

THE HYDROGENATION OF CARBON DIOXIDE IN PARTS-PER-MILLION LEVELS

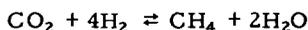
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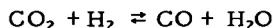
INTRODUCTION

In recent years the development of the fuel cell, a device that converts chemical energy directly into electrical energy, particularly the low-temperature, acid fuel cell that uses reformed natural gas, made it necessary to design a process that can produce a reformat gas suitable for fuel cell application.

The process is well established, but the kinetics of some of the reactions that take place during the process are not very well known. One of the reactions that could take place during the process is



However, CO may be formed by the side reaction



Early investigations of the reaction between carbon dioxide and hydrogen were either primarily qualitative in nature or attempts to determine the equilibrium of the reaction; consequently, no data suitable for kinetic analysis were presented.

The first attempt to obtain rate data for this system was made by Nicolai, d'Hont and Jungers.¹ They studied the kinetics of carbon dioxide hydrogenation on a nickel catalyst at low pressures (0.10-1.0 atm) and temperatures of 180°-300°C. Binder and White² made an extensive study of this system for the first time. The rate of the reaction was correlated by a mechanism which assumes that the major resistance to the overall process is offered by the reaction of an adsorbed carbon dioxide molecule with at least two adsorbed hydrogen molecules; thus, the surface reaction appeared to be rate-controlling. This study was extended by Dew, White and Slipevich,³ who studied the effect of total pressure and postulated a mechanism which assumes that the reaction takes place between four adsorbed molecules of hydrogen and an adsorbed molecule of carbon dioxide on the catalyst's surface.

In a search for a source of synthetic hydrocarbons, Fischer and Pichler⁴ studied the reaction between carbon dioxide and hydrogen, and carbon monoxide and hydrogen over a ruthenium catalyst. Only high-molecular-weight hydrocarbons were obtained at 100 atmospheres; methane at one atmosphere. Pichler also reported that ruthenium could not be improved by promoters or carriers. For this reason and because of its high cost, this catalyst was not tried by other investigators for the hydrogenation of carbon dioxide or carbon monoxide until a later date.

In its search for better catalysts, the Bureau of Mines^{5,6} found that ruthenium can be used on alumina in concentrations of 0.5%, at a cost no greater than commercially successful catalysts made from platinum. Ruthenium can also compete with nickel, considering the small quantities required (0.5% Ru vs. 48% Ni), and when compared to commercial nickel hydrogenation catalysts and the complexity of nickel pretreatment.

The purpose of this investigation was to obtain data over a range of temperatures, compositions, and space velocities, using a gas mixture containing carbon dioxide

(ppm) in hydrogen. Using a ruthenium catalyst impregnated on an alumina support for data at atmospheric pressure would yield an expression for the kinetics of the hydrogenation of carbon dioxide.

EXPERIMENTAL

The basic description of the experimental apparatus has been presented elsewhere.⁷ The reactor was fabricated from a 22-in.-long, stainless steel, Type-304 tube, having a 1/2-in. ID and a 1-in. OD. The thickness of the wall ensured longitudinal isothermality. A multipoint thermocouple was placed inside the bed, with three thermocouples observing temperatures at intervals of 1/4 in. A perforated screen, functioning as a catalyst support, was welded to the thermocouple rod 1 in. from the tip. A premixed mixture of carbon dioxide and hydrogen was passed through a pressure regulator and control valve to a calibrated rotameter. Then the gases entered the top of the reactor and flowed downward through the catalyst bed.

The catalyst used in this investigation was furnished by Englehard Industries, Inc., and consisted of 0.5% ruthenium impregnated on 1/8 x 1/8-in. cylindrical alumina pellets. Catalyst pellets (2 cc) dispersed in an equal volume of alumina pellets were used for every run. The catalyst was activated prior to a run sequence by passing H₂ over it at 450°C for approximately 2 hours. Because of the dispersed nature of the catalyst and the low gas concentrations, the reactor behavior was isothermal, with the temperature variance in three thermocouples never exceeding 1°C, even under conditions of maximum conversion. Steady-state conversions were achieved within 30 minutes for all variations of temperature and gas flow rate.

The product gases, after leaving the reactor, flowed through a condenser and were continuously monitored until a steady state was achieved. Two nondispersive, infrared analyzers (MSA Lira Model 300) were used to determine the concentrations of carbon monoxide and methane. The infrared analyzers were calibrated to read in the ranges of 0-100, 0-500, and 0-3500 ppm of CO and CH₄ and were never permitted to drift beyond 5 ppm on the 0-3500 ppm scale. The units were calibrated at the beginning of each run sequence (constant temperature with varying space velocities) with hydrogen used as the zero calibration gas. Five different gas mixtures were used to check the calibration scale of each of the Liras. The calibration gases were mixed and analyzed by The Matheson Co. and were accurate to within 2 ppm. All of the premixed and analyzed gases containing 1150, 2060, and 3580 ppm carbon dioxide in hydrogen were also supplied by The Matheson Co.

RESULTS

In this investigation, the runs are grouped into three different sets, each having a different feed composition: 1150, 2060, and 3580 ppm CO₂ in H₂. For each set five runs were made with varied flow rates and at constant temperature. The temperature range investigated was 200°-450°C; the gas flow rates used were 10, 30, 50, 70, and 100 cu cm/s, corresponding to the variation of residence time from 0.2 to 0.02 $\frac{\text{cu cm catalyst}}{\text{cu cm gas/s}}$. The pressure was maintained at 1 atmosphere for all the runs. Selected runs were repeated to check reproducibility and for catalyst deactivation. All the data taken were reproducible to $\pm 2\%$; no noticeable decrease in the catalytic activity was observed over the runs' durations.

Each run was obtained under steady-state conditions and consisted of an analysis of effluent gases at a given feed rate, temperature, pressure, and the quantity of the catalyst: The duration of each run was approximately 40 minutes. The quantity of the catalyst was kept constant throughout all the runs. The effects of the variables involved are discussed below.

Effect of Temperature. The number of moles of carbon dioxide converted per mole of carbon dioxide in the feed gas for all gas mixtures, and the corresponding number of moles of methane and carbon monoxide formed for selected gas mixtures at different temperatures are shown in Figures 1-5.

The production of methane per mole of CO₂ fed is maximum for the gas mixture containing 1150 ppm CO₂: The ratio reaches 1 at temperatures around 450°C and a residence time of $0.2 \frac{\text{cu cm catalyst}}{\text{cu cm gas/s}}$. The conversion of carbon dioxide and the production of methane and carbon monoxide exhibited characteristic S-shaped curves, showing an increase in conversion with an increase in temperature.

The formation of carbon monoxide is favored by an increase in temperature; however, at temperatures below 350°C there is negligible formation. Above this temperature, the amount of carbon monoxide in the effluent progressively increases.

At higher temperature ranges note that all three gases exhibit asymptotic behavior regarding conversions. It is apparent that the selection of a temperature range for this experiment almost spans the entire range for carbon dioxide methanation at these concentrations.

Effect of Feed Gas Composition. The effect of feed gas composition on hydrogenation reactions is significant over the ruthenium catalyst. The carbon dioxide conversion increases with decreasing amounts of carbon dioxide in the feed gas at any temperature and for all residence times. The asymptotic values of conversion decreased from ~1 for 1150 ppm CO₂ to about 0.8 for 3580 ppm CO₂. The amount of methane produced per mole of carbon dioxide in the feed also increases with the decrease in amount of carbon dioxide in the feed gas. It was interesting to note that the formation of carbon monoxide increases with an increase in the concentration of carbon dioxide in the feed. Consequently, the conversions may be increased by either raising the temperature to ~450°F, or by decreasing the amount of carbon dioxide in the feed gas.

Effect of Residence Time. In each case the conversion of carbon dioxide increases with an increase in residence time. At any given temperature, the production of methane also increases with an increase in the residence time. This would naturally indicate conventional reactor behavior.

However, the effect of residence time on the formation of carbon monoxide displayed a rather unconventional characteristic. Figure 5 shows an increase in the formation of carbon monoxide with a decrease in residence time over the entire range of temperatures and concentrations investigated.

DISCUSSION

It appears possible that the following reactions are taking place:



Several investigators have shown^{2,3} that, at higher concentrations of carbon dioxide in the feed, the methanation of carbon dioxide takes place directly by Reaction 1; carbon monoxide is formed by the side reaction, Reaction 2. It appears from our results that the methanation of ppm concentrations of carbon dioxide does not occur directly by Reaction 1, since we found that at any particular temperature carbon monoxide is produced by increasing the flow rate. This would mean that the reverse shift reaction (Reaction 2) reaches equilibrium almost instantaneously; the

methanation of carbon monoxide proceeds with time. More carbon monoxide is produced (Reaction 2) as the methanation of carbon monoxide takes place until the steady-state condition is reached. Nicolai, d'Hont and Jungers¹ pointed out that carbon dioxide does not react in the presence of carbon monoxide. In one of the studies at the Institute of Gas Technology¹⁰ on the selective methanation of carbon monoxide using a gas mixture containing hydrogen, carbon dioxide, and carbon monoxide, it was also pointed out that ruthenium is the best selective methanation catalyst and that the reaction of carbon dioxide does not proceed in an appreciable amount until the level of carbon monoxide in the mixture reaches a certain minimum level. In the present investigation this is indeed the case. As soon as the carbon monoxide methanation reaches a steady state, leaving the concentration of carbon monoxide in the reacting mixture above this minimum, the conversion of carbon dioxide ceases completely, as indicated by Figures 1-3.

For finding the overall empirical rate expression valid for the change of conversion and corresponding rate constants at various temperatures for these reactions, an expression of the type

$$-r_{\text{CO}_2} = kC_{\text{CO}_2}^n$$

was tried for reasons given by Levenspiel,⁸ who suggested the use of simple empirical rate expressions in chemical reactor design work. The use of such a power law rate equation is also supported by catalytic combustion studies at U.C.L.A.⁹ Although the reaction rate should depend upon the concentration of hydrogen in addition to the concentration of carbon dioxide in the system, this term has been omitted from the rate expression used here, since hydrogen is in excess and is treated essentially as a constant.

