TEMPERATURE PROGRAMMED DESORPTION TECHNIQUE TO PREDICT THE CARBON OXYGEN REACTION

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Abstract — The kinetics of the reaction of oxygen with a sucrose char particle size: (88 μm$<d_p<$105 μm) has been studied using a thermogravimetric analyzer (TGA) and a mass spectrometer (MS) to measure weight change and CO and CO_2 formation rates during reaction. Experiments were performed to determine the surface oxide formation rate and to determine the mechanism of CO desorption in the temperature range of 762 K to 851 K and for oxygen pressures of 0.04 to 0.3 atm, respectively. When the reaction rate at 30% conversion was used in the Arrhenius plot, an activation energy of 34±3 kcal/mol was obtained and the CO/CO_2 ratio was found to increase with increasing reaction temperature. Analysis of the rate of formation of CO and CO_2 shows the activation energy for CO formation is greater than for CO_2 formation. Temperature programmed desorption (TPD) studies of the surface oxides were made to provide a better understanding of the carbon oxidation process. The activation energy distribution function for desorption was approximately Gaussian and the average activation energy is 55 Kcal/mol for a preexponential factor of 10^{13} 1/sec. The peak of the energy distribution function shifts to higher activation energies for surface complexes formed at higher reaction temperature.

Key words: Oxidation, TPD, Gasification, Surface Complexes, Activation Energy Distribution

INTRODUCTION

The carbon oxygen reaction is a complex molecular process and includes many elementary reaction steps. The surface complex (C-O) is the principle reaction intermediate, and the measurement of the desorption rate of the surface complex is one way to characterize the surface complex.

Initially the oxygen atom is adsorbed on the edge carbon atoms and forms a carbon-oxygen surface complex. Subsequently carbon-carbon bonds are broken resulting in the loss of carbon as CO and CO_2.

This process produces TPD spectra which can be interpreted in terms of the energetic state of chemisorbed surface complexes and interaction phenomena occurring within the carbon structure during the TPD process.

The TPD (temperatured programmed desorptrion) method is an experimental technique widely used in the field of heterogeneous catalysis, and recently has been applied to studies of gas-solid reaction. Du et al. [1990, 1991] and Calo and Hall [1989] have used TPD to determine the activation energy distribution of the surface oxygen complex. They found that the fraction of the oxygen on the surface is very tightly bound with activation energies for desorption greater than 85 Kcal/mol. They also found the energy barrier for CO desorption decreases with increasing amount of oxygen surface coverage.

This model is an approximate method for determining the desorption of activation energy distribution of the (C-O) complexes. Suuberg [1983] had earlier developed a method to accurately desorb with the evolution of volatile products in non-isothermal coal pyrolysis. Suuberg [1983] had assumed a Gaussian distri-

buted activation energy in his devolatilization model. The model used in this study can determine the activation energy distribution from the experimental data directly and does not require any assumption for the form of the distribution.

EXPERIMENTAL EQUIPMENT AND PROCEDURES

1. Materials

The char used in this study was a sucrose char which was prepared by pyrolyzing small quantities of reagent grade sucrose under nitrogen. It has a surface area of 700-900 m²/g, by the Brunauer-Emmett-Teller method, a micropore volume of 0.3 cm³/cm³, and no measurable macroporosity. A particle size of 88 μm$<d_p<$105 μm was used in these experiments. The char used in the experiment was heat treated to different temperature prior to an experiment.

The elemental analysis data of the sucrose char particle which was performed by Huffman Laboratories is given in Table 1.

2. Experimental Procedure and Apparatus

An Omnitherm 1500 Thermogravimetric Analyzer (TGA) and a VG quadrupole mass spectrometer were used in obtaining the kinetic data. The TGA system consists of a balance, furnace, temperature programmer and digital recorder.

The data are recorded by a Bascom-Turner Model 4100 two channel digital recorder which receives signals from both the temperature and the balance control unit. The ultimate sensitivity of the recorder is 1 μV (0.01 μg) and the maximum data acquisition rate is 10 data points per second. The data are stored on a 8″ magnetic disc and used for derivation of weight versus time curve. Software programs built in to the operating program of the recorder can be used to analysis of experimental data. The Bascom-Turner recorder is connected to the computer using an

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Table 1. Sucrose char characteristics

| Conversion | | O/C | Weight (%) | | | BET surface area | | Pore volume |
(weight basis)	(carbon basis)	atom ratio carbon remaining	C	H	O	(m²/g) weight remaining basis	carbon remaining basis	(sec/mg) weight remaining basis
0.0	0.0	0.023	96	1	3	<300	<300	
55	10.1	0.064	91.3	1a	7.8	740(1.4)	810	0.177
21	31.7	0.11	86.3	1	12.8	1180(1.4)	1370	0.288
41d	41	0.023	96	1	3c	1190(1.5)	1240	0.304
66	71.1	0.16	81.5	1	17.5	1160(1.8)	1420	0.279

particle size: 90-106 μm. Char heat treated to 800℃ for 10 min before activation

RS-232 interface and the data, which stored in the recorder, can be transfered to the computer for additional processing.

