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A NEW PROCESS FOR PRODUCING
CARBON MONOXIDE AND HYDROGEN

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FINAL TECHNICAL REPORT ON
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ABSTRACT

The kinetics of phosphorus pentoxide with carbon have been studied in a fixed bed of activated carbon at temperatures between 925 and 1050°C, and at 1 atm pressure. Phosphorus pentoxide vapors were passed into the reactor with helium as a carrier gas. Principal products were carbon monoxide and phosphorus. Data acquisition was using both the differential and integral techniques. The effects of changes in particle size and density were studied. The reaction rate was found to be first order with a resulting activation energy of 45.1 Kcal/mole. The data indicated a chemical reaction controlled mechanism in the entire range of temperature with mass transfer and diffusion effects being small.

INTRODUCTION

Coal gasification processes are presently in various stages of development, ranging from those that are commercially available to those that are formulated conceptually and are yet to be tested. Several recent discoveries now in the research stage show promise. One of these discoveries is a new process conceived by Handwerk (1975) which is significantly different in concept and flexibility from existing processes. The primary products from the proposed process are equal quantities of high purity hydrogen and carbon monoxide. Hydrogen is produced by oxidation of phosphorus with steam as shown in the equation:

The phosphorus for this reaction is regenerated by reducing the resulting phosphorus oxides with carbon to produce the carbon monoxide and elemental phosphorus according to the following reaction:

The phosphorus produced here is later recycled to the oxidation step. Essentially no phosphorus is consumed. The consumed raw materials are carbon (or char) and water. The overall process had good potential for commercial coal conversion.

Reaction (1) has been extensively studied by Bruanauer and Schultz(1950). This reaction is exothermic and can be carried out in a fixed bed reactor. All reactants and products are

in the vapor phase at reactor conditions.

Reaction (2) has been demonstrated only once by Heuer and Burnha (1972). No other attempt has been made until the present work to continue the study of this reaction and no kinetic data have been published in the literature.

The primary objective of the present investigation has been to obtain basic kinetic data for reaction (2) and to study the effect of different experimental conditions on the rate of reaction.

EXPERIMENTAL SECTION

Equipment

The equipment used can be divided into three main subsystems: phosphorus pentoxide feed system, carbon reactor and receiver unit. Figure 1 shows a schematic representation of the whole system.

The phosphorus pentoxide supply system was used to regulate the appropriate concentration of phosphorus pentoxide in the gas feeding the carbon bed reactor. It consisted of a helium supply bottle and a phosphorus pentoxide vaporizer. A Parr bomb heater by Honeywell was used to control the vaporizer temperature within $\pm 0.5^{\circ}\text{C}$. The phosphorus pentoxide was placed in a 0.5 liter, three-necked Pyrex flask fitted with a thermowell, helium inlet tube and manometer attachment. The phosphorus pentoxide

used was of type 'H' crystalline form, commonly found in commerce. The flow of phosphorus pentoxide was controlled with a three way valve and it was swept into the reactor with helium. Heating tapes were used to control temperature between the vaporizer and the carbon bed reactor. The temperature of this reaction was measured with 6 inch long type K thermocouples. The flow of helium through the vaporizer was closely regulated with a Whitey metering valve and measured with a rotameter.

The entire reactor assembly consisted of a 1 inch diameter tube which was 24 inches long. The reactor tube itself was a 0.98 ID, 20 in. long, Mullite tube, welded at both ends with joints. A 14 inch long Mullite thermowell was centered into the reactor tube in which two thermocouples were placed 4 inches apart to sense the reaction temperature. Temperatures sensed by type K thermocouples were monitored with an Omega model 175 digital indicator within $\pm 2.5^{\circ}\text{F}$ overall error. The middle section of the reactor contained the packed bed of particles to be reacted. The upstream section of the reactor was filled with 1/2 inch ceramic spheres to preheat the gas mixture. The discharge section of the reactor was also filled with Mullite spheres. Both end sections were heated with 100 watt heating tapes up to 300°C . A Lindberg high-temperature electric furnace, model 5342, was used to control the temperature in the carbon-bed reactor. For safety reasons the reactor was enclosed in a fume hood.

The receiver unit consisted of two specially designed traps and a receiver bath container filled with a mixture of dry ice and acetone. Each trap was filled with 1/2 inch ceramic balls to provide high surface area of condensation. The condensable oxides and pure phosphorus are collected at the bottom of the trap. Off gases exiting from the receiver unit are passed through a sampling valve where gas samples were withdrawn for analysis in the gas chromatograph. The chromatograph had a thermal conductivity detector and a 1/8 inch diameter, 3 foot long column, packed with porapak Q thermostatted at 25°C. The carrier gas was helium at a flow rate of 60 cc/min. This column essentially analyzed CO and CO₂.

