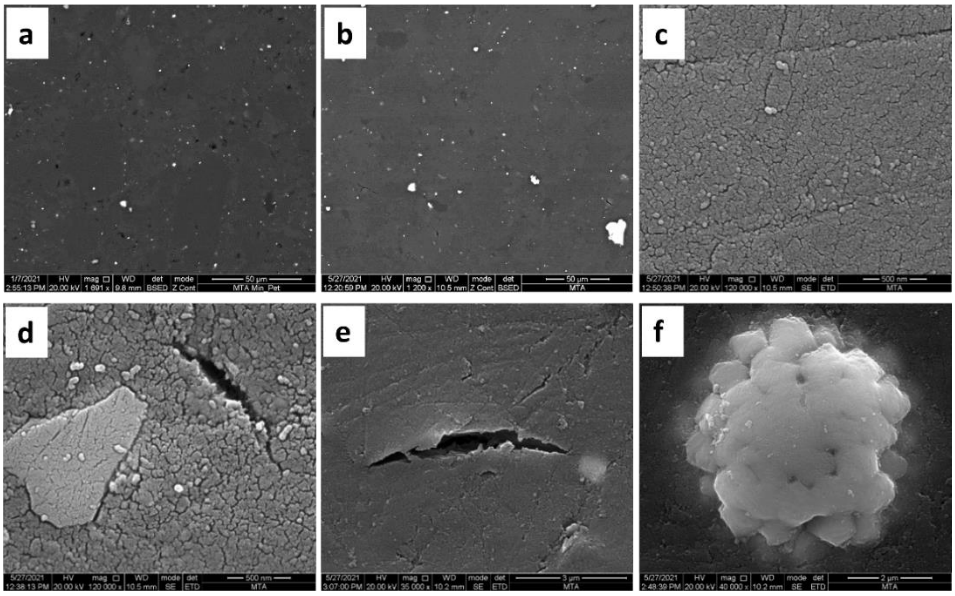

Fig. 3. SEM images of pressed Oltustone, a). Top surface b). Cross-sectional surface c). Nano pores d). Meso and macropores e). Macro pores. f). Framboidal pyrite filled with mobilized liptinite content

The proximate analysis results indicated that the Oltu-stone is rich in volatile matters. It is because of the liptinite content, especially the resin-rich component, which is primarily volatile, and volatile matters are necessary for Oltu-stone. Heating has a more significant impact on such macerals than pressure. As a result, the pressed Oltu-stone was examined at both the lowest and maximum heating time under same pressure. After cleaning, the quantity of volatile matter was 63.5%, which was decreased to 5% approximately after agglomeration. The pressed Oltu-stone obtained at 5 minutes showed a 5% decrease in volatile content, while the pressed Oltu-stone obtained at 60 minutes indicated a 6.1% reduction in volatile matters (Table 1). The longer the heating time under pressure, the lower the volatile content, resulting in increased coal maturity.

Table 1. Proximate analysis of Oltu-stone samples

Sample	Proximate Analysis		
	Volatile matters (%)	Ash (%)	Fixed carbon (%)
Oltu-stone waste (OW)	54.02	12.3	30.9
Stanadard Oltu-stone (SO)	64.5	2.5	30.2
Cleaned Oltu-stone wastes	63.5	1.78	32.79
Pressed Oltu-stone (P=450Mpa, T= 5 min)	58.5	3.2	36.5
Pressed Oltu-stone (P=450Mpa, T= 5 min)	57.4	3.58	37.15

T = Pressing time, P = Pressure

The FTIR spectra of pressed Oltu-stone obtained under different pressure and pressing time conditions are shown in Fig. 4. According to previous sections characterization results, the change in pressure affects overall indirect tensile strength but reveals similar surface mechanical properties. At the same time, the change in pressing time did not affect on overall indirect tensile strength but showed small changes in volatile amounts. The change in pressing time under controlled heating conditions, on the other hand, affected chemical characteristics. As a result, the sample with the shortest pressing time (5 minutes) and the longest pressing time (60 minutes) was discussed for FTIR investigation (Fig. 4).

