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THE HEAT OF OXYGEN CHEMISORPTION ON CARBONACEOUS CHAR

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ABSTRACT

The first step in the combustion of a char that has been formed from the pyrolysis of oil shale, lignite, or coal is the chemisorption of oxygen onto the active sites formed during the fragmentation reaction. This chemisorption process can be associated with the way that the char was formed. It is definitely a function of the rate at which the raw material was pyrolyzed and the maximum pyrolysis temperature. Studies have been made which show that the chemisorption kinetics follow the theory normally associated with the chemisorption of gases on catalytic surfaces. However, when trying to determine the energy associated with the chemisorption of oxygen on chars, experimental difficulties were encountered which necessitated equipment and experimental changes for studying this type of reaction. A discussion of the problem and some of the observations are presented in this paper.

INTRODUCTION

When organic materials such as coal, lignite, or an oil shale are pyrolyzed in an inert atmosphere, the devolatization of the polymer structure leads to the formation of chain fragments. These fragments are highly reactive with many active sites. Given time, these active sites find each other and a graphitic-type char forms. However, if oxygen is introduced while these active sites exist, the oxygen will be chemically adsorbed to these sites initiating an intense exothermic reaction. The energy release occurs in a very short period of time and this highly exothermic reaction must be studied if retorts for the pyrolysis of organic materials depending on this energy release are to be properly designed.

An investigation of the chemisorption of oxygen on Michigan oil shale [1] showed that the kinetics follow a modified Elovich equation exactly like that proposed by Scholten et al. [2] for the chemisorption of nitrogen on pure iron catalysts. After determining these kinetics, it was felt that it would be very important to find out how much heat is released during the combustion process. Unfortunately, the heat released is so intense that it was impossible to follow it with the equipment available. Therefore, only the heat generated during the chemisorption process is reported in this paper.

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In using a Perkin-Elmer TGA system, the dead volume is quite large so some of the initial reaction is lost when changing atmospheres. The DSC-II system has much less dead volume and so the changing of the atmosphere permits one to see the initial stages of the reaction. However, there were experimental difficulties which will be discussed in this paper.

EXPERIMENTAL

A study of oxygen chemisorption on fossil fuel fragments obtained during the pyrolysis of that material is complex and very time consuming. One only needs to consider that the amount and the reactivity of the fragments is governed by the pyrolysis rate and the final temperature to which the material is pyrolyzed. The material can be pyrolyzed at a number of different rates to different pyrolysis temperatures and this leads to many combinations of just these two variables. Add to these variables the rate at which the material is quenched to one of several temperatures where the chemisorption process is to be studied under isothermal conditions and one sees the enormity of the problem. It takes 48 h just to determine a reliable estimate of how much oxygen will be adsorbed by a specific specimen and these experiments should be replicated. It took six months to determine the kinetics of chemisorption reported in ref. 1, therefore, none of the research reported in this paper is considered to be complete. Excerpts from various studies are used to illustrate the experimental methodology thus far developed and to encourage others to comment and suggest improvements.

In setting up the Perkin-Elmer DSC-II for these experiments, ultrapure nitrogen at a given flow rate (usually 1.33×10^{-6} m^3 s^{-1}) was flushed through the apparatus, then, without a sample present, the nitrogen was replaced by air at the same flow rate. A three-way cock was used for making this change over. The change over was almost instantaneous with only a small perturbation in the flow rate. It had been hoped that this small upset in the system would lead to small spike on the readout from the DSC-II. What actually happened is shown as curve C in Fig. 1. This curve could not result from the perturbation caused by the change over of the streams and this was confirmed by interchanging nitrogen streams.

The reason for the curve that results on the interchanging of nitrogen and air is seen upon the examination of the gas-flow splitter that Perkin-Elmer use in their DSC-II, as shown in Fig. 2. One stream has a straight-through passage, whereas the other stream goes through the branch of a tee and around a sharp corner. This will cause an imbalance in the two flow rates. Air will reach one cell before it reaches the other and until the system has the same gas composition in both cells, there is a differential signal as depicted by curve C (Fig. 1). Once the system is in balance for air, then nitrogen can be re-introduced and the same phenomenon occurs except that it is in the negative direction.

