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KINETIC STUDIES ON THERMAL DEGRADATION OF TREATED AND UNTREATED RICE HULLS

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ABSTRACT

The kinetics of thermal degradation of treated and untreated rice hulls over a temperature range of 350–900°C were studied. The treatment of rice hulls (addition of iron) comprised impregnating the rice hulls in ferrous sulphate solution then soaking them in ammonia solution.

The results of thermogravimetric analysis revealed that the thermal degradation of rice hulls is completed in two steps: the volatilization of volatile matter and the oxidation of carbon. The fraction of volatile matter and carbon evolved from the treated sample is greater than that from untreated one. The calculated activation energies for the two steps of degradation over the temperature range 500–900°C are 1.042 and 6.457 kcal mol^{-1} for the treated sample and 1.198 and 7.916 kcal mol^{-1} for the untreated one, respectively. Further amorphous silica with low proportions of deleterious contaminants was produced by this process.

INTRODUCTION

Rice hulls constitute one of the major waste products of the agricultural industry. In Egypt the "Rice Centres" produce annually about 400 000 tonnes of rice hulls as a by-product of rice milling. It is bulky and creates a problem of storage due to high fire risk.

The approximately 20% of silica present in the rice hulls constitutes a unique source of relatively high-grade silica. The silica from hulls must compete with other cheap energy sources such as sand, bentonite and diatomaceous earth, however, it frequently offers advantages because of minimal amounts of unwanted elements other than silica. Further, the rice hulls appear very attractive as raw materials, particularly in integrated systems where the raw material is used to produce energy while the resultant silica is marketable at higher prices than the raw material.

It is known that rice hulls are flame retarding and, at ordinary temperatures, self-extinguishing. Neither ignition nor distillation of rice hulls completely removes the carbon residue from the cinder of rice hulls to produce

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carbon-free silica. Low-carbon and white rice-hull ash are prepared [1,2] by first removing volatile constituents (furfural, water vapour and gas) by heating the rice hulls to a relatively low temperature below their ignition point. Fixed carbon is then oxidized in the presence of air or O_2 by heating the hulls to a second temperature below the crystallization temperature.

The authors [3] studied the effect of the addition of iron on the coking process of rice hulls (in the absence of air) and on the ease of carbon combustion in the coked rice hulls. The addition of iron was made by impregnating the rice hulls with ferrous sulphate solution, followed by soaking in ammonia and coking in the absence of air. The results revealed that iron strongly affects the combustion of carbon for the coked rice hulls, especially at high coking temperatures (700–900°C).

The aim of the present work is to study the effect of treatment process on the kinetics of thermal degradation of the green rice hulls in order to produce a carbon-free silica with a low proportion of deleterious contaminants to enable the greater utilization of silica in manufacturing refractories and building materials.

EXPERIMENTAL

Materials

The materials used were rice hulls (~ 17% 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.% Fe_2SO_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. The treated rice hulls were left to dry in air. Chemical analysis of the treated and untreated rice hulls was performed to determine carbon, silica and metal oxides [4].

Combustion process

A weighted amount of both treated and untreated rice hulls was placed in a platinum crucible. The crucibles and contents were inserted into a furnace at combustion temperature (350, 500, 700 and 900°C). Mass changes of the samples were measured at intermittent periods of firing at the desired temperatures. The mass change represents the mass of volatile matter and carbon removed.

Some representative samples were examined by X-ray diffraction and infrared analysis. X-ray diffractometer runs were made using a Philips X-ray diffractometer with Ni-filtered Cu$K\alpha$ radiation at 1.54 Å. The scanning rate was 2°C min^{-1}. Infrared spectra were run for some samples on a grating spectrophotometer, a Beckman recording double beam IR spectrometer, using the KBr pellet method.

RESULTS AND DISCUSSION

Figures 1 and 2 show the loss in weight in static air for both treated and untreated rice hulls as a function of time of heating at different temperatures. The loss in weight can be attributed to the evolution of volatile matter and also to the oxidation reactions occurring at such high temperatures [5]. It is evident that the fraction of volatile matter and carbon evolved from the treated sample is greater than that from the untreated one. This effect appears in the samples fired at 500–900°C. The loss in weight versus time of heating curves at all temperatures approximate classical parabolic behaviour. This can be represented by the following equation

$$(\Delta m/m)^2 = Kt + C \tag{1}$$

in which Δm represents the loss in weight, m the mass of volatile matter and carbon content, and t the time of heating. K is the parabolic rate constant and C is a constant to account for the initial reaction. The value of C equals zero because the samples were inserted in the furnace at the desired temperature. Then the parabolic equation becomes $(\Delta m/m)^2 = Kt$. The results are