The rate expression can also be stated in a different form

$$-r_{\text{CO}_2} = -\frac{dC_{\text{CO}_2}}{\left(\frac{V}{V_0}\right)} = kC_{\text{CO}_2}^n$$

which, when integrated, yields the expression -

$$k(n-1) \frac{V}{V_0} = C_{\text{CO}_2}^{1-n} + (C_{\text{CO}_2})_0^{1-n} \text{ for } n \neq 1$$

$C_{\text{CO}_2}^{1-n}$ was plotted against $\frac{V}{V_0}$ for various values of n . The value of n giving the best straight line was used as the reaction order for the hydrogenation of the carbon dioxide reaction. The rate constants could then be calculated from the slopes of the lines. The best value of n was found to be 1.5. A typical plot of $C_{\text{CO}_2}^{1-n}$ versus $\frac{V}{V_0}$ for this value of n is shown in Figure 6 for a feed of 1150 ppm CO_2 .

The reaction velocity constant is related to the reaction temperature in accordance with the Arrhenius equation

$$k = k_0 e^{-E/RT}$$

The Arrhenius plots for this reaction are given in Figure 7. The empirical frequency factor, k_0 , and the activation energy for this reaction are tabulated in Table 1. All of the Arrhenius plots are linear in the temperature range considered.

Table 1. ACTIVATION ENERGIES AND SPECIFIC REACTION RATE CONSTANTS AS A FUNCTION OF THE INLET-GAS COMPOSITIONS

Concentration of CO ₂ in Feed, ppm	E, kcal/ mole	k ₀ , $\frac{\text{cu cm gas (ppm CO}_2\text{)}^{-0.5}}{\text{cu cm catalyst/s}}$
1150	10.8	5700
2060	11.4	4250
3580	11.5	2800

Unlike the methanation of carbon monoxide on ruthenium,⁷ where only one Arrhenius plot was obtained for all the concentrations of carbon monoxide, three different plots are obtained for the three concentrations of carbon dioxide considered. This can be explained by the way in which the methanation of carbon dioxide takes place. Since it occurs by the reverse shift reaction, all we are dealing with is the methanation of carbon monoxide and the effect of the various amounts of carbon dioxide on such a reaction. Thus the decrease in k values, due to an increase in the concentration of carbon dioxide in the feed, can be compared to Cohen and Nobe's¹¹ work dealing with the effect of an increasing concentration of water vapor on the catalytic oxidation of carbon monoxide on nickel oxide. (This phenomenon is explained below.)

Every catalyst has a number of active sites where the reaction takes place. In the case of the hydrogenation of carbon dioxide these sites are occupied by carbon monoxide, which is reacting with hydrogen to form methane, and by carbon dioxide, which remains unreacted. As the concentration of carbon dioxide is increased, more of the sites are occupied by unreacted carbon dioxide, thus making fewer sites available for the reaction of carbon monoxide. Therefore, one would expect a decrease in the reactivity of carbon monoxide with hydrogen to form methane when carbon dioxide is present in the reacting mixture. This effect of increasing the amount of carbon dioxide is reflected in the decreasing values of the reaction constant, k.

CONCLUSION

The hydrogenation of carbon dioxide at very low concentrations over a 0.5% ruthenium catalyst was studied. The empirical rate expression, valid for the change of conversion of CO₂ in the overall reaction, was found to follow the simple expression

$$-r_{\text{CO}_2} = k \text{CO}_2^{1.5}$$

where k obeyed the Arrhenius temperature dependence for each concentration at all temperatures.

The methanation of carbon dioxide took place in two steps: the formation of carbon monoxide and the subsequent hydrogenation of carbon monoxide to methane. The effect of an increasing amount of carbon dioxide in the feed was reflected in the decreasing values of the reaction constant, k.

ACKNOWLEDGMENT

The authors wish to thank the Institute of Gas Technology which sponsored this work through its basic research program.

NOMENCLATURE

- C_A = concentration of species A in effluent, ppm
- (C_{A_0}) = concentration of species A in feed, ppm
- E = activation energy, cal/g-mole
- k = reaction rate constant, $\frac{(\text{cu cm gas})(\text{ppm CO}_2)^{-0.5}}{(\text{cu cm catalyst})(\text{s})}$
- k_0 = Arrhenius frequency factor, $\frac{(\text{cu cm gas})(\text{ppm CO}_2)^{-0.5}}{(\text{cu cm catalyst})(\text{s})}$
- n = reaction order
- r_A = rate of change of conversion of species A, $\frac{(\text{cu cm gas})(\text{ppm CO}_2)}{(\text{cu cm catalyst})(\text{s})}$
- R = gas constant, cal/mole - °K
- T = temperature, °K
- v_0 = volumetric flow rate of gas, cu cm/s
- V = volume of catalyst, cu cm
- x_A = moles of A converted or produced per mole of CO₂ in feed

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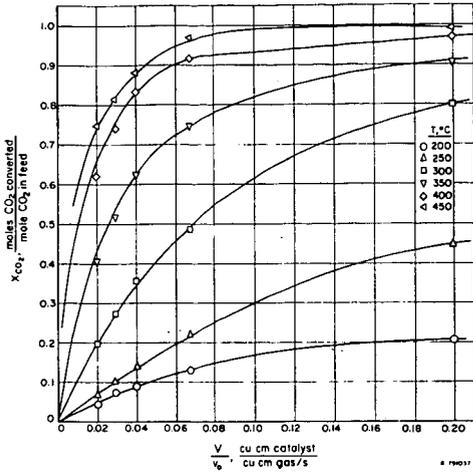


