Manufacture of Silicon Tetrachloride from Rice Hulls

Raw rice hulls contain about 20% silica in very finely dispersed form. Pyrolyzed hulls can be chlorinated at 1000°C to give a nearly quantitative yield of silicon tetrachloride free of most other inorganic chlorides. Solid, organic, chlorine-containing species have been found to be reaction intermediates. Commercial application appears economically attractive.

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SCOPE

Rice grows in a form such that an outer coating, or hull, surrounds the edible grain. These hulls are removed from the grain at the mill and constitute a waste product. Rice hulls vary somewhat in composition, depending on the conditions of growth but are composed primarily of cellulose, lignin, and ash (Houston, 1972). Table 1 shows the range of compositions of ash which has been reported. The ash is typically about 92% SiO_2. The silica is generally dispersed throughout the hull, with higher concentrations being found near the inner and outer surfaces. Rice hulls are 4 to 5 mm in length, 1 to 2 mm in width, and about 0.5 mm in thickness. They are woody and have a low bulk density, 96-160 kg/m^3.

The conventional means of disposal has been burning, which produces a large quantity of particulates because of the high silica content. Burning is no longer permissible in California, and the rice mills in the state are confronted with the need to dispose of 200,000 tons of hulls per year at a cost of about $5 per ton. This project was undertaken as part of the effort to find profitable alternatives to rice-hull burning.

The cheapest raw materials for the manufacture of silicon tetrachloride by conventional means are sand, chlorine, and coke. A survey of the methods of manufacturing silicon tetrachloride has been presented elsewhere (Base, 1972). All methods using the above raw materials require temperatures in excess of 1,300°C. Electrical energy in one form or another is required. Very fine dispersal of the coke and sand by grinding is also necessary. The potential advantages of using rice hulls as the raw material for making silicon tetrachloride are lower cost, dispersion much finer than possible by mechanical means, and the resultant lower temperature of chlorination.

The current U.S. production of silicon tetrachloride is about 82,000,000 lb/yr, and the price is 9 to 15¢/lb. Production of this entire amount from rice hulls would consume only about 15% of California's yearly crop. A major new market, such as use as an intermediate in silicones manufacture, would be required for silicon tetrachloride manufacture to become a major method of disposing of rice hulls. A sufficient reduction in the cost of manufacture could warrant such a development.

CONCLUSIONS AND SIGNIFICANCE

Nearly quantitative conversion of rice-hull silica to silicon tetrachloride occurs when pyrolyzed hulls are chlorinated at 1,000°C under the proper flow conditions and reactor geometry. Evidence was found for a highly exothermic reaction sequence in which carbon dioxide is a primary product. There is also evidence for the formation of a solid chlorine-carbon reaction intermediate. It is not known whether there is one reaction path or several in parallel. Carbon monoxide in the gas phase was shown to be ineffective as a reducing agent for the reductive chlorination of silica in the temperature range 800° to 1100°C. Phosgene, which can appear in the reactor off-gas, was shown to be a satisfactory source of chlorine when recycled to the reaction zone. Conditions which promote heat transfer from the reaction zone result in a decreased conversion of silica, which appears to react rapidly or not at all when exposed to chlorine.

The use of rice hulls as a raw material for the production of silicon tetrachloride could lead to lower operating costs because of the cheapness of the hulls at a mill site and because electric power is not required to reach reaction temperature. Capital costs are expected to be comparable to or slightly less than those for a conventional plant.

CHEMISTRY

The first step in the manufacture of $SiCl_4$ from rice hulls must be the pyrolysis of the hulls. In this step drying occurs, followed by decomposition of cellulose and saccharides to carbon and water vapor, and cracking of other organic compounds to carbon and volatile substances. The pyrolysis gas thus contains a variety of organic compounds, some of which are condensable, but it is essentially free of inorganic particulates. Residual hydrogen content must be very low to prevent excessive consumption of chlorine, and residual water must be negligible to prevent hydroly-

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sis of $SiCl_4$ after it is formed. About 55 to 60% of the mass of the rice hull is lost during pyrolysis, but its size and shape remain essentially unchanged. The pyrolyzed hulls still mirror the shape of the rice kernal and are rather strong. There is no apparent sintering or agglomeration.

The two possible overall reactions between carbon, silica, and chlorine are

$$SiO_2 + C + 2Cl_2 \rightarrow SiCl_4 + CO_2 \quad (1)$$

$$\Delta H^\circ_{1300^\circ K} = -42.54 \text{ kcal/mol}$$

$$\Delta F^\circ_{1300^\circ K} = -56.53 \text{ kcal/mol}$$

$$SiO_2 + 2C + 2Cl_2 \rightarrow SiCl_4 + 2CO \quad (2)$$

$$\Delta H^\circ_{1300^\circ K} = -2.46 \text{ kcal/mol}$$

$$\Delta F^\circ_{1300^\circ K} = -70.12 \text{ kcal/mol}$$

The thermodynamic data were calculated from values given in the JANAF tables (Stull, 1960). At temperatures below 600°C (873°K), reaction (1) has the greater negative value of ΔF°.

