EXPERIMENTAL INVESTIGATION OF SILICON CARBIDE FORMATION FROM HIGH ENERGY BALL-MILLED RICE HUSKS VIA PYROLYSIS

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ABSTRACT

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In this thesis work, it was aimed to optimize the conditions to produce silicon carbide (SiC), from rice husks from Turkish Thrace Region, via pyrolysis.

Rice husks, coked at 500°C, were high energy ball-milled prior to pyrolysis, in order to investigate the effects of ball-milling on pyrolysis temperature, pyrolysis time and morphology of the SiC produced.

Samples of rice husks subjected to different ball milling conditions, were pyrolyzed at temperatures varying from 1500°C to 1600°C and for times varying from ½ hour to 2 hours. Results of experiments showed that, ball-milling reduced the pyrolysis temperature and pyrolysis time to some extent. It was also experimentally shown that ball-milling favored the formation of SiC particles rather than formation of SiC whisker.

Key words: Silicon Carbide, Rice Husks, Pyrolysis, High Energy Ball-Milling

ÖZ

YÜKSEK ENERJİLİ BİLYALI DEĞİRMENDE ÖĞÜTÜLEN PİRİNÇ KABUKLARINDAN PİROLİZ YÖNTEMİYLE SİLİSYUM KARBÜR ELDE EDİLMESİNİN DENEYSEL İNCELENMESİ

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Bu tez çalışmasında, ülkemiz Trakya Bölgesi'nde hasat edilen pirinç kabuklarından, piroliz (ısıl bozunma) yöntemiyle, silisyum karbür (SiC) elde edilmesi koşullarının optimize edilmesi amaçlanmıştır.

500^{o}C de koklaştırılmış pirinç kabukları, piroliz sıcaklığı, piroliz süresi ve elde edilen SiC nin morfolojisi üzerindeki etkilerinin araştırılması maksadıyla, piroliz öncesinde yüksek enerjili bilyalı değirmende öğütülmüştür.

Farklı öğütme sürelerine tabi tutulan pirinç kabuğu örnekleri, 1500^{o}C ve 1600^{o}C arasında değişen sıcaklıklar ve ½ saat ile 2 saat arasında süreler kullanılarak piroliz edilmiştir. Deney sonuçları, bilyalı değirmende öğütmenin piroliz sıcaklığını ve piroliz süresini belirli oranda azalttığını göstermiştir. Öğütmenin SiC nin çubuksu (whisker) yapı yerine parçacık şeklinde oluşumunu desteklediği de deneysel olarak gösterilmiştir.

Anahtar Kelimeler: Silisyum Karbür, Pirinç Kabuğu, Piroliz, Yüksek Enerjili Bilyalı Değirmen

To My Parents,

To My Wife

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CHAPTER 1

INTRODUCTION

Rice husk is a by-product of rice milling process and generally considered as an agricultural waste. It has a few low-value applications in steel casting, chicken farming or as fuel. On the other hand, rice husk contains a number of organic constituents that will yield carbon when thermally decomposed, high silica content in the ash with small amounts of alkalis and other trace elements. Owing to the high silica content together with high carbon content, it becomes a natural and ideal source material for production of SiC, as long as the reduction of silica by carbon is achieved.

Unlike rice husks, SiC is a high technology material and it has wide industrial application due to its excellent mechanical properties, high thermal shock resistance, excellent chemical and oxidation resistance and high wear resistance. The main and industrialized synthesis method of SiC is a carbothermal reduction of silica sand with green petroleum coke at a high temperature between 1600 and 2500˚C, known as Acheson process. This process uses a very high temperature and the product has a large grain size (> 1 mm), which requires extensive grinding to reduce the powder to sinterable size (Romero et al., 1996). Extensive milling makes the cost of SiC powder higher, therefore, preventing the use of SiC products in the consumer markets.

It is reported that, about 0.2 million tons of rice husks are generated in Turkey annually and the price of rice husk in the market is around 140 $/ton. On the other hand, SiC is totally imported to Turkey (5400-5500 tons/year) and it has a price of 1400-4500 \$/ton (depends on purity and particle size). To manufacture such a value-added product, silicon carbide, from a low valued material, rice husks are subjected to pyrolysis (thermal decomposition). In pyrolysis process, rice husks is generally heated at a high temperature (> 1400˚C), where a reaction occurs between silica and carbon resulting in the formation of SiC, under protective atmosphere (inert gas flow during process). The possible reactions of such a process can be written as;

$$C(s) + SiO_2(s) \rightarrow SiO(g) + CO(g) \quad (1)$$
$$SiO_2(s) + CO(g) \rightarrow SiO(g) + CO_2(g) \quad (2)$$
$$C(s) + CO_2(g) \rightarrow 2CO(g) \quad (3)$$
$$2C(s) + SiO(g) \rightarrow SiC(s) + C(g) \quad (4)$$

which results in the overall reaction:

$$SiO_2 \text{ (amorphous)} + 3C \text{ (amorphous)} \rightarrow SiC + 2CO \text{ (g)} \quad (5)$$

The silicon carbide made from rice husks is usually a mixture of silicon carbide powders and whiskers, but through control of the reaction conditions, silicon carbide whiskers can be obtained as the main product and also compared with traditional processing, this method is simpler and more economical and it can dispose of unused part of rice husks without pollution (Sacher, 1988). Therefore, rice husk is the most economical and promising raw material for producing silicon carbide.

The main problem of the carbothermic reduction process is the particle size of reactants and the need for an intimate contact among them. The low density and the space in the raw rice husks facilitate the production of silicon carbide, further grinding of rice husks in a planetary ball mill (high energy ball-milling) is expected to favor the silicon carbide formation. Since, as the milling time increases, particle size is decreasing and the specific surface area increases. Also, energy introduced by high energy ball milling prior to pyrolysis, is also expected to improve the conditions of pyrolysis in terms of temperature and time.

In this thesis study, it was aimed to optimize the silicon carbide formation from high energy ball-milled rice husks, which were obtained from Thrace Region of Turkey. It was also aimed to investigate experimentally, the effect of high energy ball-milling on pyrolysis conditions and morphology of the silicon carbide produced.

Literature reviews and the works published on pyrolysis of rice husks to produce SiC are presented in Chapter 2, experimental procedures are summarized in Chapter 3, results obtained and discussion are given in Chapter 4, conclusions of the study are reported in Chapter 5 and recommendations and suggestions regarding further work on this topic are presented in Chapter 6.

CHAPTER 2

LITERATURE SURVEY

In this chapter, results of literature survey regarding silicon carbide, rice husks, pyrolysis, silicon carbide whiskers, high energy ball-milling and alternative methods of silicon carbide production were reviewed and discussed.

2.1 General Information about Silicon Carbide

Silicon carbide (SiC), also known as carborundum, is a compound of silicon and carbon with chemical formula SiC. It occurs in nature as the extremely rare mineral moissanite. Pure SiC is colorless, the brown to black color of industrial product results from iron impurities (Kumar et al., 2011). Silicon carbide is one of the most important non-oxide ceramic materials which are produced on a large scale in the form of powders, molded shapes and thin film (Boulos et al., 1994).

Main properties of SiC at room temperature, as listed in the webpage of Insaco Incorporated, are given in Table 2.1.

Table 2.1 Properties of SiC at room temperature (Insaco Incorporated)

Property	**Value**
Molar Mass	40.1 g/mol
Density	3.1 - 3.2 g/cm^3
Melting Point	2730°C (decomposes)
Hardness	2550 - 2800 Knoop kg/mm^2
Modulus of Elasticity	58 - 65 psi x 10^6
Coefficient of Thermal Expansion	3.9 – 4.5 x 10^{-6} /°C
Thermal Conductivity	71 - 130 W/m°K

SiC is a semiconductor and the electrical conductivity of SiC can be increased by the addition of boron and nitrogen. The high sublimation temperature of SiC makes it useful for bearings and furnace parts. There is currently much interest in its use as a semiconductor material in electronics, where its high thermal conductivity, high electric field breakdown strength and high maximum current density make it more promising than silicon for high-powered devices (Zhang et al., 2001). Some other critical applications of SiC are;

- Wear resistant applications (nozules, car brakes and clutches)
- Casting filters, casting (melting) pot
- As ballistic ceramics in armor applications
- Used in abrasive machining (cutting, grinding, honing, sandblasting)
- Mirror material for astronomical telescopes
- Used to measure gas temperatures in an optical technique called thin filament pyrometry
- Used for ultrafast, high-voltage Schottky diodes, and high temperature thyristors for high-power switching.

2.2 General Information about Rice Husks

Rice husks, the coating for the seeds, or grains of the rice plant, consist of organic and inorganic parts. The organic part of rice husks constitutes mainly cellulose and lignin totally contains 51-52 %C, 40-42 %O and 6-7 %H by weight (average values and depends on region). The inorganic part comprises of a number of metal ions such as B, Mn, Na, K, Al, Mg, Fe, Ti all in different quantities (Karera, 1986).

In addition, rice husks have a high ash content varying from 13 to 29 % depending on the variety, climate and geographic location. Some industrial uses of rice husk ash are given in Table 2.2.

The ash is composed largely of silica (87-97 %) with small amount of alkalis and other trace elements. Silica is in an hydrated amorphous form and bound in the inner layer to organic constituents (Williams, 1984).

Silicon enters the rice plant through its root in a soluble form, probably as a silicate or monosilicic acid and then moves to the outer surface of the plant, where it becomes concentrated by evaporation and polymerization to form a cellulose silica membrane. There is quite general agreement that the silica is predominantly in inorganic linkages, but some of the silica is also covalently bonded to the organic compounds. This portion of the silica can not be dissolved in alkali and can withstand to very high temperatures. Silica is mainly localized in the tough interlayer (epidermis) of the rice husks and it also fills in the spaces between the epidermal cells (Sun and Gong, 2001).

Table 2.2 Uses of Rice Husk Ash (Rao, 1980; Proctor et al., 1995).

Feature	Application
Absorbent	For oils and chemicals
Insulator	As insulation powder in steel mills In homes and refrigerants In the manufacture of refractory bricks
Release agent	As a release agent in the ceramics industry
Pozzolan	Cement industry Concrete industry
Repellents	As repellents in the form of "vinegar-tar"
Aggregates and fillers	Aggregates and fillers for concrete
Soil ameliorant	Soil ameliorant to help break up clay soils and improve soil structure
Source of silicon	Manufacture of industrial chemicals like silica, sodium silicate, zeolite and refractory material such as SiC, Si_3N_4
Substitute for micro silica / silica fumes	RHA can also replace silica fume in high strength concrete
Water purifier	To filter arsenic from water
As a vulcanizing agent	Vulcanizing agent for ethylene-propylenedieneterpolymer (EPDM)

2.3 Production of SiC via Pyrolysis of Rice Husks

In recent years, ceramic-matrix or metal matrix composites have become of great interest because of their high temperature strength retention as well as thermal stress resistance coupled with their light weight. As a consequence, different types of Si-based ceramic materials such as SiC, Si_3N_4 and Si_2N_2O are available commercially (Ray et al., 1991).

SiC whiskers, useful in reinforcing metal matrix and ceramic matrix composites are already reported to be produced using rice husks. For the production of SiC, Si_3N_4 and Si_2N_2O, both the important raw materials SiO_2 and carbon are present in rice husk with intimate contact and they possess a high surface area. Therefore, it is not surprising that, due to the ease of further processing, rice husk was reported to be used in the production of SiC, Si_3N_4 and Si_2N_2O (Shen et al., 1995).

Rice husks were, first, used by Lee and Cutler (1975) as a starting material for the production of silicon carbide. Since the rice husk route appears to be promising, much attention has been paid to it and many studies have been reported (Patel, 1991; Ray et al. 1991; Romera and Reinso 1996; Moustafa et al. 1997; Krishnarao et al. 1998; 1999; Panigrahi et al. 2001). Almost all the processes investigated so far involve two process steps;

(i) coking at lower temperature (400–800˚C) in a controlled manner to remove volatiles and
(ii) reacting the coked rice husk at high temperature (> 1400˚C) to form SiC.

Romera and Reinso (1996) determined that; during the prolysis of coked rice husks, there were four competitive processes occurring; crystallization of amorphous silica, crystallization of amorphous carbon, reduction of SiO_2 and formation of SiC whiskers and particles.

The silica and carbon in rice husks start to crystallize at 900˚C and the crystallization of amorphous silica is accelerated with increase in temperature from 1100-1200˚C.

Lee and Cutler (1975) also reported that, heat energy for the reaction is provided by available energy sources in the rice husk itself; that is, the excess carbon present in the husk. This, of course, means that some port of combustion system is required for the rice husks. An upper temperature limit of about 1700˚C was reported as an approximate economic limit for the temperature of such a combustion system. To be economically processed near the source of the rice husks, the reaction must occur at a reasonable rate at temperatures somewhat below 1700˚C.

Shanma and Williams (1984) carried out a work on the distribution of Si in rice husks to understand the formation of SiC whiskers by thermal decomposition and reaction of natural materials in it. Scanning electron microscopy, Auger electron spectroscopy and energy-dispersive X-ray analysis confirm the presence of a major amount of Si in the outer and inner epidermal regions of the rice husks. The Si is present as a hydrated amorphous form of silica which is evidently bound in the inner layer to organic constituents, placing it adjacent to a source of carbon (Yücel, 1997).

Hanna et al. (1987) reported that formation of β-SiC occurred at temperatures above 1300˚C and amount of SiC was increased as the pyrolysis temperature was increased up to 1500-1600˚C.

Limthongkul et al. (2006) experimetally showed that, for the heat treatment temperatures between 1140˚C – 1170˚C, the diffractograms were very similar to that of the raw rice husks; no crystalline phase could be detected. As the heat treatment temperature increased, crystallization of the amorphous phases occurred. By inspecting the starting and the final products by using XRD and SEM, it has been found that SiC formed at temperatures at and above 1330˚C.

Peaks corresponding to that of cristobalite SiO_2 (strong peak at $2\theta = 21.9^o$, 28.4^o, 31.4^o and 35.9^o) and graphite (strong peak at 26.4^o) were found for the samples fired at temperatures between 1330˚C and 1425˚C. At firing temperatures above 1130˚C, small amount of β-SiC was detected ($2\theta = 35.7^o$, 60.0^o, 71.8^o) along with cristobalite and graphite phases. As the temperature increases to 1450˚C and 1635˚C, peaks from the cristobalite phase disappeared, and β-SiC was dominant phase.

The microstructures of SiC were found to vary from nano-size whiskers to fine particulates with increasing temperature and pressure. Limthongkul et al. (2006) also reported that, as the pyrolysis temperature was increased to 1360˚C, a large quantity of whiskers was observed. As the pyrolysis temperature increased further, a lesser quantity of the SiC whiskers and a larger quantity of SiC particulates were found along with beading up of whiskers to particles. The particles were found to be agglomerated and some were found to still retain the starting structure of the inner epidermal layer which consisted of only carbon for the samples fired at lower temperatures. This indicates that these SiC particles were formed through the solid vapor interaction (possibly SiO (g) and C (s)). The slower formation of the SiC from this area of the husk is probably due to a less abundant silicon source at this part of the epidermal layer, therefore, longer diffusion paths are required for the formation of SiC. It was also found that a higher amount of whiskers was found for sample fired at lower pressure.

