

PYROLYSIS AND COMBUSTION OF TREATED AND UNTREATED RICE HULLS

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ABSTRACT

The presence of iron in coked rice hulls accelerates the formation reaction of silicon carbide from the hulls at a relatively low temperature (1500 °C). The addition of iron was made by impregnating the rice hulls with ferrous sulphate solution, followed by soaking in ammonia solution and coking in the absence of air.

Firstly, the effect of pretreating rice hulls (addition of iron) on the amount of volatile matter and residual carbon present after the coking process was studied. The results revealed that there is more volatile matter for the treated than for the untreated rice hulls. The char after coking the untreated sample has a 30% higher carbon content than that of the treated sample. This difference decreases with increasing coking temperature from 350 to 900 °C.

Secondly, the effect of the treatment process on the readiness of carbon combustion in the coked rice hulls was studied. The results of thermogravimetric analysis revealed that iron strongly affects the combustion of carbon for the coked rice hulls, especially at high coking temperatures (700–900 °C).

The present results were discussed on the basis of changes occurring in the crystal structures of silica, carbon and iron oxide during the coking process, and the reactions in which iron oxide may participate.

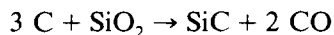
INTRODUCTION

At present silicon carbide is manufactured from coal and quartz sand in an electric furnace [1]. The furnace is heated by resistance of the electrical current to temperatures in the order of 2500 °C. Much of the electrical current is utilized in the endothermic formation of the silicon carbide crystals.

Recently, much attention has been paid to the use of rice hulls as a starting material for the production of silicon carbide [2–6]. Rice hulls consist of silica (~ 20 wt.%) and cellulose, which will yield carbon when thermally decomposed. With the very high surface area and intimate contact available from carbon and silica in the rice hulls, it is possible to form silicon carbide at a relatively low temperature (1500 °C) [6].

The formation of silicon carbide from rice hulls is completed in two steps [6]. In the first step, the rice hulls are coked in the absence of air at a

relatively low temperature (700 °C). This step decomposes the cellulose into amorphous carbon and removes any volatile matter. In the second step, the coked rice hulls are fired at high temperatures (≥ 1500 °C) in an inert or reducing atmosphere to cause the carbon and silica to react according to the following equation



The presence of iron in the coked rice hulls accelerates the formation reaction of silicon carbide from the rice hulls [5]. The addition of iron was made by impregnating the rice hulls with ferrous sulphate solution, followed by soaking in ammonia solution. The treated rice hulls were coked and then fired.

The coking, or pyrolysis, of rice hulls is an important industrial process. Through this process, the rice hulls can be used as a source of energy in the form of the high calorific value gases and oils evolved during the coking process. The carbon/silica ratio of the coked rice hulls should be near that needed for the formation of silicon carbide according to previous equation ($\text{C}/\text{SiO}_2 = 3 : 5$), since excess carbon in the product requires an additional industrial process, i.e., combustion, to remove this carbon. It is therefore favourable to boil off the maximum possible carbonaceous materials during the coking process. Furthermore, the coking temperature may affect the nature of the reactants (carbon and silica) and consequently the formation of SiC. Thus, the first aim of the present work is to study the effect of the pretreatment of rice hulls on the amount of volatile matter evolved during the coking process, and the nature of the residue after this process.

It is further proposed [7] to make use of rice hulls in an integrated system of pyrolysis to produce clean energy sources of gases and vapours, and then to combust the coked hulls to produce a residual white ash, which is mainly silica, representing important industrial material. Thus, the second aim of the present work is to study the effect of the treatment process on the readiness of carbon for combustion and the nature of the silica residue after the combustion process.

EXPERIMENTAL

Materials

The materials used were rice hulls (16.55% silica) and ferrous sulphate, which is a waste product of the steel industry in Egypt. A chemical analysis of the ferrous sulphate gives: FeSO_4 , 28.79%; H_2SO_4 , 14.22%; H_2O , 57%.

