THE UTILIZATION OF WHEAT HULL ASH FOR THE PRODUCTION OF BARIUM AND CALCIUM SILICATES

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***Abstract*—Wheat is the world's second most produced grain because of its high consumption rate, easy growth, multipurpose use and important role in the human diet. Every year, abundant amounts of wheat hull are obtained after shell process of the wheat as a waste material. Wheat hull, a by-product of the food industry, has low economic value. The utilization of wheat hull ash in various areas of industry can contribute to both financial and waste management strategies. In the present study, wheat hull ash that contains a high proportion of silica (43.22%), was utilized for barium and calcium silicate production. The wheat hull ash based barium and calcium silicate had a BET surface area of 30 and 54 m^2/g, respectively. There has been no research on barium and calcium silicate production from wheat hull. So, this study will present originality on this area.**

***Keywords*—Agricultural waste; barium silicate; calcium silicate; silica; wheat hull ash.**

I. INTRODUCTION

Today, silica "a chemical combination of silicon and oxygen" has been widely used in pharmaceutical products, ceramics, electronics, polymer material industries, oil refining and detergents, rubber and photoelectric material industries, such as thixotropic agents, thermal insulators, composite fillers and chromatograph column packing (Proctor *et al*., 1975; Liou, 2004; Zhang *et al.*, 2010). Ultra-fine silica powders can be applied in many technological fields because of their small particle diameter and high surface area (Pijarn *et al.*, 2010). Silicate is made up of silicon, oxygen, and other elements such as aluminum, magnesium, sodium, etc. Sodium silicate, the precursor for silica production is currently manufactured by smelting quartz sand with sodium carbonate at 1300°C (Brinker and Scherer, 1990; Iler, 1979). Although silica and silicates can be produced from different inorganic resources, wheat hull ash is also a source of silicate because it contains high amounts of silica (Terzioglu and Yucel, 2012; Zhang and Khatib, 2008). Therefore, wheat hull ash can be presented as a new renewable silica source and sodium silicate can be produced easily and economically by using wheat hull ash.

Wheat is the world's second most produced and consumed grain. The global wheat production and consumption values are presented in Table 1. Wheat "the raw material of various products such as flour, bread etc." is also produced in Turkey with high amounts. In 2009, 20 million 600 thousand tons of wheat were produced in Turkey (Boyacıoğlu, 2009; Akbaşı *et al.*, 2010).

Table 1.The global production and consumption values of wheat (million tone) (Boyacıoğlu, 2009).

	2006	2007	2008	2009
Production	621	598	609	674
Consumption	625	611	614	647

Table 2. The chemical composition of wheat hull (dry base,%) (Hoseney, 1994).

Material	Ash (%)	Protein (%)	Lipid (%)	Cellulosic material (%)
Wheat hull	2	6	0.5	20

Wheat hull is a natural fiber which can be defined as a polymeric compound containing cellulose, hemicelluloses, lignin, protein, starch, lipid and ash (Bledzki *et al.*, 2010). Wheat hull constitutes almost 5% of the total grain which consists of approximately 6% protein, 2% ash, 20% cellulose and 0.5% fat and non-starch polysaccharides (Hoseney, 1994). The results are presented in Table 2 (Hoseney, 1994).

Wheat hull ash is usually obtained by burning wheat hull (the rest of the wheat crust after husking) in air atmosphere. Ash contains mainly K, P, Mg, Cl, Ca, Na, Si and small amounts of Zn, Ni, Mn, Cu, Co, F, Se, Br, I, B and Al. The amounts of these inorganic elements vary depending on environmental conditions, largely on the type of soil, rainfall condition and the type and amount of used fertilizer (Hoseney, 1994). In a study, Zhang and Khatib (2008) investigated the chemical composition and physical properties of wheat hull ash obtained by burning at 450-500°C for production of construction material. It was found that wheat hull ash contains 53.94% SiO_2, 13.23% Al_2O_3, 4.40% CaO, 4.10% Fe_2O_3, and 1.58% MgO (Zhang and Khatib, 2008).