It is unlikely that either reaction (1) or (2) proceeds without intermediate steps. Reactions involving the formation of Si, SiO, or SiC appear improbable on the basis of large positive values of ΔF°. For this reason intermediate steps involving compounds of chlorine and carbon seem to be the only possibilities. The chlorination experiments to be discussed below indicate that solid compounds containing chlorine are indeed formed during the chlorination of pyrolyzed hulls. Their identity has not been established.

APPARATUS AND EXPERIMENTAL TECHNIQUES

The pyrolysis experiments were carried out in a sealed stainless steel pot through which nitrogen could be passed. The pot was heated in an electric crucible furnace. Temperatures were measured at the wall and at three positions within the pot. The effluent gas passed through a series of ice-water-cooled condensers and then through a wet test meter. The quantities of condensable liquids and net noncondensable gases were measured as a function of time during a run. All pyrolyses were carried out at essentially atmospheric pressure.

The chlorination experiments were carried out in two sets of runs in equipment which was essentially identical except for size. The general layout is shown schematically in Figure 1. In any given run a sample of pyrolyzed rice hulls was placed in a tubular reactor made of mullite (aluminum silicate). The reactor was then placed in an electric furnace and the indicated gas flow lines were attached. The reactor was brought up to temperature while being purged with nitrogen, then the desired flow of gases was started. A small mullite tube (3.2 mm O.D., 1.6 mm I.D.) running longitudinally through the reactor allowed axial temperature measurements with a chromel-alumel thermocouple.

The initial experiments were done in a reactor 9.5 mm I.D. Sample sizes were generally about 2 g and occupied a length of about 4 cm in the reactor. Pure chlorine was used for the chlorination. The axial temperature in the absence of reaction was essentially uniform over this length during a run. The purpose of these runs was to establish the extent of reaction and some indication of reaction kinetics. Effluent gas samples were not taken, but the presence of $SiCl_4$ in the effluent was established qualitatively. The percent conversion as noted in the figures was obtained by oxidizing the carbonaceous residual and comparing the ash with the ash obtained from unchlorinated material. If the ash were pure SiO_2, this would correspond to the percent conversion of SiO_2.

The second set of experiments utilized a mullite reactor of 44.5 mm I.D. and pyrolyzed rice hull samples of 5 to 15 g. The length of the packed section was reduced correspondingly. The method of operation was essentially the same except

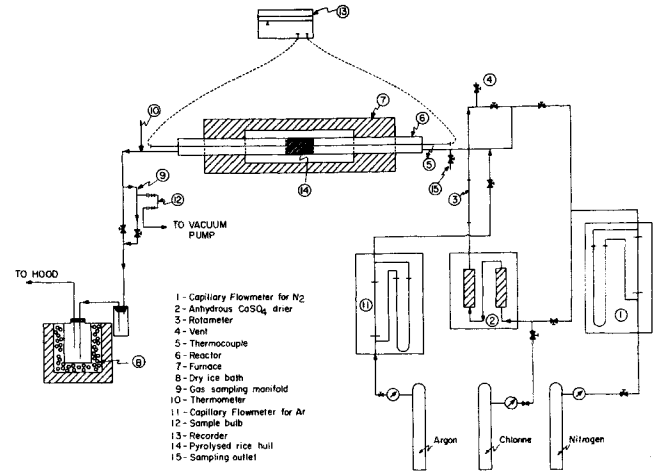

Fig. 1. Schematic of the 44.5 mm reactor system.

TABLE 1. AVERAGE COMPOSITION OF RICE HULL ASH

Constituent	Weight-% (dry basis)
SiO_2	86.9-97.3
K_2O	0.58-2.5
Na_2O	0.0-1.75
CaO	0.2-1.5
MgO	0.12-1.96
Fe_2O_3	trace-0.54
P_2O_5	0.2-2.85
SO_3	0.1-1.13
Cl	trace-0.42

TABLE 2. ANALYSIS OF PYROLYZED RICE HULLS*

(Temperature of Pyrolysis—900°C)

	Wt-%
Ash	46.4
Carbon	53.2
Hydrogen	0.4

* This quantitative analysis was done by the Analytical Laboratory, College of Chemistry, University of California, Berkeley.

that during a run samples were taken of the reactor effluent and were subsequently analyzed for $SiCl_4$, $COCl_2$, Cl_2, CO, CO_2, N_2, and Ar. The argon was added as a tracer to allow calculation of flow rates and monitoring of any changes in flow rate during a run.

The method of analyzing the gas sample has been reported previously (Basu et al., 1972). The solid residues were routinely analyzed for carbon and unreacted silica by weighing, ashing in a muffle furnace, and reweighing. Unreacted silica was determined from these weights and a knowledge of the initial composition of the ash. Some solid samples were analyzed gravimetrically for residual chlorine.