Impregnation process

The green rice hulls were impregnated with ferrous sulphate solution (1.5 wt.% FeSO_4) for 1 h. After draining the FeSO_4 solution, the rice hulls were

soaked in ammonia solution (10 wt.%) for 1 h, followed by washing thoroughly with water to fix the iron within the swelled cellulose structure.

Coking process

Both treated and untreated rice hulls were dried in air at ambient temperature and then placed in a platinum dish. Air was excluded from the dish by a tightly sealed lid. The dish and contents were inserted into a furnace at coking temperature (350, 500, 700 and 900 °C), soaked for 1 h at each firing temperature, then quenched in air. The loss in weight after this process represents the mass of volatile matter removed. Chemical analysis of the black rice hulls was performed using a procedure described elsewhere [4]. The procedure includes the determination of carbon (volatiles were considered as mainly carbon), silica and iron. Carbon was determined by heating the sample in air at 700 °C for 0.5 h. Silica was determined by heating the residue with HF. The residue was fused by KHSO₄ and dissolved in HCl, and the iron was volumetrically estimated in the solution using the EDTA method.

Combustion process

A weighed amount of each coked sample was placed in the furnace at room temperature. The temperature was increased with a program of 10 °C min⁻¹ to the top temperature (350, 400 or 500 °C) for 2 h and then quenched in air. Mass changes of the samples were measured at intermittent periods of firing at the desired temperatures.

X-ray diffraction analysis

X-ray diffraction analysis was carried out for some representative samples after each process using a Philips X-ray diffractometer. Powder samples were analyzed by CuK_α radiation at 1.54 Å. The scanning rate was 2 °C min⁻¹.

RESULTS AND DISCUSSION

Figure 1 shows the amounts of volatile matter and residual carbon in the ash as a function of coking temperature for both treated and untreated rice hulls. It is evident that the amount of volatile matter evolved from the treated sample is greater than that from the untreated sample. The difference decreases as the coking temperature increases, from 350 to 900 °C. It is about 10% of the yield of untreated hulls at 350 °C and about 1.5% at 900 °C. On the other hand, the amount of residual carbon in the char decreases in an opposite manner to the increase of volatile matter evolved

from the treated rice hulls. The char, after coking the untreated sample, has a 30% higher carbon content than the treated sample. This difference decreases at higher coking temperatures.

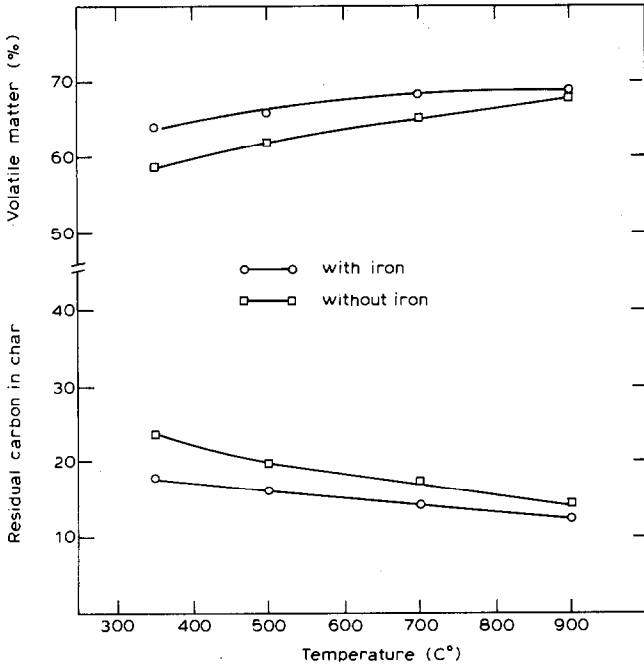


Fig. 1. Effect of coking temperature on the amounts of volatile matter and residual carbon in the ash.