Procedure

Both the differential and integral reactors were weighed before and after each run to determine the amount of carbon reacted. Phosphorus pentoxide usage, based on prior tests, was determined as a function of vaporizer temperature and helium flow. Condensibles in the reactor discharge traps (phosphorus oxides and phosphorus) were dissolved by benzene and analyzed by standard wet chemistry techniques detailed by Zerpa (1980). The gas analysis chromatograph was calibrated for both carbon monoxide and carbon dioxide using four calibration mixtures.

The reactor was purged with helium for about two hours as the temperature was equilibrated at the desired level.

A second stream of helium, containing phosphorus pentoxide was input to the bed to begin the reaction. Most of the data runs required 120 to 180 minutes. Condensable discharge gases were collected in each of the parallel cold traps for periods between 30 minutes and one hour. Chromatograph samples were taken every fifteen minutes. After the reaction, cooling occurred under a pure helium purge.

EXPERIMENTAL RESULTS AND DISCUSSION

The primary products of the C-P₄O₁₀ reaction were carbon monoxide and phosphorus. Carbon dioxide and phosphorus tetraoxide (P₄O₈) were formed in small quantities. No other phosphorus oxides or phosphine were detected with the chemical analysis used. The presence of phosphine is unlikely since water vapors were eliminated during heat up. From the overall mass balances, an average stiochiometric ratio of C: P₄O₁₀ equal to 9.2 ± 0.54 was botained.

The experimental weight loss data for carbon was obtained in two different ways: measuring the carbon loss in the reactor by weighing the carbon before and after the run, and measuring the carbon in the outlet gases as CO and CO₂. The quantities of carbon loss obtained agreed within $\pm 3\%$. The experimental weight loss data was transformed into fractional carbon conversion and is presented in Figure 2, at different temperatures. The slope of these graphs represents the rate of reaction. The effect of temperature

on the rate is quite marked. For instance, the time required for 35% carbon conversion was drastically reduced from 200 minutes at 977°C to 90 minutes at 1050°C. The overall rate reflects the combined effects of surface reaction and gas residence time in the bed.

Solid Structure

The manner in which particle size and density change during reaction from their initial values is shown in Figure 3 and 4. These results indicate that particle diameter decreases. At 50% conversion the average ratio of the particle diameter to initial particle diameter is 0.83, which gives 0.57 for the ratio of particle volume to initial particle volume. At the same time the density decreases as shown in Figure 4. At 50% conversion the ratio of density to the initial density is 0.82. The reduction in volume is therefore more pronounced than the reduction in density. It is concluded that the reaction took place principally on the outer surface of the particle.

The limiting case of a particle reacting at almost constant density is described by the following relation:

$$\frac{d_p}{d_p} = (1 - x)^{1/3}$$

Figure 5 shows that the above relation approximates the data, particularly in the early stages of reaction.

In calculating the rate coefficient it is necessary to

have a knowledge of true surface area on which reaction occurs. This however is very difficult to measure for every reacting sample. Field (1969), Wen and Dutte (1977) and Johnson (1977) expressed the rate of reaction per unit external geometrical surface by using the surface area of a sphere of the same volume as the particle. This form is also compatible with the equations for diffusion and conduction between a particle and the gas. The external surface of a spherical particle per unit volume is given by:

$$S = \frac{6}{d_p} \quad (4)$$

By using experimental values of particle diameter and equation 4, the external surface area is calculated. The results may be adequately represented by the expresion:

$$\frac{S}{S_0} = (1 - X)^{2/3} \quad (5)$$

A comparison with experiment is shown in Figure 6. Equation 5 represents the variation of surface area with conversion that would be expected for a truly monosize group of particles reacting externally, but no particular inference need be drawn from this since there is an inevitable spread of sizes in the bed and some internal reaction is known to occur. The result is regarded here as an empirical relation to facilitate the estimation of mean surface area during reaction. The choice of two-third power law is not critical for the calculation of reaction rate. Two alternatives that have been examined, (a) $S/S_0 = 1$ and (b) $S/S_0 = (1 - X)$ give reaction rates that are respectively 17 per cent lower and 13 per cent higher than

the two-third power law when the extent of reaction is 50 per cent.

Integral Reactor

The change in concentration of phosphorus pentoxide, phosphorus, carbon monoxide and carbon dioxide as a function of residence time within the bed were studied at 925, 977, 1011 and 1050°C. The residence time was varied by alternately changing the gas flow rate (700, 1200, 1800 cc/min) or the reactor length (2.60, 10.65, 21.27 cm). The concentration of phosphorus pentoxide in the gas phase was 9.78×10^{-7} mole/cc (1 atm, 300 °K).

The amount of phosphorus pentoxide decomposed ranged up to 90%, depending on the gas flow rate, the length of the reactor tube, the temperature, and the extent of reaction.