Wheat hull ash is called "waste product of food industry" and it causes environmental pollution because it taken to land fill areas. Wheat hull can be also evaluated to produce biofuels such as biochar and bio-oil (Bledzki *et al.*, 2010; Motojima *et al.*, 1995). Moreover, it was used to produce the fibers of Si_3N_4 by Motojima *et al.* (1995). Wheat hull ash is also used as concrete additive in the construction industry (Mani *et al.*, 2004). The utilization of wheat hull ash in various areas of industry will contribute to both economic and also waste management strategies. Different silica-based materials such as barium silicate and calcium silicate can also be produced from wheat hull ash. Barium silicates are special materials which can be used in the ceramics, glaze and glass industry. Recently, it is being used in the solar-cell production as an important ingredient because of its special properties. It is not easy to find barium silicate as mineral in nature. Barium silicate is frequently produced from the reaction of barium carbonate ($BaCO_3$) and silicon dioxide (SiO_2) at 1600°C for industrial purpose (Fericiana *et al.*, 2002). Barium silicate production from wheat hull silica will be an economic alternative for this method since this method is a high energy required method

There are various types of calcium silicates which are obtained by reacting calcium oxide and silica in various molar ratios. Calcium silicates have a wide variety of application areas. They can be used as insulation boards, as constituents in refractory ceramics, in paper industry and cements, as adsorbents and fillers, etc. (Taylor, 1990; Wang *et al.,* 2005).

Therefore, in this study a new application area for the efficient evaluation of this waste type is presented. There has been no study about the evaluation of amorphous silica of wheat hull ash for barium and calcium silicate production in the literature. In the present study, a novel utilization area for wheat hull ash is proposed. Barium silicate and calcium silicate are produced from the wheat hull ash containing a high proportion of silica.

II. MATERIALS AND METHODS

A. Materials

The wheat hull sample (Fig. 1) obtained from Doruk Marmara Flour Factory located in the Marmara region of Turkey. The wheat hull ashes (Fig. 1) obtained by burning these hulls in laboratory were used in this study. Burning process was carried out using an incineration ash furnace (Protherm, Turkey). All of the chemicals used in experiments were of analytical reagent grade (Merck).

B.Moisture Content of Wheat Hull

The wheat hulls were dried at 110°C till constant weight to determine moisture content.

$$\text{Moisture}(\%) = \frac{(m_1 - m_2)}{m_3} \times 100, \tag{1}$$

m_1, m_2 and m_3 were weight after drying, tare weight of crucible, original sample weight (*g*), respectively.

C. Ash Content of Wheat Hull

10 g of wheat hull was put into a tared crucible. It was burned at 550°C for 12 hour in an incineration furnace (Protherm, Turkey) and waited to open furnace until the temperature had dropped to at least 250°C. The door of the furnace was opened carefully to avoid losing ash.

Fig. 1. Wheat hull and wheat hull ash.

Crucible was taken quickly to a dessicator and allowed to cool down (Nielsen, 1993).

The ash content was calculated as follows:

$$\text{Ash}\,(\%, \text{dry basis}) = \frac{(m_1 - m_2)}{(m_3 \times m_4)} \times 100, \tag{2}$$

m_4 was the dry matter coefficient of wheat husk.

D.Silicate Extraction from Wheat Hull Ash

Silica was extracted from wheat hull ash using the method of Kalapathy *et al*. (2000). 600 ml of 1 N NaOH was added to 100 g of wheat hull ash which was obtained by burning at 600°C for 5h**.** The mixture was boiled in an Erlenmeyer flask for 1 h with constant stirring to dissolve the silica to produce a sodium silicate solution. This solution was filtered and washed with 50 ml of boiling water. The sodium silicate solution was allowed to cool to room temperature. Samples were kept in plastic pots and used as necessary.