EXPERIMENTAL RESULTS

Pyrolysis

Pyrolysis of an organic substance typically results in the production of a combustible gas mixture containing H_2, CO, CH_4, CO_2, C_2H_2, etc., a condensable fraction containing acids, alcohols and high-boiling organic compounds, and a solid residue containing carbon and the inorganics. The amounts of the various fractions and their composition depends on a number of factors, such as the nature

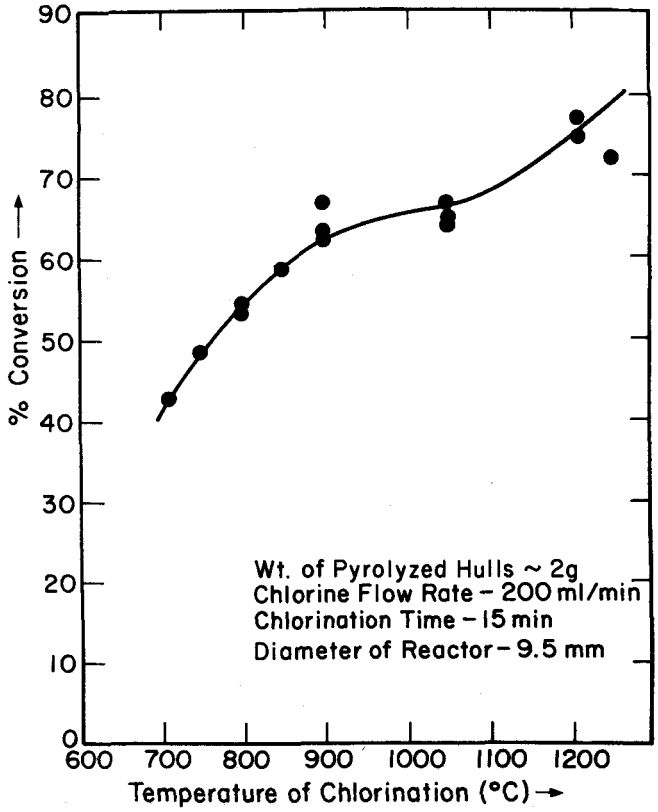

Fig. 2. Effect of temperature on the conversion of rice hull ash.

of the carbonaceous material being pyrolyzed, heating rate and maximum temperature attained during pyrolysis, and the type of equipment used (for example, batch or continuous).

The effect of heating rate, nitrogen flow, and final temperature on gas evolution, liquid production, and final weight for the pyrolysis of rice hulls is reported elsewhere (Basu, 1972). The determination of the composition of the gases and liquids evolved was outside the scope of this project. Pertinent to the project was the determination that the rice hulls reached an essentially constant weight after pyrolysis for two hours at 600°C. Variation of the pyrolysis temperature between 600° and 1,300°C had no effect on the subsequent chlorination. Pyrolysis at 1,400°C reduced the rate of chlorination.

The analysis of pyrolyzed hulls is given in Table 2. The ash of raw hulls used in this work was analyzed, and the fractions of the various constituents were found to fall in the ranges given in Table 1. The ash of pyrolyzed hulls was not found to differ significantly from this composition.

Experiments in 9.5 mm Reactor

Figure 2 shows the results of chlorinations at different temperatures. Each data point represents a different run in which the hulls were chlorinated for 15 minutes. The conversion of SiO_2 to $SiCl_4$ increases markedly with temperature.

In each of these runs a substantial excess of chlorine was used. It was found that the bulk of the reaction occurred in about 5 minutes and that the subsequent rate of chlorination was very small. At 1050°C, for instance, increasing the time of chlorination from 5 minutes to 190 minutes increased the conversion from 68% to 80%. Grinding the residue and rechlorinating had no effect.

Mixtures of CO and Cl_2 were ineffective in chlorinating rice hull ash and produced no improvement in chlorinating pyrolyzed hulls. This indicates that CO is not effective as a reducing agent in the reductive chlorination of silica in the temperature range 750° to 1100°C.

Model rice hulls were made by pyrolyzing mixtures of starch and silica having various size ranges. The resulting carbon/silica ratio approximated pyrolyzed hulls. The silicas used were colloidal silica (0.007-0.06 μ), diatomaceous earth (101.5 μ), Ottawa Beach Sand (−325 mesh) and Monterey Beach Sand (−80 mesh). The results are shown in Figure 3 where the decrease in conversion with increasing particle size is clearly evident.

Experiments in 44.5 mm Reactor

The first experiments in the larger reactor duplicated the temperature conditions and method of analysis used before. It was found that the conversion of the silica to $SiCl_4$ was substantially greater at all temperatures. Further experiments were performed to determine the effect of chlorine content and gas velocity on the conversion. Some of these results are shown in Figure 4. Again, each point represents the result of a single run. In each run, at least twice the amount of chlorine necessary for complete conversion of silica was passed through the reactor.