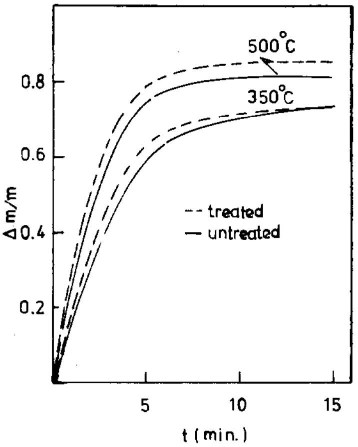

Fig. 1. Loss in volatile matter and carbon vs. time curves for treated and untreated rice hulls at 350 and 500°C.

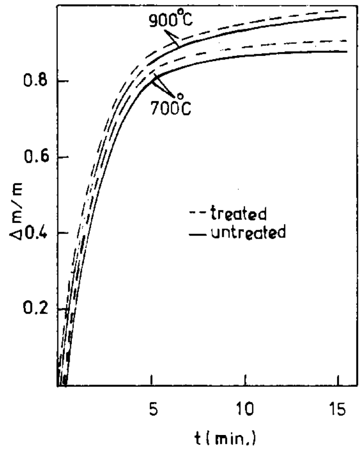

Fig. 2. Loss in volatile matter and carbon content vs. time curves for treated and untreated rice hulls at 700 and 900°C.

shown in Figs. 3 and 4 in a parabolic plot of $(\Delta m/m)^2$ versus t. It is clear that the straight lines obtained, which represent a region of parabolic degradation behaviour, are divided into two groups. This indicates that the thermal degradation of rice hulls takes place through two main steps. The

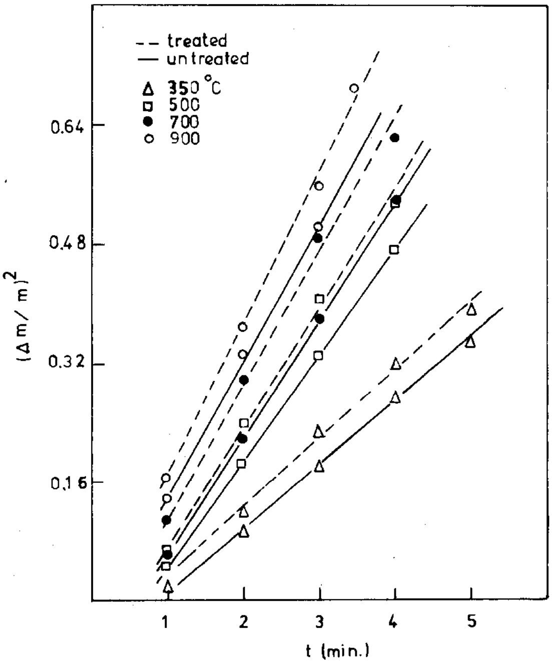

Fig. 3. Parabolic plots for evolution of volatile matter.

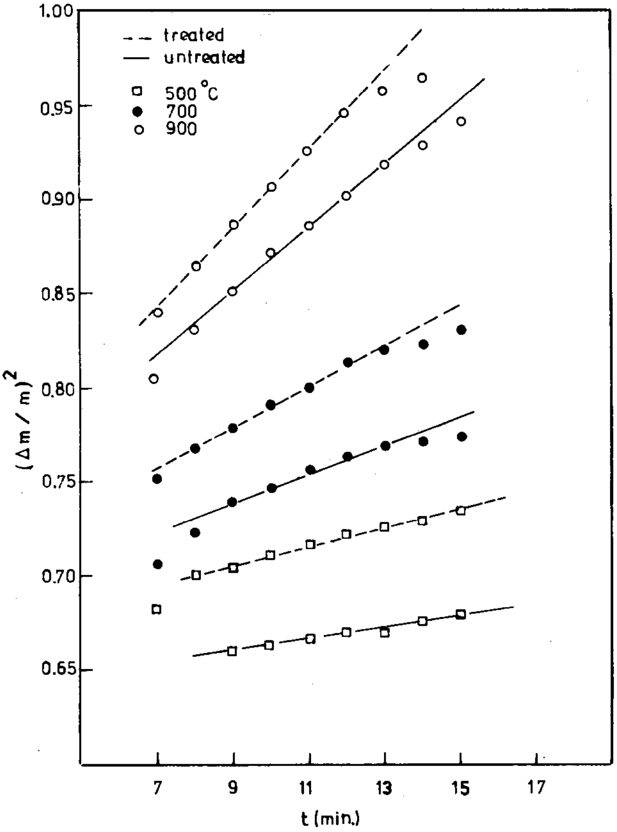

Fig. 4. Parabolic plots for oxidation of carbon.