Typical results are shown in Figure 7. The effect of temperature on the production of CO is shown in Figure 8. These results are consistent with other gasification reactions in that the production of CO increases with temperature. The effects of external mass transfer were studied based on the fact that resistance to mass transfer between the fluid stream and the outer particles surface is markedly reduced as the fluid velocity is increased. Results presented in Table 1, show almost the same degree of conversion for two beds of different depths and same contact time (space velocity). In this case, the linear velocity will be greater in the deeper bed showing small effect on degree of conversion, so, the effects of external mass transfer can be considered small. The effect of

particle size on P_4O_{10} conversion is observed in Figure 9, and is negligible. This fact also suggests that film boundary diffusion was not very important under the experimental conditions employed.

Differential Reactor

Reaction data over a small section of the bed reactor was obtained with 5g of carbon bed at 925, 949, 977, 1011 and 1050 °C., and at constant gas flow rate of 1800 cc/min (1 atm, 300 °K). At each temperature, two series of runs were made; one with a P_4O_{10} initial concentration of 6.52×10^{-7} mole/cc. A maximum of about 60% of the carbon was removed at 1050 °C. At long reaction times (180-240 min) the extraction of condensables from the cold traps was complicated by the large amounts of unreacted P_4O_{10} present.

The data in this study was correlated by the shrinking core model and first order law. Other models such as the grain model (Szekely and Evans, 1972), the homogeneous model (Wen, 1967) and the pore model (De Matos, 1978) were tested, but the one used was preferred because of its simplicity and because it correlates the data better over the range of experimental conditions.

This expression was:

$$(1 - E) \frac{dX}{dt} = b k S_o (1 - X)^{2/3} \bar{C}_A \quad (6)$$

Typical experimental values are plotted in Figure 10 as $M(x)$ against time, where $M(x) = 3 (1 - (1-X)^{1/3})$ was obtained from equation 6. The slope of these graphs may be used for obtaining the intrinsic rate constant k at different temperatures.

These values were then plotted in Figure 11 using a simple Arrhenius correlation. The resulting activation energy was 45.1 Kcal/mole and the frequency factor determined was 1.46×10^7 cm/min. The data points used in the Arrhenius plot were found to have an experimental error within $\pm 8.1\%$ with a 99% confidence limit as determined from an error analysis performed using MonteCarlo simulation. When the slope ratio in Figure 11 is compared to the ratio of initial gas concentrations, the values agreed within $\pm 5\%$ difference. This results also support the assumption of a first order law.

The high value obtained for the activation energy, around 45.1 Kcal/mole, suggests that pore diffusion was not very important. Pore diffusion in a porous solid as activated carbon is always present to some extent, however, the nature of the chemical reaction and the conditions of the experiment may will produce some hindering effects that reduce or minimize the effects of internal diffusion. If diffusion rates within the particles influenced the reaction rate, this was not manifested by change in particle size because destruction of macropores upon particle shrinking could have diminished any effect that particle size may have had. If some pore diffusion still occurs, this would be reduced by a diffusional hindering effect to the escape of CO that is formed inside the particles and to the P_{40}^{10} molecules that are trying to diffuse inside the micropores. Also because of the type of transport within the pores, a net generation of gas molecules (11 moles of product gas for 1 mole of gas reactant), results in an outward flow of gaseous products and reduces the rate of diffusion of the reactant into the solid. Similar hindered

effects have been reported by Weekman and Gorrington (1965). They reported calculated results of the effect of net generation or consumption of gas at constant pressure.

Conclusions

Based upon experimental work, it was concluded that a reaction temperature range of 925 - 1050 °C. and at atmospheric total pressure, the carbon-phosphorus pentoxide reaction data fit first-order kinetics. The activation energy of 45.1 Kcal/mole with the principal products being carbon monoxide and phosphorus. Carbon dioxide and phosphorus tetroxide were considered secondary products.

The reaction is almost entirely surface reaction controlling in this temperature range with mass transfer and pore diffusion resistance being very small.

Nomenclature

b	= stoichiometric coefficient for Carbon/ P_4O_{10}
C_A	= concentration of P_4O_{10} mole/cm ³
$\bar{C}_A$	= average concentration of P_4O_{10} mole/cm ³
C_{A_0}	= initial concentration of P_4O_{10} mole/cm ³
d_p	= diameter of particles, cm
d_{p_0}	= initial diameter of particles, cm
k	= reaction rate constant, cm/min
$M(X)$	= correlation function
S	= surface area, cm ² /g
S_0	= initial surface area, cm ² /g
T	= reaction temperature, °C
t	= time, min
X	= extent of reaction or conversion
Z	= reactor length, cm
ϵ	= void space factor
ρ	= density, g mole/cm ³

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