Figure 1. CONVERSION OF CO₂ AS A FUNCTION OF RESIDENCE TIME FOR 1150 ppm FEED GAS

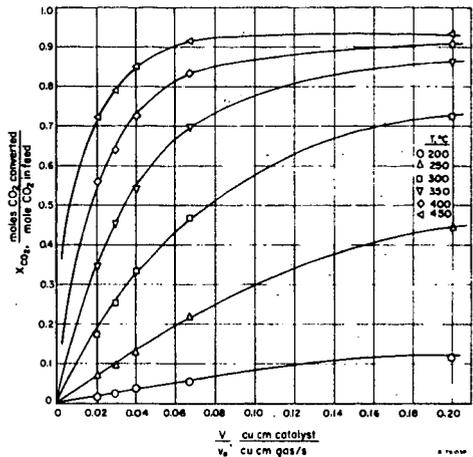


Figure 2. CONVERSION OF CO₂ AS A FUNCTION OF RESIDENCE TIME FOR 2060 ppm FEED GAS

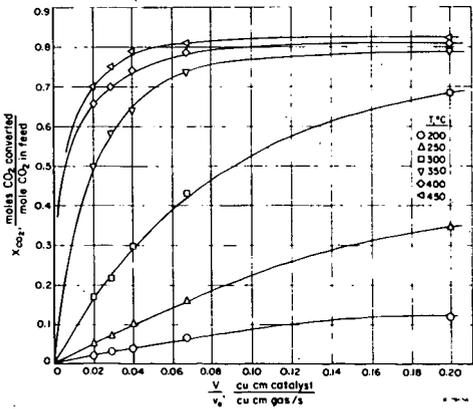


Figure 3. CONVERSION OF CO₂ AS A FUNCTION OF RESIDENCE TIME FOR 3580 ppm FEED GAS

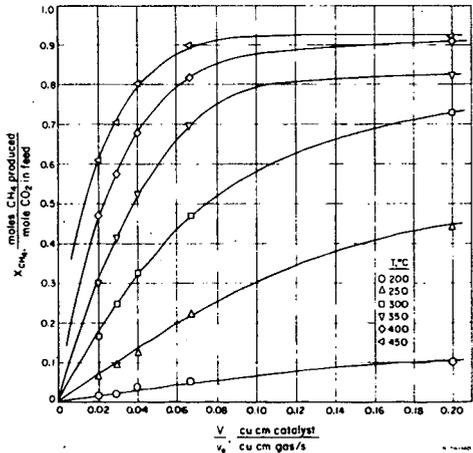


Figure 4. PRODUCTION OF CH₄ AS A FUNCTION OF RESIDENCE TIME FOR 2060 ppm FEED GAS

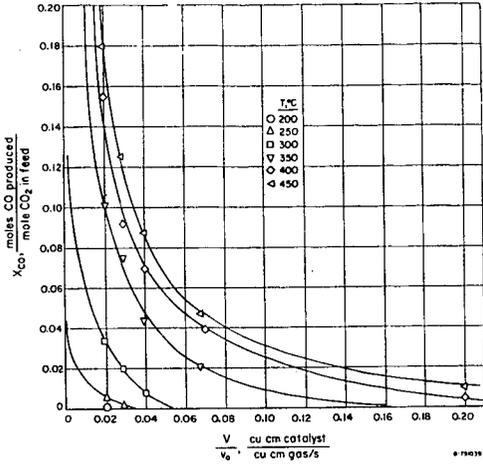


Figure 5. CO PRODUCTION AS A FUNCTION OF RESIDENCE TIME FOR 3580 ppm FEED GAS

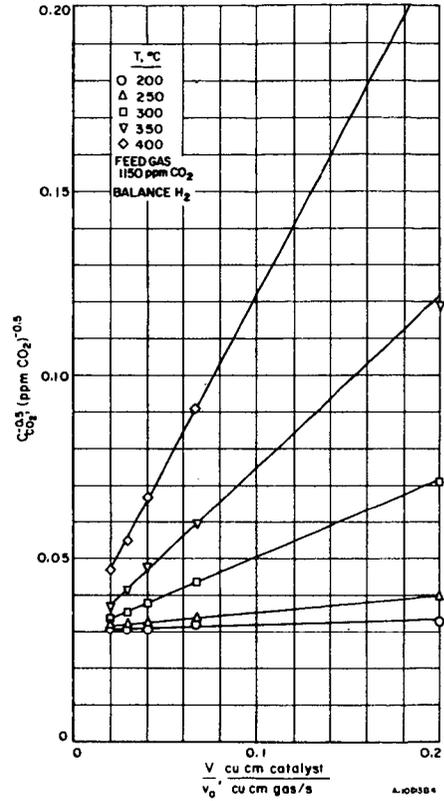


Figure 6. VARIATION IN $C_{CO_2}^{-0.5}$ WITH RESIDENCE TIME FOR 1150 ppm FEED GAS

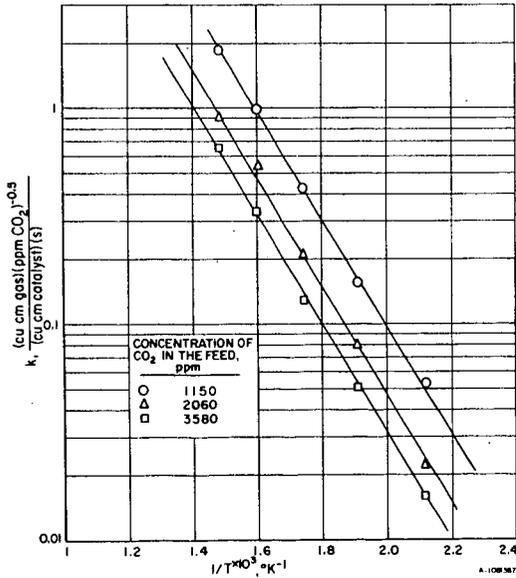


Figure 7. ARRHENIUS PLOT FOR HYDROGENATION OF CO_2

METAL HYDRIDES AS A SOURCE OF HYDROGEN FUEL

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Hydrogen has the potential of being a cheap and non-polluting fuel which could be used in a variety of energy converters. It is particularly attractive for use in fuel cells, where it is the preferred fuel, but it could also be used in any type of combustion engine, although in the latter case some modification of conventional designs would be required. However, a major problem involved in using hydrogen as a common fuel is the difficulty encountered in storing and transporting it. To store and transport hydrogen as a cryogenic liquid or as a compressed gas for such use does not appear practical either from an economic or a safety standpoint.

Recent studies¹⁻³ on the equilibrium relationships between hydrogen and certain metals and alloys suggest that the reversible metal hydrides formed in these systems may serve as a convenient, safe, and cheap means of storing hydrogen. In this regard the use of magnesium hydride as a source of hydrogen fuel for internal combustion engines has already been discussed.⁴ The object of this paper is to describe how such metal hydrides may be used to supply hydrogen for use as a fuel in an electrochemical cell.

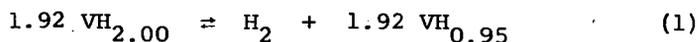
In its most simple form such a storage system consists of a vessel containing a reversible metal hydride of the type described below, a means by which heat may be added to or removed from the system, and a tap for withdrawing or adding hydrogen gas. In operation, as hydrogen is withdrawn from the system, the hydrogen pressure drops below the equilibrium dissociation pressure of the metal hydride which will then dissociate in order to re-establish equilibrium conditions. During the hydrogen evolution step heat must be added to the system since the dissociation reaction is endothermic. Dissociation will continue under these conditions as long as the designated hydride phase exists (it is possible to have more than one hydride phase present in certain systems). In order to regenerate the hydride the procedure is reversed; hydrogen is added to the

system and the hydrogen pressure is maintained above the dissociation pressure. Heat must be removed from the system during this step.

In Table 1 the pertinent properties of three candidate metal hydrides are listed and can be compared to corresponding figures for cryogenic and compressed gas storage. These compounds are vanadium dihydride (VH_2), magnesium nickel hydride (Mg_2NiH_4) and MgH_2 . It is interesting to note that on a volume basis the hydrogen content of the solids is greater than that of liquid hydrogen and much greater than that of compressed hydrogen at 100 atm. pressure and 25°C . We wish to point out that a detailed discussion of the properties and synthesis of these compounds has already been given;¹⁻³ here we shall only discuss these properties briefly and in connection without particular intent.

Vanadium Dihydride - A Low Temperature Hydrogen Reservoir

Vanadium dihydride is capable of supplying hydrogen at a pressure of >1 atm. to a fuel cell at any temperature above $\sim 10^\circ\text{C}$. It has a grey metallic appearance, is very brittle and can easily be ground to a fine powder. It is not pyrophoric, indeed in the presence of air its decomposition is inhibited. It can be synthesized by the direct reaction of hydrogen with the metal or with vanadium monohydride. It will decompose to form vanadium monohydride and hydrogen as follows:³



A plot showing the equilibrium dissociation pressure (P_d) vs composition, expressed as the ratio of H atoms/total metal atoms (H/M), is shown in Fig. 1. Reaction (1) refers to the reaction taking place in the plateau region which lies between the limits $\text{VH}_{0.95}$ - $\text{VH}_{2.00}$. In this region the P_d is essentially constant and not dependent on the solid composition. Above $\text{VH}_{2.00}$ the isotherm does not rise vertically but has a slight slope to the right which is due to the nonstoichiometric character of vanadium dihydride. Below a composition corresponding to $\text{VH}_{0.95}$ the P_d drops precipitously as only the vanadium monohydride phase is present which is quite stable.

The dissociation pressure (P_d) of VH_2 is very sensitive to the type and amount of impurities present in the starting vanadium. Thus, it has been found that the P_d of VH_2 made from commercial grade vanadium (Union Carbide Corp., Materials System Division) was higher by a factor of >2 than that made from high purity vanadium.³ Since a higher P_d is desirable for our purposes we shall specify that the VH_2 used in the systems described here be made from commercial vanadium; the data presented here has been obtained with VH_2 using this as the starting material. Qualitative observation also indicated that these impurities have a catalytic effect, increasing both the rate of decomposition and formation of VH_2 .

A plot of the reciprocal temperature vs the P_d for the composition range $VH_{0.95}$ to $VH_{2.00}$ yields a straight line (Fig. 2) which obeys the equation $\log P_{atm} = \frac{-1989}{T_{oK}} + 7.3795$. From these data the following thermodynamic quantities for reaction (1) can be calculated:

$$\Delta H_{298} = +9.10 \text{ Kcal}$$

$$\Delta S_{298} = +33.76 \text{ eu}$$

$$\Delta F_{298} = -0.96 \text{ Kcal}$$

Thus, the decomposition of VH_2 is endothermic and heat must be supplied. However, at 298°K the free energy change is negative and the reaction is spontaneous. Even at a temperature as low as 0°C the equilibrium dissociation pressure is slightly above 1 atm. (1.25 atm.). Consequently, VH_2 can supply hydrogen at a usable pressure by extracting heat from the surrounding environment if the ambient temperature is above 0°C . While this may be convenient in certain circumstances it is probably more efficient to utilize the waste heat of the energy converter to effect decomposition.

An idealized schematic of an integrated H_2 -air fuel cell and a table of compatible metal hydride-fuel cell systems is shown in Fig. 3. As an example of a low temperature system, consider a fuel cell of the type described previously by Bartosh⁵ but with H_2 supplied by the decomposition of VH_2 . The cell was a 500-watt H_2 -air cell operating at 74°C with an aqueous KOH electrolyte. Hydrogen originally was supplied by a companion reforming-purification unit which required a low sulfur, hydrocarbon feed. The volume of the reforming unit was 1.4 ft^3 .

weighed 47 lb, including fuel and water, and at maximum cell power the rate of H_2 feed was 0.0632 lb/hr or 14.23 g mole/hr. We may replace the reformer with a reservoir containing VH_2 and at this rate of consumption, 14.45 Kg (31.8 lb) of VH_2 will last 10 hr. The volume of the fuel reservoir required for this amount, assuming a 50% void space, is 5.78 l (0.20 ft³). The amount of energy required to provide the heat of dissociation is 129.5 Kcal/hr (513 Btu/hr). The waste heat generated by the cell, at 55% efficiency, is 351 Kcal/hr (1393 Btu/hr). The only significant difference between the cell described here and that of Bartosh is that we propose to have a circulating electrolyte which is used to transfer the waste heat of the cell to the hydride bed. Considering that the waste heat is in excess by a factor of almost 3 over that required to dissociate VH_2 and the large temperature difference between the hydride bed and the fuel cell, it is quite possible that simpler means of heat transfer would suffice, e.g. locating the hydride bed in an air stream previously used to cool the fuel cell. Thus, the design as shown in Fig. 3 appears quite conservative and allows a considerable degree of flexibility.

As far as start-up procedure is concerned, we would note that the dissociation pressure of VH_2 is high enough to supply hydrogen at the cell operating pressure of 28 psia down to ambient temperature of 7°C. Of course, the bed will tend to cool as the hydride decomposes and the pressure will drop, but the sensible heat of the bed should be sufficient to supply the heat required until some heat is available from the cell. In addition as the bed cools below the ambient temperature some heat will be extracted from the surrounding environment.

When the VH_2 content of the reservoir is exhausted it can be regenerated by supplying H_2 at a pressure of >200 psia at a bed temperature of 25°C. It is necessary to conduct the regeneration reaction at a pressure substantially above the P_d since there is appreciable hysteresis in the system. Further, the rate of regeneration at any fixed temperature is pressure dependent and pressures of 200-300 psia above the P_d are recommended to attain reasonably fast reaction rates. In the latter case qualitative observation suggests that the hydride can be 90% regenerated in about 1 hr, provided sufficient cooling capacity is available to maintain the bed at 25°C.

It is possible to adapt the hydride storage concept to a more conventional scheme also shown in Fig. 3. In this case VH_2 is used to provide a ballast effect in a reformer system. Hydrogen is manufactured from a hydrocarbon fuel and purified in the usual manner by passing it through palladium-silver membrane. The hydrogen may be conducted to the hydride reservoir to regenerate VH_2 , or directly to the fuel cell, or both. Under peak loads the system can be designed so that some VH_2 will decompose to supply the required extra hydrogen. If the fuel cell operation is intermittent, the hydride reservoir may carry most of the load during cell operation and is regenerated when the cell is down. Such an arrangement has several advantages over conventional hydrocarbon reforming-fuel cell systems which are summarized as follows:

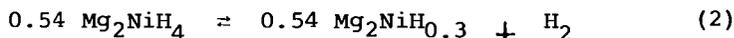
1. The reformer size is determined by the average hydrogen consumption, not peak consumption.
2. The size of the palladium silver diffuser is also determined by the average hydrogen consumption.
3. The reformer can be run continuously and hydrogen stored in the hydride bed for future use.
4. The VH_2 bed can supply H_2 immediately upon start-up.

The actual design of such a system will depend a great deal upon the use pattern envisioned for the fuel cell. However, it can be seen that the incorporation of a relatively small hydride reservoir should result in a practical fuel cell system having a greater degree of flexibility than any previously known.

