

# Novel Porous Refractory Synthesized from Diatomaceous Earth and Rice Husk Ash

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## Abstract

Refractory materials are products used in thermal equipment to protect the fire and prevent heat loss to the outside environment. Thermal equipment such as driers, ceramic kilns, glass or metal furnaces and others always consume high heat in the combustion of the fuel. If the thermal equipments have a high heat loss which cause wastes of the fuel and increases production costs. Therefore, researchers are always looking for a solution to minimize heat loss for the kiln. In which, refractory materials significantly influence to the heat loss of the kiln and they have been studied a lot in recent years. This study focused on utilization of locally available raw materials to produce the novel porous refractory composites. The products have high porosity based on choosing the suitable raw materials and forming process. The refractory has high porosity and low thermal conductivity repended to the requirements of saving energy for the thermal equipments. More important, the novel porous refractory products have high shape stability when observed by heating microscope in a range of room temperature to over 1400°C.

**Keywords:** Diatomaceous earth, Rice husk ash, Porous Refractory, Heat loss, Thermal conductivity

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## INTRODUCTION

Refractory is a material that retains its physical and chemical properties at high temperature (over 1000°C) for a long time and not deformed under mechanical load. Refractory materials are widely used in industries such as metallurgy, chemicals, thermal power plant, ceramic, glass, cement production and others. Refractory materials are limited in special process technologies to reduce heat loss of the furnaces. During the operation of the equipment, researchers always find solutions to increase the quality of refractory bricks, prolong the usage time of bricks in the kiln. This contributes to increasing equipment productivity, reduce heat consumption, increase quality and decrease prices of products [1-4].

Today, there have been many novel refractory materials to meet the demands of technical progress. These are super-advanced materials used in supersonic aircraft technology, modern rockets, materials in

nuclear reactors, in spacecraft and others. There are different ways to classify refractory materials known as:

According to the chemical and physical properties of the initial raw materials, refractory materials are classified into 3 main groups: acidic refractories (silica, aluminosilicate, and zirconia); basic refractories (magnesite, dolomite, magnesia-chrome); and neutral refractories (carbon graphite, chromite, alumina) [5-9].

According to fusion temperature, refractory materials are classified into 3 main groups: Normal refractories with fire resistant temperature are in the range of 1580-1780°C; High refractories with fire resistant temperature are in the range of 1780-2000°C; Super refractories with fire resistant temperature are over 2000°C.

In addition, refractory materials are also classified according to method of manufacture;

shaped or unshaped; refractoriness; thermal conductivity [10-18].

Diatomaceous earth (DE) is a lightweight mineral with the density around 0.25-0.50 ton/m<sup>3</sup> formed million years ago by diatom algae groups. DE contains high silica (60-97%) with amorphous porous structure. There is a vast DE reserve available all over the world. The United States, China, and other countries have DE reserves of about 250, 110 and 550 million tons, respectively, up to 2012 [19]. In another report, total DE reserves of the world are around 918.9 million tons estimated before 2006 [20].



**Fig. 1:** Open-cast DE mine was exploited in Lam Dong province, Vietnam.

In Viet Nam, DE minerals are detected in many local known as Hai Phong city, Lam Dong, Phu Yen provinces and others with different reserves. However, the raw material has low quality with a lot of impurities, especially clay minerals. Therefore, it will be costly to treat and use it like as the other diatomite in the global market. Hence, Vietnamese researchers are looking for the most appropriate solutions to exploit and use effectively this abundant resource [21].

Rice husk ash (RHA) is high – silica material made from burning rice husk. Rice husk takes up about 20% weight of rice and its compositions include 15 – 20% SiO<sub>2</sub>, the others are cellulose and lignin [22-23]. Therefore, after burning process, total weight of obtaining RHA is near 20% weight of rice husk. This characteristic mainly depends on burning conditions such as temperature, holding time. In 2011, rice production was

over 700 million metric tons all over the world, where more than 90% belong to Asea countries such as China, India, Indonesia, Bangladesh, Vietnam, Burma, Thailand, and Philippines. Hence, total estimated RHA reserves are over 28 million metric tons every year [23-24].



