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Abstract

In this paper oxidative torrefaction of sunflower husk pellets in the kaolin layer was firstly investigated. Besides, influence of kaolin without use of special additives on limitation of the oxygen flow from environment into the sunflower husk was analyzed. Torrefaction temperature, torrefaction time, and height of kaolin layer over the range of 240-280 °C, 30-60 min, and 3-5 cm, respectively were varied. Analysis showed that increase of temperature led to more significant influence of layer height on mass yield. Energy yield gradually decreased with increasing torrefaction temperature and torrefaction time, and height of kaolin layer had the opposite effect on the energy yield. With the increase of torrefaction intensity, drier fuel with higher hydrophobicity was formed. Torrefaction resulted to biomass destruction, although the fiber structure was retained.

Keywords

Sunflower husk pellets, oxidative torrefaction, kaolin layer, mass yield, energy yield, fuel properties.

1. Introduction

Sunflower (*Helianthus annuus L*) is a large herbaceous crop, widely cultivated throughout the world with a total production of about 48 million tons. Sunflower husk is by-product of the sunflower oil industry and makes up 45-60% of the seed weight [1-3]. Typically sunflower husk is used as animal feed, but the annually growing production capacities does not allow utilizing large volume of the husk as feed additive, therefore, oil and fat industry plants need to the development other processing methods [4-7]. It is known that raw sunflower husk has some disadvantages such as low heating value and low bulk density, high moisture and volatile matter contents; its energy density is lower than that of fossil fuel [5-7]. Research have shown [2, 8-12], that for effective use of biomass as energy feedstock in thermochemical conversion processes requires its pretreatment. Torrefaction combined with granulation can convert biomass into the attractive fuel with high energy density, lower biodegradability, and improved mechanical durability that also provides better economic viability for transport and handling [13-18]. To reduce energy consumption for pelletizing, it is better to use raw biomass than torrefied biomass [19].

Torrefaction is moderate thermochemical treatment of biomass at temperatures of 200-300 °C in the oxidizing and non-oxidizing atmosphere [20, 21]. At the present time, most studies of sunflower husk torrefaction focused on the use of non-oxidizing atmosphere: torrefaction of sunflower residues in a tabletop heated reactor [22], torrefaction of sunflower seed shell in a tube furnace [23], torrefaction of sunflower seed shells in a thermogravimetric analyzer [24], torrefaction in a vertical reactor with external heating by combustion products [14], torrefaction in a multi-hearth furnace [25]. Non-oxidative torrefaction is rather energy-intensive and expensive process due to the use of inert gas (nitrogen) [26], which also dilutes the gaseous products, which makes it difficult for their condensation and combustion after torrefaction [27].

In the case of oxidative torrefaction, using air as a carrier gas reduces the cost of inert gas consumption and maintenance [24, 28]. Active oxygen from the air stream is burned together with volatile matters and, thus, additional thermal energy is generated, which can be useful for conversion of torrefaction into the self-sustaining thermal process [27]. Oxidative torrefaction also provides higher content of fixed carbon in biomass than non-oxidative torrefaction [29]. Currently there are few studies in the literature about oxidative torrefaction of sunflower husk. Perhaps, this is due to the fact that oxidative torrefaction occurs in temperature range close to the onset of exothermic processes in biomass during its heating [30], and sunflower husk contains a significant amount of xylan [24]. It is known that the thermal decomposition of xylan produces furfural, which is easily ignited and can serve as a catalyst that causes a sharp increase in temperature and self-heating of biomass [31]. In the literature, there are mainly articles on oxidative torrefaction of sunflower husk in fluidized bed [11, 30-32]. Studies have shown that excess oxygen content in gas phase leads to significant decrease in mass and energy yield of biomass [33]. A moderate amount of oxygen can contribute to torrefaction process by increasing released internal energy and energy efficiency of the process, but effective removal of excess heat from the reaction zone is required. There is also difficulty of ensuring the required residence time of biomass in a fluidized bed reactor operating in an ideal mixing mode [30]. Thus, in connection with some advantages of oxidative torrefaction over non-oxidative torrefaction, it becomes necessary to study more detail the methods of torrefaction of sunflower husk with limited oxygen content.

The oxygen concentration can be controlled by increasing or decreasing its diffusion into the biomass through the layer of mineral matter [34-36]. According to this technology, oxygen diffuses from the environment through the mineral layer towards biomass and takes part in torrefaction process. Due to immobility of all components in the reactor, it is possible to use biomass in the form of pellets without risk of their destruction. Depending on the changing torrefaction conditions (temperature, residence time, layer height) and type of mineral filler, properties of torrefied products can vary in a quite wide range [27]. This torrefaction technology was studied only on wood biomass [37]. Therefore, there is insufficient data in the literature on the effect of oxidative torrefaction in the mineral layer on the fuel properties of sunflower husk.

Kaolin is suitable to use as mineral filler, because it is cheap, environmentally friendly material and retains its heat-resistant properties at high temperatures [38, 39]. It is assumed that kaolin shouldn't have a catalytic effect, since it doesn't subject to special treatment (activation, dehydroxylation, etc.) [40-41] and torrefaction is carried out at temperatures below 400 °C [42]. Therefore, the aim of this work is to study oxidative torrefaction of sunflower husk pellets in the kaolin layer and investigate whether kaolin without the use of special additives effects on the suppression of oxidation reactions. Torrefaction temperature, torrefaction time, and height of kaolin layer over the range of 240-280 °C, 30-60 min, and 3-5 cm, respectively were varied. Also, such properties of sunflower husk as mass yield (MY), higher heating value (HHV), energy yield (EY), hydrophobicity and morphology were studied.

Materials and methods

Materials

The granulated sunflower husk under study was collected from Russian oil extraction plant. Sunflower pellets had a diameter of 8 mm and a length of about 20 mm. Before the experiment; pellets were dried at 105 °C for 1 h. After this dried sunflower pellets were stored in sealed plastic bags for further experiments. Density of the untreated pellets was 1000-1400 kg/m^3. Kaolin with thermal and chemical resistance was used as a mineral layer. Before torrefaction kaolin was dried at 200 °C for 2 h. In this study, torrefied sunflower husk is denoted as SA-B-C, where the parameter A indicates torrefaction temperature, B denotes torrefaction time and C denotes height of kaolin layer. For example, S240-30-3 indicates torrefied sunflower husk which was obtained by torrefaction at 240 °C for 30 min inside of 3 cm kaolin layer.

Material characteristics

CHNS contents were determined using elemental analyzer (EuroEA3000, Eurovector SpA, Italy). The tests were repeated at least twice to ensure the repeatability of test results, which was within ±0.4%. Oxygen content was determined by deducting from 100% of CHNS and ash contents. Moisture, ash content and volatile matter content per dry weight of sunflower husk samples were determined using standard methods of analysis [43-45]. All the measurements were carried out at least three times with the error of measurement ± 7%. The obtained values were calculated by averaging. Fixed carbon content was calculated according to ASTM standard D7582 by subtracting the percentage of volatiles, moisture and ash contents from the initial sample weight:

$$F_c = 100 - (VM + MC + AC), \quad (1)$$

where VM - percentage of volatile matter; MC – percentage of moisture content; AC - percentage of ash.