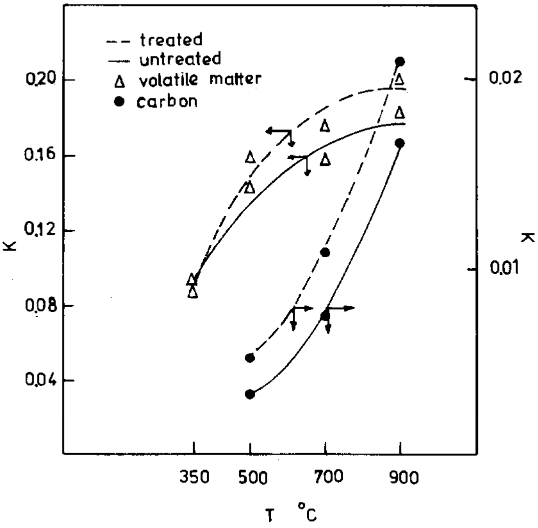

Fig. 5. Variation of rate constant for degradation of rice hulls with temperature.

first step is the volatilization of volatile matter and the second is the oxidation of carbon in the residual rice hulls char. The values of parabolic rate constant, K, for the degradation of rice hulls, which are obtained from the slopes of the straight lines, are shown in Fig. 5 as a function of firing temperature. It is evident that the degradation rate of untreated samples is slower than that of treated rice hulls in the temperature range 500–900°C. Another observation is that the volatilization of volatile matter proceeds more rapidly than the process of carbon oxidation.

The parabolic rate constants are compared in the Arrhenius equation (Fig. 6)

$$K = A\exp(-E/RT)$$

where E is the activation energy, R is the normal gas constant and T is the absolute temperature. The calculated activation energies for the two steps of degradation of rice hulls were found to be 1.042 and 6.457 kcal mol^{-1} for the treated sample and 1.198 and 7.916 kcal mol^{-1} for the untreated rice hulls, respectively. Further, it is found experimentally that the treated samples still show earlier degradation than the untreated sample when the volume of rice hulls is increased. This difference in thermal behaviour of the two samples could be due to the iron present in the rice hulls. Iron was fixed with hull fibres as iron hydroxides. It is possible that the thermal decomposi-

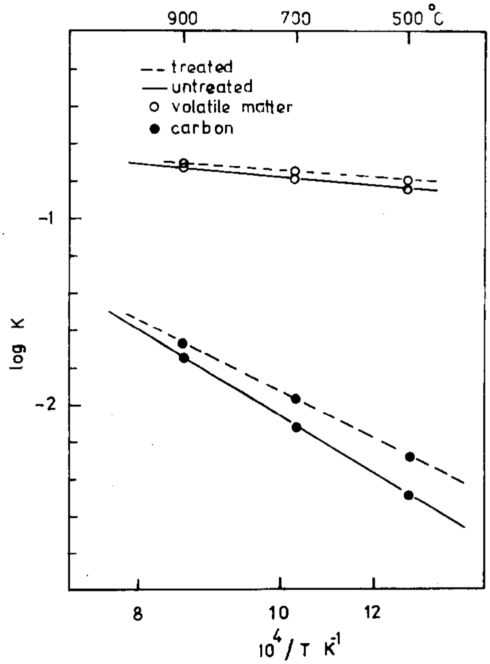

Fig. 6. Arrhenius plot of parabolic rate constants for degradation of treated and untreated rice hulls.

TABLE 1

Gasification of carbon with iron

Ref.	Carbon characteristics	Reaction	Fe amount (%)	ΔE (kcal mol^{-1})	
				without Fe	with Fe
7	Natural single crystal	$C + CO_2$ 550–700°C	Colloidal Fe = ?	46	10
8	Coke	$C + CO_2$ 700–900°C	Fe > 20	95	55–70
9	Charcoal	$C + CO_2$ 700–900°C	Ash = 3.5	66	38
10	Sugar carbon	$C + CO_2$ 600–900°C	Fe = 7	61.2	22.8

tion of ferric hydroxide to ferric oxide may cause openings in the structure of rice hulls and increase the volatile matter. Further, ferric oxide may react with carbon, hydrogen and hydrocarbons at temperatures < 500°C to form ferrous oxide and volatile matter (CO and H_2O) [6]. These reactions increase the amount of volatile matter, and at the same time decrease the carbon content in silica ash.