High Temperature Systems

Both the Mg_2NiH_4 and MgH_2 may be considered in the present context as high temperature systems. They cannot abstract the heat required for decomposition from the environment; rather, such heat must come from the waste heat of the energy converter, provided its operating temperature is high enough, or from some other high temperature heat source. The most efficient arrangement is to use the waste heat of the converter and we will limit our discussion to that particular alternative.

Mg_2NiH_4 is a rust-colored powder having a non-metallic appearance. It is not pyrophoric and it decomposes slowly in water but rapidly in a slightly acidified solution. A pressure composition isotherm for the Mg_2NiH_4 system is shown in Fig. 1. Unlike VH_2 almost all the hydrogen is available except for a small amount which dissolves in the Mg_2Ni decomposition product. The decomposition reaction is as follows:



A plot of the dissociation pressure vs the reciprocal temperature is shown in Fig. 4. It is a straight line and obeys the relationship $\log P_{atm} = -3360/T^{OK} + 6.389$. For reaction (2) the following thermodynamic values have been determined²:

$$\Delta H_{298^{\circ}} = +15.4 \text{ Kcal}$$

$$\Delta F_{298} = +6.7 \text{ Kcal}$$

$$\Delta S_{298} = +29.2 \text{ eu}$$

The reason for including Mg_2NiH_4 in this discussion is that it could be used to supply hydrogen to Bacon type fuel cells operating near $300^{\circ}C$. The high cell temperature would require that the electrolyte be a highly concentrated KOH solution (at least 85 wt % KOH). The advantage of Mg_2NiH_4 over VH_2 in this situation is that it contains 3.3 wt % available hydrogen vs 2.1 wt % for the latter. However, it is only useful in a relatively narrow temperature range from $\sim 275^{\circ}C$ where its P_d is 1.81 atm. to $325^{\circ}C$ at which point the P_d of MgH_2 is 2.8 atm. The latter, of course, contains much more hydrogen on weight basis and for this reason would be the preferred fuel. Unfortunately Bacon type cells operate at temperatures which are too low to utilize the waste heat in order to dissociate MgH_2 . Thus, making the assumption that Bacon cells were available of the same rating and H_2 fuel requirement as the low temperature cell discussed above, the equivalent amount of Mg_2NiH_4 necessary would be 8.56 Kg (18.8 lb) and would require a reservoir volume of 6.66 liters (0.23 ft^3) assuming a 50% void space. The hydride regeneration procedure is similar to that previously described for VH_2 except that the regeneration temperature should be above $250^{\circ}C$ in order to attain an acceptable reaction rate.

For high temperature fuel cells such as those using molten carbonates or solid electrolytes, MgH_2 could be used as the source of hydrogen fuel. However, the preparation of pure MgH_2 by direct reaction with hydrogen is difficult and requires a temperatures of $\sim 400^\circ C$ and ~ 100 atm. pressure.⁴ In addition, the product is quite inert. However, it has been found that if a magnesium alloy containing 5-10 wt % Ni or Cu is used as the starting material the synthesis reaction is greatly accelerated and the product very active.^{1,2} For hydrogen storage purposes, an alloy of 95% Mg and 5% Ni is recommended. Hydrogen will react with this material to form both MgH_2 and Mg_2NiH_4 . Decomposition will take place in two steps; first Mg_2NiH_4 decomposes as shown above in reaction (2), followed by the known reaction:



A pressure composition isotherm for such a system is shown in Fig. 1. The short upper plateau is due to the presence of Mg_2NiH_4 .

A plot of the P_d vs the reciprocal temperature for MgH_2 is shown in Fig. 4. It is a straight line and can be represented by the equation $\log P_{atm} = -4045/T + 7.224$. Assuming Mg_2NiH_4 (or Mg_2Ni) acts purely as a catalyst and that there is no solubility of H_2 in the Mg phase, the following thermodynamic functions have been calculated for reaction (3):²

$$\Delta H_{298^\circ K} = +18.5 \text{ Kcal}$$

$$\Delta F_{298^\circ K} = +8.7 \text{ Kcal}$$

$$\Delta S_{298^\circ K} = +33 \text{ eu}$$

The equilibrium dissociation pressure of MgH_2 at $325^\circ C$ is 2.85 atm. and this material could be used in any system provided the waste heat could be extracted at that temperature or above. It appears to be quite suitable for high temperature cells using molten carbonate electrolytes which operate above $400^\circ C$. However, since the optimum MgH_2 temperature is about $350^\circ C$ ($P_d = 5.4$ atm.), the fused salt electrolyte cannot be used as a heat transfer medium because this temperature is about $50^\circ C$ below the melting point of the lowest melting eutectic mixture of sodium,

lithium and potassium carbonates. The operation of the metal hydride reservoir at 400°C, where the P_d is 16.4 atm., is not recommended because it is in a temperature and pressure region where the strength of materials may be a problem and leaves no safety margin as far as the molten salt is concerned. Thus a secondary heat transfer medium would have to be used, perhaps a liquid metal (e.g. mercury or sodium), or gas (i.e. air).

The great advantage of MgH_2 is, of course, its high hydrogen content. In this case, in order to power a high temperature cell, similar to the 500-watt cell described above, the total weight of material (91.2% MgH_2 , 8.8% Mg_2NiH_4) required to give the same operating characteristics would be 3.950 Kg (8.69 lb), having a volume (50% void space) of about 5.4 liters (0.19 ft³). Because of the presence of the ternary hydride, the hydrogen content of the mixture is 7.3 wt % rather than 7.6 wt % as it is in pure MgH_2 . In calculating the volume we made no correction for the probable increase in density resulting from the presence of Mg_2NiH_4 and have assumed the density of the mixture is the same as that of pure MgH_2 , i.e. 1.45 g/cc.

A hydride reservoir containing Mg_2NiH_4 or MgH_2 could also be used to give a ballast effect in a reformer system as described above using VH_2 . The higher hydrogen content of these compounds vs VH_2 is somewhat offset by the higher decomposition temperature required for the former, otherwise the same advantages would accrue as those enumerated above.

Conclusions

We have shown how several reversible metal hydride systems may be used to supply hydrogen to several types of electrochemical fuel cells. In our judgment VH_2 is the preferred material for such use because of its convenience, flexibility and the ease with which it could be integrated with the most advanced fuel cell type, i.e. aqueous, low temperature systems. However, the large hydrogen content of MgH_2 could be a determining factor in certain circumstances where weight may be an over-riding consideration. The ternary hydride Mg_2NiH_4 is of interest primarily because it could be used in conjunction with high temperature Bacon cells.

It is our contention that these compounds have the potential to solve a serious and long-term problem associated

with the development of a practical and economical fuel cell, i.e. the storage and generation of hydrogen. It is also apparent that they could be used in a number of alternative schemes not discussed here, where these properties would constitute an important advantage and improvement.

Acknowledgment

The authors wish to thank Messrs. J. B. Hughes and A. Holtz for their expert assistance in the laboratory.

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Table 1

	<u>VH₂</u>	<u>Mg₂NiH₄</u>	<u>MgH₂</u>	<u>H₂ Gas</u>	<u>Liq. H₂</u>
Available Hydrogen Wt %	2.1	3.3	7.6	100	100
Density g/ml	~5	2.57	1.45	7.2×10^{-3}	7×10^{-2}
Available Hydrogen g/ml of Volume	0.105	0.085	0.110	7.2×10^{-3}	7×10^{-2}

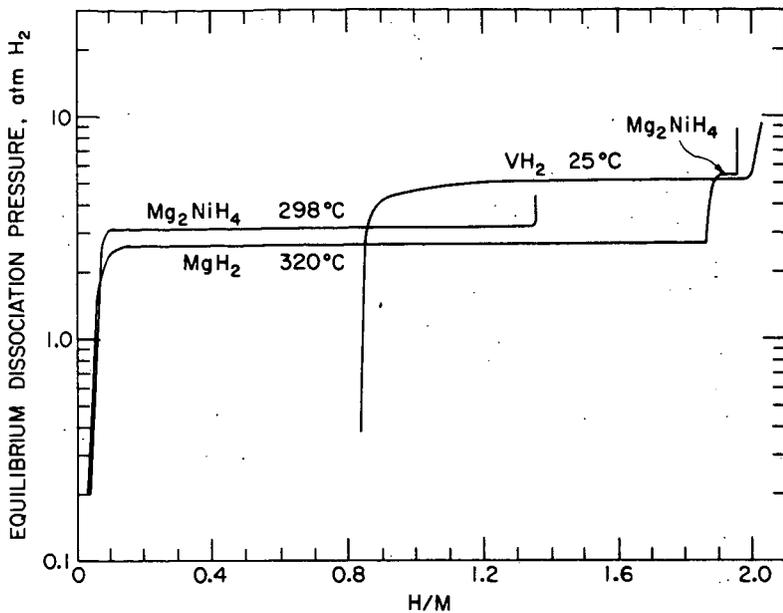


Fig. 1
Pressure-Composition Isotherms
for Systems Indicated.