E. Silica Content

Silica content was determined gravimetrically by lowering the pH of 50 ml sodium silicate solution from 12 to 7 to precipitate silica (Kalapathy *et al*., 2000). Silica precipitate was washed twice with 100 ml water, dried at 110°C for 12 h, and weighed.

F.Barium and Calcium Silicate Production

Barium silicate production was performed at room temperature with barium salt ($BaCl_2 \bullet 2H_2O$). A stoichiometric quantity of barium salt was solved completely in distilled water in a flask and sodium silicate solution (Na_2SiO_3) was poured on it by a pipette. During the reaction a constant stirring (1250 rpm) was applied with a magnetic stirrer (Heildolph MR 3000, Germany). Immediately, a white precipitate appeared. After reaction was completed, the mixture was filtered under vacuum. The remaining part on filter paper was washed with 1000 ml of distilled water to eliminate impurities. The precipitate was dried at room temperature. Also, the same procedure was applied for calcium silicate production by using calcium salt ($CaCl_2 \bullet 2H_2O$).

G.Characterization of Samples

Characterization of wheat hull, wheat hull ash, barium and calcium silicate samples was performed by using various methods and equipments. The surface properties of the samples were obtained with the use of a Scanning Electron Microscope (CamScan- Oxford Instruments, France) and a Costech 1042 Sorptometer, Italy for the BET measurements. Fourier transform infrared spectra of wheat hull ash based silicates were obtained with use of a SHIMADZU, IR Prestige 21 (USA) device in the range of 800 to 2000 cm^{-1}. X-ray diffraction patterns of samples were obtained with an X'Pert PRO PANalytical (Holland) XRD system using an acceleration voltage of 40 kV and current of 45 mA. The sample was scanned from 5° to 90° 2θ, with a step size of 0.003.The chemical properties of wheat hull ash were determined using ICP system (Perkin Elmer Optical Emission Spectrometer Optima 2100 DV, USA). Before ICP analysis, solving process of ash was done in a Microwave oven (BERGHOF, Speed wave TM MWS-3, Germany).

Table 3. The SiO_2 content % of ash obtained at 400, 500, 600°C.

Temperature (°C)	400	500	600
SiO_2(%)	38.36	37.72	43.22

III.RESULTS AND DISCUSSION

The moisture and ash content of wheat hull were found to be consecutively 7, 7 % and 9, 95 %.

Sodium silicate is generally produced by the reaction of quartz sand and sodium carbonate at 1300-1400°C. This process requires a lot of energy. Therefore, as an alternative to this process, Kamath and Proctor (1998) have produced the sodium silicate solution at low temperature by using rice husk ash (that contains amorphous silica). Silica in rice husk ash (SiO_2) is found as an amorphous structure at temperatures below 600 °C and this amorphous silica can be easily solubilized in alkaline conditions. Reacting with amorphous silica and sodium hydroxide results in the formation of sodium silicate solution and water:

$$\mathbf{nSiO_{2\,(s)} + 2NaOH_{(aq.)} \longrightarrow Na_2O{\bullet}nSiO_{2\,(aq.)} + H_2O}$$

In this study, the sodium silicate solution is obtained by using wheat hull ash according to the method of Proctor *et al.* (1995). Although there is only one study about the evaluation of amorphous silica of wheat hull ash in the literature (Terzioğlu and Yucel, 2012), there are a lot of studies obtaining silicate compounds from rice hull ash (Proctor *et al.,* 1995; Kalapathy *et al*., 2000). There are many factors affecting the solubility of silica such as its form (amorphous, quartz and crystallite, tridymite, coesite, stishovite, opal orlechatelerite), pH of the solution, temperature and presence of other ions (Tarutani, 1989). The solubility of amorphous silica is high and simple compared to crystalline silica. On the other hand, the experiments of silica extraction were made in alkaline conditions, because the solubility of amorphous silica increases rapidly at pH=10 and above 10 (Proctor *et al.,* 1995). Kamath and Proctor (1998) easily obtained sodium silicate and silica gel in alkaline conditions by taking advantage of this feature of rice hull ash's silica. As can be seen in the literature studies, ashes with high silica content are obtained at higher temperatures than 400°C (Kamath and Proctor, 1998). Therefore, firstly, the wheat hulls were burned at 400, 500, 600, 700 and 800°C for 5 hours. The SiO_2 percentage content of ash obtained at 400, 500, 600°C is given in Table 3. However, it was determined that there was an amorphous structure of silica in wheat hull ash obtained at 600°C and temperatures below 600°C. At this point, 600°C was determined as the best experimental condition and sodium silicate solution was produced from wheat hull ash obtained in this condition (600°C, 5h). Figure 2 shows that wheat hull fibers have rounded corners and are long-shaped. The micrographs of wheat hull and wheat hull ash obtained by burning at 600°C are given in Fig.3.