It was found that increasing the gas velocity or decreasing the chlorine content of the gas reduces the conversion. The latter effect is much more pronounced. However, reducing the chlorine content does not produce a linear decrease in conversion. Instead, there is a fairly abrupt shift from the high level of reactivity to a lower one as the fraction of chlorine drops from 50% to 25%. Comparison of Figures 3 and 4 shows that this lower level of reactivity corresponds very closely to that found for the

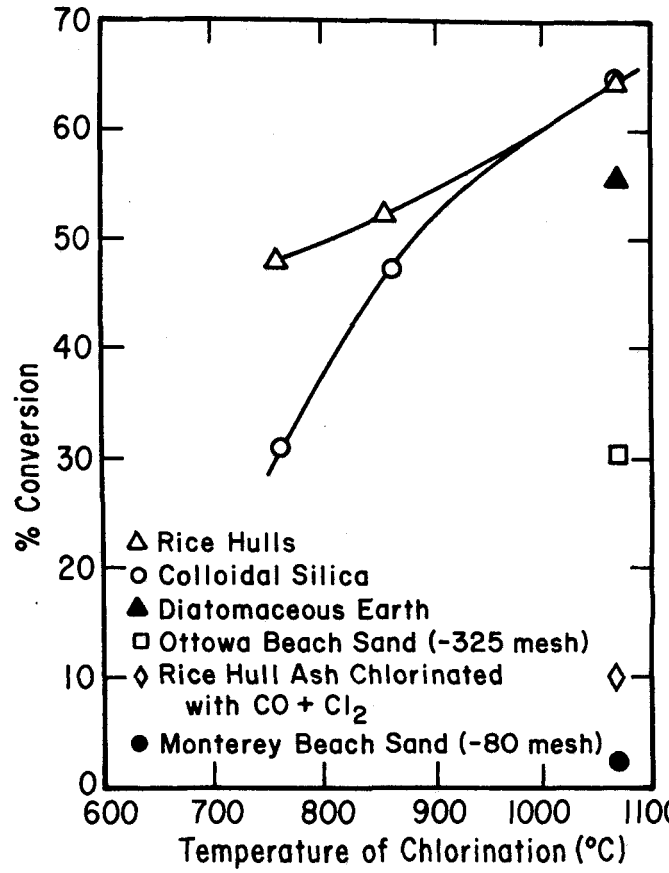

Fig. 3. Effect of particle size on chlorination of silica (9.5 mm reactor).

9.5 mm reactor. This behavior is in accordance with the reaction model discussed in a later section.

A number of runs were made at temperatures ranging from 600° to 1200°C in which the effluent gas stream was analyzed at intervals during the chlorination. For these runs nearly pure chlorine was used at a flow rate of only about 100 ml/min in order to facilitate sample taking. The gas compositions were determined chromatographically and normalized. The residence time for the gas in the reactor was calculated from the flow for each run and the total reactor volume. This residence time is indicated in Figure 5 and agrees well with the time required to purge the nitrogen from the reactor after the chlorine flow has started. It should be noted that the rice hulls occupied a section in the middle of the reactor tube which was 12% or less of the total reactor volume (see Figure 1). The contact time of a given element of gas with the hulls was thus substantially less than one minute.

The results of these runs are presented in full elsewhere (Basu, 1972). Typical of them is the run at 1000°C, which is shown in Figure 5. These composition-versus-time curves display several noteworthy features. First is the presence of CO_2 throughout the run. This was found for all runs, even at 1200°C, despite the fact that one would predict reaction of CO_2 with the residual carbon at these temperatures. The CO_2 is present at about 20 times its equilibrium concentration relative to CO and C at the point of maximum CO content in Figure 5.

Second is the presence of a considerable quantity of phosgene. The phosgene curve, which reached a maximum near the intersection of the CO and Cl_2 curves, is not shown in Figure 5 because it is believed that $COCl_2$ was

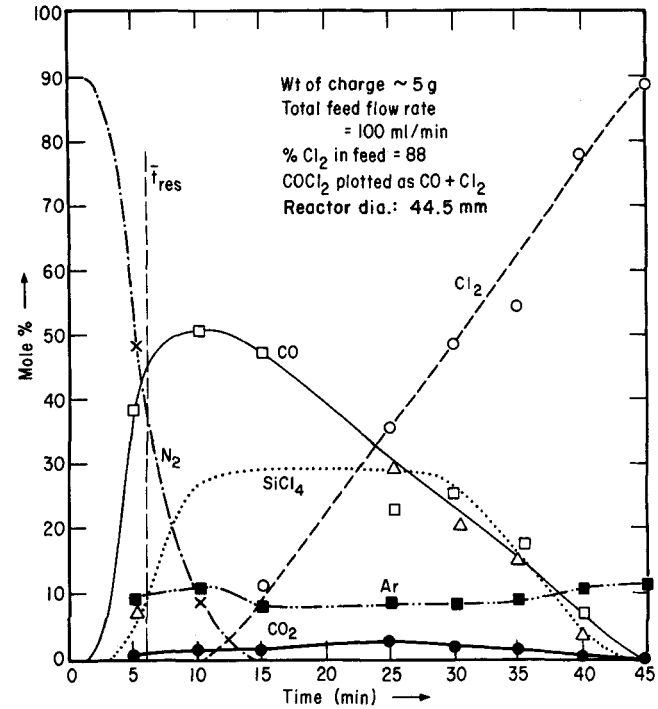

Fig. 5. Composition of effluent gas from chlorination reactor—1000°C.