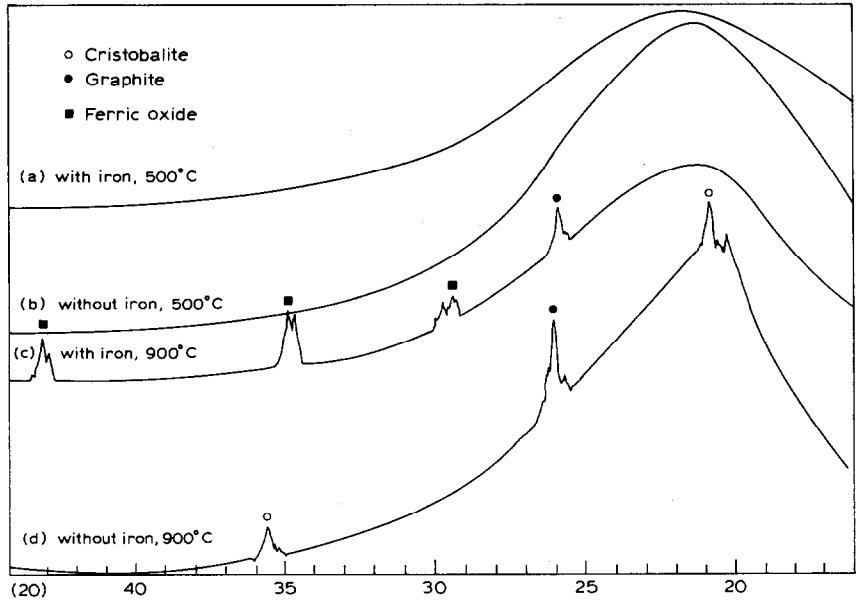


Fig. 2. The X-ray diffraction patterns of samples coked at different temperatures.

The carbon/silica ratio is changed in the treated sample from 0.9 to 0.6 and in the untreated one from 1.2 to 0.7 as the coking temperature is increased from 350 to 900 °C, respectively. These values illustrate how the ratio approaches the carbon/silica ratio necessary for the formation of silicon carbide from coked rice hulls ($C/SiO_2 = 0.6$).

The X-ray diffraction patterns of samples coked at 500 and 900 °C for 1 h are shown in Fig. 2.

The X-ray pattern of the treated sample, which is coked at 500 °C represents a curve with no characteristic peak. This curve has a maximum at $2\theta = 22^\circ$, characteristic of silica forms. Its height increases, with a slight shift in its d -spacings, to a higher value as the coking temperature increases from 500 to 900 °C (Fig. 2a, c). While iron appears in the form of ferric oxide in the sample coked at 900 °C, there is no indication of its presence in crystalline form in the sample coked at 500 °C. Further, the sample coked at 900 °C shows an additional X-ray peak at $2\theta = 26.70^\circ$, corresponding to graphite. This means that the reducing conditions are suitable for the crystallization of part of the carbon in the graphite form. The X-ray patterns of iron-free samples (Fig. 2b, d) show an increase in the crystallinity of silica and carbon in comparison with the treated samples. This is clear from the

