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ACTIVE SITES IN CHAR GASIFICATION

Final Technical Report

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NOMENCLATURE

Symbol	Description
a	the Elovich constant, as defined by eqn (1) in Chap.4 [kg char/g O ₂],
A _p	specific external area of the particle [cm ² /g],
b	the Elovich constant, as defined by eqn (1) in Chap.4 [g O ₂ /(kg char-hr)],
B	sample burn-off [%],
ASA	active surface area [m ² /g],
C	gas concentration [g/cm ³],
C _s	gas concentration at the surface [g/cm ³],
C _f	a free active site,
C(O), C(O ₂)	oxygen surface complex,
CO ₂ /CO	molar ratio of CO ₂ to CO in gaseous products of gasification,
d	particle diameter [Å, μm],
D _e	effective diffusivity through the pores [cm ² /s],
D _k	Knudsen diffusivity [cm ² /s],
E	activation energy [kcal/mol],
E _A	activation energy of thermal annealing [kcal/mol],
F	number of active sites with a unique activation energy E _A ,
k	pre-exponential in the Arrhenius rate expression [s ⁻¹ , hr ⁻¹],
k _A	pre-exponential in the Arrhenius rate expression for annealing [s ⁻¹ , hr ⁻¹],
m	sample mass [g],

n	amount of adsorbate [mol/g char]; reaction order,
n_m	monolayer capacity [mol/g char],
N_{Av}	Avogadro's number,
P	total pressure [atm, torr],
P/P_0	ratio of partial pressure of an adsorbate to saturation partial pressure at the same temperature,
P_c	critical pressure [atm],
P_{O_2}	oxygen partial pressure [torr, atm],
q	oxygen uptake during chemisorption [g O ₂ /kg char],
Q	heat of adsorption [kcal/mol],
r	reaction rate [g/(g·hr)]; pore radius [Å],
r_m	meniscus curvature [Å],
r_p	particle radius [Å],
s	(= 1 or 2) denotes single or dual site adsorption,
s'	(= 1 or 2) denotes single or dual site desorption,
S	total number of active sites,
t	time [s, hr],
T	temperature [°C, K],
T_c	critical temperature [K],
T_D	desorption temperature [°C, K],
T_p	pyrolysis temperature [°C, K],
TSA	total surface area [m ² /g],

V_o	pore volume [$\text{cm}^3/\text{g char}$],
V_l	molar volume of the liquid adsorbate [cm^3/mol],
V_p	specific particle volume [cm^3/g],
γ	surface tension [dyn/cm]; a constant in the Temkin isotherm (see eqn(11), Chap.4),
ε	char porosity,
η	effectiveness factor,
θ	surface coverage,
Θ	wetting angle [$^\circ$],
ρ	density [g/cm^3],
σ	condensation coefficient,
Φ, Φ_n	Thiele modulus,

Chapter I

BACKGROUND

Gasification and combustion of carbonaceous solids are both likely to remain key industrial processes for many years to come. It is also likely that many different kinds of technologies and feedstocks will be of interest in response to various economic and other factors. This suggests that there is value in research which contributes to the flexibility of design procedures for such processes.

Among the key variables in the design of gasifiers and combustors is the reactivity of the chars which must be gasified or combusted. Significant loss of unburned char is unacceptable in virtually any process; the provision of sufficient residence time for complete conversion is essential. While mass transfer considerations may play a major role in determining the required residence time in some cases, in others, the inherent chemical reactivity is the primary consideration (particularly in gasification processes). A very wide range of reactivities are observed, depending upon the nature of the char in a process. The chars may be produced within the processes themselves, by devolatilization of various carbonaceous materials, or they may be fed directly into reactors as feedstock.

It is not surprising then that gasification of carbonaceous solids has historically been and remains an area of significant scientific and technological interest [1-7]. The current work focuses on furthering the understanding of gasification reactivities of chars. It has been well established that the reactivity of char to gasification generally depends upon three principal factors: (a) the concentration of "active sites" in the char; (b) mass transfer

within the char; and (c) the type and concentration of catalytic impurities in the char. The present study primarily addresses the first factor.

The subject of this research is the origin, nature, and fate of active sites in chars derived from parent hydrocarbons with coal-like structure. This kind of information will ultimately help in understanding what factors contribute to development of active sites in chars derived from coals or any similar hydrocarbon precursors. The nature and number of the active sites and their reactivity towards oxygen are examined in "model" chars derived from phenol-formaldehyde type resins. How the active sites are lost by the process of thermal annealing during the heat treatment of chars are studied, and actual rate for the annealing process is derived. Another focal point of this project is examination of the relationship between low temperature oxygen chemisorption on the char surface and char reactivity towards gasification. Oxygen chemisorption has been widely used as a tool for active surface area determination, but several problems are evident, especially in the application of this technique to chars with low degree of crystallinity, i.e., "young chars."

Since intrinsic char reactivities are of primary interest in the present study, a fair amount of attention was given to the model char synthesis and handling so that the effect of catalytic impurities and oxygen-containing functional groups in the chemical structure of the material were minimized, if not completely eliminated.

The project would not be considered complete without comparing characteristic features of synthetic chars with kinetic behavior exhibited by natural chars, including coal chars.

1 THE NATURE OF ACTIVE SITES.

The gradual pyrolytic evolution of hydrocarbons (possibly including heteroatoms) to highly carbonaceous solids is accompanied by dramatic changes in the gasification reactivity of such materials. Here we are concerned with the gasification behavior of chars that have already undergone active pyrolysis in which most hydrocarbon gases and tars are evolved. The issues involved in transient high rate hydrogasification or steam reactivity during pyrolysis (e.g., [1,8,9]) are not addressed here.

Active sites in relatively pure carbons are normally thought to be associated with various types of imperfections in the carbon structure. Work with graphite has suggested the important role of carbon crystallite edges or dislocations. The majority of mechanistic theories of carbon gasification are based on the "pure-carbon-surface- with-imperfections" model. This is appropriate for chars that have been heat-treated at high temperatures for extended periods of time and thus have relatively low residual oxygen and hydrogen contents (i.e., "old" chars). Some caution must be exercised in applying results obtained from pure carbons to "young" chars.

Carbon gasification theories are based largely upon chemisorption-desorption mechanisms (some also allow for surface diffusion of intermediates). The same type of oxygen-carbon complexes appear to be involved in oxygen, steam, and carbon dioxide gasification [2, 10]. A correlation has also been demonstrated between active sites involved in hydrogen gasification and those involved in carbon dioxide gasification, although there is no direct proof that the sites involved are indeed the same in both cases [1].

There have been numerous attempts to measure active site concentrations in carbons and chars. In one such study [11], the total active surface area (ASA) was estimated by exposure of a char surface to oxygen at low temperatures (ca. 300°C). Under these conditions, surface carbon oxides are not released, so all the absorbed oxygen was assumed to be chemisorbed on active sites. Heating the char to 950°C released the adsorbed oxygen, and the ASA was calculated assuming each oxygen atom released had been chemisorbed on an edge-type carbon atom of 8.3 Å². In this manner, it was determined that the ratio of ASA to total surface area (TSA) increased by about an order of magnitude during oxidation of a graphitized char. Another study suggested that the variation in this ratio was actually rather small during combustion of many heat-treated chars [12]. Other work involving steam gasification of various chars pointed out that the $\frac{\text{ASA}}{\text{TSA}}$ might vary by an order of magnitude among different materials [13]. This point is addressed further below.

1.2 EFFECT OF TEMPERATURE ON ACTIVE SITE CONCENTRATION.

There exists a distinction between "active" sites that are reactive and those that are nonreactive at a given temperature. The reactive "active" sites are responsible for the release of surface carbon oxides, while the nonreactive "active" sites will chemisorb oxygen, but will not release surface oxides at the temperature under consideration. Raising the temperature of the carbon can convert some nonreactive to reactive "active" sites [5, 11]. This mechanism,

combined with the expected Arrhenius-type enhancement of chemical reaction rates, results in increasing gasification rate with temperature.

The preceding effect, however, is not always observed, and thus other factors must also play a role. For example, it has been observed that the rate of carbon combustion normally increases with increasing temperature, up to about 1200°C. In the 1200-1700°C temperature range, however, it has often been noted that the rate of combustion actually decreases with increasing temperature [5, 14-17]. One explanation for this behavior is known as "thermal annealing" [3, 5, 18-20]. This same effect has also been postulated as being responsible for a decrease in reactivity towards other gases as well [1, 21, 22]. There is a trend towards lower reactivity with increased time and temperature of char heat treatment [1, 23-29]. This behavior reflects a progressive and continuous ordering of the remaining carbon, and is actually an extension of the pyrolysis process, some aspects of which have recently been explored in a study on coal chars; it has been noted that more highly heat treated chars have a more highly ordered structure, based on an electrical conductivity increase, with increasing severity of pyrolysis. This electrical conductivity was seen to be uniquely related to a measure of reactivity in oxygen [30].

It would, therefore, seem logical to associate the temperature dependence of the annealing process in chars with the activation energies of the latter phases of pyrolysis; i.e., 100 to 200 kcal/mol, typical for high temperature H₂ release [31] and graphitization [32], respectively. In fact, this range is consistent with the results of a few annealing studies on pure, relatively graphitic carbons [15, 20]. In another recent study, the oxygen reactivity of chars seemed to correlate with the remaining hydrogen content of the chars [33, 34].

Thus, again the activation energy for annealing might be expected to be that for H_2 release during pyrolysis. The values of annealing reaction activation energies derived from experiments with "younger" chars have been generally lower than those for pyrolytic H_2 release, however; in the case of annealing of chars with respect to gasification by hydrogen, activation energies have been reported in the range of 9-20 kcal/mol [1, 35, 36]. The same range has been observed for annealing with respect to oxidation reactions, but the activation energies for annealing of a given char with respect to oxygen attack are not always the same as for annealing with respect to hydrogen [36]. Such low values of the activation energy for annealing may be an artifact of the model used to describe the annealing process. In almost all of the cases cited, annealing was treated as a simple, single, first order chemical process (thus described by a single activation energy). More realistically, however, annealing in "young" chars involves a wide spectrum of pyrolytic reactions, ranging from those involving gas evolution to those responsible for graphitization. It is well known that modelling a set of independent, parallel chemical reactions by a single, first order rate model can give rise to a pseudo-activation energy lower than any of the "true" activation energies in the set of reactions (e.g., see [37]). Of course, there is no direct proof that this was the case in the studies cited. The issue is further complicated by the fact that in the case of chars derived from natural products, the annealing process may also be accompanied by changes in the form of catalytic impurities [36].

The accurate prediction of thermal annealing rates depends upon having a proper model of the processes involved. While a single, first order reaction model may be quite adequate for predictive purposes within a narrow

range of heating rates, it may perform quite unsatisfactorily when applied to situations in which heating rates are quite different. Recently, there has been increased interest in the reactivity of chars produced at high heating rates. These studies have shown that as heating rate is increased, char reactivity increases [23, 38], possibly by the promotion of more chaotic crystallite growth.

The annealing reactions can affect the activation energy of gasification reactions [39]. When corrected for mass transfer effects, the activation energy for oxidation reactions seems to decrease with increasing char pretreatment temperature [5], thereby suggesting a shift in the stability of the remaining active sites. Another study found, however, that more highly ordered, heat treated materials had higher activation energies for oxidation [40]. There seems to be a mild disagreement on "typical" activation energies for chars. The compilation of reactivities of a large variety of chars by Smith [40] has shown a relatively "constant" activation energy of 43 kcal/mol over a wide range oxidation of temperatures. Another study found a value of 34 kcal/mol for many chars of many reactivities [33]. In compilations of data on a large number of chars, the subtle variation of activation energy with the "age" of individual chars may not be noticeable.

1.3 THE RELATIONSHIP BETWEEN PRECURSOR MATERIAL AND ACTIVE SITES.

There exists significant evidence that the nature of the parent hydrocarbon material has a major influence on both the concentration and the

active sites for gasification. The differences are greatest during the early phases of pyrolysis, decreasing thereafter as the carbon increases in purity as a result of heat treatment. In the case of coals, there is a marked trend towards decreased hydrogasification activity with increasing rank [1] (a similar trend has been reported in another study, but with more scatter; [41]). This effect is at least partially attributable to the variation of available surface area with rank, although probably also to differences in inherent reactivity of the carbons. The rates of steam, carbon dioxide, and oxygen gasification are, likewise, known to depend to some extent upon the parent material of the char [1, 13, 23-25, 42]. It is important to account separately for variation in total surface area, catalytic effects due to impurities, and the chemical nature of precursor material (e.g., see review [43]).

The ratio of active to total surface area has been previously noted to be a function of the type of char [13]. This ratio may vary from a few percent [11] to near unity for thin layers of pyrolytic carbon [44].

It has been established that during low temperature oxidation of coal, the non-aromatic sites are attacked preferentially [45]. Exactly how long, during the course of pyrolysis, these originally non-aromatic sites retain their identity as active sites, has not been established. In the case of graphites, it is well known that the formation of etch pits reflects a preferential attack on edge atoms (e.g., see review [46]). The carbon atoms on the edges of the large parallel layers in graphite are considerably more reactive with respect to oxidation than those located on the basal plane (at temperatures of 727°C and above; [47]). Non-graphitic carbons are generally comprised of a mixture of crystallographically-ordered aromatic regions and disordered carbon. It has

been observed that during oxidation of carbon blacks and partially graphitized carbons, the disordered regions are more reactive (review [48]).

Thus, it is clear that differences exist in the reactivity of different physical regions in the char. The question of whether or not these differences correlate with particular chemical features of the char precursor has not been thoroughly explored. Among the few examples are suggestions of correlations between char reactivity and organic oxygen content [30, 49, 50]. The amount and chemical nature of oxygen in the char is unquestionably related to the structure of the parent materials. The problem of understanding and predicting char reactivity is thus closely related to the study of the formation of carbons by pyrolysis (e.g., review [51]; the role of mesophase, [52]; graphitization [32, 53]; ESR studies, [54]; general physical properties of non-crystalline carbons, [55].

1.4 CHANGES IN THE NATURE AND CONCENTRATION OF ACTIVE SITES WITH GASIFICATION.

In only a relatively few cases is it known exactly how the nature of active sites changes with extent of gasification. It has been observed that graphites oxidize or gasify primarily via edge atom attack. For carbons containing both ordered and disordered regions, the disordered regions usually burn off first [48]. The same conclusion may be inferred from data on oxidation of pyrolyzed phenol-formaldehyde resins [56]. The reported crystallite dimensions of the chars (an indicator of the average size of the ordered regions) was not observed to change even up to 40% burn-off. This

implies that the reaction occurred primarily in the disordered regions. This same study [56] also sheds some light on the annealing process. As expected, char reactivity was observed to decrease with increasing preparation temperature. The fact that this decrease was not accompanied by large changes in either the size of the ordered regions or the total surface area, suggests that annealing probably involves processes in the disordered regions (perhaps a "shifting" of carbon from disordered to ordered regions, with a preferential average crystallite size). Unfortunately, the fraction of carbon in disordered versus ordered regions was not reported.

Direct measurements of the ratio of active to total surface area have been performed as a function of extent of gasification or burn-off [11, 57]. In both these cases, the ratio appears to increase with increasing extent of gasification. In another study, the ratio of reactivity to active surface area has been reported as constant, over a wide range of burn-off [58], as has the activation energy for oxidation [59]. In the case of highly graphitized chars, this behavior can be explained in terms of an increase in the fraction of edge atoms with burn-off, or alternatively, by the "co-operative effect" (i.e., edge atoms becoming more reactive with increasing depth of the etch pit [60, 61]. In chars with small crystallite regions and much disordered structure, the decrease in reactivity with loss of disordered carbon might be compensated for by changes promoting greater reactivity in the remaining carbon.

1.5 OBJECTIVES OF THIS STUDY AND AN OVERVIEW OF METHODOLOGY.

At the inception of this project, the intention was to produce a variety of chars from polymeric materials with structures similar to phenol-formaldehyde resins--that is, with small aromatic units joined by methylene bridges. These materials were felt to be reasonable "models" for coals, but could be conveniently produced in-house in relatively pure form. The purity issue is important, insofar as assuring that catalytic mineral effects are negligible. In the present phase of the study, only chars from one type of phenol-formaldehyde resin were studied, since these materials proved to be interesting enough in behavior to warrant an entire project on them. A few benchmark experiments were performed under similar conditions on lignite chars in order to validate the selection of these materials as "models" for coals. Work on the question of the role of variations in chemical structure of the parent resin on subsequent char reactivity must await a future study.

The synthesis of the resin is described in detail in subsequent chapters. Despite great efforts to assure the purity of this material, some catalytic elements nevertheless are present at low levels in the char. A typical "average" char sample contained 144 ppm Na, 57 ppm K, and 22 ppm Ca. As of this writing, work continues on trying to establish whether such low levels of impurity are at all significant in affecting the reactivity of these model chars. At the relatively mild oxidation conditions of interest in this study, some recent work on bituminous coal chars suggests that with reactive chars such as these, the effects of mineral impurities may be small [34, 62],

and of course, the present materials have much lower mineral contents than do some typical demineralized coal chars. Another recent study has shown that acid demineralization of a lignite does substantially reduce its low temperature oxidation reactivity [63], so it would be inappropriate to conclude that reactivity enhancement does not exist under these conditions. It is only suggested that the level of impurity in the present phenol-formaldehyde chars is so low as to not be of importance. Thus, this report is written in line with the present view that mineral effects are negligible.

The model chars studied were extensively characterized with respect to:

1. Elemental analysis
2. Surface areas (N_2 and CO_2)
3. Active surface area (by O_2 chemisorption)
4. Low temperature O_2 chemisorption kinetics ($T < 250^\circ C$)
5. Low temperature O_2 gasification kinetics ($T > 250^\circ C$)

This report will focus on these measurements and offer conclusions concerning the effect of heat treatment temperature and burn-off on these factors. This sort of preliminary, fundamental study of a model material is a necessary prerequisite to further studies, in which the additional complication of changes in the initial chemical composition on the char properties are to be studied.

It is appropriate to note at the outset that these chars are indeed reasonable models for coal chars, based on a number of comparisons with these latter materials. A sample of phenol-formaldehyde char was tested using the non-isothermal reactivity test of Solomon et al. [30, 33] and found to obey the

same general correlation between electrical resistivity and reactivity (as measured by a "critical temperature") as do a variety of coal chars [30].

A comparison can also be made of the reactivity of these model chars with the general correlation of char oxidation reactivity, as developed by Smith [40]:

$$r(\text{g/m}^2\text{hr}) = 1.098 \times 10^{10} \exp (-42800/RT)$$

where $R = 1.987 \text{ cal/mol-K}$. The correlation was developed for oxidation at 1 atm partial pressure of oxygen, for which conditions data are available from this study. The comparison is as follows (r in $\text{g/m}^2\text{hr}$):

<u>Toxidation (K)</u>	<u>Heat Treatment Temp. (K)</u>	<u>r measured</u>	<u>r predicted</u>
573	1273	9.2×10^{-7}	5.1×10^{-7}
573	1673	1.3×10^{-7}	
623	1273	8.7×10^{-6}	1.0×10^{-5}
623	1673	1.5×10^{-6}	
673	1673	1.3×10^{-5}	1.4×10^{-4}

The correlation does not take into account variations between different kinds of chars, and as a result has at least an order of magnitude uncertainty inherent in it. The main conclusion from this comparison can then only be that the phenol-formaldehyde resin char is a fairly "typical" char, whose reactivity is reasonably well predicted by the correlation when its heat

treatment is "mild" (1273K for about 2 hours) and whose reactivity is less than that predicted by the correlation by almost an order of magnitude upon heat treatment at 1673K for 2 hours.

The activation energy for the oxidation reactions of the phenol-formaldehyde char have been determined to be in the range from 24 to 36 kcal/mol. This compares well with several recent studies on oxidation of true coal chars which have yielded values of 34.8 kcal/mol [33], 29 kcal/mol [59], 31 kcal/mol [34], and 29 to 42 kcal/mol [64]. This point will be discussed further in Chapter 4.

In addition to the kinetic behavior, the porosity of the phenolic resin char is also similar to those found in coal chars. In summary, it appears that the phenolic resin char is a good model for coal chars, but without the heterogeneities and difficult-to-remove mineral impurities that the latter materials contain.

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chapter II

MATERIAL CHARACTERIZATION

2.1. CARBONS DERIVED FROM PHENOLIC RESINS -- CHEMICAL CHANGES OCCURRING DURING CARBONIZATION

Phenol-formaldehyde resin formation can be represented as follows:

Either basic or acidic catalysts can be used and the resulting polymer is termed resol or novolac, respectively. By varying the phenol-to-formaldehyde ratio, nonlinear polymers with different degrees of cross-linking can be obtained.

The process of phenolic resin carbonization consists in a thermal treatment of the resin under non-oxidizing atmospheres (an inert gas or vacuum) up to temperatures as high as 3000°C. Carbonization has been customarily divided into two steps: the so-called curing, which occurs at temperatures between the temperature of formation and 400°C, followed by a high-temperature pyrolysis. Chemical changes in the carbonaceous material during carbonization will be briefly reviewed in this section. No claim of completeness is made, however, and the reader is referred to more extensive reviews in the literature [1,2].

Although the reaction between phenol and formaldehyde was known as early as 1872 [3], the structural features of the cured resin remained a mystery for nearly a century. The obvious reason for such a failure to understand the chemistry of many thermosetting resin systems is the fact that these materials are insoluble, infusible, high-molecular weight polymers that are difficult to analyse by conventional techniques of analytical chemistry. It was only after implementation of more sophisticated methods, such as infrared and nuclear magnetic resonance spectroscopies, isotopic labelling of monomers, x-ray crystallography, as well as chromatographic techniques, that some insights into the structure of cured polymers could be made. The results thus obtained were combined with the knowledge of gaseous products of phenolic resin thermal decomposition, to lead to

various formulations of chemical pathways in the process of degradation.

Ouchi and Honda have studied the structural changes of phenol-formaldehyde resins during carbonization [4-10]. It was determined that the primary gaseous products of pyrolysis were methane, water, carbon monoxide and hydrogen. Methane was produced as a result of decomposition of methylene bridges, while water was formed from hydroxyl groups; water and the decomposed bridge radicals ($\text{---CH}_2\text{---}$) reacted to yield carbon monoxide. It was demonstrated that about 70% of carbon atoms present in the carbon bridges remained in the residual carbon. Differences in the condensation type of the original material (linear versus weakly or strongly cross-linked) were found to be inconsequential with respect to carbonization. The carbonaceous materials produced below 700°C had unpaired electrons and no large condensed aromatic rings. In the temperature range $700 - 1400^\circ\text{C}$, however, the hydrogen atoms bonded directly to the benzene nuclei began to split off and condensation of aromatic rings followed. The carbon formed between 1400 and 2000°C was found to have large condensed aromatic rings and a two-dimensional graphite-like lattice. A qualitative description of high-temperature graphitization of char can be found in [11]. Further evidence of dehydration involving hydroxyl groups and aromatic ring condensation was given by Wolfs *et al.* [12]. It was also found that the "aromatic" hydrogen was released during the secondary carbonization, partly as methane.

An important contribution to the study of thermal degradation of phenolic resins was the work done by Conley *et al.* [13-15]. It was determined that oxidation was the primary mechanism of degradation even though carbonization was carried out in an atmosphere of argon or in a vacuum. The presence of water produced during curing, and possibly oxygen and water adsorbed from the air by pre-dried samples, were believed to be responsible for the original oxidation of methylene bridges $\text{---CH}_2\text{---}$ to benzophenone $>\text{C}=\text{O}$. This remarkable observation, later verified and supported by other researchers (e.g. see [16,17]), led to the statement that "...It is virtually impossible to study a phenolic resin system on a purely nonoxidative basis" [2]. This mode of oxidation from within, or auto-oxidation, also agrees with previous evidence of spontaneous oxidation of phenolic resins [18]. A more comprehensive picture of structural changes during curing and pyrolysis could now be presented [10, 13-15].

Three functional group species seem to predominate in the original uncured polymeric system: the methylene linkage (A), the methylol linkage (B), and the dibenzyl ether linkage (C), with the methylene linkages being the major functional group.

(A)

(B)

(C)

Infrared spectra show no presence of benzophenon-type, quinone-type, carboxyl, or carbonyl species in the cured resin [14]. The following are the major reactions which occur below 400°C:

(1)

and

trimer

(2)

in contrast to the mechanism proposed in [10]

(3)

for which no experimental verification has been found (e.g. diphenyl ether linkages in infrared spectra). This reaction is known to occur above 400°C, however.

The cured phenolic resin contains methylene linkages, residual methylol groups, dihydroxybenzophenone linkages from oxidation during curing (see eqn (4) below), and substituted salicylic acid moieties resulting from methylol oxidation (see eqn (5) below).

Other typical reactions for resin decomposition are presented in Fig. 2.1 [14].

As far as the gaseous products of resin degradation are concerned, it has been already noted that water and paraformaldehyde are major products below 400°C . Carbon dioxide, methane and carbon monoxide begin to be evolved at temperatures of 300, 400 and 500°C , respectively. The following char formation mechanism was postulated to account for these changes, with methane evolution pathway illustrated in Fig. 2.1.

This mechanism is consistent with the fact that carbon monoxide is not evolved at lower temperatures, and is further substantiated by hydroxyl and carboxyl groups detected in the charred material at 700°C. The last step of eqn (6) does not seem to be well-understood, even its stoichiometry is incorrect, and indeed very little is known about mechanisms involved in formation of polyaromatic structures in chars. Thermal decomposition through quinone-type linkages was deduced from char formation occurring simultaneously with the appearance of carbon monoxide.

Thermogravimetric and elemental composition studies of char formation were reported by Lochte *et al.* [19]. The results show a remarkable constancy of weight loss during pyrolysis, which varied between 40.0 and 43.8% for ten samples of phenolic resins having different degrees of cross-linking and different curing histories. The elemental composition of both the cured resin and char formed at 800°C also turned out to be independent of the starting material, which is evident from data shown in Table 2.1. Samples A and B were prepared using $\text{Ca}(\text{OH})_2$ as a catalyst and had phenol to formaldehyde ratios of 0.42 and 0.36, respectively. Resin C was a commercial product (CTL-91-LD, obtained from the American Reinforced Plastics Company, Los Angeles,

California) as was resin D (SC-1008, obtained from the Monsanto Company, Plastics Division, Springfield, Massachusetts). Curing was carried out in air under the following conditions: 72hr at 74°C, 2.5 hr increasing from 74 to 108°C, and finally 19hr at 127°C; an additional curing step (post-curing) was employed and it involved 6 hr at 149°C, 8 hr at 177°C, 8 hr at 199°C, 30 min. increasing from 199 to 232°C, and 30 min. at 232°C. Traces of nitrogen present in commercial grade resins were not included in elemental analysis data.

Table 2.1 Elemental composition of phenolic resin heat-treated to various temperatures (heating rate 3.3°C/min. in argon) [19].

SAMPLE A					
T [°C]	wt %			Atomic Ratio × 100	
	C	H	O*	O/C	H/C
as cured	72.81	5.49	21.70	22.35	90.0
180	71.38	5.19	23.43	24.62	87.6
260	73.22	5.15	21.63	22.12	84.0
320	72.04	4.82	23.14	24.08	80.4
420	73.33	4.68	21.99	22.50	76.8
460	75.94	4.61	19.45	19.20	73.2
490	78.60	4.61	16.79	16.05	70.8
520	82.25	4.51	13.24	12.08	66.0
560	85.65	4.23	10.12	8.85	58.8
610	89.31	3.58	7.11	6.00	48.0
675	90.75	2.35	6.90	5.70	31.2
705	92.56	2.10	5.34	4.35	27.6
810	93.73	1.17	5.10	4.05	14.4

SAMPLE B					
T [°C]	Wt %			Atomic Ratio × 100	
	C	H	O*	O/C	H/C
as cured	72.37	5.31	22.32	23.10	87.6
180	72.15	5.21	22.64	23.55	86.4
260	72.99	5.13	21.88	22.50	84.0
320	72.20	4.91	22.89	23.78	81.6
420	73.56	4.63	21.81	22.20	75.6
460	75.57	4.60	19.83	19.68	73.2
490	77.37	4.56	18.07	17.55	70.8
520	80.15	4.32	15.53	14.55	64.8
560	85.29	4.12	10.59	9.30	57.6
610	88.67	3.43	7.90	6.68	46.8
675	91.12	2.43	6.45	5.32	32.4
705	--	2.15	--	--	--
810	94.12	1.13	4.75	3.75	14.4

SAMPLE C

T [°C]	wt %			Atomic Ratio × 100	
	C	H	O*	O/C	H/C
as cured	75.78	5.60	18.62	18.45	88.8
180	75.41	5.37	19.22	19.12	85.2
260	74.49	5.15	20.36	20.48	82.8
320	72.85	4.83	22.32	22.95	79.2
420	74.99	4.67	20.34	20.32	74.4
460	76.43	4.71	18.86	18.52	74.4
490	79.04	4.64	16.32	15.45	70.8
520	81.81	4.58	13.61	12.45	67.2
560	85.44	4.22	10.34	9.08	58.8
610	88.70	3.46	7.84	6.60	46.8
675	90.45	2.44	7.11	5.92	32.4
705	90.75	2.17	7.08	5.85	28.8
810	93.88	1.25	4.87	3.90	15.6

SAMPLE D

T [°C]	wt %			Atomic Ratio × 100	
	C	H	O*	O/C	H/C
as cured	76.63	5.57	17.80	17.40	87.6
180	74.77	5.12	20.11	20.18	81.6
260	74.49	5.24	20.27	20.40	84.0
320	72.82	4.80	22.38	23.02	79.2
420	74.67	4.74	20.59	20.70	75.6
460	76.79	4.51	18.70	18.30	70.8
490	78.93	4.82	16.25	15.45	73.2
520	81.77	4.37	13.86	12.68	63.6
560	85.43	4.10	10.47	9.22	57.6
610	90.79	3.63	5.58	4.58	48.0
675	91.32	2.34	6.34	5.18	31.2
705	91.25	2.06	6.69	5.48	27.6
810	93.42	1.24	5.34	4.28	15.6

* by difference

Changes in elemental composition of studied resins clearly reflect progressive carbonization of the material with increasing temperature of treatment. Carbon content continuously increases with severity of pyrolysis (or extended curing), whereas concentrations of oxygen and hydrogen decrease due to breakdown of hydroxyl groups and evolution of gaseous species.

The degradation processes occurring at elevated temperatures were interpreted to be dependent upon the stability of the dihydroxydiphenylmethane unit. This is why all the studied polycondensates (including some commercial resins) showed a similar chemical behaviour once the curing process is completed. It should be noted here that this is

consistent with the mechanism postulated in [14] (see eqns (4) and (6) above).

A detailed infrared analysis of phenolic resin degradation was reported by Ouchi [20]. In this work, few or no changes were found to occur in the original structure of the phenolic resin up to about 300°C. Above this temperature dehydration via the reaction paths (7) and (8) occurs:

Diphenyl ether linkages were observed to appear at 400°C and vanish above 500°C, which was inferred from a rapid increase of the absorption band near 1256 cm^{-1} at about 400°C, and from its practical disappearance above 500°C. Reaction of sodium metal in liquid ammonia produced a reduction of intensity in that region, indicating cleavage of diphenyl ether type linkages and providing strong evidence for reaction (8).

Significant changes were reported at the methylene bridges above 400°C: they decomposed and formed carbonyl and methyl groups; the concentration of the former was found to exhibit a maximum at 500°C. The ratio of aromatic to aliphatic hydrogen was followed and was found to decrease slightly with temperature up to 400°C and increase sharply at higher temperatures. This was explained by a breakdown of methylene bridges and the concomitant evolution of hydrogen, methane and carbon monoxide:

The intermediate stages proposed for reactions (9) and (10) are [20]:

The simultaneous appearance of a weak carbonyl band at 1660 cm^{-1} (cf. $\nu_{\text{C=O}}$ at 1667 cm^{-1} in anthrone [21]) and a methyl band at 1385 cm^{-1} provide some support for these suggestions. From 600°C onward, the aromatic hydrogen also began to be eliminated and the spectra became structureless, perhaps due to aromatic ring condensation. The oxygen remaining at this stage is believed to be present as inner-ring oxygen, as in diphenylene oxide. Paranthetically, evolution of hydrogen reported by Ouchi and Honda [10] was not observed by Jackson and Conley [14], who implied that perhaps the former workers used phenolic resin from commercial sources. Such materials are known to contain propanol as a solvent.

It should be noted that although this mechanism differs from the one proposed by Jackson and Conley [14], both of them contain the idea of auto-oxidation. It is beyond the scope of this work to resolve the dispute between Conley and Ouchi over reaction (3), i.e. whether diphenyl ether structures occur during phenolic resin degradation or not. It should

be pointed out, however, that Morterra and Low did report such linkages in phenolic resin cured at 360°C in vacuum, but curing in nitrogen at 350°C did not produce this kind of evidence [22]. Diphenyl linkages were observed by these workers above 500°C irrespective of whether pyrolysis was carried out *in vacuo* or in nitrogen, and this in turn contradicts disappearance of these structures above 500°C observed by Ouchi [20]. It is even suggested that oxygen bridges of the aryl-aryl type may survive high temperature carbonization and remain present in condensed, polyaromatic domains formed after the final collapse of the phenol-formaldehyde network [22]. The significance of the 1260 cm⁻¹ band for identification of diphenyl ether linkages does not seem to be in question as, apart from the convincing sodium metal test carried out by Ouchi [20], absorption in this region is assigned to aryl ether by standard reference books on infrared spectral analysis [23,24].

Composition and kinetics of the volatile products of the thermal degradation of phenolic resins were studied by Shulman and Lochte [16]. Spectrometric thermal analysis to 800°C (a linearly programmed heating cycle) was the method employed and activation energies for the formation of each product as well as for degradation of the polymer were determined.

Kobayashi *et al.* [25] carried out an x-ray diffraction study of crystalline characteristics of chars derived from phenolic resins. They found that such resins produce a hard (i.e. non-graphitizing) type of carbon. The spacing $d(110)$ was found to be constant in the range of heat treatment temperature 1000 - 1400°C, and to increase gradually with temperatures above 1400°C. The crystalline thickness $L_c(002)$ exhibited the same behaviour as $d(110)$. The crystalline size $L_a(100)$, however, was found to increase slowly with heat treatment temperature, showing some plateaux in the ranges of 1000 - 1400°C and 2000 - 2500°C.

The formation of glass-like carbon by thermal decomposition of three-dimensional cross-linked polyfurfuryl alcohol resin, phenolic resin, and mixtures thereof, was found to be independent of the chemical structure of these resins [26]. In each temperature range (up to 1200°C), no pore formation was detected by light and electron microscopy, from which it was concluded that the pore diameter of the chars was less than 30 Å. Both the micropore volume and the BET total surface area (TSA) exhibited maxima at 700°C (the micropore volume and TSA were 4 mm³/g and 125 m²/g, respectively). However, a commercial "glassy carbon" was also examined at various stages of pyrolysis, and pores with diameters from 2 to 20 µm were found. It seems to be more reasonable to term these as macroscopic cracks rather than pores, and they are certainly inconsequential in finely

ground and sieved material that is the subject of most studies.

Carbonization of phenol-formaldehyde resin labelled with deuterium and ^{13}C was studied by Yamashita and Ouchi [27]. The following de-watering reactions were found to prevail below 400°C :

The relative importance of these reactions is shown in Table 2.2 [27]:

Table 2.2. Proportion of dewatering reactions (11) - (13)

SAMPLE	200-300°C			340-400°C		
	REACTION (11)	REACTION (12)	REACTION (13)	REACTION (11)	REACTION (12)	REACTION (13)
Ph(--OD)	50.0%	43.0%	7.0%	0%	97.0%	3.0%
Ph(--CD ₂ --)	50.0%	43.4%	6.6%	0%	95.6%	4.4%

The Ph(--OD) and Ph(--CD₂--) runs should be treated as two independent experiments here, since no isotopic effects are involved.

Methane was found to be primarily a product of methylene bridge decomposition, while carbon monoxide was proposed to be liberated according to the following mechanism:

A schematic representation of the entire process of carbonization, as suggested in that study, is presented in Fig. 2.2 [27].

Thermal degradation of a novolac-type resin was investigated by means of infrared spectroscopy by Morterra and Low [22]. It was found that, unlike for resols studied by Conley *et al.* [13-15] and Ouchi [20], the auto-oxidative mechanism did not represent an important reaction pathway in thermal degradation of novolac resins. A similar conclusion had been previously reached by Camino *et al.* [28], and it was based on the apparent absence of absorption near 6.2 μm , i.e. 1613 cm^{-1} ($>\text{C}=\text{O}$). CO_2 rather than CO was found in the products of thermal degradation, however, and the authors admit that "an

oxidation process takes place. Thus -- they continue -- it is confirmed that the resin itself acts as a source of oxygen for the oxydation process." Apart from this, Morterra and Low did observe the $>C=O$ absorption in the infrared spectrum and they based their conclusion of unimportance of auto-oxidation upon the weakness of absorption near $6.2\ \mu\text{m}$. In any case, the studies by Morterra and Low and by Camino *et al.* might suggest that the way in which the starting material is synthesized may be of some importance to the nature of chemical changes occurring during carbonization. They offer no explanation, however, as to why resols should behave differently from novolacs.

The degradation reactions proposed by Morterra and Low are presented below [22]:

--curing ($T \cong 360^\circ\text{C}$, vacuum):

The formation of diphenyl ether linkages was deduced mainly from a sharp band growing near $1260\ \text{cm}^{-1}$, assigned to the aryl-ether $\text{C}-\text{O}-\text{C}$ assymetric stretching mode.

Fragmentation reactions also occur, involving cleavage of some methylene bridges, with subsequent elimination of fragments competing with the branching and cross-linking of some of the chains in the residue at the active ring positions:

These reactions were inferred from the CH stretching region ($3100\text{--}2800\ \text{cm}^{-1}$) being more readily observable and clearly defined than in the original resin. According to the authors, the extent of this change cannot be ascribed only to a decreased overlapping with the OH

stretching band. In particular, the aliphatic component absorbing below 3000 cm^{-1} appeared to be slightly shifted, better resolved, and increased in intensity, which was paralleled by an increase in intensity of a band near 1470 cm^{-1} attributed to a CH_n deformation mode. Some other changes in the IR spectrum were consistent with the proposed scheme but the authors admit that this mechanism "may appear to be somewhat speculative on the basis of the 360°C data." It is interesting to note that the thermal degradation described above occurred only in a vacuum cured resin. No major change was observed in the spectrum of a novolac resin heat-treated at 350°C in the stream of nitrogen, and it is not quite clear why such a different behaviour was observed. It is probable that at the lower temperatures, vacuum was more efficient in removing evolved material than the stream of nitrogen; at temperatures above 500°C , both methods of pyrolysis were found to give identical results [22].