CHO index proposed by Mann et al. [46] to describe oxidation state of organic carbon in organic materials was calculated as:

$$CHO_{Index} = \frac{2\cdot[O]-[H]}{[C]} \quad (2)$$

where [O], [H] and [C] are number of oxygen, hydrogen and carbon atoms in a molecule, respectively. The CHO index can vary from -4 to +4. Higher CHO index values have more oxidized compounds, and lower CHO index values are associated with decrease in the number of atoms in oxidized compounds [47].

Mass yield measures the amount of solid product releases in the torrefaction process. The mass yield was calculated as the ratio of torrefied biomass mass to the initial mass of untreated biomass:

$$\text{Mass yield (MY)} = \frac{(m_{\text{torrefied biomass}})}{(m_{\text{untreated } biomass})} \cdot 100\% \quad (3)$$

Higher heating value of biomass samples was calculated according to the correlation proposed by Bychkov et al. [48].

$$\text{HHV [MJ/kg]} = 0.00355\cdot C^2 - 0.232\cdot C - 2.230\cdot H + 0.0512\cdot C\cdot H + 0.131\cdot N + 20.600 \quad (4)$$

where C, H and N are the content of carbon, hydrogen and nitrogen (wt.%), respectively.

Energy density ratio and energy yield were calculated as [49]:

$$\text{Energy density ratio (EDR)} = \frac{\text{HHV}_{\text{torrefiedbiomass}}}{\text{HHV}_{\text{untreatedbiomass}}} \quad (5)$$

$$\text{Energy yield} = \text{MY} \cdot \frac{\text{HHV}_{\text{torrefied biomass}} \cdot m_{\text{torrefied biomass}}}{\text{HHV}_{\text{untreated biomass}} \cdot m_{\text{untreated biomass}}} \quad (6)$$

To compare the hydrophobicity of fuels, sunflower husk pellets were immersed in a vessel with distilled water in a mesh strainer at room temperature for two hours. Further samples were air-dried for an hour, prior to the determination of its moisture content [50]. SEM analysis was carried out to study changes in structure of the samples due to the torrefaction using a SEM HITACHI TM-1000 with a magnification of up to 10,000 and a resolution of 30 nm.

Torrefaction process

Torrefaction of sunflower husk pellets was carried out inside of 100 ml glass beaker filled with the kaolin layer (Fig.1). The beaker was heated inside a muffle furnace. In this case, the beaker was not sealed during the torrefaction process. Oxygen from the furnace chamber diffused through the kaolin layer towards biomass and took part in torrefaction process. Initially, a small part of kaolin was poured into the bottom of the glass beaker, and then pellets were put down, and then were covered with remaining kaolin. Sunflower husk pellets did not touch each other inside the kaolin layer. The muffle furnace was heated to the desired temperature for 30-40 minutes. Torrefaction experiments were performed at different torrefaction temperatures (240, 260, 280 °C), residence time (30, 60 min), and height of kaolin layer (3, 4, 5 cm). Torrefaction experiment at each operating condition was repeated three times to ensure experimental repeatability. Biomass with kaolin layer after torrefaction was cooled to room temperature in a desiccator. After cooling, torrefied sunflower pellets were easily cleaned from the kaolin, weighed, and stored in sealed plastic bags for further analysis.

Results and discussion

Fuel properties of biomass

According to technology, kaolin layer was used to limit oxygen access to the sunflower husk samples from the environment [35]. At the same time, varying height of kaolin layer made it possible to control diffusion flow of oxygen to biomass, as a result of which the properties of the torrefied biomass changed. Moreover, properties of untreated and torrefied sunflower husk depended on torrefaction temperature and torrefaction time. Fig. 2 presents photographic images of sunflower husk pellets before and after torrefaction under varying variable combinations.

The results of proximate and ultimate analysis of sunflower husk samples are obtained. It can be observed from Table 1 that torrefied sunflower husk pellets had significantly lower moisture content (1.2-1.3%) compared to untreated samples (7.0%). Torrefied sunflower husk pellets had a larger ash residue than untreated biomass. Ash content slightly increased depending on increase in temperature and torrefaction time.

The increase of kaolin layer height had the opposite effect due to a decrease in the access of oxygen to the biomass [37]. Untreated sunflower husk contained 77.6% volatiles and 12.5% fixed carbon. With increase in temperature and torrefaction time, a tendency towards decrease in volatiles and increase in fixed carbon was observed and kaolin layer height had the opposite effect. The increase of ash content and fixed carbon leads to a clear carbonization phenomenon due to thermal destruction of cellulose in biomass [51, 52]. FC/VM (fuel ratio) increased as the volatiles decreased due to the torrefaction. This ratio in untreated biomass is only 0.16 that is too low for being a promising solid fuel. However, torrefaction improved this ratio to 0.52 (for S280-60-3) which made it a better fuel quality.

As shown in Table 2, after torrefaction carbon content increased while hydrogen and oxygen contents decreased. The lower content of oxygen and hydrogen in the torrefied sunflower husk samples may indicate about removal of light volatiles, physically bound moisture and the decrease of the hemicellulose content [53]. The decrease in oxygen content is favorable for fuel quality since higher oxygen content makes the biomass more hydrophilic and minimizes its storage time. Nitrogen content was not high and sulfur was not detected in the samples, which gives importance to biomass, as nitrogen reduces HHV and sulfur causes equipment corrosion and pollution. It can be noted that a comparison of the elemental composition of biomass obtained by torrefaction inside bentonite and talc [37] and torrefaction inside kaolin showed that the elemental composition differed insignificantly. This indicates that the kaolin itself has not affected the torrefaction reactions and its main purpose was to change the oxygen diffusive flux to the biomass from the environment.

As a result of torrefaction, the higher heating value of sunflower husk samples increased significantly. It can be noted that HHV was affected by all three parameters of torrefaction (temperature, layer height, and torrefaction time). The maximum HHV of torrefied biomass (22.06 MJ/kg) was obtained for S280-60-4. This is probably due to the fact that there was maximum carbon content under the given torrefaction conditions in biomass. Since vibrations of the elemental composition were observed, that in turn affected the values of HHV, which also varied irregularly. Note that the HHV values are within the results obtained in the case of oxidative torrefaction of sunflower husk in fluidized bed [30, 32].

Additional information of changes in the chemical composition of torrefied sunflower husk samples can be observed in the Van Krevelen diagram (Fig. 3), which shows the obtained profiles of the H/C ratio depending on the O/C ratio. Oxidative torrefaction in the kaolin layer led to an obvious decrease in the O/C and H/C ratio. The figure also shows changes leading to the movement of fuel towards the position of the peat. It can be assumed that torrefaction may provide an opportunity for biomass substitution in the co-firing systems [23].

Fig. 4 shows the CHO index values of sunflower husk samples. It is observed that the CHO index values ranged from -0.45 to -0.20, which means these biomass samples have a relatively lower amount of oxygen and higher amount of relative hydrogen content. It is also observed that the different torrefaction conditions can affect the value of CHO index in a rather broad range.

Mass yield

Influence of various parameters on mass yield when using kaolin as the mineral layer was analyzed. Since the main purpose of the mineral layer is to limit the access of oxygen to biomass from the environment thereby repressing oxidation reactions and do not allow mass yield to decrease excessively [27].