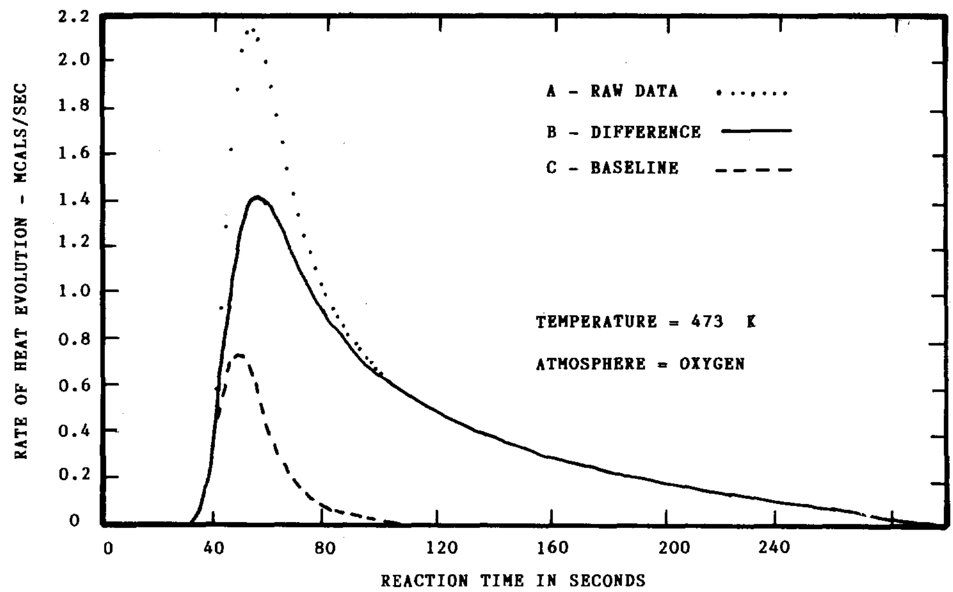

Fig. 1. Experimental data for the chemisorption of oxygen on lignite char.

At first this phenomenon was considered to be a difficulty for the intended research, but rather, it proved to be very helpful. For a given flow rate of gases, this particular response was reproducible and when oxygen was substituted for air the height of the curve was found to be directly proportional to the height observed when air was used. If this proportionality holds true for low concentrations of oxygen, the instrument could detect oxygen in nitrogen to about 20 ppm. A further advantage was obtained because the onset of the imbalance was very sharp and the time to this onset was directly

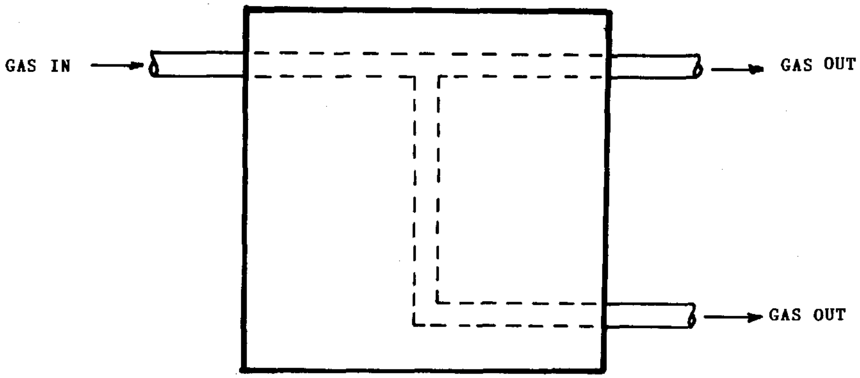

Fig. 2. DSC II gas splitter.

proportional to the gas flow rate. This gave a check on the rotameter settings.

To determine the heat of oxygen chemisorption, the sample (3–5 mg) was pyrolyzed to a prescribed temperature (973 K for the data presented in this paper) in a nitrogen atmosphere. After reaching the final pyrolysis temperature, the sample was quenched at 2.67 K s^{-1} to the temperature where the chemisorption study was to be made (473 K). As soon as the temperature stabilized at the set point, either air or oxygen was introduced and the reaction proceeded as shown by curve A in Fig. 1. The computer was set to take 20 pieces of data and average them to obtain each reported data point. This was done every 2 s. When the reaction was deemed to be over, nitrogen was re-introduced and, after the system stabilized, the oxygen-containing atmosphere was again introduced and the baseline was established (curve C). The difference between the two sets of data represents the rate of energy released during the chemisorption process (curve B). The total energy of chemisorption was determined by evaluating the areas under curves A and C and subtracting.

DISCUSSION OF RESULTS

Lignite was pyrolyzed at various heating rates to 973 K and the results are shown in Fig. 3. These data are typical of data seen for coal and oil shale. The chemisorption was done in an oxygen atmosphere at 473 K. The heat release is lowest when the material is heated at the slowest heating rate and increases as the pyrolysis heating rate is increased. The heat release passes through a maximum and then decreases. The total heat release for the various runs is presented in Fig. 4. In Fig. 4 two sets of data are presented: one for runs terminated after five minutes and one for runs terminated after ten minutes. In each case the reaction seemed to be over because the rate had reached a constant value typical of the establishment of a new baseline. Since there is a substantial weight gain which may be as high as 10% for some chars, a shift from the original baseline might be expected. However, because the chemisorption reaction continues for a considerable period of time, the establishment of a true baseline is difficult to achieve. Data were taken over longer time periods showing a still greater increase in the energy release, but an insufficient amount of data has been accumulated to establish the true total amount of energy released during the chemisorption reaction.