The results obtained by Limthongkul et al. (2006), were consistent with the results obtained from the weight loss experiment in which above 1450˚C, SiC and carbon were the only phases found with no remaining SiO_2 phase. Effects of pressure were also studied between 0.5 – 2 atm at 1650˚C. It was found via XRD that the dominant phase of the husk after the treatment in the pressure range was β-SiC.

Krishnarao (1992) reported that, crystallization of silica and its conversion to SiC are two dominant processes at 1200˚C. Therefore, heating at lower temperatures at 900-1200˚C slowly or holding the coked rice husks at lower temperatures cause the rate of release of SiO and the rate of SiO deposition on carbon substrate, and the rate of SiC formation from SiO reduction are probably low enough for the preferred formation of SiC whiskers. Likely, some researchers (Subrahmanyam et al. 1995, Jagadishkumar et al. 1996) regulated the pyrolysis conditions to increase the reaction rate and the production rate and found that; instead of slow heating and holding for a long time at pyrolysis temperatures, rapid heating (300 ± 25˚C /min) and holding for a short period at high temperatures (1300-1600˚C) increases the production rate in continous operation.

In contrast with rapid heating, multistep pyrolysis, which involves the maintenance of different temperatures for different periods of time during the heating process, was found to result in an even higher production rate (Krishnarao et al., 1992).

As another approach to the synthesis of SiC from rice husks, Romera and Reinso (1996) investigated the use of catalysts (iron, cobalt and nickel) and claimed that the introduction of the catalyst increased the reaction rate, the yield becoming up to three times that for the uncatalysed reaction and increased the proportion of β-SiC from 95% to 99%. However, Patel (1989) disclosed the reason that a catalyst was not necessary because of the existence of trace elements in rice husks, some of which (iron, magnesium, etc.) could impart a catalytic effect.

Nakata (1989) showed that potassium in rice husks originate from K_2O in fertilizers, which causes surface melting and accelerates crystallization of amorphous silica to cristobalite. Potassium polysilicate with a melting point at a lower temperature was formed by reaction of SiO_2 and K, which included carbon causing the ashes to melt and the color of the ashes changing to gray or black. Na_2O is also to be thought to have the same behavior as K_2O. It was also stated by Yücel (1997) that presence of K in rice husks caused increase in surface melting profoundly and the existence of crystallization started to form at lower temperature, about 900^{o}C. It was further stated by Yücel that, K and Na in rice husks helped to the formation of SiC in whisker form.

Effect of the rate of heating on the morphology of SiC experimentally showed by Yücel and Geveci (1997) that, when heating rate was low enough (7.11°C/min.) between 900-1200°C, the more whisker formation occurred but at high heating rate (37.23°C/min.), between 900-1200°C, the release rate of SiO and the rate of of SiC formation were probably higher and favored, and a significant amount of SiC particles were formed.

Pure SiC whiskers without the presence of particulates or any amorphous phases are preferred for some composites and therefore, efforts were made to remove (dissolve) the metallic particulates from the product by a technique involving ultrasonic vibration and acid wash (HF + HCl). Raju and Verma (1997) suggested that cleaning the pyrolyzed product with an acid treatment removed small amounts of amorphous material to leave it consisting essentially of smooth β-SiC whiskers with needle like morphology.

Trace elements can also be removed at the beginning of the process. It was analyzed by many authors (Chakraverty et al., 1988) that preliminary leaching of rice husk with solution of HCl, HNO_3, H_2SO_4, NaOH, NH_4OH, boiled before thermal treatment with temperature ranging from 500-1400°C, for various time intervals (Rao et al., 1996, Boaterg, 1990) was effective in removing most of the metallic impurities. The acid treatment of rice husk did not affect the amorphousness of the silica. Real et al. (2001), found that the preliminary leaching of rice husks with a solution of HCl before combustion at 600°C could result in relatively pure silica (approximately 99.5%) with a high specific surface area (approximately 260 m^2/g). Other acids like sulfuric, oxalic, and citric acids can also be used for leaching of rice husk but experimental results showed that silica produced by hydrochloric acid possesses higher surface area than that of sulfuric, oxalic, and citric acids (Liou et al., 2011).

2.4 General Information about Silicon Carbide Whisker

Characterization of the product by X-ray diffraction, scanning electron microscopy, infrared spectroscopy and chemical analysis confirmed that the formation of β-SiC whiskers as the major component with a small amount of particulate material of the same composition (Raju and Verma, 1997).

As a class of ceramic materials, SiC whisker-reinforced ceramic composites were developed for potential structural applications because of the significant improvements in the mechanical properties these materials offered as compared to the monolithic materials. Compared with particulates, SiC in whisker form has been shown to be an excellent reinforcement material in ceramic and glass matrix composites, giving better high temperature properties and therefore improving the potential of the materials for use in high temperature applications (Tiegs, 1986).

Lightweight metal matrix composites, such as aluminum reinforced with SiC particulates, whiskers or discontinuous fibers have shown better electrical properties, thermal conductivity, oxidation resistance and impact strength than basic matrix material and therefore are potentially more suitable as strong structural materials for automotive and other applications such as SiC whisker reinforced composites of alumina, mullite and zirconia matrices have been extensively studied and Al_2O_3 – SiC composites have been tried in machine tool applications (Rohatgi, 1991).

Silicon carbide whiskers have been interested as a reinforcing material for use in plastics, metals and ceramics to produce strong and tougher composite ceramics and light metal alloys because they are fine structure and have a mechanical strength close to theoretical (Jia and Tong, 2011).

Lee et al. (1994), studied on the effects of sintered porosity, volume fraction and particle size of silicon carbide particles on the abrasive wear resistance of powder metallurgy (P/M) aluminium alloy 6061 matrix composites. Aluminium alloy 6061 manufactured following the same route was also included for direct comparison. The results show that the beneficial effect of hard SiC, addition on wear resistance far surpassed that of the sintered porosity in the P/M composites. The wear rates of composites decreased as the amount of SiC, increased.

2.5 Structure of SiC Produced via Pyrolysis

Silicon carbide exists in about 250 crystalline forms. The polymorphism of SiC is characterized by a large family of similar crystalline structures called polytypes. They are variations of the same chemical compound that are identical in two dimensions and differ in the third. Thus, they can be viewed as layers stacked in a certain sequence. Alpha silicon carbide (α-SiC) is the most commonly encountered polymorph; it is formed at temperatures greater than 1700˚C and has a hexagonal crystal structure (similar to Wurtzite). The beta modification (β-SiC), with a zinc blende crystal structure (similar to diamond), is formed at temperatures below 1700˚C (Kollo, 2010). The transition temperature from one modification to the other has not been determined. Some resarchers consider that β-SiC is unstable above 2000˚C and is converted into α-SiC (Taylor, 1957). The crystal structure properties of SiC polytypes are summarized in Table 2.3.

Table 2.3 Crystal Structure Properties of SiC Produced via Pyrolysis (Kollo, 2010).

Properties	**3C (β) Structure**	**6H (α) Structure**
Crystal structure	Zinc blende (cubic)	Hexagonal
Lattice constants (Å)	4.3596	3.0730;15.11

The characteristic color of silicon carbide whiskers are described as green (Mortensen, 2007) which is given by nitrogen used as inert gas and impurities or the lack of them can cause the color of silicon carbide whiskers to vary from albino (colorless) to blue to black. Li et al. (2001) also reported the color of silicon carbide whiskers produced in their study was also green due to nitrogen doping.

2.6 High Energy Ball-Milling

Nanoscience and nanotechnology has become the buzz-word in recent years. It has appeal of miniaturization: also, it imparts enhanced electronic, magnetic, optical and chemical properties to a level that can not be achieved by conventional materials (Bhushan, 2004; Kohlar et al., 2004). A variety of ways have been reported to synthesize nano level materials such as plasma arcing, chemical vapor deposition, electro deposition, sol-gel synthesis, high intensity ball milling etc (Cao, 2004). Among these methods, high-energy milling has advantages of being simple, relatively inexpensive to produce, applicable to any class of materials and can be easily scaled up to large quantities (Baraton, 2003).

In this mechanical treatment, powder particles are subjected to a severe plastic deformation due to the repetitive compressive loads arising from the impacts between the balls and the powder. This produces novel crystalline and amorphous materials with crystallite sizes at the nanometer scale (Koch, 2006).

As the milling time increases, particle size is decreasing and the specific surface area increases; and also surface roughness of the silicon carbide increases. The increased surface roughness supports the higher surface energy of the ball milled silicon carbide. This favors the generation of Vander Waal’s interactions. The increased surface roughness supports the increased wettability of the surface and also is expected to promote its compatibility with the polymer or metal matrices when it is used as reinforcing nano-structured filler. This change is beneficial for the applications such as particulate nano-structured filler in polymeric or metallic matrices. Hence, the enhanced amorphous and rough surface content is very encouraging as it may lead to better compatibility with various metallic and polymeric matrices (Bhowmick et al., 1995).

The size reduction of silicon carbide from micrometer level to nanometer levels (from 120 nm to 26 nm) has been achieved by high-energy ball milling for the period of 50 hrs. The percentage of crystallinity reduces from 74% to 49%. The silicon carbide becomes more amorphous and the crystallite size reduces drastically. The lattice strain was increased with increasing the milling time. The SiC phase is the maximum sufferer during milling; hence, with increasing the milling time SiC peak height shifts to the lower levels and also broadening of the diffraction pattern occurs, with increasing milling time the peak height intensity shift slightly to the lower heights and increasing the peak broadening. This is the indication of high energy milling decreases the crystallinity of the silicon carbide, thus increasing the amorphous phase in it (Rao et al., 2011).

From the above and currently available literature conclusion can be drawn that very limited literature is available in the production and characterization of nano structured reinforcements by high energy ball milling method; for instance the production of nano structured silicon carbide powder (Rao et al., 2011).

2.7 Alternative Methods

Some other processes for SiC synthesis include plasma-arc synthesis, continuous feed through an induction furnace, batch reaction of silica and carbon in CO or inert gas, decomposition poly-carbosilanes, and chemical vapor deposition (CVD). However, the variable costs for these fine reactive powders are an order of magnitude higher than those for materials produced with Acheson furnace. This has restricted wide-scale commercialization (Sun et al., 2001).

Alternative ways of producing SiC have been reported including that from direct reaction between Si metal with carbon, or by reacting carbon with other sources of silica such as that form clay (Lee et al., 1994).

Several alternate methods such as sol-gel Meng, et al. (2009), thermal plasma Tong and Reddy (2006), and microwave Satapathy, et al. (2005) have been reported in the literature for the synthesis of SiC powders.

Sol-gel process requires expensive precursor solutions and complicated process while the thermal plasma synthesis, laser synthesis and microwave synthesis have very high operating costs with expensive equipment.

CHAPTER 3

EXPERIMENTAL PROCEDURE

Throughout this chapter, aim of the experiments, equipment and set-ups used, and procedures followed while the experiments were being performed, are discussed.

Multistep pyrolysis (coking process prior to the pyrolysis) was proceeded as experimental method in order to obtain maximum SiC yield and catalysts were not introduced during the process since iron present in the rice husks was assumed that it was acting like catalyst and it was also assumed that presence of potassium favored the silicon carbide formation as stated in the previous studies (Nakata, 1989 and Yücel,1997). In this thesis study, as a new approach to SiC formation from rice husks, coked rice husks were ball-milled prior to pyrolysis (additional energy was introduced to the system) and pyrolysis was done without providing a protecting atmosphere (no inert gas flow).

3.1 Raw Materials

Rice husks from the Thrace Region were used as raw materials for the synthesis of silicon carbide via pyrolysis. Rice husks were sieved by shaking through 2 screens with apertures of 4.75 mm and 1.40 mm, respectively. Raw rice husks were eliminated from foreign materials; residues, splinters and sands were removed via sieving and eye control.

Particle size distribution of rice husks was;

-1.40 mm : 11 wt. %
+1.40 mm – 4.75 mm : 87 wt.%
+4.75 mm : 2 wt.% (removed)

3.1.1 Proximate Analysis

In order to determine the proximate analysis of the rice husks used in the experiments,

(i) raw husks were firstly coked at 500˚C under Argon gas flow to remove volatiles and moisture,

(ii) then, coked rice husks were burnt at 800˚C, 1 hour for combustion of the fixed carbon,

(iii) following each step, samples were weighed and the mass loss was allocated to related substance,

(iv) finally, remaining mixture was the ash and it was also analysed by inductively coupled plasma mass spectrometry (ICP-MS) to determine the oxides in it.

Results obtained are given in Table 3.1 and the ash analysis is given in Table 3.2.

Table 3.1 Proximate Analysis of Rice Husks (Mass %)

Matter	Average %
Volatile and Moisture	58-60
Fixed Carbon	26-28
Ash	12-14

Table 3.2 Ash Analysis (Mass %)

Oxide	Average %
SiO_2	89-92
Fe_2O_3	3-4
K_2O+ CaO+MgO	3-4

3.1.2 Pure Silicon Carbide

SiC with 99.08% purity obtained from the market was taken as the reference material in order to compare the phases obtained at the end of the experiments and to examine the oxidation resistance of silicon carbide under the same conditions with the combustion of excess carbon.

3.2 Coking

At the first step, raw rice husks were coked in order to remove the volatile matter and to decompose the cellulose into amorphous carbon.

3.2.1 Equipment and Experimental Set-Up

Geveci and Timuçin (1994) suggested coking parameters as 600 ˚C for 1 hour under argon. In another study, Nakata (1989) found that the weight loss began at about 200˚C and the largest weight loss can be seen at 346 ˚C, at a temperature over 500˚C a gradual decrease could be seen.

Considering the parameters given in the literature, it was evaluated that coking at 500˚C would be sufficient to remove volatiles. An electrically heated crucible furnace of Hoskins was used for coking.

3.2.2 Experimental Procedure

- Rice husks were put into reaction chamber in alumina crucibles and chamber was equipped with inlet and outlet for Argon gas.
- Type R thermocouple was placed into the furnace to measure the temperature.
- Furnace was switched on and voltage was regulated in terms of mV considering temperature compensation.
- Chamber was flushed with Argon gas for 15 minutes prior to coking process and Argon flowed throughout the coking.
- Raw rice husks were put into reaction chamber in 3 alumina crucibles as one batch. Total 50 grams sample of rice husks were coked at each batch.
- Chamber was heated to 500˚C for 1.5 – 2 hours and when 500˚C was reached, the furnace was switched off.
- Coked rice husks were cooled to room temperature in the furnace.

3.3 High Energy Ball-milling and Pyrolysis

At second stage of experiments, the rice husk cokes were first ground in a high energy ball-mill and then pyrolyzed in order to obtain SiC. The purpose was to study the effect of ball-milling on the pyrolysis time and temperature, to produce SiC from coked rice husks.

3.3.1 Equipment and Experiment Set-Up

A high energy ball-mill, Retsch PM-100, was used for grinding of coked rice husks. An AISI 4340 steel bowl with a volume of 250 ml and 6 stainless steel balls each having a diameter of 20 mm, were used. Figure 3.1 shows the stainless steel balls put into the bowl. 10 g coked rice husks with a volume of 150 ml were ball-milled at each batch.