The mass yield was obtained at three values of torrefaction temperature: 240, 260 and 290 °C. Experimental results show that the mass yield increased with the height of mineral layer. At the low height of mineral layer, mass yield was affected by oxygen diffusion, and at the higher height - concentration of water vapor inside the glass beaker [27]. Fig. 5 (a,b) shows that at lower temperature (240 °C), when realized kinetic regime of torrefaction [54] influence of layer height on the mass yield was not significant. Leontiev et al. [34] mentioned that the similar results were for woody biomass; as the comparison showed, at 240 °C and 60 min, mass yield was consistent with the results when using bentonite with sodium bicarbonate as inhibitor. The decomposition of hemicelluloses and removal of low molecular weight aromatic compounds mainly occurred at this temperature [55, 56].

During torrefaction temperature increased to 260 °C the decrease in mass yield became more obvious. This is probably due to the fact that at temperatures above 250 °C the rate of decomposition of hemicellulose is high, and the reactions of depolymerization and devolatilization in hemicellulose become considerable [51]. The increase in mass yield with height of kaolin layer was observed. The influence of kaolin layer height was insignificant due to the rate limit of hemicellulose decomposition in sunflower husk by chemical kinetics [27]. In the case of temperature increasing to 280 °C (the diffusive regime of torrefaction) process was mainly characterized by depolymerization of lignin, cellulose, and hemicellulose [57] that was led to a maximum decrease in mass yield. The increase in the height of kaolin layer significantly affected mass yield.

The increase in torrefaction time also affected the mass yield at constant temperatures. Longer torrefaction time caused the decrease in mass yield due to raised heat release [37]. The difference in mass yield from 30 to 60 min at 240 °C was almost negligible. At 260 °C and 280 °C, the mass yield decreased more visibly with an increase in the torrefaction time. Thus, the decrease in height of kaolin layer as well as the increase in temperature and torrefaction time resulted in the reduction of the mass yield. Comparison with results of mass yield during torrefaction of wood pellets inside bentonite layer [34], all other conditions being equal, showed similar results, and the difference was 2-5%.

Energy yield

Energy density ratio could be used to determine the densification of torrefied biomass energy content. Fig. 6 (a,b) shows the EDR values at three heights of kaolin layer: 3, 4, and 5 cm for 30 and 60 min. In most cases, there was a tendency to decrease the EDR with increasing the kaolin layer height. The effect of kaolin layer height increased with temperature at 240 and 260 °C. On the other hand, increase in temperature to 280 °C had the opposite effect. Note that the effect of torrefaction time on energy density ratio was not typical. Thus, energy density ratio increased when torrefaction time increased from 30 to 60 min.

Energy yield determines amount of energy remains in the torrefied sunflower husk samples after torrefaction. Fig.7 (a,b) shows that energy yield gradually decreased with increasing torrefaction temperature. Since energy yield depends on the mass yield, which decreases with the temperature increasing. The lowest values of energy yield were obtained at 280 °C for both torrefaction times. The kaolin layer height had the opposite effect on the energy yield. Moreover, energy yield decreased with an increase in the torrefaction time, which is associated with a significant decline in the mass yield.

Hydrophobicity

As a result of torrefaction, changes take place in the organic structure of the biomass. As a rule, under more severe conditions of torrefaction, the structure of torrefied biomass increasingly resembles the structure of common solid fuel (for example, the hydrocarbon structure of coal), acquiring also the hydrophobic properties typical of nonpolar hydrocarbons [22].

Fig. 8 shows dependence of moisture absorption on the kaolin layer height at different temperatures and torrefaction times. A general tendency towards a decrease in the content of absorbed moisture can be noted with an increase in torrefaction temperature and torrefaction time. On the other hand, content of absorbed moisture increased with the height of kaolin layer. The smallest amount of absorbed moisture for each temperature and torrefaction time was obtained at the lowest kaolin layer height (3cm). Note that untreated sunflower husk sample had the highest water absorption (213%). Torrefaction significantly reduced the hydrophilicity of sunflower husk. The minimal content of absorbed moisture (25.8%) was found for S280-60-3. Obviously, a drier and less hydrophilic solid product was formed under more severe torrefaction conditions. This simplifies the requirements for the storage and transportation conditions of torrefied biomass and preserves its energy value.

This result is consistent with Aslam et al. [51], where the hydrophobicity of torrefied rice husks was investigated at different temperatures (200, 250, 300 °C), and a decrease in the biomass tendency to swell in water was observed with an increase in torrefaction temperature from its initial value of 308% to 92%.

Morphological features

SEM micrographs of sunflower husk samples before and after torrefaction at three values of temperature: 240, 260, and 280 °C were obtained (Fig. 9). Sunflower husk is a woody plant tissue, homogeneous in physical structure [58]. As a rule, due to thermal effect there are physical changes in the structure and cell tissue of biomass. At the same time, there is no generally accepted agreement in the literature on morphological changes in biomass during torrefaction [23]. Earlier, in the process of preliminary grinding and granulation, the fiber structure of the original sunflower husk was significantly destroyed. As a result of the high pressure during pressing, the pieces of fibers began to stick together due to the newly formed intermolecular bonds. In the micrograph, the untreated material had the generally compact structure with a fibrillar organization of smooth, homogeneous parts and some roughness on the outer surface (a). It is possible to notice the internal structure with some porous ovals (b).

The fiber structure was retained in the torrefied sunflower husk samples, cracks and irregularities can be observed on its surface. In the range of 200-300 °C, melting of cell wall cellulose occurred. Torrefied sample at 240 °C had visible destruction of the external structure and exfoliation of microfibril fibers (c). Destruction to the biomass structure became more significant as the torrefaction temperature increased. The large exfoliation of microfibrils and curling of their edges were clearly visible at 260 °C (d). On the sample torrefied at 280 °C (e), some microporous structure was visible on leaf-shaped surfaces with well-defined porous ovals formed by the removal of volatiles and moisture from the interior of cells. These new pores differed from those observed in micrographs of untreated biomass as they were more rounded. An increase in the torrefaction time led to a deeper release of volatiles, a thinning of the cell walls, the development of cracks. Bilgic et al. [23] compared the SEM-images of untreated and torrefied at 300 °C sunflower husks, and they pointed out that torrefaction led to fragility и fractal structure of the samples due to formed cracks. This increased the specific surface area and porosity of samples, which can positively affected the rate and efficiency of fuel combustion [59].

Conclusion

Oxidative torrefaction of sunflower husk pellets in the kaolin layer was firstly investigated. Kaolin was used to limit oxygen diffusive flux to the biomass from the environment and did not affect the torrefaction reactions. The main attention in the work is how temperature, torrefaction time, and kaolin layer height effects on the fuel properties, mass yield, energy yield, hydrophobicity and morphology of biomass. According to obtained results, the following conclusions are formulated.

1. Temperature, torrefaction time and kaolin layer height had different effects on the fuel properties of sunflower husk. The torrefied sunflower husk pellets had a larger ash residue than untreated biomass. The tendency towards a decrease in volatiles and an increase in fixed carbon was observed. The fuel ratio increased from 0.16 to 0.52 that improves biomass fuel quality.