The mass spectrometer used in this experiment is a VG-quadrupole mass spectrometer. It consists of an analyser, RF generator and control unit. Vacuum is maintained by a turbo molecular pump and a rotary backing pump.

The masstorr analyser has three main section; the ion source, the quadrupole mass filter and the detector.

The mass spectrometer (MS) is connected to the computer using a National Instruments interface (IEEE-488). Both data control of the mass spectrometer and data acquisition can be done through the interface.

The masstorr interface performs peak search, automatic signal ranging, total pressure measurements, and partial pressure of outgassing measurements. As soon as communication is established between an external device and the masstorr computer, via the IEEE488 interface, commands may be sent to operate the mass spectrometer. The interface has 16 channels, each programmable for mass number, accuracy of measurement and gain range (pressure range). When the machine passes from the local (masstorr) state to the remote control state (the computer has control of the mass spectrometer), the computer performed all the actions necessary for measuring the pressures at the mass numbers of all enabled channels and return the results in simple ASCII strings. Measurements were taken at constant intervals timed by interrupts from a programmable timer module. After the sample was placed on the sample pan, the pressure of mass analyser and capillary sample line were checked. The operating pressure of the mass spectrometer was less than 1×10^{-7} mbar.

Product gases were sampled by the use of heated capillary tube connecting the TGA furnace to the enclosed ion source of the mass spectrometer. The pressure in the capillary tube was maintained at 170 micron using a rotary vacuum pump. The mass spectrometer, which is connected to the computer was switched to the remote state, and the computer interface performed all the actions necessary for measuring the pressures at the mass numbers of all enabled channels and returning the results in simple ASCII strings to the computer.

The following is an example command: "C1 = M28 = IK100 = G 10 = A3 = N". Here C1 represent a channel 1, M28 represent mass 28 (CO and N₂), IK100 represents the Secondary Electron Multiplier (SEM) voltage, G10 represent the gain range of partial pressure and A3 represents the accuracy of the measurements. In Faraday detector mode the display is calibrated in torr, however the display indicates the measured current in amps when switched to the multiplier detector. By adjusting the voltage applied to the SEM, the instrument can be calibrated so that the reading gives the partial pressure directly.

During a mass spectrometer run, an oscilloscope was used to look at the mass scan, which are mass 12 (carbon), mass 17 (OH), mass 28 (CO & N₂), mass 32 (O₂) and mass 44 (CO₂). In these studies 6 channels were measured during a run: total pressure, mass 12 (carbon), mass 17 (OH), mass 28 (CO), mass 32 (O₂) and mass 44 (CO₂).

In a temperature programmed desorption experiment, the char was heated in argon from the reaction temperature (starting desorption temperature) to 1113 K at a heating rate of 50℃ /min and held at 1113 K for 10 minutes to remove the surface oxides. The (C-O) complexes which formed by oxygen chemisorption on carbon are thermally decomposed as CO and CO₂. The desorption data (CO and CO₂) were obtained from the MS and plotted as a function of time or temperature (for the non-isothermal period).
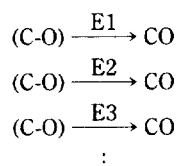
RESULTS AND DISCUSSION

1. Desorption Model

During the TPD process the (C-O) complexes which are formed by chemisorption of oxygen on the carbon surface are thermally decomposed to CO and CO₂. It is assumed that the (C-O) complexes have a range of activation energies for desorption. The energy distribution function, f(E), is introduced to describe the distribution of desorption activation energies, where f(E)ΔE represent the fraction of total (C-O) complex with activation between E and E + ΔE. The integration of f(E) were the entire range of activation energy is set equal to 1:

$$\int_0^\infty f(E)dE = 1 \tag{1}$$

The thermal decomposition of (C-O) complexes on carbon surface is assumed to be a set of independent parallel reactions. These reactions have their own activation energy. For each activation energy, the rate is assumed to be proportional to the amount of unreacted material remaining.

$$(C\text{-}O) \xrightarrow{\ E1\ } CO$$
$$(C\text{-}O) \xrightarrow{\ E2\ } CO$$
$$(C\text{-}O) \xrightarrow{\ E3\ } CO$$
$$\vdots$$