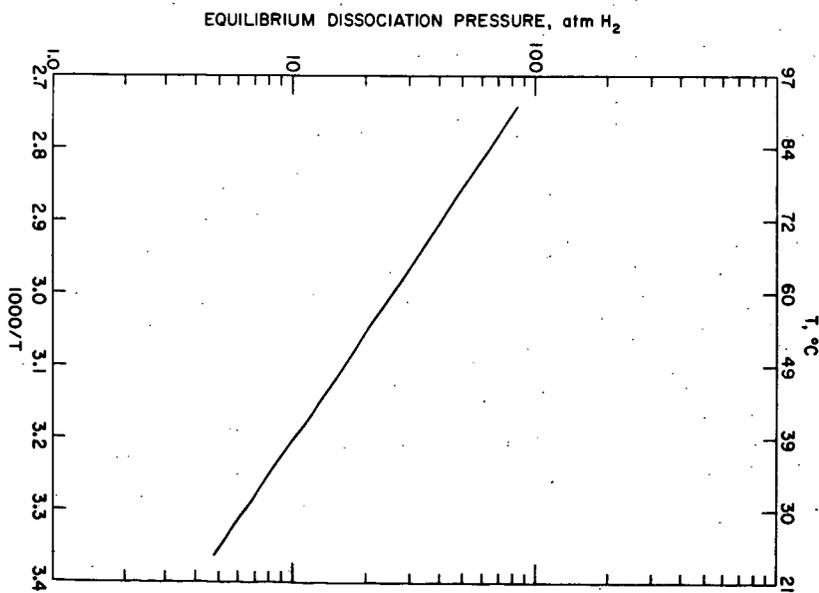
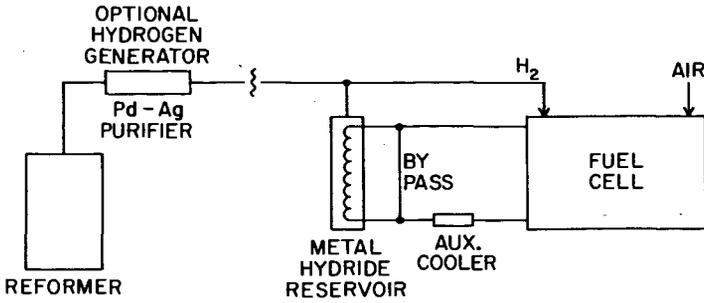


Fig. 2
Equilibrium Dissociation Pressure
of VH₂ vs 1000/T^oK



METAL HYDRIDE	TEMP. °C	EQUIL. PRESS. atm	FUEL CELL	
			TEMP. °C	H ₂ FEED PRESS. atm
VH ₂	25	5	75	2
Mg ₂ NiH ₄	290	2.6	300	"
MgH ₂	340	5	>400	"

Fig. 3
Schematic of Integrated
Metal Hydride - Fuel Cell System

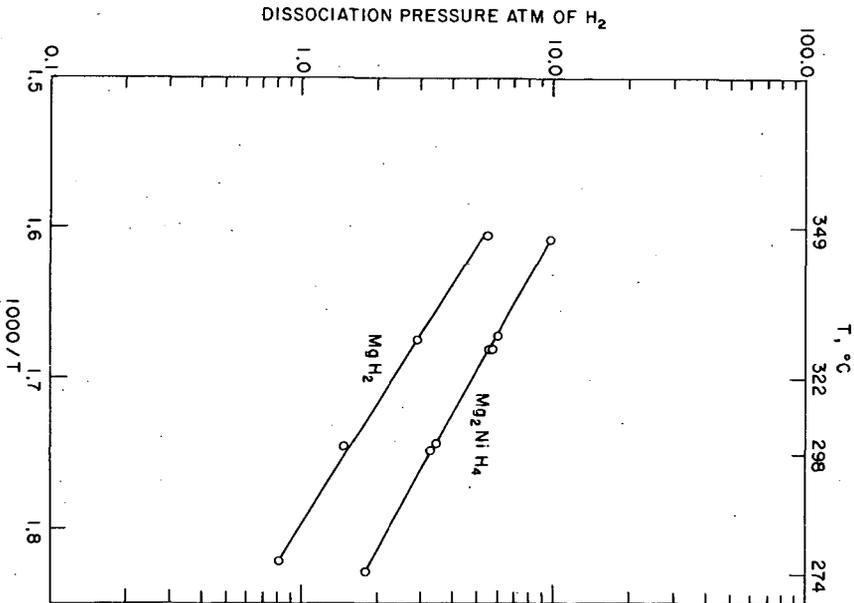


Fig. 4
Dissociation Pressure of
MgH₂ and Mg₂NiH₄ vs 1000/T⁰K

SELF-HEATING OF CARBONACEOUS MATERIALS

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INTRODUCTION

For quite a few years, Great Lakes Carbon Corporation has produced semi-calcined petroleum coke on a commercial scale. This coke is calcined to a maximum temperature of about 1600°F. For many years previous to this, both raw petroleum coke and fully calcined petroleum coke were handled in quantity and essentially no difficulty was encountered with spontaneous combustion. However, experience has demonstrated that semi-calcined coke is much more liable to spontaneous combustion and special precautions are necessary in handling this material. The present investigation was undertaken in connection with this phenomena.

Because of the importance of spontaneous combustion, particularly with respect to the storage of certain coals and lignites, quite a number of investigations have been conducted. There were a number of investigators who worked early in this century. Among the earliest workers to study the self-heating of coal under adiabatic conditions were Davis and Byrne⁽¹⁾. In their investigation the sample was charged to a vacuum insulated container which was surrounded by an oil bath controlled to follow the temperature of the sample under test. All of their investigations

were conducted using dry coal and dry oxygen. The tests were started at approximately 70°C and usually terminated at about 140°C. They concluded that the heating tendencies of coals high in oxygen are greater in general than those of coals low in oxygen, although the heating tendency is not in all cases proportional to the oxygen content. The heating tendencies of coals of a similar rank are approximately the same. More recent work was done by Heusinger and Muenzner⁽²⁾. In their study tests were made at different starting temperatures with coal of high pyrite content. At >70°C, they found that the heat of oxidation in air gave a temperature rise which would lead to self-ignition in a few days.

In 1928, Rosin⁽³⁾ published a very comprehensive article concerned with spontaneous combustion of semi-coke from brown coal. He pointed out the difference between ignition temperature and liability to spontaneous combustion which are often confused. Ignition temperature is the temperature at which ignition takes place under defined conditions, and is dependent upon the conditions. Liability to spontaneous combustion is a property possessed by a substance of heating spontaneously to the ignition temperature whereupon combustion ensues. A low ignition temperature is not the primary cause of spontaneous combustion. The quantitative work conducted by Rosin required rather large samples of coke - approximately 24 pounds which were held in insulated containers. Rosin recognized the importance of moisture and of humidity control, although it is not clear to what extent humidity was

controlled in the gases passed over the semi-coke. He concluded that moist, semi-coke absorbs more oxygen than dry semi-coke, and that it is more liable to spontaneous combustion. Also, that semi-coke is an activated carbon containing unsaturated compounds which absorb oxygen and that the absorption raises the temperature of the semi-coke to a temperature of dangerous oxidation, which finally results in combustion. Based on the work of others, he concluded the heat of wetting is sufficient to raise the temperature of semi-coke to the temperature of dangerous oxidation.

The use of D. T. A. for classifying coals on the basis of their self-heating characteristics was fully investigated by Banerjee and Chakravorty⁽⁴⁾.

The present paper is concerned with the measurement of the self-heating rates of carbonaceous materials when exposed to a stream of nitrogen, oxygen or CO₂ with controlled humidity.

EXPERIMENTAL WORK

Description of Apparatus

In designing the equipment the objective was to provide simple apparatus sufficiently well insulated so that the rather small heat of absorption or reaction could be followed by the rise in temperature of the carbonaceous material under test. It was desired to accomplish this without the necessity of having the ambient temperature closely follow the temperature rise of the sample, and without the necessity of using a very large sample.

A sketch of the apparatus is shown in Figure 1. It consists of a one-quart, wide mouth Dewar flask in an oven which may be held at constant temperature. The gases, nitrogen, oxygen or carbon dioxide, were supplied from tanks and the flow measured with a rotameter at room temperature. The gas then flowed to a flask filled with water, fitted with an electric heater in which the gas was dispersed by means of a fritted disc and allowed to rise through the water so as to saturate it.

Heat input was automatically controlled by the water temperature. The water saturated gas then flowed through a coil contained within the temperature controlled oven just ahead of the Dewar flask. The temperature of the gas was measured just prior to its entrance into the Dewar flask, using a thermocouple. A thermocouple was also mounted approximately one inch from the bottom of the sample contained in the Dewar flask. The steel tube which supplied the gas stream to the Dewar flask was fitted with a perforated platform at its base which closely fitted the inside diameter of the Dewar flask. The sample was placed on the platform which provided distribution of the gas.

In early tests some difficulty was encountered in obtaining satisfactory Dewar flasks due to insufficient insulation. Prior to placing a Dewar flask in use, its behavior was checked using a standard sample. It was found that heavy walled Pyrex Dewars were best for this particular application, as they provided maximum insulation.

The silvered Dewars used were 70 mm. I. D., 90 mm O. D., 250 mm. deep and contained no separation pads at the base. The evacuation was approximately 1×10^{-7} mm. of mercury.

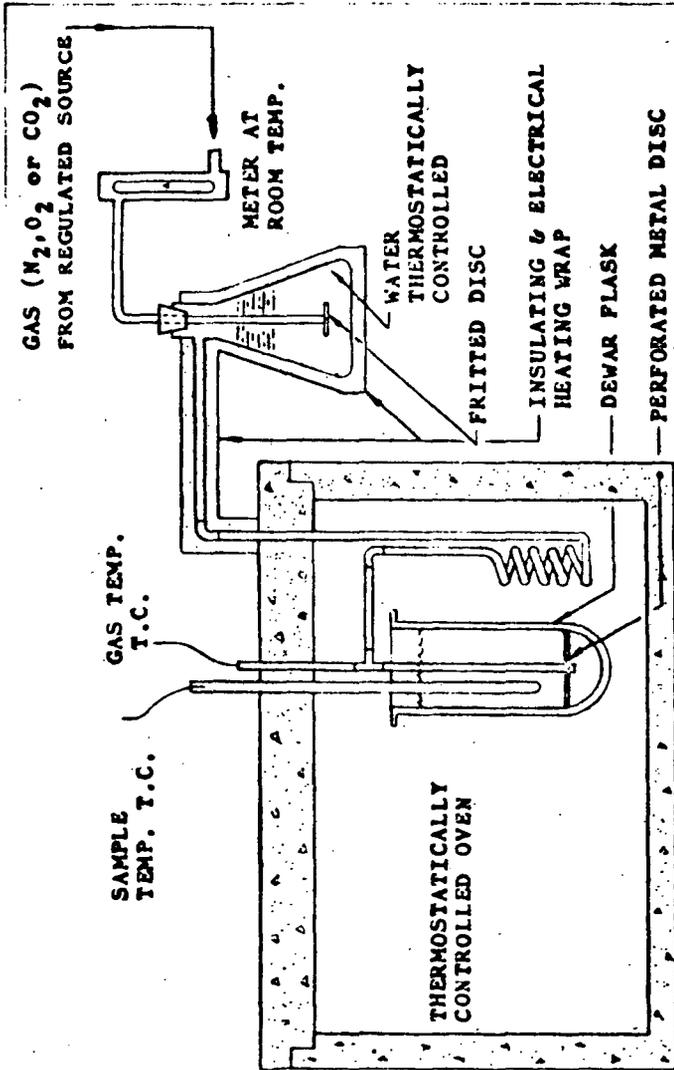


FIG. 1.
APPARATUS FOR SELF-HEATING OF CARBONACEOUS MATERIALS

Sample Preparation

The as-received semi-calcined petroleum coke was carefully crushed to produce a maximum of -3 on 14 mesh particles. In order to standardize test conditions, the majority of the tests were made using coke samples which were air-dried at 220°F. Vacuum drying and drying in an inert atmosphere were investigated. The temperature rise and the shape of the temperature versus time curve were within the limit of reproducibility of the test regardless of the method of drying.