not present in the reaction zone, but that the CO and Cl_2 reacted subsequently to form it. Support for this belief was obtained from a run in which the reactor was packed with mullite bits instead of rice hulls and $COCl_2$ was fed instead of Cl_2. Both CO and Cl_2 were found in the effluent. Furthermore, the relative quantities of $COCl_2$, CO, and Cl_2 found in the samples depended on the time elapsed between sample taking and analysis on the chromatograph. Samples analyzed after 24 hours were found to contain only $COCl_2$. Since the rate of the reaction involved is finite at room temperature, it seems reasonable to assume that equilibrium prevails at 1000°C and that virtually no $COCl_2$ was present in the reaction zone. For this reason the data of Figure 5 are drawn with $COCl_2$ assumed to be dissociated into CO and Cl_2.

The third striking feature of this run is the manner in which CO precedes the $SiCl_4$ leaving the reactor and the difference in sharpness of the Cl_2 front when compared with the N_2 tail and the CO and $SiCl_4$ fronts. This behavior is believed to indicate that the chlorine reacts initially with the carbon of the pyrolyzed rice hulls, forming at least part of the CO or CO_2 immediately, but not releasing $SiCl_4$ until some time has elapsed. This feature was less marked in reactions at 1,200°C and was more pronounced at temperatures below 1,000°.

In these runs the silica lost from the residues was compared to the $SiCl_4$ yield obtained by integrating the composition curves. The agreement in general was quite good, the standard deviation being only 9.4 percentage units. At 1,000°C a carbon balance showed that about 1.8 atoms C were removed from the pyrolyzed hulls for each atom of Si. As is seen from Figure 5 the agreement between chlorine fed and chlorine-containing species in the effluent is quite good.

The efficacy of phosgene as a chlorinating agent was tested and found to be equivalent to that of chlorine. Of additional importance was the determination that the loss of carbon by the pyrolyzed rice hulls was equally great

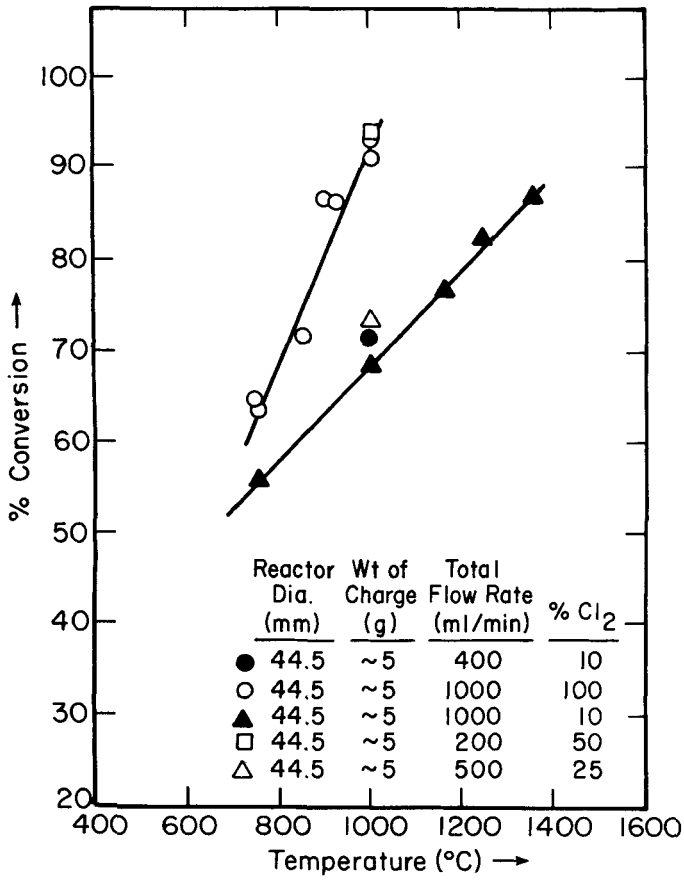

Fig. 4. Effect of concentration of Cl_2 on the conversion of rice hull ash.

with either $COCl_2$ or Cl_2 as chlorinating agent. This indicates again that the CO of the phosgene does not take part in the reductive chlorination.