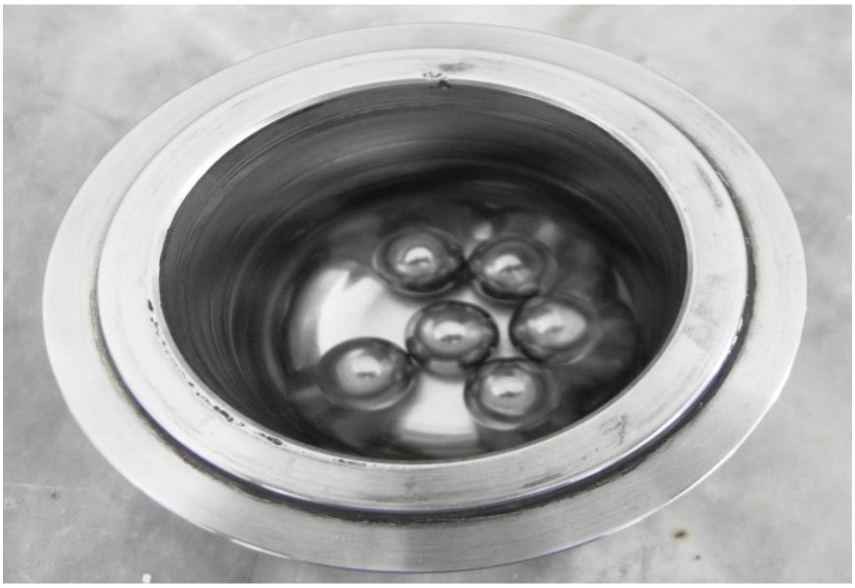

Figure 3.1 Stainless steel milling balls in the milling bowl

Total filling level (coked rice husks together with 6 balls) was 175 ml, which was 70% of the milling bowl volume as shown in Figure 3.2.

Figure 3.2 Coked rice husks inserted into the milling bowl

The bowl placed in the high energy ball-milling machine is shown in Figure 3.3. The speed of the machine was set to 300 rpm, at each batch.

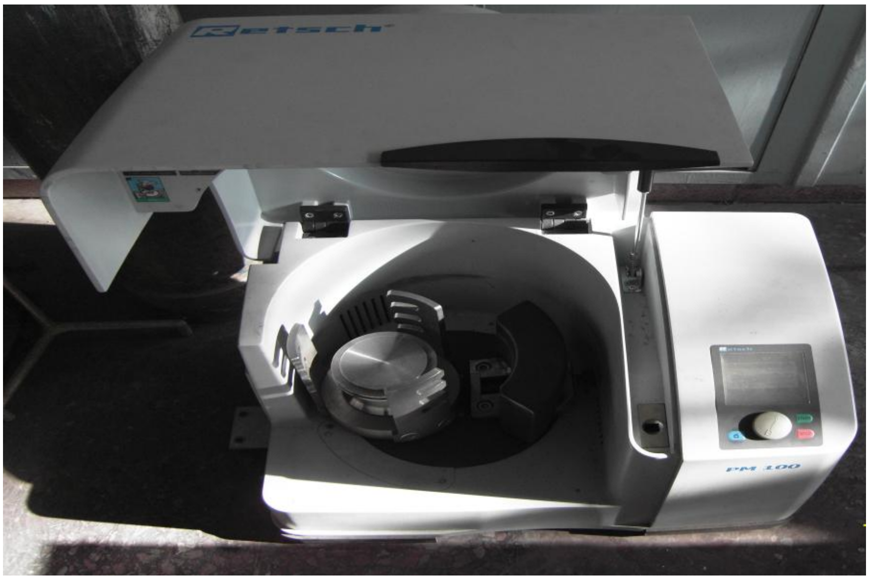

Figure 3.3 Ball-milling machine (with milling bowl placed in it)

An electrically heated muffle furnace of SFL brand, as shown in Figure 3.4, was used for pyrolysis. The furnace had a reaction chamber with dimensions of 30 cm in width, 30 cm in depth and 20 cm in height and the inner volume of the chamber was 18 lt. Coked rice husks were put into cylindrical graphite crucibles, with 7.5 cm diameter and 9 cm height and 1 cm wall thickness, before placing in the muffle furnace. Graphite crucibles were closed up with a graphite lid with 7.5 cm diameter and 1 cm in thickness. Graphite crucible and the lid used are shown in Figure 3.5.

Figure 3.4 Muffle Furnace

The door of the muffle furnace was shut down, during pyrolysis. There was no inlet of inert gas or protective atmosphere. Pyrolysis took place in reducing atmosphere provided by the graphite crucible while the crucible burned or reacted slowly.

Figure 3.5 Graphite crucible and graphite lid

3.3.2 Experimental Procedure

The formation of SiC from coked rice husks depends on the temperature and the time. Geveci and Timuçin (1994), determined the optimum condition for pyrolysis process as; 1700 ˚C for 30 minutes, under Argon gas flow.

In order to the determine the optimum conditions to obtain SiC from rice husks, two samples of coked rice husks, which were not ball-milled, were pyrolyzed at 1550˚C and 1600˚C for reference, and, eight samples of coked rice husks, which were ball-milled at different durations, were pyrolyzed to determine the effect of ball-milling on SiC formation temperature and time. Samples and experimental procedures are as given in Table 3.3.

Table 3.3 Experimental Procedures

Sample	Experimental Procedure
Reference 1	Pure SiC (99.08 %)
Reference 2	Coked rice husks without ball-milling, pyrolyzed at 1550˚C for 2 hours.
Reference 3	Coked rice husks without ball-milling, pyrolyzed at 1600˚C for 2 hours.
Sample 1	Coked rice husks ball-milled for 5 minutes at 300 rpm, then pyrolyzed at 1550˚C for 2 hours.
Sample 2	Coked rice husks ball-milled for 10 minutes at 300 rpm, then pyrolyzed at 1550˚C for 2 hours.
Sample 3	Coked rice husks ball-milled for 15 minutes at 300 rpm, then pyrolyzed at 1550˚C for 2 hours.
Sample 4	Coked rice husks ball-milled for ½ hour at 300 rpm, then pyrolyzed at 1500˚C for 2 hours.
Sample 5	Coked rice husks ball-milled for 1 hour at 300 rpm, then pyrolyzed at 1500˚C for 2 hours.
Sample 6	Coked rice husks ball-milled for 15 minutes at 300 rpm, then pyrolyzed at 1550˚C for 1 hour.
Sample 7	Coked rice husks ball-milled for 15 minutes at 300 rpm, then pyrolyzed at 1600˚C for 1 hour.
Sample 8	Coked rice husks ball-milled for 15 minutes at 300 rpm, then pyrolyzed at 1600˚C for ½ hour.

During the experiments, muffle furnace was programmed; to heat the sample to 1200˚C with a rate of 10˚C/min., hold at this temperature for 10 minutes, continue heating to the required final temperature and keep at this temperature for 2 hours. Following the pyrolysis of coked rice husks for 2 hours, muffle furnace was cooled down to 1200˚C with a rate of 10˚C/min. and then the furnace was switched off and cooled down to room temperature.

At each experiment, 9.8-10 g of coked rice husks were pyrolyzed in the muffle furnace without inert gas flow.

The cooled samples were then placed in another muffle furnace that was kept at 800˚C, in a rectangular boat, and excess carbon that might have remained after reactions or taken from graphite crucibles, was burned out.

CHAPTER 4

RESULTS AND DISCUSSION

In order to determine the phases included, pure SiC (%99.08) and coked rice husks were analyzed by X-ray Diffractometer type; Rigaku SA-HF3 X-Ray Diffractometer which has 20 kHz high voltage power supply and 400 Hz filament power supply generates an out-put of 3 kW and designed for use with a sealed off X-ray tube.

Particle size change, depending on ball-milling time was tried to be determined by Scanning Electron Microscope (SEM), JSM-6400 Scanning Microscope. The microscope was equipped with an Energy Dispersive Spectrometer (EDS) which was used to determine the impurity elements after pyrolysis. SEM images of both coked and pyrolyzed rice husks and EDS spectrums were obtained.

The samples were analyzed by X-ray diffractometer (Rigaku SA-HF3) to determine the phases formed after pyrolysis. XRD patterns were also analyzed in terms of unreacted silica amount for each experiment to decide the optimum condition for SiC synthesis from ball-milled and non-ball-milled coked rice husks.

The amount of unreacted silica were calculated with the use of a curve fitting software called Curve Expert Professional, which is a cross-platform solution for curve fitting and data analysis (downloaded from http://www.curveexpert.net). Raw data from XRD diffractograms were modeled using a toolbox of linear regression models, nonlinear regression models, smoothing methods, or various kinds of spline and then the most convenient curves, with 95 % accuracy, fitted to the peaks were decided.

Since the equations of the curves already existed in the database of software, the areas under the curves were calculated by taking the integral of the curves. The ratio of area silica peak, or curve, to total area of the all existence peaks resulted in the percentage of unreacted silica in the Samples.

Weight loss calculations, to determine the efficiency of pyrolysis was also done after the combustion of excess carbon. Pure SiC was also analyzed in terms of oxidation resistance in order to determine the SiC losses during the combustion of excess carbon after pyrolysis.

4.1 Particle Size

The size and shape of the non-ball-milled as well as ball-milled rice husk coke were studied using Scanning electron microscopy (SEM). Figure 4.1 shows the SEM image of non-ball-milled rice husk coke. Figure 4.2 - Figure 4.4 show the SEM images of 5 min., 10 min. and 15 min., ball-milled rice husk coke, respectively.