Some other workers reported a significant decrease in the activation energy for the gasification of carbon with iron as shown in Table 1.

Long and Sykes [9] postulated that the vaporisation of carbon (by desorption of CO from the surface of graphite) would be enhanced if electrons were transferred from the graphite to a catalyst. They suggested that transition elements (of which iron is one) accept electrons due to the non-stoichiometric character of their oxides. Another factor that may be of great importance in catalysis by transition metals is their unfilled *d*-orbitals. As a result of these unfilled orbitals, the transition metals are believed to be able to accept electrons. They would, therefore, be able to catalyse the oxidation of graphite by accepting its electrons, thereby enhancing desorption of CO in a manner similar to that proposed by Long and Sykes [9].

Another possible mechanism for the catalysis of the $C–CO_2$ reaction by iron is suggested in the work of Pettit et al. [11]. They concluded that CO_2 dissociates over Fe to give CO and adsorbed oxygen atoms. These atoms are probably highly mobile on the Fe surface where they would react to produce

TABLE 2

Chemical constitution of treated and untreated silica

Sample	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)
Untreated	94.32	1.70	0.20	0.09	0.74	0.78	0.48	1.68
Treated	94.72	0.47	2.13	0.06	1.20	0.59	n.d.	n.d.

gaseous CO. This means that there are two possible mechanisms by which iron can interact with reactants: electron transfer mechanism and oxygen transfer mechanism.

The present results also revealed that the treatment process offers the advantage of the ability to produce a carbon-free silica with a minimal number of unwanted elements. This could be deduced from the chemical composition of the silica obtained from treated samples in comparison with that produced from untreated rice hulls. Table 2 shows that the impurity content was reduced by the treatment process. The reduction of the amount of these impurities may be due to the impregnation process in which the rice hulls were soaked in $FeSO_4$ solution containing H_2SO_4 and then in ammonia solution. This means that some impurities were leached by these solution treatments [12]. The reduction of the unwanted impurities has a great effect on the high temperature application of silica, e.g., the presence of only 0.7% alumina hinders the quartz conversion to cristobalite and it and alkaline lower the refractoriness of the fired silica brick [13]. On the other hand, it is known that iron is one of the promoters added to silica in order to accelerate the conversion reaction of quartz to cristobalite which is of great importance in the technology of silica and siliceous refractories. The conversion reaction of silica progresses completion at a uniformly rapid rate in the presence of iron [13]. Further, the addition of a small amount of iron to silica has no dangerous effect on the melting point of silica. The phase diagram for the system $FeO-SiO_2$ [14] shows an immiscibility and only a small drop in the melting point of silica (~ 25°C) with up to 40% substitution by ferrous oxide. Another observation is that the amount of iron in the silica ash could be controlled by changing the conditions of impregnation process [4]; the concentration and temperature of $FeSO_4$ solution, the concentration of ammonia solution and the time of impregnation.

The IR patterns of the silica obtained from treated rice hulls at 500°C showed the following bands: 470, 810, 1100, 1600 and 3420 cm^{-1} (Fig. 7a). This pattern is similar to that obtained from the untreated rice hulls at the

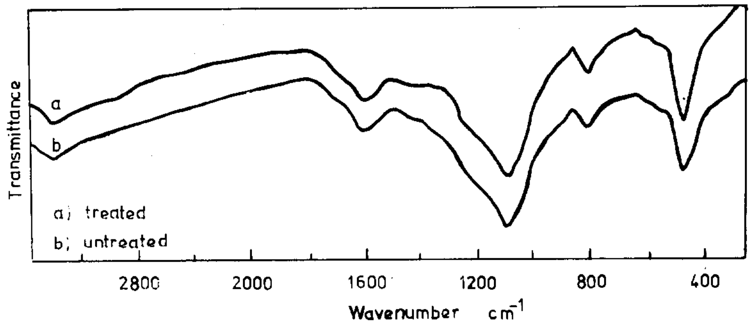

Fig. 7. Infrared absorption spectra of silica obtained from (a) treated and (b) untreated rice hulls at 500°C.

same temperature (500°C) (Fig. 7b). The X-ray diffraction pattern of the silica obtained at 500°C showed a curve without any characteristic peak. This means that it is in an amorphous form at this temperature. In previous work [3], it has been found that the free silica obtained from the treated coked rice hulls at 1200°C consists mainly of cristobalite with a small amount of tridymite. The formation of tridymite was reduced in comparison with that formed from the untreated sample. This may be due to the reduction of impurities in the sample by the treatment process (Table 2). This means that the treatment process decreases the formation of tridymite at high temperatures.

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