--pyrolysis ($T \cong 500^\circ\text{C}$)

(It should be noted that the reaction "B" was previously hypothesized by Ouchi *et al.*[10,20], although no experimental evidence for it was found at that time.) Pyrolysis at higher temperatures brought about condensation into large polyaromatic domains and the resulting char was found to be much like other intermediate temperature chars.

Concluding, one must admit that the study of chemical changes occurring during the carbonization of phenolic resins has not led to a complete knowledge of the chemical structure of the resulting chars. A number of unresolved questions remain: e.g., the presence or absence of diphenyl ether linkages and temperature ranges where they allegedly occur; the role of novolac versus resol type precursors; evolution of hydrogen, propanol, etc.; the various reaction paths postulated, etc. It seems that the initial stages of curing are relatively well understood, while all that can be said about extensively pyrolysed materials is that they contain condensed polyaromatic rings with unknown functionalities. It appears that the characteristics of the original phenol-formaldehyde resin have little or no effect upon the structure of the resultant char. It is unfortunate that no quantitative data are available on numbers of --OH, --COOH, >C=O, etc. groups remaining, as a function of pyrolysis temperature. Some additional light may perhaps be shed on the chemistry of carbon by direct examination of char surfaces by means of various spectroscopic techniques. It is well-known, however, that such studies are very difficult and often inconclusive in the case of chars. On the basis of the reviewed literature, the following conclusions about the nature of chars pyrolysed at and above 1000°C can be made:

- (1) all hydroxyl, methylol and methyl groups are gone;
- (2) dibenzyl ether linkages as well as methylene linkages do not occur;
- (3) low hydrogen-to-carbon atomic ratio implies highly condensed aromatic structures;
- (4) oxygen survives thermal treatment mainly in the form of carbonyl and quinone-type linkages; diphenylene oxide is probably present, and diphenyl ether is most probably gone.

2.2 SYNTHESIS, CURING AND PYROLYSIS OF PHENOL-FORMALDEHYDE RESIN

Since the interest in phenolic resins dates back to the end of the previous century there is a great deal of information on phenolic resin production available in the literature. None of the common laboratory or industrial procedures could be directly applied in this work, however, due to high standards of purity that had to be met by the starting material for the model char. These specific requirements are:

- (a) uniform chemical structure throughout the model compound and virtual absence of non-carbon groups that could act as active sites;
- (b) no inorganic impurities that might exhibit catalytic activity;
- (c) the resin should not be oxidized as it is believed that there is a correlation between char reactivity and the amount, as well as the chemical nature, of oxygen present in the char;
- (d) the resultant char should be thoroughly characterized as far as its total and active surface areas and elemental analysis are concerned.

Although there is a non-catalytic procedure for phenolic resin production quoted in the literature [29-32], it was found that the method described did not work in practice. The mixture of reactants (phenol + formaldehyde) was heated at 100°C for several days giving no sign of resin formation, although, according to the above-mentioned sources, the product should be obtained after about 8 hours. This can be explained by the fact that crude carbolic acid, probably containing pyridine and other bases, was originally used, and the catalytic properties of these impurities were not realized by the early workers. Unfortunately, the use of high purity reactants did not lead to desirable ends and, therefore, catalytic methods had to be employed.

Both acid and basis can be utilized as catalysts for the formation of phenolic resin, and although there are certain differences in the properties of resultant resins, none of these types is particularly preferential for the purpose of this project. The primary criteria for catalyst selection were the ease with which a given catalyst could be removed from the reaction mixture and the effect it might have on char gasification reactivity. In this way such catalysts as NaOH were eliminated, since even a trace amount of sodium can have a significant effect on the gasification reaction kinetics. Acetic acid, on the other hand, might

result in incorporation of carboxyl groups (--- COOH) in the structure of the final product.

Careful consideration of all the options led to the selection of NH_4OH as the catalyst of choice. Although it is true that some nitrogen-containing intermediates could be formed, it was believed that both their concentration and effect on char reactivity were low enough to be negligible. Three such intermediates were isolated by Shono [33] in 1929, and their chemical formulae are given below.

It was hoped that at least part of this organically bound nitrogen would be evolved as ammonia during the process of curing. A series of experiments were run to determine an optimum phenol-to-formaldehyde ratio, as well as the amount of catalyst that would yield the lowest nitrogen concentration in the product. An excess of phenol could not be used since it was desirable to remove all the unreacted species from the resin; formaldehyde could be easily washed out of the solution or evolved in the curing step. The following laboratory procedure was used to synthesize a parent material for the chars used in this study.

150 g of phenol is mixed with 500 ml of 40% vol. solution of formaldehyde (40g of formaldehyde in 100 ml of solution) in a 1 litre flask, which corresponds to formaldehyde-to-phenol molar ratio of 4.33. 50 drops of 30% NH_4OH are added as a catalyst. The flask is attached to a reflux condenser and is heated in a hot water bath until the contents of the flask turn milky in appearance (about 16 hours). In order to avoid oxidation

during the condensation reactions, the flask is continuously flushed with argon, which is permitted to bleed out of the system through the reflux condenser. Then the flask is cooled down (still under the flow of argon) and after about 24 hours two phases are clearly discernible in the liquid. The upper phase (water + methanol + unreacted formaldehyde) is decanted, and the catalyst in the lower phase (resin) is neutralized by adding about 30 drops of glacial acetic acid. This creamy, resinous material is thoroughly washed with distilled water and dissolved in acetone.

This procedure has been scaled down and somewhat modified recently to make it more suitable for isotopic studies that are planned in the near future. The new proportions in which reactants are mixed are: 1.5 g of phenol, 1 ml of 40% vol. solution of formaldehyde, 1 ml of H_2O , and 25 μ l of 30% NH_4OH ; the reaction is carried out in a 10 ml flask. The resultant resin is much harder than before, and is produced with the yield of about 88%. The yield after the curing step of 2 hr at 60°C, 12 hr at 120°C in vacuum, and 3hr at 300°C in helium, is approximately 70%. All the resin used in this work was synthesized using the old procedure described above.

The literature contains no standard curing procedure for phenol-formaldehyde resins. Curing in air is unacceptable due to excessive oxidation, and thus vacuum or inert atmospheres had to be considered. It turned out that the conditions used for curing did have an effect on both nitrogen and oxygen levels in the model char, as determined by elemental analysis. The results of these tests are summarized in Table 2.3.

Table 2.3 Phenolic resin elemental compositions

Expt	Curing Conditions	wt %				Atomic Ratios $\times 100$		
		N	C	H	O ^a	O/C	N/C	H/C
	uncured	0.2	66.2	6.4	27.2	31.0	0.25	116
A	Vacuum, 3 hr @ 120°C	0.4	73.0	5.8	20.8	21.3	0.43	95
B	Vacuum, 3 hr @ 120°C + 1 hr @ 200°C	0.4	74.5	5.5	19.6	19.6	0.42	89
C	Vacuum, ~4 hr @ 130°C +	0.35	68.0	5.8	25.9	28.5	0.44	102

	1/3 hr @ 195°C							
D	Vacuum, ~4 hr @ 130°C + 1/3 hr @ 195°C	0.35	76.9	5.6	17.1	16.6	0.39	87
E	Vacuum, 1 hr @ 85°C + 3 hr @ 125 + 2/3 hr @ 200°C	0.3	74.3	5.8	19.4	19.5	0.3	94
F	Vacuum, 2hr @ 65°C + 12 hr @ 120°C + 2 hr @ 200°C	0.1	55.7	5.6	38.3	51.5	0.2	121
G	Vacuum, 2hr @ 65°C + 12 hr @ 120°C + 2 hr @ 200°C	0.1	75.2	5.7	18.8	18.8	0.1	91
H	Vacuum, 2hr @ 65°C + 12 hr @ 120°C + 2 hr @ 200°C	0.1	74.3	5.8	19.6	19.8	0.1	94
I	N ₂ , 3 hr @ 120°C + 1 hr @ 400°C	0.4	85.6	5.1	8.9	7.9	0.36	71
J	N ₂ , 3 hr @ 120°C + 1 hr @ 200°C	0.24	58.3	5.7	35.9	46.1	0.37	117
K	He, 2 hr @ 60°C + 12 hr @ 120°C + 2 hr @ 200°C	0.3	73.9	5.7	19.9	20.2	0.3	93
L	He, 2 hr @ 60°C + 12 hr @ 120°C + 2 hr @ 200°C + 2 hr @ 400°C	0.2	80.0	5.3	14.4	13.4	0.2	80
M	Vacuum, 2 hr @ 65°C + 12 hr @ 120°C + He, 2 hr @ 200°C + 2 hr @ 400°C	0.2	80.5	5.4	13.7	12.8	0.2	80
N	Vacuum, 2 hr @ 60°C + 12 hr @ 120°C + He, 2 hr @ 300°C	0.1	76.1	5.4	18.4	18.1	0.1	85

*by difference

It is clear from these results that there is a wide variability in the O/C ratio, depending upon the curing conditions. It is apparent that the lowest O/C ratio resins are attained in processes involving curing at 400°C. It is worth noting that these resins were produced using a formaldehyde-to-phenol molar ratio of 4.33. The theoretical O/C ratio of a highly

cross-linked, cured phenolic resin is given by:

$$\frac{1}{(n+6)} = (O/C),$$

where n is the number of formaldehyde groups associated with each aromatic ring (assumed to contain a single $---OH$ group). For $n = 4.33$, the theoretical O/C ratio would be 0.097, which is in a neighbourhood of the results obtained in experiments I, L, M and N of Table 2.3. One can conclude that curing at temperatures above $200^{\circ}C$ is necessary in order to allow proper cross-linking of the resin.

It may also be shown that a properly cross-linked resin should have a H/C ratio of unity. The resins cited generally have a H/C ratio of 0.7 to 0.85, indicating that perhaps some carbonyl groups exist in the cured resin, or that some pyrolysis to more highly condensed systems has occurred. There is some evidence of the former from the infrared spectra shown in Fig. 2.5, Fig. 2.6 and Fig. 2.7 ($6.2\ \mu m$ region). Since the runs were carried out in oxygen-free atmospheres, the resin itself must have acted as a source of oxygen for oxidation reactions (auto-oxidation). This is consistent with the reaction mechanism proposed by Conley, Bieron and Jackson [13,14]. In light of this, a slight oxidation seems to be inevitable, although there are cases of non-oxidized products reported in literature [14]. The authors admit, however, that this happens only "occasionally," implying a chance occurrence of such resins. In this work, a reasonable reproducibility of synthesized material was required and traces of carbonyl groups in the cured resin were found acceptable, especially that the O/C ratio was expected to further decrease during carbonization. An infrared spectrum of a "non-oxidized" phenolic resin synthesized by Jackson and Conley [14] is shown in Fig. 2.8; it is quite clear that apart from the weak carbonyl absorption band near $1660\ cm^{-1}$ the resins produced in the present work have the same structural features as the non-oxidized resin of Jackson and Conley [14]. It can be noted that the $---CH_2OH$ groups were successfully eliminated by the $200^{\circ}C$ step in the curing procedure (compare Fig. 2.3, Fig. 2.4, Fig. 2.5, Fig. 2.6 and Fig. 2.7 in the $9.5-10\ \mu m$ region) and that the $---OH$ absorption band ($\sim 3\ \mu m$ region) decreases with increasing severity of curing. The dispersive IR spectra were taken using a model 735 B Perkin-Elmer infrared spectrophotometer.

The presence of nitrogen turned out to be more persistent than expected and the N/C ratio was generally found to increase during curing. Nevertheless, a low temperature phase of curing was observed to favour low values of N/C, with the more successful procedures of experiments L, M and N preserving the level of nitrogen unchanged compared to the raw

resin. This implies volatilization of some nitrogen during curing.

In view of these considerations, the following final curing procedure was proposed (experiment N in Table 2.3):

- (a) 2 hr at 60°C in vacuum,
- (b) 12 hr at 120°C in vacuum,
- (c) 2 hr at 300°C in helium.

Steps (a) and (b) were carried out in a vacuum oven, whereas a tube furnace was used for the last step. Helium was chosen rather than nitrogen to reduce the chances of unintentional oxidation. Even if the carrier gas is of a high purity grade, it may contain enough trace oxygen to react with the sample over several hours of continuous flow. Helium is less likely to contain oxygen in trace impurities as it is derived from natural gas, not from the air as is the case with nitrogen. A number of batches of resin cured under the conditions given above were made. The elemental composition of each batch was independently determined and those having unacceptably high nitrogen or oxygen contents were eliminated from further experiments. The remaining batches were mixed and thus obtained material formed a basis for char preparation.

It is clear that the selected curing régime N compares favourably with other curing conditions reported in Table 2.3. Extensive thermal treatment of this particular resin resulted in its IR spectrum losing most of its sharpness. However, a high resolution FTIR spectrum, taken with a 60SX Nicolet spectrophotometer, reveals very similar structural features to the spectra described previously (see Fig. 2.9).

Resin pyrolysis was carried out in a tube furnace and four pyrolysis temperatures were used, $T_p = 1000, 1111, 1243$ and 1400°C ; each sample was pyrolysed for 2 hours at the final temperature. The heating and cooling rates were approximately $3.3^\circ\text{C}/\text{min}$. The weight loss during pyrolysis was found to be independent of pyrolysis temperature, and equal to about 41%. It is in excellent agreement with data reported by Lochte [19], and also with the weight loss observed during pyrolysis of demineralized North Dakota lignite at 950°C for 2 hours, which was found to be approximately 40%. It is evident from the char reactivity data presented in Appendix A, that oxidation rates varied by as much as an order of magnitude between chars pyrolysed at 1000 and 1400°C . This result made it particularly convenient to examine the phenomenon of thermal annealing of the phenolic resin char. The elemental composition of the chars studied is given in Table 2.4.

Table 2.4. Elemental composition of phenolic resin chars.

T _p [°C]	wt %				Atomic Ratio × 100		
	N	C	H	O	O/C	N/C	H/C
1000	0.4	97.1	0.8	1.7	1.3	0.4	9.9
1111	0.2	97.9	0.7	1.2	0.9	0.2	8.6
1243	0.2	98.5	0.3	1.0	0.8	0.2	3.7
1400	0.1	98.8	0.3	0.8	0.6	0.1	3.6

Comparison of elemental composition of chars and resins used in this work (Tables 2.3 and 2.4) with the data reported by Lochte *et al.* [19] (Table 2.1) shows that elemental composition of chars pyrolysed at 1000, 1111, 1243 and 1400°C forms a logical extension of the trend present in Table 2.1, i.e. a continuous increase in concentration of carbon, and a decrease in oxygen level with increasing pyrolysis temperature. It supports the view that early stages of curing have very little, or no effect on final elemental composition of chars. At lower temperatures, however, curing conditions play more important a role and this is why agreement between the data from Tables 2.1 and 2.3 is much less impressive, although still very reasonable. Differences between various curing regimens in Table 2.3 can be explained in the same way.

Fig. 2.10 provides at least partial justification for using phenolic resin chars to model the structure and behaviour of real coals. Data from the papers by Kobayashi [34], Suuberg [35], Lochte [19], and from the present study were combined to show the relevance of the model compound approach to coal reaction studies. This view is further supported by the apparent agreement of weight loss during pyrolysis observed in phenolic resin chars and in demineralized North Dakota lignite, as stated above. The question of correspondences between model chars and materials coming from natural sources should not be overlooked and it will be pursued further later on.

It is evident from Tables 2.3 and 2.4 that the nitrogen content does not decrease during carbonization, as was expected, and thus the effort and time spent on minimizing concentration of nitrogen in the original resin can be appreciated. The nitrogen contaminant level in char is of the order of a fraction per cent and it is believed that this does not appreciably affect gasification reactivity. In this way a material of high degree of purity and uniform and fairly well-characterized chemical structure was produced for the studies reported herein.

Demineralized North Dakota lignite was also examined in this study, primarily for the purpose of comparison with the model chars derived from phenol-formaldehyde resin. Elemental composition of the as-received lignite (on a weight percent, dry basis) is given below:

C	65.6%
H	3.6%
N	1.1%
S	0.8%
ash	11.0%
O	17.9%

Demineralization was accomplished by washing the sample with HCl, followed by HF, and again followed by HCl, according to the technique of Bishop and Ward [*Fuel* 37, 191 (1958)]. The residual mineral matter content of the lignite was determined to be approximately 0.8%.

At this point, based on both elemental analysis and current knowledge of phenolic resin char chemistry (see section 2.1), a conceptual model of the chemical structure of the chars used in this study can be formulated. No claim of absolute chemical rigour is made, of course, but it is believed that such considerations are helpful to understanding the chemical and physical changes which occur on the char surface, which is the subject of subsequent chapters. Since it is well-known that chars are composed of lamellae, the model presented in Fig. 2.11 is a fragment of a platelet believed to represent chemical structure of chars used in this study. The figure was drawn in such a way that it reflects the true atomic ratios O/C, N/C, and H/C of the phenolic resin char pyrolysed at 1000°C. Perhaps the most prominent feature of this structure is a high degree of aromatic ring condensation, necessary to guarantee the correct value of H/C. The molecular weight of the fragment is 3144 g/mol, but the entire molecule is certainly even larger. It is interesting to see that only a small fraction of the surface is occupied by oxygen and nitrogen-containing groups. Since the molecular diameter of nitrogen is 3.0 Å [36], and the dimension of an aromatic ring in a crystalline network is about 2.5 Å [37], it is clear that nitrogen can adsorb only on the sides of rings, and not at the corners. Thus, the maximum theoretical N₂ BET surface area of this char was calculated to be 962 m²/g, assuming that the entire surface was covered by nitrogen and that the top and bottom parts of the lamella do not participate in adsorption. In reality, of course, porosity reduces the access of an adsorbate to the surface, whereas the tops or bottoms of certain lamellae are certainly

exposed to adsorption. Apart from this, chars also contain non-crystalline, disordered regions which are the source of additional adsorption sites. Notwithstanding the above-mentioned shortcomings, the presented picture gives some idea about the chemical nature of the chars studied and about the magnitude of specific surface area to be expected. It is also worth mentioning, that the amount of oxygen chemisorbed on the char surface during the oxygen chemisorption experiments turned out to be of the same order of magnitude as the amount of oxygen already present upon formation of the char.

2.3 SPECIFIC SURFACE AREA, ADSORPTION ISOTHERMS AND PORE SIZE DISTRIBUTIONS OF PHENOLIC RESIN CHAR

Specific surface area, as well as its accessibility to gaseous reactants are of paramount importance for heterogeneous reactions occurring at the char surface. There are basically two classes of methods of surface area determination: measurement of the heat of wetting in methanol or other liquids [38, 39], and vapour and gas adsorption. The reliability of the former method is still debated as it was found that in some cases there exist specific interactions between oxygen-containing functional groups present in carbonaceous materials and the hydroxyl group of methanol or water [38, 39-41]. Methods based on gas adsorption were applied in this study to determine the specific surface area of the phenolic resin char.

Accessibility of surface is governed by the pore structure of a given material, more specifically by the pore size distribution. In large enough pores (i.e. those with radii of at least 10 Å), the Kelvin equation is used to relate the equilibrium vapour pressure of adsorbate to the radius of a pore filled by the condensed adsorbate:

$$\ln \frac{P}{P_0} = - \frac{2\gamma V_l}{RT \cdot r_m} \cdot \cos \Theta \quad (1)$$

where P and P_0 are the equilibrium and saturation vapour pressures at temperature T , r_m is a meniscus curvature (pore radius minus thickness of the adsorbed film), γ and V_l are the surface tension and molar volume of the liquid adsorbate, respectively, and Θ is the wetting angle, here assumed to be 0° for N_2 on char (i.e., complete wetting). It should be noted that with N_2 adsorbate the Kelvin equation is valid in the range of pore radius between about 10 and 250 Å; the lower limit of P/P_0 ratios implied by this size range is $P/P_0 = 0.35$, whereas near $P/P_0 = 1$ the equation is of limited utility because of the low accuracy of P/P_0 determination. Pore size distribution calculations always involve an assumption of pore geometry (usually cylindrical), and detailed procedures are reviewed in standard textbooks on surface area analysis, e.g. [42, 43]. It should also be noted that the form of pores (tortuous, multiple intersecting, etc.) may also influence accessibility of surface.

The following classification of pores with respect to their average width was proposed by Dubinin [44], and later adopted by the International Union of Pure and Applied Chemistry [45]:

micropores: width $< 20 \text{ \AA}$,

mesopores: $500 \text{ \AA} < \text{width} < 20 \text{ \AA}$,

macropores: width $> 500 \text{ \AA}$.

Other definitions are frequently used in the coal literature, but the IUPAC convention is followed here.

This division is somewhat arbitrary since the behaviour of a porous material interacting with an adsorbate also depends on the nature of the latter; thus the upper limit of size at which a pore begins to function as a micropore depends on the effective diameter of the adsorbate in a particular adsorbent: $d_{\text{max}} = 1.5s$ for slit-like pores, and $d_{\text{max}} = 2.5s$ for cylindrical pores, where s is the diameter of an adsorbate molecule[42].

Adsorption isotherms, i.e. plots of adsorbate uptake versus P/P_0 (at specified constant temperature), are the usual way of characterizing adsorbent-adsorbate pairs. Brunauer, Deming, Deming and Teller [46] suggested grouping the most common shapes of such curves into five classes, types I through V, as they are frequently referred to (see Fig. 2.12). The stepped isotherm, designated as Type VI, was later added to this classification due to a special theoretical interest it inspired. Most of the adsorption isotherms encountered in practice fall into one of the six categories, but there are certainly other cases that are difficult, if not impossible, to classify.

Type I isotherms are characteristic of microporous materials, for which the very concept of surface area appears to be controversial, as will be explained subsequently. It is possible, however, to determine the total micropore volume, as well as a crude estimate of pore size distribution. A Type II isotherm usually describes adsorption on what are termed "non-porous" solids, with capillary condensation unimportant, whereas the Type IV behaviour indicates developed mesoporosity with capillary condensation which is responsible for hysteresis. Both Type II and Type IV isotherms are amenable to surface area determinations, provided no special complications occur, and the standard technique used is nitrogen adsorption at its boiling point temperature of -196°C . From Type IV isotherms, pore size distributions are routinely obtained on the basis of the Kelvin

equation. Isotherms of Type III and Type V characterize solids exhibiting rather weak interactions with the adsorbate, and they do not occur as frequently as the others. Type III isotherms are usually obtained from non-porous or macroporous solids, whilst Type V isotherms imply meso- or micro-porous adsorbents. Surface area interpretation of adsorption data for these systems is not straightforward.

2.3.1. *Gas Adsorption*

Before reviewing kinetic models of the adsorption of gases on solids, it is useful to examine the properties of nitrogen and carbon dioxide, the two most common adsorbates used in char or coal surface area determination. Nitrogen is believed to belong to the class of gases that adsorb non-specifically on most solid surfaces [47, 48] (i.e., without other than dispersion and repulsion forces involved), and this feature makes it a particularly attractive adsorbate. It was found, however, that the heat of adsorption for nitrogen was significantly higher on some adsorbents, such as alumina or hydroxylated silica, due to a possible quadrupole interaction with the surface [47, 49]. However, specific interactions are usually of no concern for the adsorption of nitrogen on carbonaceous materials. Carbon dioxide, on the other hand, has a much higher quadrupole moment than nitrogen, which makes strong interactions with oxygen-containing functional groups of char much more likely [50, 51]. There is some evidence that the amount of CO₂ adsorbed (as measured from N₂ isotherms), and the heat of adsorption of CO₂ increase with the fraction of surface covered by hydroxyl groups [51]. Another study has shown that the amount of CO₂ adsorbed on carbon blacks at -78 °C relative to N₂ adsorbed at -196 °C increases with increasing oxygen content, and that the surface area of lampblack, as measured by CO₂ adsorption, is about 4 times higher than that measured by N₂ adsorption [50]. The enhanced adsorption of CO₂ was attributed to the chemical interaction between the adsorbate and the carbon surface. There is certainly some confusion concerning the role of CO₂-surface interaction reported in the literature. Ramsay [52], for instance, showed that although gamma irradiation of an anthracite in air increased the oxygen content by about 40%, the CO₂ surface area increased by only 5%. He concluded that CO₂ adsorption could be used for surface area determination of even highly oxygenated coals. Marsh [39] suggested that because of enhanced adsorption potential in microporous coals, the additional effect of oxygen functionalities on CO₂ adsorption is slight. This view is supported by the data published by Walker and Kini [53], who showed that Xe surface areas measured at 0 °C were in reasonable agreement with those measured by CO₂ adsorption at -78 and 25 °C (see Table 2.5).

Table 2.5. Surface areas of coals [m^2/g] as measured by different adsorbates and at different temperatures [53].

C [% maf]	N ₂ (-196°C)	Kr (-78°C)	CO ₂ (-78°C)	Xe (0°C)	CO ₂ (25°C)
95.2	34	176	246	226	224
90.0	Nil	96	146	141	146
86.2	Nil	34	107	109	125
83.6	Nil	20	80	62	104
79.2	11	17	92	84	132
72.7	22	84	198	149	139

CO₂ at -78 °C should be used with caution, however, because CO₂ is assumed to be in the supercooled liquid phase for calculating the molecular area of the adsorbed gas, a_m [54]. Walker and Kini [53] argue that this cannot be the case when adsorption occurs in very fine pores. According to them, the true state of adsorbed CO₂ at -78 °C is intermediate between a perfect bulk liquid and a perfect bulk solid. There is a wide variation in a_m values reported in the literature; those listed by McClellan and Harnsberger [54] range from 14.1 to 22.0 Å² at -78 °C (a_m from liquid density = 16.3 Å²). There is also the possibility of CO₂ chemisorption on certain adsorbents [42]. In spite of these disadvantages, Anderson *et al.* [50] recommend adsorption of CO₂ at -78 °C rather than N₂ at -196 °C due to slow adsorbate diffusion through pores at low temperatures. It was suggested [55, 56] that at -196 °C the system of fine pores in coals is inaccessible to N₂ molecules because of an activated diffusion process and shrinkage of pores. Nandi and Walker [57] found that nitrogen had a higher activation energy for micropore diffusion than carbon dioxide.

2.3.2. Langmuir equation

Adsorbate uptake, n , expressed in moles per gram of char, can be measured experimentally as a function of partial pressure of vapour P , or alternatively, P/P_0 . In order to convert this quantity to specific surface area, an assumption about the way the adsorbate fills pores must be made. Langmuir [58] developed a model based upon an equilibrium between the rate at which molecules arrive at, and condense on the surface of adsorbent, and the rate at which they leave the surface. If the fraction of sites occupied by the adsorbate is θ_1 , and the fraction of bare (unoccupied) sites $(1 - \theta_1)$, then the rate of condensation per unit area of surface is $a_1 \cdot \kappa P(1 - \theta_1)$, where κ is a constant given by the

kinetic theory of gases, a_1 is the condensation coefficient, i.e. the fraction of incident molecules which actually condense on the surface. The evaporation of an adsorbed molecule is an activated process, in which the activation energy may be equated to the isosteric heat of adsorption. Hence, at equilibrium,

$$a_1 \kappa P (1 - \theta_1) = z_m \theta_1 v_1 e^{-q_1/RT} \quad (2)$$

where z_m is the number of sites per unit area (so that $z_m \theta_1$ is the corresponding number of adsorbed molecules) and v_1 is the frequency of oscillation of the molecule in a mode normal to the surface. Substitution of $\theta_1 = n/n_m$ in eqn (2), where n_m is the monolayer capacity, yields:

$$\frac{n}{n_m} = \frac{BP}{1 + BP} \quad (3)$$

where $B = \frac{a_1 \kappa e^{-q_1/RT}}{z_m v_1}$. In practice, however, B is determined experimentally. It

should be pointed out that the principal assumption in Langmuir's model is that adsorption is confined to a monolayer. The Langmuir equation may be rewritten in the linear form

$$\frac{(P/P_0)}{n} = \frac{1}{C n_m} + \frac{(P/P_0)}{n_m} \quad (4)$$

where $C = P_0 B$, and thus a plot of the lefthand side of eqn (3) versus P/P_0 yields a straight line with a slope of $\frac{1}{n_m}$. Specific surface area can then be determined from

$$TSA = n_m a_m N_A v \quad (5)$$

where $N_A v$ denotes Avogadro's number. The Langmuir equation often reproduces experimental isotherms of microporous adsorbents (Type I).

2.3.3. The BET equation

An extension of Langmuir's approach to multilayer adsorption by Brunauer, Emmett and Teller [59] gave rise to the celebrated BET equation:

$$\frac{(P/P_0)}{n(1 - P/P_0)} = \frac{1}{n_m C} + \frac{(C - 1) P/P_0}{n_m C} \quad (6)$$

It turns out that eqn (6) describes Type II isotherms very well, but it has been extensively used for other types of isotherms as well. Unfortunately, the limitations of this equation

have not always been fully realized. The mobility, or delocalization, of adsorbed molecules is crucial for the value of a_m to be governed by the molecular size of the adsorbate rather than by the lattice parameters of the adsorbent. Another important assumption is the complete coverage of the monolayer. These two factors are reflected in the optimum value of constant C in the BET equation being in the range between 50 and 150 [42]. The chars studied here typically had C values in the range from - 100 to + 50.

The geometrical similarity between Type II and Type I isotherms should be noted here, as well as a particularly steep slope of the low partial pressure part of Type I isotherm and a flat, practically horizontal middle part of the isotherm. Introducing microporosity to a non-porous adsorbent causes a Type II isotherm distortion in the low-pressure region, reflected in an increase in C , and the value of TSA derived from the BET procedure is erroneously high due to a process similar to capillary condensation in pores [42, 60, 61]. In particular, a BET specific surface area in excess of about $500 \text{ m}^2/\text{g}$ should be taken as a warning that considerable microporosity may be present. Also, the value of C of the order of several hundreds is a strong indication of either the presence of microporosity, or adsorption on active sites, or even chemisorption [42].

A number of tests for the presence of microporosity have been proposed [62, 63]. The so-called α_s - plot seems to be particularly useful, α_s being defined as the ratio of n to $n_{(0.4)}$, where $n_{(0.4)}$ is the value of adsorbate uptake at $P/P_0 = 0.4$. A plot of n versus α_s obtained from a non-porous material (instead of plotting n versus P/P_0) should give a straight line with zero intercept for non-porous adsorbents, and a straight line with a non-zero intercept for microporous materials (see Fig. 2.13). Although a similar non-porous material is recommended as a reference adsorbent for the best accuracy, it is also possible to use any experimental Type II isotherm obtained from a non-porous solid to convert values of P/P_0 to α_s [42]. It should also be pointed out that microporous systems do not necessarily have to exhibit a flat middle portion in the adsorption isotherm, as shown in Fig. 2.13.

2.3.4. *The Dubinin - Radushkevich equation*

The concept of mono- or multilayer surface coverage is of questionable validity in micropores, and a mechanism of pore filling with liquid phase adsorbate appears to be a more adequate description of adsorption in micropores. Dubinin and Radushkevich [64] proposed an equation for the estimation of the micropore volume from the low and medium pressure regions of the adsorption isotherm. They adapted Polanyi's theory of adsorption

[65] in their treatment and, assuming a Gaussian pore size distribution, derived the following relation,

$$\log V = \log V_0 - D \log^2(P/P_0) \quad (7)$$

V is the amount adsorbed expressed as a liquid volume ($V = nM/\rho_1$, where ρ_1 is the density of the bulk liquid adsorbate), V_0 is the total volume of micropores, and D is a constant. It should be emphasized that only the volume of micropores, and not specific surface area, can be calculated from the Dubinin-Radushkevich equation. There exists another "version" of the Dubinin-Radushkevich equation proposed by Kaganer [66], and hence sometimes termed the DRK equation, in which the original fractional pore filling (V/V_0) is replaced by the surface coverage (n/n_m). Such an approach is tantamount to saying that all the liquid adsorbate that fills the pores covers pore walls with a monolayer, which is inconsistent with the assumed pore filling rather than the surface coverage mechanism used in deriving the equation. Thus the significance of this approach is obscure and the validity of reporting surface areas for microporous adsorbents is in question [42, 61, 67]. In spite of this, the values of specific surface areas for such materials have been reported in the literature, but it should be remembered that they ought to be used merely for the purpose of comparison.

2.3.5. *Results and discussion*

Adsorption isotherms, pore size distribution and surface areas of the phenolic resin chars have been obtained at several burn-offs by means of a dynamic, continuous flow method, using both N_2 and CO_2 . The measurements were made using a commercial instrument (Quantasorb, Quantachrome Corp.), described in detail in Appendix E.

Adsorption isotherms for the resin chars were found to be of Type I up to about 50% burn-off (see Fig. 2.14). Despite some scatter of the data and an inability to obtain the steep part of the curve at low values of P/P_0 , it is clear that the data points lie on nearly horizontal lines. It is only in the case of samples burnt-off to 28.4 and 49.7% that a slight curvature of the isotherms can be discerned. The virtual constancy of the amount of nitrogen adsorbed above $P/P_0 \approx 0.1$ (somewhat more in the case of char burnt-off to 50% mass loss) implies that practically all pores have radii less than about 15 Å. Thus the Kelvin equation, and the classic pore size distribution analysis, cannot be employed. From the data presented in Appendix A (Tables A1 and A2), it is possible, however, to estimate the contribution of pores larger than 15 Å to the specific surface area of chars. This

contribution is largest in the 50% burn-off char, of course, but even in this case it accounts only for as little as 8% of the total BET surface area. The presence of microporosity was confirmed by an α_s - plot (Fig. 2.15) and by relatively high values of BET specific surface area. Standard data for the adsorption of nitrogen at -196°C on non-porous hydroxylated silica [68] were used in preparing the α_s - plot. It may be concluded that reactions of phenolic resin char oxidation do occur inside micropores at temperatures up to 400°C and $P_{\text{O}_2} = 1$ atm, and that there is no mass transfer limitation involved that would be large enough to prevent oxygen from penetrating into the microporous structure of the char. This is consistent with mass transfer calculations presented in Appendix B.

The Langmuir and Dubinin-Radushkevich plots are shown in Fig. 2.16 and Fig. 2.17, respectively, and specific surface areas obtained from these, as well as from other measurements, are presented in Table A2 (Appendix A), as well as in Figs. 2.18 through 2.22. The following general observations can be made:

- (1) a rapid increase of TSA with burn-off at low burn-off;
- (2) $\text{TSA}(\text{CO}_2) > \text{TSA}(\text{N}_2)$; (both BET and Dubinin-Radushkevich), especially at low burn-off; at higher burn-off, the difference between $\text{TSA}(\text{CO}_2)$ and $\text{TSA}(\text{N}_2)$ is normally much less than 10%;
- (3) $\text{TSA}(\text{Langmuir}) = \text{TSA}(\text{Dubinin - Radushkevich})$; (both N_2 and CO_2)

Furthermore, it is apparent from Fig. 2.22 that surface area does not seem to depend on temperature of pyrolysis, the char prepared at 1000°C being the only exception. This different behaviour of that material can be explained by oxygen chemisorption occurring on the surface and blocking the sites that would be otherwise available for physical adsorption. Chemisorption at room temperature is undoubtedly very slow and severely limited only to the most reactive sites, it can nevertheless be of some import if a char is exposed to the ambient air for a few months. Since chars pyrolysed at relatively low temperatures are more active towards chemisorption than chars heat-treated at higher temperatures (e.g., see oxygen uptake data in chapter IV), it is not surprising that the char pyrolysed at 1000°C exhibited consistently lower surface area due to this effect. Oxygen chemisorption interfering with surface area measurements was also reported by Taylor [69].

The existence of a "universal" surface area curve for all the chars studied in this work turned out to be particularly convenient in interpolating values of surface area among scattered data points. However, the steep slope of the curve for burn-off less than about

5%, as well as experimental error involved in obtaining low burn-off samples, made values resulting from interpolation in this region rather unreliable. On a few occasions, it was more reasonable to normalize reaction rates with respect to mass rather than total surface area, i.e. express them in $\text{g}/(\text{g}\cdot\text{hr})$ rather than in $\text{g}/(\text{m}^2\cdot\text{hr})$.

A remarkable agreement between pore volume determined from Dubinin-Radushkevich plots and the one directly measured in adsorption experiments is evident (see Table A2 and Figs. 2.23 through 2.26). Pore volume increases by an order of magnitude by 50% burn-off, as a result of pore enlargement due to carbon consumption at the surface. It is not surprising that specific surface areas determined from the Langmuir and Dubinin-Radushkevich plots show good agreement. Both of them are derived from the same measured quantity, that is from the amount of adsorbate taken up by char, and both approaches assume monolayer coverage of the surface. As mentioned previously, however, this method of surface area determination is questionable, especially in the case of highly microporous materials. Thus a reliable determination of pore volume may lead to dubious, if not completely erroneous values of surface area. This is particularly evident in the case of a few unrealistically high surface areas reported in Table A2. It is believed that more reliable values were obtained from the BET equation, which is based on a concept of multilayer surface coverage.

These data suggest a number of important points that help in the interpretation of the gasification rates obtained during this study, but at the same time raise some questions. It is noted from Fig. 2.18 that the N_2 and CO_2 surface areas, regardless of the basis of calculation, approach each other very rapidly at relatively low extents of burn-off. Apparently, there is a structural feature of microporosity that is being dramatically changed by the removal of only a few percent of carbon atoms. Whether this means that a small number of carbon atoms "block" access to micropores is not yet clear, but this is certainly one possible explanation for the data. Alternatively, oxidation might change the structure of the char in some other way (e.g. removal of strained carbon linkages that hold lamellar planes close enough together so that N_2 cannot penetrate).

Once the burn-off exceeds a few percent, there is little argument about the correct magnitude of microporous surface area, enabling one to calculate rates of gasification on that basis without concern for whether N_2 or CO_2 is "right." Furthermore, as noted above, the data suggest that burn-off occurs mainly in the micropores. There is simply no quantitative way that the large changes in surface area noted with burn-off could be due to changes in meso- and macroporosity without dramatic changes in the shape of the

adsorption isotherm. This does not necessarily mean, however, that there exist no mass transfer limitations on this level of porosity. Depending upon the length of the micropores and the number of active sites per length, some portions of the microporosity might still be oxygen starved.