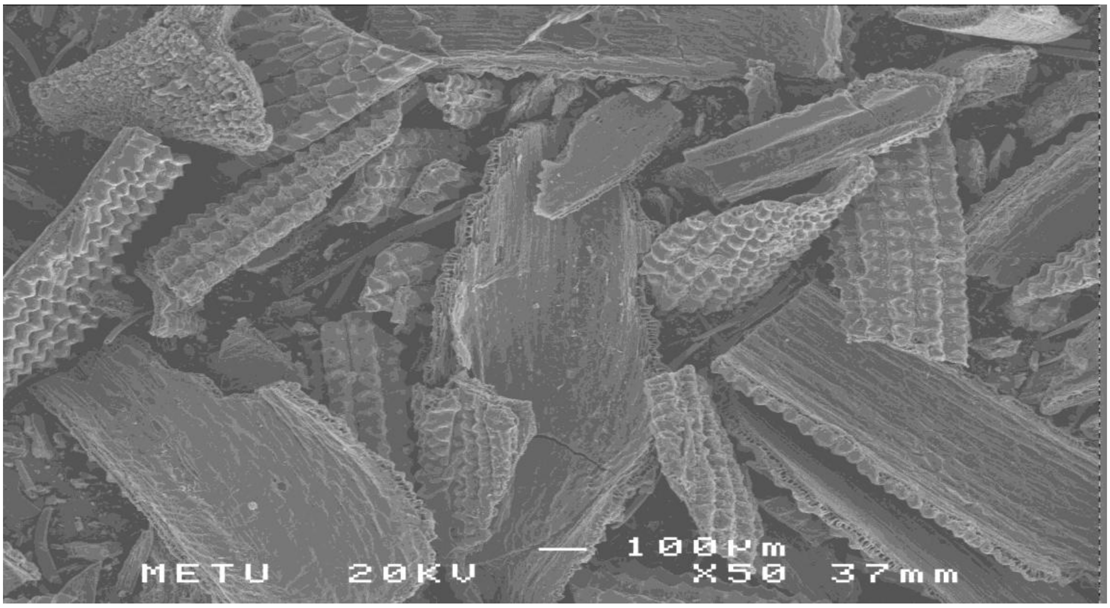

Figure 4.1 SEM Image of Non-ball-milled Coked Rice Husks

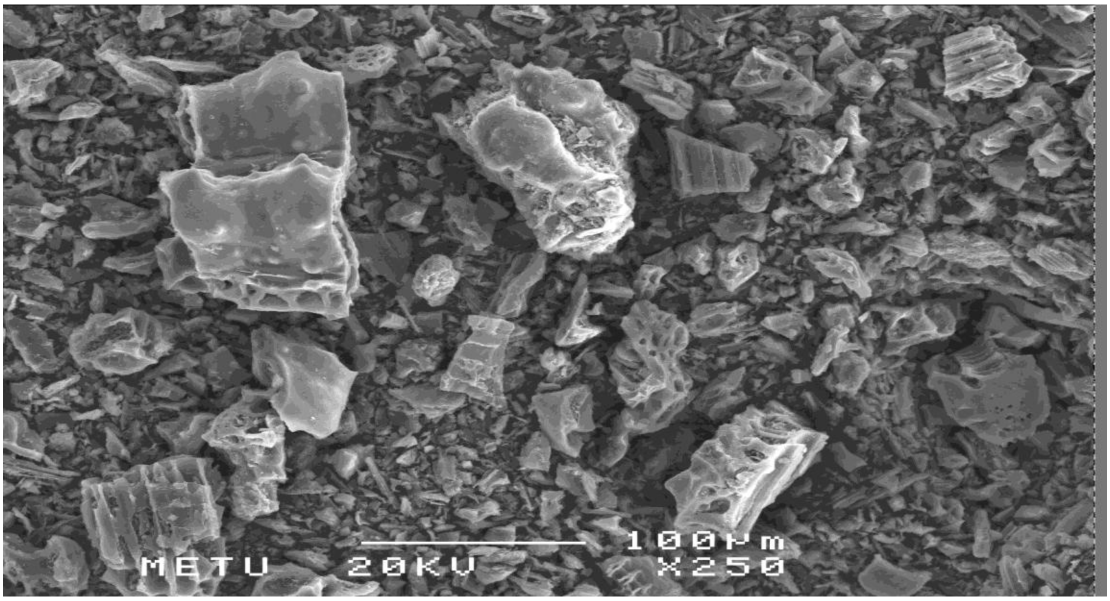

Figure 4.2 SEM Image of Coked Rice Husks, Ball-milled for 5 minutes

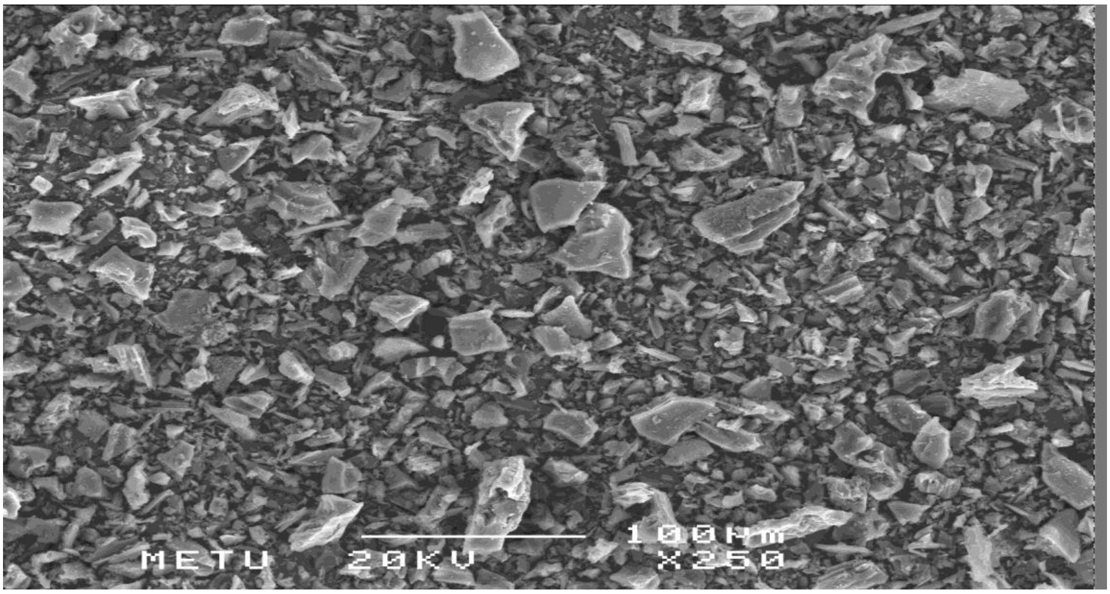

Figure 4.3 SEM Image of Coked Rice Husks, Ball-milled for 10 minutes

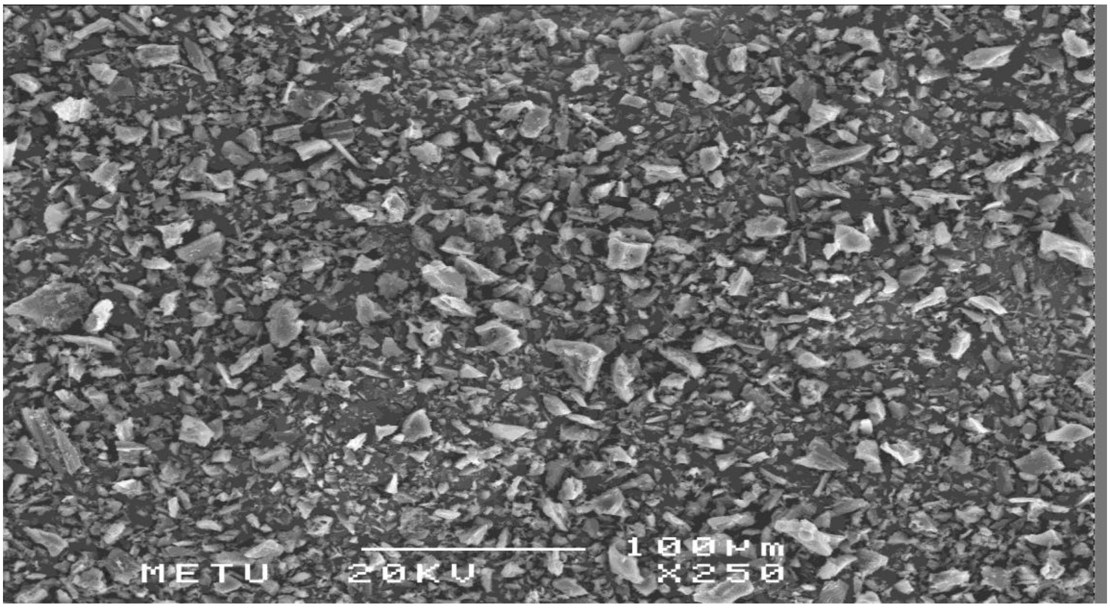

Figure 4.4 SEM Image of Coked Rice Husks, Ball-milled for 15 minutes

Here the whisker structure of rice husk coke has been destroyed; the flake shaped particles were further crushed by intense impacts of the balls; hence the decrease in particle size occurred with increasing milling time as shown in Table 4.1. As shown in Figure 4.4, the final shape of the particles was mostly angular and the surface morphology was rough.

Table 4.1 Particle Size

Sample	Particle Size		
	Length(µm)	Width(µm)	length/width
Coked RH ball-milled for 5 min	3 – 60	2 – 35	1.5 – 4
Coked RH ball-milled for 10 min	2 – 40	2 – 30	1 – 2.5
Coked RH ball-milled for 15 min	1 – 20	1 – 10	1 – 2.0

4.2 Coking Results

Totally 20 g of coked rice husks were obtained from 50 g of initial raw rice husks, after coking and average weight loss was determined as 60 % after each coking process.

X-ray diffractogram belonging to coked rice husk is given in Figure 4.2.

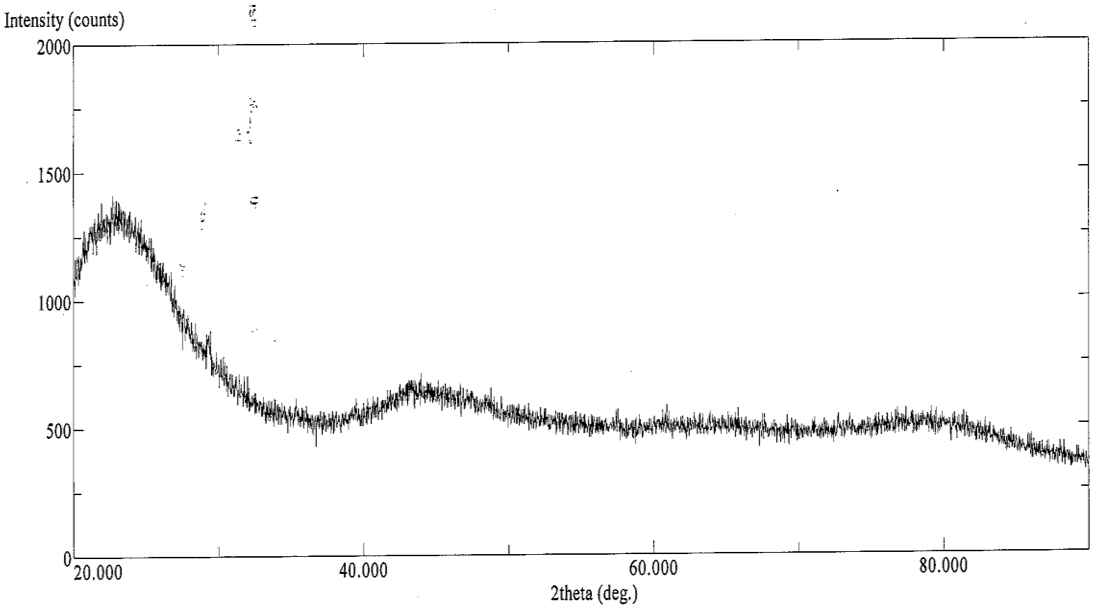

Figure 4.5 X-ray Diffractogram of Coked Rice Husk

It can be concluded from Figure 4.5 that no crystallographic phase occurs after coking, but the amorphous silica can easily be seen at 2θ degrees 20-21°.

4.3 Pure SiC

X-ray Diffractograms and peaks detected belonging to pure SiC is given in Figure 4.6. As it is clearly seen on the diffractogram, SiC constitutes of two phase; β-SiC, α-SiC, however β-SiC is the expected phase after pyrolysis, since the pyrolysis temperature is below 1700˚C.

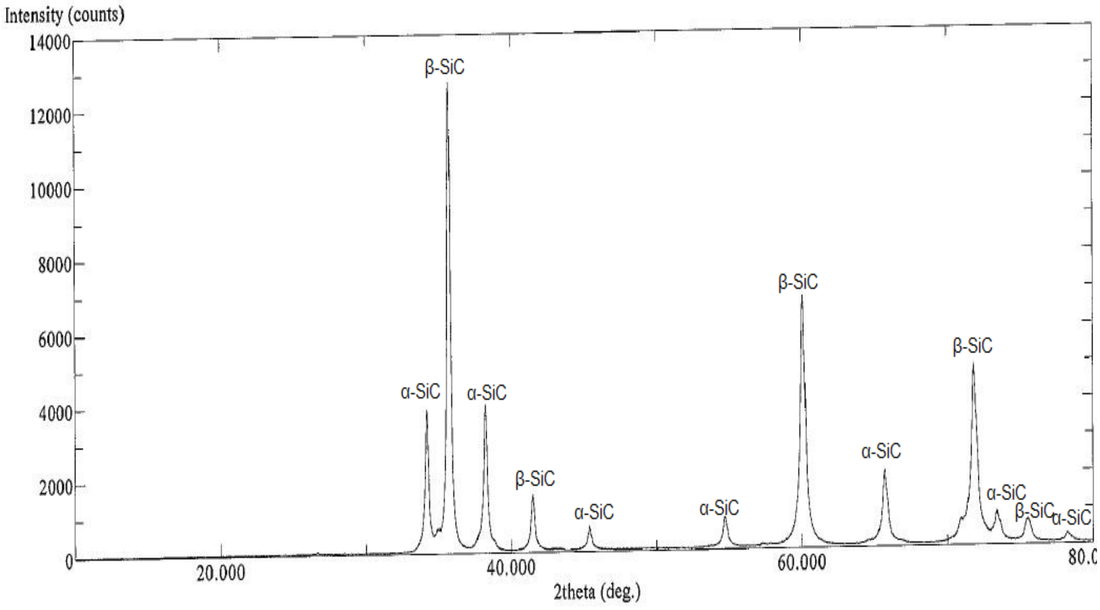

Figure 4.6 X-ray Diffractogram of Reference 1 (Pure SiC)

In addition to X-ray analysis, two samples of pure SiC powder weighing 5.17 g and 5.00 g were heated up to 800˚C for 40 min. in a pot weighing 144.35 g in a muffle furnace to determine whether SiC oxidizes or not, at the same condition for combustion of excess carbon.

Sample 1:
Mass before combustion: 144.35 + 5.17 = 149.52 g
Mass after combustion: 149.50 g

Sample 2:
Mass before combustion: 144.35 + 5.00 = 149.35 g
Mass after combustion: 149.32 g

It was experimentally shown that SiC is highly resistant against oxidation, since the initial mass and final mass were almost the same. So, SiC loss would not be expected due to oxidation during experiments.

4.4 X-ray Diffractograms After Pyrolysis

The phases formed after pyrolysis were mainly β-SiC, α-SiC, unreacted silica and graphite (in the case of incomplete reduction and the presence of excess carbon), which are labeled on each X-ray diffractograms, which are given in Figures 4.7 to 4.14.

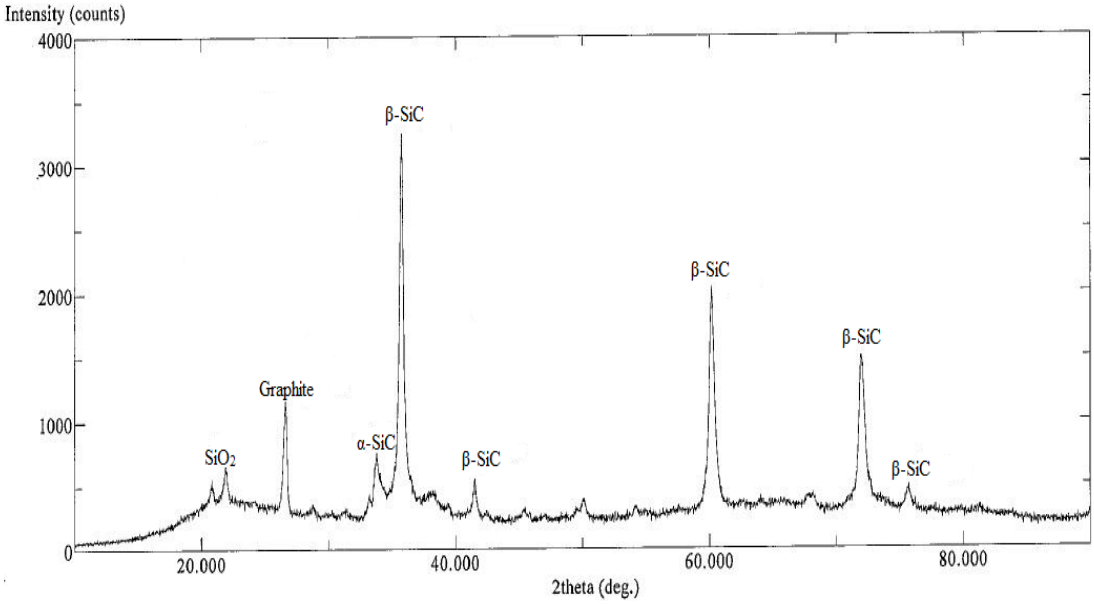

Figure 4.7 X-ray Diffractogram of Reference 2
(Non-ball-milled, pyrolyzed at 1550˚C for 2 hours)

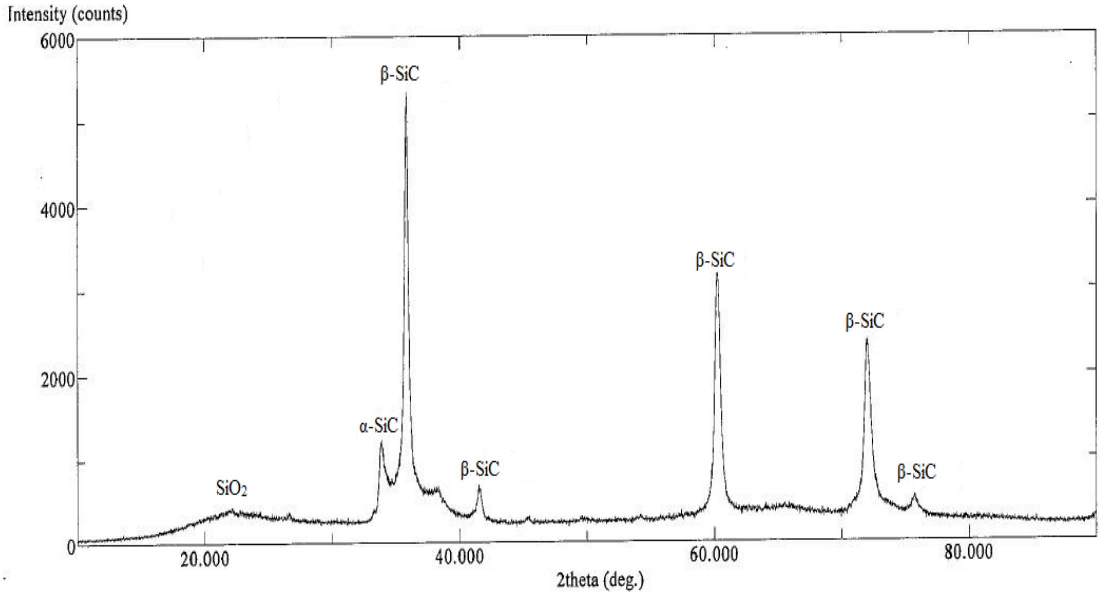

Figure 4.8 X-ray Diffractogram of Reference 3
(Non-ball-milled, pyrolyzed at 1600˚C for 2 hours)

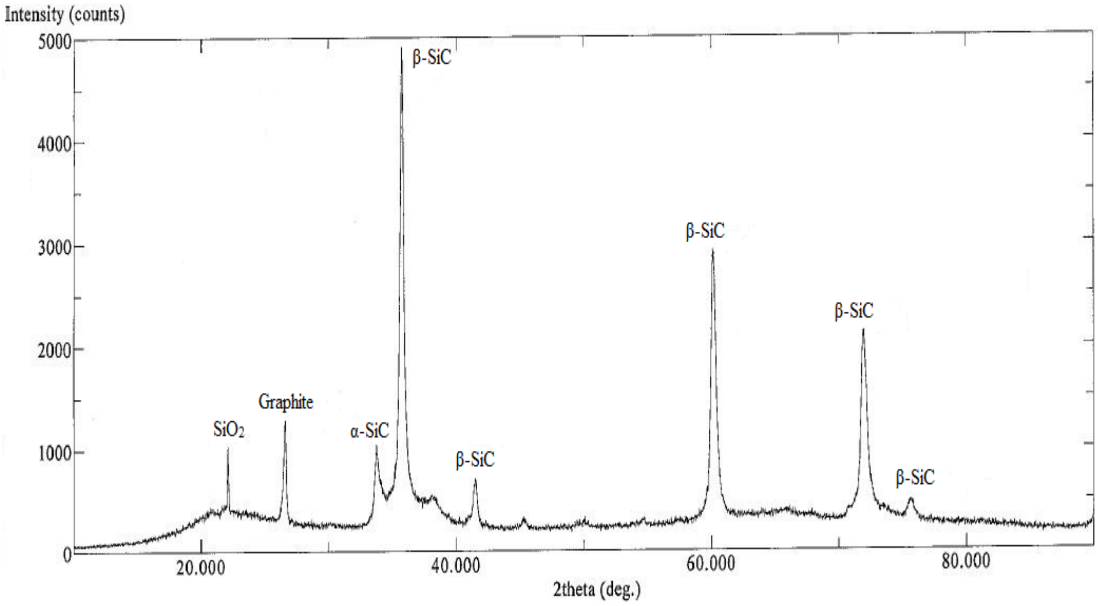

Figure 4.9 X-ray Diffractogram of Sample 1
(Ball-milled for 5 minutes, pyrolyzed at 1550˚C for 2 hours)