Figure 3 (200x and 1000x) shows the wheat hull ash, that appears as a heterogonous mass of filamentous sheets. In Fig. 3 (200x), mostly stalactite-like and circular structures are observed in the flat surface. When

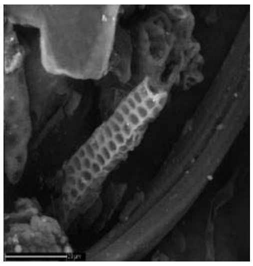

Fig. 2. Scanning electron micrographs of wheat hull (1500x).

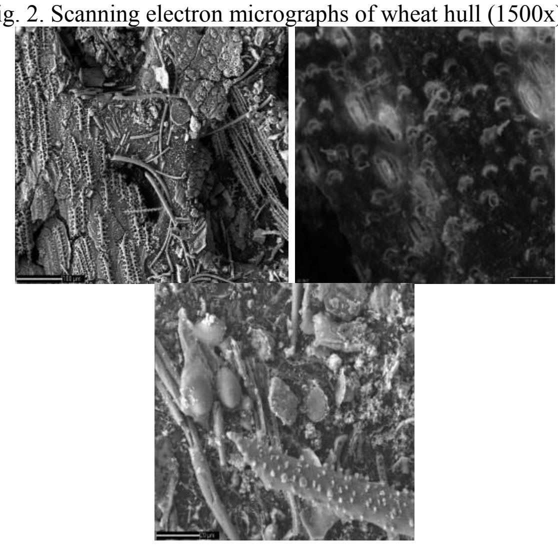

Fig 3. SEM images of wheat hull ash burned at 600°C for 5 h (200x, 350x and 1000x).

looking at the semi-quantitative results of the SEM device, K and Si elements are more in stalactite-like structure than in the circular portion. In Fig. 2 (1500x), structures like as corn cob are seen. It is known that the amorphous silica in the construction of rice hull takes place on the mound of hull. Since a similar image with rice hull was observed for wheat hull, it can be thought that silica is concentrated in the structure of wheat hull. By the way, the fibrous structure is also observed in the wheat hull images in addition to corn cob structure. Samples were covered with gold to obtain the better micrographs of wheat. As can be seen from Fig. 3, the characteristic micrograph structure for silica based materials is also obtained for wheat hull ash. The SEM images in Fig. 3 indicate that wheat hull ashes have a corn cob structure. Also, in Fig. 3 (350x) the protuberances indicates the presence of silica (Ikram and Akther, 1988). And, these images prove that silica is found in the structure of wheat hull ash.

In the study, silica content of sodium silicate solution was found to be 2.44%. Ash content was determined according to standards in the literature (Nielsen, 1993). Ash content was found to be 9.95% for wheat hull. When the ash content of the wheat hull in this study is compared with the literature value (Hoseney, 1994), the ash content is higher than the literature value (2%).

The chemical composition of wheat hull ash obtained at 600°C is given in Table 4. The silica content of ash is found to be 43.22 % in this study. The silica content of wheat hull ash obtained at 600°C in this study (43,22%) was lower than the literature value (53.94%) or the silica content of wheat hull ash burned at 450-500°C (Zhang and Khatib, 2008). The other major components of wheat hull ash were found as K_2O and CaO which were similar to the literature values. The difference between the chemical compositions of hulls depends on many factors such as geographical conditions, climatic conditions, type of wheat, and the quantity of fertilizer used (Govindarao, 1980).