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Fig. 2.1

Typical reactions proposed for resin decomposition at elevated temperatures. (Route I) oxidative degradation process; (Route II) fragmentation reactions; (Route III) formation of benzenoid species [14].

Fig. 2.2

Carbonization mechanism of phenol-formaldehyde resin, as suggested by Yamishita and Ouchi [23].

Fig. 2.3 Infrared spectrum of an uncured phenolic resin.

Fig. 2.4 Infrared spectrum of phenolic resin cured in vacuum at 120°C for 3 hr.

Fig. 2.5 Infrared spectrum of phenolic resin cured in vacuum at 120°C for 3 hr and then at 200°C for 1 hr.

Fig. 2.6 Infrared spectrum of phenolic resin cured in nitrogen (at 60°C for 1 hr, then at 120°C for 3 hr and at 200°C for 1 hr).

Fig. 2.7

Infrared spectrum of phenolic resin cured in vacuum at about 150-200°C for 6.5 hr.

Fig. 2.8

Infrared spectrum of a non-oxidized phenolic resin cured in vacuum at 400°C for 1 hr [14].

Fig. 2.9 FTIR spectrum of phenolic resin cured in vacuum at 60°C for 2 hr, at 120°C for 12 hr and then in helium at 300°C for 3 hr.

Fig. 2.10 Comparison of H/C and O/C ratios for pyrolysis of different samples of bituminous coal, lignite, and phenolic resin char [19, 34, 35].

Fig. 2.11 Chemical structure of phenolic resin chars used in this study.

Fig. 2.12 The five types of adsorption isotherm, I to V, in the classification of Brunauer, Deming, Deming and Teller [46], together with Type VI, the stepped isotherm.

Fig. 2.13 Effect of microporosity on the isotherm and an α_S -plot. (a) (A) is the isotherm of a non-porous sample of the adsorbent; (B) is the same solid when micropores have been introduced into it; (b) an α_S -plot corresponding to the isotherms of (a); (schematic only) [42].

Fig.2.14 Adsorption isotherms.

$T_p = 1000\text{ }^{\circ}\text{C}$

• B = 0%

$$y = 0.309 + 0.074x$$

♦ B = 16%

$$y = 6.497 + 0.201x$$

■ B = 28.4%

$$y = 7.526 + 0.901x$$

× B = 37.0%

$$y = 7.416 + 1.447x$$

$T_p = 1400\text{ }^{\circ}\text{C}$

◊ B = 0%

$$y = 0.762 + 0.097x$$

□ B = 49.7%

$$y = 10.341 + 2.913x$$

Fig. 2.15 α_s -plots.

$T_p = 1000^\circ\text{C}$

- $B = 0\%$
 $y = 83.378 + 2312.566x$
- ◆ $B = 16\%$
 $y = 0.473 + 147.454x$
- ◇ $B = 28.4\%$
 $y = 0.251 + 116.538x$
- $B = 37.0\%$
 $y = 2.120 + 104.852x$

$T_p = 1400^\circ\text{C}$

- $B = 0\%$
 $y = 15.409 + 1102.403x$
- $B = 49.7\%$
 $y = 11.699 + 4.038x$

Fig. 2.16 Langmuir plots.

$T_P = 1000^\circ\text{C}$

- $B = 0\%$
 $y = -1.851 - 0.057x$
- ◆ $B = 16\%$
 $y = -0.630 - 0.014x$
- $B = 28.4\%$
 $y = -0.525 - 0.034x$
- ◇ $B = 37.0\%$
 $y = -0.494 - 0.046x$

$T_P = 1400^\circ\text{C}$

- $B = 0\%$
 $y = -1.510 - 0.043x$
- $B = 49.7\%$
 $y = -0.298 - 0.098x$

Fig. 2.17 Dubinin-Radushkevich plots.

Fig. 2.18 Specific surface area vs burn-off (char pyrolysed at $T_p = 1000^\circ\text{C}$).

Fig. 2.19 Specific surface area vs burn-off (char pyrolysed at $T_p = 1111^\circ\text{C}$).

Fig. 2.20 Specific surface area vs burn-off (char pyrolysed at $T_p = 1243^\circ\text{C}$).

Fig. 2.21 Specific surface area vs burn-off (char pyrolysed at $T_p = 1400^\circ\text{C}$).

Fig. 2.22 Specific surface area of the chars used in this study, as determined by the CO₂ BET method.

Fig. 2.23 Pore volume vs burn-off (char pyrolysed at $T_p = 1000^\circ\text{C}$).

Fig. 2.24 Pore volume vs burn-off (char pyrolysed at $T_p = 1111^\circ\text{C}$).

Fig. 2.25 Pore volume vs burn-off (char pyrolysed at $T_p = 1243^\circ\text{C}$).

Fig. 2.26 Pore volume vs burn-off (char pyrolysed at $T_p = 1400^\circ\text{C}$).

chapter III

EXPERIMENTAL

A thermogravimetric analyser, herein referred to as a TGA, was extensively used for both char reactivity studies and the oxygen chemisorption runs. A schematic of the apparatus is shown in Fig. 3.1. The Cahn 113 microbalance (Cahn Instruments Inc.) is the central part of the apparatus. The operating range for weight measurement was 10 μ g to 1000 mg, and the typical sample size varied between 50 and 100 mg. The char sample was suspended in a quartz bucket inside a hangdown tube surrounded by a furnace equipped with a temperature controller. It was also possible to place several hundred milligrams of material in a close proximity to the quartz bucket to increase the size of a sample during thermal desorption in the TGA. The weight of the additional material was not determined, however, but it was used to increase the amount of CO and CO₂ evolved during thermal desorption runs, thereby improving the sensitivity of the gas analysis. Both temperature and sample weight could be monitored continuously and recorded on a strip-chart recorder. A K-type thermocouple was placed about 5 mm from the sample. The system was equipped with a Microcon 823 programmer to facilitate temperature profile control.

The microbalance was enclosed in a Pyrex, gas-tight housing that could be evacuated and filled with gases through a manifold. Continuous purging was also possible by flowing an inert gas through the TGA to the vent. The system operated at a pressure slightly above atmospheric to avoid possible air leaks into the TGA. Various partial pressures of oxygen were obtained by *in situ* mixing of oxygen or air with helium. To facilitate this operation, two pressure gauges were installed to measure pressure inside the vessel. The total volume of the system was about 5 litres, large enough to make changes in oxygen partial pressure occurring during chemisorption negligible.

Unless stated otherwise, all samples were outgassed prior to each run by overnight pumping on the TGA at room temperature, followed by helium purge and thermal surface cleaning. The helium purge consisted of an eightfold evacuation of the system and subsequent filling with helium at 100°C, after which a flow of helium through the TGA was maintained for an hour to allow the volume of gas equal to about 10 times the volume of TGA to be swept from the system. Only high purity gases were used in all the experiments, with the flow of helium passing additionally through a cryogenic trap. These precautions were taken to prevent sample oxidation during thermal surface cleaning. It was necessary to remove all the oxygen surface complex from the surface of each sample to carry out meaningful oxygen chemisorption runs.

Surface cleaning was done by heating char in a quiescent atmosphere of helium to 950°C at the rate of about 20-30 °C/min., keeping the temperature at 950°C for 2 hours, and cooling the sample down to the chemisorption temperature in 1-2 hours.

Oxygen chemisorption was performed by sudden evacuation of the TGA and filling it with oxygen containing mixture of gases, or with pure oxygen. Chemisorption was carried out in the range of 150-250°C. Char reactivity runs followed oxygen chemisorption and were initiated by raising the temperature to the desired level.

Desorption of surface oxides was preceded by the helium purge described before, after which temperature was raised stepwise to 950°C. Changes in weight were followed gravimetrically, and after each increase in temperature the desorbed carbon oxides were swept out of the TGA with a stream of flowing helium and trapped in a cryogenic trap. The ratio of CO to CO₂ was subsequently determined using a Hewlett-Packard gas chromatograph, model 5730A, and a 3380A Hewlett-Packard integrator. The CO peak was obtained at 30°C, after which the temperature was cycled to 100°C for evolution of CO₂. Calibration was performed after each measurement by injecting 1:1 CO/CO₂ mixture.

Specific surface area measurements were carried out using a dynamic, continuous method. A commercial instrument (Quantasorb, Quantachrome Corp.) was utilized to determine N₂ and CO₂ surface areas as well as adsorption isotherms. Prior to surface area analysis, all samples were outgassed in a flow of nitrogen at 300°C for 3 hours.

Elemental composition of char samples was determined using a 240 B Perkin-Elmer elemental analyser. Concentrations of hydrogen, carbon and nitrogen were determined directly, whereas the amount of oxygen was calculated by difference.

Detailed descriptions of all experimental procedures used in this study are given in Appendix E, and a method of phenolic resin synthesis, curing and pyrolysis is discussed in section 2.2.

Fig. 3.1 Schematic of the TGA apparatus.

chapter IV

ACTIVE SURFACE AREA AND THE CARBON-OXYGEN REACTION KINETICS

4.1 GENERAL STATEMENT OF THE PROBLEM

The introduction of the concept of active surface area (ASA) as measured by oxygen chemisorption [1] has led in recent years to various attempts to correlate char reactivity towards oxygen, or oxygen-containing agents such as CO_2 or steam, with the amount of oxygen taken up by a given carbonaceous material in an oxygen chemisorption experiment. It has been shown, or at least implied, by the results of various workers that active surface area is a better predictor of char reactivity than is total surface area (TSA) [1-3]. It has been stated, either explicitly or implicitly, that the very same sites involved in the adsorption of oxygen at relatively low temperatures are also involved in gasification reactions occurring at elevated temperatures. In this way, oxygen chemisorption soon became the most frequently employed technique available for active surface area determination in chars [1-9]. As may be seen from the literature review presented in the next section, this approach has met with some, although not universal, success; theories have been advanced which suggest that only a portion of active sites may participate in actual gasification reactions (e.g., see [1]). At the core of the problem remains a significant lack of understanding of the precise nature of active sites.

A wide variety of conditions have been used for measurement of ASA, generally involving temperatures in the range from 100°C to 350°C and oxygen partial pressures from fractions of a torr to atmospheric. Only in few cases have these conditions been critically evaluated. In this study, a series of experiments has been carried out to establish the importance of these conditions on determining the ASA of "young" chars. If oxygen uptake during chemisorption depends upon such parameters as temperature and oxygen partial pressure, then what is it that one actually measures? What conditions should be employed to obtain meaningful information on ASA from an oxygen chemisorption run? Is it always possible to extract such information from chemisorption data, and if not, in what cases is oxygen uptake at low temperature indicative of char reactivity towards high temperature gasification? These and similar questions are addressed in subsequent sections of this chapter in order to arrive to an understanding of the applicability of oxygen chemisorption as a tool for measuring the ASA of chars.

The analysis is based on a series of reaction rate measurements, and reactivities are compared with the amount of oxygen chemisorbed by a given char in separate experiments. Oxygen partial pressure and temperature were varied to see if, and in what way, these parameters affected oxygen chemisorption kinetics. Chars pyrolysed at different temperatures were used to study changes induced by thermal annealing in both char reactivity and oxygen chemisorption behaviour. Apart from this, reaction order and activation energy of low temperature char gasification, as well as the CO₂/CO ratio during thermal decomposition of surface complexes, were determined so that some inferences could be made about the effect of thermal annealing upon the reaction mechanisms involved. A qualitative interpretation of phenomena occurring on a char surface during oxygen chemisorption and gasification are given, and recommendations for further work are made.

4.2 RELEVANT LITERATURE SURVEY

4.2.1 The O₂ chemisorption technique for determining ASA

The heterogeneous reactions of oxidizing gases such as CO₂ and steam on carbonaceous materials are generally believed to proceed via a carbon-oxygen surface complex, [C-O] (e.g., Walker *et al.* [10]); e.g.,

where the products of desorption are carbon monoxide and a regenerated active site, C_f, required to carry on the gasification reaction through further steps. The most generally accepted view of carbon reactivity envisages the formation of these surface complexes taking place on certain preferred carbon surface sites, known as "active sites." For the more highly graphitized carbons, there is enough experimental evidence to indicate that these "active sites" are localized at the edges and discontinuities of the graphitic basal planes (e.g., see Meyer [11]). These preferential sites of reaction represent a rather small fraction of the total internal char surface area, as determined by standard gas adsorption techniques; e.g., for Graphon, Laine *et al.* [1] found total active surface areas (TASA) ranging from 0.3% (at 0% burn-off) to 3% (at 35% burn-off) of the total surface area (TSA). Thus, the TASA is distinct from and significantly less than the TSA. However, the TASA has been found to more satisfactorily account for vast differences in reactivity found for wide ranges of carbonaceous materials (Radović *et al.* [2]), since it is a more direct measure of the

carbon atoms available for attack.

The initial impetus for applying O₂ chemisorption to the model compound chars in the current study, derived from the work of Walker and co-workers, and primarily the paper by Laine, Vastola, and Walker [1], who first quantified the technique. A qualitative description of the mechanism of the process is as follows: Molecular oxygen adsorbs onto active carbon sites to form an intermediate or unstable surface complex. It was believed that this is the rate-determining step in the over-all process of chemisorption. These transitory complexes were postulated to immediately form one of three reaction products: carbon dioxide, carbon monoxide, or a stable carbon-oxygen surface complex. This latter complex consists of one oxygen atom bonded to one carbon atom, which is in turn bonded to other surface carbons such that the surface complex is most probably immobile. [Mobility of the surface complex would allow for the prompt formation and desorption of carbon dioxide, and, consequently, the complex would then be unstable at reaction (adsorption) temperature.] The stable complex builds up on the surface with the stoichiometry of one oxygen atom associated with each active carbon site. As active sites become occupied by stable surface complexes, they are no longer available for chemisorption, and thus the O₂ uptake rate decreases. These surface complexes can be removed from the carbon surface by heating the material to temperatures higher than their formation temperature. Upon heating, the complex desorbs as either carbon monoxide or carbon dioxide, depending on the desorption temperature. CO₂ formation has been found to have a lower activation energy than CO formation, but at higher temperatures, more of the surface complexes attain the necessary activation energy to desorb as CO, so the CO/CO₂ product ratio increases with temperature.

In the work of Laine *et al.* [1], clean Graphon surfaces were exposed to 0.5 torr of O₂ at 300°C for 24 hours. The amounts of CO and CO₂ desorbed after 3 hours at 950°C were determined with a mass spectrometer. The adsorption data were interpreted assuming that the surface complex consisted of one oxygen atom per edge carbon atom, and that these atoms lay in the [100] plane, thereby occupying 0.083 nm². Since this work, this value of area/atom has been applied by many workers to other carbonaceous materials, some not very highly graphitized, which might have resulted in some systematic quantitative experimental errors. In any case, the uptake of oxygen per unit mass has been taken as a qualitative indicator of relative carbon reactivity. Once the surface area per active site has been assumed, the total active surface area (TASA) can be determined via an oxygen balance by assuming that all the surface complexes are desorbed as either CO,

CO₂, or the specified combination of the two. By fitting their chemisorption rate data to expressions directly proportional to TSA, as determined by standard BET methods, and to TASA, Laine and co-workers found that effective rate constants based on the former varied considerably with burn-off, whereas rate constants based on TASA were essentially constant over the burn-off range studied.

Subsequent to this work, Hart *et al.* [5] reported that the amount of surface complex formed was a strong function of temperature, at least at pressures less than 0.5 torr. For Graphon, two distinct plateaux in the amount of O₂ chemisorbed were found; one between 25 and 200°C, and the other between 300 and 500°C. These data were interpreted as being due to two different groups of active sites; one type of site at low temperature (type 1), and two types of sites at the higher temperatures (types 1 and 2). Moreover, after repeated chemisorption runs at low temperature, another type of fast initial adsorption was observed to develop. These latter sites seemed to appear at the expense of the higher temperature type 2 sites. However, O₂ treatment at 500 - 625°C was observed to eliminate the fast initial adsorption and produce an active site distribution similar to that which existed initially without the fast adsorption sites. Therefore, it was concluded that low temperature O₂ adsorption followed by desorption activates that carbon surface differently than by direct combustion at higher temperatures. The rate of adsorption on the type 1 sites was reported to be proportional to the square of the unoccupied ASA, with an activation energy of 7.4 kcal/mol O₂.

Another study of the chemisorption of O₂ on Graphon was carried out by Lussow *et al.* [6]. These workers also reported a plateau in the amount of O₂ adsorbed in the temperature range 300-400°C. The TASA corresponding to this uptake was similar to that found by Laine *et al.* [1]. However, somewhat differently from Hart *et al.* [5], these workers found a progressive increase in chemisorption following this plateau up to 550°C. The amount adsorbed at 550°C was approximately three times the quantity adsorbed during the lower temperature plateau. Lussow *et al.* [6] reported an activation energy of 28.9 kcal/mol O₂ for chemisorption between 450 and 675°C. However, significant gasification of Graphon, occurring concurrently with chemisorption, was observed above about 400°C.

Bansal *et al.* [7] also investigated O₂ chemisorption on Graphon over a range of temperatures and found several linear sections in Elovich isotherms that were interpreted as different stages of chemisorption. These data led these workers to conclude that there were at least five different groups of active sites on the Graphon surface. The activation energies

estimated for these groups varied from 3.1 to 12.4 kcal/mol O₂.

All the work described thus far was focused on highly graphitic carbons. But perhaps more relevant to the current work is that with much less graphitic materials. Along these lines, Allardice [12] examined the adsorption of oxygen gravimetrically on brown coal char (prepared from an Australian Yallourn brown coal) over the temperature range 25-200°C, and at pressures up to 1 atm. Adsorption was found to occur by two separate processes, one reversible and the other irreversible. The reversible adsorption was found to be physical, while the irreversible uptake was found to be chemisorption conforming to the Elovich isotherm. A mechanism for the chemisorption was suggested that involved rate control via surface migration.

Radović *et al.* [2] studied a range of carbonaceous materials increasing in degree of crystallinity from a demineralized North Dakota lignite (PSOC-246) char (referred to hereafter as dem-char), a Saran char, to Monarch 700 carbon black, V3G graphitized carbon black, and SP-1 spectroscopically pure natural graphite. TASA for these carbons was determined using O₂ chemisorption at 102°C and 750 torr of air for periods of 12 hours. An oxygen balance on the oxides of carbon desorbed at 952°C for 3 hours was used to determine TASA, assuming a value of 0.083 nm² for the surface area occupied by the oxygen atom in the surface complex. The difference in reactivity over this range of chars was found to be about five orders of magnitude. O₂ chemisorption capacity was found to decrease with pyrolysis severity. It was clearly shown that TSA is not a relevant normalization parameter for char reactivity. For example, a difference of a factor of twelve in reactivity among samples of the demineralized lignite char was reduced to about a factor of three when the rate constants were expressed in terms of TASA rather TSA. Similarly differences in observed reactivities of almost three orders of magnitude between Saran char (and also dem-chars) and V3G, and four orders of magnitude between SP-1 graphite and the more reactive chars were reduced to within an order of magnitude when the respective TASA's were taken into account.

In another interesting study involving dissimilar carbons, Taylor [13] investigated the reactivity behaviour of Saran char and V3G. Low temperature (100°C) O₂ chemisorption was used to measure TASA in a fashion similar to that employed by Laine *et al.* [1]. For the Saran char, it was found that the specific reactivity increased with burn off. Although this was attributed to an increase in TASA with burn-off, O₂ chemisorption measurements at 100°C did not reflect this trend. In fact, TASA via "oxygen surface areas actually decreased slightly from 50.4 m²/g at 0% burn-off to 39.7 m²/g at 89.1% burn-off.

Furthermore, at the higher burn-offs the "oxygen surface areas" even exceeded the TSA's as measured by N₂ and CO₂ adsorption.

Taylor [13] offers some possible explanations for this anomaly. One was that perhaps the use of 0.083 nm² per adsorbed oxygen atom is inappropriate for some carbons. The number of oxygen atoms per edge carbon site may be greater than unity on average. FTIR results indicated large quantities of carboxyl groups on the surface of the Saran chars, in which case, two oxygen atoms would be bound to each carbon. Thus, if all the surface oxygen complex for the Saran chars were carboxylic acid groups, the "oxygen surface areas" would be reduced by a factor of two. However, not all surface oxygen is involved in carboxylic acid groups. A significant amount of the CO formed on heat treatment may have been present as either bridge-type oxygen or ether linkages. If atoms of oxygen bridge across two edge carbon sites, an area of 0.083 nm² could be assigned to each oxygen. However, if oxygen atoms bridge across two carbon atoms within the basal plane, each oxygen would be assigned an area of 0.053 nm², thereby tending to reduce the calculated oxygen areas. Another explanation put forth was that the surface area accessible to oxygen attack at 375°C was different from that accessible to N₂ and CO₂ at -196°C and 25°C, respectively. A large fraction of the TSA could have been covered by oxygen complex following ambient atmospheric reaction and may not have been measured via gas adsorption.

In any case, these results clearly imply that the stable oxygen complex formed during the atmospheric gasification runs greatly exceeded the stable oxygen complex formed at low temperature over the entire burn-off range. This behaviour completely contradicts the hypothesis of Laine *et al.* [1] that TASA would never be entirely covered by a stable oxygen complex at gasification temperatures. Thus, these results completely rule out the model of gasification reactivity control via fractional coverage of active sites for Saran char.

Taylor [13] advanced three possibilities that individually or in aggregate could account for this apparent discrepancy. First, that the Saran char exhibits a significant distribution of active sites such that at 100°C only the most active sites can chemisorb oxygen. Indeed, Bansal *et al.* [7] noted such a distribution in activation energies for O₂ chemisorption on graphitized carbon black at low temperatures. Second, it is possible that during carbon gasification, new carbon edge atoms are continuously being generated. It is known that these sites are very active since they possess an unpaired electron. However, these sites can subsequently re-hybridize to less active sites by localizing π -electrons forming an in-plane σ -pair. If, however, oxygen can attack the site prior to re-

hybridization, then it will behave as a very active site for gasification. This effect would obviously increase with increasing O₂ partial pressure, and thus relatively large surface coverages of surface oxygen complex can be realized at higher pressures. Third, Yang *et al.* [14] have concluded that oxygen can be bound on the basal plane (long thought to be inert) at a temperature of 650°C. Presumably this oxygen is atomic and originates from O₂, first dissociating on other active sites and then finding its way onto the basal plane. In this manner, the basal planes can act as a sink for atomic oxygen. At lower temperatures, however, this "spillover" would not occur to any appreciable extent.

It was also shown for Saran char that during stepwise desorption of surface complexes the amount of unoccupied active surface area increased with temperature to a maximum, whereupon it once again decreased; these data were interpreted as indicative of a definite decrease in the number of active sites due to annealing at temperatures as low as 727°C.

The behaviour of the V3G carbon was contrasted to that of the Saran char in the same work by Taylor [13]. Like the Saran chars, the V3G carbons exhibited an increase in specific reactivity with burn-off. However, unlike the Saran chars, the O₂ chemisorption measurements of TASA were also found to increase with increasing burn-off, as had been originally expected. Thus these results are consistent with the previous work of Laine *et al.* [1]. Examination of the V3G carbon over a range of temperatures from 300°C to 575°C indicated that the formation of stable complexes on clean V3G surfaces involves a distribution of active sites.

From the preceding it seems clear that the absolute values of TASA, as determined by O₂ chemisorption, must be carefully evaluated for each type of char and are not automatically to be taken literally for all chars under all conditions. There are definite differences in mechanism and sources of active sites between low temperature chemisorption conditions and those that exist during actual gasification, for some chars at least. It has also been shown that the O₂ chemisorption capacity is a function of temperature and pressure, and, under certain conditions, competes with other simultaneously occurring processes, such as gasification. On the other hand, at this point in its understanding, it has been shown to be one of the best measurements for correlating reactivity for many chars. The precise interpretation of the data from the application of this technique to the model compound chars being used in the current study is still not completely resolved, and is the subject of active investigation.

4.2.2 *The Elovich equation*

There exists a voluminous literature on chemisorption, and on the celebrated Elovich equation which is believed to describe this process best of all known formulations. The most comprehensive reviews are undoubtedly those by Hayward and Trapnell [15] and Low [16], and the reader is referred to these sources for more information. Only the most important features of chemisorption will be summarized here, with particular emphasis placed on material relevant to oxygen chemisorption on chars.

The differences between physical and chemical adsorption, as well as criteria useful in distinguishing between these two processes are listed below [15]:

- (1) Physical, or van der Waals, attraction forces involved in physical adsorption versus formation of chemical bonds responsible for chemisorption.
- (2) The magnitude of the heat of adsorption: high for chemisorption, typically 15 - 20 kcal/mol, low for physical adsorption (in the neighbourhood of heats of liquefaction, i.e. typically below 6 kcal/mol).
- (3) The temperature range in which the adsorption proceeds: near, or below, the boiling point of the adsorbate for physical adsorption, far above the boiling point for chemisorption.
- (4) Chemisorption, as every chemical reaction, requires some activation energy and thus would not occur at appreciable rates below a certain minimum temperature, whereas physical adsorption requires no activation energy and should be exceedingly rapid at any temperature and take place as fast as the adsorbate reaches the surface.
- (5) No case of chemisorption of more than a single layer is known, whereas no such limitation applies in the case of physical adsorption. (This is why surface cleaning is of paramount importance in chemisorption studies.)

The rate of chemisorption often follows the Elovich equation:

$$\frac{dq}{dt} = B \cdot \exp[-Aq] \quad (1)$$

where q is the amount of adsorbate adsorbed at time t , and A and B are constants. Eqn (1) can be integrated between the limits t_0 , t and q_0 , q to give

$$q = \frac{1}{A} \left\{ \ln \left[(t-t_0) + \frac{\exp(Aq_0)}{AB} \right] - \ln \left(\frac{1}{AB} \right) \right\} \quad (2)$$

or alternatively,

$$q = \frac{1}{A} \left\{ \ln[(t-t_0) + C] - \ln C \right\} + q_0 \quad (2a)$$

where C is defined as $C \equiv \frac{\exp[Aq_0]}{AB}$.

Now eqn (2) can be substituted in eqn (1) to obtain another form of the Elovich equation,

$$\frac{dq}{dt} = \frac{\frac{1}{A}}{(t-t_0) + \frac{\exp[Aq_0]}{AB}} \quad (3)$$

A frequent initial condition is $t_0 = q_0 = 0$, which leads to the following simplified formulation,

$$q = \frac{1}{A} \ln(t + T_0) - \frac{1}{A} \ln T_0 \quad (4)$$

and

$$\frac{dq}{dt} = \frac{\frac{1}{A}}{t + T_0} \quad (5)$$

where $T_0 \equiv 1/AB$. It is clear from eqn (4) that a plot of q vs. $\ln(t + T_0)$ should yield a straight line, the so-called Elovich plot, and this is the method usually used to determine the Elovich constants A and B . It should be noted that a two-parameter fitting procedure is required, unless simplifying assumptions are made. A similar technique can be employed in the more general case of $t_0 \neq q_0 \neq 0$ (see eqns (2) and (2a)). It follows from eqns (1) and (3) that the Elovich constants B and A can be interpreted as the initial rate of chemisorption and a parameter inversely proportional to the reaction rate at $t \gg t_0$, respectively. In this way the rate of chemisorption is originally governed by the magnitude of parameter B , whereas the constant A becomes increasingly important as the reaction

proceeds.

Although the Elovich equation was first proposed as a purely empirical formula, it has been widely interpreted on theoretical grounds. Thus, according to Hayward and Trapnell [15], adsorption may occur whenever gas molecules possessing the necessary activation energy E collide with surface sites available for chemisorption. The chance that such collisions result in adsorption is known as the condensation coefficient σ . The velocity of adsorption depends on four factors: the rate of collision with the surface, which is equal to $\frac{P}{\sqrt{(2\pi mk_B T)}}$, per unit area at pressure P , m being the mass of the gas molecule,

k_B Boltzmann's constant and T temperature; the magnitudes of σ and E ; and upon the chance that collisions take place at available sites. Since this probability usually depends on the fraction of the surface covered, θ , it is designated $f(\theta)$. The rate of chemisorption is then

$$\frac{d\theta}{dt} = \frac{\sigma P}{\sqrt{(2\pi mk_B T)}} f(\theta) \cdot \exp[-E/RT] \quad (6)$$

By a similar argument, the rate of desorption of a chemisorbed species can be expressed as

$$\frac{d\theta}{dt} = K \cdot f'(\theta) \cdot \exp[-E'/RT] \quad (7)$$

where K is a velocity constant. In writing the rate of adsorption $\frac{dq}{dt}$ as $\frac{d\theta}{dt}$, a tacit assumption of proportionality between the amount of gas chemisorbed, q , and the surface coverage, θ , has been made. Although such an assumption seems to be intuitively correct and justified, it is by no means obvious as will be demonstrated below. It is worth mentioning that in general E , E' , K and σ vary with θ and that two separate reasons for this variation are possible:

- (1) The variation may arise from repulsive interactions in a layer, which clearly depend on interatomic distance and hence on θ . In this case, the surface may be treated as uniform, i.e. in adsorption into a layer of given θ , all available sites will have the same E and σ values, and in desorption K and E' will be the same at all available sites. The velocities of adsorption and desorption can be obtained by inserting in eqns (6) and (7) the functional dependence of E , E' , K and σ upon θ .

- (2) Probably a more frequent cause of the variation of E , E' , K and σ is that surfaces are heterogeneous, i.e. there is a variation of adsorptive property from site to site, with different sites possessing different values of these four properties. In this case it is necessary to divide up total surface area into a number of small uniform elements, $d\chi$, each containing n_χ sites of type χ , and to each of which eqns (6) and (7) apply. The total chemisorption velocities are then obtained by integration over all elements of the surface, giving

$$\frac{d\theta}{dt} = \frac{P}{\sqrt{(2\pi m k_B T)}} \int n_\chi \sigma_\chi \cdot f(\theta_\chi) \cdot \exp[-E_\chi/RT] d\chi \quad (8)$$

and

$$\frac{d\theta}{dt} = \int n_\chi K_\chi \cdot f(\theta_\chi) \cdot \exp[-E'_\chi/RT] d\chi \quad (9)$$

If adsorption is dissociative, as it is believed to be in the case of oxygen chemisorption on carbonaceous materials, then $f(\theta) = (1 - \theta)^2$; desorption of surface carbon oxides does not involve dissociation of molecules, however, and thus $f(\theta) = \theta$.

One way of deriving the Elovich equation is by combining Polanyi's theory [17] with the Temkin isotherm [18]. Polanyi's expression relates activation energy, E , to the heat of adsorption, Q , in the following way:

$$E = E_0 - \Phi Q \quad (10)$$

where E_0 and Φ are empirical parameters. The Temkin isotherm holds that the heat of adsorption decreases linearly with surface coverage θ :

$$Q = Q_0(1 - \gamma\theta) \quad (11)$$

where Q_0 is the heat of adsorption at zero coverage and γ is an empirical parameter. Substituting eqn (11) in eqn (10) and combining with eqn (6) gives

$$\frac{dq}{dt} = \frac{d\theta}{dt} = \text{const.} \cdot f(\theta) \cdot \exp \left[-\frac{E_0 + \gamma\theta}{RT} \right] \quad (12)$$

which is of the form of eqn (6) with the additional term $f(\theta)$ if σ is constant. If now $f(\theta) = (1 - \theta)$ or $f(\theta) = (1 - \theta)^2$, then $f(\theta)$ has a small variation in comparison with the exponential

term, provided $\theta \ll 1$. Thus the Elovich equation is obtained from elementary theoretical considerations.

Another derivation was proposed by Taylor and Thon [19], who assumed that there is a nonlinear increase of surface coverage, θ , with the amount of adsorbate chemisorbed, q . In particular, the following relationship was suggested:

$$\frac{dq}{dt} = A(1 - \theta) \quad (13)$$

which upon integration gives:

$$\theta = 1 - \exp[-Aq] \quad (14)$$

This shows that the assumption used previously that θ is proportional to q may only be true for small q . If eqn (6) expresses the rate of adsorption defined as $\frac{dq}{dt}$, if both σ and E are assumed constant, and if furthermore $f(\theta) = (1 - \theta)$, as for the Langmuir isotherm, then

$$\begin{aligned} \frac{dq}{dt} &= \text{const.} \cdot (1 - \theta) \\ &= \text{const.} \cdot \exp[-Aq] \end{aligned} \quad (15)$$

which has the form of the Elovich equation. Moreover,

$$\frac{dq}{dt} \frac{d\theta}{dq} = \frac{d\theta}{dt} = \text{const.} \cdot A(1 - \theta)^2 \quad (16)$$

which has the form of the classic kinetic expression for a chemical reaction occurring on a surface.

Despite these theoretical interpretations, significant criticism of the Elovich equation still remains. First of all, the Elovich equation does not account for surface saturation at $t \rightarrow \infty$, implying that chemisorption should continue *ad infinitum*, which is rather counterintuitive. A theory has been advanced, however, according to which sites are continually created upon contact with adsorbate [19].

Secondly, there are irregularities in Elovich plots reported in the literature, most commonly in the form of sharp changes in gradient (see e.g. [20-23]). These are very often interpreted as indicating a change in adsorption mechanism. On a few occasions these results were later explained more satisfactorily on the basis of another kinetic model (see e.g. [24]). On the other hand, Parravano and Boudart [25] maintain that the wide

applicability of the Elovich equation also constitutes its major weakness, since a number of different processes, such as bulk or surface diffusion and activation or deactivation of catalyst surfaces, as well as chemisorption may be represented by the semilogarithmic formulation. They conclude that it appears futile to explain the applicability of this formulation in terms of any unique mechanism. A similar view was presented by Harris and Evans [26].

Thirdly, the dependence of the Elovich constants upon temperature and pressure is not established. There are significant inconsistencies even in the qualitative trends exhibited by these relationships [16]. It appears that the chemisorption rate constant b has been often reported to be first or fractional order with respect to partial pressure of adsorbate.

Another difficulty, associated more with a practical aspect of chemisorption experiments than with the nature, or validity of the Elovich equation, is an extremely slow adsorption rate at high surface coverages, to the extent that it is virtually impossible to tell whether and when the process of chemisorption ceases to proceed.

Concluding, one must admit that there is still very little known about kinetics of chemisorption in general, and about oxygen chemisorption on chars in particular, including the well-studied Elovich equation, which far too often has to be reduced to a mere exercise in curve fitting. What follows is a brief review of experimental endeavours to establish the dependence of oxygen chemisorption on carbonaceous solids upon temperature and oxygen partial pressure.

The effect of temperature on the amount of oxygen chemisorbed by a char has been studied only to a limited extent. An Australian brown coal char pyrolysed for more than 10 hours at 1000°C showed a trend of increasing oxygen capacity with increasing temperature of chemisorption between 25 and 200°C [12]. Experiments with a higher rank coal char prepared at similar temperatures showed that oxygen capacity increased with temperature only up to about 100°C [9], while a 550°C cellulose char showed increasing oxygen uptake with increasing temperature up to at least 207°C [27]. An activated Graphon (highly graphitized carbon black) showed increasing chemisorption capacity with increasing temperature up to at least 550°C [6]. The actual temperature dependence of saturation amounts of uptake was concluded to be quite complex [5]. Bansal *et al.* [7, 28] investigated the influence of temperature on the USA fractional coverage (the unreacting fraction of the ASA, which is covered by adsorbed oxide film; this is where reaction

initially takes place) and, from the results of their investigations, suggested the existence of several different types of active sites. The adsorption isotherms obtained were found to obey the Elovich equation, and to consist of a series of linear sections. The different stages appeared only after a definite quantity of oxygen had been adsorbed, and this quantity was independent of temperature: the effect of increased temperature was to simply speed the completion of each stage. This would seem to imply that the adsorption is mobile, with the sites of lowest potential energy (highest energy of formation) always filling up first.

The effect of oxygen partial pressure on chemisorption behaviour has also been studied only to a limited extent. It was found, for 1000°C Australian brown coal char, that both reversibly sorbed and chemisorbed oxygen increased with increasing oxygen pressure (from 161 torr to 760 torr) [12]. On the other hand, a sample of higher rank coal char which had been pyrolysed at 1000°C showed no variation in oxygen chemisorption capacity for pressures ranging from about 7.6 torr to 760 torr [9]. In another study, a Graphon sample displayed an oxygen chemisorption capacity which was markedly pressure dependent in the pressure range 0.5 torr to 700 torr [6]. An increase in oxygen chemisorption with oxygen pressure was also observed at high temperatures (615°C) [29].

A study of cellulose char, pyrolysed at 550°C, showed data on oxygen uptake at temperatures between 74 and 207°C to be reasonably fit by the Elovich equation, and implied a linear increase in chemisorption activation energy from 13 to 25 kcal/mol with increasing extent of uptake [27]. These data were interpreted, together with ESR data, to suggest that far more oxygen is chemisorbed than there are free radical sites initially available. A chain reaction via peroxy radicals was ruled out on the basis of the high activation energies. A Diels Adler reaction was postulated, but not vigorously supported. This is representative of the uncertainty concerning oxygen uptake mechanisms on chars. The mere fact that the Elovich equation fits data does little to establish a mechanism; as has been pointed out, the Elovich equation may be consistent with several different types of sorption isotherms.

4.2.3 *Experimental kinetic data.*

Out of all gas reactions of carbon, the one with oxygen seems to be most confusing and troublesome [30-31]. Not only is the reaction mechanism obscure, but also the experimental data published over last decades often show major discrepancies, misunderstandings and lack of coherence in presentation. The source of most difficulties lies in the rapid reaction rate, which makes the kinetic measurements hard to perform.

Table 4.1 Activation energies and reaction orders for the reactions of carbon with oxygen and air.