**Fig. 2:** Rice husk ash was Discharged after after the Boiler Combustion Process.

In Vietnam, rice husks are used as fuel for the drying of agricultural products or to burn boilers. The temperature of the burning process is only around 600°C in a very short time (less than 15 minutes) causing incomplete combustion of the ash. Therefore, the quality of rice husk ash is very low in order to be used it as a raw material for other industries. This ash is used only as a filler in fertilizer production or is poured directly onto the plant stumps. This reduces the value of the rice husk ash and wastes the high silica resources. However, RHA has high porosity and contains high silica in its chemical composition. Therefore, this study has utilized the rice husk ash as a main raw material supplying silica in the manufacture of refractory materials.

Besides, the study also used sawdust (SD) as an additive to aid the heating process and increase the porosity of the final product. Sawdust is a byproduct of the wood processing industry. The sawdust has the small particle size and uneven distribution so it has rarely used in life and only considered as waste to discharge in the environment. Sawdust has the potential to pose problems of health hazards. Wood dust is a human carcinogen and some

types of wood and their dust contain toxins that can cause severe allergies. Therefore, using sawdust is a useful solution to both improve product porosity and save fuel for the burning process. Moreover, this solution also contributes to environmental protection by reducing solid waste throw away into the environment and community health protection.

That is the reason to proceed the study and obtain a refractory product with better than expected properties

## MATERIALS AND METHODOLOGY

### Materials and Mix Design

The study used DE from Lam Dong province, Vietnam. This material has white or light yellow finely ground and passed through a 90µm sieve. It is then dried to prepare it for mixing and shaping.

RHA was used from the kiln of Loc Troi Group – formerly An Giang Plant Protection Joint Stock Company (AGPPJS) which is the leading agricultural manufacturer and service supplier in Vietnam market with the sustainable value chain from research, production, trading of seed products, crop chemicals and biological – organic products. Rice husk ash with the color of gray or dark, white was finely ground and passed through a 90µm sieve to prepare for the mixing and forming of products.

Sawdust was from a local wood production facility in Binh Chanh town, Ho Chi Minh city, Vietnam, which was dried at 110°C for 24 hours and passed through a 250µm sieve to prepare for the mixing and forming of products.

**Table 1:** Mix Design for Raw Materials in Porous Refractory (% wt).

Samples	Raw materials		
	DE	RHA	SD
M0	50.0	50.0	0
M5	47.5	47.5	5.0
M10	45.0	45.0	10.0
M15	42.5	42.5	15.0
M20	40.0	40.0	20.0
M25	37.5	37.5	25.0
M30	35.0	35.0	30.0
M35	32.5	32.5	35.0

The mixtures were designed with changes of ratios sawdust, DE and RHA as shown in Table 1.



**Fig. 3:** The Refractory Samples after Forming.

Water was added with 40% of the mixtures to get the plasticity meals. It is noted that the samples with over 40% SD can not formed because the mixtures did not have the plasticity required for forming. The refractory samples were formed into bricks with sizes of 220x110x65 (mm) from the plasticity meals. The forming process was carried out with a pressure of 10MPa and obtained specimens as shown in Figure 3. These wet samples were dried naturally in a warehouse at a temperature about 30°C for 72 hours (3 days) and then dried in oven at 60°C for 24 hours (1 day). Finally, the dried samples were heated at 1200°C as mentioned below.

### Evaluation and Determination of the Heating Regime for Refractory Products

In this study, the sample with 35%SD (M35) was chosen to carry out for thermal analysis (DTA-TG) with the results shown in Figure 4.

The sample M35 was heated from room temperature (25°C) to 1200°C with heating rate at 5°C/minute. During the heating process, the sample M35 had been decreased mass over 40% related to evaporation of physical absorbed water (drying); decompositions of organic matter including sawdust; dehydration of clay minerals; phase structure changes of quartz and alumino-silicate compounds and sintering process over 1100°C.