In speculating as to why there is a maximum in the amount of energy released, one might argue that, at the slow heating rates, the active sites have time to inter-react forming a more graphitic matrix with fewer active sites available for oxygen adsorption. However, it must be remembered that when a sample is heated at different rates to the same final pyrolysis temperature, the amount of material that is pyrolyzed is different. Thus, a material heated

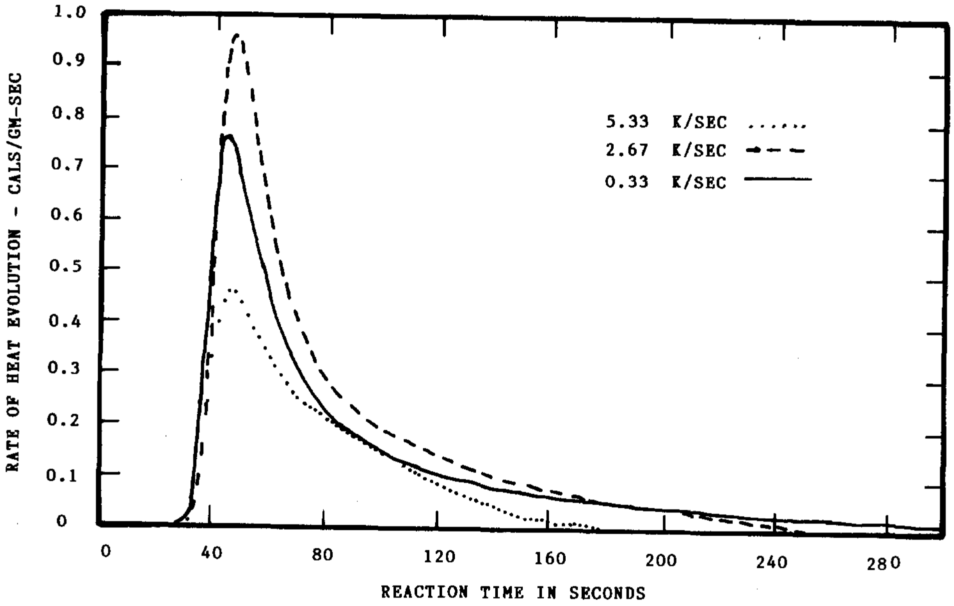

Fig. 3. The effect of pyrolysis heating rates on the energy evolved during chemisorption.

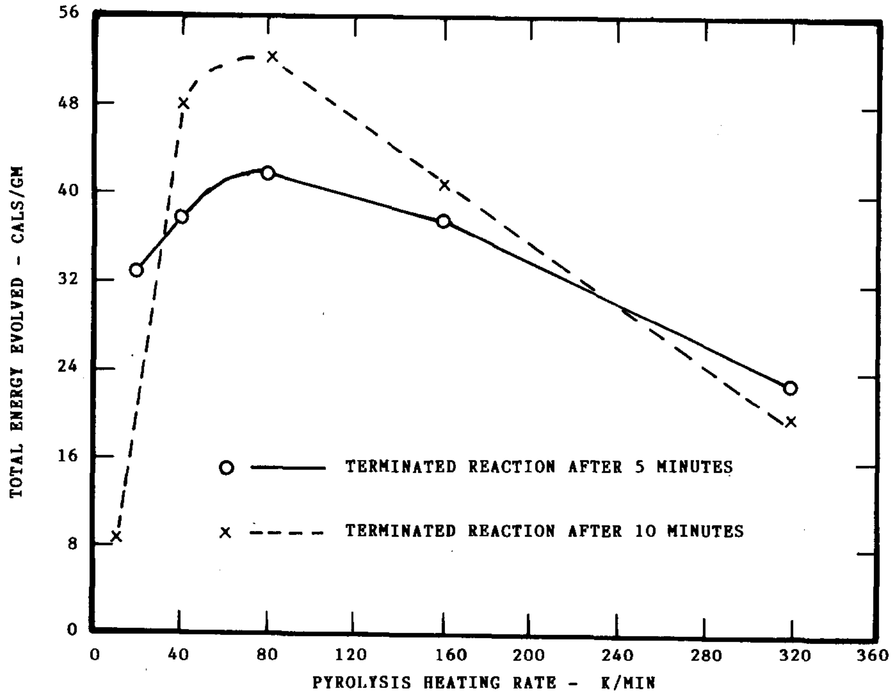

Fig. 4. The total energy evolved for the chemisorption reaction.

at a low pyrolysis rate will lose much more weight than materials heated at more rapid rates. So the results obtained for the chemisorption of oxygen at low pyrolysis rates may be the result of less material being available for oxygen chemisorption. Also, since more material has been pyrolyzed, the sample will tend toward a graphitic structure with fewer active sites available. At the highest heating rate, the sample never reaches a pyrolysis state where a sufficient amount of active sites are formed. Rather than heating the material to a specific temperature, it would be better to heat it to a given final weight remaining. This could be done if TG data are available which correlate sample weight remaining to heating rates and final pyrolysis temperatures.