Investigator	Ref.	React on	Carbon Type	Pressure	Temp. Range	Activation Energy (kcal/mole)	Reaction Order		Evaluation Equation	Experimental Method
							Experi- mental	Assumed		
<i>Reaction with Air and Oxygen</i>										
Acharya and Olander (1973)	33	O ₂	Pyrolytic graphite	1 atm. 10 ₂ , 0.05-1%	1100-2000 K	34.1 (basal plane); 56.5 (prism plane) for T < 1400 K	0 (basal plane), 0.25-0.6 (prism plane)		Nagle and Strickland-Constable	Rotating disk
Ayling and Smith (1972)	34	Air	Coal (pulverized) (semianthracite)	1 atm	1400-2200 K	18.8	—	1	Semiempirical with simple Arrhenius	Upflow furnace tube
Béer et al. (1964)	35	Air	Anthracite	1 atm	1500-1750 K	18.9	—	1	Simple Arrhenius	Plug-flow furnace
Coward and Lewis (1967)	36	Air	Vitreous carbon	1 atm	700-850°C	32	—	—	(Unstated)	(Unstated)
Day et al. (1958)	37	O ₂	5 Rod carbons (manufactured)	1 atm	1500-2000 K	5.3, dropping to 2.3 with increased velocity	1	—	Simple Arrhenius	High-velocity jet
Dutta and Wen (1977) II	38, 39	O ₂ /N ₂	6 Gasification chars	1 atm	400-1100°C	31		1	First-order, semiempirical with Arrhenius	Thermobalance (multiple particle)
Espen et al. (1977)	40	Air	2 Cokes, 1 coal	1 atm	950-1550°C	50 for C/CO ₂ reaction		1	Arrhenius	Flow through, fixed bed (combustion pot)
Essenhigh (1970) (Béer (1964) data)	41	Air	Anthracite	1 atm	1350-1750 K	22 and 44	0	—	Arrhenius	Plug flow furnace
Essenhigh et al. (1965) (Hottel (1934) data)	42	Air	Carbon	1 atm	900-1600°C	40 (T < 1100°C); 3.4 (T > 1250°C)		0 (T < 1100°C); 1 (T > 1250°C)	Modified Langmuir	Thermobalance, (single sphere)
Evans and Enimons (1977)	43	Air	Wood charcoal	1 atm	750-1100°C	18		1	Simple Arrhenius	Jet
Field (1969)	44	C ₂ /N ₂	Anthracite char (pulverized)	1 atm	1200-2000 K	30-10 for increased T	1		Empirical	Drop (isotherm) tube

Table 4.1 - cont.

Investigator	Ref.	Reaction	Carbon Type	Pressure	Temp. Range	Activation Energy (kcal/mole)	Reaction Order		Evaluation Equation	Experimental Method
							Experi- mental	Assumed		
Reaction with Air and Oxygen (continued)										
Field (1970)	45	Air	11 p.c. chars	1 atm	1200-2000 K	Linear rise of rate constant with T	1		(Incomplete evaluation)	Drop (isotherm) tube
Gray et al. (1974)	46	Air	Coal chars	1 atm	1200-2000 K	37 ($n = 0$); 6 ($n = 1$)		0 1	Langmuir-Hinshelwood	Drop tube
[Field (1969) data] Hamor et al. (1973)	47	Air	Brown coal (pulverized)	1 atm	630-2200 K	16.2 (dia > 25 μ m) (T > 760K)	0.5		Empirical nth-order with simple Arrhenius (Detailed flow analysis)	Upflow furnace tube
Hawtin and Murdoch (1964)	48	Air	Graphite (pile grade A)	1 atm	400-550°C	23.5 as measured 45.4 (corr. for diffusion)	0.6		(Detailed flow analysis)	Flow tube
Hawtin et al. (1964)	49	Air	Graphite (pile grade A)	1 atm	400-500°C	44.5 (corr. for diffusion)	0.6		(Detailed flow analysis)	Flow tube
Hawtin and Gibson (1966) I	50	Air	Graphite (pile grade A)	1 atm	550-675°C	25 (appt) 48.6 (corr. for diffusion)	0.8 (appt); 0.6 (true)		(Detailed flow analysis)	Flow tube
Hawtin and Gibson (1966) II	51	Air	Baked carbon	1 atm	300-420°C	55.2 (falling with T)	0.78		(Detailed flow analysis)	Flow tube
Howard and Essenhigh (1966, 1967)	52, 53	Air	Coal	1 atm	500-1500° C	30-65		1	Simple Arrhenius	Plug-flow furnace
Jenkins et al. (1973)	54	Air	21 Heat-treated coal chars	1 atm	500°C	—	—	1	Rate $\propto$ weight with simple Arrhenius	Thermobalance

Table 4.1 - cont.

Lambert (1936)	55	O ₂ /N ₂	Diamond, graphite, anthracite char, coconut char	1 atm	500-800 K	44, 49, 31, 29 (respectively)	1	Arrhenius	Flow through multiple particle bed
Lee et al. (1962)	56	Air	Soot	1 atm	1300-1700° C	39.3	1	First-order Arrhenius	Flame (soot)
Leesley and Hedley (1972)	57, 58	Air	Anthracite (13 size cuts)	1 atm	1200-1600° C	20	0.87	Computer fit. on surface reaction	Plug-flow flame
Lewis et al. (1964)	59	O ₂ /N ₂ (dry)	Graphite (pile grade A)	1 atm	575-655°C	Not reported	0.54-0.6	Empirical nth order	Flow over single cylinder
Lewis et al. (1965)	60	O ₂ /N ₂ (moist)	Graphite (pile grade A)	1 atm	575-655°C	Not reported	0.65	Empirical nth order	Flow over single cylinder
Magnussen (1971)	61	Air	Soot	1 atm	1300-1700° C	39 for adsorption	1 (O ₂)	Langmuir	Flame (soot)
[Lee et al. (1962) data]									
Froberg (1967)	62	Air, O ₂	Graphitized carbon (L-56 III)	1 atm	600-1100° C	45 (Zone I), 22.5 (Zone II)	0 0.5	Arrhenius	Thermobalance (single sphere)
Kurylko and Essenhigh (1973)	63	Air, O ₂	Graphitized carbon (L-56 III)	1 atm	600-1100° C	48.1 (Zone I), 25.5 (Zone II)	0 0.5	Arrhenius	Thermobalance (single sphere)
Matsui et al. (1975)	64	Air	Carbon	1 atm	1000-1800 K	47 and 53	—	1	Fluid mechanics analysis
Nagle and Strickland Constable (1963)	65	O ₂ or O ₂ /N ₂	1 Carbon, 2 graphites	up to 0.6 atm	1000-2000° C	30 (T < 1400°C)	1 (O ₂ adsorption)	Nagle and Strickland- Constable	Electrically heated rods
Okada and Ikegawa (1953)	66	Air	Artificial graphite	1 atm	700-2000° C	12.7 (T < 800°C)	0	Arrhenius	Electrically heated rods
Parker and Hottel (1936)	67	Air	Brush carbon	1 atm	1000-1400 K	44	1	"Resistance"	Thermobalance (single cylinder)
Popov (1959)	68	Air	Carbon	1 atm	1000-1400° C	19.4	1	"Resistance"	Thermobalance (single sphere)

Table 4.1 - cont.

Investigator	Ref.	Reaction	Carbon Type	Pressure	Temp. Range	Activation Energy (kcal/mole)	Reaction Order		Evaluation Equation	Experimental Method
							Experimental	Assumed		
Reaction with Air and Oxygen (continued)										
Sebastian and Mayers (1937)	69	Air	15 Cokes	1 atm	200-600°C	10-38 function of coal-type	—	1	Crossing point analysis	Crossing point (ignition)
Sergeant and Smith (1973)	70	Air	3 Coal (bituminous) chars, pulverized	1 atm	800-1700 K	27		1	Empirical n th order with Arrhenius	Drop (isotherm) tube
Smith (1970)	71	Air	Anthracite (pulverized)	1 atm	1400-2200 K	18.8		1	Empirical n th order with Arrhenius	Upflow furnace tube
Smith (1971) I	72	Air	Anthracite, coke, char (pulverized)	1 atm	1200-2270 K	16-18 (for 3 fuels)		1	First order with Arrhenius	Upflow furnace tube
Smith (1971) II	73	Air	Semianthracite (pulverized)	1 atm	1400-2200 K	19		1	First order with Arrhenius	Upflow furnace tube
Smith and Tyler (1972)	74	Air	Semianthracite (pulverized)	1 atm	1400-2200 K	20		1	First order with Arrhenius	Upflow furnace tube
Smith and Tyler (1974)	75	Air	Brown coal char (pulverized)	1 atm	630-1812 K	32.6		0	Empirical n th order with Arrhenius	Upflow furnace tube
Tu et al. (1934)	76	Air	Graphite (brush carbon)	1 atm	900-1700 K	40 ($T < 1000^\circ$ K)		1	"Resistance"	Thermobalance (single sphere)
Udayakar, and Williams (1976)	77	O ₂ and N ₂	Electrode carbon	1 atm	2000-3500 K	18			Empirical n th order with Arrhenius	Laser ignition of free particles
Walls and Strickland Constable (1964, 1965)	78, 79	O ₂	2 Pyrographites	1 atm	900-2400° C	30 for O ₂ adsorption	—	—	Nagle and Strickland-Constable	Electrically heated rods with jet impingement

Table 4.2 Intrinsic kinetic data for carbon and char combustion [30].

<u>Investigation</u>	<u>Sample</u>	<u>T [K]</u>	<u>P_{O2} [atm]</u>	<u>n</u>	<u>E [kcal/mol]</u>
Field <i>et al.</i> [79]	carbon	950-1600	0.01-0.21	1	36
Mulcahy and Smith [80] (overall kinetic data)	anthracite, petroleum coke, bituminous and lignite chars	1000-2300	0.20	1*	~15
Blyholder and Eyring [81]	graphite	875-1075	10 ⁻⁶ -10 ⁻⁴	0	80
Blyholder and Eyring [82]	graphite	1075-1575	10 ⁻⁶ -10 ⁻⁴	0.5	2-80†
Walker <i>et al.</i> [10]	carbon, chars	--	--	1	46-58
Thring and Essenhight [83]	carbon, chars	800-1550	~0.2	0	25-45
Laine <i>et al.</i> [1]	carbon	850-950	5·10 ⁻⁵	1*	44
Laine <i>et al.</i> [84]	carbon	575-950	(4-66)·10 ⁻⁵	1*	43-46
Rosner and Allendorf [85]	graphite	1100-1300	~10 ⁻³	0.5	62
		1450-1700	~10 ⁻³	1	0
Mulcahy and Smith [86]	graphite	1200-1600	--	0.5	35-60
Rodriguez-Reinoso <i>et al.</i> [87]	graphite	775-875	(8-79)·10 ⁻³	0.5-0.6	47-53

* n = 1 assumed

† E approaches 2 kcal/mol at the highest temperatures

Another problem presents itself in a fairly complicated pattern of mass transfer phenomena occurring during combustion of coal: resistance in a boundary layer, molecular, Knudsen, or even activated diffusion within pores may lead to erroneous data interpretation if not realized as process controlling effects; this was in fact the case with nearly all early research endeavours [30]. The influence of catalytic impurities and complex surface phenomena, such as dissociation of oxygen on active sites, surface complex formation, evolution, and its decomposition as carbon oxides, form a separate group of difficulties. It was shown by Smith [32] that despite elimination of effects of different pore sizes and surface areas, reactivities of various carbonaceous materials may still differ by as much as four orders of magnitude. The behaviour of reacting carbon-oxygen systems is by no means simple.

Tables 4.1 and 4.2, compiled by Essenhight [31] and Laurendeau [30], provide a rather complete overview of reaction kinetics studies. It can be observed that the reaction order varies between zero and unity, the result predicted by Langmuir-Hinshelwood rate expression, discussed in the next section. Secondly, nearly all data collected at relatively low temperatures ($T < 700^{\circ}\text{C}$) exhibit a fractional order kinetics, with reaction order m typically in the range 0.5-0.6. There seems to be some indication that low temperature favours lower reaction order. Thirdly, zero order reactions have rather high activation energies ($E = 40 - 80 \text{ kcal/mole}$), for fractional (mostly half-) order reactions, activation energies range roughly from 20 to 50 kcal/mole, whereas first order reactions are characterized by relatively low activation energies ($E = 3-30 \text{ kcal/mole}$) [31]. Since activation energies for oxygen adsorption (chemisorption in fact) and surface complex desorption are approximately $E_a = 15-20 \text{ kcal/mole}$ and $E_d = 70-80 \text{ kcal/mole}$, one may conclude that zero order oxidation is desorption-controlled, while reactions exhibiting first order kinetics are controlled by adsorption.

4.2.4 Langmuir-Hinshelwood kinetics and surface reaction mechanisms for char gasification [15,30,89]

The simplest mathematical model applicable to high temperature ($T > 250^{\circ}\text{C}$) gas-solid reactions was developed by Langmuir (for a single site mechanism); Hinshelwood later extended the model to dual site mechanisms. The following three assumptions must be added to the usual ones denoted above:

- (1) The surface is homogeneous, i.e. a uniform average activity can be defined for the entire surface (a uniform distribution of active sites).

(2) No interaction occurs among adsorbed species, i.e. the amount adsorbed has no effect on the adsorption rate per site.

(3) Surface migration is either nonexistent or so rapid that only adsorption and desorption can be rate-controlling.

The above assumptions imply that E_a and E_d remain constant in time as well as from site to site.

The intrinsic rate of adsorption is

$$r_a = k_a \cdot C \cdot (1 - \theta)^s, \quad s = 1, 2 \quad (17)$$

where θ is the fraction of active surface covered by adsorbed species, C is the local gas concentration [g/cm^3], $s = 1, 2$ denotes single and dual site adsorption, respectively, and

$$k_a = A_a \cdot \exp[-E_a/RT] \quad (18)$$

The rate of desorption can be written as

$$r_d = k_d \cdot \theta^{s'}, \quad s' = 1, 2 \quad (19)$$

where $s' = 1, 2$ refers to single and dual site desorption, respectively, and

$$k_d = A_d \cdot \exp[-E_d/RT] \quad (20)$$

Consider the $s = s'$ case; assuming steady state, isothermal conditions, we have $r_a = r_d$ and thus from eqns (17) and (19),

$$[\theta/(1 - \theta)]^s = A \cdot C \quad (21)$$

where

$$A = k_a/k_d = A_a/A_d \cdot \exp[(E_d - E_a)/RT] \quad (22)$$

Note that for homogeneous, non-interacting surface, A is solely a function of temperature

and independent of θ . Rearranging eqn (21), we obtain

$$\theta = \frac{(A \cdot C)^{1/s}}{1 + (A \cdot C)^{1/s}}, \quad s = 1, 2 \quad (23)$$

Assuming $s = 1$ and substituting eqn (23) into eqn (19), the intrinsic surface rate becomes

$$r = r_a = r_d = \frac{k_a C}{1 + AC} \quad (24)$$

It is clear that depending upon temperature and partial pressure of oxygen, r can become either first or zeroth order.

$$(1) \quad AC \ll 1 \quad \text{---->} \quad r = k_a C \quad [m = 1]$$

$$(2) \quad AC \gg 1 \quad \text{---->} \quad r = k_d \quad [m = 0].$$

Thus if we fit a global intrinsic expression $r = kC^n$ to a system controlled by Langmuir kinetics, the true order will fall in the range $0 < n < 1$ depending on temperature and oxygen partial pressure. In general, first order kinetics, i.e. adsorption control, is promoted by lower reactant concentrations (eqn (24)) and higher temperatures (eqn (22)). Note that either first or zeroth order kinetics also arise for $s = s' = 2$. For $s = 2$ and $s' = 1$ (dissociative chemisorption and single site desorption), a more complex situation occurs, which offers the possibility of half order kinetics in addition to $n = 0$ and $n = 1$.

A number of surface reaction mechanisms have been proposed to explain experimental data on char gasification and combustion. A few of them will be mentioned here to illustrate possible chemical processes that can occur on char surfaces, and how they account for various reaction orders reported in the literature.

Spokes and Benson [90], following von Fredersdorff and Elliott [91] and Nagle and Strickland-Constable [65], suggested the following mechanism,

where C_f denotes a free active site, $C(O)$ is a surface complex, C_t is an active site in contrast to C_i , which is an inactive site that has lost its reactive properties due to thermal annealing, expressed by eqn (R4). By assuming a steady-state concentration of $C(O)$, it can be shown that this model is consistent with reaction order $n = 0$ or $n = 1$.

An alternative mechanism [92], relying on $C(O_2)$ rather than $C(O)$ is given by

but the second reaction is probably not elementary [30].

Since the late 1950s, evidence has accumulated [83,87,89], showing that $n = 0.5$ in the temperature range 800-1300°C. More recent work [75,88,93] indicates that a half-order reaction can apply in general for even larger temperature ranges (400-1500°C). Table 4.1 gives more examples of half-order kinetics for char gasification. Based on these results, a suitable mechanism for char combustion must allow for true orders of zero, one-half and unity, and such a mechanism must be characterized by dissociative chemisorption and surface migration [30]. Blyholder and Eyring [83] recommend the following:

where $C'(O)$ is another type of a surface complex.

This mechanism is consistent with quantum mechanical calculations which favour mobile (two-site) chemisorption [94]. Reaction (R6) has also been postulated by Marsh *et al.* [95] and Walker *et al.* [4, 96]. Blyholder and Eyring [83] suggest that $C'(O)$ represents a mobile ionic bond, while $C(O)$ represents an immobile covalent (carbonyl) bond. The reversibility of O_2 adsorption implied by eqn (R5) has been questioned, however [1, 15, 97].

An alternative mechanism was proposed by Laurendeau [30], and this mechanism will be discussed here in more detail. The model suggested by Laurendeau involves the following reactions:

Reaction (R7) is an attempt to provide faster conversion to CO at lower temperatures than allowed by reaction (R3). Reaction (R8) has been found by Walker et al. [96] to be responsible for primary CO₂ formation. Using isotope tracer methods at low pressures, these investigators not only found positive evidence for reaction (R8), but also eliminated previous suggestions such as,

In addition, reaction (R8) is consistent with Blackwood and McTaggart's observation that CO₂ is produced during reaction between carbon and atomic oxygen [98].

Application of the steady-state approximation to both C'(O) and C(O) gives,

$$\Delta_1 \Theta^2 - \Delta_2 \Theta + \Delta_3 = 0 \quad (\text{L1})$$

where

$$\Delta_1 = 2k_5(1 + k_3/k_6)^2[\text{C}_t]\text{C} - 2k_8(k_3/k_6)^2[\text{C}_t]$$

$$\Delta_2 = 4k_5(1 + k_3/k_6)[\text{C}_t]\text{C} + k_3(1 + k_7/k_6)$$

$$\Delta_3 = 2k_5[\text{C}_t]\text{C}$$

and k_3 , k_5 , k_6 , etc., are reaction rate constants for reactions (R3), (R5), (R6), etc., $[\text{C}_t]$ is surface concentration of active sites in $[\text{sites}/\text{m}^2]$, C is concentration of oxygen in the gas phase, and Θ is defined as $[\text{C}(\text{O})]/[\text{C}_t]$.

The intrinsic global rate can be approximated by

$$r \approx m_c[\text{C}_t]k_3(1 + k_7/k_6)\Theta \quad [\text{g}/\text{m}^2\cdot\text{s}], \quad (\text{L2})$$

where Θ is given by eqn (L1), and m_c is mass of carbon atom in $[\text{g}/\text{site}]$. Two cases can be considered:

$$(1) \quad |\Delta_1| \ll \Delta_2 \\ \therefore \Theta = \Delta_3/\Delta_2$$

$$(2) \quad \Delta_2 \ll |\Delta_1| \\ \therefore \Theta = \sqrt{-\Delta_3/\Delta_1}$$

For case (1), we have two subcases:

$$(A) \quad 4k_5(1 + k_3/k_6)[C_t]C \gg k_3(1 + k_7/k_6) \\ \therefore \Theta = 1/2(1 + k_3/k_6)$$

and thus

$$r = \frac{m_C[C_t]k_3}{2} \left(\frac{1 + k_7/k_6}{1 + k_3/k_6} \right) \quad (L3)$$

$$(B) \quad 4k_5(1 + k_3/k_6)[C_t]C \ll k_3(1 + k_7/k_6) \\ \therefore \Theta = 2k_5[C_t]C/k_3(1 + k_7/k_6)$$

and thus

$$r = 2m_Ck_5[C_t]^2C \quad (L4)$$

For case (2), if we assume further

$$2k_8(k_3/k_6)^2[C_t] \gg 2k_5(1 + k_3/k_6)^2[C_t]C,$$

we have $\Theta = (k_6/k_3)(k_5C/k_8)^{1/2}$ and thus,

$$r = m_C[C_t]k_6(1 + k_7/k_6)(k_5/k_8)^{1/2}C^{1/2} \quad (L5)$$

Eqns (L3)-(L5) demonstrate that the suggested mechanism does indeed allow $n = 0$ (low temperatures), $n = 0.5$ (intermediate temperatures) and $m = 1$ (high temperatures). Furthermore, the following simplifying assumptions can be made:

@ low temperature	$k_3/k_6 \gg 1$	$k_7/k_6 \gg 1$
@ intermediate temperature	$k_3/k_6 \gg 1$	$k_7/k_6 \ll 1$
@ high temperature	$k_3/k_6 \ll 1$	$k_7/k_6 \ll 1$

to obtain ,

$$\begin{aligned}
 n = 0 & \quad r = m_c [C_L] k_7 / 2 \\
 n = 1 & \quad r = 2 m_c k_5 [C_L]^2 C \\
 n = 0.5 & \quad r = m_c [C_L] k_6 (k_5/k_8)^{1/2} C^{1/2}
 \end{aligned}$$

Hence, mobile site desorption controls at low temperatures, dissociative chemisorption at high temperatures and site migration at intermediate temperatures.

A number of other models predicting zero, first and half-order gasification kinetics have been proposed recently (e.g., Ahmed and Back [99], Calo [100]), no mechanism is known, however, that would account for other than 0, 1 and 0.5 reaction orders over wide ranges of oxygen partial pressure.

4.3 OXYGEN CHEMISORPTION AS A TOOL FOR CHARACTERIZING "YOUNG" CHARS

Since gasification reactions occur at active sites, it is clear that gasification rates are a strong function of active site concentration, often expressed in terms of active surface area, ASA. Thus the knowledge of this variable is central to modelling char gasification and combustion kinetics, and, ultimately, for the design of coal gasifiers or combustors. As outlined in the previous section, oxygen chemisorption has been proposed as a viable technique for measuring active surface area of carbonaceous materials, and it has been extensively used for this purpose in the past. Unfortunately, there are some questions as to its universal validity, primarily due to temperature and pressure dependence of oxygen uptake. The evidence for the relationship between the amount of oxygen chemisorbed and gasification rates have come mainly from a series of very careful studies on very "old" chars, oxidized at moderate temperatures [1,4-7]. The few studies of "young" chars that have been done [12, 27] involved materials containing potentially catalytic components, and it was found that the concentration of catalytic additives has an effect on both oxygen chemisorption behaviour and gasification rates (e.g., see [27, 101]). Work on high purity "young" materials was needed for better understanding of fundamentals underlying the chemisorption-gasification relationship. This issue is addressed in this section.

Two different kinds of char were examined in the course of this study. One was prepared by pyrolysis of a previously demineralized North Dakota lignite (see section 2.2 for elemental analysis), the other was derived from a phenol-formaldehyde resin, carefully synthesized to avoid cation contamination (see section 2.2).

Both samples were pyrolysed at similar conditions under an atmosphere of flowing helium. The resin samples were heated at a rate of 4 to 5°C/min. to a maximum temperature of 950°C, held at this temperature for 2 hours, and then cooled to room temperature at a rate of 2 to 25°C/min. The lignite was heated at a rate of about 3°C/min. to 1000°C, held at this temperature for 2 hours, and then cooled to room temperature at a rate comparable to the heating rate. The weight loss during pyrolysis was about 40% for the resin char and 42% for the lignite. Samples were never exposed to oxygen at elevated temperatures, except during the actual chemisorption experiments. Prior to chemisorption, samples were outgassed under helium at 950°C for 2 hours.

Two tests were performed with these chars to determine the effects of temperature and oxygen partial pressure on chemisorption capacity. In both experiments, chars with

initially clean surfaces (see chapter III for the surface cleaning procedure) were subjected to oxygen and then to a stepwise increase in temperature or oxygen partial pressure. Figs 4.1 through 4.4 show the results of these tests.

As shown in Fig. 4.1, for the resin char there is evidence of increased oxygen chemisorption capacity with increasing temperature up to 300°C, at which temperature the mass begins to decrease due to decomposition of surface oxides. In the case of the lignite char, as shown in Fig. 4.2, the effect of temperature is much less pronounced and mass loss becomes evident at 250°C.

Thus it must be concluded that the effect of temperature on chemisorption may vary from char to char, and there is a legitimate question as to exactly what is measured at any arbitrary condition. Depending upon the situation, the maximum uptake may be an artifact due to competing processes of continued chemisorption and desorption of complexes.

It is apparent from Figs 4.3 and 4.4 that the partial pressure of oxygen has a marked influence on the rate of oxygen uptake and, evidently, on the ultimate oxygen capacity of the sample. It is noted that the rate of oxygen uptake becomes immeasurably small after about 24 hours of continuous exposure to oxygen at low values of partial pressure (i.e., $P_{O_2} = 0.66$ and 3.9 torr). It is quite obvious that the amount of oxygen chemisorbed at, say 0.66 torr cannot attain the uptake level observed at higher partial pressures on any reasonable experimental time scale. Therefore, it is concluded that oxygen chemisorption can hardly be termed a "site-specific" analytical technique, at least when applied to young chars. However, the fact that apparent oxygen capacities are sensitive to temperature and pressure does not necessarily imply that oxygen chemisorption is not useful as a correlative tool; it has been demonstrated in several cases (see e.g., [1, 2]) that active site concentrations, as measured by chemisorption of oxygen, do correlate reasonably well with char reactivity.

Despite the expected problems associated with such an endeavour, an attempt was made to correlate reactivities of "young" phenolic resin chars with ASA's measured under certain selected conditions. A number of oxygen chemisorption experiments, as well as reaction rate measurements, were carried out to obtain the necessary data for this analysis. The results are presented in Tables 4.3, 4.4, and in section A.4 (Appendix A). Active surface area was calculated assuming that each atom of oxygen chemisorbed occupies 8.3 Å² of surface, and the value of oxygen uptake, q , refers to the amount of O₂ chemisorbed during 24 hours. The surface oxide species were removed from the surface of all the char

Table 4.3 Oxygen chemisorption data (char pyrolysed at 1000°C).

	P _{O2} = 160 torr			P _{O2} = 760 torr			
	150°C	200°C	300°C [†]	150°C	150°C*	200°C	300°C [‡]
B [%]	4.3	3.3	4.2	4.2	43.1	4.1	4.3
TSA (CO ₂ BET) [m ² /g]	417	407	417	417	720	417	417
q [g O ₂ /kg char]	7.4	9.39	11.0	10.4	14.2	12.3	12.68
q/TSA · 10 ⁵	1.8	2.3	2.6	2.5	2.0	2.9	3.0
ASA [m ² /g]	23.1	29.3	34.4	32.5	44.4	38.4	39.6
ASA/TSA · 100%	5.5	7.2	8.2	7.8	6.2	9.2	9.5
a [kg char/g O ₂]	1.00	0.77	0.57	0.83	0.60	0.68	0.56
a · TSA · 10 ⁻⁵	4.2	3.1	2.4	3.5	4.3	2.8	2.3
b [g O ₂ /(kg char·hr)]	55.4	81.8	165.4	204	352	196	1388
b/TSA · 10 ⁵	13.3	20.1	39.7	48.9	48.9	47.0	333

* extrapolated (chemisorption data collected for 8.2 hr)

[†] zero mass gain reached after 17.6 hr (concurrent O₂ chemisorption and gasification)[‡] zero mass gain reached after 2.85 hr (concurrent O₂ chemisorption and gasification)

Table 4.4 Oxygen chemisorption data (chars pyrolysed at 1111, 1243, and 1400°C).

	$T_p =$	T = 150°C P _{O2} = 760 torr				T = 200°C P _{O2} = 160 torr	
		1111°C	1243°C*	1400°C	1400°C	1400°C	1400°C
B [%]		0.24	0.12	0.21	12.9	47.5	0.14
TSA (CO ₂ BET) [m ² /g]		70	36	123	560	900	107
q [g O ₂ /kg char]		4.84	1.81	0.52	6.85	20.7	0.29
q/TSA · 10 ⁵		6.9	5.0	0.42	1.2	2.3	0.27
ASA [m ² /g]		15.1	5.7	1.6	21.4	64.7	0.91
ASA/TSA · 100%		21.6	15.8	1.3	3.8	7.2	0.85
a [kg char/g O ₂] 1.00		2.31	12.4	1.32	0.508	9.22	
a · TSA · 10 ⁻⁵		0.70	0.83	15.3	7.3	4.6	9.9
b [g O ₂ /(kg char·hr)]		4.68	1.15	1.63	260	2674	0.0698
b/TSA · 10 ⁵		6.7	3.2	1.3	46.4	297	0.065

* extrapolated (chemisorption data collected for 17.5 hr)

samples prior to chemisorption by desorption at 950°C in helium, in the manner described in chapter III. Initial burn-off of about 3.3-4.3%, 0.24%, 0.12% and 0.14-0.21% resulted from the cleaning procedure in the case of chars prepared at 1000, 1111, 1243 and 1400°C, respectively.

It is evident from Tables 4.3 and 4.4 that ASA increases with burn-off, especially for the char heat-treated at 1400°C, and this is why reactivities measured at the lowest possible burn-offs were chosen for comparison of data. In spite of this, corrections for burn-off were necessary in the case of char pyrolysed at 1400°C, and they were made using linear interpolation of ASA values taken from Table 4.4. Thus ASA's of 4.1, 6.4 and 6.6 m²/g were found for B = 1.1%, 2.9% and 3.0%, respectively. The values of TSA were determined using the "universal" TSA (CO₂ BET) vs burn-off curve approach discussed in section 2.3, while ASA was determined from oxygen chemisorption at T = 150°C and P_{O₂} = 760 torr. Oxygen uptake after 24 hours was used as the basis for the calculations. The relevant data for comparison of reaction rates are presented in Table 4.5.

As noted above, the active surface area of the 1000°C char is relatively constant with burn-off, whereas it increases dramatically with burn-off in the case of the 1400°C char, presumably because any molecular order promoted by heat treatment can be destroyed by removal of carbon by gasification. The increase in disorder in the 1000°C char is not significant, because this char is highly disordered to begin with.

It can be seen that the reaction rates expressed on a mass basis differ by as much as the factor of 8.0 between the most and the least reactive chars. This factor is reduced to only 7.1 by normalizing the reactivities with respect to TSA. Reaction rates expressed on an ASA basis, however, show the largest discrepancy to be a factor of 2.1. Furthermore, this difference is attributed primarily to a lack of burn-off correction data for ASA available for the char pyrolysed at 1243°C. No such data are needed for the two "youngest" chars, as it has already been concluded that appreciable changes in ASA with burn-off occur only in the case of "older" chars. Indeed, the corrected ASA-based reactivities for the char prepared at 1400°C show very good agreement with reactivities of the chars pyrolysed at 1000 and 1111°C, whereas the uncorrected reaction rates of the char pyrolysed at 1243°C exhibit consistently highest values.

Variation of reaction rates with burn-off was also examined, and the results are presented in Table 4.6. It was found that reaction rates normalized with respect to ASA remain constant with changing burn-off in the case of the char pyrolysed at 1000°C. For

Table 4.5 Oxidation reactivities of the phenolic resin chars ($P_{O_2} = 760$ torr).

	T = 300°C			
	$T_p = 1000^\circ\text{C}$	$T_p = 1111^\circ\text{C}$	$T_p = 1243^\circ\text{C}$	$T_p = 1400^\circ\text{C}$
B [%]	4.5	3.6	0.3	2.9
TSA (CO_2 BET) [m^2/g]	402	467	143 ^a	388
ASA [m^2/g]	32.5	15.1	5.7	6.4
$r \cdot 10^4$ [g/(g·hr)]	3.7	1.6	0.83	0.52
$r/\text{TSA} \cdot 10^7$	9.2	3.4	5.8	1.3
$r/\text{ASA} \cdot 10^4$	0.11	0.11	0.15	0.081

	T = 325°C			
	$T_p = 1000^\circ\text{C}$	$T_p = 1111^\circ\text{C}$	$T_p = 1243^\circ\text{C}$	$T_p = 1400^\circ\text{C}$
B [%]	7.9	3.3	2.0	3.0
TSA (CO_2 BET) [m^2/g]	422	421	384	390
ASA [m^2/g]	33.5	15.1	5.7	6.6
$r \cdot 10^4$ [g/(g·hr)]	12.0	6.0	3.3	1.8
$r/\text{TSA} \cdot 10^7$	28.4	14.3	8.6	4.6
$r/\text{ASA} \cdot 10^4$	0.36	0.40	0.58	0.27

	T = 350°C			
	$T_p = 1000^\circ\text{C}$	$T_p = 1111^\circ\text{C}$	$T_p = 1243^\circ\text{C}$	$T_p = 1400^\circ\text{C}$
B [%]	17.4	2.1	1.5	1.1
TSA (CO_2 BET) [m^2/g]	495	390 ^b	352	368 ^c
ASA [m^2/g]	36.5	15.1	5.7	4.1
$r \cdot 10^4$ [g/(g·hr)]	43.0	17.8	11.0	5.4
$r/\text{TSA} \cdot 10^7$	86.9	45.6	31.3	14.7
$r/\text{ASA} \cdot 10^4$	1.2	1.2	1.9	1.3

^a based on the $T_p = 1400^\circ\text{C}$ TSA data, may be larger yet ($\sim 200 \text{ m}^2/\text{g}$)^b based on the $T_p = 1243^\circ\text{C}$ TSA data^c based on the $T_p = 1000^\circ\text{C}$ TSA data

Table 4.6 Effect of burn-off on phenolic resin char reactivity ($P_{O_2} = 760$ torr).

$T_p = 1000^\circ\text{C}$				
$T [^\circ\text{C}]$	$B [\%]$	$r \cdot 10^4 [\text{g/g}\cdot\text{hr}]$	$\text{ASA} [\text{m}^2/\text{g}]$	$r/\text{ASA} \cdot 10^4$
300	4.5	3.7	32.5	0.11
300	23.9	3.3	38.5	0.086
300	30.5	4.8	40.5	0.12
300	42.3	5.2	44.2	0.12
350	17.4	43	36.5	1.2
350	29.3	40	40.1	1.0
350	41.5	59	43.9	1.3
350	55.1	65	48.1	1.4
$T_p = 1400^\circ\text{C}$				
$T [^\circ\text{C}]$	$B [\%]$	$r \cdot 10^4 [\text{g/g}\cdot\text{hr}]$	$\text{ASA} [\text{m}^2/\text{g}]$	$r/\text{ASA} \cdot 10^4$
300	0.3	0.46	3.0	0.15
300	2.9	0.52	6.4	0.081
300	35.4	1.1	49.3	0.022
325	0.4	1.8	3.2	0.56
325	2.9	1.5	4.6	0.33
325	3.0	1.8	6.6	0.27
325	35.3	3.6	49.1	0.073
350	1.1	5.4	4.1	1.3
350	2.9	5.3	6.4	0.83
350	35.1	12	48.9	0.25
375	2.4	16	5.8	2.8
375	35.8	38	49.8	0.76
400	1.7	46	4.9	9.4
400	20.3	96	24.2	4.0
400	36.4	110	50.6	2.2

the 1400°C char, however, the ASA-normalized rates exhibit stronger variation with burn-off than the rates related to sample mass. This can possibly be explained by limited accessibility of active sites to oxygen during gasification due to a mass transfer limitation. Since molecular and Knudsen diffusion have been found not to be rate limiting (see Appendix B), it is hypothesized that activated diffusion in micropores can be of importance. Another indication that activated diffusion may be involved is the plot of the Elovich parameter a vs $1/T$ (Fig. 4.5). If activated diffusion is rate controlling, then the rate of chemisorption, which is proportional to $1/a$, is expected to decrease with temperature. A slight curvature in the a vs $1/T$ plots suggests that this may be actually the case.

Successful correlation of reactivities with active surface area, as determined by oxygen chemisorption, does not change the fact that this technique is, in general, inadequate for *quantitative* ASA measurements. It is apparent that the number of "active sites" depends upon the conditions of the experiments. Therefore, ASA, as measured by oxygen chemisorption, is merely an index of chemisorption reactivity which can, if determined under standardized conditions, usually be used to obtain good correlation with gasification reactivity. At present we cannot claim a fundamental understanding of what constitutes ASA. However, the following observations can be made about the values obtained for ASA:

- (1) Low temperatures and oxygen partial pressures give low apparent ASA values. This is not to imply that a value of ASA obtained at, say 150°C, is any less "correct" than an ASA obtained at 200°C, but the values will be different.
- (2) The use of temperatures above 250°C runs the risk of promoting gasification simultaneously with chemisorption. The actual temperature at which gasification becomes appreciable depends both upon the char and the oxygen partial pressure.
- (3) There is no well-defined endpoint for the experiment. Generally, an arbitrary choice is made to terminate chemisorption; many workers seem to use 24 hours as the endpoint.

Since all three crucial parameters: temperature, partial pressure of oxygen, and time scale of the experiment are very material dependent and practically impossible to determine *a priori*, it seems more reasonable to resort to direct reaction rate measurements, since reactivities are exactly what is needed in most cases anyway. Oxygen chemisorption may

still, however, find successful applications in studying surface reaction phenomena occurring in heterogeneous reactions of "young" chars.

At this point some comments are given regarding the variation of the Elovich constants with temperature, pressure, and sample pyrolysis conditions. It can be inferred from eqns (1) and (12) that the constant a , as well as the logarithm of b , should be proportional to $1/T$. Figs 4.5 and 4.6 show that these relationships are only crudely satisfied. The proportionality of b to partial pressure of oxygen, implied by eqn (6), is satisfied only approximately. The ratios of b (760 torr) to b (160 torr), calculated from data presented in Table 4.3, are 3.7, 2.3, and 8.4, instead of the expected 4.75. This discrepancy can be explained in terms of experimental error involved in the exact determination of the beginning of each oxygen chemisorption run. As mentioned in the previous section, the parameter b represents the initial rate of chemisorption, and thus is very sensitive to any experimental uncertainty involved in determining the slope of the oxygen uptake curve during the initial stages of chemisorption.

No variation of a is expected with P_{O_2} and, indeed, it is quite clear from Table 4.3 that a is constant at different partial pressures of oxygen for the same material and for the same chemisorption temperature.

An important conclusion can be drawn from the variation of b with the pyrolysis temperature. It is evident from Tables 4.3 and 4.4 that b , measured at $P_{O_2} = 760$ torr, decreases as pyrolysis temperature increases. Since the parameter b is a measure of the collision frequency between gas molecules and active sites, and since P_{O_2} was not varied in this experiment, it follows that the number of active sites apparently decreases with severity of heat treatment. Therefore, it is postulated that the process of annealing is responsible for the diminishing population of active sites. No clear trend of variation of a with T_p was observed; there seems to be a minimum involved but there are too few data points to draw a firm conclusion.