The rate of CO formation due to the desorption of a surface complex energy E to E + ΔE is:

$$-\frac{d[C\text{-}O]_E}{dt} = \frac{d[CO]_E}{dt} = k_E[C\text{-}O]_{E,t} \tag{2}$$

where k_E is the rate constant for desorption of sites of energy
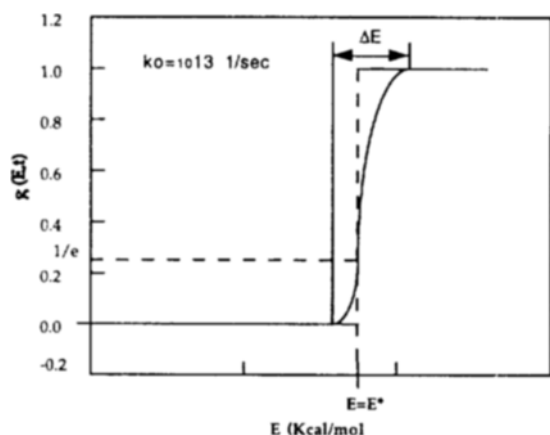
Fig. 1. Plot of small interval of activation energy.

E, $[C-O]_E$, is the number of (C-O) complexes remaining on the carbon surface with activation energy between E and E + ΔE.

$$[CO]_E(t) = [C-O]_{E,0} \exp(-\int_0^t k_E t \, dt) \tag{3}$$

where k_E is a function of temperature, and is not consistant in a non isothermal desorption experiment.

$$\text{if } [C-O]_{E,0} = C_T f(E) \, dE \tag{4}$$

where $[C-O]_{E,0}$ is the number of C-O complexes of energy E on the surface of the carbon, C_T is the total number of complexes and f(E) is the density distribution of the sites with activation energy E.

$$[CO]_E(t) = C_T f(E)[\exp(-\int_0^t k_E t) dt] dE \tag{5}$$

Eq. (5) can be integrated over all sites to obtain

$$[CO]t = C_T \int_0^\infty f(E) \exp(-\int_0^t k_E dt) dE \tag{6}$$

Du et al. [1990], suggested approximaing $\exp(-\int_0^t k_E dt)$ in Eq. (6) by a step function such that

$$\exp(-\int_0^t k_E dt) = \exp[-k_0 \exp(-E/RT)] \tag{7}$$

The Eq. (7) equal to 0 if E<E*, equal to 1 if E>E*. The point at which the step function goes from 0 to 1 is chosen to be at 1/e.

The rational for this approximation is that this function increase rapidly over a small interval of activation energy. This is shown in Fig. 1. Eq. (6) can then be written as follow:

$$\frac{[CO](t)}{C_T} = \int_{E^*}^\infty f(E) dE \tag{8}$$

$$\text{or } \frac{d[CO](t)}{dt} = -\frac{dE^*}{dt} f(E)C_t \tag{9}$$

Other choices for the jump point could also be employed, but the choice for the jump point will not appreciably alter the final expression for E* which is given below.

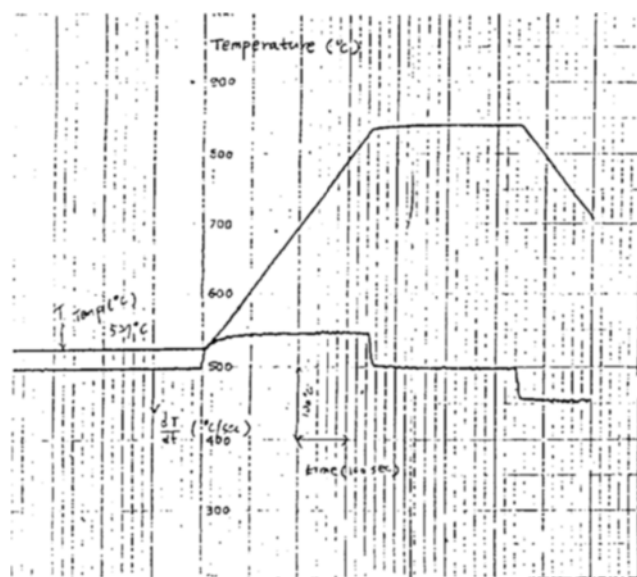E* is evaluated by obtaining the asymptotic solution for the integration Eq. (7), to give:

Fig. 2. Temperature profile as a function of time in TPD experiment (T vs t and dT/dt vs t).
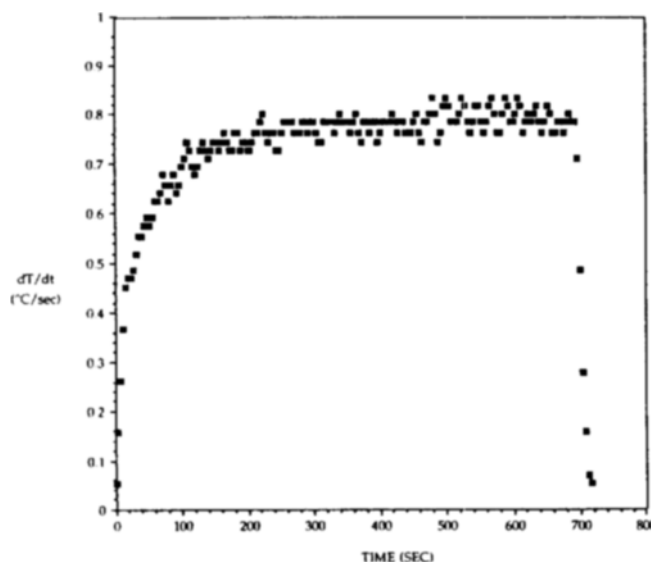

Fig. 3. Temperature profile as a function time in TPD experiment (dT/dt vs t).

$$E^* = RT(t)[a - \ln(a) + \ln(a)/a] \text{ where } a = \ln[k_0 |T(t)/T'(t)|].$$

$$\text{and } dE^*/dt = RT'(t)[a - \ln(a) + \ln(a)/a] = E^* T'(t)/t(t) \tag{10}$$

(d[CO]/dt) and C_T can be obtained from experiment measurement and the distribution function dE*/dt can be calculated by the use of Eq. (10):

$$f(E^*) = (d[CO]/dt)/C_T/(dE^*/dt) \tag{11}$$

Therefore energy distribution function can be obtained using the desorption experiment data and the Eq. (10).

2. Desorption Experimental Data

The temperature profile used in the desorption experiments is shown in Fig. 2. The derivation of the temperature profile (dT/dt) is also shown in Fig. 3. The rate of complex desorption
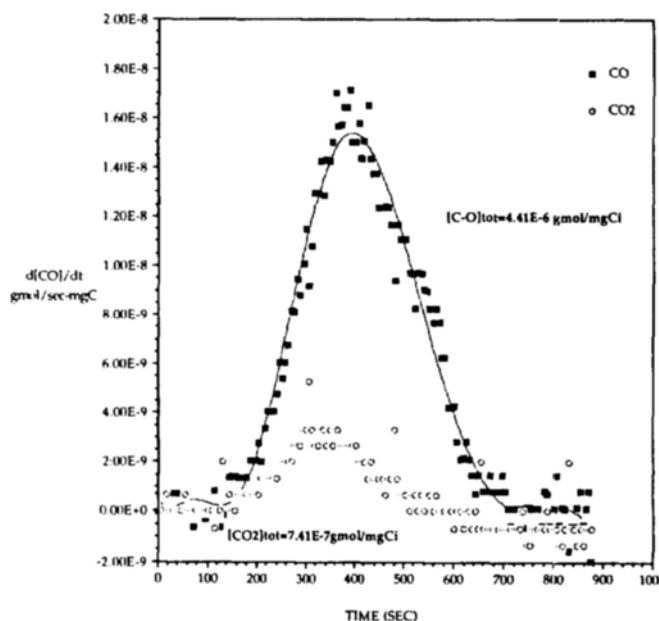
Fig. 4. Experimental TPD spectra of sucrose char at 686 K as a function of time; 4% O_2 and 30% conversion (50°C/min).
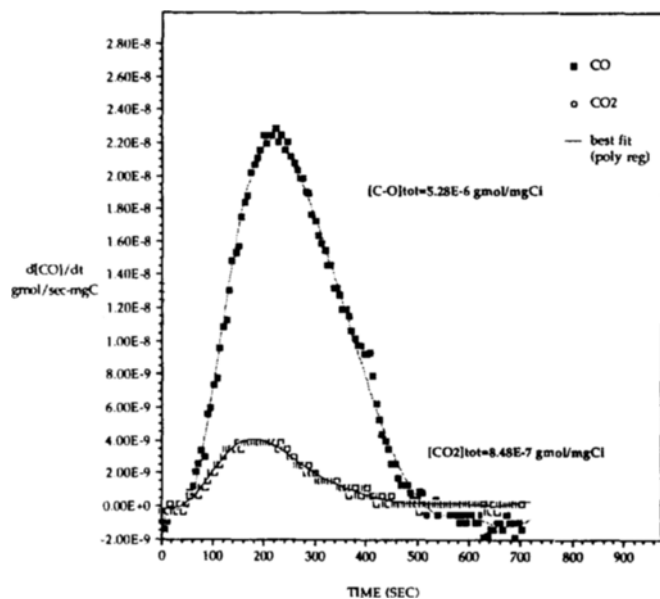

Fig. 6. Experimental TPD spectra of sucrose char at 801 K as a function of time; 4% O_2 and 30% conversion (50°C/min).