The X-ray diffraction patterns of wheat hull ash obtained by burning at 600 and 800°C for 5 h are given in Fig. 4 and 5. In Fig. 4, the XRD pattern of wheat husk ash does not show a well-defined sharp peak, indicating that silica in ash is amorphous when formed at 600°C (Singh *et al.*, 2008). As can be seen from Fig. 6, the XRD pattern shows a diffused peak at about 2θ =22° corresponding to a disordered cristobalite structure (Della *et al.*, 2002). Therefore, the ash obtained at 800°C has an heterogeneous structure containing both amorphous and crystalline silica.

Table 4.The chemical composition of wheat hull ash obtained at 600°C.

Compound	Value (%)
SiO_2	43,22
K_2O	11,30
MgO	0,99
Fe_2O_3	0,84
Na_2O	0,16
Cr_2O_3	0,0004
MnO_2	0,02
CaO	5,46

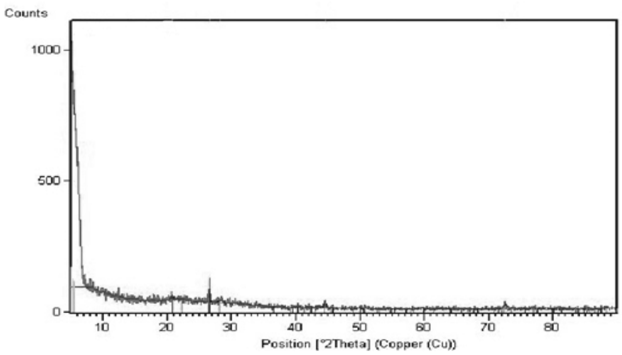

Fig. 4.The X-ray diffraction pattern of wheat hull ash obtained by burning at 600°C for 5h.

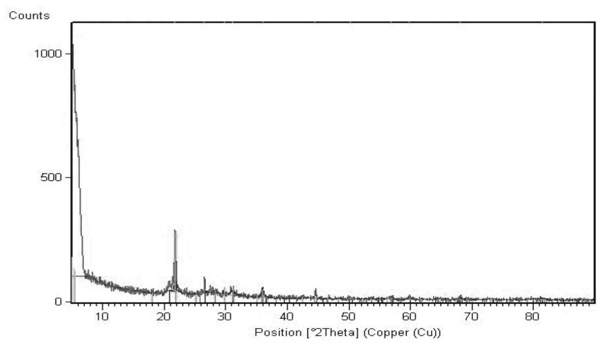

Fig. 5.The X-ray diffraction pattern of wheat hull ash obtained by burning at 800°C for 5h.

Table 5. BET surface area of barium and calcium silicates

Type of Silicate	BET Surface Area (m^2/g)	Source
Dicalcium	39	Hagymassy *et al.*,1972
Tricalcium	84	Hagymassy *et al.*,1972
Calcium	120	Anonymous (2012b)
Calcium	200-225	Anonymous (2012a)
Dibarium	35	Hanna *et al.*, 2007

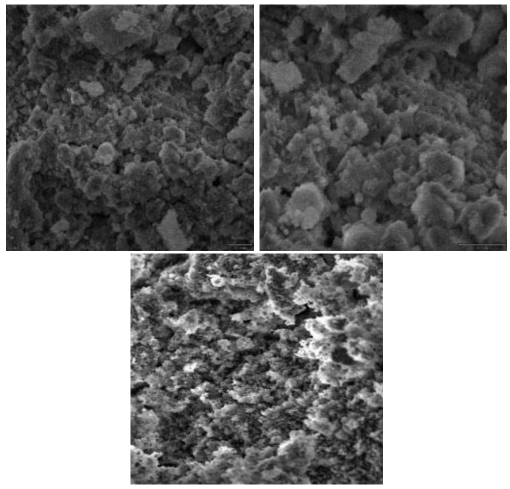

Fig. 6.SEM images of barium silicate (1000x, 2000x and 3000x).