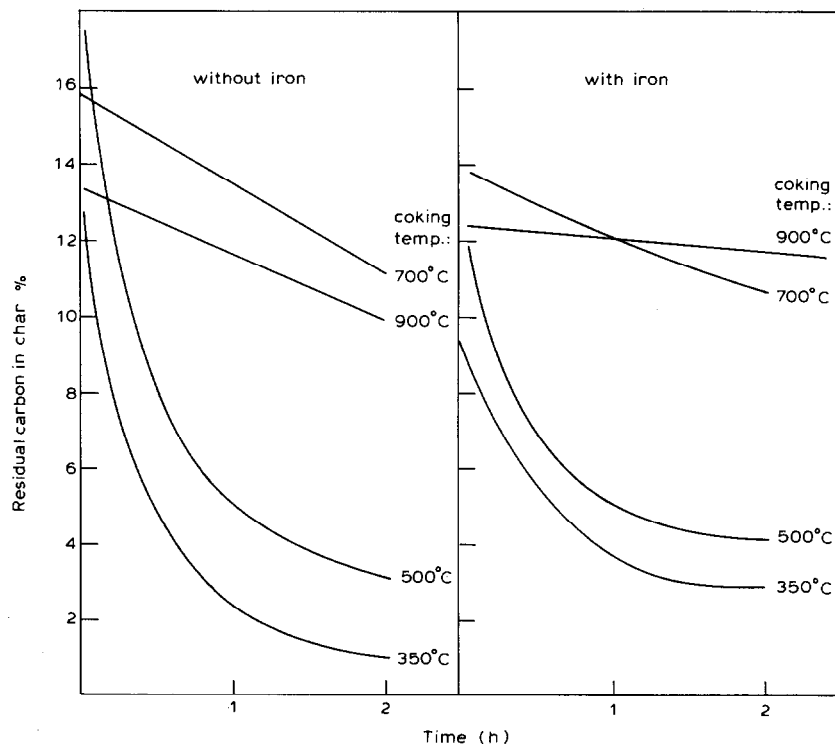


Fig. 3. The change in weight of the residual carbon in the char as a function of the time of heating in static air at 350 °C.

X-ray analysis of the iron-free samples coked at 900°C. The appearance of the 200 peak of cristobalite indicated that silica, in the absence of iron, starts to convert to a low form of cristobalite. Another observation is the increase in both the amount and the crystallinity of the graphite formed.

The rice hulls coked at 350–900°C for 1 h were then fired in static air at 350, 400 and 500°C for 2 h at each temperature; Figs. 3–5 illustrate the change in the carbon content as a function of the time of heating at these temperatures.

As the rice hulls are coked at a relatively high temperature, e.g., 900°C, it is difficult to remove their carbon on firing. This is more clearly observed in the sample coked at 900°C and then fired in static air at a relatively low temperature (350°C, Fig. 1). This means that the increase in the coking temperature favours the fixation of carbon in the black rice hulls' ash. Another observation is the thermal behaviour of treated samples compared to untreated samples. The carbon of the treated sample shows less readiness to combustion than the untreated sample. This thermal behaviour is clearly observed as the coking temperature is increased from 350 to 900°C and the combustion temperature is decreased from 500 to 350°C. This may be due to the effect of iron on the crystallinity of carbon and silica and consequently on the fixation of carbon in the coked rice hulls which will be discussed later.