The -3 on 14 mesh size fraction was also used for all other raw materials tested.

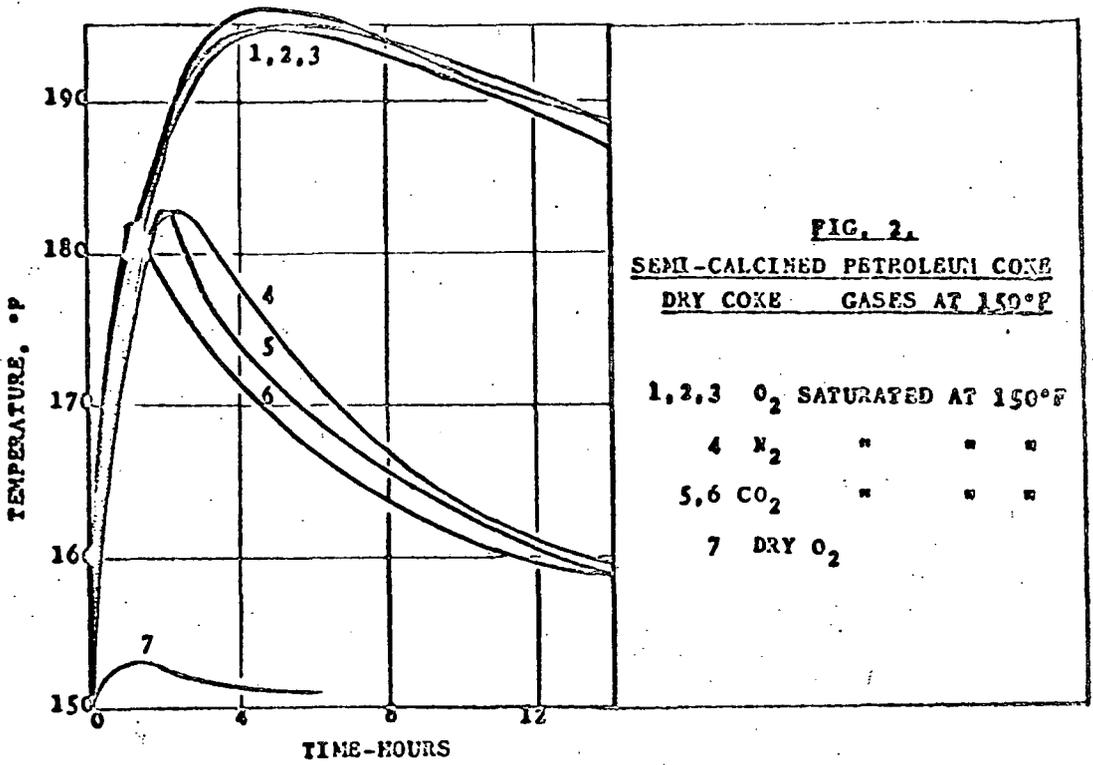
Test Procedure

Due to the extremely low rate of heat transfer between the oven and the sample contained in the Dewar, it was necessary to charge the sample at approximately 150°F. Dried samples at 220°F were allowed to cool to approximately 150°F and then charged to the Dewar. A 600 g. sample was used. The temperature of the sample was then adjusted to 150°F by passing dry nitrogen gas through to either cool or heat the sample. To make certain the system was in equilibrium, it was held for at least ten minutes at 150°F prior to starting a run. The desired gas was then passed through the sample at a controlled flow rate, usually 0.5 cu.ft./hr. and was saturated with water at 150°F, if desired. The furnace temperature, inlet gas temperature, and temperature of the sample at a point one inch above the bottom of the sample were recorded, versus time.

RESULTS AND DISCUSSION

In Figure 2 is shown a graph for a number of runs conducted on a sample of semi-calcined petroleum coke. All runs were made with representative portions of the same sample of coke. Curves 1, 2 and 3 were runs in triplicate made with oxygen, Curve 4 was a run made with nitrogen and Curves 5 and 6 duplicate runs made with CO₂. In all runs the gases were at 150°F and saturated with water vapor. The agreement between duplicate runs is quite good and demonstrates the reproducibility of the test procedure. We may attribute the difference between the temperature versus time relationship of Curves 1, 2 and 3 versus the curves for the runs with nitrogen and CO₂ to the presence of oxygen versus nitrogen or CO₂. There is a definite increase in the maximum temperature obtained of about 12°F when oxygen is used rather than the more inert gases. The shape of the curves after the peak temperature has occurred is of interest. With oxygen there is a tendency for the temperature to be sustained for a longer period of time indicating that the oxygen continues to be absorbed or to react, liberating heat, while with nitrogen or CO₂, after the peak is reached, there is a much sharper decrease in temperature with respect to time. These data indicate that the temperature rise due to absorption of water vapor is about 33°F, while that due to O₂ is about 12°F.

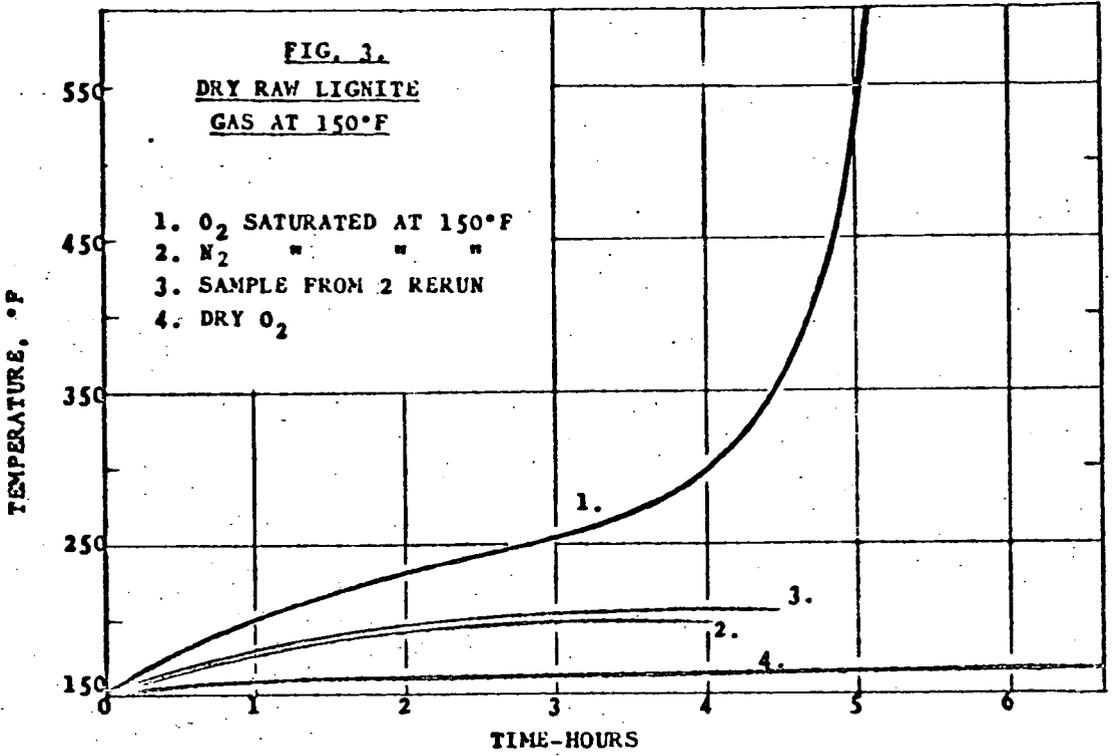
Curve 7 is for a run using dry oxygen at 150°F. The maximum temperature attained was well below that of any of the curves made with saturated gases and indicates that there is little or no reaction or absorption of oxygen in the absence of moisture.