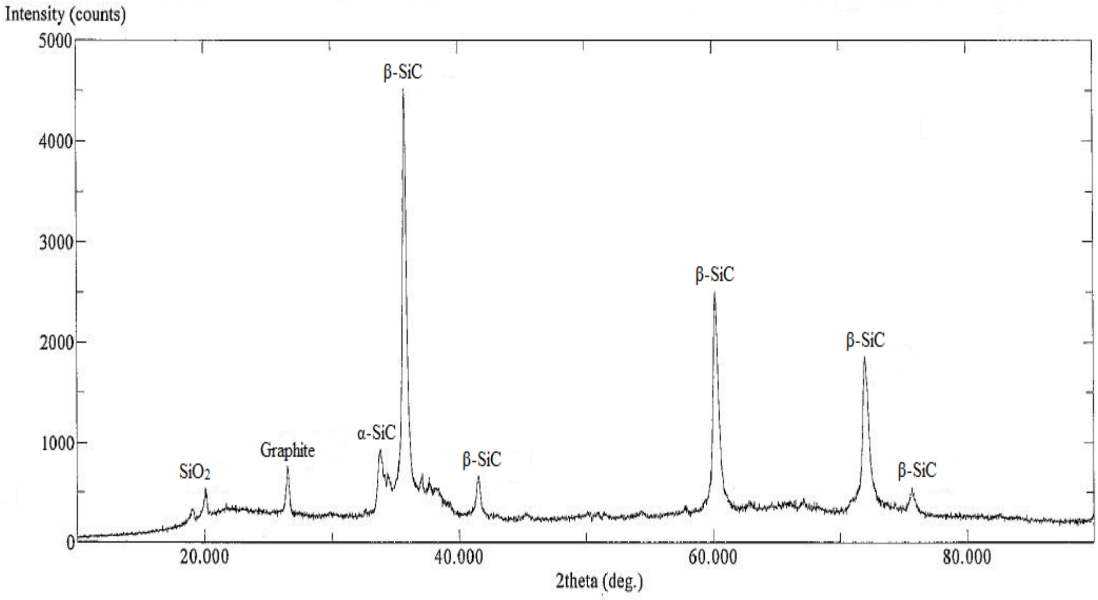

Figure 4.10 X-ray Diffractogram of Sample 2
(Ball-milled for 10 minutes, pyrolyzed at 1550˚C for 2 hours)

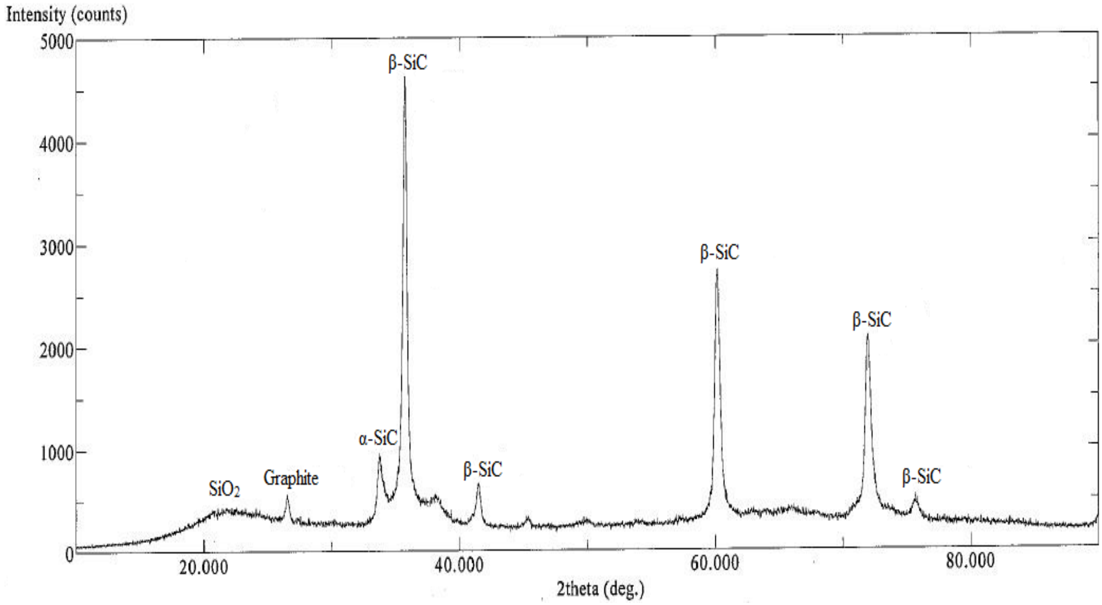

Figure 4.11 X-ray Diffractogram of Sample 3
(Ball-milled for 15 minutes, pyrolyzed at 1550˚C for 2 hours)

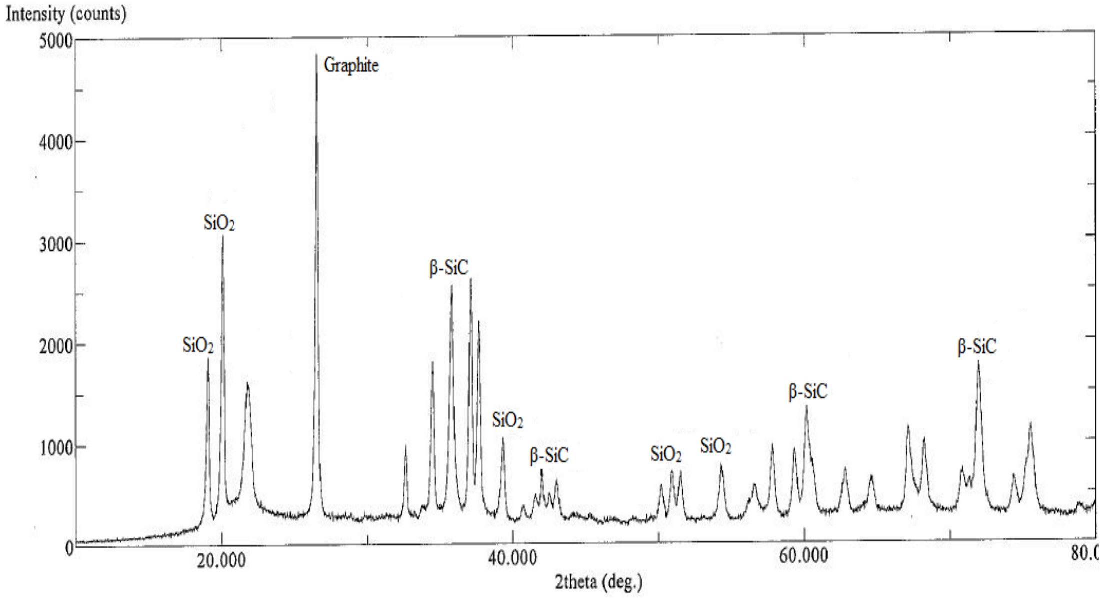

Figure 4.12 X-ray Diffractogram of Sample 5
(Ball-milled for 1 hour, pyrolyzed at 1500˚C for 2 hours)

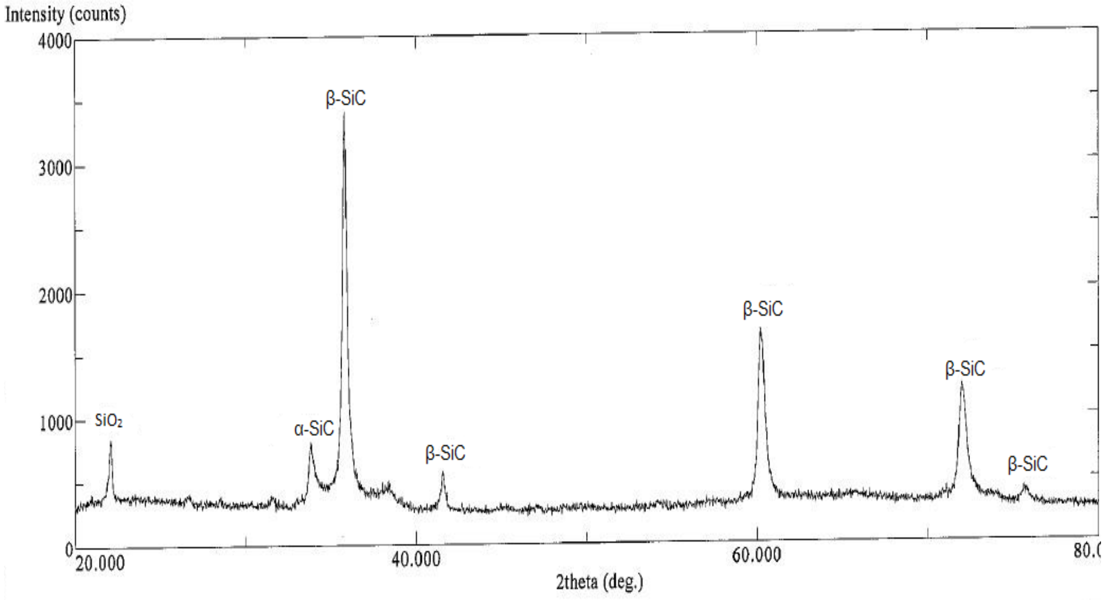

Figure 4.13 X-ray Diffractogram of Sample 6
(Ball-milled for 15 minutes, pyrolyzed at 1550˚C for 1 hour)

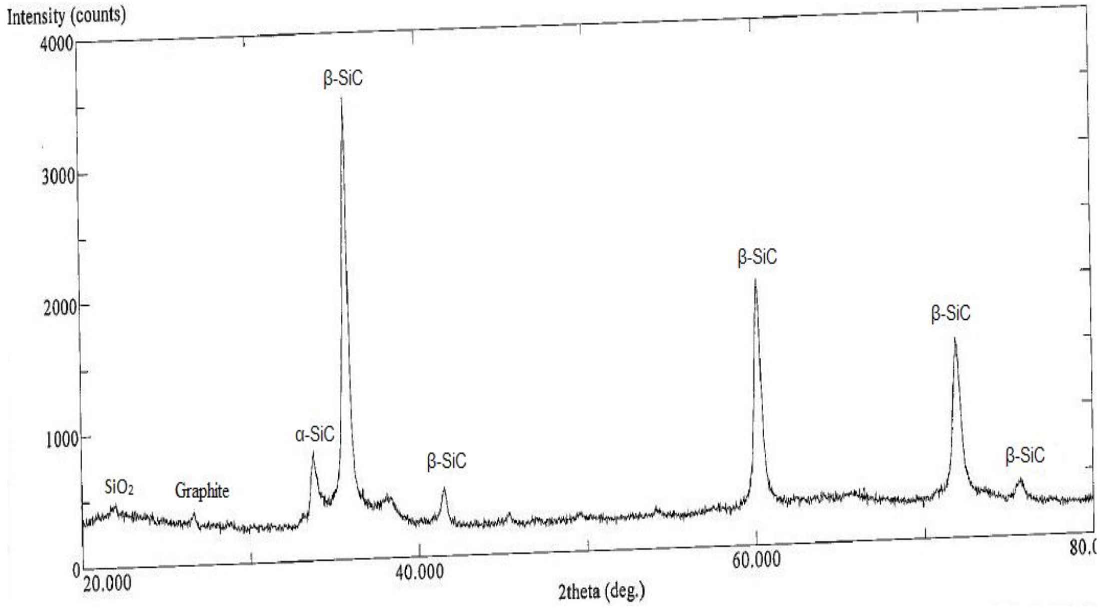

Figure 4.14 X-ray Diffractogram of Sample 7
(Ball-milled for 15 minutes, pyrolyzed at 1600˚C for 1 hour)

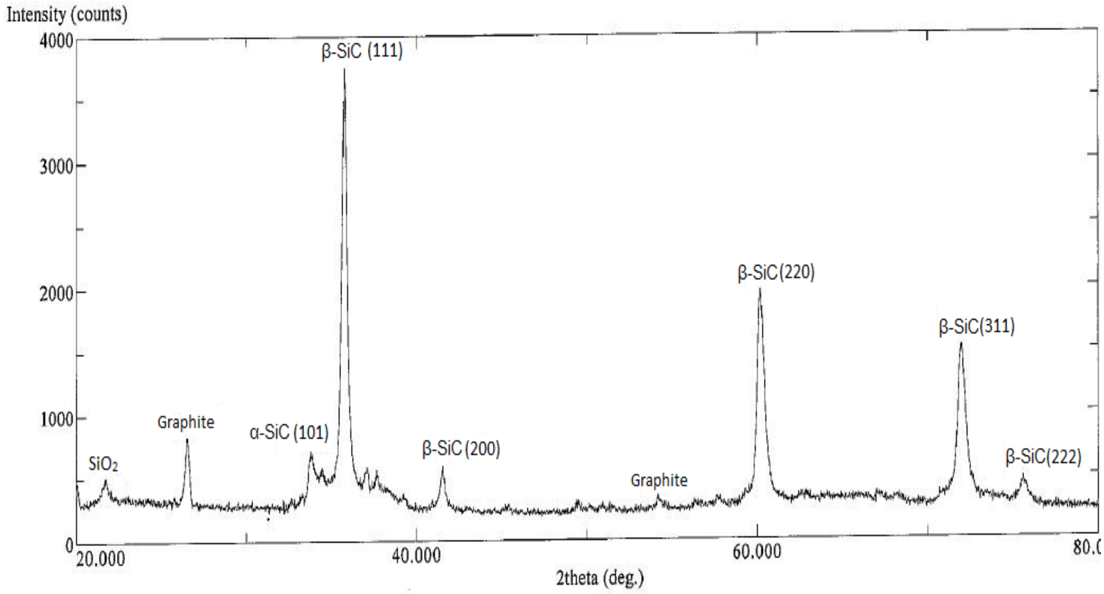

Figure 4.15 X-ray Diffractogram of Sample 8
(Ball-milled for 15 minutes, pyrolyzed at 1600˚C for 1/2 hour)

In the X-ray diffractograms, intense peaks in the (111), (220), (311) and (101) directions at 2θ degrees of 35.74, 60.16, 71.96 and 33.78, respectively from β-SiC and α-SiC, were observed.

In the experiments; Reference 3, Sample 3 and Sample 7, only amorphous silica remained as unreacted, however in the rest of experiments silica as crystalline phase remained as unreacted due to incomplete reduction of silica.