Figure 6 shows the X-ray patterns of some coked samples after firing in air

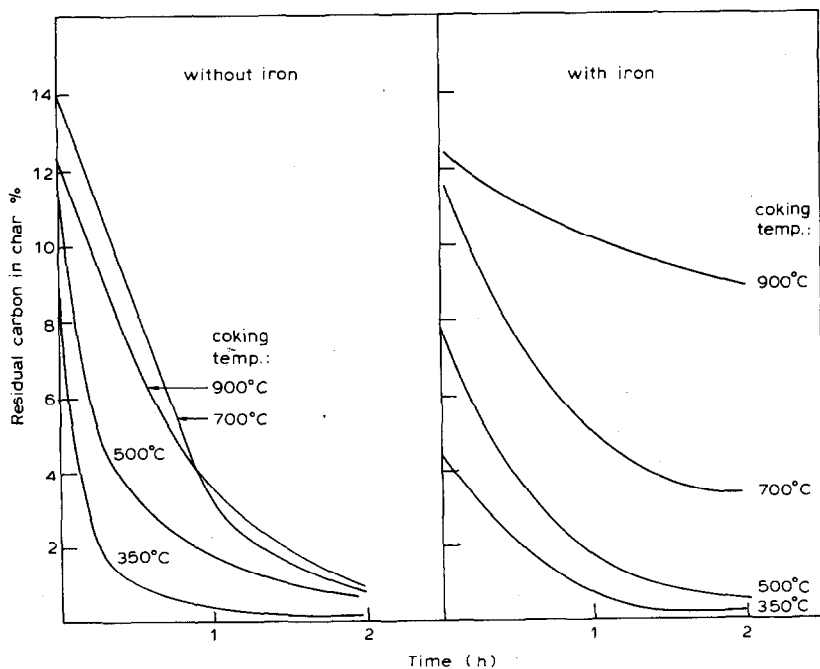


Fig. 4. The change in weight of the residual carbon in the char as a function of the time of heating in static air at 400°C.

static air for 2 h at different temperatures. Similar X-ray patterns were obtained for the treated and untreated samples which were coked at 350 °C for 1 h and then fired in static air at 500 °C for 2 h (Fig. 6a, b). However, the treatment process affects decrease of the degree of crystallinity of the silica

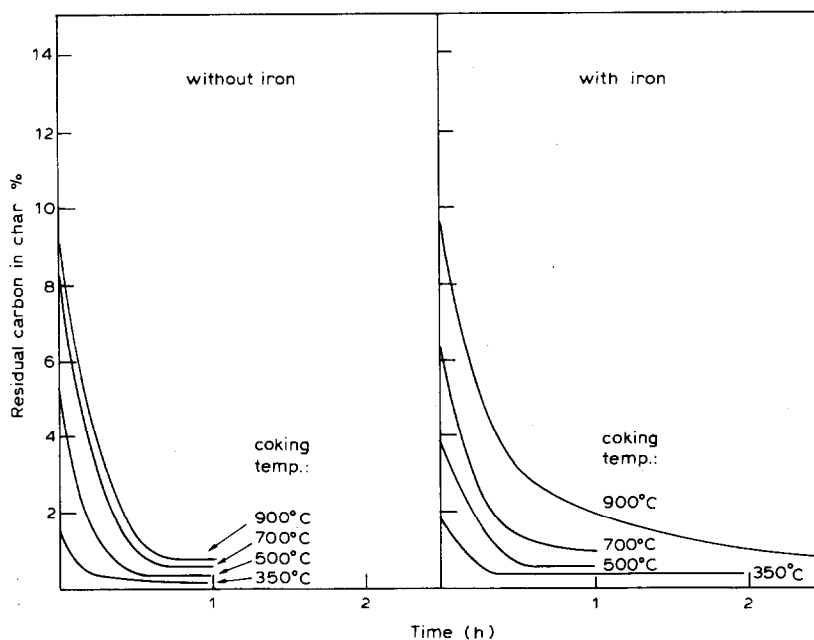


Fig. 5. The change in weight of the residual carbon in the char as a function of the time of heating in static air at 500 °C.

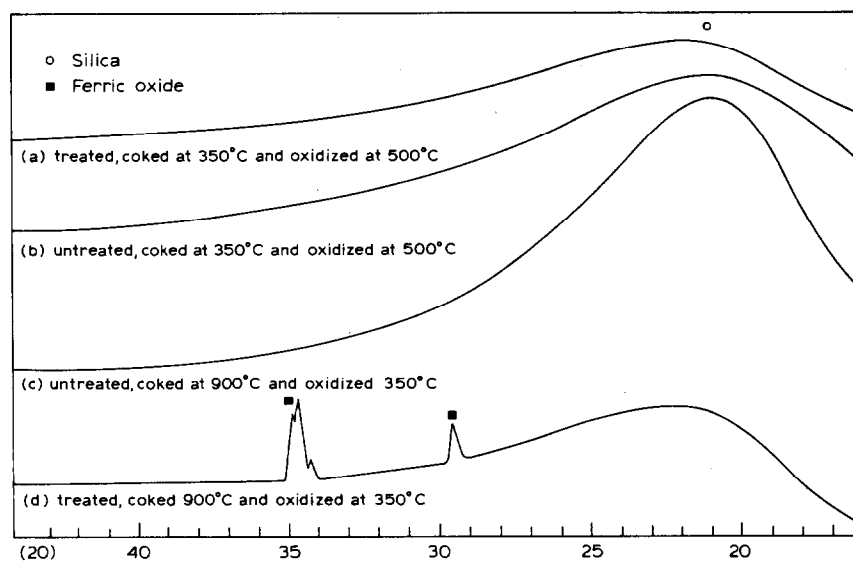
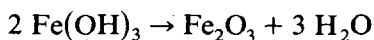