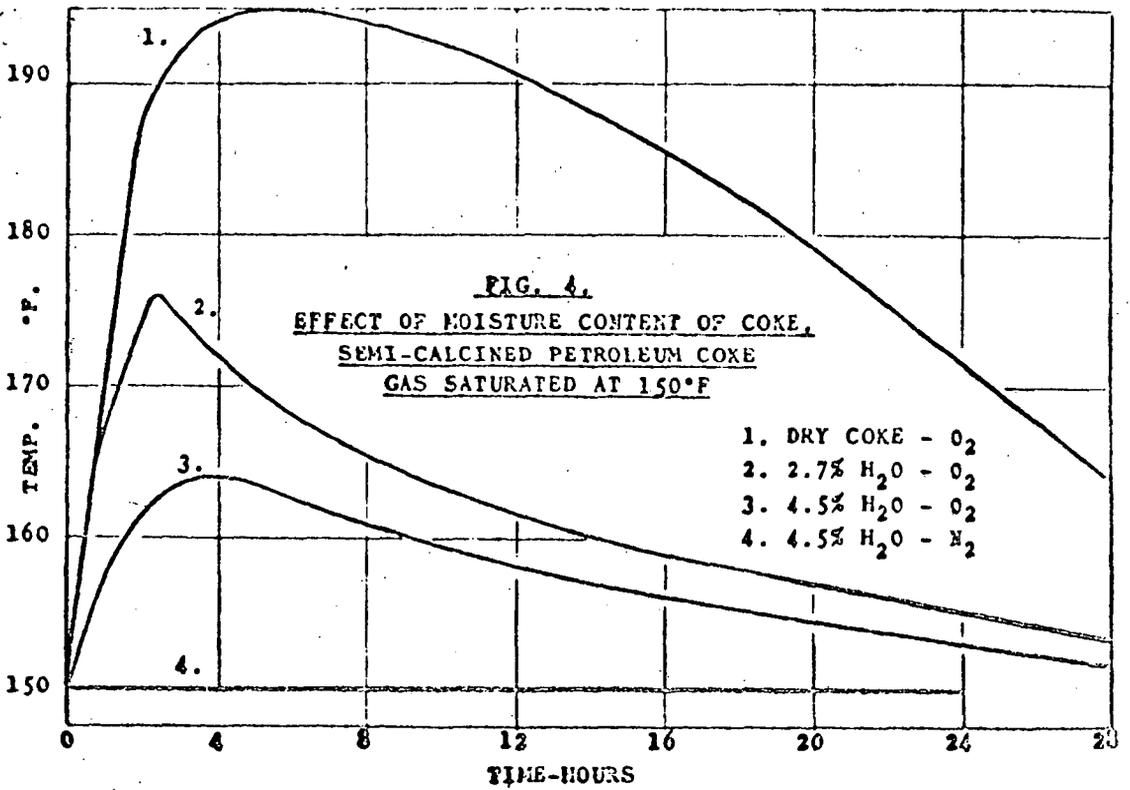


The importance of the role of water in the self-heating of carbonaceous materials is shown more strikingly in Figure 3 in which the sample was dry raw lignite. All runs were made with the gas stream at 150°F. Curve 1 was made with oxygen saturated with water vapor, Curve 2 and 3 with nitrogen saturated with water vapor and Curve 4 with dry oxygen. With dry oxygen the maximum temperature rise was 18°F, with saturated nitrogen 48°F and with saturated oxygen the sample ignited spontaneously in less than 5 hours.

All runs of Figure 4 were conducted using representative portions of a sample of semi-calcined petroleum coke. In runs 1, 2 and 3, the gas was oxygen saturated with water vapor at 150°F; in run 4, it was nitrogen saturated with water vapor. The combination of dry coke exposed to saturated oxygen gave a temperature rise of about 45°F in 5 hours, and as expected, moisture addition to the coke lowered the temperature rise in an atmosphere of saturated oxygen. In run 4 made with saturated nitrogen and coke containing 4.5% water, there was no measurable temperature rise.

From the runs of Figure 2 the contribution of O₂ and water vapor to the temperature rise of semi-calcined petroleum coke was estimated based on the difference between the total rise with saturated O₂ and that with saturated N₂ using dry coke. This amounted to 12°F. In the experiments presented in Figure 4, the coke was saturated with water and the temperature rise due to O₂ measured directly. This amounted to about 14°F,

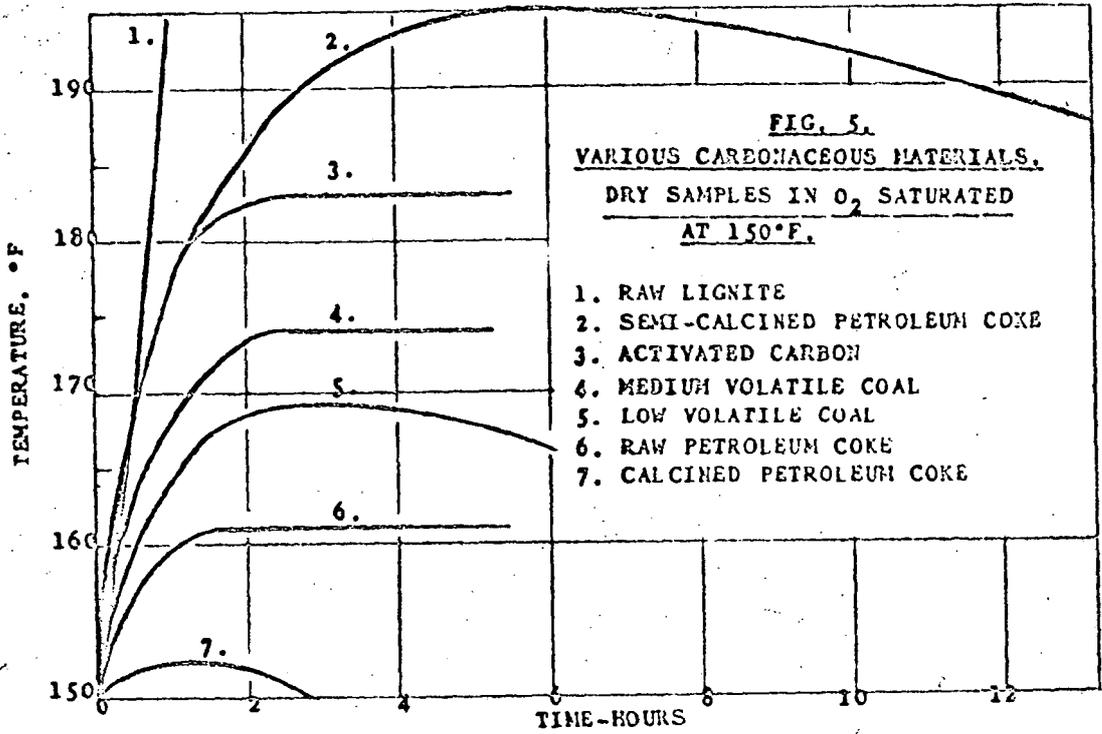




while the rise due to water vapor by difference amounted to 31°F. These are in good agreement with the estimates from Figure 2.

In Figure 5 are shown temperature versus time curves for a variety of carbonaceous materials subjected to a stream of oxygen at 150°F saturated with water vapor. From an examination of the curves it is apparent that lignite, which can be stored with safety only under water, shows the greatest tendency for self-heating in the test apparatus and actually ignites spontaneously in less than five hours. The next most active material is semi-calcined petroleum coke, which shows a maximum temperature rise of about 45°F in five hours. Surprisingly enough this material exhibits a greater temperature rise than a commercial grade of activated carbon which shows a temperature rise of about 33°F. Below this in decreasing order of temperature rise are: a medium volatile (27%) bituminous coal, a low volatile (17%) coal, raw petroleum coke with a volatile matter content of 12%, and finally calcined petroleum coke which exhibits no temperature rise under these conditions. The results of Figure 5 are in good agreement with the known behavior of the various carbonaceous materials upon storage in the field⁽⁵⁾.

The behavior of the activated carbon is of course an exception. Although it exhibits a rather high temperature rise in this test, it is not subject to spontaneous combustion. This is due to the fact that it is well devolatilized and does not contain an appreciable amount of hydrocarbons which are



available for combination with oxygen at temperatures in the range from about 300°F to its ignition point. Thus, it is believed that when this test with oxygen at 150°F saturated with water vapor is applied to materials which are capable of combining with oxygen in the temperature range of 300°F to their ignition temperature, it provides a good measure of the liability of the material to spontaneous ignition.

SUMMARY AND CONCLUSIONS

A simple procedure for the determination of the self-heating rates of various carbonaceous materials has been developed. For those materials which contain sufficient hydrocarbons to combine with oxygen at 300°F and thus ignite at relatively low temperatures, the maximum temperature rise determined in this test correlates with the liability to spontaneous ignition in the field. In a completely dry system there is no serious self-heating evident for any of the materials tested, even in pure oxygen. The absorption of water vapor by the dry carbonaceous material provides the major heating effect in the temperature range from 150°F to about 190°F. This temperature rise will occur even though the moisture be carried by an inert gas such as nitrogen or CO₂. With semi-calcined petroleum coke it has been demonstrated that if oxygen is used, a higher temperature rise of approximately 14°F occurs due to absorption or reaction of the oxygen in the presence of moisture.

The importance of moisture is best illustrated by the behavior of raw lignite which in dry oxygen at 150°F shows a temperature rise of only 18°F in about 5 hours. However, if the oxygen is saturated with water vapor at 150°F, the rate of temperature rise is of the order of tenfold greater, and the lignite ignites in less than 5 hours. Of all of the carbonaceous materials investigated, raw lignite shows the greatest temperature rise in oxygen saturated with water vapor at 150°F. The next most reactive material was semi-calcined petroleum coke which is more active than any of the bituminous coals tested, and in agreement with field experience with this material where considerable difficulty is encountered with spontaneous ignition unless great care is exercised to insure proper cooling prior to storage and to exclude the access of air insofar as possible.

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PRODUCTION AND CHARACTERIZATION OF
CARBON DERIVED FROM COMPOUNDS OF INDENE (U)

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The advances in structural design associated with reactor, aerospace, and related technologies increase, in turn, demands for speciality forms of structural materials. One material that is finding special and strategic application in these areas is carbon. Increased use of carbon for other, more domestic applications is projected for the future. Interest in carbon as a fabrication material is prompted by the following: (1) high temperature heat resistance, (2) resistance to chemical attack, (3) constancy of properties with time, (4) the diverse properties which carbon can exhibit and the variety of product-type into which it can be made.

Since the properties exhibited by carbon can significantly vary, use of this material necessitates control of these properties. Our efforts involve two aspects of control: (1) reproducibility, with emphasis on use of synthetic raw materials as carbon precursors, (2) manipulative control, which would allow one to make carbon with specific and preselected properties by the appropriate choice of precursor and processing conditions. It is known that chemical, mechanical, electrical, and thermal properties of carbon, or parts fabricated from carbon, are greatly influenced by the carbon type; as is well known, carbon is generally classified in terms of amorphous, graphitic, and diamond structures. Properties associated with any given classification suggest a range of values. More specifically, properties of a graphitic carbon are a function of the degree of graphitization and certain other microstructural properties.

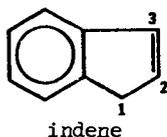
Have you considered the factors which contributed to the diverse properties exhibited by our natural deposits of carbon and carbonaceous products? Generalization will allow us to narrow the effects to two factors: (1) the nature of the organic matter from which the carbon was derived, (2) the conditions (pressure, temperature, time, etc.) under which the organic matter was converted to carbon. In our evaluation of carbon precursor materials, we have considered the same two factors. More specifically, we have attempted to correlate carbon properties with (1) the properties of the precursor material, with emphasis on effects attributed to molecular composition and structure, and (2) the processing conditions employed in converting the organic material into carbon, including the effect of temperatures up to 3000° C.