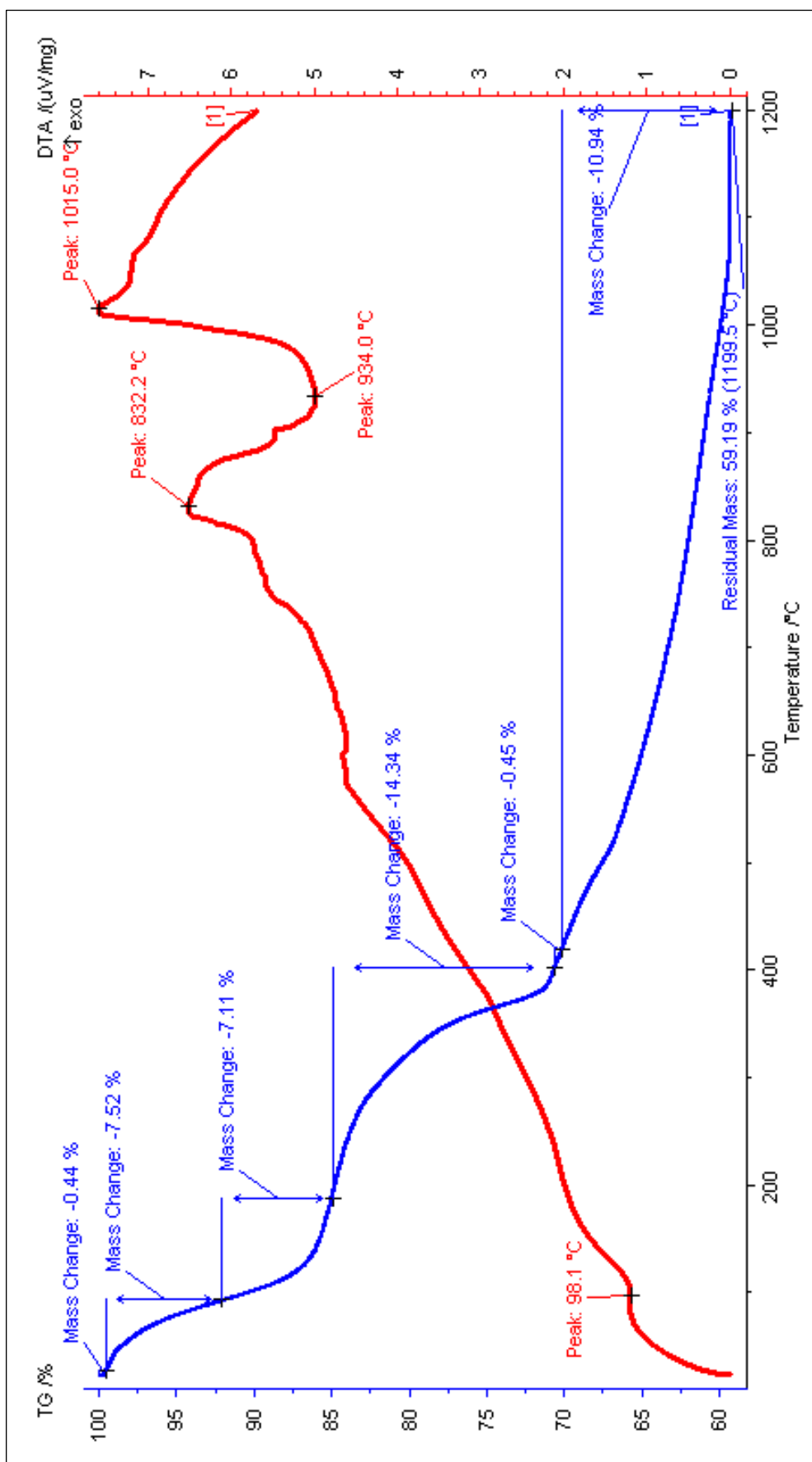


Fig. 4: Thermal Reactions and Mass Changes of the Sample M35 using DTA-TG.