Fig. 6. The X-ray patterns of coked samples after firing in static air at different temperatures.

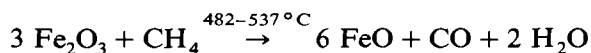
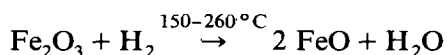
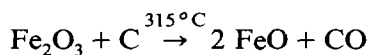
residue. This was detected from the difference in the curve height in the region of the maximum peak characteristic of the silica forms.

The two other patterns (Fig. 6c, d) are for two samples coked at 900 °C for 1 h and then fired in static air at 350 °C for 2 h. On comparing their X-ray patterns with those before the combustion process (Fig. 2c, d) the following deductions can be made: (i) graphite disappeared in the two samples as a result of its oxidation in air; (ii) there is an obvious decrease in the degree of crystallinity of silica in both samples. However, silica in the untreated rice hulls still shows a higher degree of crystallinity than that in the treated hulls.

Silicon atoms are assimilated in the rice plant. They probably replace the carbon atoms in the organic compounds [8]. As a result of firing, silicon atoms are first transformed into amorphous silica. The thermal decomposition of the cellulose structure resulted in amorphous carbon. Silicon atoms attach to oxygen atoms forming a siloxane group, Si-O, or a silanol group, Si-OH [9]. On increasing the coking temperature, rice hulls lost their OH groups, and the Si-O groups became attached to each other to produce a low form of cristobalite. In a reducing atmosphere, amorphous carbon begins to crystallize as graphite. Iron was fixed with hull fibres as iron hydroxide, Fe(OH)₃. The latter is thermally converted to ferric oxide according to



It is possible that the decomposition of ferric hydroxide to ferric oxide may cause openings in the structure of rice hulls and promote the pyrolysis process. It was found experimentally that the amount of volatile matter increases with increasing iron content. Further, any reaction that iron oxide participates in or influences, may play a significant role in the pyrolysis process of rice hulls. The following reactions may occur between ferric oxide and carbon, hydrogen and hydrocarbons [10]



These reactions increase the amount of volatile matter, and at the same time decrease the carbon content in rice hulls.

It was found that increasing the coking temperature increases the crystallinity of both silica and carbon (Fig. 2), i.e., decreases their activities to react with each other at higher temperatures ($\geq 1500^\circ\text{C}$) to form silicon carbide. This means that a low coking temperature is preferable for the formation of silicon carbide from rice hulls. It was found experimentally that, in the

presence of iron, the crystallinity of the reactants (silica and carbon) decreased (Fig. 2). This may lead to an increase in the rate of silicon carbide formation at higher temperatures. Simply, for the same coking temperature, the crystallinity of both silica and carbon decreases as the iron content increases. Thus, increasing the amount of iron promotes the formation of silicon carbide from rice hulls [6].

Another observation is the effect of coking temperature on increasing the crystallinity of iron oxide. It was found that iron oxide at 500 °C was in the amorphous form and at 900 °C was in a highly crystalline ferric oxide form. Therefore, the catalytic effect of iron addition on the formation of silicon carbide decreases when the rice hulls were coked at a relatively high temperature, e.g., 900 °C.