Fig. 5. Experimental TPD spectra of sucrose char at 748 K as a function of time; 4% O_2 and 30% conversion (50°C/min).

Fig. 7. Experimental TPD spectra of sucrose char at 686 K as a function of temperature; 4% O_2 and 30% conversion (50°C/min).

(measured as the rate of CO formation) $d[CO]/dt$ was obtained from the mass spectrometer data and $[C-O]_T$ was calculated by integrating the $[CO]$ evolution rate over time.

Typical temperature programmed desorption spectra are shown in Fig. 4 to 6 as a function of time for different desorption starting temperatures. The area under each curve in Fig. 4 to 6 corresponds to the total CO and CO_2 generation during a TPD run. Fig. 7 and 8 show the temperature dependence of the programmed desorption spectra. In all figures, the points represent the experimental data, and the line is a best fit polynomial curve to the experimental data.

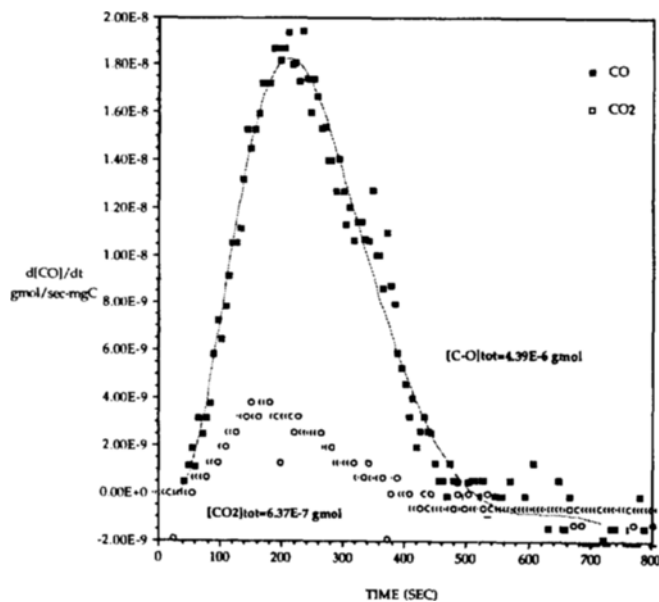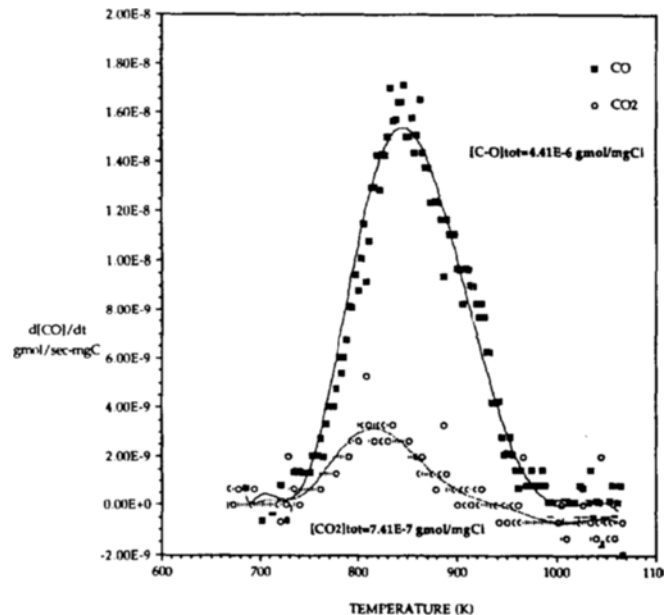The CO evolution in the figures consists of a peak centered