It is based on evaluations of DTA-TG, the study has provided a solution for the heating regime of the refractory specimens. The products were heated at 1200°C for 2 hours to ensure for completely sintering. From room temperature to 600°C, there have been many physico-chemical reactions happened in combination with combustion and thermal decomposition of saw dust. Therefore, the heating rate should be slow at 1°C/ minute to avoid deformation of the specimens. From 600 to 1200°C, there are phase structure changes of quartz and alumino-silicate compounds and sintering process, mass loss was around 5%, the heating rate was adjusted at 2°C/ minute. The cooling process was carried out according to the rate of cooling of the furnace with cooled rate at 3°C/minute. The entire thermal regime of the porous refractory products is indicated by a heating curve diagram as shown in Figure 5. Finally, the refractory specimens manufactured (Figure. 6.) were tested for engineering and thermal properties. In which, the engineering properties included volumetric weight ( $\text{g/cm}^3$ ), porosity (%), bending and compressive strength (MPa); thermal properties were tested for thermal shrinkage (%), thermal shock resistance (time), thermal conductivity (W/m.K).

## RESULTS AND DISCUSSION

After cooled process, the specimens of refractory composite were removed from the

furnace to test for the required properties. In this study, the samples were focused on testing for engineering and thermal properties.

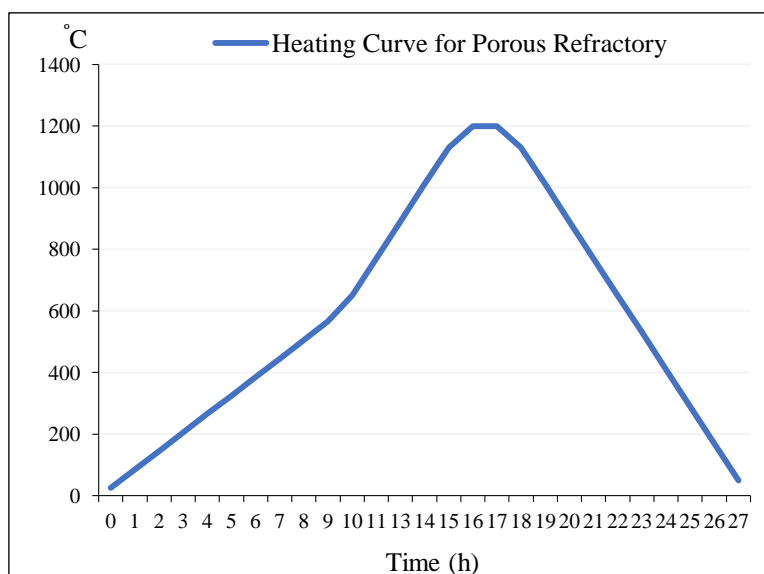
### Engineering Properties of the Porous Refractory Composite

The engineering properties of the products are physical and mechanical properties known as volumetric weight ( $\text{g/cm}^3$ ), porosity (%), bending and compressive strength (MPa).

**Table 2:** The Values of Volumetric Weight ( $\text{g/cm}^3$ ) and Porosity (%) for the Porous Refractory.

Samples	Engineering Properties	
	Volumetric Weight ( $\text{g/cm}^3$ )	Porosity (%)
M0	0.66	75.32
M5	0.61	74.28
M10	0.57	78.13
M15	0.53	81.64
M20	0.48	83.08
M25	0.44	86.76
M30	0.41	88.51
M35	0.37	92.45

The novel refractory composites have the values of the volumetric weight from 0.37 to 0.66  $\text{g/cm}^3$  which have belonged to the group of lightweight materials. In addition, the porosity of the products is really high from 74.28 to 92.45% as shown in Table 2. This is explained that the porous refractory composites were formed from raw materials which have high porosity as known DE and RHA.



**Fig. 5:** The Heating Curve for the Porous Refractory from Diatomaceous Earth and Rice Husk Ash.



**Fig. 6:** The Porous Refractory Products of the Study after Heating at 1200°C.

The second reason come from using sawdust which after combustion will reduce the mass of the material and leave more pores. Moreover, the water was added and water in clay minerals also has a role similar to sawdust.