Experiments on Reaction Mechanism (44.5 mm Reactor)

A number of partial chlorinations were carried out in an effort to learn more about the mechanism of the chlorination reaction. The results of one such run are shown in Figure 6. In this run at 750°C the flow of chlorine was stopped after 15 minutes and the reactor was purged with nitrogen for another 15 minutes. The temperature control on the electric oven was then set to bring the reactor to 1,000°C. As the temperature rose with nitrogen still the sole feed gas, significant additional quantities of both $SiCl_4$ and CO were evolved. A similar experiment with the reactor initially at 1,000°C and subsequently heated to 1,200°C failed to show a similar behavior.

In a group of related runs, the pyrolyzed hulls were removed from the reactor and analyzed gravimetrically after partial chlorination at various temperatures. Pyrolyzed rice hulls chlorinated for 15 minutes at 650°C and purged with N_2 for another 15 minutes at the same temperature contained 15 to 16% Cl (by weight). Pyrolyzed hulls chlorinated for 15 minutes at 750°C and then purged with N_2 for another 15 minutes at the same temperature contained 11 to 12% Cl by weight. For chlorinations carried out at temperatures at 1,000°C, or higher, where 95 to 97% conversion was obtained, very little (< 1%) chlorine was held up in the solids.

To determine the nature of the Cl held up in the solids at the lower temperatures, chlorinated hulls were washed thoroughly with 5% NaOH solution, dried in an oven at 105°C and then reanalyzed for Cl. It was found that only 30 to 35% of the chlorine content of the solids could be removed by the alkaline washing. The Cl so removed was found to include little or no elemental chlorine but was essentially all chloride ion.

Hulls which had been partially chlorinated at 750°C, flushed with nitrogen, then heated to 1,000°, were found to contain no chlorine in the solid residue. Chlorine once bound in the solid thus appears able to react further to give $SiCl_4$ if sufficient time and temperature are provided.

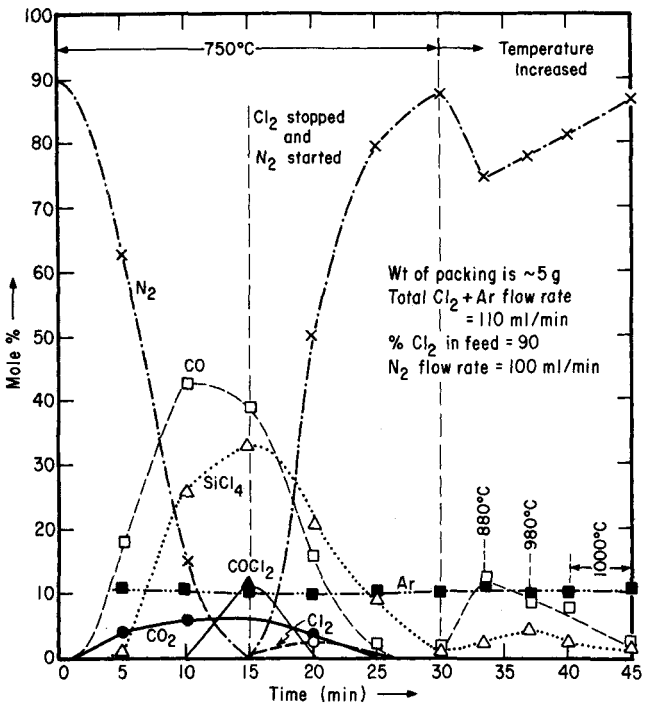

Fig. 6. Effect of short chlorination time and subsequent heating on composition of effluent gas from chlorination reactor.

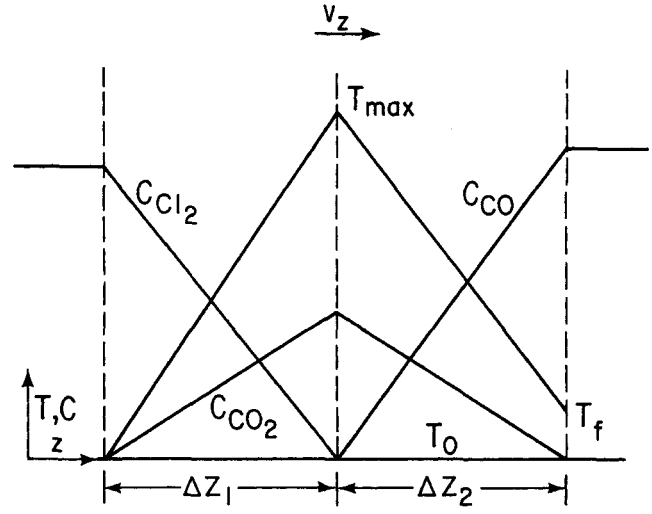

Fig. 7. Schematic representation of the temperature wave theory: C, concentration; T, temperature; $\bar{t}_{res}$, residence time; V_Z, velocity; and Z, distance coordinate.