2. The decrease in kaolin layer height, as well as the increase in temperature and torrefaction time, resulted in the reduction of mass yield. The kaolin effectively reduced the diffusion of oxygen to the sunflower husk without using special additives and suppressed oxidation reactions. The energy yield gradually decreased with increasing torrefaction temperature and torrefaction time; the height of kaolin layer had the opposite effect.

3. Torrefaction improved the physical property of sunflower husk by increasing its hydrophobicity. The smallest amount of absorbed moisture for each temperature and torrefaction time was obtained at the lowest kaolin layer height.

4. Changes in the morphological structure of sunflower husk before and after torrefaction were analyzed by the microscopic method. The fiber structure was retained in the torrefied biomass samples, cracks and irregularities can be observed on its surface. Destruction of the fiber structure of the sunflower husk became more significant as the torrefaction temperature increased.

This study revealed that oxidative torrefaction can lead to some improvements in the fuel properties of sunflower husks. However, the torrefaction conditions should be optimized.

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Declarations

Ethical Approval This article does not contain any studies with human participants or animals performed by any of the authors.

Informed Consent Informed consent was obtained from all individual participants included in the study.

Conflicts of Interest The authors declare no competing interests.

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Figures

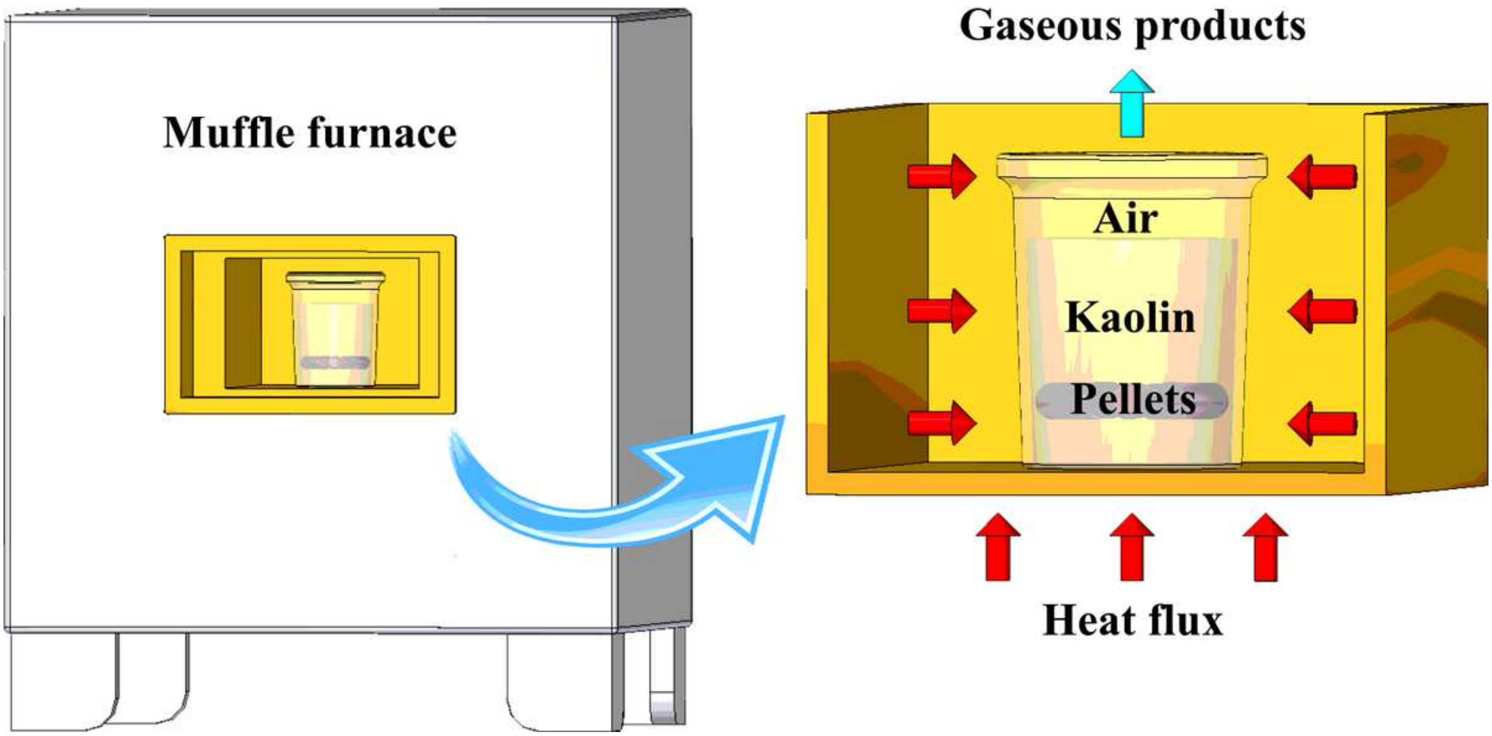

Figure 1

Torrefaction process of sunflower husk pellets in the kaolin layer

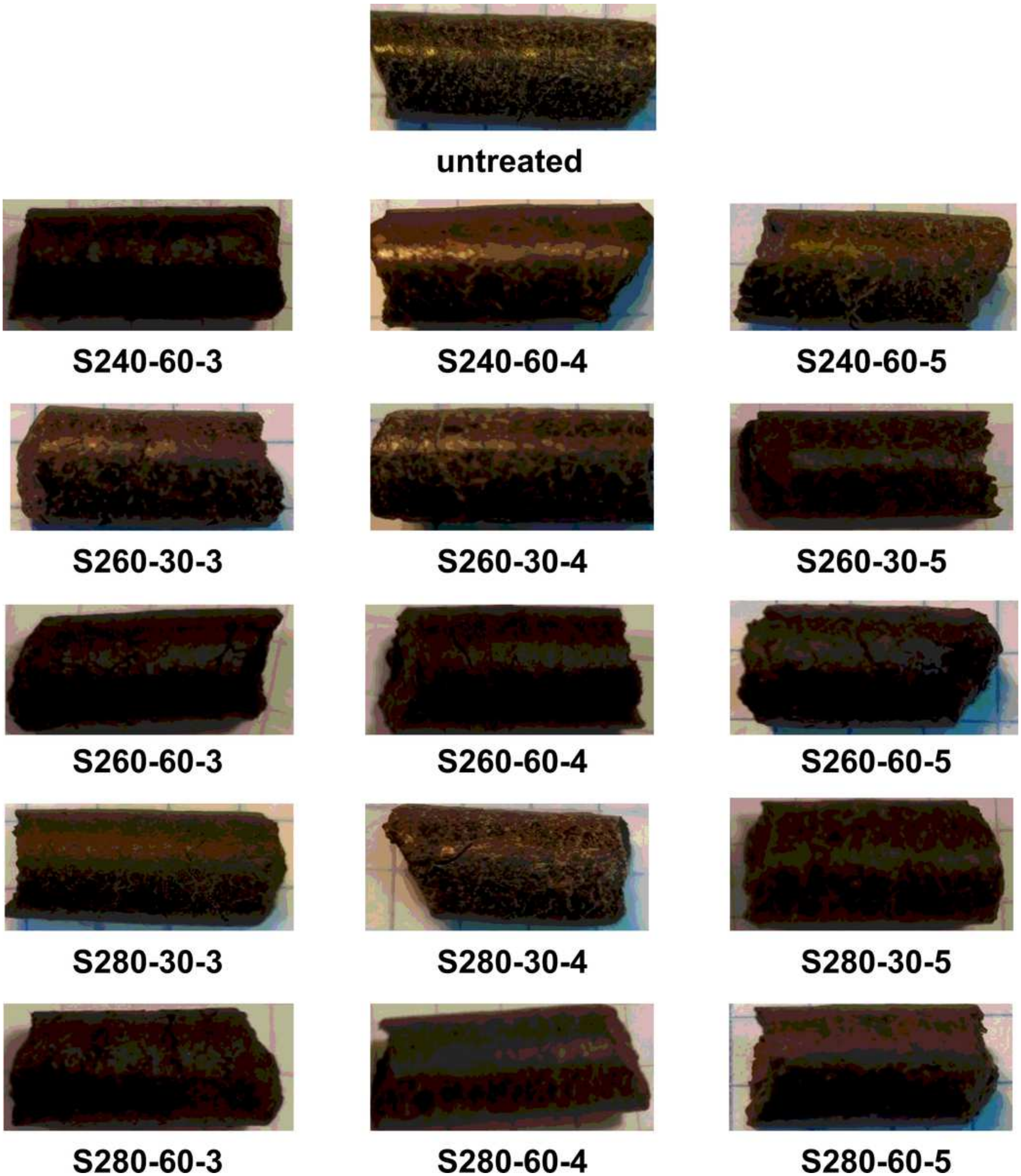

Figure 2

Photographic images of sunflower husk samples

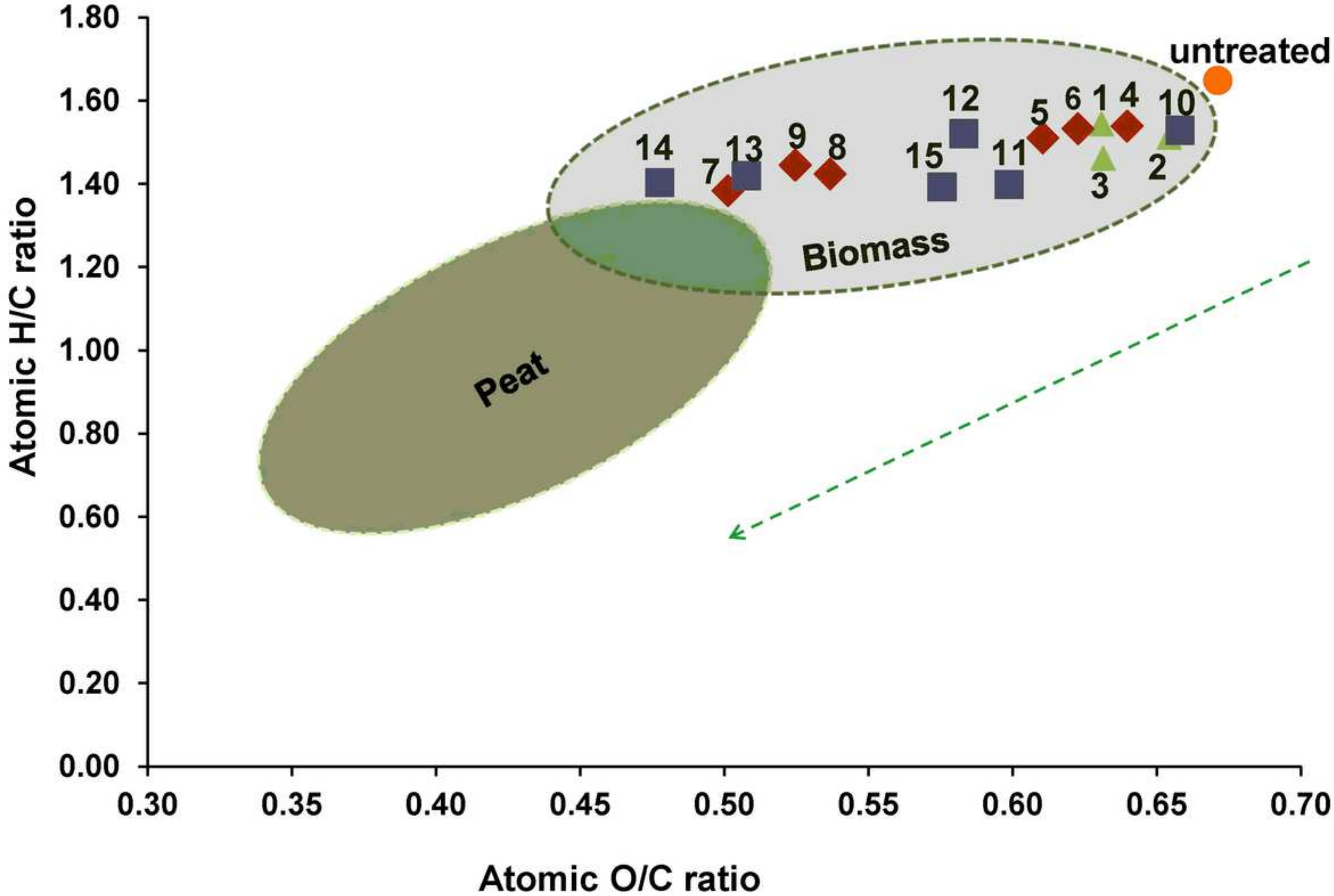

Figure 3

Van Krevelen diagram of sunflower husk samples

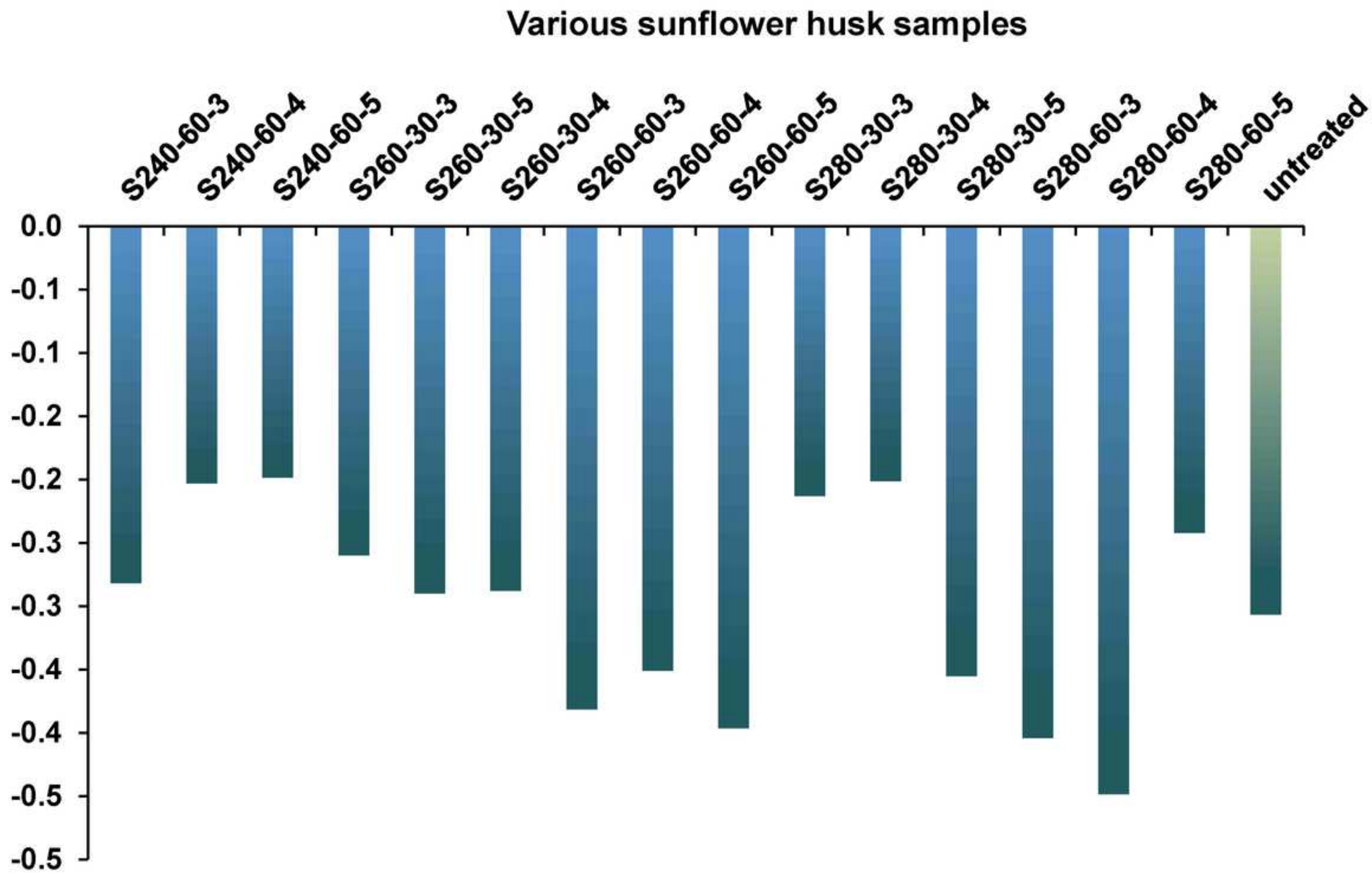

Figure 4

CHO index values of sunflower husk samples

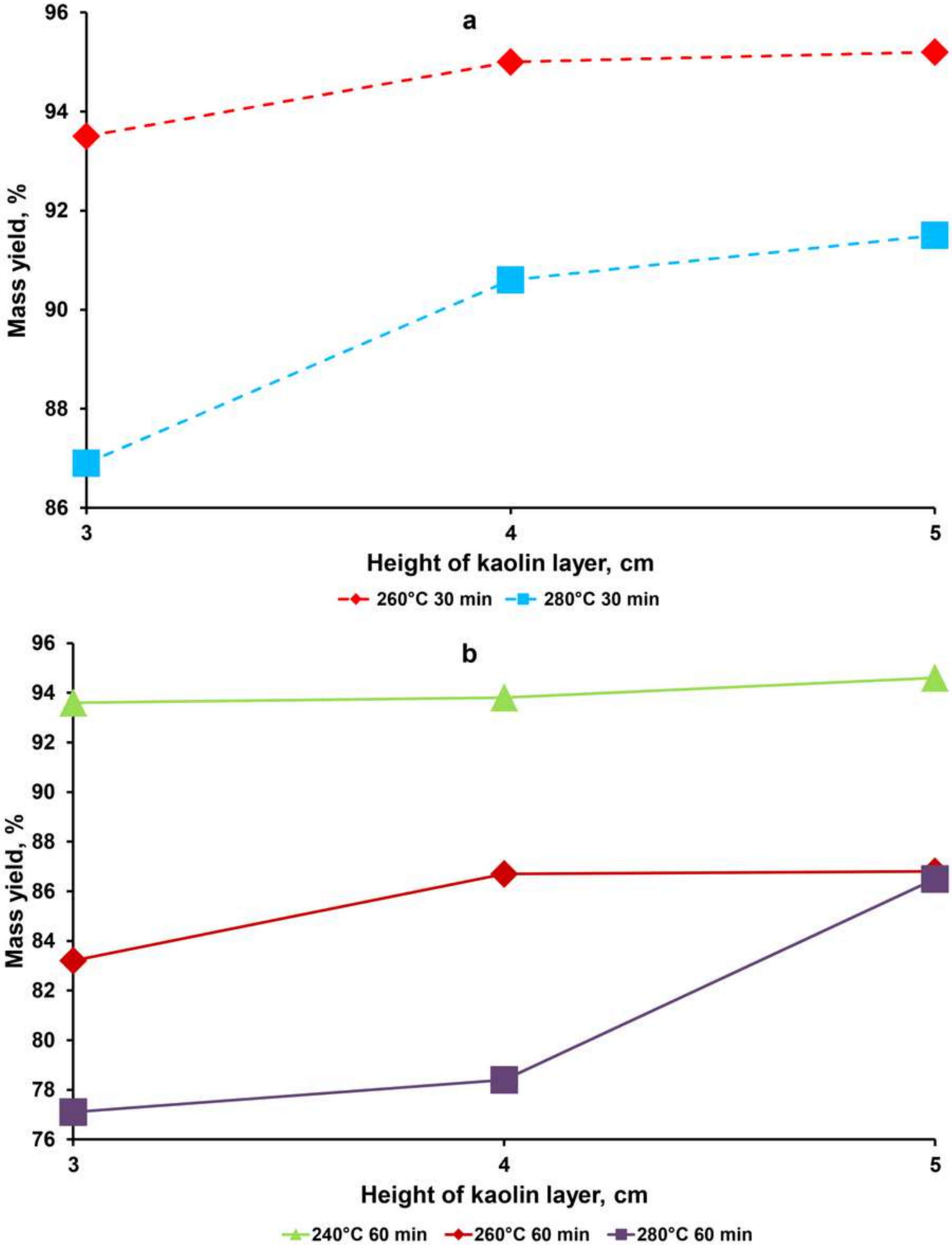

Figure 5

Influence of kaolin layer height on mass yield: (a) 30 min; (b) 60 min

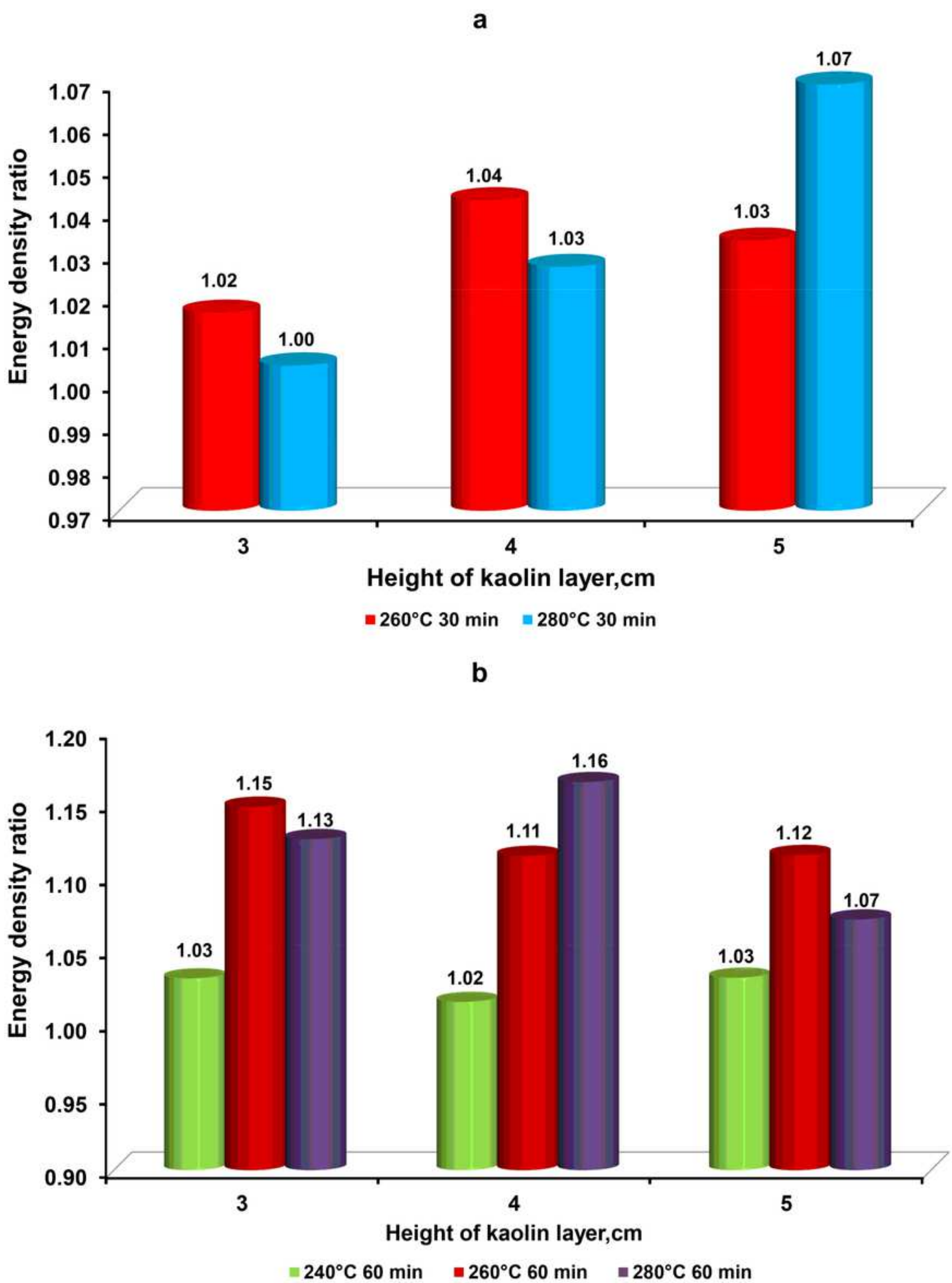

