Simulation of Carbon Gasification Kinetics Using an Edge Recession Model

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An edge recession modeling method is proposed as a new approach to the prediction of carbon gasification kinetics. Using this method, the variations in reactive surface area (RSA) and specific reactivity (R) with conversion were simulated for several polynuclear aromatic molecules adopted as models of carbon crystallites. The effects of crystallite size and shape, edge site reactivity and vacancies on the changes in RSA and R with conversion were investigated. As a result, RSA and R were found to be essentially independent of crystallite shape, but to depend on crystallite size and the presence of vacancies. Good agreement was obtained between model predictions and experimental data for several kinds of model carbon crystallites. In the case of structurally disordered carbons (such as chars), simultaneous gasification of model crystallites of two different sizes gave better predictions than that of single-size crystallites. The edge recession model is proposed as an alternative, or at least complementary, approach to the more conventional (and, arguably, less physically meaningful) pore structure development models.

Introduction

Modeling of carbon gasification kinetics has been a popular and rewarding research activity, particularly in the last decade (Ballal and Zygourakis, 1987a, b; Bhatia and Perlmutter, 1980; Delikouras and Perlmutter, 1991; Gavalas, 1980; Reyes and Jensen, 1986; Simons, 1982; Tseng and Edgar, 1989; Zygourakis and Sandmann, 1988). Practically all the efforts to understand why and how the rate of this deceptively simple reaction changes with time (conversion) have been directed toward predicting the evolution of the pore structure of disordered, nongraphitic carbons (such as coal chars). The early models considered the evolving surface area to arise from the straightforward enlargement of single cylindrical pores (Petersen, 1957). Subsequently, the important processes of initiation (birth) of new pores and coalescence (death) of existing adjacent pores were included using a population balance approach, albeit at the expense of introducing too many adjustable parameters (Hashimoto and Silveston, 1973). Perhaps the best compromise between physical reality and the number of (adjustable) parameters has been achieved with the random-pore models (Bhatia and Perlmutter, 1980; Gavalas, 1980). More recently, percolation models (Reyes and Jensen, 1986; Sahimi and Tsotsis, 1988) and a discrete structural model (Zygourakis and Sandmann, 1988) have been proposed to treat in a more rigorous way the phenomenon of pore overlap and coalescence during reaction.

The carbon gasification models mentioned above rely on the assumption that all the surface carbon atoms are both accessible to and equally reactive toward the gaseous reactant(s). In particular, the success in predicting the rate vs. conversion behavior (reactivity profiles) has been attributed to the fact that some of them can account for the experimentally observed maxima in the variation of total surface area (*TSA*) with conversion (Su and Perlmutter, 1985). Nevertheless, in the absence of experimental artifacts, such as diffusional limitations, catalyst deactivation and initially concomitant mass gains due to oxygen chemisorption (Lizzio et al., 1988), the specific gasification rate (in g consumed/g remaining/s) is found, more often than not, to increase monotonically with conversion (Lizzio et al., 1990). Furthermore, in the chemically controlled kinetic regime, the pore structure of the solid is relevant only

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to the extent that it has an effect on the amount of reactive surface available for reaction at any given time.

The specific gasification rate (R) at a given level of conversion (X, %) and at constant reactant gas pressure can be expressed in the following form (Lizzio et al., 1990; Radovic et al., 1983):

$$R = \frac{1}{100\text{-}X}\frac{dX}{dt} = kC_s \tag{1}$$

where t and k are the gasification time and rate constant, respectively, and C_s is the surface concentration of carbon. We have recently proposed that there is a need for using the following fundamental rate expression (Lizzio et al., 1990),

$$R = kC_s = k\ (RSA) = k\ (TSA)\ \frac{ASA}{TSA}\frac{RSA}{ASA} \tag{2}$$

where TSA, ASA, and RSA are the total, active and reactive surface area of the carbon, respectively. Only a portion of the TSA is active (chemisorbs oxygen); and only a portion of the chemisorbed oxygen (ASA) is reactive at any given time during gasification. The term RSA thus represents the number of reactive carbon atoms or, equivalently, the surface area of the carbon material covered by the carbon-oxygen reaction intermediate under gasification conditions (Lizzio et al., 1990; Meijer, 1992; Radovic et al., 1991; Zhu et al., 1989).