The reason for the presence of graphite are; contaminations by graphite crucibles in which rice husks were pyrolyzed or incomplete combustion of excess carbon after pyrolysis.

4.5 Unreacted Silica

XRD patterns were analyzed in terms of unreacted silica amount, as an indicator for the efficiency of SiC synthesis. Peaks were assumed as curves having a certain equation and the ratio of the area calculated under the silica curve (silica peak) to total calculated area of the all curves on the XRD pattern gave the (%) portion of the unreacted silica phase. The results were normalized, by omitting the areas of graphite phase, if exists. Figure 4.16 illustrates the areas calculated on the XRD pattern.

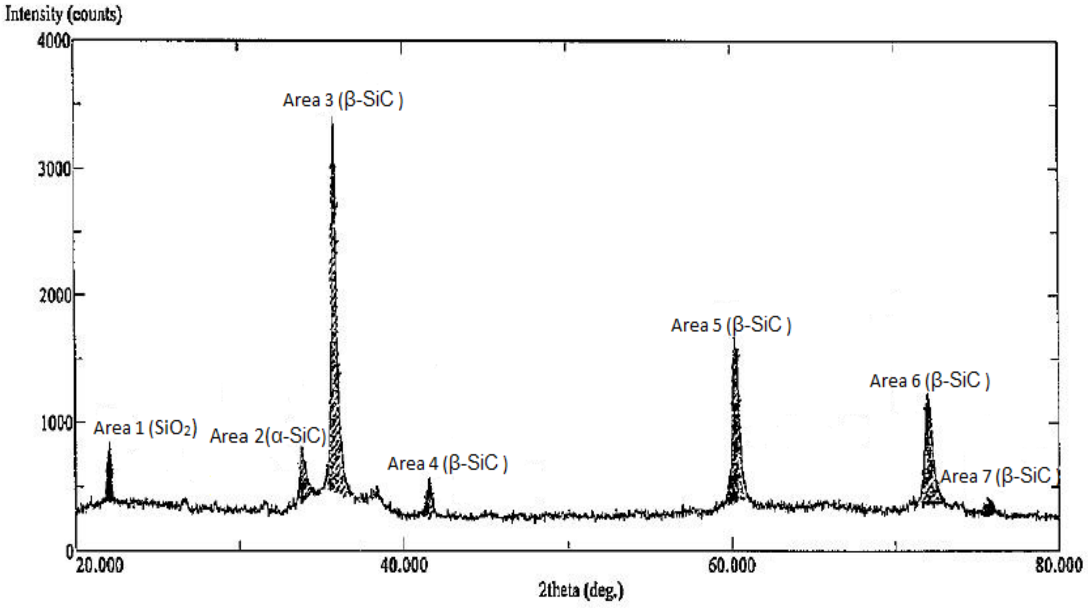

Figure 4.16 Areas of Phases (Curves)

% Unreacted Silica = [(Area 1) / ∑ (Area 1 to Area7)] x 100

Areas under the peaks were calculated by running the curve fitting software called, Curve Expert Professional. Calculated amounts of unreacted silica detected after each pyrolysis conditions are tabulated in Table 4.2.

Table 4.2 Unreacted Silica (%)

Sample	Unreacted silica (%)
Reference 2 (without ball-milling, pyrolysis at 1550˚C for 2 hrs)	7.2
Reference 3 (without ball-milling, pyrolysis at 1600˚C for 2 hrs)	1.5
Sample 1 (ball-milled 5 min. at 300 rpm, pyrolysis at 1550˚C for 2 hrs)	2.6
Sample 2 (ball-milled 10 min. at 300 rpm, pyrolysis at 1550˚C for 2 hrs)	2.0
Sample 3 (ball-milled 15 min at 300 rpm, pyrolysis at 1550˚C for 2 hrs)	1.2
Sample 6 (ball-milled 15 min. at 300 rpm, pyrolysis at 1550˚C for 1 hr)	6.2
Sample 7 (ball-milled 15 min. at 300 rpm, pyrolysis at 1600˚C for 1 hr)	1.7
Sample 8 (ball-milled 15 min. at 300 rpm, pyrolysis at 1600˚C for 1/2 hr)	3.9

As it can be seen from Table 4.2, the unreacted silica amount varied between 1.2 % and 7.2 %. Considering the unreacted silica content obtained from samples, the optimum conditions (unreacted silica content below 2 %) were decided as;

- without ball-milling, pyrolysis at 1600˚C for 2 hrs (reference condition),
- ball-milling for 15 min. at 300 rpm then, pyrolysis at 1550˚C for 2 hrs,
- ball-milling for 15 min. at 300 rpm then, pyrolysis at 1600˚C for 1 hr.

The intensities of the peaks from SiC, the amorphous phase were compared by Raju and Verma (1997) and indicated that the amorphous phase content was no more than 2-3 %, after pyrolysis at 1500˚C. Based on this fact, total amount of unreacted silica content was assumed as 4-5% at optimum conditions.

When it is compared to reference condition, it can be concluded that, ball-milling prior to pyrolysis;

- reduces the reaction temperature at the same pyrolysis durations or,
- reduces the pyrolysis durations at the same reaction temperatures, by some extent.

However, further ball-milling times; 1/2 hour and 1 hour pyrolysis times experienced in Sample 4 and Sample 5, could not lead to further decrease in pyrolysis temperature at 2 hours of pyrolysis time. As it is clearly seen on the X-ray diffractogram of Sample 5, which was ball-milled for 1 hour, then pyrolzed at 1500˚C for 2 hours, the amount of unreacted silica was so high that there was no need to calculate for comparison. Based on this experimental fact, it was decided that 15 minutes of ball-milling time was the optimum duration, for efficient pyrolysis.

Likely, further reduction on pyrolysis time was not achieved; 3.9 % of unreacted silica obtained as a result of experimental investigation of Sample 8.

X-ray analysis showed that formation of silicon carbide from rice husk was strongly temperature and time dependent process, which indicates that longer diffusion paths are required for the formation of SiC, by the reaction;

$$2C(s) \quad + \quad SiO(g) \quad \rightarrow \quad SiC(s) + C(g) \qquad (6)$$

The effect of ball-milling on unreacted silica content, at pyrolysis temperature 1550˚C and 2 hours of pyrolysis time, is illustrated in Figure 4.17.

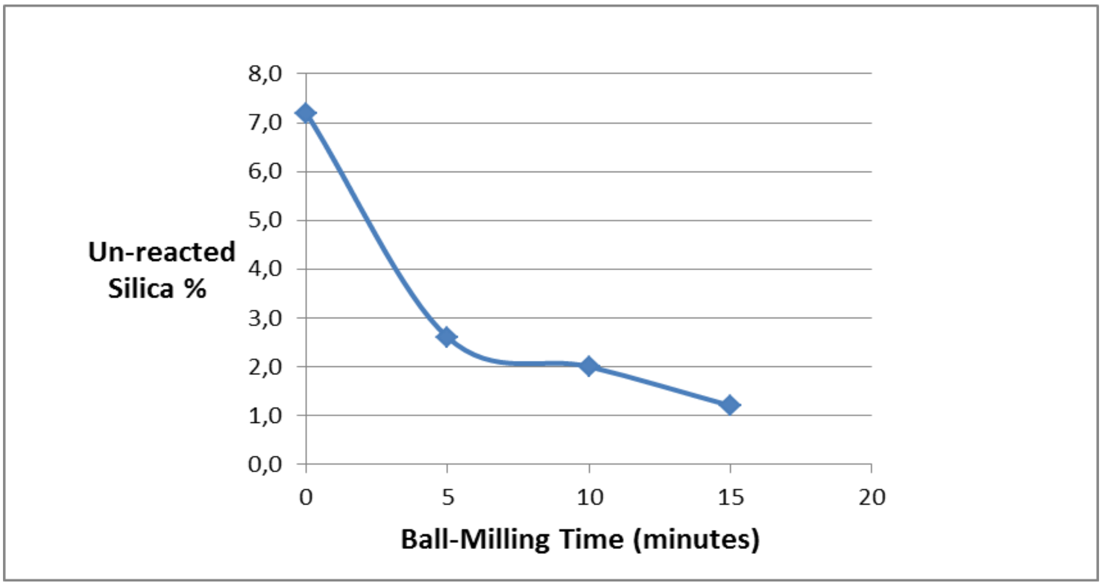

Figure 4.17 Unreacted Silica vs. Ball-Milling Time (T=1550˚C)

As it is seen on Figure 4.17, while ball-milling time increases the amount of unreacted silica decreases. Unreacted silica content was 7.2 %, 2.6%, 2.0% and 1.2% when ball-milling time was 0 minutes, 5 minutes, 10 minutes and 15 minutes, respectively.

4.6 SEM Images After Pyrolysis

The outer surface of coked rice husk was highly roughened and shows linear ridged structures which were punctuated with prominent domes, as shown in Figure 4.18. The silica is mainly localized in the tips of the domes, whereas a lower amount of silica can be found in other regions of the rice husk. High silica content, provides strength and stiffness to the husk (Park et al., 2003; Ruseckaite et al., 2007).

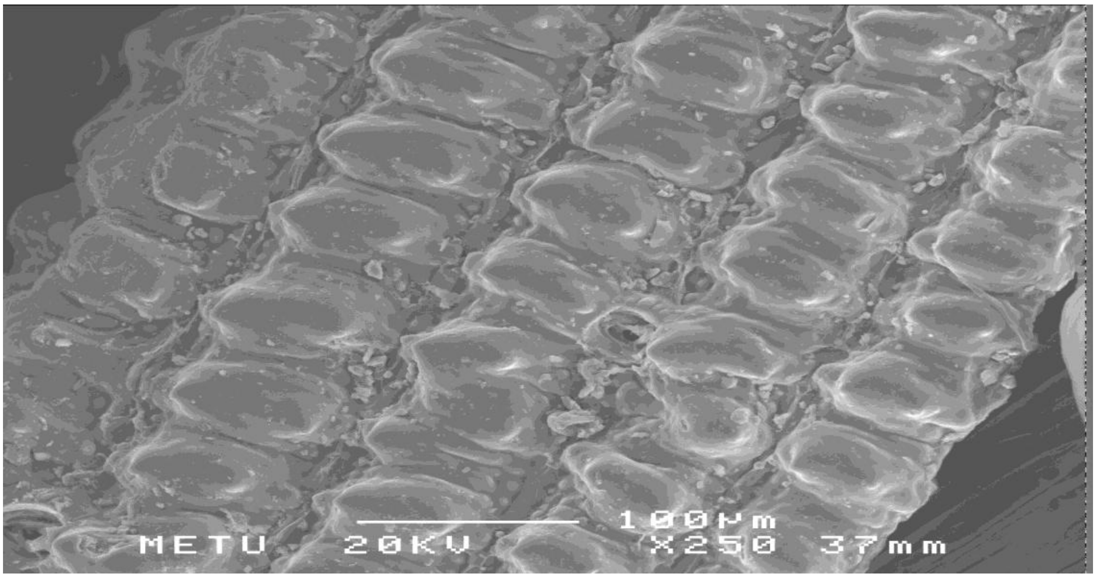

Figure 4.18 SEM Image of Non-ball-milled Coked Rice Husk Before Pyrolysis

As shown in Figure 4.19, the globular structure (domes) of coked rice husk was significantly changed by pyrolysis of non ball-milled rice husk at 1600˚C for 2 hours (Reference 3). Domes disappeared almost completely. However, the sample texture was preserved to some extent due to absence of mechanical disturbing effect of ball-milling. As a result, the final structure consists of a larger quantity of β-SiC whiskers and a lesser quantity of silicon carbide particles. β-SiC whiskers are obviously seen in Figure 4.20.

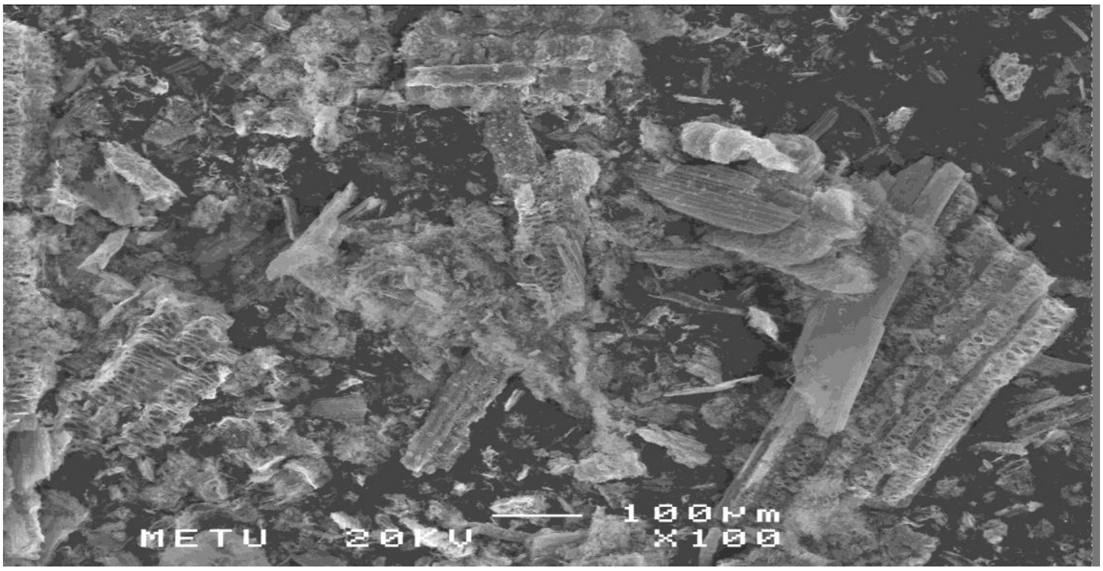

Figure 4.19 SEM Image of Reference 3
(Non-ball-milled, pyrolyzed at 1600˚C for 2 hours)

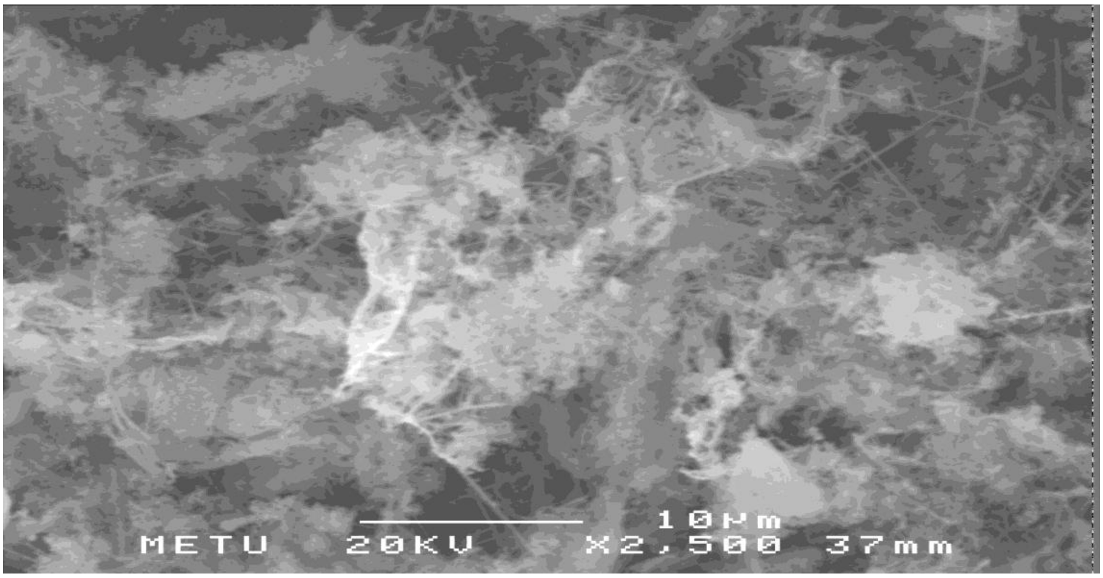

Figure 4.20 SEM Image of β-SiC Whiskers (Reference 3)

However, SEM analysis of Sample 3 and Sample 7, which were ball-milled for 15 minutes prior to the pyrolysis, showed that; the whisker structure of coked rice husks was destroyed. Ball-milling resulted in a final structure consisting a lesser quantity of SiC whiskers and a larger quantity of SiC particles, as shown in Figures 4.21 to 4.24, this is opposite to non ball-milling condition.