For a given char, the quantity b increases with increasing burn-off in all cases, implying a creation of active sites with burn-off. Furthermore, there seems to exist a correlation between variation of b with burn-off and the effect of burn-off on oxygen uptake, q . A remarkable constancy of b over the burn-off range 4.2-43.1% is reflected by relative constancy of q for the char pyrolysed at 1000°C. On the other hand, a rapid increase of b with burn-off is accompanied by a definite increase of q in the case of char prepared at 1400°C. The ratio of b to q is not constant, however, and it increases with

burn-off.

The Elovich plots are shown in Figs 4.7 through 4.19. Most of them are linear, but some exhibit a slight curvature, especially at extensive surface coverages. This latter kind of behaviour has been frequently reported in the literature (e.g., see [16]), and attributed to variations in the function $f(\theta)$ (eqn (6)). Plots of oxygen uptake, q , versus time are presented in Figs 4.20 through 4.23, and they illustrate the effects of pyrolysis conditions, temperature, oxygen partial pressure and burn-off on the measured active surface area of the phenolic resin chars studied, as discussed above.

4.4 KINETICS OF GASIFICATION AND THERMAL ANNEALING

One of the conclusions arrived at in the previous section is that the number of active sites decreases significantly with increasing pyrolysis temperature. The primary objective of this part of the study is to find out whether thermal annealing causes any changes in the nature of processes occurring on the char surface, or whether reduced reactivities of chars heat-treated at high temperature result merely from a lower active surface area. The secondary objective is to further verify usefulness of model char compounds for kinetic studies of naturally occurring carbonaceous materials.

A series of experiments was performed to determine the reaction rate order and activation energy of a low temperature oxidation of phenolic resin chars. The thermogravimetric technique outlined in chapter III, and the TGA apparatus described in Appendix D were used to continuously monitor mass loss versus time of phenolic resin char samples. Reaction rates derived from such plots were used to determine reaction orders with respect to oxygen partial pressure, as well as activation energies, from the following fundamental relation,

$$r \equiv -\frac{1}{m} \frac{dm}{dt} = k_0 \cdot \exp[-E/RT] \cdot P_{O_2}^n, \quad (25)$$

where:

- m = sample mass,
- t = time,
- k_0 = pre-exponential factor,
- E = activation energy,
- R = gas constant,
- T = temperature,
- P_{O_2} = oxygen partial pressure,
- n = reaction order.

In addition, the ratio of CO_2 to CO from the gas thermal desorption of surface oxides was determined by gas chromatography (see chapter III and Appendix D for a detailed description of the procedure). Gasification reaction rates, as well as CO_2/CO ratios are given in Appendix A.

Plots of $\ln r$ versus $\ln P_{O_2}$ used for reaction order determination are presented in Figs 4.24 through 4.32, and the results are summarized in Table 4.7.

Table 4.7 Reaction order of phenolic resin char oxidation

T_p [°C]	T [°C]	B [%]	n	Fig.
1000	300	4.9-9.6	0.64	4.25b
1000	325	7.9-15.6	0.69	4.27b
1000	350	17.4-39.2	0.62	4.28
1243	300	0.3-0.6	0.76	4.24
1400	325	0.4-4.5	0.67	4.30b
1400	350	1.1-4.6	0.66	4.31b
1400	375	2.4-4.7	0.73	4.32
1400	400	1.7-5.5	0.66	4.33b

Reactivity data were grouped according to the burn-off ranges indicated in Table 4.7 in order to minimize the effect of this parameter on reaction order.

One difficulty encountered was in the measurement of reaction rates at low partial pressures (i.e., at $P_{O_2} = 3.9$ and 21.3 torr). Not only were the reaction rates under these conditions very low, but also an effect of slow, transient surface complex decomposition was found to interfere with the steady-state measurement. It was found necessary to conduct the low partial pressure runs after sample exposure at higher oxygen partial pressures due to the extremely low rate of oxygen chemisorption at low P_{O_2} . A typical run involved thermal surface cleaning at 950°C in helium, followed by exposure of the sample to oxygen at relatively high temperature (e.g., 350°C). Under these conditions, initial oxygen chemisorption proceeded relatively quickly; the sample mass reached its maximum after several hours, thereafter decreasing due to gasification. After a few hours the slope attained a steady-state value and reaction rate measurements could begin.

Switching from high to low oxygen partial pressure, however, requires re-establishment of the steady-state concentrations of surface oxides at lower levels via slow desorption of oxides of carbon. At low oxygen partial pressures, however, this rate was found to be comparable to that of the eventual steady-state gasification rate, thereby enhancing the apparent mass loss. When this problem was realized, the rate of surface complex decomposition was measured by following the mass loss due to desorption in an

atmosphere of helium at the same conditions, and appropriate corrections to the measured reaction rate were made. The corrected and uncorrected reactivities were plotted for one such run and the result is presented in Fig. 4.24.

Since the rate of surface complex decomposition depends upon the temperature, pressure, the state of char surface (i.e., on the sample history), and since it is also expected to depend on the nature of char, such corrections made on the basis of a single measurement could not be quantitatively extended to other runs. The results of this experiment, however, justify disregarding the other rates measured at $P_{O_2} = 3.9$ torr, which all fall consistently above the fitted straight line, when uncorrected for surface complex desorption. The 3.9 torr data point in Fig. 4.28 is the only one in which no correction seems to be necessary. This can be explained by the fact that the char pyrolysed at 1000°C is the most reactive of all phenolic resin chars studied, and that at 350°C , its reactivity is several orders of magnitude higher than the reaction rates exhibited by the other samples, such that presumably the rate of surface complex desorption is negligible in comparison. Data presented in Figs 4.26 and 4.29 were too scattered to interpret them in a meaningful manner, the latter set of data being below the range of accurate gravimetric measurement (low char reactivity combined with low reaction temperature), especially in the case of low oxygen partial pressures.

The results presented in Table 4.7 indicate that the measured values of reaction order are in the range 0.62 - 0.76. This is consistent with the values reported in the literature (e.g., see Table 4.1), but not with any of the known models of carbon-oxygen surface reactions, which all predict reaction orders of 0, 0.5, or 1 (e.g., see [30]). Although the Langmuir-Hinshelwood-type form does account for virtually any value of n between 0.5 and 1.0, it does not explain the constancy of this quantity over a three orders of magnitude variation in oxygen partial pressure (see eqn (24)). Since reaction orders of 0.62-0.76 determined in this study were found to be statistically different from 0.5 at 95% confidence level, they cannot be viewed as "approximately equal to 0.5," and thus it must be admitted that no theoretical interpretation of these data is known. It can also be proven that the difference between $n = 0.62$ and 0.76 is statistically significant at the 95% confidence level, which leads to the conclusion that a change in reaction order is involved. The mechanism responsible for this variation is not known, however. In addition, no simple trend, or dependence on such parameters as T_p , or temperature was observed. Since such a behaviour, as well as the range of reaction order variation, is also typical for other chars, it can be concluded that, once again, the phenolic resin model chars were found to behave

very much like natural carbonaceous materials.

Activation energies, as determined from the Arrhenius plots in Figs 4.34 through 4.46, are presented in Table 4.8. The values between 24 and 36.4 kcal/mol that were found are also quite typical for other chars and coals (see Table 4.1). It is interesting to note that for the phenolic resin char pyrolysed at 1000°C, the global activation energy of the oxidation reaction is significantly lower at low P_{O_2} than for any other char studied under a variety of conditions. Since at low oxygen partial pressures, it has been demonstrated that desorption of surface oxides can play a significant role, it is hypothesized that there may be a difference in the nature of desorption between chars pyrolysed at low and high temperatures (e.g., $T_p = 1000^\circ\text{C}$ vs 1400°C).

Table 4.8 Activation energies for oxidation of phenolic resin char.

T_p [$^\circ\text{C}$]	P_{O_2} [torr]	E [kcal/mol]	Fig.
1000	3.9	28.2	4.34
1000	21.3	24.0	4.35
1000	160	34.4	4.36
1000	430	35.4	4.37
1000	760	35.2	4.38
1000	760	32.8*	4.39
1111	760	34.0	4.40
1243	760	34.8	4.41
1400	3.9	36.4	4.42
1400	21.3	34.8	4.43
1400	160	33.6	4.44
1400	430	33.8	4.45
1400	760	34.6	4.46

* char surface was not cleaned prior to reaction rate measurements

This point was further pursued by examination of CO_2/CO molar ratios obtained upon thermal desorption of surface oxides following chemisorption. The chars pyrolysed at 1000°C and 1400°C were subjected to oxygen chemisorption at 200°C and $P_{O_2} = 160$ torr for a few days. Then the TGA was purged with helium and the temperature was raised stepwise to 950°C. The system was purged with helium after each desorption step, and CO and CO_2 were collected in a cryogenic trap. The CO_2/CO ratio was subsequently determined by gas chromatography. The data collected in this experiment are shown in

Table 4.9 and in Fig. 4.47.

Table 4.9 CO₂/CO molar ratio and mass loss during a stepwise desorption of surface oxides.

$T_p = 1000^\circ\text{C}$

T_D range [$^\circ\text{C}$]	$\frac{\Delta m_D}{m_0} 100\%$	CO ₂ /CO
200-350	0.33	1.9
350-450	0.39	0.84
450-550	0.45	0.35
550-650	0.38	0.155
650-750	0.45	0.072
750-850	0.42	0.034
850-950	0.17	0.024

$T_p = 1400^\circ\text{C}$

T _D range [°C]	$\frac{\Delta m_D}{m_O} 100\%$	CO ₂ /CO
200-350	0.030	2.9
350-450	0.012	0.73
450-550	0.018	
550-650	0.015	
650-750	0.023	0.11
750-850	0.014	0.047
850-950	0.043*	

*an air leak into the TGA system occurred and this value is not reliable

It is evident from Fig. 4.47 that below 600°C, relatively more carbon dioxide is evolved from the surface of the char prepared at 1400°C than from that pyrolysed at

1000°C. It cannot be concluded, however, that the process of desorption follows two different mechanisms in each case, although it is certainly a possibility. An alternative explanation is that desorption involves parallel reaction pathways and that annealing changes the relative distribution of active sites participating in each route. Both differences in activation energies and in CO₂/CO ratios imply that desorption of surface oxides is certainly affected by annealing. This conclusion is further supported by comparison of relative amounts of surface complex released from surfaces of both chars in particular intervals of T_D, as measured by the ratio of mass loss in a given interval of T_D to the total mass loss up to 850°C. In terms of percentages of total mass desorbed, more desorption occurs at temperatures between 200 and 300°C in the case of the 1400°C char than in the case of the 1000°C char (more total mass is, however, desorbed at all temperatures by the 1000°C char than by the 1400°C char).

An approach proposed by Suuberg [102] was used to evaluate activation energy of annealing. If F represents a number of active sites with a unique activation energy E_A , the rate of annealing of F can be represented as

$$\frac{dF}{dt} = -k_A \cdot F \cdot \exp[-E_A/RT] \quad (26)$$

where t is time, R the gas constant, T temperature, and k_A the Arrhenius pre-exponential. The amount of F at any time t_f is obtained by integration:

$$\frac{F}{F_0} = \exp \int_0^{t_f} -k_A \cdot \exp[-E_A/RT] dt, \quad (27)$$

where F_0 is the value of F at zero time, which is an arbitrary point of reference. Let S_0 represent the total number of active sites, of all possible activation energies, and this quantity is proportional to measured reaction rates; then the fraction that will decompose with the activation energy within dE_A of E_A is $S_0 f(E_A) dE_A = F_0$, where $f(E_A)$ is a distribution of activation energies. It is assumed that there is a unique value of the Arrhenius pre-exponential k_A regardless of the activation energy. This assumption has been made throughout the literature, although in one case k_A has been assumed to be a distributed parameter as well [103]. In general, however, the scarcity of data does not allow to study models with distributed values of k_A in a meaningful manner. Much less variation is expected in k_A than in the activation energy, however, since a pre-exponential factor of approximate order 10^{13} s^{-1} has basis in general chemical principles related to

bond vibration frequencies [104]. It appears reasonable then to assume a constant pre-exponential term and study distribution of activation energies.

The remaining number of active sites can be represented as

$$S = \int_0^{\infty} F dE_A = \int_{-\infty}^{\infty} F dE_A \quad (28)$$

The extension of the lower limit of integration adds nothing to the value of the integral, since $E_A > 0$. Substituting eqn (27) into eqn (28), one obtains after rearrangement

$$\frac{S}{S_0} = \int_{-\infty}^{\infty} \exp \left[\int_0^{t_f} -k_A \exp[-E_A/RT] dt \right] \cdot f(E_A) dE_A \quad (29)$$

This is the usual starting point for distributed activation energy analyses [105]. This integral can be solved analytically for a nondistributed activation energy (i.e., for $f(E_A)$ equal a delta function at E_{A0}) and such a solution was tried with reaction rate data, r/TSA , from Table 4.5. The derived equation includes pyrolysis occurring during linear heating and cooling of the sample, the rates of which are designated as m_h and m_c , respectively.

$$\ln \frac{S}{S_0} = -k_A \exp[-E_A/RT] \cdot \left[\frac{RT^2}{E_A} \left(\frac{1}{m_h} + \frac{1}{m_c} \right) - t_f \right] \quad (30)$$

This attempt turned out to be unsuccessful, however, since no physically meaningful combination of activation energy and pre-exponential could be found. Then a solution of the problem with a Gaussian distribution of activation energies was tried; i.e.,

$$f(E_A) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left[-\frac{(E_A - E_{A0})^2}{2\sigma^2} \right], \quad (31)$$

where E_{A0} is the mean activation energy and σ the standard deviation. An approximate method of solving eqn (29) was used, as described in [102]. The parameters were systematically varied in the following ranges,

$$k_A = 10^6 - 10^{13} \text{ [s}^{-1}\text{]},$$

$$E_A = 30 - 100 \text{ [kcal/mol]},$$

$$\sigma = 5 - 30 \text{ [kcal/mol]},$$

and a numerical search was conducted. Some combinations of parameters and corresponding sums of errors are presented in Table 4.10. They are presented in this form to emphasize the complicated nature of the surface over which optimization is performed, leading to many candidate parameter sets that are quite different but almost equally "good". A more sophisticated optimization is not warranted until a larger data set is available for fitting.

Table 4.10 Best parameter sets for eqn (29)

k_A	σ	E_{A0}	$SSE \cdot 10^2$
10^{13}	35	55	8.32
10^{13}	30	72	10.6
10^{13}	25	90	13.7
10^{12}	35	40	7.8
10^{12}	30	60	9.6
10^{11}	35	35	8.8
10^{11}	30	50	8.6
10^{10}	30	40	7.9
10^9	30	30	7.6
10^8	25	40	8.8
10^7	25	30	9.2
10^6	20	35	8.8
10^{12}	35	42	7.6
10^{13}	30	72	10.0

* sum of squared errors

The parameter set $k_A = 10^9 \text{ [s}^{-1}\text{]}$, $\sigma = 30 \text{ [kcal/mol]}$, and $E_{A0} = 30 \text{ [kcal/mol]}$ gives the best fit but it has to be discarded on the basis of physical interpretation of this set of values; i.e., 67% of all the active sites are included in the interval $E_A = E_{A0} \pm \sigma$, and 95% in $E_A = E_{A0} \pm 2\sigma$, which leads to negative values of activation energy. Discarding all other sets for which $E_{A0} < 2\sigma$ on the same basis, the best set of meaningful parameters is: $k_A = 10^{13} \text{ [s}^{-1}\text{]}$, $E_{A0} = 72 \text{ [kcal/mol]}$, and $\sigma = 30 \text{ [kcal/mol]}$. These values can then be used to predict reaction rates of phenolic resin chars prepared at various temperatures, and comparison of rates obtained in this way with actual rates is presented in Table 4.11. The "correct" rate is assumed at 1000°C, and all other rates are calculated from the computed

rate ratios.

Table 4.11 Example of application of the computed activation energy for predicting char reactivities ($T = 325^{\circ}\text{C}$, $P_{\text{O}_2} = 760$ torr).

T_p [$^{\circ}\text{C}$]	$(r/\text{TSA}) \cdot 10^7$ actual	$(r/\text{TSA}) \cdot 10^7$ predicted
1000	28.4	28.4
1111	14.3	17.4
1243	8.6	8.8
1400	4.6	3.4

The model slightly overpredicts the temperature dependence of annealing, but agreement between the actual and computed rates is reasonable.

A similar procedure of data fitting was carried out using directly the values of ASA from Tables 4.3 and 4.4 rather than char reactivities. Again, a number of parameter sets were found to fit the data, almost equally well, and the best two fits are given below,

k_0	E_{A0}	σ	$\text{SSE} \cdot 10^2$
10^{13}	65	25	0.89
10^{12}	55	25	0.67

When compared with the previous result of $E_{A0} = 72$ [kcal/mol], $k_0 = 10^{13}$ [s^{-1}] and $\sigma = 30$ [kcal/mol], the parameter set with $E_{A0} = 65$ [kcal/mol], $k_A = 10^{13}$ [s^{-1}], and $s = 25$ [kcal/mol] seems to imply a strong correlation between the number of active sites and char reactivities, as expected. The other parameter set, however, is significantly different and, from a strictly mathematical viewpoint, the fit is undoubtedly better.

The comparison of predictions of the two parameter sets is shown below, with 1 and 2 referring to the first and the second sets, respectively; ASA is expressed in [m^2/g]. Again, the value at 1000°C is taken as a measured value at all times, and other values are referenced to it.

T_p [°C]	$(ASA)_{\text{measured}}$	$(ASA)_1$	$(ASA)_2$
1000	32.5	32.5	32.5
1111	15.1	16.0	15.9
1243	5.7	6.0	6.0
1400	1.6	1.5	1.6

It is clear that no firm conclusion can be drawn as to the numerical value of activation energy of annealing from fitting just four data points, especially in view of multiple minima of the objective function. Further work is certainly needed.

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Fig. 4.1 Effect of temperature changes on oxygen chemisorption behaviour of a phenolic resin char ($T_p = 950^\circ\text{C}$).

Fig. 4.2 Effect of temperature changes on oxygen chemisorption behaviour of lignite char ($T_P = 1000^\circ\text{C}$).

Fig. 4.3 Effect of oxygen partial pressure changes on oxygen chemisorption behaviour of a phenolic resin char ($T_p = 950^\circ\text{C}$).

Fig. 4.4 Effect of oxygen partial pressure changes on oxygen chemisorption behaviour of lignite char ($T_p = 1000^{\circ}\text{C}$).

Fig. 4.5 Effect of temperature on the Elovich parameter a .

Fig. 4.6 Effect of temperature on the Elovich parameter b .

Fig. 4.7 Elovich plot ($T_p = 1000^\circ\text{C}$, $T = 150^\circ\text{C}$, $P_{\text{O}_2} = 160 \text{ torr}$, $B = 4.3\%$).

Fig. 4.8 Elovich plot ($T_p = 1000^\circ\text{C}$, $T = 200^\circ\text{C}$, $P_{\text{O}_2} = 160$ torr, $B = 3.3\%$).

Fig. 4.9 Elovich plot ($T_p = 1000^\circ\text{C}$, $T = 300^\circ\text{C}$, $P_{\text{O}_2} = 160$ torr, $B = 4.2\%$).

Fig. 4.10 Elovich plot ($T_p = 1000^\circ\text{C}$, $T = 150^\circ\text{C}$, $P_{\text{O}_2} = 760 \text{ torr}$, $B = 4.2\%$).

Fig. 4.11 Elovich plot ($T_p = 1000^\circ\text{C}$, $T = 150^\circ\text{C}$, $P_{\text{O}_2} = 760 \text{ torr}$, $B = 43.1\%$).

Fig. 4.12 Elovich plot ($T_p = 1000^\circ\text{C}$, $T = 200^\circ\text{C}$, $P_{\text{O}_2} = 760 \text{ torr}$, $B = 4.1\%$).

Fig. 4.13 Elovich plot ($T_p = 1000^\circ\text{C}$, $T = 300^\circ\text{C}$, $P_{O_2} = 760 \text{ torr}$, $B = 4.3\%$).

Fig. 4.14 Elovich plot ($T_p = 1111^\circ\text{C}$, $T = 150^\circ\text{C}$, $P_{\text{O}_2} = 760 \text{ torr}$, $R = 0.24\%$).

Fig. 4.15 Elovich plot ($T_p = 1243^\circ\text{C}$, $T = 150^\circ\text{C}$, $P_{\text{O}_2} = 760 \text{ torr}$, $B = 0.12\%$).

Fig. 4.16 Elovich plot ($T_p = 1400^\circ\text{C}$, $T = 150^\circ\text{C}$, $P_{\text{O}_2} = 760 \text{ mm}$, $B = 0.21\%$).

Fig. 4.17 Elovich plot ($T_p = 1400^\circ\text{C}$, $\bar{T} = 150^\circ\text{C}$, $P_{\text{O}_2} = 760 \text{ torr}$, $B = 12.9\%$).

Fig. 4.18 Elovich plot ($T_p = 1400^\circ\text{C}$, $T = 150^\circ\text{C}$, $P_{\text{O}_2} = 760 \text{ torr}$, $B = 47.5\%$).

Fig. 4.19 Elovich plot ($T_p = 1400^\circ\text{C}$, $T = 200^\circ\text{C}$, $P_{\text{O}_2} = 160 \text{ torr}$, $B = 0.14\%$).

Fig. 4.20 Effect of pyrolysis temperature on oxygen chemisorption behaviour of phenolic resin chars.

Fig. 4.21 Effect of temperature on oxygen chemisorption behaviour of a phenolic resin char ($T_p = 1000^\circ\text{C}$, $P_{\text{O}_2} = 160$ torr).

Fig. 4.22 Effect of pressure on oxygen chemisorption behaviour of a phenolic resin char ($T_p = 1000^\circ\text{C}$, $T = 150^\circ\text{C}$).

Fig. 4.23 Effect of burn-off on oxygen chemisorption behaviour of a phenolic resin char ($T_p = 1400^\circ\text{C}$, $P_{\text{O}_2} = 760$ torr, $T = 150^\circ\text{C}$).

Fig. 4.24 Reaction order plot ($T_p = 1243^\circ\text{C}$, $T = 300^\circ\text{C}$, $B = 0.3\text{-}0.6\%$)

Fig. 4.25a Reaction order plot ($T_p = 1000^\circ\text{C}$, $T = 300^\circ\text{C}$, $B = 4.9\text{-}9.6\%$, $P_{O_2} = 3.9$ torr included).

Fig. 4.25b Reaction order plot ($T_p = 1000^\circ\text{C}$, $T = 300^\circ\text{C}$, $B = 4.9\text{-}9.6\%$, $P_{O_2} = 3.9 \text{ torr}$ omitted).

Fig. 4.26a Reaction order plot ($T_p = 1000^\circ\text{C}$, $T = 300^\circ\text{C}$, $B = 20.5\text{--}42.3\%$, $P_{O_2} = 3.9 \text{ torr}$ included).

Fig. 4.26b Reaction order plot ($T_p = 1000^\circ\text{C}$, $T = 300^\circ\text{C}$, $B = 20.5\text{--}42.3\%$, $P_{O_2} = 3.9$ torr omitted).

Fig. 4.27a Reaction order plot ($T_p = 1000^\circ\text{C}$, $T = 325^\circ\text{C}$, $B = 7.9\text{-}15.6\%$, $P_{O_2} = 3.9 \text{ torr}$ included).

Fig. 4.27b Reaction order plot ($T_p = 1000^\circ\text{C}$, $T = 325^\circ\text{C}$, $B = 7.9\text{-}15.6\%$, $P_{O_2} = 3.9$ torr omitted).

Fig. 4.28

Reaction order plot ($T_p = 1000^\circ\text{C}$, $T = 350^\circ\text{C}$, $B = 17.4\text{--}39.2\%$, $P_{O_2} = 3.9 \text{ torr}$ included).

Fig. 4.29

Reaction order plot ($T_p = 1000^\circ\text{C}$, $T = 350^\circ\text{C}$, $B = 17.4\text{-}39.2\%$, $P_{O_2} = 3.9 \text{ torr}$ included).

Fig. 4.29b Reaction order plot ($T_p = 1400^\circ\text{C}$, $T = 300^\circ\text{C}$, $B = 0.3\text{--}4.3\%$, $P_{O_2} = 3.9 \text{ torr}$ omitted).

Fig. 4.29c Reaction order plot ($T_p = 1400^\circ\text{C}$, $T = 300^\circ\text{C}$, $B = 0.3\text{--}4.3\%$, $P_{O_2} = 3.9 \text{ torr}$ and $P_{O_2} = 21.3 \text{ torr}$ omitted).

Fig. 4.30a Reaction order plot ($T_p = 1400^\circ\text{C}$, $T = 325^\circ\text{C}$, $B = 0.4\text{--}4.5\%$, $P_{O_2} = 3.9$ torr included).

Fig. 4.30b Reaction order plot ($T_p = 1400^\circ\text{C}$, $T = 325^\circ\text{C}$, $B = 0.4\text{--}4.5\%$, $P_{O_2} = 3.9$ torr omitted).

Fig. 4.31a Reaction order plot ($T_p = 1400^\circ\text{C}$, $T = 350^\circ\text{C}$, $B = 1.1\text{--}4.6\%$, $P_{O_2} = 3.9 \text{ torr}$ included).

Fig. 4.31b Reaction order plot ($T_p = 1400^\circ\text{C}$, $T = 350^\circ\text{C}$, $B = 1.1\text{--}4.6\%$, $P_{O_2} = 3.9$ torr omitted).

Fig. 4.32 Reaction order plot ($T_p = 1400^\circ\text{C}$, $T = 375^\circ\text{C}$, $B = 2.4\text{--}4.7\%$).

Fig. 4.33a Reaction order plot ($T_p = 1400^\circ\text{C}$, $T = 400^\circ\text{C}$, $B = 1.7\text{-}5.5\%$, $P_{O_2} = 3.9 \text{ torr}$ included).

Fig. 4.33b Reaction order plot ($T_p = 1400^\circ\text{C}$, $T = 400^\circ\text{C}$, $B = 1.7\text{-}5.5\%$, $P_{O_2} = 3.9$ torr omitted).

Fig. 4.34 Arrhenius plot ($T_p = 1000^\circ\text{C}$, $P_{\text{O}_2} = 3.9$ torr).

Fig. 4.35 Arrhenius plot ($T_p = 1000^\circ\text{C}$, $P_{\text{O}_2} = 21.3$ torr).

Fig. 4.36 Arrhenius plot ($T_p = 1000^\circ\text{C}$, $P_{\text{O}_2} = 160$ torr).

Fig. 4.37 Arrhenius plot ($T_p = 1000^\circ\text{C}$, $P_{\text{O}_2} = 430$ torr).

Fig 4.38 Arrhenius plot ($T_p = 1000^\circ\text{C}$, $P_{O_2} = 760$ torr).

Fig. 4.39 Arrhenius plot ($T_p = 1000^\circ\text{C}$, $P_{O_2} = 760$ torr, surface uncleaned).

Fig. 4.40 Arrhenius plot ($T_p = 1111^\circ\text{C}$, $p_{\text{O}_2} = 760$ torr).

Fig. 4.41 Arrhenius plot ($T_p = 1243^\circ\text{C}$, $P_{\text{O}_2} = 760$ torr).

Fig. 4.42 Arrhenius plot ($T_p = 1400^\circ\text{C}$, $P_{\text{O}_2} = 3.9 \text{ torr}$).

Fig. 4.43 Arrhenius plot ($T_p = 1400^\circ\text{C}$, $P_{O_2} = 21.3$ torr).

Fig. 4.44 Arrhenius plot ($T_p = 1400^\circ\text{C}$, $P_{O_2} = 160$ torr).

Fig. 4.45 Arrhenius plot ($T_p = 1400^\circ\text{C}$, $P_{O_2} = 430$ torr).

Fig. 4.46 Arrhenius plot ($T_p = 1400^\circ\text{C}$, $P_{O_2} = 760 \text{ torr}$).

Fig. 4.47 CO₂/CO molar ratio as a function of desorption temperature ($T_p = 1000^\circ\text{C}$ and 1400°C).

Chapter V

CONCLUSIONS

● High purity model chars derived from phenol-formaldehyde resin were synthesized and their behavior in low temperature oxidation was studied. It was found that their properties successfully model those of naturally occurring carbonaceous materials. In particular, pore structure reactivity towards oxygen, reaction order, activation energy and surface deactivation due to annealing were concluded to exhibit both qualitative and quantitative similarities with natural chars. This conclusion was reinforced by direct comparison of phenolic resin chars with North Dakota lignite char.

● Reactivities unaffected by catalytic impurities were measured. The low temperatures used made it possible to eliminate most mass transfer limitations from consideration, but the possibility of micropore diffusion limitations cannot be ruled out.

● The chemical structure of phenolic resin chars was found to involve highly condensed aromatic rings and a conceptual model of such a structure was formulated.

● Oxygen chemisorption, as a tool in active surface area determination, was critically evaluated, especially in its application for studying "young" chars. It was concluded that this technique is not a quantitative surface titration technique, primarily due to strong dependence of oxygen uptake upon arbitrarily selected conditions of temperature and pressure. Classical measurements of ASA under arbitrary conditions, however, proved to correlate favorably with oxidation reaction rates (much better than with total surface

area).

● Thermal annealing of phenolic resin chars was also studied. It was determined that this process is associated with a dramatic decrease in the number of active sites available for gasification. Changes in activation energy, as well as in the CO_2/CO ratio, indicate that annealing also affects the nature of surface oxide evolution. Details of this relationship are not known, however, and further study of this question is very much needed. The annealing was found to be reasonably modeled only with a distributed activation energy model.

Successful application of phenolic resin chars as a model compound is encouraging, and the next phase of this program will involve a study involving isotopic labelling of carbon atoms. More specifically, methylene bridges in the original resin can be labelled with ^{13}C , and the gas products of gasification can be analyzed for distribution of ^{12}C and ^{13}C using mass spectrometer. Such an experiment may shed some light on the nature of active sites and how they evolve from a particular parent hydrocarbon.

In addition, other DOE-sponsored programs will address further questions having to do with the distribution of active sites and their energetics, and the role of micropore diffusion in gasification.

This study can be viewed as only the first step in a more comprehensive program that hopefully will begin to answer many of the questions raised in this early phase of the work.

Appendix A EXPERIMENTAL DATA

A.1 ADSORPTION ISOTHERMS

Nitrogen adsorption data are presented in Table A1. T_p stands for pyrolysis temperature, B is extent of char burn-off, $\frac{P}{P_0}$ is the ratio of nitrogen partial pressure to the saturation partial pressure of this adsorptive, V is the volume of nitrogen adsorbed at about 77 K per gram of char, and n is the same amount of adsorptive expressed in terms of moles. Molar volume of 34.68 [cm³/mol] was assumed for liquid nitrogen.

Table A1. Adsorption isotherms.

$\frac{P}{P_0}$	$T_p = 1000^\circ\text{C}, B = 0\%$	
	V [cm ³ /g]	n·10 ³ [mol/g]
0.96	0.0147	0.424
0.95	0.0145	0.418
0.90	0.0144	0.415
0.85	0.0149	0.430
0.80	0.0145	0.418
0.75	0.0145	0.418
0.70	0.0143	0.412
0.65	0.0140	0.404
0.60	0.0135	0.389
0.55	0.0134	0.386
0.50	0.0139	0.401
0.45	0.0131	0.378
0.40	0.0129	0.372
0.35	0.0131	0.378
0.30	0.0143	0.412
0.25	0.0134	0.386
0.20	0.0130	0.375
0.15	0.0127	0.366
0.10	0.0122	0.352
0.05	0.0116	0.334

$\frac{P}{P_0}$	$T_p = 1000^\circ\text{C}, B = 16.0\%$	
	V [cm ³ /g]	n·10 ³ [mol/g]
0.96	0.2414	6.961
0.95	0.2266	6.534
0.90	0.2355	6.791
0.85	0.2352	6.782
0.80	0.2335	6.733
0.75	0.2331	6.721
0.70	0.2328	6.713

0.65	0.2329	6.716
0.60	0.2346	6.765
0.55	0.2330	6.719
0.50	0.2441	7.039
0.45	0.2330	6.719
0.40	0.2326	6.707
0.35	0.2312	6.667
0.30	0.2293	6.612
0.20	0.2301	6.635
0.10	0.2278	6.569

$T_p = 1000^\circ\text{C}$, $B = 28.4\%$

$\frac{P}{P_0}$	$V [\text{cm}^3/\text{g}]$	$n \cdot 10^3 [\text{mol/g}]$
0.96	0.2900	8.362
0.95	0.2898	8.356
0.90	0.2939	8.475
0.85	0.3029	8.734
0.80	0.3009	8.676
0.75	0.3053	8.803
0.70	0.2982	8.599
0.65	0.3001	8.653
0.60	0.3004	8.662
0.55	0.3113	8.976
0.50	0.2885	8.319
0.45	0.2968	8.558
0.40	0.2913	8.400
0.35	0.2943	8.486
0.30	0.2906	8.379
0.20	0.2830	8.160
0.10	0.2781	8.019

$T_p = 1000^\circ\text{C}$, $B = 37.0\%$

$\frac{P}{P_0}$	$V [\text{cm}^3/\text{g}]$	$n \cdot 10^3 [\text{mol/g}]$
0.96	0.338	9.746
0.95	0.318	9.170
0.90	0.320	9.227
0.85	0.323	9.314
0.80	0.320	9.227
0.75	0.322	9.285
0.70	0.322	9.285
0.65	0.322	9.285
0.60	0.317	9.141
0.55	0.319	9.198
0.50	0.316	9.112
0.45	0.313	9.025
0.40	0.313	9.025
0.35	0.310	8.939
0.30	0.306	8.824
0.25	0.303	8.737
0.20	0.300	8.651
0.15	0.297	8.564
0.10	0.285	8.218
0.05	0.274	7.901

$T_p = 1400^\circ\text{C}, B = 0\%$		
$\frac{P}{P_0}$	$V [\text{cm}^3/\text{g}]$	$n \cdot 10^3 [\text{mol/g}]$
0.96	0.0307	0.885
0.95	0.0303	0.874
0.90	0.0336	0.969
0.85	0.0321	0.926
0.80	0.0295	0.851
0.75	0.0297	0.856
0.70	0.0300	0.865
0.65	0.0305	0.879
0.60	0.0323	0.931
0.55	0.0307	0.885
0.50	0.0299	0.862
0.45	0.0307	0.885
0.40	0.0300	0.865
0.35	0.0309	0.891
0.30	0.0294	0.848
0.25	0.0290	0.836
0.20	0.0308	0.888
0.15	0.0293	0.845
0.10	0.0281	0.810
0.05	0.0258	0.744

$T_p = 1400^\circ\text{C}, B = 49.7\%$		
$\frac{P}{P_0}$	$V [\text{cm}^3/\text{g}]$	$n \cdot 10^3 [\text{mol/g}]$
0.96	0.5816	16.770
0.90	0.5091	14.680
0.80	0.5057	14.582
0.70	0.4926	14.204
0.60	0.4711	13.584
0.50	0.4775	13.769
0.40	0.4748	13.691
0.30	0.4609	13.290
0.20	0.4309	12.425
0.10	0.4177	12.044

A.2 SURFACE AREA AND PORE VOLUME

Table A2 contains specific surface area and pore volume data. The BET, Langmuir and modified Dubinin-Radushkevich (DRK) equations were used to compute surface area from nitrogen and carbon dioxide adsorption data. The following physical properties of N_2 and CO_2 were used:

	a_m $\text{\AA}^2$	ρ_l $\frac{\text{g}}{\text{cm}^3}$	V_l $\frac{\text{cm}^3}{\text{mol}}$
N ₂	16.2	0.81	34.68
CO ₂	19.5	1.10	40.0

V_0 (a.i.) in Table A2 denotes pore volume determined from adsorption isotherms. All the samples were outgassed for 3 hours at 300°C prior to measurement, but it was found that outgassing for an hour was sufficient.

Table A2 Surface area and pore volume of phenolic resin char.