The above nomenclature highlights the instructive analogy of uncatalyzed carbon gasification to a heterogeneous catalytic reaction (Carberry, 1987). The term TSA has, of course, the same meaning in both disciplines. Its value is obtained from a physisorption isotherm, in conjunction with a suitable adsorption model [such as BET layer-by-layer adsorption or Dubinin-Radushkevich theory of micropore filling (Dubinin and Stoeckli, 1980)]. The term ASA or oxygen chemisorption capacity (under more or less arbitrary conditions of temperature and pressure) is analogous to the *catalyst* surface area (or catalyst dispersion). The term RSA is analogous to the *catalytic* surface area. [If the ratio RSA/ASA is not constant, carbon gasification becomes a structure-sensitive reaction (Boudart and Djega-Mariadassou, 1984; Carberry, 1987).] For a typical coal char, experiments show that the total surface area is of the order of $10^2\ m^2/g$; out of every 1,000 surface carbon atoms, ~ 100 are active and ~ 1-20 are reactive (Radovic et al., 1991a).

Our modeling is based, therefore, on the following generally accepted mechanism for carbon gasification: the gas molecules (O_2, CO_2 or H_2O) dissociatively chemisorb on the reactive carbon atoms at the edges of carbon crystallites to form the surface reaction intermediates (oxygen complexes), which then decompose to form CO and/or CO_2. As a result of this removal of carbon atoms, new reactive edge atoms are exposed and are subsequently gasified. More specifically, the modeling concept explored in this article is based on the premise that there may exist a straightforward explanation for the monotonically increasing gasification rate with conversion. It is well known that the majority of reactive sites are located at the edges of the carbon crystallites. An extensive literature exists on the experimental aspects of carbon edge recession in both catalyzed and uncatalyzed gasification, as revealed by optical, scanning and transmission electron microscopy (Baker, 1986; Hennig, 1966; Thomas, 1965; Yang, 1984). As a crystallite is consumed, the ratio of the number of reactive sites to the total number of (surface) carbon atoms increases monotonically. Our initial attempts to model this process (Radovic et al., 1991a) have been encouraging. Here, we report the results of a more extensive and more detailed study of the edge recession model of carbon gasification.

The Computer Program

Brown (1988) has introduced a BASIC program that can simulate the above described gasification process for a single layer of graphite. He used it to show on a computer screen how vacancies in the basal plane grow into equilateral hexagons. In the present study, we created a new program based on Brown's concept and used it to simulate reactivity and RSA variations with conversion for several kinds of model carbon crystallites. Furthermore, we compare the results of this edge recession model to actual carbon gasification cases.

The program is written in Microsoft Quick BASIC (Version 4.5). The following assumptions are made:

(1) The crystallites are composed only of sp_2 carbon atoms; no other type of carbon atoms or heteroatoms is considered.

(2) Gasification occurs only at crystallite edge atoms which are bonded to one and two adjacent atoms; furthermore, the singly bonded ("dangling") edge atoms are so reactive that they are gasified as soon as they are formed.

(3) The basal-plane carbon atoms are not reactive and therefore cannot be gasified directly.

Furthermore, it was assumed that the above outlined two-dimensional procedure can readily be extrapolated to a three-dimensional case.

We adopted the algorithms used in Brown's program (Brown, 1988) as the way in which a computer simulates the gasification of an edge atom, and as the basis for distinguishing among the different types of edge sites. Briefly, all the atoms in a crystallite are interrogated, and only singly bonded edge atoms are first removed (gasified). The doubly bonded edge atoms are classified into one of postulated three types of sites (Figure 1); they are subsequently gasified according to their assigned reaction probabilities (site reactivities) using a random number generator, and additional edge atoms are thus formed. In our program, we introduce the concept of gasification time. The sequence of site type interrogation is repeated until all atoms are completely consumed. The gasification time step is counted by the number of calculation loops in this sequence. Since the gasification time thus obtained cannot be converted to actual time, we set it to be dimensionless. Furthermore, we use a different coordinate system to locate the position of each carbon atom on a polynuclear aromatic molecule plane. Figure 2 shows a typical example of the coordinate points for a single carbon hexagon. This coordinate system reduces the program size substantially and decreases the calculation time.