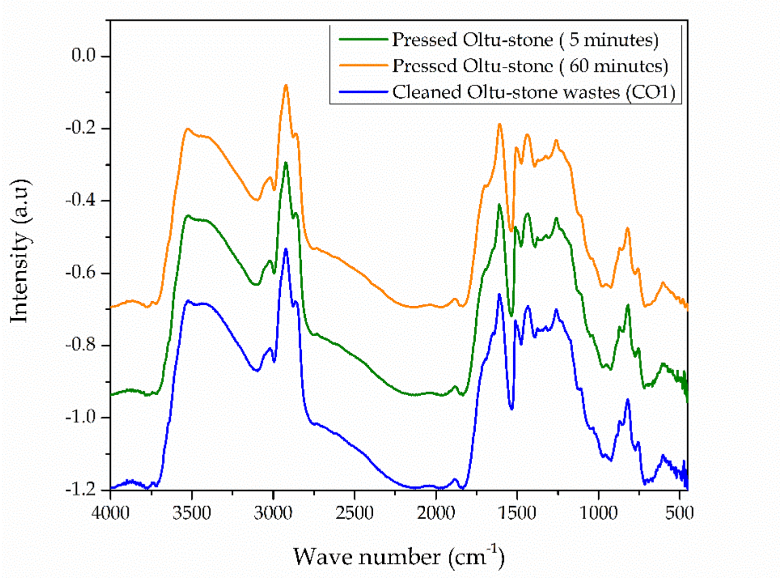

Fig. 4. FTIR spectra of cleaned Oltu-stone and pressed Oltu-stones

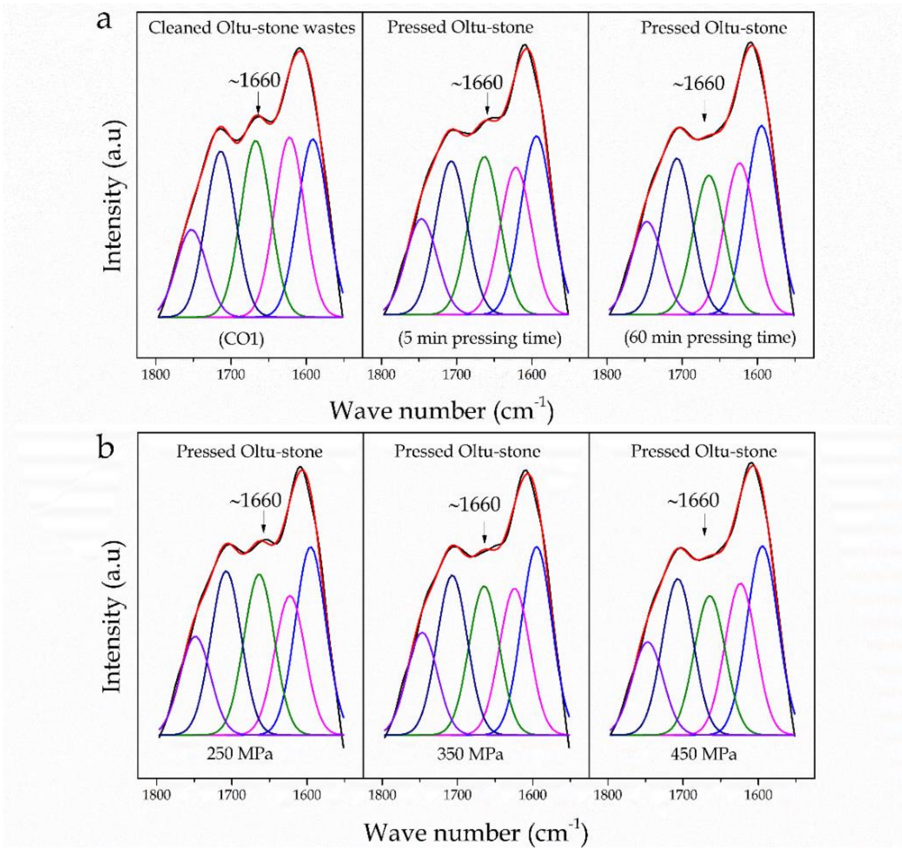

Fig. 5. a) Oxygenated group region fitted curve of figure 4. b) oxygenated group fitted curves of pressed Oltu-stone under different pressures conditions with constant time (60 minutes)

Except for the unsaturated double bonds or conjugated carbonyl at 1660 cm^{-1}, the agglomeration of cleaned Oltu-stone wastes did not effect on chemical structure. The aliphatic area has not altered much, suggesting that the liptinite maceral structure (mainly the resinite content) has been less impacted by agglomeration. The band at 1660 cm^{-1} began to decrease at 5 minutes and eventually disappeared when the time approached 60 minutes, and it is more evident in the fitted curve of the selected region (Fig. 5a). The heating action enhanced the carboxylic bands in low-rank coal (Mursito et al., 2018; Wang et al., 2010). The band between 3550 cm^{-1} and 3400 cm^{-1} became more pronounced, suggesting a rise in OH groups due to hydrogen bonding. According to a previous study (Han et al., 2013), acidic functional groups are essential in coal structures because they are the most reactive sites. Carboxylic groups (COOH) contributed to hydrogen bonds, resulting in high strength. According to Olugbade and Ojo (2021), the hydroxyl groups (3600-3100 cm^{-1}) include COOH–COOH; OH–N, Cyclic, OH–O, ether; OH–OH; and OH– linkages rise with the number of small particles. Consequently, the rate of hydrogen bond formation increased. The greater the degree of hydrogen bonding generated, the stronger the agglomeration. Furthermore, the different pressure conditions similarly affect conjugated carbonyl (Fig. 5b) as observed under different pressing times. Therefore, no effect was seen under different pressure and pressing conditions.

For preliminary evaluation of pressed Oltu-stone as an alternative market product, the pressed Oltu-stone was processed and made by the ateliers, as in Fig. 6. Based on hardness and polishing characteristics, ateliers reported that the product made from pressed Oltu-stone has similar properties compared to standard Oltu-stone. Therefore, it can be used as an alternative product.

Fig. 6. a) Pressed Oltu-stone disc obtained from high-pressure binderless agglomeration b) beads made by Oltu ateliers from pressed Oltu-stone c) polished stone for necklace prepared by Oltu ateliers from pressed Oltu-stone

4. Conclusions

In this study, the pressed Oltu-stone obtained from high-pressure binderless agglomeration was comparable to standard Oltu-stone and acceptable for ateliers. Pressed Oltu-stone has nearly identical bulk density and indirect tensile strength with standard Oltu-stone, if it is pressed at high pressure i.e., 450Mpa. Despite the physical and strength characteristics, there was little effect on chemical structure and thermal properties. The quantity of volatile matter decreased by around 5-6%, increasing fixed carbon. Pressed Oltu-stone has a high concentration of aliphatic carbon, which has a polymeric and alicyclic structure less influenced by heating. However, conjugated carbonyl groups and exocyclic structure disappeared, whereas coal maturity and carboxylic structure increased. Heating enhanced the carboxylic structure of low-rank coals to a considerable degree. This research was carried out with a fixed dimension of pressed Oltu-stone, 20 mm diameter, and 5mm thickness. The effect of the size of the pressed Oltu-stone on their properties should be investigated.

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