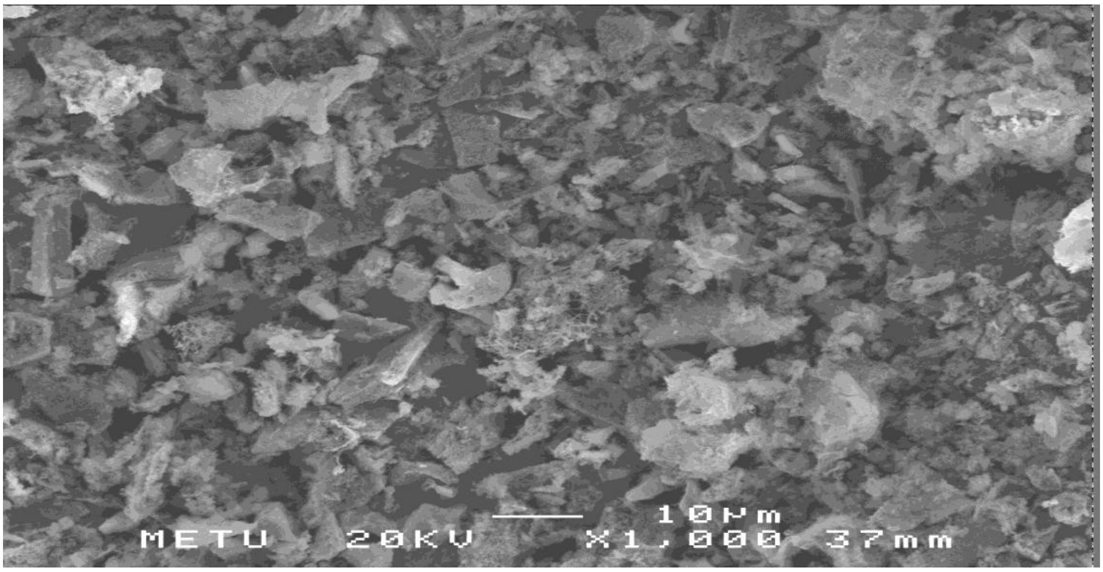

Figure 4.21 SEM Image (x 1000) of Sample 3
(Ball-milled for 15 minutes, pyrolyzed at 1550˚C for 2 hours)

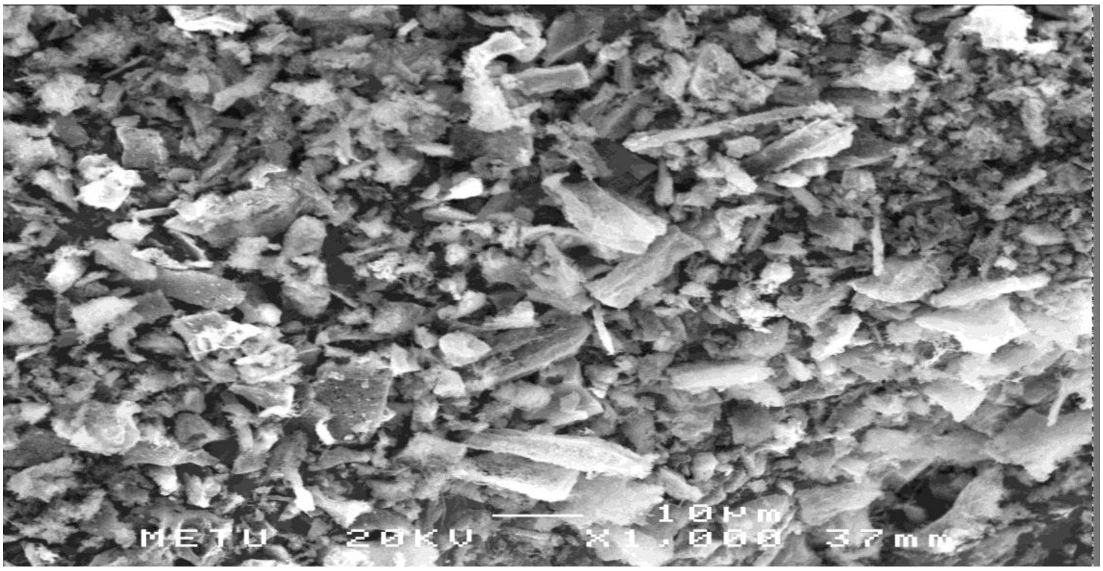

Figure 4.22 SEM Image (x 1000) of Sample 7
(Ball-milled for 15 minutes, pyrolyzed at 1600˚C for 1 hour)

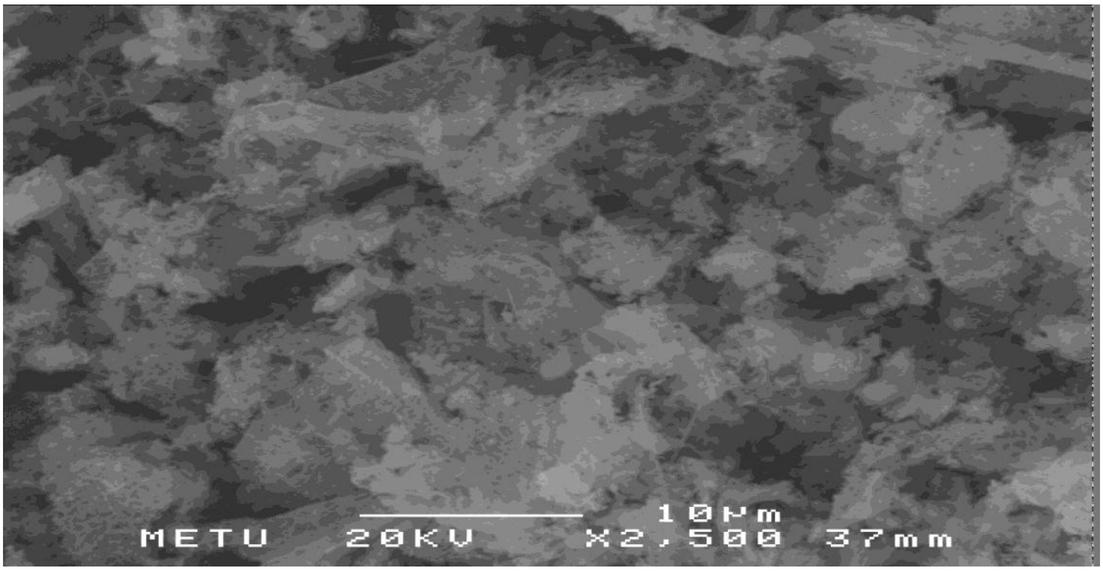

Figure 4.23 SEM Image (x 2500) of Sample 3
(Ball-milled for 15 minutes, pyrolyzed at 1550˚C for 2 hours)

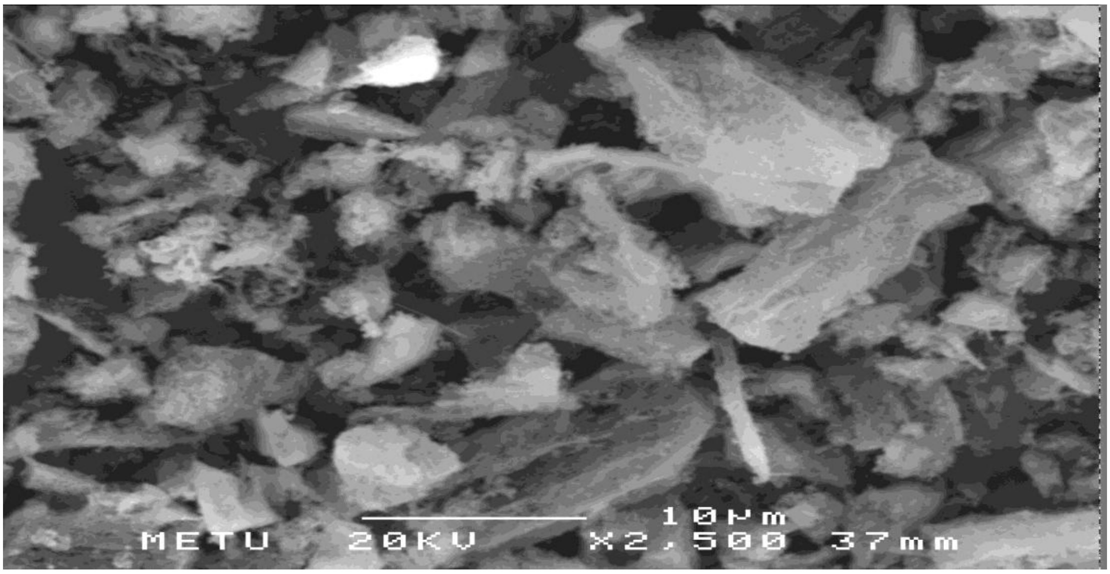

Figure 4.24 SEM Image (x 2500) of Sample 7
(Ball-milled for 15 minutes, pyrolyzed at 1600˚C for 1 hour)

Microstructural analysis on the Sample 3 and Sample 7 via SEM also showed that, microstructures obtained after pyrolyis at 1550˚C and at 1600˚C, were similar.
SEM images of Sample 1, Sample 2 and Sample 3, which were ball-milled 5 minutes, 10 minutes and 15 minutes, respectively, showed that; as the ball-milling time increased the number of silicon carbide particles also increased, this was also an expected result. Decreases in the particle size are obviously seen in Figure 4.25 to Figure 4.27.

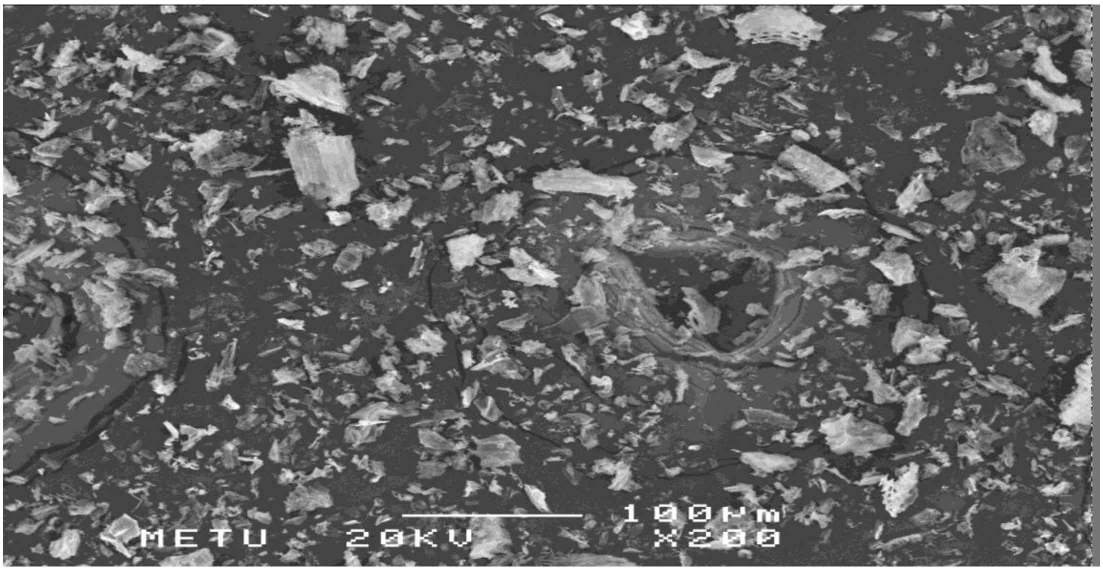

Figure 4.25 SEM Image (x 200) of Sample 1
(Ball-milled for 5 minutes, pyrolyzed at 1550˚C for 2 hours)

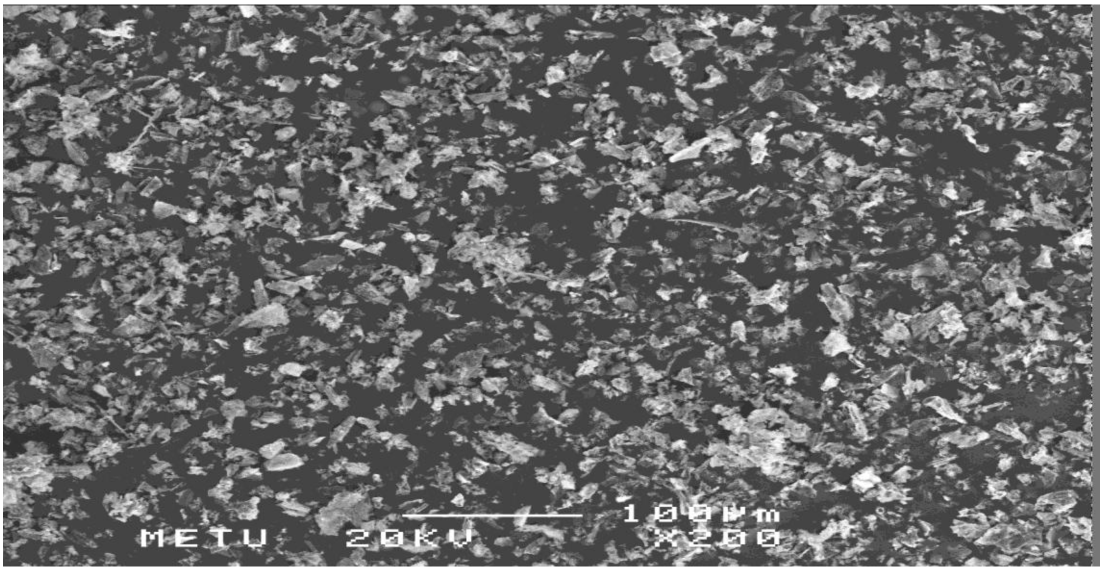

Figure 4.26 SEM Image (x 200) of Sample 2
(Ball-milled for 10 minutes, pyrolyzed at 1550˚C for 2 hours)

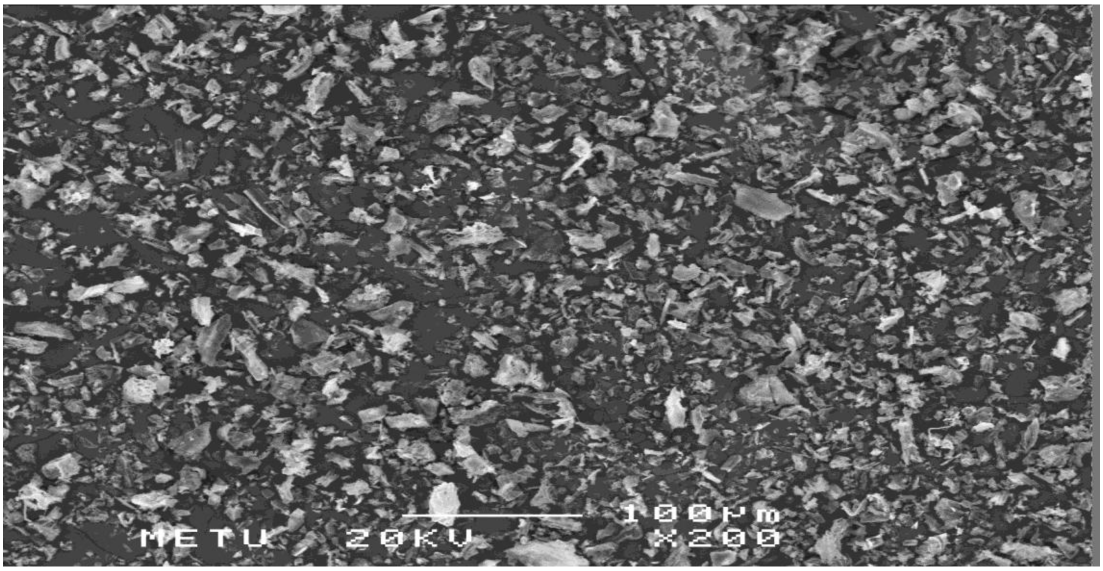

Figure 4.27 SEM Image (x 200) of Sample 3
(Ball-milled for 15 minutes, pyrolyzed at 1550˚C for 2 hours)

4.7 Energy Dispersive Spectrometer (EDS) Analysis

The elemental analysis showed that, Figure 4.28 to Figure 4.31, SiC particles were mainly consist of carbon, oxygen and silicon. Also, trace elements such as Mg, Al, Ca, K and Fe are also present in the product. Trace element content was evaluated as uncritical since, they can be removed and SiC can be purified by HF+ HCl acid treatment as stated in the previous studies (Raju and Verma, 1997, Yücel and Geveci ,1997).