REACTION MODEL

Consideration of the data presented in the foregoing sections and elsewhere (Basu, 1972) leads to the following picture of chlorination of pyrolyzed rice hulls in a packed-bed reactor: a significant fraction of the reaction follows Equation (1), in which CO_2 is the primary product. It has been found by others (Bridger and Appleton, 1948) that the presence of Cl_2 inhibits the endothermic reduction of CO_2 to CO. Since reaction (1) is highly exothermic, a temperature wave is produced in the bed. The length of the wave is a function of the velocity of the gas; the amplitude depends on the relative rate of heat loss and the fraction of chlorine present. As the CO_2 formed proceeds through the bed it reacts with carbon to form CO according to the reaction

$$CO_2 + C \rightarrow 2CO \qquad (3)$$

$$\Delta H^\circ_{1300^\circ K} = +\ 40.04 \text{ kcal/mol}$$

Once the temperature wave has passed a given point in the bed, further reaction occurs only very slowly.

An idealized model of this theory is shown in Figure 7. At steady state the reaction zone moving through the bed of pyrolyzed hulls with velocity v_z is divided into two parts, ΔZ_1 and ΔZ_2. In ΔZ_1 chlorine reacts to completion forming only CO_2 as in Equation (1). The temperature, initially at T_0, reaches T_{max}. In ΔZ_2 CO_2 reacts with carbon to form CO. The temperature drops to T_f in ΔZ_2 because the reaction is endothermic and because heat is lost to the surroundings.

A derivation based upon this model (Basu, 1972) shows that a temperature rise within the reaction zone of several hundred degrees, as implied by the experimental results, would be anticipated. As v_z increases, ΔZ_1 must increase in direct proportion, and as ΔZ_1 increases the heat-loss to the surroundings increases and a greater distance is required to reach a steady state temperature profile in the wave. If the bed is short, the wave will exit before reaching the steady state value, and the yield will drop. Also,

the presence of CO_2 in the exit gas indicates that the zone ΔZ_2 is diffuse, rather than being well defined as is indicated in Figure 7.

In the chlorination run corresponding to Figure 5, 5 g of pyrolyzed hulls were chlorinated, requiring 2200 ml of chlorine for complete conversion of the silica. The flow rate of chlorine was 88 ml/min, and the time required for the flow of stoichiometric chlorine into the reactor was therefore 25 minutes. From Figure 5 one finds that $SiCl_4$ first appears in the effluent gas 4 minutes after chlorine was turned on, while Cl_2 first appears after 12 minutes. During this 8-min period the reaction zone is totally within the bed of hulls and has not reached the end. An additional 30 to 35 minutes is required for the concentration of Cl_2 in the effluent to reach the value in the feed. During a large part of this time the reaction zone must extend through most of the bed, since the residence time of the gas within the bed is less than one minute. It is thus likely that this bed was too short for a true steady state reaction zone to be established.

This reaction-zone theory is in accordance with a number of observations: (1) The presence of the large quantities of CO_2 found can only be explained if it is a primary product of reaction. (2) The higher yield found with high chlorine content in the large reactor indicates relatively low heat loss from the reaction zone. Diluting the chlorine reduces the temperature rise and hence lessens the extent of reaction. Reducing the diameter of the reactor increases the heat loss to the wall, having the same effect. (3) At relatively low temperatures ($\sim$800°C) conversion in a short bed was markedly lower than in a longer bed (Basu, 1972). At the lower temperature, there is insufficient distance for the wave to reach its steady state amplitude in a short bed. (4) Photomicrographs of rice hull residues from runs in which high yields were obtained at 1,000°C (Basu, 1972; Thomas et al., 1972) show evidence of fusion of the silica (m.p. $\sim$1,600°C). This was not visible in hulls chlorinated with lower yield at the same temperature. (5) A temperature rise of about 30°C was observed during chlorination at 1,000°C. This low value of Δt is thought to be due to the long response time produced by the mullite shielding tube which is essential to operation of any thermocouple in chlorine at that temperature.

It is not known whether one or more reaction paths are involved during chlorination. As was noted above, the existence of chemically bound chlorine as an intermediate in the reaction was established. About one-third of this chlorine was hydrolyzable, possibly but not definitely indicating bonding to silicon. The other two-thirds was not hydrolyzable, which almost certainly indicates bonding to carbon. However, the chlorine content was found to be dependent upon the presence of reactable silica, since chlorinated residues will absorb no more chlorine once the silica is gone. This rather interesting chemistry was not pursued further.

COMMERCIAL APPLICATION

The attractiveness of the commercial application of rice hulls to silicon tetrachloride manufacture lies in their low cost, the high reactivity of their silica content, and the low level of impurities which would have to be removed from the product. Rice hulls present a disposal problem and hence are worth less than nothing at the mill. However, because of their low bulk density, shipping any appreciable distance is unlikely to be economically feasible. Their use thus probably dictates a plant site very near a rice mill.