860 K and CO/CO_2 ratio is 5.95 for starting desorption temperature of 686 K. These TPD results are showed to be typical for oxygen gasified chars and are similar to those of Lizzio and Radovic [1989] who investigated the effect of conversion level on TPD profiles of Saran char in 1 atm air. In their studies the CO/CO_2 ratio is 5.9 and the peak temperature of CO is 913 K. When Calo and Hall [1989] investigated the TPD spectra from a Pittsburgh #8 coal char sample, gasified to 11.5% burn-off in 0.1 MPa O_2 at 723 K the CO peak was centered at 1000 K and the peak had high temperature shoulder. Du et al. [1990] also investigated the TPD spectra on ST1 sample at three different heating rate. The total amount of $[C-O]$ in the slow and fast heating rate runs
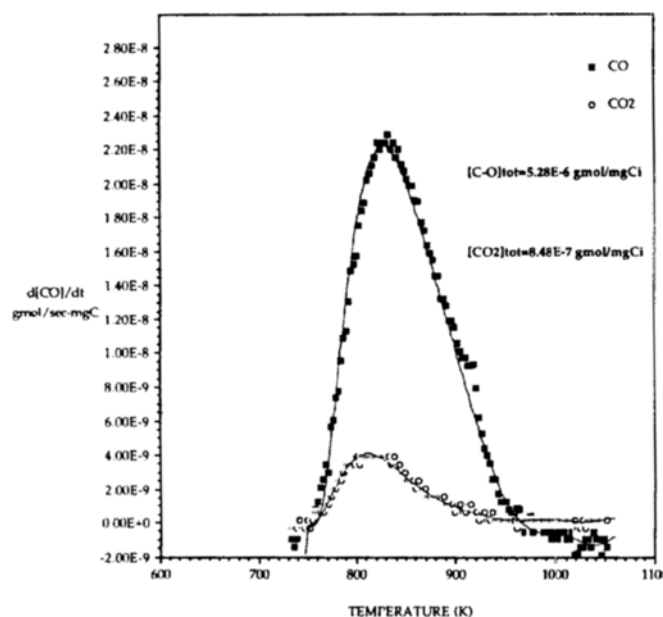
Fig. 8. Experimental TPD spectra of sucrose char at 748 K as a function of temperature; 4% O₂ and 30% conversion (50°C/min).
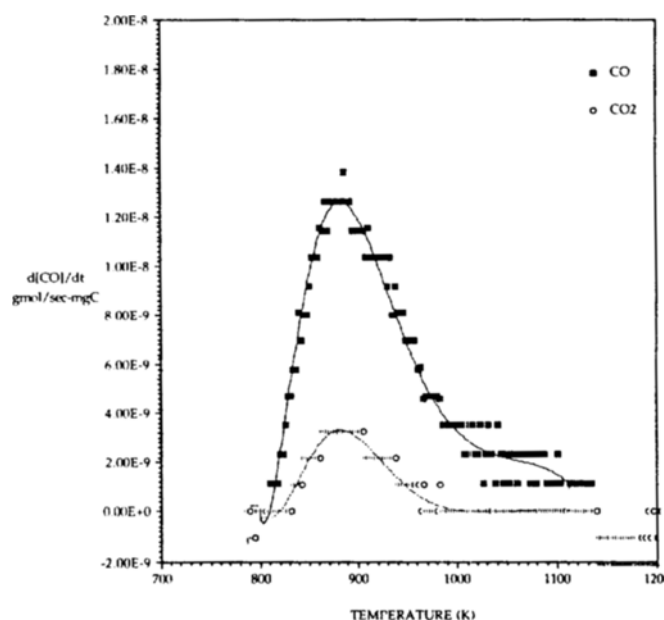

Fig. 10. Experimental TPD spectra of heat treatment sucrose char at 803 K as a function of temperature; 4% O₂ and 30% conversion (50°C/min).
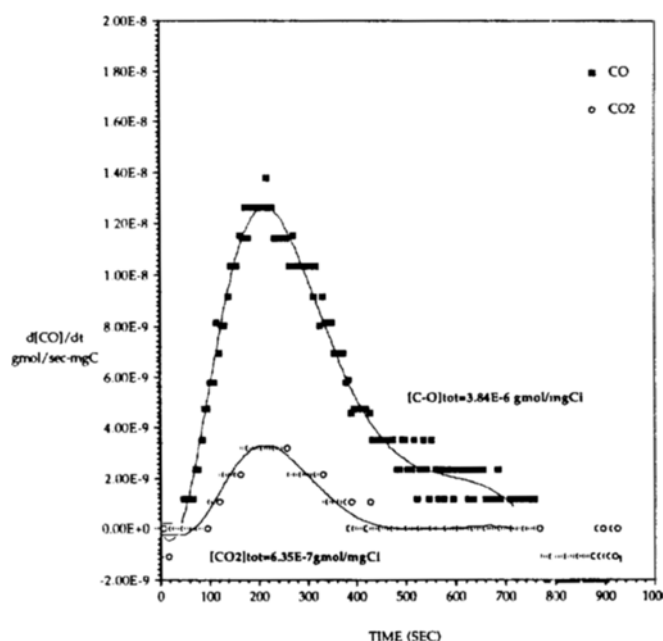