As mentioned above, iron acts as an inhibitor for the crystallization of silica and carbon during the coking process in the range 350–900 °C. Thus, the depression in the degree of crystallinity for silica and carbon favoured the fixation of carbon in the black rice hulls' ash especially at a high coking temperature (900 °C). Although the fixation of carbon is beneficial for the production of silicon carbide from coked rice hulls, the latter show less readiness to yield white ash with less carbon content on firing at a relatively low temperature, e.g., 350 °C. To obtain white silica from the coked rice hulls, the coking temperature must be lowered (350–500 °C) in order to decrease the fixation of carbon and hence remove most of the carbon at a low temperature.

Continuing the firing of the two samples (Fig. 6a, b) in an atmosphere of static air up to 1200 °C for 2 h, the main crystalline silica phase present in the white ash of the treated rice hulls was cristobalite (Fig. 7b). Tridymite

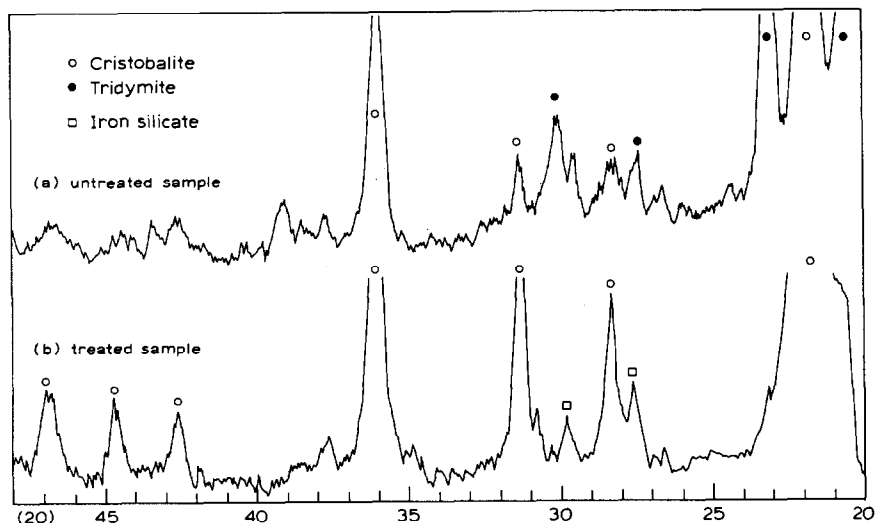


Fig. 7. The X-ray patterns of treated and untreated samples coked at 350 °C for 1 h and then fired in static air at 1200 °C for 2 h.

was also detected by X-ray diffraction analysis as a minor constituent of the silica ash. On the other hand, the white ash obtained from firing untreated rice hulls at the same temperature (1200°C for 2 h) constituted mainly tridymite with a smaller amount of cristobalite (Fig. 7a). It is known that both the amount of impurities present in rice hulls and the temperature govern the amount of tridymite formed. The impurities present enter the lattice of silica, forming a kind of solid solution, which favours the formation of tridymite [11]. The treatment process may leach some of the impurities. Thus, the formation of tridymite was reduced in comparison with that formed from the untreated rice hulls. A similar result was obtained [9] when rice hulls were boiled in water.

CONCLUSIONS

(1) While the treatment process increases the volatile matter evolved during the coking process, it decreases the amount of residual carbon in the char. This effect decreases as the coking temperature is increased.

(2) The addition of iron inhibits the crystallinity of both silica and carbon during the coking temperature, and hence favours the fixation of carbon in the black rice hulls' ash.

(3) The treatment process greatly affects the combustion of carbon of the coked rice hulls, especially when rice hulls are coked at high temperature.

(4) The treatment process leaches some of the impurities from the rice hulls and consequently, the formation of tridymite at high temperatures is lowered.

(5) A low coking temperature is preferable for the formation of silicon carbide from rice hulls, since the activities of silica and carbon to react with each other, and the catalytic effect of iron increase.

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