EDS spectrums also showed that, as the ball-milling duration was increased, intensities of oxygen decreased. Oxygen detected on the spectrums was mainly due to the presence of unreacted silica. It was shown by the x-ray analysis that as ball-milling duration was extended the amount of unreacted silica reduced. It may be concluded that, EDS results are consistent with x-ray result in terms of the effect of ball-milling on the amount of unreacted silica remained after pyrolysis.

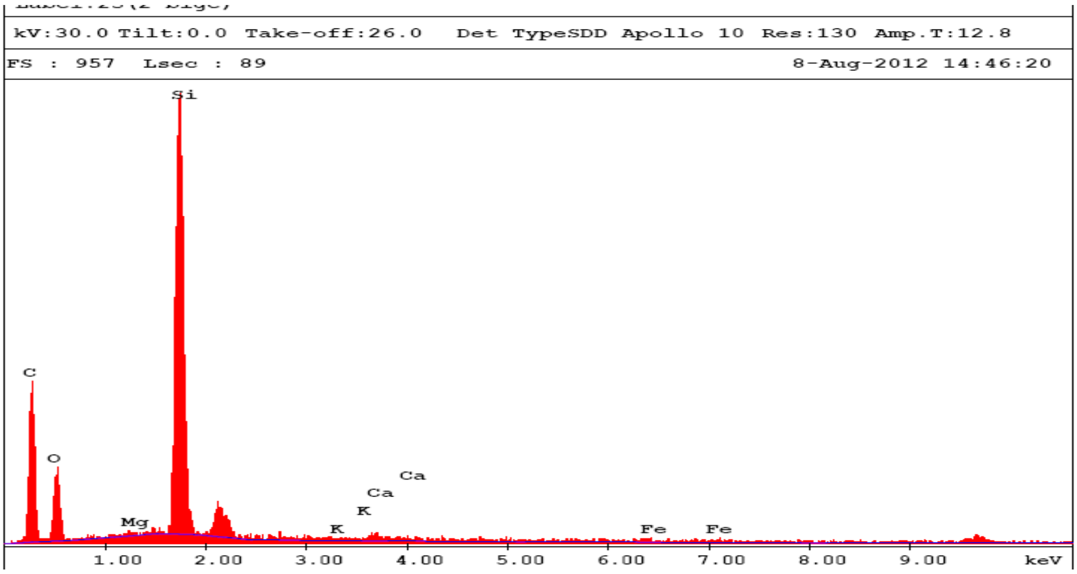

Figure 4.28 EDS Spectrum of Reference 2 (Full Scale: 957)
(Non-ball-milled, pyrolyzed at 1550˚C for 2 hours)

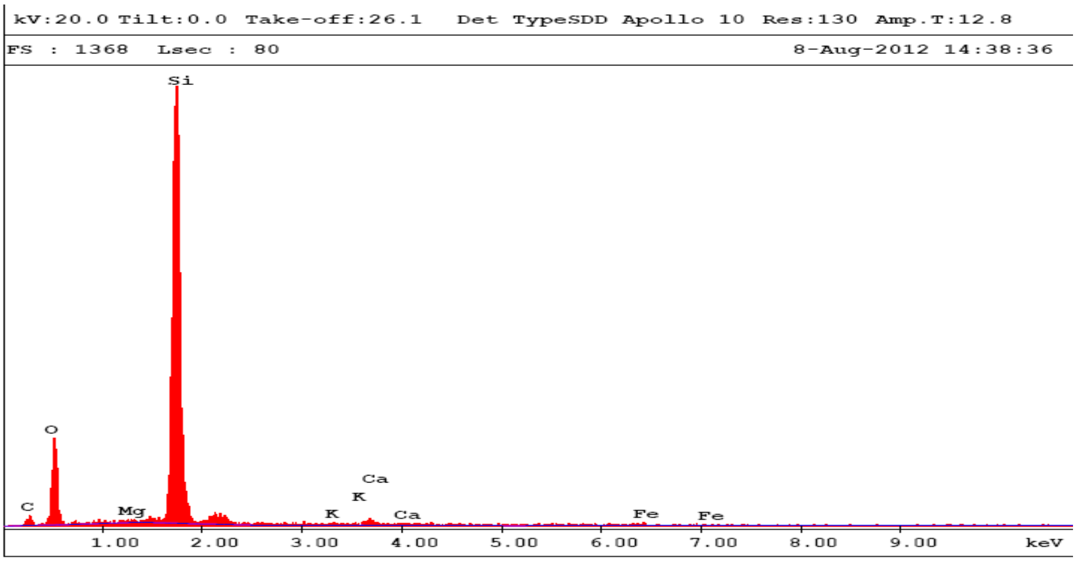

Figure 4.29 EDS Spectrum of Sample 1 (Full scale: 1360)
(Ball-milled for 5 minutes, pyrolyzed at 1550˚C for 2 hours)

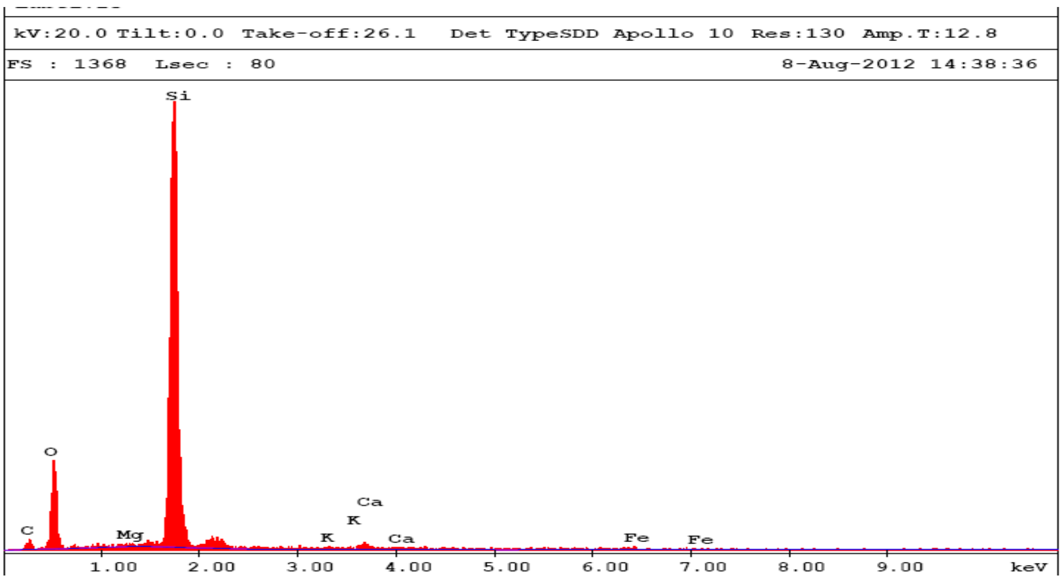

Figure 4.30 EDS Spectrum of Sample 2 (Full Scale: 1368)
(Ball-milled for 10 minutes, pyrolyzed at 1550˚C for 2 hours)

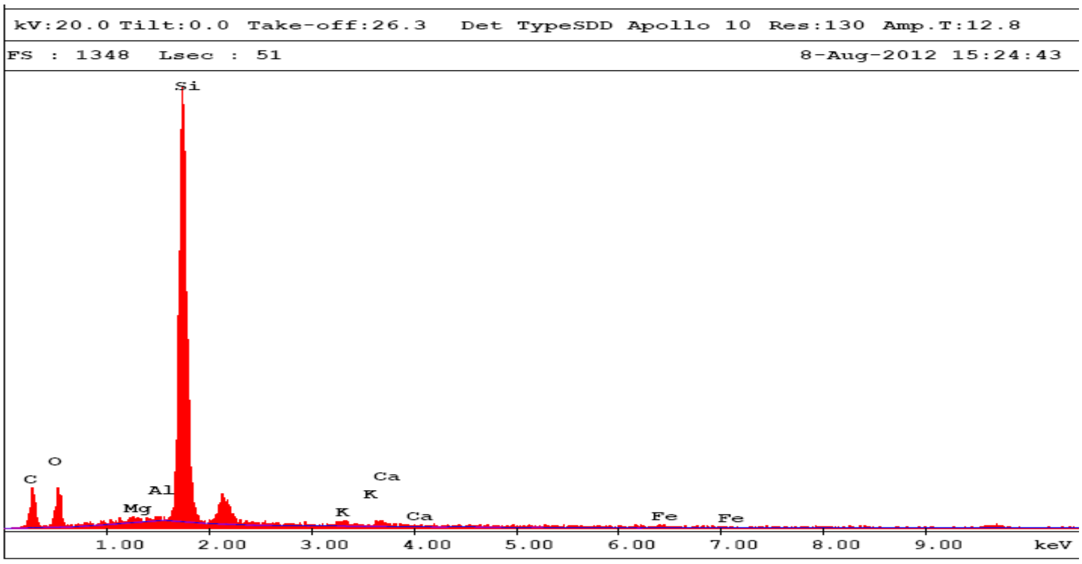

Figure 4.31 EDS Spectrum of Sample 3 (Full scale: 1340)
(Ball-milled for 15 minutes, pyrolyzed at 1550˚C for 2 hours)

4.8 SiC Yield

Samples were weighed before and after the pyrolysis, weight losses due to pyrolysis are given in Table 4.3*;*

Table 4.3 Weight-Loss After Pyrolysis

Sample	Before Pyrolysis (g)	After Pyrolysis (g)	Weight Loss %
Reference 3	9.9	3.8	61.7
Sample 3	9.8	3.5	64.3
Sample 7	10.0	3.3	67.8

Pyrolyzed samples were also weighed after the combustion of excess carbon remained in the samples, weight losses after burning of excess carbon are given in Table 4.4.

Table 4.4 Weight-Loss After Combustion of Excessive Carbon

Sample	Before Pyrolysis (g)	After Burning (g)	Weight-Loss %
Reference 3	9.9	1.9	81.0
Sample 3	9.8	1.7	82.9
Sample 7	10.0	1.5	85.0

If it is assumed that SiC formation from rice husks was completed successfully (2-3 % of unreacted silica and oxides of trace elements are neglected) and remaining weight is taken as pure SiC, in case of Ref. Sample 3, Sample 3 and Sample 7 then weight and yield of SiC that can be obtained from the pyrolysis of rice husks (60% weight-loss was determined after coking of raw rice husks) is given in Table 4.5.

Table 4.5 SiC Yield

Sample	Raw Rice Husk (g)	SiC (g)	Yield %
Reference 3	24.8	1.9	7.4
Sample 3	24.5	1.7	6.9
Sample 7	25.0	1.5	6.0

SiC produced was grey green in color, as shown in Figure 4.32. Green color might have resulted from the nitrogen in the air and grey color might have been due to presence of impurities. It might also be concluded that the amount of trace element had little effect on color of SiC produced. It was also observed that, the color of SiC produced from ball-milled and non-ball milled samples were similar.

Figure 4.32 SiC produced

CHAPTER 5

CONCLUSIONS

In this thesis work, it was aimed to determine the optimum conditions for producing Silicon Carbide from high energy ball-milled rice husks, which were coked at about 500°C. As a result of this study the following conclusions may be drawn:

- Coked rice husks were almost amorphous; no crystalline phases appeared on x-ray analysis of rice husk ash.

- Coked rice husks were elongated in form prior to ball-milling however, morphology turned into angular particle form as ball-milling time extended.

- SiC obtained has high oxidation resistance; after SiC was fired at 800°C for 40 minutes, there was no SiC loss. This also meant that there would be no SiC loss during combustion of excess carbon after pyrolysis.

- Ball-milling prior to pyrolysis;

    i) reduces the reaction temperature at the same pyrolysis durations or,
    ii) reduces the pyrolysis durations at the same reaction temperatures, to some extent.

- It was experimentally shown that as the ball-milling time increases the amount of unreacted silica decreases. At pyrolysis temperature of 1550˚C and 2 hours of pyrolysis time; unreacted silica content is 7.2 %, 2.6%, 2.0% and 1.2% when ball-milling time is 0 minutes, 5 minutes, 10 minutes and 15 minutes, respectively.

- In non-ball-milled condition, the final structure consisted of mainly silicon carbide whiskers and a lesser quantity of silicon carbide particles. On the other hand, it was seen that, as a result of ball-milling the whisker structure of coked rice husks was destroyed and the final structure contained less quantity of SiC whiskers and a larger quantity of SiC particles.

- As the ball-milling times were increased the number of silicon carbide particles also increased, as expected.

- SiC obtained at successful experiments (Reference 3, Sample 3 and Sample 7) were 7.4, 6.9 and 6.0 weight percentages of initial raw rice husks, respectively.

CHAPTER 6

RECOMMENDATIONS AND FURTHER STUDIES

High energy ball-milling has promising effects on the parameters of pyrolysis, like making the process possible at a lower temperature than 1600°C, e.g.1550°C or at shorter pyrolysis times than 2 hours, e.g. 1 hour, without introducing protective atmosphere e.g inert gas flow.

In further studies, use of high energy ball-milling on pyrolysis performed under protective atmosphere like Argon can be investigated to further optimize the silicon carbide formation from rice husks.

Economical feasibility of silicon carbide formation from rice husks might be discussed in further studies including the cost of energy consumption during coking, pyrolysis and ball-milling and the cost of purification of silicon carbide produced.

Finally, another study under Argon can be performed to see the effect of addition of minor elements like iron, calcium, potassium and magnesium, on the efficiency of SiC formation from rice husks, using the starting minor element analysis values for the chosen Thrace region rice husks.

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