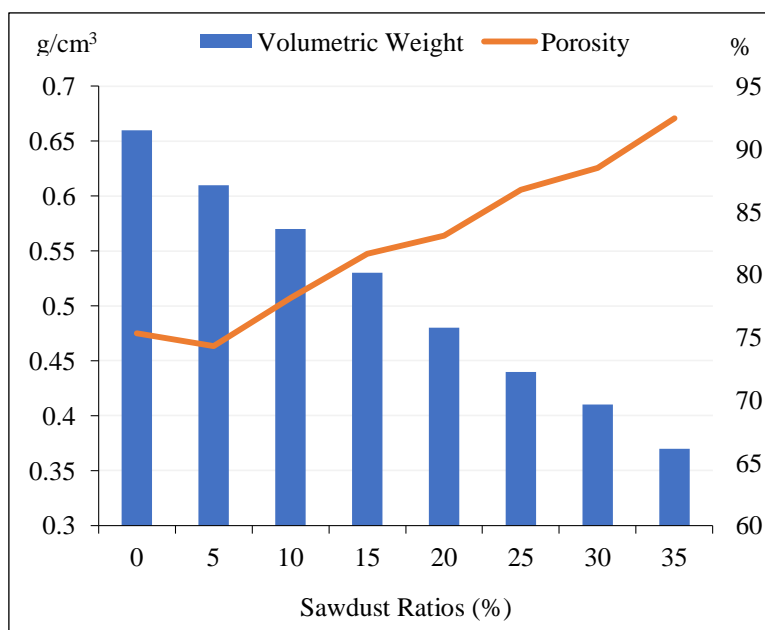
In this research, the values of the volumetric weight decreased to 0.37 g/cm<sup>3</sup> when the sawdust ratios were increased to 35%. This caused the porosity of the products was improved and reached to 92.45% as shown in Figure 7. Therefore, the porous refractory

composite with 35% sawdust (M35) has the lowest value of volumetric weight and the highest value of porosity.

**Table 3:** The values of Bending and Compressive Strength (MPa) for the Porous Refractory.

Samples	Mechanical Properties	
	Bending strength (MPa)	Compressive Strength (MPa)
M0	1.78	17.35
M5	1.75	17.24
M10	1.72	17.03
M15	1.72	16.84
M20	1.70	16.68
M25	1.68	16.41
M30	1.66	16.11
M35	1.61	15.78

The porous refractory specimens were tested for mechanical strength with the strength values decreased when the increase of sawdust ratios or porosity. In which, the values of bending strength were gone down to 1.61 MPa from 1.78 MPa and the values of compressive strength were reduced from 17.35 MPa to 15.78 MPa as shown in Table 3 and Figure 8. The mechanical strength of the product is obtained by the solid phase reactions, diffusion and sintering among solid powders together during the heating process at 1200°C.



**Fig. 7:** Relationships among Sawdust Ratios with Volumetric Weight and Porosity of the Porous Refractory Composite.

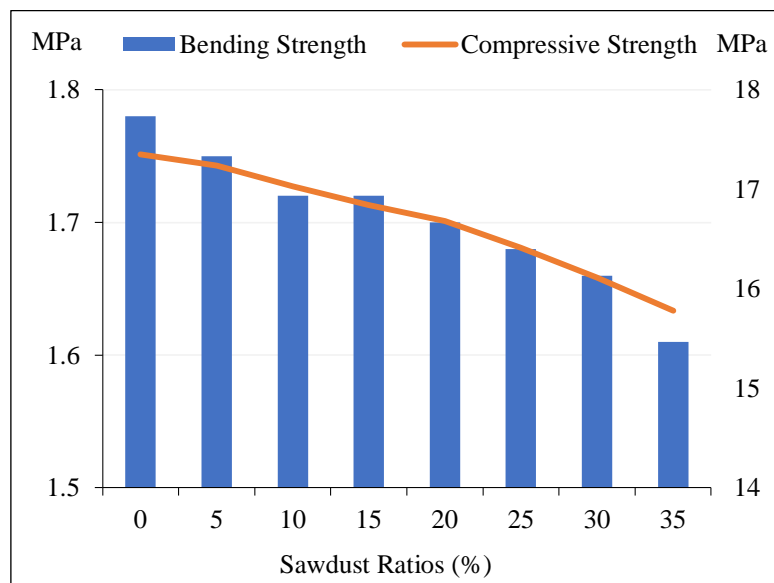


Fig. 8: Relationships among Sawdust Ratios with Mechanical Strength of the Porous Refractory.