Figure 6

Values of energy density ratio of sunflower husk samples: (a) 30 min; (b) 60 min

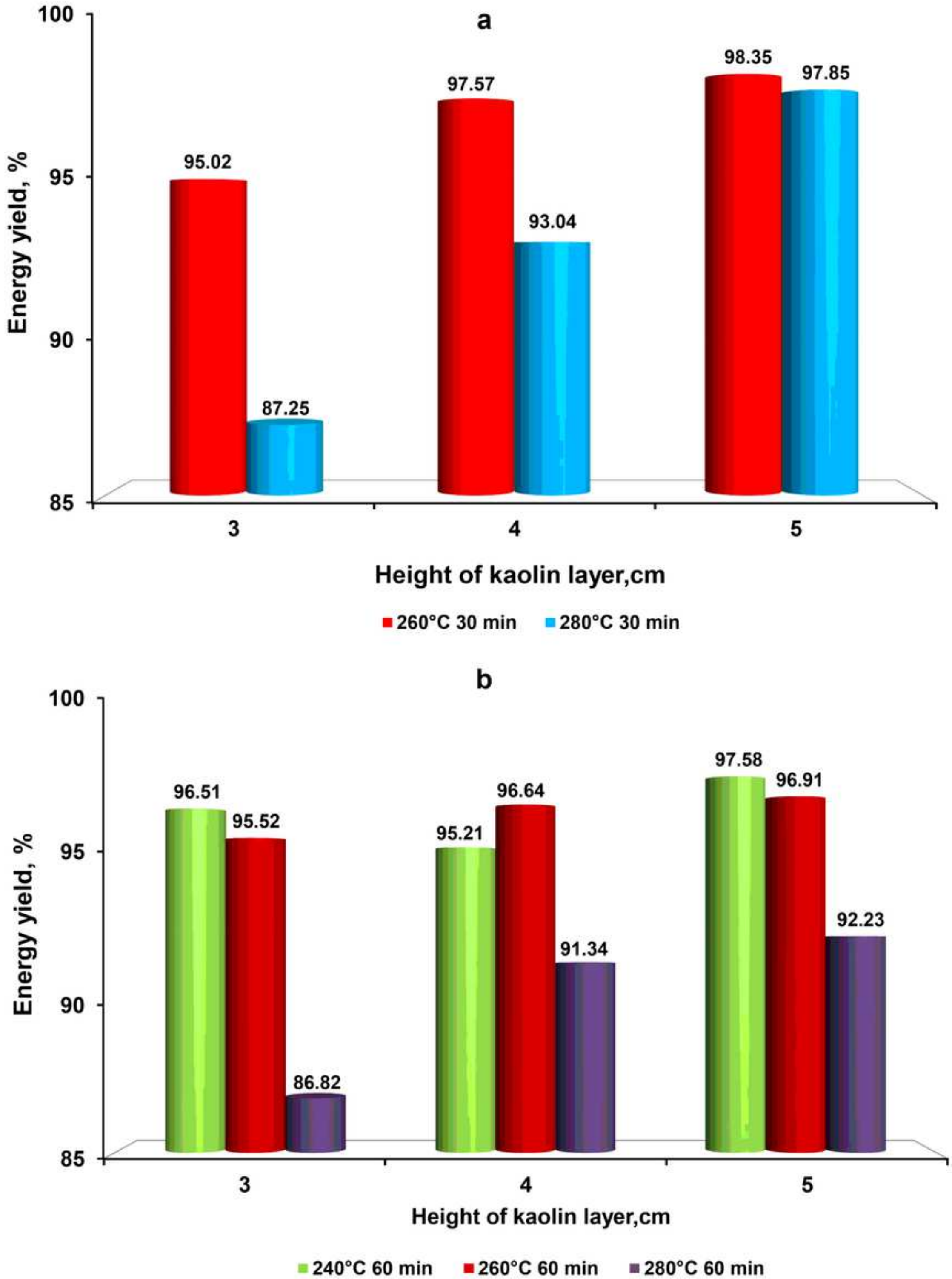

Figure 7

Values of energy yield of sunflower husk samples: (a) 30 min; (b) 60 min

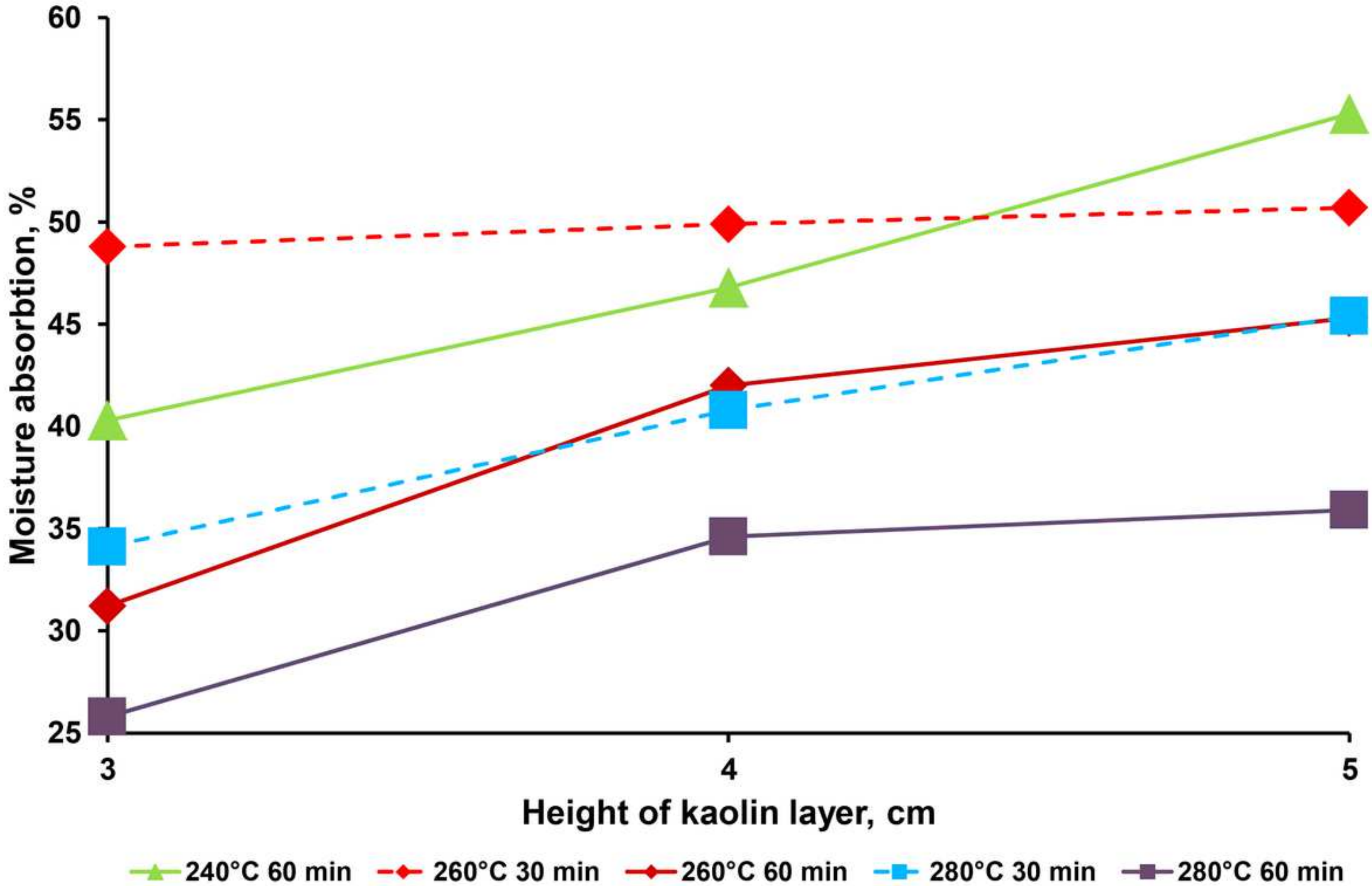

Figure 8

Dependence of moisture absorption on the kaolin layer height

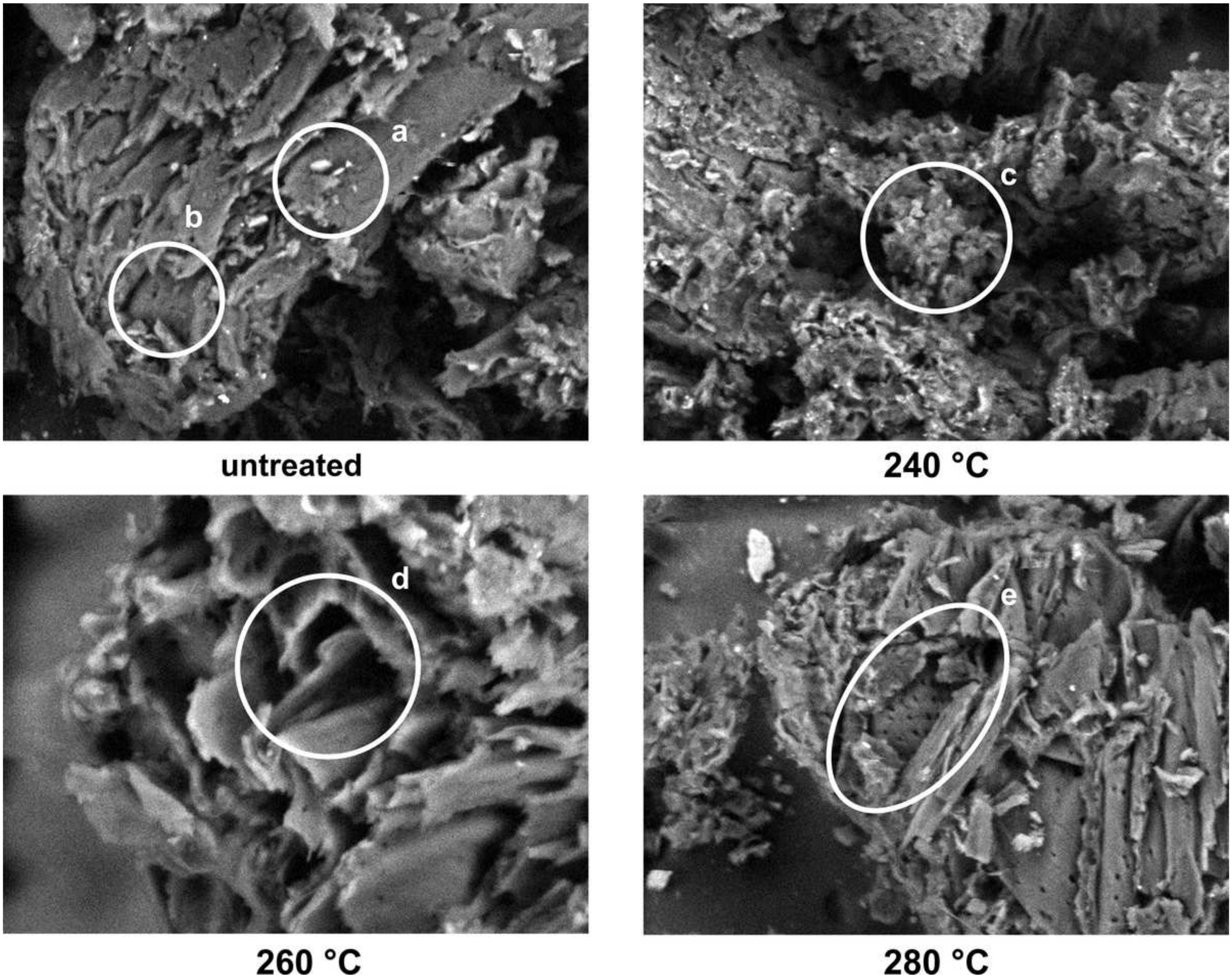

Figure 9

SEM micrographs of sunflower husk pellets before and after torrefaction process

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Table1.xlsx
- Table2.xlsx