Fig. 9. Experimental TPD spectra of heat treatment sucrose char at 803 K as a function of time 4% O₂ and 30% conversion (50 °C/min).
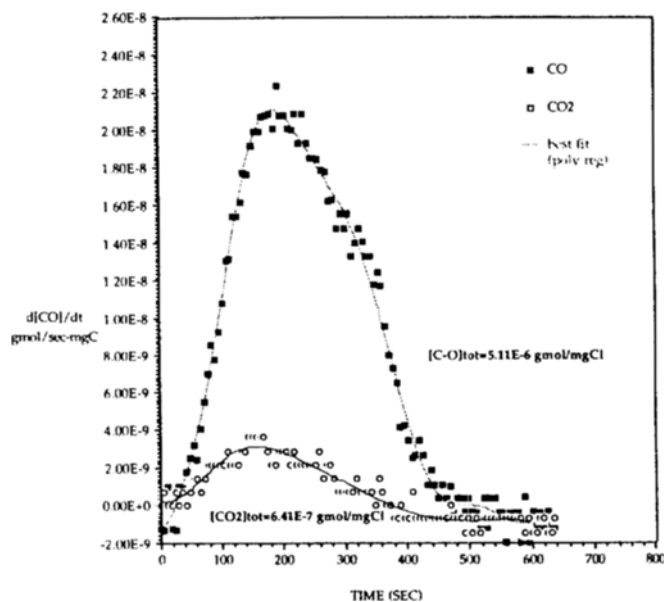

Fig. 11. Experimental TPD spectra of sucrose char at 803 K as a function of time; 4% O₂ and 30% conversion (50°C/min).

are approximately the same. This result gives evidence that the distribution curves for [CO] desorption curves are independent of the heating rate used to generate the desorption data.

Fig. 9 and 10 show the desorption spectra for a sucrose char heat treated at 1115 K. The $[C-O]_{tot}$ for heat treatment sucrose char is 3.84E-6 gmol/mgCi while from the Fig. 11, $[C-O]_{tot}$ was obtained as 5.11E-6 gmol/mgCi. Less oxygen surface complex is formed in heat treatment sucrose char compared to the sucrose char without heat treatment.

When the TPD model was used to obtain desorption spectra

at different starting temperatures the following TPD spectra are obtained as shown in Fig. 12.

The activation energy distribution, f(E), calculated using Eq. (11) are shown in Fig. 13. The preexponential k_0 was taken as 10^{13} 1/sec in the TPD process. From this figure the activation energy distribution function f(E) is approximately Gaussian and the average desorption activation was obtained to be 55 Kcal/mole. When the reaction rate at 30% conversion was used, an activation energy of 34 ± 3 kcal/mol was shown in Fig. 14. Approximately 90% of surface complexes are desorbed as CO: the remainder are desorbed as CO₂.
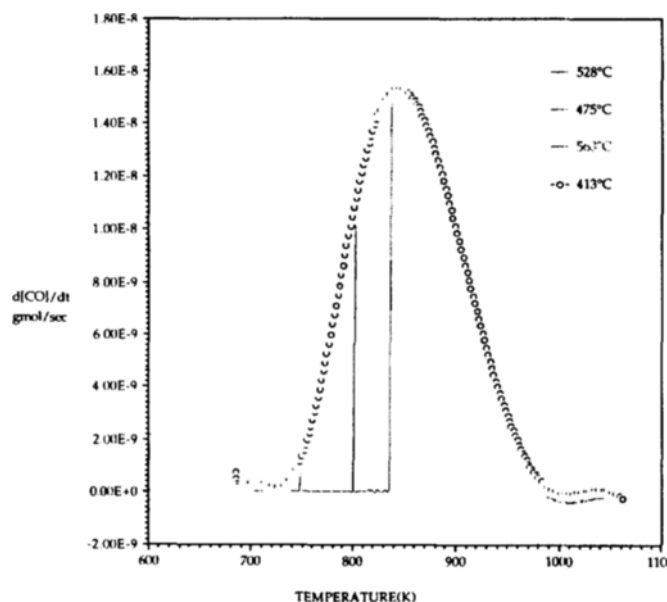
Fig. 12. Experimental TPD spectra of sucrose char at different start-
ing temperature; 4% O_2 and 30% conversion (50°C/min).

Fig. 14. Arrhenius rate plot for sucrose char oxidation at 30% conver-
sion and 4% oxygen pressure.

2. When the reaction rate at 30% conversion was used, an acti-
vation energy of 34 ± 3 kcal/mol was obtained. The product ratio
(CO/CO_2) was found to increase with increasing reaction tempera-
ture.

3. The rate of chemisorption of oxygen on sucrose char is initia-
lly rapid. The oxygen to carbon ratio increase with carbon conver-
sion, however, with greater oxygen coverage there is no change
in the reactivity of the carbon.