### Thermal Properties

The thermal properties of porous refractory composites were carried out with the experiments for testing of thermal shock resistance (time), thermal conductivity (W/m.K), shape factor and changes of area using heating microscope for sample M35.

Table 4: The Values of Thermal Properties for the Porous Refractory.

Samples	Thermal Properties	
	Thermal Shock Resistance (Time)	Thermal Conductivity (W/m.K)
M0	78	0.1035
M5	75	0.1024
M10	72	0.1003
M15	72	0.0984
M20	70	0.0968
M25	68	0.0941
M30	66	0.0911
M35	61	0.0878

In this study, the tests of thermal shock resistance were conducted at 1000°C with the results over 61 times for all of the specimens. These values are higher than comparable products on the market and meet the requirements of the TCVN standard (TCVN 6530-4:1999 and TCVN 6530-7:2000) on refractory materials. It is noted that the samples for testing thermal shock resistance were prepared in Seger cone. In specially, the higher the thermal shock resistance of the sample is, the smaller the porosity is. Because

when heated, the sintering process was still continuously happened which caused the sample with a high porosity had strong arrangement and disturbance and the seger cone was easily deformed.

The porous refractory composites have really low values of thermal conductivity from 0.0878 to 0.1035W/m.K. The values significantly reduced and reached to the lowest values at 0.0878 W/m.K corresponding to increase of porosity in the materials as shown in Table 4 and Figure 8. The low thermal conductivity of the refractory product will ensure heat savings for the furnaces with high efficiency to the fuel burning process. This is a solution with high economic efficiency for industries that use thermal equipment.

More specifically, this study used a heating microscope to observe changes in the product shape (sample M35) at high temperatures. Figure 9 shows the porous refractory had no change of the shape from room temperature to 1110°C as indicated on the line S. The sintering process occurred over 1110°C upto 1282°C as showed on the line A. At 1282°C, the sintering caused shrinkage of the sample with shape factor at 0.738, changes of area at 65.1%, height at 78.7%, and width of 86.6%.

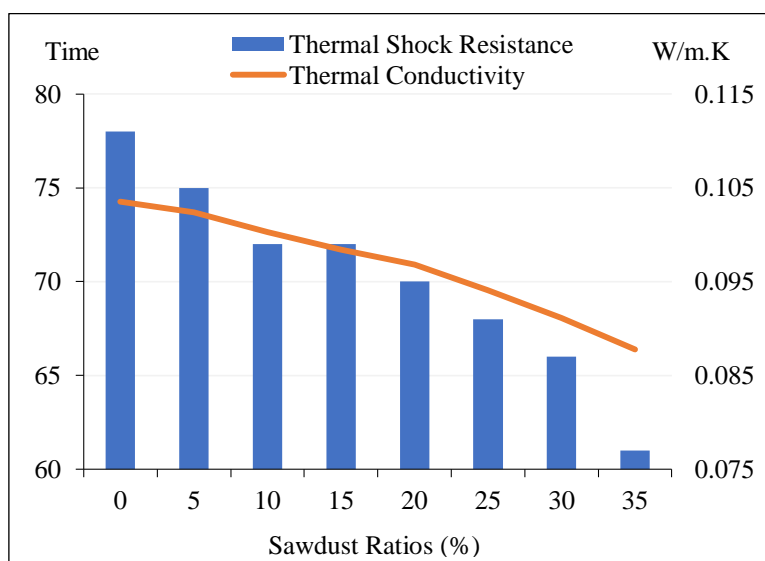


Fig. 8: Relationships among Sawdust ratios with Thermal Shock Resistance, Thermal Conductivity of the Porous Refractory Composites.