Tp (C)	B [%]	N2 BET	CO2 BET	N2 Langmuir	CO2 Langmuir	N2 (DR)	CO2 (DF)	Vd (N2 DR) [cm3/g]	Vd (CO2 DR) [cm3/g]	Vd (a.i.) [cm3/g]
1000	0	29.0	216.7	44.1	341.0	43.8	326.4	0.0155	0.111	0.0147
	0	27.8		42.2		39.8		0.0141		
	1.2	250.0	381.4	373.8	593.6	379.0	594.0	0.134	0.202	
	10.3	413.7	437.0	642.6	681.3	634.9	674.2	0.224	0.230	0.240
	16.0	440.3	472.7	676.6	740.5	674.0	727.4	0.239	0.248	
	16.0	422.6		661.3		661.7		0.234		
	22.9	503.2	582.3	778.4	924.8	772.1	907.4	0.274	0.309	0.290
	28.4	541.9	596.3	833.6	947.5	827.3	926.4	0.293	0.315	
	28.4	540.1		836.8		842.7		0.299		
	32.7	589.2	636.3	920.1	1026.2	907.1	992.6	0.321	0.338	0.338
	37.0	598.5	631.4	886.0	970.0	875.5	945.8	0.311	0.322	
	60.3	916.6	1054.5	1490.1	1966.8	1413.3	1606.2	0.502	0.547	
1111	0	1.8	42.1	2.9	92.2	2.8	62.8	0.001	0.021	0.031
	3.7	457.7	456.8	707.7	718.1	701.9	717.4	0.249	0.244	
	8.4	498.3		766.9		759.0		0.270		
	8.4	526.0		808.5		802.1		0.285		
	8.4	523.8	566.4	803.4	887.0	798.5	866.5	0.284	0.295	
	12.7	637.9	670.4	986.8	1030.3	973.3	1061.2	0.346	0.361	
1243	0	1.6	8.0	2.6	14.3	2.5	12.2	0.001	0.004	0.031
	1.5	521.3	359.6	493.2	555.5	490.1	551.8	0.174	0.188	
	2.9	430.5	427.9	662.3	866.1	653.5	846.8	0.232	0.288	
	4.3	494.0	514.0	752.9	796.4	743.4	783.0	0.264	0.267	
	9.5	572.1	598.2	886.3	934.3	871.5	932.8	0.310	0.318	
	21.1	757.2	782.0	1226.6	1300.8	1164.8	1246.8	0.414	0.425	
1400	0	57.4	75.5	90.9	127.6	88.4	119.9	0.031	0.041	0.509
	0	60.9		88.4		87.2		0.031		
	0.60	181.6	210.3	280.8	335.1	278.8	326.4	0.099	0.111	
	2.7	350.1	385.6	546.2	627.6	537.3	605.0	0.191	0.206	
	5.2	439.4		671.0		681.2		0.242		
	5.2	426.8	423.4	661.1	635.6	656.5	648.3	0.233	0.221	
	19.9	613.5	651.5	963.8	1120.1	940.3	970.0	0.334	0.330	
	49.7	868.2	926.3	1323.6	1821.6	1313.0	1441.4	0.467	0.491	

A.3 PHENOLIC RESIN CHAR REACTIVITIES

A.3.1 Char pyrolysed at 1000°C

T [°C]	PO ₂ [torr]	B [%]	r [g/g hr]
250	760	23.6	0.19
250	760	26.9	0.18
275	760	22.6	0.81
275	760	26.8	0.81
300	3.9	5.5	0.22
300	3.9	20.7	0.68
300	21.3	36.8	0.90
300	21.3	9.6	0.35
300	160	5.3	1.1
300	160	5.6	1.1
300	160	20.7	1.6
300	430	4.9	2.3
300	430	6.2	2.0
300	430	20.9	2.5
300	760	4.5	3.7
300	760	6.9	3.1
300	760	20.5	4.9
300	760	23.9	3.3
300	760	25.1	3.9
300	760	30.5	4.8
300	760	33.6	5.3
300	760	34.5	5.5
300	760	36.0	5.6
300	760	42.0	5.1
300	760	42.3	5.2
323	760	23.3	11
323	760	26.0	11
323	760	6.1	11
323	760	9.6	11
325	3.9	10.9	0.56
325	21.3	37.6	2.2
325	21.3	9.6	1.0
325	160	10.4	3.8
325	160	11.4	3.5
325	430	9.2	7.6
325	430	12.3	6.7
325	760	7.9	12
325	760	13.3	11

325	760	15.6	12
350	3.9	22.3	1.6
350	21.3	39.2	4.9
350	21.3	10.7	1.9
350	160	21.5	15
350	160	23.5	14
350	430	20.5	27
350	430	25.1	27
350	430	26.1	28
350	760	17.4	43
350	760	27.6	50
350	760	28.8	52
350	760	22.4	40
350	760	28.0	42
350	760	29.3	40
350	760	41.5	59
350	760	55.1	65

A.3.2 Char pyrolysed at 1111°C

T [°C]	PO ₂ [torr]	B [%]	r [g/g hr]
250	760	2.6	0.093
275	760	2.7	0.44
300	760	2.5	1.6
300	760	3.6	1.6
325	760	3.3	6.0
350	760	2.1	17.8

A.3.3 Char pyrolysed at 1243°C

T [°C]	PO ₂ [torr]	B [%]	r [g/g hr]
300	3.9	0.3	0.016
300	21.3	0.4	0.060
300	160	0.4	0.31
300	430	0.5	0.61
300	760	0.3	0.83
300	760	0.6	0.95
275	760	0.7	0.24

325	760	2.0	3.3
350	760	1.5	11
375	760	2.8	32
400	760	4.3	84

A.3.4 Char pyrolysed at 1400°C

T [°C]	PO ₂ [torr]	B [%]	r [g/g hr]
300	3.9	3.0	0.011
300	3.9	3.0	0.021
300	3.9	3.0	0.023
300	21.3	3.2	0.014
300	21.3	3.4	0.0064
300	21.3	3.4	0.023
300	21.3	3.4	0.026
300	160	3.6	0.21
300	430	4.3	0.37
300	760	0.3	0.46
300	760	2.9	0.52
300	760	35.4	1.1
325	3.9	3.0	0.16
325	21.3	3.3	0.15
325	160	3.6	0.68
325	430	4.4	1.2
325	430	4.5	1.2
325	760	0.4	1.8
325	760	2.9	1.5
325	760	3.0	1.8
325	760	35.3	3.6
350	3.9	3.1	0.38
350	21.3	3.3	0.51
350	160	3.7	2.0
350	430	4.6	3.9
350	760	1.1	5.4
350	760	2.9	5.3

350	760	35.1	12
375	21.3	3.5	1.2
375	160	3.8	5.8
375	430	4.7	11
375	760	2.4	16
375	760	35.8	3.8
400	3.9	3.2	2.5
400	21.3	3.4	4.2
400	160	4.0	17
400	160	4.3	16
400	430	5.5	30
400	760	1.7	46
400	760	20.3	96
400	760	36.4	110
450	760	30.8	740

A.4 OXYGEN CHEMISORPTION DATA

run # 27
 $T_{p1} = 900^{\circ}\text{C}$ (0.5 hr)
 $T_{p2} = 950^{\circ}\text{C}$ (1.33 hr)
 $B = 4.5\%$
 $P_{O_2} = 160$ torr

$T = 150^{\circ}\text{C}$

t [hr]	q [mg O ₂]	q [gO ₂ /kg char]
0.000	0.000	0.000
0.100	0.130	2.031
0.200	0.180	2.812
0.400	0.230	3.594
0.600	0.263	4.109
0.800	0.287	4.484
1.000	0.302	4.719
1.200	0.318	4.969
1.400	0.330	5.156
1.600	0.340	5.313
1.800	0.350	5.469
2.000	0.360	5.625
2.200	0.368	5.750
2.400	0.374	5.844
2.600	0.382	5.969
2.800	0.387	6.047
3.000	0.393	6.141
4.000	0.419	6.547
5.000	0.439	6.859
6.000	0.455	7.109
7.000	0.469	7.328
8.000	0.482	7.531
9.000	0.492	7.688
10.000	0.502	7.844
11.000	0.510	7.969
12.000	0.520	8.125
13.000	0.527	8.234
14.000	0.535	8.359
15.000	0.542	8.469
16.000	0.550	8.594
17.000	0.555	8.672
18.000	0.560	8.750
19.000	0.568	8.875
20.000	0.572	8.938
21.000	0.578	9.031
22.000	0.583	9.109
23.000	0.589	9.203
24.000	0.593	9.266

T = 200°C

t [hr]	q [mg O ₂]	q [gO ₂ /kg char]
24.000	0.593	9.266
24.200	0.597	9.328
24.400	0.601	9.391
24.600	0.606	9.469
24.800	0.612	9.562
25.000	0.616	9.625
25.200	0.621	9.703
25.400	0.626	9.781
25.600	0.630	9.844
25.800	0.635	9.922
26.000	0.640	10.000
26.600	0.655	10.234
27.000	0.663	10.359
28.000	0.682	10.656
29.000	0.696	10.875
30.000	0.710	11.094
31.000	0.724	11.312
32.000	0.735	11.484
33.000	0.745	11.641
34.000	0.755	11.797
35.000	0.763	11.922
36.000	0.766	11.969
37.000	0.772	12.062
38.000	0.778	12.156
39.000	0.785	12.266
40.000	0.797	12.453
41.000	0.806	12.594
42.000	0.813	12.703
43.000	0.818	12.781
44.000	0.823	12.859
45.000	0.828	12.938
46.000	0.833	13.016
47.000	0.837	13.078
48.000	0.837	13.078

T = 200°C

t [hr]	q [mg O ₂]	q [gO ₂ /kg char]
48.000	0.837	13.078
48.200	0.840	13.125
48.400	0.843	13.172
48.600	0.846	13.219
48.800	0.849	13.266
49.000	0.852	13.313
49.400	0.857	13.391
50.000	0.866	13.531
51.000	0.877	13.703
52.000	0.887	13.859
53.000	0.895	13.984
54.000	0.902	14.094
55.000	0.907	14.172
56.000	0.912	14.250
57.000	0.916	14.313
58.000	0.918	14.344
59.000	0.918	14.344
60.000	0.922	14.406
61.000	0.925	14.453
62.000	0.928	14.500
63.000	0.930	14.531
64.000	0.930	14.531

65.000	0.930	14.531
66.000	0.931	14.547
67.000	0.933	14.578
68.000	0.933	14.578
69.000	0.934	14.594
70.000	0.934	14.594
71.000	0.935	14.609
72.000	0.936	14.625

run # 28

$T_{p1} = 900^{\circ}\text{C}$ (0.5 hr)

$T_{p2} = 950^{\circ}\text{C}$ (1.33 hr)

$B = 16.0\%$

$T = 200^{\circ}\text{C}$

$P_{O_2} = 0.66$ torr

t [hr]	q [mg O ₂]	q [gO ₂ /kg char]
0.000	0.000	0.000
0.250	0.110	1.950
0.500	0.215	3.812
0.750	0.247	4.379
1.000	0.260	4.610
1.500	0.273	4.840
2.000	0.276	4.894
3.000	0.285	5.053
4.000	0.292	5.177
5.000	0.297	5.266
6.000	0.304	5.390
7.000	0.308	5.461
8.000	0.313	5.550
9.000	0.317	5.621
10.000	0.321	5.691
11.000	0.325	5.762
12.000	0.328	5.816
13.000	0.333	5.904
14.000	0.336	5.957
15.000	0.339	6.011
16.000	0.342	6.064
17.000	0.345	6.117
18.000	0.347	6.152
19.000	0.351	6.223
20.000	0.353	6.259
21.000	0.355	6.294
22.000	0.357	6.330
23.000	0.359	6.365
24.000	0.362	6.418
25.000	0.365	6.472
26.000	0.366	6.489

$P_{O_2} = 3.9$ torr

t [hr]	q [mg O ₂]	q [gO ₂ /kg char]
26.000	0.366	6.489
26.250	0.432	7.660
26.500	0.467	8.280
26.750	0.487	8.635

27.000	0.497	8.812
27.500	0.505	8.954
28.000	0.507	8.989
29.000	0.512	9.078
30.000	0.515	9.131
31.000	0.518	9.184
32.000	0.522	9.255
33.000	0.525	9.309
34.000	0.528	9.362
35.000	0.533	9.450
36.000	0.536	9.504
37.000	0.538	9.539
38.000	0.543	9.628
39.000	0.545	9.663
40.000	0.547	9.699
41.000	0.550	9.752
42.000	0.553	9.805
43.000	0.555	9.840
44.000	0.557	9.876
45.000	0.558	9.894
46.000	0.560	9.929
47.000	0.563	9.982
48.000	0.563	9.982
49.000	0.565	10.018
50.000	0.565	10.018

$P_{O_2} = 160$ torr

t [hr]	q [mg O ₂]	q [gO ₂ /kg char]
50.000	0.565	10.018
50.250	0.593	10.514
50.500	0.622	11.028
50.750	0.644	11.418
51.000	0.658	11.667
51.500	0.685	12.145
52.000	0.707	12.535
53.000	0.738	13.085
54.000	0.761	13.493
55.000	0.778	13.794
56.000	0.792	14.043
57.000	0.804	14.255
58.000	0.812	14.397
59.000	0.820	14.539
60.000	0.827	14.663
61.000	0.832	14.752
62.000	0.838	14.858
63.000	0.842	14.929
64.000	0.846	15.000
65.000	0.849	15.053
66.000	0.848	15.035
67.000	0.848	15.035
68.000	0.849	15.053
69.000	0.850	15.071
70.000	0.849	15.053
71.000	0.853	15.124
72.000	0.855	15.160
73.000	0.857	15.195
74.000	0.859	15.230
75.000	0.860	15.248
76.000	0.863	15.301
77.000	0.864	15.319
78.000	0.864	15.319
79.000	0.862	15.284

80.000	0.860	15.248
81.000	0.859	15.230
82.000	0.859	15.230
83.000	0.858	15.213
84.000	0.858	15.213
85.000	0.857	15.195

run # 55
 $T_p = 1000^{\circ}\text{C}$ (2 hr)
 $B = 4.3\%$
 $T = 150^{\circ}\text{C}$
 $P_{O_2} = 160$ torr

t [hr]	q [mg O ₂]	q [gO ₂ /kg char]
0.000	0.000	0.000
0.002	0.023	0.276
0.007	0.043	0.515
0.012	0.059	0.707
0.018	0.073	0.875
0.022	0.080	0.959
0.032	0.096	1.151
0.042	0.113	1.355
0.052	0.123	1.474
0.062	0.133	1.594
0.072	0.143	1.714
0.082	0.152	1.822
0.092	0.160	1.918
0.102	0.165	1.978
0.112	0.173	2.074
0.122	0.177	2.122
0.132	0.183	2.194
0.142	0.188	2.254
0.152	0.193	2.314
0.162	0.197	2.362
0.182	0.205	2.457
0.202	0.213	2.553
0.222	0.219	2.625
0.242	0.224	2.685
0.262	0.231	2.769
0.282	0.235	2.817
0.302	0.241	2.889
0.312	0.243	2.913
0.362	0.253	3.033
0.412	0.263	3.153
0.462	0.271	3.249
0.512	0.276	3.309
0.562	0.284	3.404
0.612	0.292	3.500
0.662	0.297	3.560
0.712	0.303	3.632
0.762	0.307	3.680
0.812	0.313	3.752
0.862	0.316	3.788
0.912	0.322	3.860
0.962	0.324	3.884
1.012	0.326	3.908
1.062	0.330	3.956
1.112	0.333	3.992
1.212	0.339	4.064
1.312	0.345	4.136
1.412	0.352	4.220

1.512	0.357	4.280
1.612	0.363	4.351
1.712	0.368	4.411
1.812	0.373	4.471
1.912	0.376	4.507
2.012	0.380	4.555
2.062	0.381	4.567
3.062	0.414	4.963
4.062	0.440	5.275
5.062	0.460	5.514
6.062	0.480	5.754
7.062	0.493	5.910
8.062	0.498	5.970
9.062	0.515	6.174
10.062	0.528	6.329
11.062	0.535	6.413
12.062	0.544	6.521
13.062	0.552	6.617
14.062	0.560	6.713
15.062	0.569	6.821
16.062	0.576	6.905
17.062	0.580	6.953
18.062	0.589	7.061
19.062	0.593	7.109
20.062	0.600	7.193
21.062	0.602	7.216
22.062	0.609	7.300
23.062	0.612	7.336
24.062	0.619	7.420

run # 52
 $T_p = 1000^{\circ}\text{C}$ (2 hr)
 $B = 4.2\%$
 $T = 1500^{\circ}\text{C}$
 $P_{O_2} = 760$ torr

t [hr]	q [mg O ₂]	q [gO ₂ /kg char]
0.0000	0.000	0.000
0.0125	0.166	2.112
0.0275	0.213	2.710
0.0475	0.243	3.092
0.0725	0.272	3.461
0.1225	0.309	3.931
0.1725	0.332	4.224
0.2225	0.352	4.478
0.2725	0.366	4.656
0.3225	0.380	4.835
0.3725	0.391	4.975
0.4225	0.401	5.102
0.4725	0.407	5.178
0.5225	0.414	5.267
0.5725	0.422	5.369
0.6225	0.430	5.471
0.6725	0.435	5.534
0.7225	0.442	5.623
0.7725	0.448	5.700
0.8225	0.452	5.751
0.9225	0.462	5.878
1.1725	0.484	6.158
1.4225	0.504	6.412

1.6725	0.517	6.578
1.9225	0.530	6.743
2.1725	0.542	6.896
2.4225	0.552	7.023
2.6725	0.562	7.150
2.9225	0.572	7.277
3.1725	0.580	7.379
3.4225	0.587	7.468
3.347	0.589	7.494
4.347	0.616	7.837
5.347	0.637	8.104
6.347	0.656	8.346
7.347	0.672	8.550
8.347	0.686	8.728
9.347	0.700	8.906
10.347	0.712	9.059
11.347	0.722	9.186
12.347	0.733	9.326
13.347	0.742	9.440
14.347	0.749	9.529
15.347	0.757	9.631
16.347	0.765	9.733
17.347	0.772	9.822
18.347	0.778	9.898
19.348	0.785	9.987
20.348	0.794	10.102
21.348	0.798	10.153
22.448	0.804	10.229
23.348	0.812	10.331
23.552	0.814	10.356

run # 46
 $T_p = 1000^\circ\text{C}$ (2 hr)
 $B = 43.1\%$
 $T = 150^\circ\text{C}$
 $P_{O_2} = 760$ torr

t [hr]	q [mg O ₂]	q [gO ₂ /kg char]
0.000	0.000	0.000
0.030	0.130	3.886
0.080	0.168	5.022
0.130	0.189	5.650
0.180	0.203	6.069
0.230	0.216	6.457
0.280	0.225	6.726
0.380	0.242	7.235
0.480	0.252	7.534
0.630	0.269	8.042
0.780	0.281	8.401
0.930	0.290	8.670
1.080	0.299	8.939
1.280	0.310	9.268
1.530	0.320	9.567
1.780	0.329	9.836
2.130	0.340	10.164
2.530	0.349	10.433
2.980	0.360	10.762
3.530	0.370	11.061
4.130	0.380	11.360
4.780	0.390	11.659
5.580	0.400	11.958

6.530	0.410	12.257
7.580	0.420	12.556
8.180	0.424	12.676

run # 60

 $T_p = 1000^{\circ}\text{C}$ (2 hr)

B = 3.3%

T = 200°C $P_{O_2} = 160$ torr

t [hr]	q [mg O_2]	q [g O_2 /kg char]
0.0000	0.000	0.000
0.0145	0.173	1.995
0.0205	0.183	2.111
0.0325	0.194	2.238
0.0385	0.201	2.318
0.0505	0.227	2.618
0.0565	0.234	2.699
0.0685	0.241	2.780
0.0745	0.245	2.826
0.0805	0.252	2.907
0.0865	0.256	2.953
0.0925	0.263	3.033
0.0985	0.267	3.080
0.1045	0.270	3.114
0.1225	0.277	3.195
0.1286	0.284	3.276
0.1406	0.292	3.368
0.1586	0.295	3.403
0.1646	0.299	3.449
0.1766	0.306	3.529
0.2006	0.310	3.576
0.2126	0.313	3.610
0.2306	0.321	3.702
0.2426	0.324	3.737
0.2726	0.328	3.783
0.2846	0.331	3.818
0.2966	0.335	3.864
0.3086	0.339	3.910
0.3326	0.346	3.991
0.3566	0.353	4.072
0.3476	0.357	4.118
0.4107	0.360	4.152
0.4287	0.364	4.198
0.4467	0.368	4.245
0.4707	0.371	4.279
0.4887	0.375	4.325
0.4947	0.378	4.360
0.5307	0.382	4.406
0.5547	0.386	4.452
0.5787	0.389	4.487
0.6087	0.393	4.533
0.6268	0.396	4.567
0.6448	0.400	4.614
0.6748	0.404	4.660
0.7168	0.407	4.694
0.7408	0.411	4.740
0.7708	0.414	4.775
0.8068	0.418	4.821
0.8308	0.422	4.867
0.8548	0.425	4.902

0.9209	0.429	4.948
0.9569	0.433	4.994
0.9809	0.436	5.029
1.0289	0.440	5.075
1.0649	0.443	5.110
1.1129	0.447	5.156
1.2090	0.451	5.202
1.2510	0.454	5.236
1.8830	0.501	5.779
2.3830	0.525	6.055
2.8830	0.547	6.309
3.3830	0.564	6.505
3.8830	0.581	6.701
4.3830	0.594	6.851
4.8830	0.609	7.024
5.8830	0.629	7.255
6.8830	0.649	7.486
7.8830	0.667	7.693
8.8830	0.680	7.843
9.8830	0.694	8.005
10.8830	0.708	8.166
11.8830	0.719	8.293
12.8830	0.729	8.408
13.8830	0.740	8.535
14.8830	0.749	8.639
15.8830	0.759	8.754
16.8830	0.767	8.847
17.8830	0.775	8.939
18.8830	0.781	9.008
19.8830	0.789	9.100
20.8830	0.797	9.193
21.8830	0.802	9.250
22.8830	0.810	9.343
23.8830	0.814	9.389
24.8830	0.819	9.446
25.8830	0.827	9.539
26.8830	0.831	9.585
27.8830	0.837	9.654
28.8830	0.841	9.700
29.8830	0.847	9.769
30.8830	0.850	9.804
31.8830	0.856	9.873
32.8830	0.859	9.908
33.8830	0.865	9.977
34.8830	0.869	10.023
35.8830	0.873	10.069
36.8830	0.877	10.115
37.8830	0.880	10.150
38.8830	0.882	10.173
39.8830	0.888	10.242
40.8830	0.891	10.277
41.8830	0.894	10.311
42.8830	0.898	10.358
43.8830	0.900	10.381
44.8830	0.904	10.427
45.8830	0.907	10.461
46.8830	0.909	10.484
47.8830	0.913	10.531
48.8830	0.917	10.577
49.8830	0.919	10.600
50.8830	0.922	10.634
51.6030	0.923	10.646
51.6330	0.925	10.681
52.6330	0.928	10.704

53.6330	0.931	10.738
55.6330	0.937	10.807
57.6330	0.941	10.854
59.6330	0.947	10.923
61.6330	0.951	10.969
63.6330	0.957	11.038
65.6330	0.960	11.073
67.6330	0.965	11.130
69.6330	0.969	11.176
71.6330	0.974	11.234
73.6330	0.978	11.280
75.6330	0.980	11.303
77.6330	0.985	11.361
79.6330	0.989	11.407
81.6330	0.993	11.453
83.6330	0.999	11.522
85.6330	1.001	11.546
87.6330	1.006	11.603
89.6330	1.009	11.638
91.6330	1.011	11.661
93.6330	1.015	11.707
95.6330	1.018	11.742
97.6330	1.020	11.765
99.6330	1.025	11.822
101.6330	1.028	11.857
102.1330	1.029	11.869

run # 58

 $T_p = 1000^\circ\text{C}$ (2 hr)

B = 4.1%

T = 200°C PO₂ = 760 torr

t [hr]	q [mg O ₂]	q [gO ₂ /kg char]
0.000	0.000	0.000
0.005	0.122	1.417
0.008	0.152	1.765
0.015	0.182	2.114
0.020	0.202	2.346
0.025	0.222	2.578
0.035	0.246	2.857
0.045	0.267	3.101
0.055	0.285	3.310
0.065	0.302	3.508
0.075	0.314	3.647
0.085	0.329	3.821
0.095	0.340	3.949
0.105	0.349	4.053
0.115	0.358	4.158
0.125	0.366	4.251
0.135	0.375	4.355
0.145	0.382	4.437
0.155	0.391	4.541
0.165	0.396	4.599
0.175	0.402	4.669
0.185	0.410	4.762
0.195	0.415	4.820
0.205	0.421	4.890
0.215	0.426	4.948

0.225	0.432	5.017
0.231	0.436	5.064
0.243	0.441	5.122
0.255	0.445	5.168
0.261	0.450	5.226
0.273	0.454	5.273
0.280	0.459	5.331
0.286	0.463	5.377
0.310	0.472	5.482
0.328	0.476	5.528
0.340	0.481	5.587
0.352	0.489	5.679
0.382	0.494	5.738
0.413	0.503	5.842
0.431	0.507	5.889
0.437	0.512	5.947
0.450	0.516	5.993
0.467	0.521	6.051
0.479	0.525	6.098
0.504	0.530	6.156
0.522	0.534	6.202
0.546	0.538	6.249
0.564	0.543	6.307
0.601	0.552	6.411
0.631	0.556	6.458
0.667	0.561	6.516
0.673	0.565	6.562
0.691	0.569	6.609
0.716	0.574	6.667
0.746	0.578	6.713
0.782	0.587	6.818
0.807	0.592	6.876
0.831	0.596	6.922
0.855	0.600	6.969
0.977	0.613	7.120
1.110	0.622	7.224
1.222	0.639	7.422
1.344	0.644	7.480
1.405	0.652	7.573
1.589	0.661	7.677
1.650	0.665	7.724
1.711	0.670	7.782
1.772	0.679	7.886
1.833	0.683	7.933
1.956	0.692	8.037
2.078	0.696	8.084
2.139	0.700	8.130
2.200	0.705	8.188
2.384	0.714	8.293
2.445	0.718	8.339
2.567	0.722	8.386
2.670	0.727	8.444
2.751	0.731	8.490
2.812	0.735	8.537
2.873	0.740	8.595
3.056	0.744	8.641
3.179	0.748	8.688
3.240	0.753	8.746
3.423	0.762	8.850
3.546	0.766	8.897
3.729	0.770	8.943
3.790	0.775	9.001
3.913	0.779	9.048
4.035	0.783	9.094

4.096	0.788	9.152
4.218	0.792	9.199
4.341	0.796	9.245
4.463	0.801	9.303
4.646	0.805	9.350
4.769	0.810	9.408
4.952	0.814	9.454
5.074	0.818	9.501
5.258	0.823	9.559
5.380	0.827	9.605
5.502	0.831	9.652
5.930	0.840	9.756
6.053	0.844	9.803
6.114	0.849	9.861
6.297	0.853	9.907
6.481	0.858	9.965
6.664	0.862	10.012
6.787	0.866	10.058
6.909	0.871	10.116
7.213	0.875	10.163
7.337	0.879	10.209
7.520	0.884	10.267
7.949	0.893	10.372
8.132	0.897	10.418
8.560	0.901	10.465
8.621	0.906	10.523
8.866	0.910	10.569
9.172	0.914	10.616
10.172	0.929	10.790
11.172	0.944	10.964
12.172	0.955	11.092
13.172	0.967	11.231
14.172	0.980	11.382
16.172	1.001	11.626
18.172	1.018	11.823
20.172	1.035	12.021
22.172	1.049	12.184
23.172	1.056	12.265
23.382	1.059	12.300

run # 57

 $T_p = 1000^{\circ}\text{C}$ (2 hr) $B = 4.2\%$ $T = 300^{\circ}\text{C}$ $P_{O_2} = 160$ torr

t [hr]	q [mg O ₂]	q [gO ₂ /kg char]
0.000	0.000	0.000
0.010	0.083	0.936
0.012	0.100	1.128
0.017	0.125	1.410
0.022	0.145	1.636
0.027	0.165	1.861
0.032	0.179	2.019
0.038	0.197	2.222
0.042	0.205	2.312
0.052	0.213	2.403
0.062	0.253	2.854
0.072	0.270	3.046
0.082	0.287	3.237
0.092	0.305	3.440

0.102	0.320	3.610
0.112	0.333	3.756
0.132	0.358	4.038
0.152	0.381	4.298
0.162	0.393	4.433
0.182	0.412	4.647
0.202	0.428	4.828
0.212	0.438	4.941
0.262	0.476	5.369
0.312	0.509	5.742
0.362	0.536	6.046
0.412	0.562	6.340
0.462	0.583	6.576
0.512	0.603	6.802
0.562	0.623	7.028
0.612	0.638	7.197
0.662	0.653	7.366
0.712	0.669	7.547
0.812	0.693	7.817
0.912	0.716	8.077
1.012	0.736	8.302
1.112	0.754	8.505
1.212	0.784	8.844
1.312	0.788	8.889
1.342	0.791	8.923
1.362	0.794	8.957
1.382	0.795	8.968
1.402	0.797	8.990
1.422	0.800	9.024
1.442	0.803	9.058
1.462	0.805	9.081
1.482	0.807	9.103
1.502	0.811	9.148
1.522	0.813	9.171
1.542	0.817	9.216
1.592	0.823	9.284
1.642	0.827	9.329
1.692	0.833	9.397
1.742	0.837	9.442
1.792	0.842	9.498
1.842	0.845	9.532
1.942	0.849	9.577
2.042	0.857	9.667
2.142	0.865	9.757
2.192	0.869	9.803
2.242	0.876	9.882
2.342	0.884	9.972
2.442	0.889	10.028
2.542	0.895	10.096
2.642	0.900	10.152
2.742	0.905	10.209
2.842	0.910	10.265
2.942	0.915	10.321
3.042	0.918	10.355
3.142	0.922	10.400
3.242	0.926	10.446
3.342	0.930	10.491
3.442	0.935	10.547
3.542	0.938	10.581
3.642	0.943	10.637
3.742	0.945	10.660
3.842	0.948	10.694
3.942	0.951	10.728
4.042	0.955	10.773

4.142	0.957	10.795
4.242	0.959	10.818
4.342	0.961	10.840
4.442	0.963	10.863
4.542	0.965	10.886
4.642	0.968	10.919
4.742	0.970	10.942
4.842	0.973	10.976
4.942	0.975	10.998
5.042	0.976	11.010
5.142	0.977	11.021
5.242	0.979	11.043
5.642	0.987	11.134
6.242	0.993	11.201
6.642	0.994	11.213
7.242	0.998	11.258
8.242	1.004	11.325
9.242	1.006	11.348
10.242	1.006	11.348
11.242	1.005	11.337
12.242	1.003	11.314
13.242	0.998	11.258
14.242	0.993	11.201
15.242	0.988	11.145
16.242	0.983	11.089
17.242	0.978	11.032
17.642	0.975	10.998

run # 53

 $T_p = 1000^\circ\text{C}$ (2 hr)

B = 4.3%

T = 300°C $P_{O_2} = 760$ torr

t [hr]	q [mg O ₂]	q [gO ₂ /kg char]
0.000	0.000	0.000
0.016	0.206	2.459
0.023	0.391	4.668
0.034	0.491	5.861
0.040	0.512	6.112
0.047	0.522	6.231
0.059	0.563	6.721
0.065	0.579	6.912
0.071	0.594	7.091
0.077	0.600	7.162
0.083	0.615	7.342
0.089	0.620	7.401
0.095	0.636	7.592
0.101	0.651	7.771
0.108	0.662	7.903
0.114	0.672	8.022
0.126	0.682	8.141
0.132	0.698	8.332
0.138	0.703	8.392
0.144	0.713	8.511
0.150	0.719	8.583
0.153	0.729	8.702
0.162	0.734	8.762
0.169	0.745	8.893
0.175	0.750	8.953
0.181	0.755	9.013

0.187	0.765	9.132
0.193	0.770	9.192
0.218	0.786	9.383
0.223	0.791	9.443
0.236	0.801	9.562
0.242	0.807	9.634
0.248	0.812	9.693
0.272	0.822	9.813
0.278	0.827	9.872
0.284	0.833	9.944
0.297	0.838	10.004
0.303	0.843	10.063
0.309	0.848	10.123
0.315	0.853	10.183
0.321	0.858	10.242
0.345	0.869	10.374
0.364	0.874	10.433
0.382	0.879	10.493
0.394	0.884	10.553
0.419	0.890	10.624
0.437	0.895	10.684
0.449	0.900	10.744
0.467	0.905	10.803
0.479	0.910	10.863
0.492	0.915	10.923
0.522	0.926	11.054
0.534	0.931	11.114
0.547	0.936	11.173
0.565	0.941	11.233
0.589	0.946	11.293
0.608	0.952	11.364
0.656	0.957	11.424
0.699	0.962	11.484
0.719	0.966	11.532
0.749	0.970	11.579
0.769	0.975	11.639
0.779	0.976	11.651
0.799	0.979	11.687
0.819	0.984	11.746
0.829	0.986	11.770
0.879	0.993	11.854
0.929	0.998	11.914
0.979	1.005	11.997
1.029	1.009	12.045
1.079	1.016	12.128
1.129	1.018	12.152
1.179	1.024	12.224
1.229	1.027	12.260
1.279	1.029	12.284
1.329	1.035	12.355
1.429	1.039	12.403
1.529	1.045	12.475
1.629	1.047	12.499
1.729	1.051	12.546
1.829	1.054	12.582
1.929	1.055	12.594
2.029	1.056	12.606
2.129	1.057	12.618
2.329	1.059	12.642
2.529	1.060	12.654
2.849	1.062	12.678

run # 51

 $T_p = 1111^\circ\text{C}$ (2 hr) $B = 0.24\%$ $T = 150^\circ\text{C}$ $P_{O_2} = 760$ torr

t [hr]	q [mg O ₂]	q [gO ₂ /kg char]
0.000	0.000	0.000
0.017	0.011	0.123
0.033	0.018	0.202
0.050	0.025	0.281
0.067	0.032	0.359
0.083	0.037	0.415
0.100	0.042	0.471
0.117	0.048	0.539
0.133	0.052	0.584
0.150	0.056	0.629
0.183	0.065	0.730
0.200	0.068	0.763
0.217	0.072	0.808
0.233	0.075	0.842
0.25	0.077	0.864
0.28	0.081	0.909
0.30	0.087	0.977
0.32	0.088	0.988
0.34	0.093	1.044
0.37	0.098	1.100
0.39	0.101	1.134
0.41	0.105	1.179
0.43	0.107	1.201
0.46	0.111	1.246
0.48	0.112	1.257
0.53	0.115	1.291
0.55	0.119	1.336
0.58	0.121	1.358
0.60	0.122	1.369
0.63	0.125	1.403
0.65	0.127	1.426
0.68	0.131	1.471
0.70	0.133	1.493
0.73	0.136	1.527
0.75	0.137	1.538
0.78	0.140	1.572
0.80	0.142	1.594
0.83	0.144	1.616
0.85	0.146	1.639
0.88	0.148	1.661
0.90	0.149	1.673
0.93	0.150	1.684
0.95	0.152	1.706
0.98	0.154	1.729
1.00	0.156	1.751
1.03	0.158	1.774
1.05	0.160	1.796
1.08	0.161	1.807
1.13	0.164	1.841
1.18	0.168	1.886
1.23	0.171	1.920
1.28	0.173	1.942
1.34	0.177	1.987
1.39	0.179	2.009
1.44	0.181	2.032
1.49	0.184	2.065

1.54	0.186	2.088
1.60	0.189	2.122
1.65	0.190	2.133
1.70	0.193	2.166
1.75	0.195	2.189
1.81	0.197	2.211
1.86	0.199	2.234
1.91	0.200	2.245
1.96	0.203	2.279
2.01	0.204	2.290
2.07	0.207	2.324
2.12	0.209	2.346
2.17	0.210	2.357
2.22	0.211	2.369
2.27	0.214	2.402
2.30	0.215	2.413
2.33	0.216	2.425
2.38	0.218	2.447
2.43	0.220	2.470
2.49	0.222	2.492
2.54	0.223	2.503
2.59	0.225	2.526
2.64	0.227	2.548
2.70	0.229	2.571
2.75	0.231	2.593
2.80	0.232	2.604
2.86	0.233	2.616
2.91	0.235	2.638
2.96	0.236	2.649
3.02	0.238	2.672
3.07	0.240	2.694
3.12	0.241	2.705
3.18	0.242	2.717
3.23	0.244	2.739
3.28	0.245	2.750
3.33	0.246	2.761
3.39	0.248	2.784
3.44	0.249	2.795
3.49	0.250	2.806
3.55	0.252	2.829
3.60	0.253	2.840
3.65	0.254	2.851
3.73	0.256	2.874
3.78	0.257	2.885
3.84	0.258	2.896
3.89	0.260	2.919
3.94	0.261	2.930
4.00	0.262	2.941
4.05	0.263	2.952
4.10	0.264	2.963
4.16	0.265	2.975
4.21	0.266	2.986
4.27	0.267	2.997
4.32	0.269	3.020
4.38	0.269	3.020
4.43	0.270	3.031
4.49	0.272	3.053
4.54	0.273	3.065
4.60	0.274	3.076
4.65	0.275	3.087
4.70	0.276	3.098
4.76	0.277	3.109
4.81	0.278	3.121
4.87	0.278	3.121

4.92	0.279	3.132
4.98	0.281	3.154
5.03	0.282	3.166
5.09	0.283	3.177
5.14	0.284	3.188
5.20	0.284	3.188
5.25	0.286	3.210
5.30	0.287	3.222
5.36	0.287	3.222
5.41	0.288	3.233
5.47	0.289	3.244
5.52	0.290	3.255
5.58	0.291	3.267
5.63	0.292	3.278
5.69	0.293	3.289
5.74	0.294	3.300
5.80	0.295	3.311
5.85	0.296	3.323
5.90	0.297	3.334
5.96	0.297	3.334
6.01	0.298	3.345
6.10	0.299	3.356
6.15	0.300	3.368
11.40	0.357	4.007
11.51	0.358	4.019
11.99	0.361	4.052
12.52	0.365	4.097
12.99	0.369	4.142
13.49	0.372	4.176
13.99	0.376	4.221
14.50	0.379	4.254
15.00	0.383	4.299
15.50	0.386	4.333
16.00	0.390	4.378
16.42	0.393	4.412
16.99	0.396	4.445
17.50	0.398	4.468
18.01	0.400	4.490
18.50	0.403	4.524
19.01	0.406	4.557
19.49	0.408	4.580
19.92	0.411	4.614
20.45	0.413	4.636
20.98	0.415	4.659
21.48	0.418	4.692
21.99	0.420	4.715
22.49	0.423	4.748
22.99	0.425	4.771
23.47	0.428	4.804
24.00	0.431	4.838

run # 50
 $T_p = 1243^\circ\text{C}$ (2 hr)
 $B = 0.12\%$
 $T = 150^\circ\text{C}$
 $PO_2 = 760$ torr

t [hr]	q [mg O ₂]	q [g O ₂ /kg char]
0.000	0.000	0.000
0.03	0.005	0.055
0.06	0.011	0.121
0.09	0.015	0.165
0.12	0.018	0.198
0.15	0.022	0.243
0.22	0.024	0.265
0.25	0.025	0.276
0.28	0.027	0.298
0.31	0.028	0.309
0.34	0.030	0.331
0.37	0.031	0.342
0.40	0.033	0.364
0.43	0.034	0.375
0.46	0.035	0.386
0.49	0.036	0.397
0.52	0.037	0.408
0.56	0.039	0.430
0.62	0.040	0.441
0.65	0.041	0.452
0.68	0.042	0.463
0.71	0.043	0.474
0.74	0.044	0.485
0.77	0.045	0.496
0.80	0.046	0.507
0.83	0.046	0.507
0.86	0.047	0.518
0.90	0.048	0.529
0.93	0.049	0.540
0.96	0.050	0.551
0.99	0.050	0.551
1.02	0.051	0.562
1.05	0.052	0.573
1.08	0.053	0.584
1.11	0.053	0.584
1.14	0.054	0.595
1.17	0.054	0.595
1.20	0.055	0.606
1.23	0.056	0.617
1.30	0.057	0.629
1.33	0.058	0.640
1.43	0.059	0.651
1.49	0.060	0.662
1.55	0.061	0.673
1.59	0.062	0.684
1.67	0.063	0.695
1.73	0.064	0.706
1.76	0.065	0.717
1.84	0.066	0.728
2.00	0.069	0.761
2.20	0.072	0.794
2.40	0.075	0.827
2.50	0.077	0.849
2.60	0.079	0.871
2.85	0.082	0.904
3.0	0.084	0.926