4. The desorption of the surface complexes (C-O) on the carbon
surface can be modeled by a site energy distribution function
f(E) which can characterize the surface heterogenity of the carbon.
The peak of energy distribution function f(E) shifts to higher acti-
vation energies with increasing temperature.

5. In sucrose char, the activation energy distribution function
f(E) is approximately Gaussian and the average activation energy
was obtained to be 55 Kcal/mole (with $k_0 = 10^{13}$ 1/sec) and almost
85% of surface complexes are desorbed as CO.
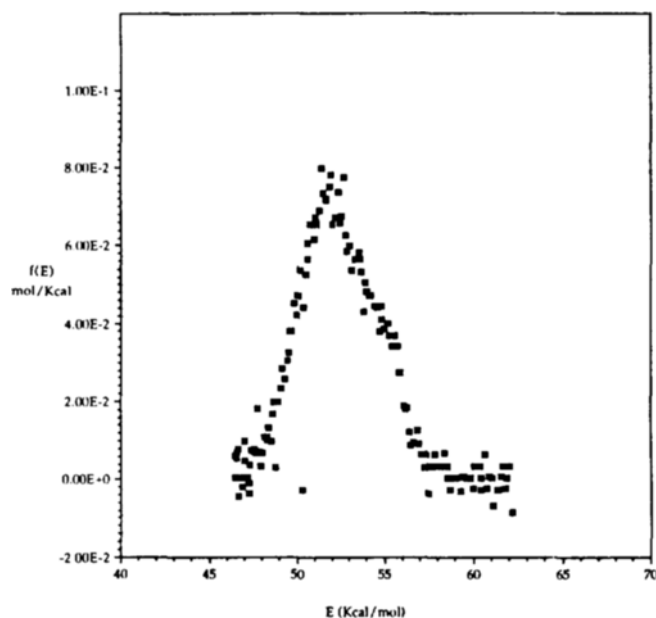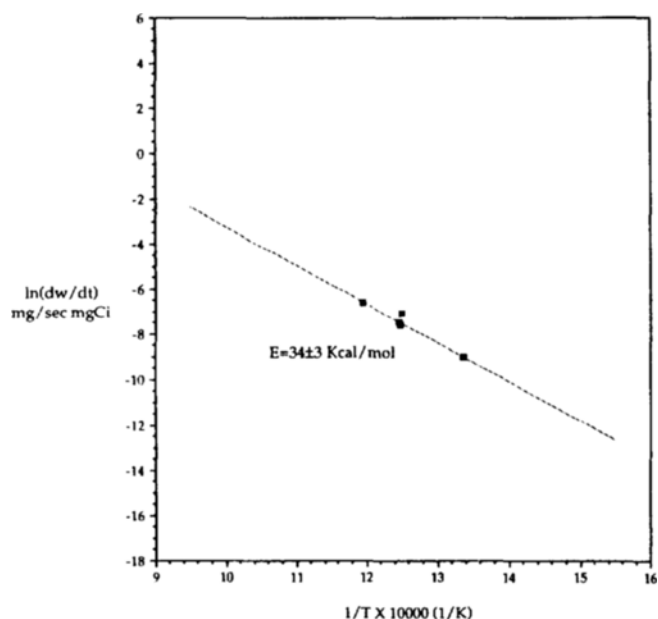

Fig. 13. Energy distribution of sucrose char at 686 K from TPD spec-
tra 4% O_2 and 30% conversion (50°C/min).

The desorption of the surface complexes (C-O) on the carbon
surface can be discussed by a site energy distribution function
f(E) which can characterize the surface heterogenity of the carbon.

CONCLUSIONS

1. Both CO and CO_2 are primary products during the carbon
oxidation. Analysis of the rate of formation of CO and CO_2 shows
the mechanism of products are different and it was found that
the activation energy for CO formation is greater than for CO_2
formation.

NOMENCLATURE

Ea   : adsorption activation energy [kcal/mole]
E_d : desorption activation energy [kcal/mole]
d_p : particle diameter
t   : time
T   : temperature [K]
R   : gas constant [(cc atm)/(gmol) (K)]
D   : diffusion coefficient
Q   : gas flow rate [scc/sec]
p   : pressure [atm]
m   : mass of a molecular
k   : reaction rate constant
C   : molar concentration
C_T : total number of complexes
T'(t) : derivation of the temperature profile [dT/dt]
f(E)   : activation energy distribution function
k_E : rate constant [1/min]

t_f : final time in TPD process
ρ : gas density
r_c : rate of carbon weight loss [gmole C/min]
r_{co} : rate of carbon monoxide evolution [gmole/min]
r_{co2} : rate of carbon dioxide evolution [gmole/min]

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