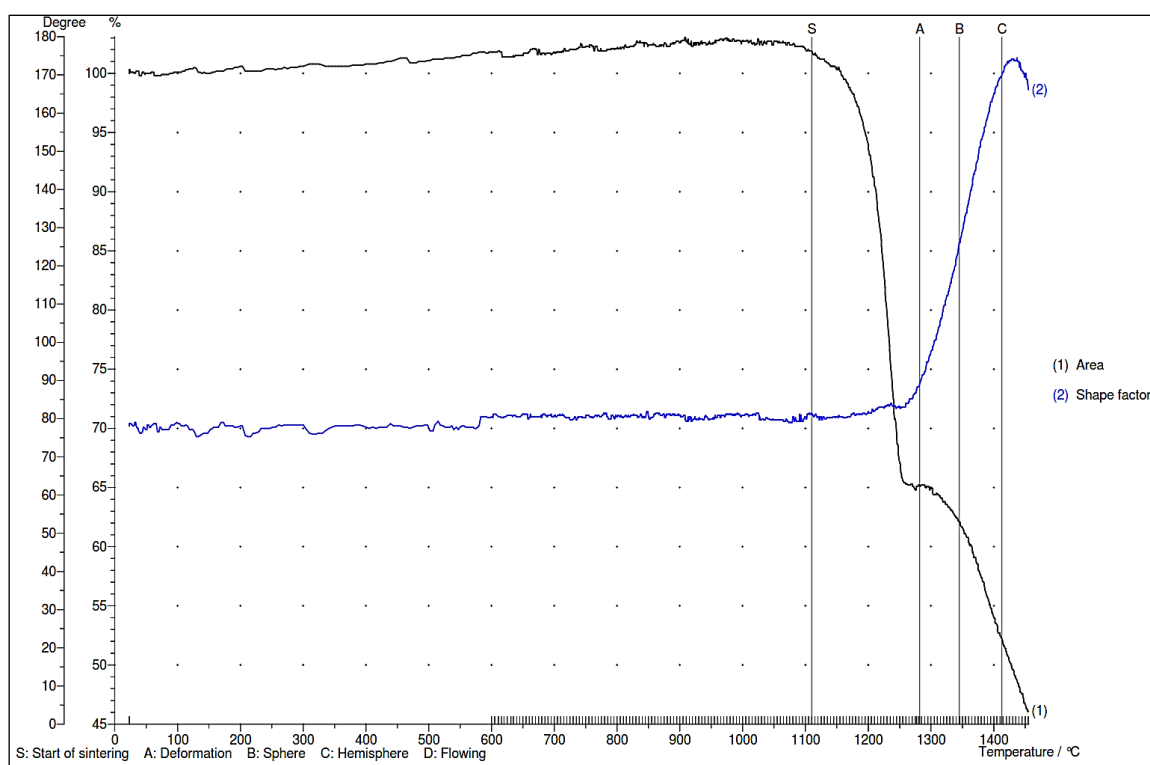


Fig. 9: Changes for the Product Shape (Sample M35) Observed by Heating Microscope.

Over 1282°C, the sample was deformation of shape as known sphere at 1345°C (the line B), hemisphere at 1413°C (the line C) and flowing at higher temperature (the line D).

**CONCLUSION**

This research utilized resource of abundant diatomite but low quality in combination

with rice husk ash and sawdust to produce porous refractory products. Both rice husk ash and sawdust are solid wastes from agro-processing and wood production industries. Therefore, using them as raw materials for refractory production is a useful solution and has many economic and environmental benefits.



The refractory products have engineering properties responded to the requirements of porous materials group with low volumetric weight and high porosity. Moreover, the tests of thermal properties also showed the novel porous refractory composites have high thermal shock resistance and low thermal conductivity. These features allows them to work in the harshest conditions of high temperature environments.

Further research should be carried out for characterizing microstructure of the novel porous refractory composites to to gain a deeper understanding of the material. In addition, future studies should also conduct tests and calculate the heat loss during the heating process for thermal equipment using this product.

#### NOMENCLATURE

- DE : Diatomaceous Earth  
RHA : Rice Hush Ask  
SD : Sawdust  
DTA : Differential Thermal Analysis  
TG : Thermogravimetric

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