3.2	0.086	0.948
3.4	0.088	0.970
3.6	0.091	1.003
3.8	0.092	1.014
4.0	0.094	1.036
4.2	0.096	1.059
4.4	0.098	1.081
4.6	0.100	1.103
4.8	0.101	1.114
5.0	0.102	1.125
5.5	0.106	1.169
6.0	0.109	1.202
6.5	0.112	1.235
7.0	0.115	1.268
7.5	0.118	1.301
8.0	0.121	1.334
8.5	0.124	1.367
9.0	0.127	1.400
9.5	0.129	1.422
10.0	0.131	1.444
10.5	0.133	1.467
11.0	0.135	1.489
11.5	0.137	1.511
12.0	0.138	1.522
12.5	0.140	1.544
13.0	0.141	1.555
13.5	0.143	1.577
14.0	0.145	1.599
14.5	0.146	1.610
15.0	0.147	1.621
15.5	0.148	1.632
15.8	0.149	1.643
16.1	0.150	1.654
16.5	0.151	1.665
17.0	0.152	1.676
17.5	0.153	1.687
17.75	0.153	1.687

run # 49B

 $T_p = 1400^{\circ}\text{C}$ (2 hr) $B = 0.21\%$ $T = 150^{\circ}\text{C}$ $\text{PO}_2 = 760 \text{ torr}$

t [hr]	q [mg O_2]	q [g O_2 /kg char]
0.000	0.000	0.000
0.200	0.013	0.154
0.400	0.016	0.195
0.650	0.018	0.219
0.900	0.020	0.237
1.400	0.023	0.270
1.900	0.024	0.288
2.400	0.026	0.305
3.000	0.027	0.320
4.000	0.029	0.340
5.600	0.031	0.367
7.600	0.033	0.392
9.600	0.035	0.414
11.600	0.037	0.434
13.600	0.038	0.450
16.600	0.040	0.473

18.600	0.041	0.486
20.200	0.042	0.497
22.200	0.043	0.509
24.000	0.044	0.521

run # 47
 $T_p = 1400^\circ\text{C}$ (2 hr)
 $B = 12.9\%$
 $PO_2 = 760$ torr

$T = 150^\circ\text{C}$

t [hr]	q [mg O ₂]	q [gO ₂ /kg char]
0.000	0.000	0.000
0.058	0.132	2.443
0.167	0.171	3.165
0.269	0.186	3.443
0.350	0.196	3.628
0.678	0.221	4.091
0.778	0.227	4.202
0.911	0.234	4.332
0.978	0.237	4.387
1.145	0.242	4.480
1.261	0.246	4.554
1.511	0.253	4.683
1.678	0.257	4.757
1.845	0.261	4.831
2.111	0.267	4.942
2.345	0.272	5.035
2.578	0.276	5.109
2.778	0.279	5.165
3.011	0.282	5.220
3.278	0.286	5.294
3.511	0.289	5.350
3.678	0.291	5.387
4.011	0.295	5.461
4.411	0.299	5.535
4.645	0.301	5.572
4.878	0.303	5.609
5.345	0.307	5.683
5.911	0.311	5.757
6.178	0.313	5.794
6.645	0.316	5.849
7.111	0.319	5.905
7.445	0.321	5.942
7.778	0.323	5.979
8.345	0.326	6.035
8.945	0.329	6.090
9.378	0.331	6.127
9.845	0.333	6.164
10.278	0.335	6.201
10.778	0.337	6.238
11.345	0.339	6.275
11.845	0.341	6.312
12.411	0.343	6.349
12.978	0.345	6.386
13.378	0.346	6.405
13.811	0.347	6.423
15.294	0.351	6.497
16.194	0.353	6.534

17.094	0.355	6.571
17.994	0.357	6.608
18.994	0.359	6.645
19.494	0.360	6.664
20.494	0.362	6.701
21.494	0.364	6.738
22.494	0.366	6.775
23.194	0.368	6.812
24.000	0.370	6.849

T = 200°C

t [hr]	q [mg O ₂]	q [gO ₂ /kg char]
24.000	0.370	6.849
24.250	0.374	6.923
24.550	0.379	7.016
25.050	0.385	7.127
25.650	0.392	7.256
26.150	0.397	7.349
26.550	0.401	7.423
27.250	0.407	7.534
27.950	0.412	7.627
28.550	0.416	7.701
29.350	0.421	7.793
30.150	0.425	7.867
30.950	0.429	7.941
31.550	0.431	7.978
32.250	0.434	8.034
32.850	0.436	8.071
33.350	0.438	8.108
34.050	0.440	8.145
34.750	0.442	8.182
35.550	0.444	8.219
36.350	0.446	8.256
37.050	0.448	8.293
37.950	0.450	8.330
38.750	0.452	8.367
39.650	0.454	8.404
40.150	0.455	8.422
40.750	0.456	8.441
41.350	0.457	8.460
42.050	0.459	8.497
43.250	0.461	8.534
44.150	0.462	8.552
44.850	0.463	8.571
45.950	0.464	8.589
46.850	0.465	8.608

run # 47C

T_p = 1400°C (2 hr)

B = 47.5%

T = 150°C

P_{O2} = 760 torr

t [hr]	q [mg O ₂]	q [gO ₂ /kg char]
0.000	0.000	0.000
0.033	0.239	7.344
0.067	0.292	8.972
0.085	0.307	9.433
0.096	0.314	9.648
0.135	0.357	10.970

0.155	0.364	11.185
0.175	0.369	11.338
0.194	0.370	11.369
0.214	0.374	11.492
0.234	0.379	11.646
0.254	0.381	11.707
0.273	0.385	11.830
0.293	0.389	11.953
0.313	0.392	12.045
0.332	0.395	12.137
0.352	0.397	12.199
0.372	0.400	12.291
0.392	0.402	12.353
0.411	0.402	12.353
0.431	0.407	12.506
0.451	0.408	12.537
0.470	0.410	12.598
0.490	0.414	12.721
0.554	0.416	12.783
0.575	0.419	12.875
0.597	0.422	12.967
0.618	0.427	13.121
0.639	0.427	13.121
0.661	0.431	13.244
0.682	0.432	13.274
0.703	0.436	13.397
0.725	0.437	13.428
0.746	0.439	13.489
0.767	0.442	13.582
0.789	0.443	13.612
0.810	0.445	13.674
0.831	0.446	13.705
0.853	0.449	13.797
0.874	0.451	13.858
0.895	0.452	13.889
0.917	0.453	13.920
0.938	0.454	13.950
0.959	0.456	14.012
0.981	0.458	14.073
1.002	0.459	14.104
1.023	0.460	14.135
1.045	0.461	14.165
1.066	0.462	14.196
1.087	0.464	14.258
1.108	0.465	14.288
1.130	0.467	14.350
1.2	0.468	14.381
1.3	0.474	14.565
1.4	0.479	14.719
1.5	0.484	14.872
1.6	0.488	14.995
1.7	0.492	15.118
1.8	0.497	15.272
1.9	0.500	15.364
2.0	0.505	15.517
2.1	0.508	15.610
2.2	0.510	15.671
2.27	0.514	15.794
2.5	0.515	15.825
2.6	0.517	15.886
2.7	0.520	15.978
2.8	0.523	16.071
2.9	0.526	16.163
3.0	0.529	16.255

3.2	0.533	16.378
3.4	0.537	16.501
3.6	0.541	16.624
3.8	0.545	16.747
4.0	0.548	16.839
4.2	0.552	16.962
4.4	0.555	17.054
4.6	0.559	17.177
4.8	0.562	17.269
5.0	0.564	17.330
5.3	0.568	17.453
5.6	0.572	17.576
5.9	0.575	17.668
6.03	0.577	17.730
6.8	0.580	17.822
7.0	0.583	17.914
7.5	0.589	18.099
8.0	0.594	18.252
8.5	0.599	18.406
9.0	0.604	18.559
9.5	0.606	18.621
10.0	0.609	18.713
10.5	0.613	18.836
11.0	0.617	18.959
11.5	0.619	19.020
12.0	0.623	19.143
13.0	0.629	19.328
14.0	0.634	19.481
15.0	0.640	19.666
15.28	0.642	19.727
15.5	0.643	19.758
16.0	0.646	19.850
17.0	0.649	19.942
18.0	0.653	20.065
19.0	0.657	20.188
20.0	0.659	20.250
21.0	0.662	20.342
22.0	0.665	20.434
23.0	0.669	20.557
24.0	0.674	20.710

run # 62
 $T_p = 1400^{\circ}\text{C}$ (2 hr)
 $B = 0.14\%$
 $T = 200^{\circ}\text{C}$
 $\text{PO}_2 = 160 \text{ torr}$

t [hr]	q [$\mu\text{g O}_2$]	q [$\text{g O}_2/\text{kg char}$]
0.00	0.0	0.000
0.05	1.0	0.011
0.10	1.8	0.019
0.15	2.2	0.023
0.20	2.5	0.027
0.25	3.2	0.034
0.30	3.8	0.041
0.35	4.1	0.044
0.40	4.2	0.045
0.45	4.4	0.047
0.50	4.9	0.052
0.55	5.1	0.054

0.60	5.7	0.061
0.65	6.0	0.064
0.70	6.1	0.065
0.75	6.7	0.071
0.80	7.0	0.075
0.85	7.1	0.076
0.90	7.3	0.078
0.94	7.4	0.079
1.14	8.2	0.087
2.14	10.8	0.115
3.14	12.7	0.135
4.14	13.6	0.145
5.14	14.4	0.154
6.14	16.0	0.171
7.14	16.9	0.180
8.14	18.0	0.192
9.14	19.0	0.203
10.14	20.0	0.213
11.14	21.0	0.224
12.14	21.9	0.233
13.14	22.8	0.243
14.14	23.3	0.248
15.14	23.7	0.253
16.14	24.1	0.257
17.14	24.3	0.259
18.14	24.6	0.262
19.14	25.0	0.267
20.14	25.6	0.273
22.14	26.4	0.281
26.14	27.9	0.297
28.14	28.9	0.308
30.14	29.1	0.310
31.14	29.5	0.314
32.14	29.9	0.319
34.14	30.3	0.323
36.14	30.8	0.328
38.14	31.2	0.333
42.14	32.0	0.341
46.14	33.1	0.353
50.14	34.1	0.364
54.14	35.4	0.377
58.14	36.0	0.384
62.14	36.9	0.393
66.14	37.5	0.400
70.14	38.3	0.408
74.14	39.0	0.416
78.14	39.4	0.420
82.14	39.9	0.425
86.14	40.7	0.434
90.14	41.4	0.441
94.14	42.0	0.448
98.14	42.5	0.453
102.14	43.0	0.458
106.14	43.6	0.465
110.14	44.0	0.469
114.14	44.5	0.474
118.14	45.1	0.481
122.14	45.7	0.487
126.14	46.4	0.495
130.14	47.3	0.504
134.14	48.1	0.513
138.14	48.8	0.520
142.14	49.4	0.527
146.14	50.0	0.533

A.5 CO₂/CO RATIO DATA

The molar, or volumetric, ratio CO₂/CO was determined from the following relations:

$$I_{\text{CO}_2} = f_{\text{CO}_2} \cdot V_{\text{CO}_2}$$

and

$$I_{\text{CO}} = f_{\text{CO}} \cdot V_{\text{CO}}$$

where I is the area under the peak (from the gas chromatographic data), f is a proportionality constant, and V is volume. Subscripts CO₂ and CO denote carbon dioxide and carbon monoxide, respectively. Dividing one of the above equations by the other gives,

$$\frac{I_{\text{CO}_2}}{I_{\text{CO}}} = \frac{f_{\text{CO}_2}}{f_{\text{CO}}} \frac{V_{\text{CO}_2}}{V_{\text{CO}}}$$

and this relation was used to evaluate $\text{CO}_2/\text{CO} \equiv V_{\text{CO}_2}/V_{\text{CO}}$. The value of $f_{\text{CO}_2}/f_{\text{CO}}$ was determined from calibration data (see Appendix D for a description of gas chromatographic measurements), and the results of the CO₂/CO determination are presented in Table A3.

Table A3 CO₂/CO ratio data

T _D range [°C]	Δm _D [mg]	T _p = 1000°C		CO ₂ /CO
		I _{CO₂} /I _{CO}	f _{CO₂} /f _{CO}	
200-350	0.30	2.77	1.40	2.0
			1.54	1.8
350-450	0.35	1.31	1.61	0.81
			1.54	0.85
			1.54*	0.85
450-550	0.41	0.54	1.54	0.35
550-650	0.34	0.24	1.60	0.15
			1.55	0.16
650-750	0.41	0.11	1.54	0.072
750-850	0.38	0.053	1.55	0.034
850-950	0.15	0.037	1.54	0.024

T_D range [°C]	Δm_D [mg]	$T_p = 1400^\circ\text{C}$		
		$I_{\text{CO}_2}/I_{\text{CO}}$	$f_{\text{CO}_2}/f_{\text{CO}}$	CO_2/CO
200-350	0.028	5.32	1.68 [†]	3.1
			1.61	3.3
			1.64	3.2
			1.52 [*]	3.5
200-350	—	4.16	1.85	2.2
			1.63	2.6
			1.64	2.5
			1.49 [*]	2.8
350-450	0.011	1.17	1.68	0.70
450-550	0.017		1.65	0.71
			1.52 [*]	0.77
550-650	0.014	0.18	1.86 [†]	0.097
650-750	0.022		1.60	0.11
			1.62	0.11
			1.55	0.12
750-850	0.013	0.073	1.58	0.046
850-950	0.040 [‡]		1.57	0.046
			1.53 [*]	0.048

* calibration without the trap (i.e. valve A in the "FILL" position)

[†]CO₂ peak overestimated (merging with the H₂O peak)

[‡] Δm_D unreliable due to an air leak into the TGA that occurred

Appendix B

MASS TRANSFER CALCULATIONS

An overall carbon-oxygen reaction rate is governed by a coupling of the intrinsic chemical kinetics with transport phenomena. The processes involved in this scheme are:

- (1) diffusion of oxygen through a boundary layer to the surface of the char particle,
- (2) diffusion of oxygen through the porous structure of the particle,
- (3) heterogeneous surface reaction between carbon and oxygen.

The term "intrinsic reactivity" refers to the situation when the third step is rate-controlling, i.e. when oxygen freely penetrates the particle (a flat O_2 concentration profile). This régime is known as "zone I," using nomenclature introduced by Wicke [1-3], and later popularized by Walker *et al.* [4]. For higher values of temperature, the reaction rate exceeds the rate of oxygen diffusion through the pores and the two come into balance at some penetration depth, where oxygen is depleted enough. The reaction does not occur in the central part of the particle due to oxygen deficiency. This is referred to as zone II.

At still higher temperature, the penetration depth shrinks to zero and the reaction retreats to the external surface of the particle (boundary layer diffusion control). This is zone III.

Zone I should be, of course, the goal for measurement of intrinsic kinetic parameters. The effect of experimental parameters on controlling mechanism is shown in Table B1 [5].

Table B1 Influence of experimental parameters on controlling mechanism for over-all char reactivity [5].

	T	P	$[C_t]$	d	ϵ
zone I	L	L	L	L	H
zone II	M	M	M	M	M
zone III	H	H	H	H	L

L indicates a low, M a medium and H a high value of each parameter, $[C_t]$ is a total number of active carbon sites, d is particle diameter, and ϵ denotes porosity.

The question that has to be addressed is whether the reaction order $n = 0.62-0.76$ reported in section 4.4 is intrinsic or apparent, i.e. influenced by diffusion through pores. The value of an effectiveness factor, defined as a ratio of the reaction rate measured experimentally to calculated intrinsic reaction rate at the temperature and composition of the bulk gas phase, is an indication of mass transfer limitation inside the porous particle. Mehta and Aris [6] demonstrated that the effectiveness factor versus Thiele modulus curves for n -th order reactions ($n > 0$) could be approximated by the first order curve (20% maximum error) if the Thiele modulus were defined as [6, 7]:

$$\Phi_n \equiv \frac{V_p}{A_p} \left[\frac{(n+1) \cdot k' \cdot C_s^{n-1}}{2\Lambda D_e} \right]^{1/2} \quad (B1)$$

where V_p [cm^3/g] is specific particle volume, A_p [cm^2/g] is specific external surface area of the particle, D_e [cm^2/s] is effective diffusivity through the pores, C_s [g/cm^3] is oxygen concentration at the surface of the particle [g/cm^3], k' is a reaction constant defined by the following equation:

$$r' = k' C_s^n \quad [\text{g}/(\text{cm}^3 \text{ s})] \quad (B2)$$

and Λ is a gravimetric stoichiometric coefficient

$$\Lambda \equiv - \frac{1}{\nu_{\text{O}_2}} \frac{M_C}{M_{\text{O}_2}} \quad (B3)$$

so that $\Lambda = 3/4$ for the reaction $\text{C} + 1/2 \text{O}_2 \rightarrow \text{CO}$ and $\Lambda = 3/8$ for $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$.

According to Youngquist [8], the combined effect of both Knudsen and molecular diffusion can be modelled to a good approximation for an isobaric system by using the over-all pore diffusion coefficient,

$$D = \left(\frac{1}{D_{AB}} + \frac{1}{D_k} \right)^{-1} \quad (\text{B4})$$

The effective diffusivity of a pore network, D_e , is related to the diffusivity of a single pore by $D_e = \frac{D \cdot \epsilon}{\tau^2}$, where τ is a tortuosity factor and ϵ porosity. Assuming $\tau = \sqrt{2}$ [9], the value of $D_e = \frac{D \cdot \epsilon}{2}$ is obtained. The relevant cross sectional area for diffusion, to which D_e is related, is the cross sectional area of the porous solid.

For a smooth pore, the diffusion coefficient for Knudsen flow can be expressed as

$$D_k = \frac{2r}{3} \left(\frac{8RT}{\pi \cdot M_{O_2}} \right)^{1/2} \quad (\text{B5a})$$

while molecular diffusivity of species A through species B can be estimated from [9]

$$D_{AB} = \frac{2.745 \cdot 10^{-4}}{P} (P_{cA} P_{cB})^{1/3} \cdot (T_{cA} T_{cB})^{5/12} \cdot \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} \cdot \left(\frac{T}{\sqrt{T_{cA} T_{cB}}} \right)^{1.823} \quad (\text{B5b})$$

where P is the total pressure of a gas mixture [atm], and subscript c refers to critical conditions for the species. D_{AB} is expressed in [cm^2/s].

Since in this work, the reaction rate expression of the form $r = k \cdot P_{O_2}^n$ [g/g hr] was used rather than eqn (B2), an appropriate conversion of k' to k must be applied. From the ideal gas law, it follows that

$$C_s = \frac{P_{O_2} M_{O_2}}{RT} = \frac{\frac{P_{O_2} [\text{torr}]}{760} \cdot 32}{82.06 \cdot T}$$

or

$$C_s = 5.13 \cdot 10^{-4} \cdot \frac{P_{O_2} [\text{torr}]}{T [\text{K}]} \quad [\text{g/cm}^3].$$

The relation of $r' [\text{g/cm}^3 \cdot \text{s}]$ to $r [\text{g/g} \cdot \text{hr}]$ is given by

$$r' = \frac{r}{3600} \rho_p,$$

where $\rho_p [\text{g/cm}^3]$ is char density. It follows then that

$$r' = \frac{k \rho_p}{3600} \left(\frac{T}{5.13 \cdot 10^{-4}} \right)^n \cdot C_s^n$$

or

$$k' = \frac{k \rho_p}{3600} \left(\frac{T}{5.13 \cdot 10^{-4}} \right)^n$$

Substituting for k' and C_s in eqn (B1), and noting that for a spherical particle $\frac{V_p}{A_p} = \frac{r_p}{3}$, one obtains

$$\Phi_n = \frac{r_p}{3} \left[\frac{(n+1)k \rho_p}{2\lambda D_e \cdot 3600} T \cdot 5.13 \cdot 10^4 \cdot P_{O_2}^{n-1} \right]^{1/2} \quad (\text{B6})$$

Char porosity can be expressed as a product of pore volume $V_o [\text{cm}^3/\text{g}]$ and char bulk density $\rho_p [\text{g/cm}^3]$. Therefore, $D_e = DV_o \rho_p / \tau^2$, and eqn (B6) can be re-written as

$$\Phi_n = \frac{r_p}{3} \left[\frac{(n+1)}{2\lambda DV_o \cdot 3600} 5.13 \cdot 10^4 \cdot k T \tau^2 \cdot P_{O_2}^{n-1} \right]^{1/2} \quad (\text{B7})$$

For the spherical geometry, the relationship between the effectiveness factor η and the Thiele modulus Φ_n is as follows [6],

$$\eta = \frac{3}{\Phi_n} \left(\frac{1}{\tanh \Phi_n} - \frac{1}{\Phi_n} \right) \quad (\text{B8})$$

Eqn (B7) cannot be used to evaluate Φ_n directly since the value of the intrinsic reaction rate k is unknown; Φ_n has to be expressed in terms of the measured reaction rate constant k_{exp} . Eqn (B1) can be re-written as

$$k' = \frac{9}{r_p^2} \frac{2\Lambda D_e}{(n+1)C_s^{n-1}} \Phi_n^2 \quad (\text{B9})$$

and from (B8) we have

$$k' = \frac{k'_{\text{exp}}}{\eta} = \frac{\Phi_n k'_{\text{exp}}}{3 \left(\frac{1}{\tanh \Phi_n} - \frac{1}{\Phi_n} \right)} \quad (\text{B10})$$

Equating right hand sides of (B9) and (B10) and making the necessary conversions from C_s to P_{O_2} and from k'_{exp} to k_{exp} , one obtains after rearrangement,

$$\frac{\Phi_n}{\tanh \Phi_n} = \frac{k_{\text{exp}}}{3600} \frac{r_p^2}{54} 5.13 \cdot 10^4 \cdot \frac{(n+1)\tau^2 T}{\Lambda D V_0} P_{O_2}^{n-1} + 1 \quad (\text{B11})$$

Eqn (B11) can be used to evaluate Φ_n and, from eqn (B8), also the effectiveness factor η . The maximum particle radius $r_p = 0.05$ cm was used in experiments involving the char pyrolysed at 1000°C , whereas the other chars were ground to the mesh size 140-325, which corresponds to the maximum radius of 0.005 cm. The values of k_{exp} and n were calculated from slopes and intercepts of plots presented in Figs 4.24-4.33 and in the case of single data points, for which no plots were available (e.g., for $T_p = 1400^\circ\text{C}$, $T = 450^\circ\text{C}$, $P_{O_2} = 760$ torr, see Table B2 below), the highest measured reaction order was assumed (i.e., 0.76) and k_{exp} was calculated using an appropriate reaction rate from Table A3. Pore volume was evaluated using data from Table A1, by means of linear interpolation or by assuming approximate values where data were not available. Knudsen diffusivity was calculated using eqn (B5a), and the pore radius of $5\text{\AA}$, $\tau = \sqrt{2}$, and $\Lambda = 3/8$ were assumed throughout the entire analysis. Molecular diffusivities turned out to be at least two orders of magnitude greater than D_k and thus D was assumed to be approximately equal to D_k (see eqn (B4)). The resulting values of the Thiele modulus, as well as the effectiveness factor, are listed in Table B2. It is clear that molecular and Knudsen diffusion did not affect kinetic measurements. In two cases ($T_p = 1000^\circ\text{C}$; $T = 350^\circ\text{C}$; $P_{O_2} = 3.9$ and 21.3 torr), transition from zone I to zone II is implied by somewhat lower values of η . Measured reaction rates are lower by only 10-15%, however, and, as it is evident from Fig. 4.28, reaction order determination was unaffected by Knudsen and ordinary diffusion.

It may be noted that for $r = 5\text{\AA}$, the Knudsen diffusion model may be suspect, and activated diffusion may be more appropriate. Nevertheless, the Knudsen model is assumed to apply here, since no information is available on activated diffusion. The analysis may be

viewed as biased against mass transfer limitations, by virtue of an assumption of the (generally faster) Knudsen diffusion rather than an activated diffusion process. It should be recalled, however, that this analysis asks if mass transfer is limiting on the scale of the particle of radius r_p . Because the particle is laced with macropores that feed the micropores, the actual value of a characteristic dimension in Φ_n may be smaller. Thus the analysis is conservative in addressing this particular question.

Suppose the pores that feed the micropores were very small, though still in the non-activated diffusion régime, could a mass transfer limitation be present? The answer is apparently that it could not. This does not mean, however, that the micropores in which diffusion is activated could not be subject to mass transfer limitations. Unfortunately, this question cannot be resolved at this time.

Some experimentally determined activated diffusivities are available in the literature, and for example Debelak [11] found that for the diffusion of CO_2 through the WYODAK lignite char at 6.1% burn-off, the ratio $D_{\text{act.}}/r_c^2$ was equal approximately 0.06 s^{-1} , where $D_{\text{act.}}$ is activated diffusivity and r_c is crystallite radius. If this ratio were similar for the diffusion of O_2 through phenolic resin char, then, using the data from Table B2 for $T = 350^\circ\text{C}$, and additionally assuming $n = 1$ and $r_c = r = 5 \text{ \AA}$, one obtains

$$\Phi_n = 1.78 \cdot \left\{ \frac{\frac{2.14 \cdot 10^{-3}}{(5 \cdot 10^{-2})^2}}{0.06} \right\}^{1/2} = 5,$$

which corresponds to $\eta \approx 0.5$. Despite crudeness of assumptions and general invalidity of applying this kind of data to different materials and different diffusing species, something can be learnt at least about the magnitude of the effect of activated diffusion.

Table B2 Effectiveness factors for phenolic resin char reactivities determined in this study.

$T_p = 1000^\circ\text{C}$							
$T [^\circ\text{C}]$	P_{C_2} [torr]	k_{exp} [g/(g·hr·torr n)]	n	D [cm 2 /s]	$\frac{\Phi_n}{\tanh\Phi_n}$	Φ_n	η
350	3.9	$6.69 \cdot 10^{-5}$	0.62	$2.14 \cdot 10^{-3}$	1.89	1.78	0.84
350	21.3	$6.69 \cdot 10^{-5}$	0.62	$2.14 \cdot 10^{-3}$	1.47	1.25	0.91
350	160	$6.69 \cdot 10^{-5}$	0.62	$2.14 \cdot 10^{-3}$	1.22	0.82	0.97
350	430	$6.69 \cdot 10^{-5}$	0.62	$2.14 \cdot 10^{-3}$	1.15	0.67	0.97
350	760	$6.69 \cdot 10^{-5}$	0.62	$2.14 \cdot 10^{-3}$	1.12	0.60	0.98
325	3.9	$1.15 \cdot 10^{-5}$	0.69	$2.10 \cdot 10^{-3}$	1.17	0.72	0.97
$T_p = 1111^\circ\text{C}$							
$T [^\circ\text{C}]$	P_{O_2} [torr]	k_{exp} [g/(g·hr·torr n)]	n	D [cm 2 /s]	$\frac{\Phi_n}{\tanh\Phi_n}$	Φ_n	η
350	760	$1.15 \cdot 10^{-5}$	0.76*	$2.14 \cdot 10^{-3}$	1.00	0.00	1.00
$T_p = 1243^\circ\text{C}$							
$T [^\circ\text{C}]$	P_{O_2} [torr]	k_{exp} [g/(g·hr·torr n)]	n	D [cm 2 /s]	$\frac{\Phi_n}{\tanh\Phi_n}$	Φ_n	η
400	760	$5.81 \cdot 10^{-7}$	0.76	$2.22 \cdot 10^{-3}$	1.00	0.00	1.00
300	3.9	$5.81 \cdot 10^{-7}$	0.76	$2.05 \cdot 10^{-3}$	1.00	0.00	1.00

$T_p = 1400^\circ\text{C}$							
$T [^\circ\text{C}]$	$\text{PO}_2 [\text{torr}]$	$k_{\text{exp}} [\text{g}/(\text{g}\cdot\text{hr}\cdot\text{torr}^n)]$	n	$D [\text{cm}^2/\text{s}]$	$\frac{\Phi_n}{\tanh\Phi_n}$	Φ_n	η
400	3.9	$5.58\cdot 10^{-5}$	0.66	$2.22\cdot 10^{-3}$	1.02	0.20	1.00
450	760	$4.78\cdot 10^{-4}$	0.76*	$2.31\cdot 10^{-3}$	1.01	0.05	1.00

* reaction order assumed to be 0.76

The following values of parameters were used in calculations: $\tau = \sqrt{2}$, $\Lambda = 3/8$, $r = 5\text{\AA}$;

(a) char pyrolysed at 1000°C : $B \approx 4.2\%$ $\Rightarrow V_O \approx 0.074 \text{ cm}^3/\text{g}$ (interpolated); $r_p \approx 0.05 \text{ cm}$;

(b) char pyrolysed at 1111°C : $B \approx 2\%$, $V_O \approx 0.015 \text{ cm}^3/\text{g}$ (assumed); $r_p \approx 0.005 \text{ cm}$;

(c) char pyrolysed at 1243°C : $B \approx 0\%$, $V_O \approx 0.015 \text{ cm}^3/\text{g}$ (assumed); $r_p \approx 0.005 \text{ cm}$;

(d) char pyrolysed at 1400°C : $B \approx 30.8\%$, $V_O \approx 0.33 \text{ cm}^3/\text{g}$; $r_p \approx 0.005 \text{ cm}$;

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Appendix C

COMPUTER PROGRAMMES

Two computer programmes were used to fit oxygen chemisorption data to the Elovich equation. One of them, written in Basic and run on a Macintosh personal computer, was used primarily to estimate starting values of a and b for the iterative procedure. This programme was particularly convenient due to a graphic representation of a fit displayed on the monitor.

The other programme was written in Fortran and executed using a VAX 11/730 computer. Most work was done using this computer.

Both programmes were based on the Gauss-Newton method, and data files for both programmes had the same layout:

Input Data

NDP -- number of data points,

t_0 -- time at which chemisorption begins ($t_0 = 0$ in most cases),

q_0 -- oxygen uptake at $t = t_0$ ($q_0 = 0$ in most cases),

$t,$	q
.	.
.	.
.	.

.

(NDP data points)

Initial Data

NK -- number of parameters (NK = 2 in the case of the Elovich equation),

P(1) -- starting value of parameter "1,"

$\delta(1)$ -- an incremental value of independent variable used in numerical determination of derivatives (not used in this work as the derivatives were evaluated by means of analytic expressions),

$\lambda(1)$ -- variable determining a step size during iterations (see the programme for details),

.

.

.

$P(NK)$

$\delta(NK)$

$\lambda(NK)$

Both programmes were executed until a maximum number of iterations was reached, unless they were aborted by the operator.

Computer programme used for numerical evaluation of the Elovich constants (Basic)

```

      DIM p(10),ss(10),s(10),F(200,10),xd(200),yd(200)
      DIM sd(10), delta(10),lambda(10)
      DIM g(10),G2(10,10),R(10),C(10),D(10)
WINDOW 4,"Graph",(10,0)-(210,150),1
WINDOW 1,"Iterations",(40,230)-(450,330),1
WINDOW 2,"INFO",(250,120)-(500,180),1
WINDOW(3),"Data Input",(250,40)-(500,80),1
WINDOW(3)
INPUT "Analytical (0) or Numerical soln. (1)";idir
INPUT "Enter the total # of iterations";imax
PRINT "Iteration limit is ";imax;
WINDOW(1)
      PRINT "The program is now reading in the data..."
INPUT "Enter the name of data file:";abc$
OPEN abc$ FOR INPUT AS #4
      INPUT #4,ndp
      INPUT #4, x0
      INPUT #4,Y0
      FOR i=1 TO ndp
      INPUT #4, xd(i),yd(i)
      NEXT i
      CLOSE #4
      PRINT

```

```

PRINT "The program is now reading in the init file..."
OPEN "INIT.DAT" FOR INPUT AS #3
INPUT #3,iout
INPUT #3,nk
FOR i=1 TO nk
  INPUT #3,p(i)
  INPUT #3,delta(i)
INPUT #3,lambda(i)
  pl(i)=p(i)
NEXT i
WINDOW(2):PRINT "Delta";"      "; "Lambda";"      "; "Parameter":FOR
i=1 TO nk:PRINT USING "#.#####  #.#####  ###.#####"
";delta(i);lambda(i);p(i):NEXT i:WINDOW(4)
CLOSE #3
GOSUB plot
PRINT
PRINT "The program is running...":PRINT
g(1)=1!
g(2)=1!
99  REM

IF iter>imax THEN maxf=1:GOTO 1000
iter=iter+1
IF iter MOD 10 = 0 THEN GOSUB plot
IF idir<>0 THEN GOTO 22
'Here lies the analytical routine...
FOR k=1 TO nk
s(k)=0!
g(k)=0!
FOR i=1 TO ndp
GOSUB model
s(k)=s(k)+((yd(i)-phi)^2)
GOSUB deriv
g(k)=g(k)+der
NEXT i
s2(k)=s(k)
p(k)=p(k)-g(k)*lambda(k)
NEXT k
GOTO 20
22  FOR k=1 TO nk
FOR i=1 TO ndp
  p(k)=p(k)-delta(k)/2!
  GOSUB model

```

```

        F(i,k)=phi
        s(k)=s(k)+((yd(i)-phi)^2)
        p(k)=p(k)+delta(k)
        GOSUB model
        F(i,k)=(phi-F(i,k))/delta(k)
        sd(k)=sd(k)+((yd(i)-phi)^2)
        p(k)=p(k)-delta(k)/2
100    NEXT i
        IF(s(k)=ss(k)AND iter>10) THEN loopf=1:GOTO 1000
        ss(k)=s(k):s2(k)=(s(k)+sd(k))/2
        g(k)=(sd(k)-s(k))/delta(k)
        s(k)=0!
        sd(k)=0!
        p(k)=p(k)-(g(k))*lambda(k)
200    NEXT k
20    REM
        PRINT " ITERATION = ";iter
        FOR kk=1 TO nk
            PRINT "Parameter #";kk;
        PRINT "=",p(kk)," deriv =";g(kk)
        PRINT "Objective ";s2(kk)
        NEXT kk
        GOTO 99
1000    REM
2000    REM
        file3$=FILES$(0,"Output data file?")
        IF file3$="" THEN GOTO out
        OPEN file3$ FOR OUTPUT AS #3

        PRINT #3," ITERATION = ";iter
        FOR kk=1 TO nk
            PRINT #3,"Parameter #";kk;
        PRINT #3,"=",p(kk)," deriv =";g(kk)
        PRINT #3, "Objective ";s2(kk)
        NEXT kk
        CLOSE #3
        out:
        WINDOW(3):PRINT: IF loopf=1 THEN PRINT "Objective not
        changing..."
        IF maxf=1 THEN PRINT "Iteration limit reached..."
        WINDOW(1)
        GOSUB plot
        PRINT " ITERATION = ";iter

```



```

    FOR kk=1 TO nk
      PRINT "Parameter #";kk;
    PRINT "=";p(kk)," deriv =" ;g(kk)
    PRINT "Objective " ;s2(kk)
  NEXT kk

```

```

tmr: GOTO tmr
plot: 'Plot subroutine
WINDOW(4)
yscal=95/yd(ndp)
CALL MOVETO (xd(1)*16,120-yd(1)*yscal)
FOR i=2 TO ndp:CALL LINETO(xd(i)*16,120-yd(i)*yscal):NEXT i
x=xd(1):GOSUB model2:CALL MOVETO (xd(1)*16,120-phi*yscal)
FOR x=(xd(1)) TO (xd(ndp)) STEP .1
  GOSUB model2:CALL LINETO((x)*16,120-phi*yscal)
NEXT x: WINDOW(1)
RETURN

```

```

model:
  phi=p(2)*LOG((xd(i)-x0)*p(1)+1!)+Y0
  RETURN

```

```

model2:
  phi=p(2)*LOG(((x)-x0)*p(1)+1!)+Y0
  RETURN

```

```

deriv:
  IF k=1 THEN GOSUB deriv1
  IF k=2 THEN GOSUB deriv2
  RETURN

```

```

deriv1:
  der=2!*(p(2)*LOG((xd(i)-x0)*p(1)+1!)+Y0-yd(i))*p(2)*(xd(i)-
x0)/(p(1)*(xd(i)-x0)+1!)
  RETURN

```

```

deriv2:
  der=2!*(p(2)*LOG((xd(i)-x0)*p(1)+1!)+Y0-yd(i))*LOG(p(1)*(xd(i)-
x0)+1!)
  RETURN

```

Computer programme used for numerical evaluation of the Elovich constants (Fortran)

PROGRAM GOWSNUTN

```

C
C   This program employs the Gauss-Newton method to
C   find the parameters to fit a user specified
C   function to a set of data points. The routine
C   is initially set up for one dependent and one
C   independent variable.
C
C   The following is a list of variables used in the
C   program:
C   -----
C   -----
C   F(I,K)   = d (Function at X(i))/d (parameter(k))
C   S(K)     = The "least squares" sum of the differences squared
C   P(K)     = Parameter(k)
C   DELTA(K) = The delta value used for each parameter for
C               derivative
C   G(K)     = d S(K)/d P(k)
C   G2(K)    = 2 x the sum of (F(i,k) x F(j,k)) over all k
C   XD(K)    = Independent data points
C   YD(K)    = Dependent data points
C   C(K),D(k)= Constraints on each parameter
C   -----
C   PHI      = User specified function defined in subroutine model
C   NK       = The number of parameters
C   NDP      = The number of data points being fit
C   -----
C
C   IMPLICIT REAL*8 (A-H,O-Z)
C   REAL*8 LAMBDA
C   character*1 nul
C   DIMENSION P(10),ss(10),S(10),F(200,10),XD(200),YD(200)
C   DIMENSION SD(10), DELTA(10),LAMBDA(10),P1(10),S2(10)
C   DIMENSION G(10),G2(10,10),R(10),C(10),D(10)
C
C DATA STATEMENTS

```

```

WRITE(5,*)'Analytical(0) or numerical (1) solution?'
READ(5,*)IDIR
WRITE(5,*)'Enter the maximum number of iterations:'
READ(5,*)IMAX
WRITE(5,*)'The program is now reading in the data...'
OPEN(UNIT=4,NAME='58t.DAT',TYPE='OLD')
READ(4,*)NDP
READ(4,*)X0
READ(4,*)Y0
WRITE(5,*)'# of data points = ',NDP
WRITE(5,997)X0
WRITE(5,998)Y0
WRITE(5,*)'The data points are:'
DO 107 I=1,NDP
  READ(4,*)XD(I),YD(I)
  WRITE(5,999)XD(I),YD(I)
107 CONTINUE
997 FORMAT(3X,'t0 = ',F15.8)
998 FORMAT(3X,'q0 = ',F15.8)
999 FORMAT(2F15.3)
CLOSE(UNIT=4,DISPOSE='SAVE')
WRITE(5,*)
WRITE(5,*)' The program is now reading in the init file...'
11 FORMAT(I2)
OPEN(UNIT=6,NAME='INIT.DAT',TYPE='OLD')
READ(6,*)IOUT
READ(6,*)NK
WRITE(5,*)'Initial values are:'
DO 5 I=1,NK
  READ(6,*)P(I)
  WRITE(5,*)'P',I,' = ',P(I)
  READ(6,*)DELTA(I)
  WRITE(5,*)'DELTA',I,' = ',DELTA(I)
  READ(6,*)LAMBDA(I)
  WRITE(5,*)'LAMBDA',I,' = ',LAMBDA(I)
  P1(I)=P(I)
5 CONTINUE

CLOSE(UNIT=6)
OPEN(UNIT=6,NAME='OUTPUT.DAT',TYPE='NEW')
nul=char(0)
WRITE(5,*)
WRITE(5,*)nul,' The program is running'

```

```

      G(1)=1.0D0
      G(2)=1.0D0
99    CONTINUE
      IF (ITER.GT.IMAX) GO TO 1000
      ITER=ITER+1
      IF (IDIR.GT.0) GO TO 22
C
C    The analytical routine
C
      DO 10 K=1,NK
      S(K)=0.0D0
      G(K)=0.0D0
      DO 15 I=1,NDP
      CALL MODEL(PHI,P,NK,XD(I),YD(I),X0,Y0)
      S(K)=S(K)+(YD(I)-PHI)**2.0D0
      IF(K.EQ.1) GO TO 17
      DER=2.0D0*(P(2)*LOG((XD(I)-X0)*P(1)+1.0D0)+Y0-YD(I))*
$ LOG(P(1)*(XD(I)-X0)+1.0D0)
      GO TO 18
17    DER=2.0D0*(P(2)*LOG((XD(I)-X0)*P(1)+1.0D0)+Y0-YD(I))*
$ P(2)*(XD(I)-X0)/(P(1)*(XD(I)-X0)+1.0D0)
18    G(K)=G(K)+DER
15    CONTINUE
      S2(K)=S(K)
      P(K)=P(K)-G(K)*LAMBDA(K)
10    CONTINUE
      GO TO 200
22    CONTINUE
C
C
C    Numerical routine
C
C    Loop to calculate first derivative of S
C
C
C    Test for convergence
C
408    FORMAT(' PARAMETER(' ,I2,' ) = ',D15.7,' First derivative
='D15.7)
410    FORMAT('/ # OF ITERATIONS = ',I7)
      DO 200 K=1,2
C

```

C Future convergence test (If G=0 then extremum found for partial deriv.)