Some understanding of the relationships existing between carbon properties and precursor properties have evolved over the years. In general, organic materials which are or become infusible prior to pyrolysis do not tend to produce graphitic carbon. This type of material is characterized by thermosetting resins or highly crosslinked polymers. Thus, crystallinity seems to be dependent upon the ability of molecules to rearrange or reorient prior to pyrolysis, and such mobility necessitates an intermediate fluid or plastic state. Research efforts involving liquid crystal and mesophase studies represent attempts to correlate degree of orientation prior to pyrolysis with graphitic properties of derived carbon. Likewise, the planarity of polynuclear aromatic molecules will be a significant factor in determining the degree of graphitization of derived carbon. Molecules or molecular fragments that retain a nonplanar structure do not tend to graphitize. This seems reasonable in light of the planar, polynuclear structure that characterizes graphite. In addition to the inherent organic structure of the precursor materials, the presence of

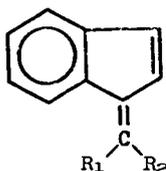
impurities such as sulfur and metallic compounds influence the graphitic properties of derived carbon.

Thus, precursor materials derived from natural sources will not be adequate for certain specialized applications since (1) they represent a complex mixture of organic structures whose composition varies with sources and refining methods, and (2) they frequently contain inorganic contaminants which vary in quantity and type with location of source.

This effort in the area of synthetic carbon precursors has included synthesis, polymerization, and carbonization studies. Much of the effort has been directed toward synthesis and evaluation of carbon precursor materials derived from indene (C_9H_8).



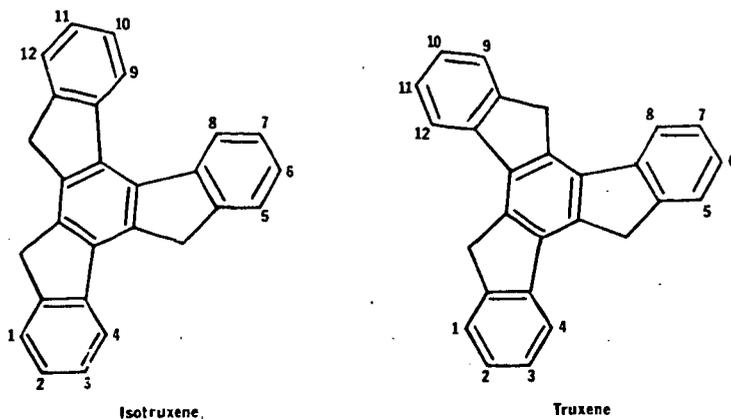
Included in the series were various indene derivatives incorporating the benzofulvene structures shown below.



	<u>R₁</u>	<u>R₂</u>	<u>Compound</u>
I	H	H	benzofulvene
II	CH ₃	CH ₃	dimethylbenzofulvene
III	H	C ₆ H ₅	benzylideneindene
IV	CH ₃	C ₆ H ₅	methylphenylbenzofulvene
V	C ₆ H ₅	C ₆ H ₅	diphenylbenzofulvene
VI	H	C ₆ H ₅ -CH=CH-	cinnamylideneindene

These compounds were synthesized by condensation reactions of indene with carbonyl compounds with the carbonyl component becoming an integral part of the benzofulvene structure.

Additional compounds that were derived from indene included α -truxene (truxene) and β -truxene (isotruxene), both of which are trimeric derivatives of indene. As shown by the structures below, the latter compounds are structural isomers.



The preparative procedures involve reactions of indene and carbonyl compounds in the presence of amine catalysts. Heretofore, only isomeric mixtures of these two compounds could be obtained by synthetic procedures involving autoclave conditions. However, procedures used in this study will allow production of either isomer under reflux conditions, and at the exclusion of the other. The specific isomer obtained will be a function of the carbonyl compound used in the formulation.

To lend emphasis to the correlations previously suggested between carbon properties, precursor properties, and processing conditions, truxene and isotruxene shall be discussed in detail. The influence of three factors on graphitizability of carbons shall be considered. These are the effect of (1) molecular structure, (2) metallic impurities, and (3) polymerization conditions.

Initially, structural effects will be considered. Though isomeric in structure, truxene yields a nongraphitic carbon while carbon derived from isotruxene tends to be graphitic. Two factors could contribute to the disoriented structure of truxene-derived carbon: (1) the planar structure that characterizes truxene molecules is apparently disrupted prior to pyrolysis and nonplanar intermediates are formed; (2) the fluid properties before and during pyrolysis were not conducive to orientation. As observed for other nongraphitizing materials, gases evolved during pyrolysis were entrapped, resulting in a cellular or foam-like carbon. Such gases tend to be freely evolved during pyrolysis of graphitizing materials, as was observed for isotruxene. These observations are indicative of the fluid properties existing during periods in which chemical change and structural realignments will be greatest. Lack of molecular mobility during these periods would tend to inhibit orientation. Attempts to control graphitic properties of carbons by blending graphitizing and nongraphitizing materials were considered. The materials must of necessity form homogeneous solutions and must yield a homogeneous carbon. For example, mixtures of isotruxene and truxene produce homogeneous carbons with properties that are dependent on composition. Data obtained by X-ray analysis of carbons derived from isotruxene and truxene-isotruxene mixtures are shown as a function of temperature in Table 1.

Table 1

CRYSTALLOGRAPHY STUDIES ON GRAPHITIC CARBONS FROM ISOMETRIC TRUXENES

Source of Carbon	Heat Treatment Temperature (°C)	d_{004} (Å)	C_0 (Å)	L_c (Å)	d_{110} (Å)	A_0 (Å)	L_0 (Å)
Isotruxene	2,800	1.6820	6.7280	314	1.2296	2.4592	259
Isotruxene	2,400	1.6845	6.7380	255	1.2299	2.4598	412
Isotruxene	2,000	1.7080	6.8320	126	1.2261	2.4522	135
Isotruxene-100	2,800	1.6317	6.7268	315	1.2294	2.4588	247
Isotruxene-truxene (75-25)	2,800	1.6914	6.7656	113	1.2300	2.4600	250
Isotruxene-truxene (75-25)	2,400	1.6946	6.7784	106	1.2290	2.4580	250

In one example of a study involving the effect of metallic impurities on graphitizability, samples of truxene-derived carbon containing induced metallic impurities were evaluated. Samples containing titanium carbide were fired to 2800° C, and were studied by X-ray analysis and photomicrography. Microstructural observation indicated large areas of graphitic carbon. As shown in Figure 1, X-ray data indicated an increased degree of graphitization as compared to the typically nongraphitic carbon derived from truxene. Other metals such as iron, nickel, chromium, or aluminum will also promote graphitization of typically nongraphitizing materials.

To show the effect that polymerization conditions can have on graphitizability, the oxidative polymerization of isotruxene will be considered. Without an oxidative cure, isotruxene yields an isotropic carbon that is not highly graphitic. After oxidative cure, X-ray analysis and microstructural examination indicate a more graphitic and a more anisotropic carbon. Changes in carbon properties with oxidative cure time are shown in Table 2.

In summary efforts to closely control properties of synthetic carbons must include close control on raw material properties and impurities, and conditions under which organic precursor materials are converted to carbon.

Table 2
EFFECT OF HEAT TREATMENT (300° C) IN OXYGEN ON THE PROPERTIES OF ISOTRUXENE AND ISOTRUXENE DERIVED CARBON(1)

Time (hrs)	Viscosity(2) (cp)	Oxygen Content(3) (%)	Melting Range (° C)	Apparent Monomer Content(4) (%)	Coke Yield at 1,000° C (%)	Carbon Properties After 3,000° C				
						g Factor	L _c (A)	d ₁₁₀ (A)	L _a (A)	
Batch 10-82-69 (O ₂ Flow Rate, 40 cc/min)										
0	18.0	0.24	202 - 212	79.2	38.5	1.7010	0.422	120	1.2287	210
24	22.0	0.43	78 - 187	81.2	42.5	1.6906	0.656	104	1.2299	289
48	32.4	0.73	89 - 123	70.9	61.5	1.6914	0.633	112	1.2308	280*
72	56.8	1.10	93 - 142	64.5	63.5	1.6854	0.767	187	1.2307	419
96	113.2	1.28	135 - 183	58.9	75.0	1.6860	0.756	187	1.2310	319
125	427.2	1.43	182 - 196	57.6	78.0	1.6865	0.744	178	1.2304	361
Batch 10-84-69 (O ₂ Flow Rate, 84 cc/min)										
0	17.2	0.31	201 - 209	82.7	45.0	1.7025	0.389	97	1.2292	200
24	26.4	0.89	85 - 178	78.9	63.5	1.6900	0.667	102	1.2302	377
48	61.2	1.29	123 - 163	64.4	61.5	1.6871	0.711	131	1.2303	362
72	137.6	1.17	132 - 168	59.9	73.5	1.6845	0.789	200	1.2304	447
91	627.2	1.09	184 - 222	58.5	83.5	1.6851	0.778	173	1.2303	424
Batch 10-92-69 (O ₂ Flow Rate, 165 cc/min)										
0	18	0.24	208 - 216	69.0	26.0	1.7004	0.433	112	1.2292	206
24	32.8	0.86	92 - 122	75.0	60.5	1.6882	0.711	122	1.2304	427
48	108.0	1.45	143 - 178	56.0	77.0	1.6871	0.733	198	1.2307	591
65(5)	-	0.62	> 300	(insoluble)	89.5	1.6882	0.711	129	1.2304	367

(1) Isotruxene was heated at 300° C with constant agitation and with O₂ gas bubbling through molten material. Samples were removed periodically for evaluation.
 (2) Measured with Brookfield viscometer.
 (3) Determined by neutron activation.
 (4) Estimated from molecular distributions shown on GPC scans.
 (5) Material solidified after 65 hours of heating at 300° C, thus no viscosity was measured.

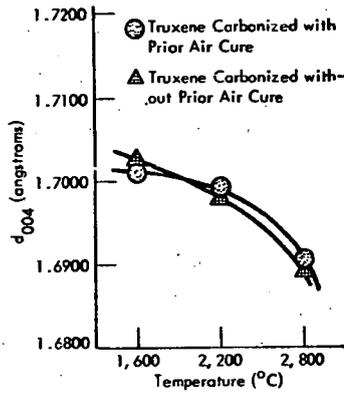


Figure 1. Correlation of Interlayer Spacing With Firing Temperature for Truxene-Derived Carbon Containing Titanium Carbide.