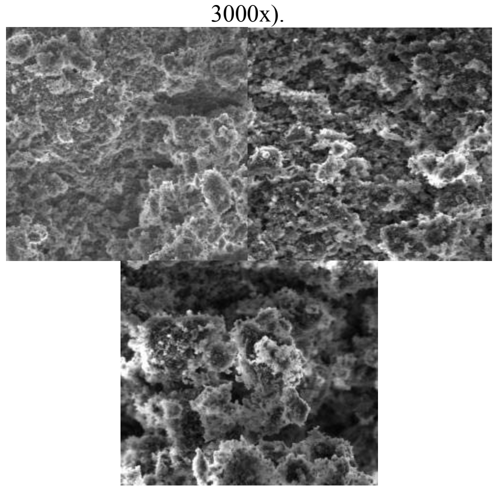

Fig. 7. SEM image of calcium silicate (1000x, 2000x and 3000x).

BET surface areas were 54 and 30 m^2/g for calcium and barium silicate, respectively. SEM micrographs of barium and calcium silicates obtained from sodium silicate solution of wheat hull ash are presented in Figs. 6 and 7. The presence of a few large sized and irregular shaped particles is seen in Fig. 6. The micrographs show in Fig. 6 the orthorhombic and euhedral crystals of barium silicates (Amritphale *et al.*, 2007). The SEM micrographs exhibit irregular-shaped particles in Fig. 7. Barium silicate sample has a more granular structure in comparison with calcium silicate sample. The particle´s physical shape and surface areas of samples can affect the usage areas of silicate samples. The BET surface area of commercial calcium silicates and literature data of barium and calcium silicates are given in Table 5. The wheat hull ash based barium silicate's BET surface

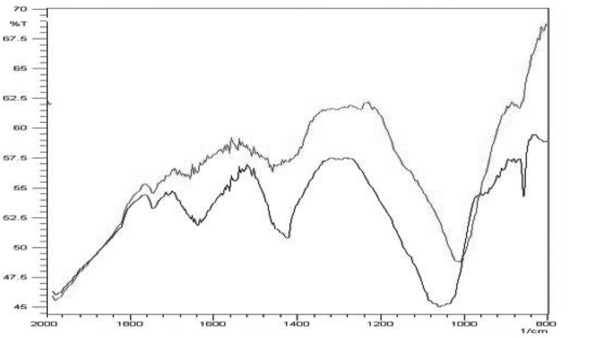

Fig. 8. FTIR spectrum of barium (grey line) and calcium (red line) silicates

area is similar to the literature value (Hanna *et al.*, 2007).

The FTIR spectra of silicates are presented in Fig. 8. They present the peak of the O-Si-O bands between 1030 and 1060 cm^{-1}. The band at 840 cm^{-1} is assigned to the Si-O-Si symmetric stretch. Both samples have the Si-O band; however, barium silicate has more Si-O in comparison with calcium silicate sample. The other absorption peak corresponds to hydroxyl (O–H) at 1600 cm^{-1}. The spectrum exhibits the peak of the Ca-O stretching band at ~1460 cm^{-1} (Booncharoen *et al.*, 2011).

IV. CONCLUSIONS

The evaluation of ash produced via burning hulls of wheat has been investigated for silica based materials production. 600°C was found to be the optimum incineration condition for the production of ash with maximum amorphous silica content. Barium and calcium silicate forming temperatures are clearly lower than the conventional production processes. The BET surface areas of barium silicate and calcium silicate were 30 and 54 m^2/g, respectively. The results have shown that this experimental work opens encouraging perspectives for the evaluation of the wheat hull ash as a silica source and to obtain the silicate products with an economical method. A novel raw material was presented on silicate production area by this study. This work can be enhanced by investigating the effect of different parameters such as reagents molar ratio, temperature, washing agent and salt type on silicates production.

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