An investigation was made where the sample upon being quenched to 473 K was held at this temperature for 3 h under a flowing nitrogen atmosphere before the oxygen was introduced. The results are shown in Fig. 5. The reduction in the reactivity of the aged material could be the result of active-site decay, but it could also be due to the presence of a minute amount of oxygen present in the nitrogen stream even though this gas was ultrapure and was passed through an oxygen trap. Appoximately one ppm of oxygen in the nitrogen would have caused the decrease in energy release observed.

Studies of the chemisorption reaction were also made using air instead of oxygen with similar results. The magnitude of the energy released during the initial stage of the reaction is, of course, less, but if the run is extended to

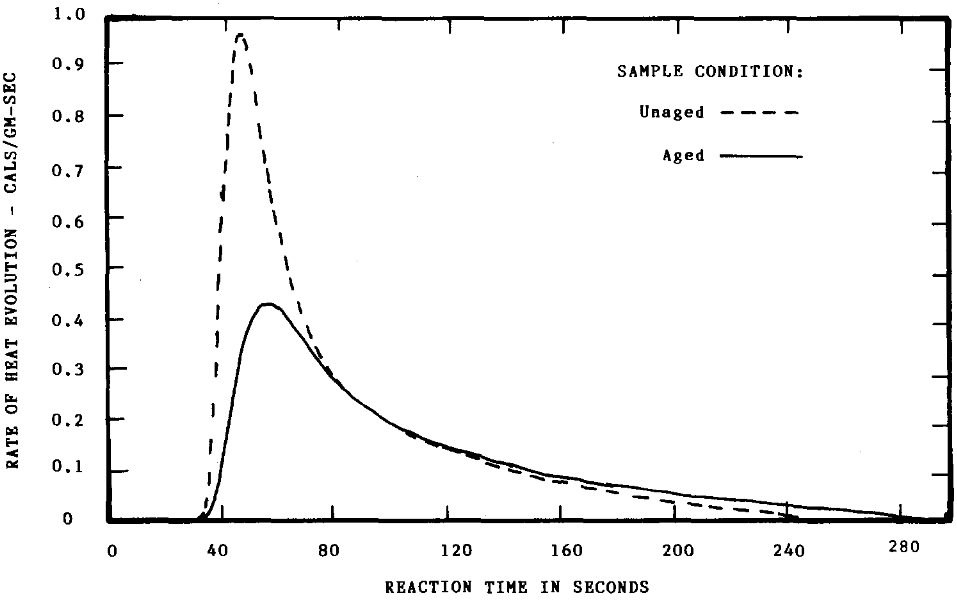

Fig. 5. The effect of ageing a specimen before introducing oxygen.

five times the length of time used in studies with oxygen, then the same total amount of energy release is obtained.

The original objective of this research was to ascertain the heat of combustion of the char as a function of time, but every attempt to study this problem met with defeat, since the initial stage of the reaction is so intense that even when the DSC-II was set at its lowest sensitivity, the data still went way off scale. the manufacturer was contacted to see if they could decrease the sensitivity by two orders of magnitude. They were unable to do this. The sample size was reduced to less than 0.1 mg in order to obtain a complete energy thermogram, but this introduced errors in measuring this weight accurately. Also, samples this small are not homogeneous and so there was a great deal of variability between the results from sample to sample. An effort was made to dilute the samples with an inert material, but again, it was impossible to obtain homogeneous samples and the results varied extensively.

CONCLUSIONS

Obviously, it is not possible to assign a specific value for the heat of oxygen chemisorption for lignite, or for any of the other materials studied. Nevertheless, the energy is high with a majority of its release occurring in the first few minutes of the chemisorption reaction. At elevated temperatures (about 723 K) the chemisorption reaction occurs over a few seconds, the fragments ignite, and the combustion reaction is quite intense.

This research points to the very geat need for a *standard* fossil fuel which could be used to investigate the many variables that are a part of the combustion reaction.

There are two interesting features that evolved during this research. If the decrease in activity for the aged sample is the result of oxygen, then one could develop a precise tool for measuring the oxygen content at extremely small concentrations in inert gas supplies. On the other hand, if the decrease in activity is the result of active-site decay, then it should be possible to study the kinetics for this rate of decay and thus gain a better understanding of the combustion process.

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