C

C IF(G(K).EQ.0.0D0)GOTO 200

DO 100 I=1,NDP

P(K)=P(K)-DELTA(K)/2.0D0

CALL MODEL(PHI,P,NK,XD(I),YD(I),X0,Y0)

F(I,K)=PHI

C WRITE(6,105)P(K),S(K)

C105 FORMAT(' P = ',D15.7,' SUM =',D15.7)

S(K)=S(K)+((YD(I)-PHI)**2.0D0)

P(K)=P(K)+DELTA(K)

CALL MODEL(PHI,P,NK,XD(I),YD(I),X0,Y0)

F(I,K)=(PHI-F(I,K))/DELTA(K)

SD(K)=SD(K)+((YD(I)-PHI)**2.0D0)

P(K)=P(K)-DELTA(K)/2.0D0

100 CONTINUE

if(s(k).eq.ss(k))goto 1000

ss(k)=s(k)

S2(K)=(S(K)+SD(K))/2.0D0

199 FORMAT(' Objective = ',D15.8)

G(K)=(SD(K)-S(K))/DELTA(K)

S(K)=0.D0

SD(K)=0.D0

P(K)=P(K)-(G(K))*LAMBDA(K)

200 CONTINUE

if (real(iter)/real(iout).eq.iter/iout)WRITE (5,410)ITER

C if (real(iter)/real(iout).eq.iter/iout)write(6,410)iter

DO 409 KK=1,2

if (real(iter)/real(iout).eq.iter/iout)WRITE(5,408)KK,P(KK),G(KK)

IF(REAL(ITER)/REAL(IOUT).EQ.ITER/IOUT) WRITE

(5,199)S2(KK)

409 CONTINUE

C

C Loop to calculate approximation to second derivative

C $G2 = dd(S)/dK(i)dK(l) = -2 (SUM) \text{ eps } dd(F)/... + 2 (SUM)$

C $[d(F)/dK(i)][d(F)/dK(l)]$

C

C

C R = The inverse of G2

C SUBROUTINE SIMUL(N,A,X,EPS,INDIC,NRC)

C

C CALL SIMUL(NK,G2,R,1.D-18,-1.D0,10)

```

C
C   FIND NEW PARAMETERS
C
      GOTO 99
1000  CONTINUE
C
C   ROUTINE COMPLETED AND CONVERGENCE FOUND !!
C
C   WRITE (6,1010)SG
1010  FORMAT(' FINISHED SUCCESSFULLY! ',D15.7)
2000  CONTINUE
      write(5,*) ' The program is completed.'
      END

      SUBROUTINE MODEL(PHI,P,NK,X,Y,X0,Y0)
C
C   SUBROUTINE FOR USER DEFINED FUNCTION
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION P(NK)
      PHI=P(2)*DLOG(P(1)*(X-X0)+1.0D0)+Y0
      RETURN
      END

```

The following programme was used to carry out a numerical search for best parameter sets characterizing thermal annealing of phenolic resin chars. Data were entered directly into the programme as R(1), R(2), R(3), and R(4), no matter whether reactivities or ASA's were considered. The parameters were varied automatically in the following ranges:

$$\begin{aligned}
 k_A &= 10^6 - 10^{13} \text{ s}^{-1} \\
 E_A &= 30 - 100 \text{ kcal/mol} \\
 \sigma &= 5 - 30 \text{ kcal/mol.}
 \end{aligned}$$

```

PA1=.254829592#
PA2=-.284496736#
PA3=1.421413741#
PA4=-1.453152027#

```

```

PA5=1.061405429#
PP=.3275911#
DEF FNPT(X)=1/(1+PP*X)
DEF FNERF(TX,X)=1-
(PA1*TX+PA2*TX^2+PA3*TX^3+PA4*TX^4+PA5*TX^5)*EXP(-X*X)
MC=.056
MH=.056
RG=1.987
TI=7200!
D=.5
DIM T(5),R(5),A(5),B(5),XC(5),YC(5),S(5),X0(5),G(5)
T(1)=1273!
T(2)=1384!
T(3)=1516!
T(4)=1673!
R(1)=28.4
R(2)=14.3
R(3)=8.6
R(4)=4.6
OUTER:
  FOR IK=13 TO 6 STEP -1
    K0=10!^IK
    LPRINT "K0=";K0; "1/SEC"
    FOR IE=30 TO 100 STEP 5
      LPRINT
      LPRINT "E0=";IE;"KCAL/MOL"
      E0=IE*1000!
      IL=IE/2
      FOR IS= 5 TO IL STEP 5
        SIG=IS*1000!
        FOR I=1 TO 4
          G(I)=1.414*SIG/(RG*T(I))
          X0(I)=E0/(RG*T(I))
          A(I)=K0*T(I)*(1/MH+1/MC)
          B(I)=K0*TI
          CALL ROOT (I,A(I),B(I))
          YC(I)=(XC(I)-X0(I))/G(I)
          PRINTYC(I)
          JA=ABS(YC(I))
          JJ=YC(I)/JA
          TX=FNPT(JA)
          S(I)=.5*(1-JJ*FNERF(TX,JA))
        NEXT I
      NEXT IS
    NEXT IE
  NEXT IK

```

```

      SSE=((S(2)/S(1))/(R(2)/R(1))-1!)^2+((S(3)/S(1))/(R(3)/R(1))-
1!)^2+((S(4)/S(1))/(R(4)/R(1))-1!)^2
      LPRINT "IS=";IS;" SSE=";SSE
    NEXT IS
  NEXT IE
NEXT IK
SUB ROOT(J,QA,QB) STATIC
  SHARED XC()
  XC(J)=25!
  DIFF=1!
  WHILE DIFF>.0001
    F=(QA/XC(J)+QB)*EXP(-XC(J))-.5
    FP=-(F+.5)-(QA/XC(J)^2)*EXP(-XC(J))
    XNEW=XC(J)-F/FP
    DIFF=ABS(XC(J)-XNEW)
    XC(J)=XNEW
  WEND
END SUB

```


Appendix D

OPERATION INSTRUCTIONS

D.1 ELEMENTAL ANALYSER OPERATOR GUIDE

1. Are the correct oxidation and reduction tubes for N-C-H analyses in place?
2. From a cold start, check the following:
 - helium tank has sufficient pressure to run for at least 48 hours (500 psi or more),
 - helium supply pressure set to 18 psi,
 - oxygen supply pressure set to 25 psi,
 - power on: allow furnace to heat to 950°C on combustion side and to 650°C on reduction side,
 - detector on: press detector reset: wait 4 hours before using,
 - allow system to flush overnight if power has been off.
3. From a warm start, check the following:
 - meter selector readings: oven = 75°C; reduction = 650°C; combustion = 950°C,
 - detector output set to "A",
 - attenuations: Hydrogen x 1: Carbon 0: Nitrogen x 1,
 - fine zeros centred,
 - extended combustion set to "4,"
 - calculator interface power on,
 - microbalance controller power on,

4. Turn on the calculator and press "CLEAR". Press "LEARN" and enter the programme posted on the wall. Press "LEARN" again to exit the programming mode.
5. If you have not established a calibration for the expected concentrations of nitrogen, carbon, or hydrogen in your samples, or for the particular sample mass range you will use, prepare your calibration sample(s) while conducting your initial blank run series.
6. Before starting a run, always check the individual detector outputs by selecting "N", "C", and "H" on the Detector Output knob and reading the value on the calculator interface display. These should be positive values in the range of 400-600 microvolts. If necessary, adjust the coarse gain pots on the upper (inside) control panel of the instrument, allow a few minutes settling time, and return the Detector Output knob to "A".
7. To begin a run, press the "START" buttons on both the instrument and the calculator. At about 2.75 minutes into the run (on programmer wheel) the inject light is supposed to come on and the programme to wait until you inject the ladle and press the "INJECT-COMBUST" button before continuing. This does not always happen, so you should be prepared to inject the ladle at the 2.75 minute point. Ladle injection (and later withdrawal) is performed with a magnet. When injecting, position the ladle such that the bulb containing the magnet is just outside the high heat zone shroud (the circular metal collar protruding from the side of the furnace). About 5 minutes into the run, the programmer will stop and wait for pressure to build in the sample mixing volume, then continue on its own. If the inject light comes on at this time, press it. At about 5.5-6.0 minutes into the run, the detector output will scan the zero level values of nitrogen, carbon, and hydrogen and the calculator will print each twice. During this time, check the calculator interface display to be sure each value is positive and greater than 100 microvolts. You should see large value spikes (switching noise) between the readings for each element. When the zero level readings have finished printing out, withdraw the ladle to its original position. At about 10-11 minutes into the programme, the detector output will again scan the sample level values for each element, and the calculator will print each reading three times. Press the calculator "STOP" and "CLEAR" buttons to put it in the immediate mode.

8. Run two or more ladle blanks to establish the blank values for nitrogen, carbon, and hydrogen. The blank values are the differences between the detector output during the zero level readings versus the detector output during the sample level readings. For very accurate work, the blank values should be well stabilized, reproducible to within a few microvolts. To evaluate the blank readings, average the sample level readings for each element, average the zero level readings for each element, and subtract the zero level value from its corresponding sample level value. You should be able to eyeball the average values, perform the subtractions on the calculator, and print the results on the tape for a permanent record. The final printed tape will look something like this:

TITLE	(optional)
489.	(N zero level)
487.	(N zero level)
513.	(C zero level)
512.	(C zero level)
523.	(H zero level)
523.	(H zero level)
3.	(calculator returns to scan mode)
566.	(N sample level)
566.	(N sample level)
564.	(N sample level)
600.	(C sample level)
601.	(C sample level)
599.	(C sample level)
607.	(H sample level)

- 607. (H sample level)
- 608. (H sample level)
- 5. (calculator returns to scan mode)
- (programme end: space)
- 77. (N blank value) or (N sample value)
- 87. (C blank value) or (C sample value)
- 84. (H blank value) or (H sample value)

To print titles and other information on the tape, hold down the "ALPHA" key while entering characters subscripted on the keyboard.

9. When you are satisfied that the blank values are stabilized (they should also each be less than 200 microvolts) you can begin your calibration or sample analyses.

CALIBRATION: Weigh out your calibration sample, using a sample mass similar to that which you intend to use for your unknowns but not exceeding 3000 μg , into a platinum boat or nickel capsule and record the mass. Remove the plug at the end of the quartz tube and extract the ladle. Carefully transfer the boat or capsule to the ladle (except behind magnet) with your fingers. Replace the ladle inside the quartz tube and reseal the ladle port. Wait two minutes for the system to flush before starting the run. When the run is finished, calculate the calibration constants as follows:

First determine the mass of each element in the sample from its formula weight percentages or molecular formula. Next determine the detector response of each element as ((X sample value) - (X blank value)) microvolts. Next divide the response by its corresponding elemental mass to obtain the response constant K_X in $\mu\text{v}/\mu\text{g}$. A diskette with software for assisting in these calculations is available for use with the Apple computers.

Run at least two ladle blanks between calibration runs to clean up the system. Repeat the calibration until you have good reproducibility and can determine the range of error present.

SAMPLE RUNS: Weigh out your unknown sample as described above. Attempt to maintain the sample mass in a close range around the mass of the calibration samples (within 2%). Transfer the sample to the ladle as described, seal the port, wait two minutes, and start the run. Calculate the elemental masses as follows:

Response ((X sample value) - (X blank value)) in μv divided by K_X in $\mu\text{v}/\mu\text{g}$ = mass of X in μg .

The mass of oxygen is taken as the difference of the sample mass and the sum of elemental masses for N, C, and H unless ash is visible in the boat after combustion, in which case you must determine the mass of ash before determining oxygen. The software will assist you in these calculations, as well as determining elemental ratios and printing results.

For survey work, only one intermediate blank run is necessary between samples. For work requiring high accuracy, two or more blank runs should be made between samples to clean up the system and the ladle.

10. Do not shut down the instrument if it will be used again within a week's time unless the gas supplies will not last. When you are finished for the day, turn off the calculator, the calculator interface, and the balance controller.

MODEL 240B ELEMENTAL ANALYZER OPERATING SEQUENCE

The steps to be performed by the analyst for operation of the Model 240B are numbered below. In the programmed portion of the sequence the instrument functions are listed at the points in the program at which they occur, with the readings that should appear on the Programmer Index Wheel when they happen. Steps and instrument functions in bold type are those which must occur before other actions are initiated.

1. Make the following initial control settings:
 - a. POWER Switch - DETECT
 - b. Programmer Index Wheel - 0
 - c. Manual Chart Drive Switch (Recorder) - Off
 - d. METER SELECTOR Switch - as desired
 - e. TEMPERATURE Controls:
 - COMBUST - 6 (for 950° C); REDUCE - 5 (for 650° C)

- f. ATTENUATION Switches:
 - M - X1;
 - C - 0;
 - N - X1
- g. ZERO Controls:
 - M, C, N - as desired

	PROGRAMMER DIAL READING ¹	
2. Push START button	0	START lamp on. Program starts.
	2 min.-20 sec.	
3. Move ladle into combustion zone (insert in ladle to edge of high heat furnace cover)	2 1/4 +	INJ-COMB lamp on. START lamp out. Program stops.
	Period determined by operator	
4. Push INJ-COMB button.	2 1/4 +	START lamp on. INJ-COMB lamp out. Program restarts.
See Note 2	30 sec.	
4a. For extended combustion period, turn the EXT-COMB switch to any desired setting (1, 2, or 4 minutes) after pushing the INJ-COMB button.	2 1/4 +	START lamp out. Program stops.
	Period determined by operator	
4b. After the extended combustion period concludes, the program resumes.	2 1/4 +	START lamp on. Program restarts.
	1 min.-20 sec.	
	3 1/4 -	High heat on.
	1 min.	
	4 1/4 -	High heat off.
	20 sec.	
	5	START lamp off. Program stops.
	60 to 180 sec. (Determined by He pressure)	
	5	START lamp on. Program restarts.
	70 sec.	
5. Return ladle into cool zone of combustion tube. Set N ZERO control as desired ^{2,3} .	5 1/4 +	READOUT lamp on. Recorder starts. N bridge connected.
	75 sec.	
6. Set C ZERO control as desired ^{2,3} .	5 1/4 -	N bridge disconnected. C bridge connected.
	25 sec.	
7. Set M ZERO control as desired ^{2,3} .	6 1/4 -	C bridge disconnected. M bridge connected.
	20 sec.	
	6 1/4 -	N bridge disconnected. Recorder stops. READOUT lamp off.
	3 1/2 min.	
8. Set H ATTENUATION switch. Note attenuation on chart.	10	READOUT lamp on. Recorder starts. H bridge connected.
	35 min.	
9. Set C ATTENUATION switch. Note attenuation on chart.	10 1/2 +	N bridge disconnected. C bridge connected.
	35 sec.	
10. Set M ATTENUATION switch. Note attenuation on chart.	11 1/4 -	C bridge disconnected. M bridge connected.
	30 sec.	
	11 1/4 -	N bridge disconnected. READOUT lamp off. Recorder off.
	20 sec.	
	0	Program stops. START lamp off.

END OF PROGRAM

NOTES

¹Dial readings which end in "+" represent a dial position 5 sec. after that indicated by the number; a "-" represents a dial position 5 sec. earlier than that shown. ²These zero adjustments are a compensation bridge longer than the programmed 2-minute, 20 second period is required in the EXT-COMB switch is set to 0. If the program continues uninterrupted and the START lamp remains on. ³It will usually be found useful to set the ZERO controls for a % to 10 division upscale displacement of the recorder pen above chart zero. This setting allows for when re-analyzing samples with the same sample material and similar sample size, the "penalty" may be recorded with the ATTENUATION section of the procedure required for the "ready".

MODEL 240B OPERATING SUMMARY

- 1) Make the following preliminary control settings.
 - a) POWER Switch - DETECT
 - b) Programmer Index Wheel - 0
 - c) DET RESET Lamp - OFF
 - d) COMBUST Control - 950°C
 - e) REDUCE Control - 650°C
 - f) H and N ATTENUATION Switch - X1
 - g) C ATTENUATION Switch - 0
 - h) EXT-COMB Switch - as desired
 - i) If a 1 mV recorder is being used, the CX10 pushbutton lamp should be lit. If a Programmable Calculator System A is used, the CX10 lamp should be off.
 - j) DETECTOR OUTPUT Switch - A

Note: The Detector Bridge signals should result in a 25% of full scale recorder deflection or, with the Programmable Calculator System A, a 500-1000 mV readout.

- 2) Purge oxygen line daily for 10 minutes by first removing the inlet fitting and installing the flow fitting plug (P-E Part No. 240-0101). Turn the programmer index wheel to setting 2 for 10 minutes. Turn the programmer index wheel to setting 1, and reinstall the standard inlet fitting. Leave the programmer index wheel at this setting for 3 minutes, then return the programmer index wheel to zero.
- 3) Before proceeding with the operating sequence, the Model 240B must be leak free and it must be conditioned. To condition the instrument, run blanks, 2 mg samples, and standards as described in Section 3 of the manual.
- 4) Perform the following procedure:
 - a) Accurately weigh the (1-3 mg) sample in the sample boat and place the sample boat in the ladle. Place the sample in the cool zone of the combustion tube.
 - b) Press the START button. The START lamp should light.
 - c) Two minutes and 20 seconds after the START lamp lights, the INJ-COMB lamp should come on and the START lamp should go off. Place the sample in the combustion zone.
 - d) Press the INJ-COMB button and the START lamp comes on. In approximately 2.7 minutes the START lamp goes off. 60 to 180 seconds later the START lamp comes on again.
 - e) Twenty seconds after the START lamp comes on the READOUT lamp comes on. When the READOUT lamp comes on, retract the ladle to the cool position.
 - f) The zeroes are scanned automatically and the READOUT lamp then goes off. Three and one half minutes later the READOUT lamp comes on again and the readout signals are recorded.
 - g) Attenuate the signals, using the C, H, and N ATTENUATION switches, as required. Less than two minutes after the READOUT lamp comes on it goes off. The START lamp goes off, and twenty seconds later the program is concluded.

Note: No attenuation is required if the Programmable Calculator is used.

D.2 PROCEDURE FOR OBTAINING ADSORPTION-DESORPTION ISOTHERMS

Before you start the experiment, you must decide on the carrier gas and adsorbent. The flow controller is versatile and can be used with two carrier gases and several adsorbents. The flow controller has two digital flow meters and each one has the capability of giving 20 cm³/min (base flow rates are set for He as carrier gas and N₂ as adsorbent. The instrument electronically corrects the density variations of gases. (With CO₂ you may get a maximum flow rate of 14.70 cm³/min.) In most cases, a total flow rate of 20 cm³/min is adequate and if needed you may use the maximum flow rate available to set your P/P₀ values. You may calculate the flow rates needed for different P/P₀'s, using the values given below:

P/P ₀	<u>Nitrogen (carrier gas -- He)</u>	
	V _{He} [cm ³ /min]	V _{N2} [cm ³ /min]
1.00	0.00	20.00
0.96	0.42	19.58
0.95	0.62	19.38
0.90	1.64	18.36
0.85	2.66	17.34
0.80	3.68	16.32
0.75	4.70	15.30
0.70	5.72	14.28
0.65	6.74	13.26
0.60	7.76	12.24
0.55	8.78	11.22
0.50	9.80	10.20
0.45	10.82	9.18
0.40	11.84	8.16
0.35	12.86	7.14
0.30	13.88	6.12
0.25	14.90	5.10
0.20	15.92	4.08
0.15	16.94	3.06
0.10	17.96	2.04
0.05	18.98	1.02

P/P ₀	<u>Carbon dioxide (carrier gas -- He)</u>	
	V _{He} [cm ³ /min]	V _{CO2} [cm ³ /min]
0.300	12.99	6.01
0.200	14.99	4.01
0.100	17.00	2.00
0.075	17.50	1.50
0.060	17.80	1.20
0.045	18.10	0.90
0.030	18.40	0.60
0.015	18.70	0.30

After you have adjusted the flow rates, switch on the Quantasorb instrument by positioning the OFF/ON switch to "ON". Now the instrument is ready for use and you should let it warm up for an hour or so.

Now, check the following on the Quantasorb:

1. Check the gas flow by placing the plastic tube (the one nearest you on the left hand side) in a beaker or water. You should observe bubbles in the beaker.
2. The float on the M3 flowmeter (upper pane, Fig. D1) should roughly be at the centre of the flow meter.
3. Make sure that the "IN" and "OUT" septa located on the lower left panel are not leaking. If you see holes in a septum, replace it with a new one.
4. Finally, check the gas syringes and needles.

If you are convinced that the instrument is working satisfactorily, you may proceed to prepare a sample for analysis.

Preparing a sample for analysis:

Quantasorb possesses an outgassing station on the left-hand side of the instrument. This can be used either to purge the sample or to outgas a sample in the 25-350°C range. (Never exceed 400°C since you may melt the U-tube.) Outgassing is carried out by placing a small amount of sample in the U-tube and heating it to the desired temperature with a slowly flowing purge gas. Heating is accomplished by placing a heating mantle around the U-tube and adjusting the temperature control on the side of the arm. Plug the heating mantle into the power outlet located on the left side of the instrument. Also insert the thermocouple lead into the jack adjacent to the power outlet. You may adjust the flow rate through the cell with N₄ (located on the lower left panel).

Unless it is absolutely essential, never exceed a temperature of 350°C. Of course, the outgassing temperature should be low enough to prevent chemical reaction. In general, it is safer to outgas at a lower temperature for a longer period of time.

If you do not intend to outgas the sample, just purge the sample for about 15 minutes prior to analysis.

Now the sample is ready for the construction of desorption-adsorption isotherms.

Experimental procedure

Remove the U-tube either after outgassing or purging and place it in the analysis station on the front of the machine. At the same time fill the dewar with liquid N₂ (for CO₂ use dry ice and acetone). Adjust the flow rates such that P/P_0 is 1.0.

At this point, allow the sample to equilibrate at the set P/P_0 (1.0.). During this equilibration, adjust the zero, threshold, bridge current and attenuation values.

The bridge current reading should be set at 150 mA.

Set the attenuation at 128 unless you suspect that the sample does not have a high surface area. If that is the case, set the attenuation at 64 and adjust the zero and threshold values.

Zero is adjusted by using the zero adjust control (R14) on the lower right panel. You must flip the S-7 switch (see Fig. D2) located on the lower right panel to zero and adjust the zero position on M-2. After zeroing M-2, switch S-7 to count. This setting need not be changed throughout the analysis. Now use coarse zero (P-2) and fine zero (P-1) knobs to readjust the zero if necessary. These are located on the lower left panel.

The threshold value should be set with a threshold knob (R26) after flipping the R14 switch into the "COUNT" position. This requires a little practice as you may be confused as to whether you should use the upper or lower divisions on meter M-2. The threshold value should be as low as possible but without considerable tails in the integrated signal. Try to use upper divisions on M-2. It is difficult to state exactly where the threshold should be since it is dependent upon the attenuation setting. Attenuation settings 32, 16 and 8 are quite noisy, in increasing order, and your threshold setting should compensate for that. Otherwise you may count the noise as sample signal. You may have to repeat the experiment (which is a very tedious task) if you are not careful with the threshold setting. The threshold setting should not be changed during an experiment. If the value has changed during an experiment, you must set it to the original position.

It is a good practice to check the threshold, zero and bridge current settings every 2 hours. They may change as you do the experiment and you should bring them to their original settings.

If for any reason you find that the threshold value needs to be changed, you must repeat the whole set of measurements at the new threshold value.

$$P/P_0 = 1.0$$

After the above settings are completed, immerse the sample U-tube in a liquid nitrogen-filled dewar. Clamp the dewar to the bar on the front of the cabinet. At this point the polarity switch should be in the "Ads" position. It is possible that you may not notice any appreciable adsorption signal. You need not be alarmed about it. Now adjust the flow rates for a P/P_0 of 0.96 or to any other value that you desire. (After a while you will notice a signal on the meter and the counter will start counting if the polarity switch is on "Des". The green light will be on since the needle would have crossed the set threshold value. This is due to the desorption of adsorbent from P/P_0 of 1.0 to 0.96.)

$$P/P_0 = 0.96$$

Desorption

Equilibrate the sample at this flow rate for five minutes. Flip the "Ads/Des" switch to "Des". Now remove the liquid nitrogen dewar and immerse the U-tube in a beaker of room temperature water. The purpose of immersing the cell in the water is to bring the cell back to ambient temperature rapidly so that the "sample" rotameter float "M3" returns to its initial reading prior to the integrator accumulating any counts. This procedure guarantees maximum accuracy by preventing integration under a varying flow rate condition. After a couple of minutes you will notice a desorption signal. Using the attenuator settings, place the signal peak about 50% of full scale. When the desorption signal is complete record the integrator number on the data sheet (V_{Des}).

Calibration

Using the precision gas sampling syringes* withdraw gas from the "OUT" septum (and clean by flushing the syringe twice) and inject it into the "IN" septum. Note the volume injected (V_{Inj}) and the integrator reading on the data sheet (V_{Cal}). Overshooting is not permissible. The needle on M-2 should not go off the scale.

* Note: During calibration isolate the sample cell by using toggle valve V_6 . Rotate by 90° and the flow will bypass the sample.

To learn more about the calibration procedure read section VI of the Quantasorb manual (pages 21-23).

Adsorption

Let the toggle valve V_6 point towards you. Flip the polarity switch to "Ads". After completing the calibration, immerse the cell in the liquid nitrogen dewar at the same P/P_0 value. Observe the adsorption signal and, using the attenuator, place the signal peak at about 50% of full scale. Note the reading on the data sheet (V_{Ads}).

When the polarity switch is at "Ads", you cannot calibrate. Calibration is possible only during desorption and only when the polarity switch is in the "Des" position. The previous calibration on desorption should be adequate. If you would like you can calibrate after desorbing and isolating the sample cell.

$$P/P_0 = 0.90$$

To obtain desorption-adsorption signals you should follow the above procedure. Now reduce P/P_0 from 0.96 to 0.90 or to any desired P/P_0 value. It is important that you change the flow rates when the sample is immersed in liquid nitrogen dewar. This assures that you are on a desorption cycle. Let the sample equilibrate for another five minutes at this P/P_0 value. Now adjust "zero" on the meter using "coarse" and "fine" zero knobs. Flip the polarity switch to "Des". Remove the liquid nitrogen dewar and immerse the sample cell in a water beaker. Observe the desorption signal and record the integrator number on the data sheet. This value is V_{Des} at a P/P_0 of 0.90 (or another set value).

Calibrate the signal by isolating the sample cell and injecting the sample (V_{Inj}) from the "OUT" septum into the "IN" septum. Record the integrator number on the data sheet. This value is V_{cal} at P/P_0 of 0.90 (or at the set value).

Note: The calibration value should agree with the sample signal (V_{Ads} or V_{Des}) within $\pm 10\%$. If it does not agree, change the injection volume until the reading is within $\pm 10\%$.

To obtain an adsorption signal, reverse the polarity and point the toggle valve V_6 towards you. Immerse the sample cell in liquid nitrogen dewar and obtain the adsorption signal, V_{Ads} . Calibrate again if you wish to, and proceed to the next P/P_0 value.

$$P/P_0 = 0.80$$

Change the polarity again, point V₆ towards you and immerse the sample cell in the liquid nitrogen dewar. Change the P/P₀ to the next lower value, say 0.80. After equilibrating at 0.80, desorb and calibrate as indicated above. Note the readings (V_{Des} and V_{Cal}). Adsorb again and obtain V_{Ads} as outlined for P/P₀'s of 0.96 and 0.90. Now you have obtained V_{Ads}, V_{Des}, V_{Cal}, and V_{Inj} readings. Repeat the above steps until you reach a P/P₀ value of 0.0. It is advisable to have at least 10 data points to construct a desorption-adsorption curve. The procedure we just followed starts with a purely adsorbed sample (100% adsorbate). We decreased the adsorbent concentration slowly, i.e., desorbed and obtained the values needed to construct a desorption-adsorption isotherm.

From the above data, you can construct desorption-adsorption isotherms. The data can also be used to calculate surface areas and to draw a pore size distribution curve.

We have a programme which can be run on an APPLE computer to calculate pore size distributions and surface areas of the powdered sample. You should go through the Quantasorb manual to understand the procedures involved in calculating pore volumes and surface areas and then use the programme. It is advisable that you go through the calculations manually at least once before using the programme.

The data sheet should contain the following columns:

P/P ₀	V _{Ads}	V _{Des}	V _{Inj}	V _{Cal}	Att
0.96					
0.90					
0.80					
.					
.					
0.15					
0.10					
0.05					

D.3 THERMOGRAVIMETRIC ANALYSER OPERATOR GUIDE

In this section frequent references are made to Fig. 3.1, in which a schematic of the TGA apparatus is presented.

1. Purge a helium inlet liquid nitrogen trap by letting helium flow through it at room temperature for about 5 min. in order to desorb air and water vapour from the packing. If the TGA has not been in use for a few days, it is advisable to raise temperature of the trap by placing it in a hot water bath, or by heating it with a heat gun. The maximum allowable temperature of desorption is about 250°C, however, since the packing degrades above this temperature. After then the trap should be filled with liquid nitrogen and the level of nitrogen ought to remain constant until purging of the system with the sample in it is over.
2. Manifold A should be purged by evacuating and subsequent filling with helium (about 5 times is sufficient if the system has not been open to the ambient air). A slow flow of He through the manifold should be kept at the time when a char sample is being prepared for analysis.
3. Quartz bucket should always be kept clean. Avoid touching it with fingers; use a set of special tools (a quartz holder and a hook) to handle the bucket. It is a good idea to clean it periodically with a cotton applicator soaked in acetone or any other degreasing agent.
4. Make sure that the system is under atmospheric pressure before you open it to place the sample inside the TGA. Otherwise, the balance can be damaged by outrushing gas. You can check the pressure using a pressure gauge and then opening the vent line to see if there is any gas going out of the system. Caution: zero on the pressure gauge scale corresponds to slightly positive pressure. This is a normal operating pressure in all the runs, but the pressure should be truly zero before opening the TGA.
5. Caution should be exercised when you detach the hang-down tube from the rest of the system so that no expensive quartz part of the TGA is broken. If you find it difficult to detach the hang-down tube, use a heat gun to heat up a ground joint.
6. Taring of the microbalance should be carried out in the 100 mg scale. It can be performed with the TGA open, but care should be taken that the hang-down wire does not touch the wall of the baffle tube. Use a zero suppression scale to tare the balance.

7. A sample of 60-95 mg should be used, unless there is a reason to use a different sample size. Make sure that a little hook at the end of the hang-down wire goes around the wire in a safety pin fashion. This prevents straightening of the hook at high temperatures and a consequent loss of the sample and a bucket.
8. After the sample is placed in the TGA, the system should be purged by evacuation to about 200 millitorr and subsequent filling with helium (2 times). Care should be taken so that the TGA is never overpressurized by more than a few psi; a serious damage may occur.
9. Following the helium purge described in (8), the sample should be left overnight under vacuum (continuous pumping, room temperature) so that water vapour is desorbed from the mechanism of the microbalance, which has been exposed to the air.
10. A more thorough system purge is required before thermal cleaning of the sample surface: the procedure described in (8) should be carried out at 100°C and repeated 8 times; afterwards helium should be let flow through manifold A, the TGA, manifold B to the vent for about an hour at 100°C. The rotameter should read between 13 and 15.
11. Surface cleaning consists in heating the sample to 950°C in about 45 min., keeping the temperature at 950°C for 2 hours, and cooling the sample down to the temperature at which oxygen chemisorption is to be carried out.
12. Oxygen chemisorption is effected by evacuating the TGA to a vacuum of 100 millitorr and subsequent filling it with a gas mixture having the desired partial pressure of oxygen. This step should be performed as quickly as possible due to a rapid initial oxygen uptake. It is advisable to increase the strip-chart recorder speed from standard 1 cm/hr to about 4-20 cm/hr, depending on the expected char reactivity.
13. When an oxygen chemisorption run is over (usually after 24 hr) and oxygen uptake very slow, the system should be evacuated and filled with helium to determine a buoyancy correction for the gravimetric measurement in atmospheres of different gases (He, and oxygen containing gas mixture).

14. Char reactivity runs should follow oxygen chemisorption if they are desired. It is a good practice to carry out as many measurements as needed (under varying conditions of temperature and oxygen partial pressure) over a narrow burn-off range to avoid significant changes in specific surface area. Always start at the highest pressure and temperature and work down.
15. Before beginning any thermal desorption of surface oxides, the sample should be left in vacuum overnight and then purged according to directions given in (10). Desorption is carried out stepwise, and after each temperature step increase the CO and CO₂ desorbed from the surface are swept out of the TGA and collected in a liquid nitrogen trap (manifold B). Except for a different vent, this operation is similar to the purging procedure described in (10). Trapped CO and CO₂ are quantitatively analysed by means of gas chromatography (see Appendix A).

Figs D3-D5 provide illustration to the above-described procedures.

D.4 GAS CHROMATOGRAPHY

A Hewlett-Packard gas chromatograph, model 5730A, was used for the CO₂/CO ratio determination. The CO peak was obtained at 30°C, whereas CO₂ was desorbed at 100°C. The controls of the instrument were set as indicated below.

- **GAS CHROMATOGRAPH**

- 5705A TC detector control panel:

- detector power sensitivity -- 5, which corresponds to the TC current of about 210 mA,
 - offset -- none
 - attenuation -- 1

- 5702A oven temperature programmer:

- oven mode -- operate,
 - time 1 -- 4 or 8 min (depending on the sample),
 - time 2 -- 8 or 16 min. (depending on a sample),
 - temperature 1 -- +30°C,
 - rate -- 32 °C/min.,
 - temperature 2 -- 100°C.

-- 18762A temperature control:

meter selector -- det 2,
detector 2 temp. -- 150°C,
inj. port temp. -- 100°C,
auxiliary temp. -- 100°C.

-- carrier gas flow: ~2.5 units on rotameter A, ~1.3 units on rotameter B; inlet He pressure on the gas tank regulator ~40 psi; valve A used to introduce the sample to the instrument (positions "FILL" and "INJECT").

• INTEGRATOR (Hewlett-Packard, model 3380A)

-- report: AREA %
-- start delay: off
-- stop timer: 60 min
-- area reject: off
-- chart speed: 0.5 cm/min.
-- slope sensitivity: auto
-- attenuation: 8-256 (depending on the sample).

Calibration followed each measurement, and it was done by injecting 50-800 μl of 1:1 CO_2/CO mixture into the calibration port of the instrument. Sample gas chromatographic traces are presented in Figs D6 and D7.

Fig. D1

Lower left and upper panels of the Quantasorb instrument.

Fig. D2

Lower right panel of the Quantasorb instrument.

Fig. D3

Surface cleaning and the beginning of an oxygen chemisorption run.

Fig. D4

The end of an oxygen chemisorption run; buoyancy correction.

Fig. D5

Desorption of surface oxides (phenolic resin char, $T_p = 1000^\circ\text{C}$).

Fig. D5 -- cont.

Desorption of surface oxides (phenolic resin char, $T_p = 1000^\circ\text{C}$).

HP 3380A
 DLY OFF
 MV/M .33

STOP 60
 ATTN 128

REJECT OFF

Fig. D6

Gas chromatographic trace ($T_p = 1000^\circ\text{C}$, $T_D = 550-650^\circ\text{C}$, CO evolved at 30°C , CO_2 at 100°C , $I_{\text{CO}_2}/I_{\text{CO}} = 0.24$, $V_{\text{CO}_2}/V_{\text{CO}} = 0.16$).

Fig. D7

Gas chromatographic trace -- calibration ($T_p = 1000^\circ\text{C}$, $T_D = 550\text{-}650^\circ\text{C}$, CO evolved at 30°C , CO_2 at 100°C , $I_{\text{CO}_2}/I_{\text{CO}} = 1.55$, $800\ \mu\text{l}$ of 1:1 CO_2/CO mixture injected).

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ACTIVE SITES IN CHAR GASIFICATION

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