The data obtained in the laboratory reactor indicate that a nearly quantitative conversion of silica to silicon tetrachloride can be obtained at a nominal reactor temperature of 1,000°C. This temperature level does not require electrical heat. Furthermore, it is likely that in a larger reactor quantitative conversion would be obtained at a nominal temperature of 800° to 900°C, since heat losses would be reduced.

The operation of the process would be energetically self-sustaining. Combustion of the carbon residue after chlorination would be more than adequate to provide both the heat needed for the pyrolysis of the hulls and that required for the preheat of the chlorine. Particulate emission from this combustion would be relatively low since 95+% of the silica would have been removed by the chlorination.

Possible reactor designs for the process include fixed bed, moving bed, and fluidized bed. One of the goals of the design will be to realize the 95+% yield at 1,000°C or lower which was demonstrated in the laboratory. This combination of high yield and relatively low temperatures appears to depend upon establishing a thermal reaction wave in the bed. The wave appears to be dissipated by conditions which promote heat transfer to the surroundings. For this reason a fluidized bed would probably be unsatisfactory. A moving bed would provide the advantages of continuous operation if the problems of solids introduction and removal at high temperature can be solved. The use of two or three batch fixed-bed reactors operated cyclically has in effect been demonstrated by the laboratory work and is therefore chosen for further discusssion.

The pyrolysis step (which may yield by-products of value) could either take place as the first part of the cycle in the chlorination reactor or be carried out as a separate operation. After chlorination the residue could be removed from the reactor by burning with dry air. The hot combustion gases could be used to preheat the chlorine and to pyrolyze a fresh batch of hulls. The heat and mass balances for this operation are presented elsewhere (Basu, 1972).

The off-gas from the chlorination step will contain CO, CO_2, N_2, Cl_2, and $COCl_2$, in addition to $SiCl_4$. The average composition should not differ substantially from that of a conventional $SiCl_4$ plant, but the composition will vary cyclically. The off-gas is cooled to a temperature low enough to condense Cl_2, $COCl_2$, and $SiCl_4$. The first two are taken as overhead from a distillation step and recycled to the process. The $SiCl_4$ product is purified by further distillation. The other off-gases, mostly CO and N_2, are scrubbed of residual chlorine and sent to a furnace. Basu (1972) also presents design calculations and a flowsheet for the recovery system.

In conclusion, the manufacture of silicon tetrachloride from rice hulls offers attractively low costs for raw materials and power. The reactors will be larger than those of a conventional plant because of the low bulk density of the rice hulls, but the lower temperature of operation and absence of the need for electrical heating is expected to lead to a reactor cost which is comparable. The separation and purification train is also expected to be about the same in cost since the off-gas will be similar in average composition. The low potential operating cost may warrant consideration of the use of silicon tetrachloride for new applications such as alkyl chlorosilane manufacture. Patent rights to this process have been assigned to the University of California.

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Permeation of Gases in Polystyrene Molded at Elevated Pressures

Atactic polystyrene was molded at pressures up to 3000 atmospheres, and the effects of this pressure history were studied by permeability measurements using helium, neon, and argon as probe molecules. The permeabilities were significantly reduced by molding at higher pressures. The diffusion coefficients decreased monotonically with molding pressure, reflecting more extensive interchain cohesion. In contrast, the solubility coefficients showed a broad minimum around a molding pressure of 1000 atm, indicating that changes in local order were induced by higher pressures. These changes were shown to affect permeation, mechanical characteristics, and other properties. An optimum molding pressure somewhat below 1000 atm is indicated for polystyrene.

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SCOPE

The growing body of work concerned with modification of polymer properties under the application of elevated pressure, reviewed recently by O'Reilly (*1*), has confirmed that this thermodynamic variable can induce major changes in polymer properties. However, only a few introductory studies (*2* to *7*) have been made of the potentially important residual effects on amorphous polymers of a high-pressure history, such as high molding pressures. Studies of this type of behavior to date have been concerned almost entirely with the residual density increase, or volume compaction effect, and with its relaxation on heating or annealing. A wider variety of techniques must be used to characterize more fully the effects of a high-pressure history in order to establish reasonable structure-property relationships. We have conducted a more extensive characterization of the effects of kilobar molding pressures on a common system-polystyrene-glasses and have reported the changes in several mechanical and relaxation properties (*8*). The observed property variations indicated that the pressure history had a strong effect on the packing and stability of the polymer structure on a molecular scale.

Further information about the nature of the polymer microstructure is presented in this paper, where diffusion and solubility measurements of simple gases were used as a molecular probe, sensitive to changes in polymer order on a scale comparable to the size of the penetrant molecule. Such measurements can be made repeatedly using probe molecules of different sizes without perturbing the inherent sample properties. The results provide information of direct importance for packaging and selective membrane separation applications. In addition, the fundamental dependence of solution and transport processes on the detailed nature of polymeric materials (*9* to