The program consists of three parts. The first part asks the user to input the information about the shape of the crystallite and the reactivities of the three types of edge sites. The program then converts the crystallite shape into a set of coordinates. In the second part, the gasification sequence is performed and the relevant parameters (number of gasified carbon atoms, number of remaining rings, and number of sites of each type) are recorded. Each simulation run is repeated 10-50 times to obtain statistically meaningful values for these parameters. In

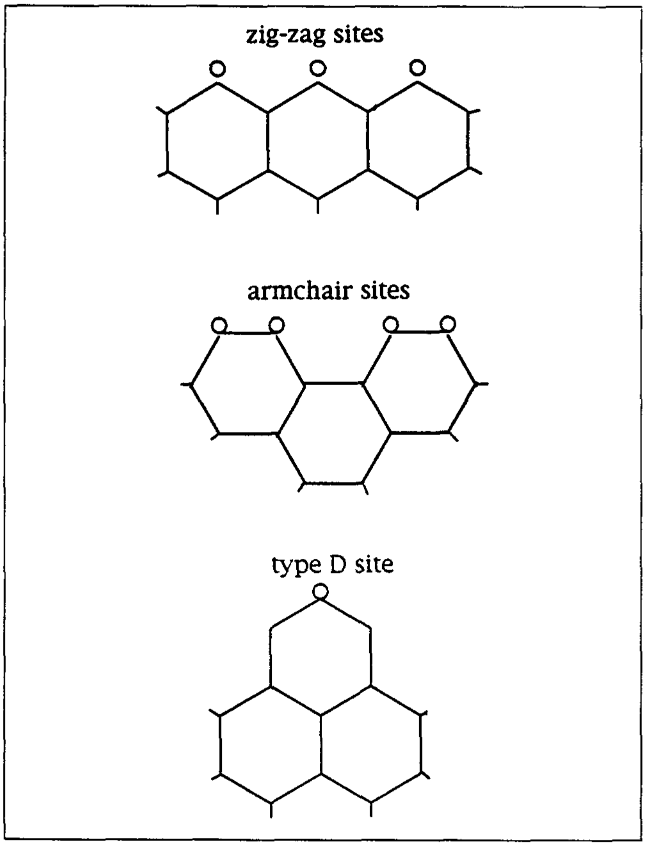

Figure 1. Representation of three types of reactive carbon sites at crystallite edges.

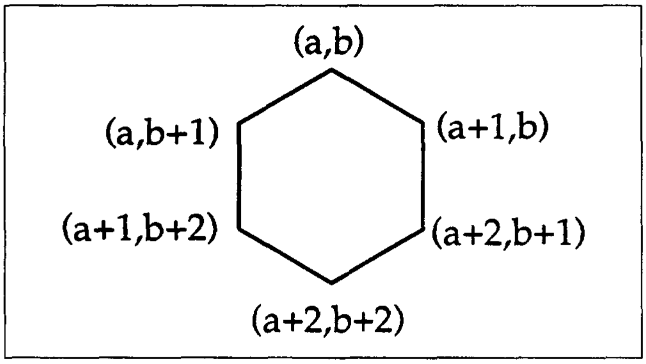

Figure 2. Example of coordinate system in the case of a single carbon hexagon (*RSA* = 100%).

the third part of the program, the data generated are stored on a hard disk in such a way that any spreadsheet software can read, arrange and analyze them after a run is completed.

Modeling of carbon structure and reactivity

The structures adopted for a single carbon crystallite, along with the corresponding number of zig-zag, armchair and type D sites and the average crystallite sizes (L_a), are given in Table 1. The structures of models A, B, B_a, and B_p are similar to the one suggested by Wigmans (1986) as typical of a char, with 80 carbon atoms arranged in 30 polyaromatic hydrocarbon rings. Models B, B_a and B_p have very similar L_a values. They, however, differ in shape: while model B is a rectangle, models B_a and B_p have anthracene-like and phenanthrene-like edges, respectively (Figure 3). These three models were used to analyze the effect of crystallite shape on gasification behavior. To simulate the heterogeneous nature of chars, a larger model crystallite (model C) was also studied. The L_a values of model samples A-C are in the range of 1-2 nm, which falls within the common values for basal plane surfaces of the nongraphitic chars. More ordered carbons are represented by models D and D_v, whose L_a values are similar to those of heat-treated ('graphitized') carbon blacks, such as Graphon (~7 nm) and V3G (~8 nm). Although the two model structures have the same

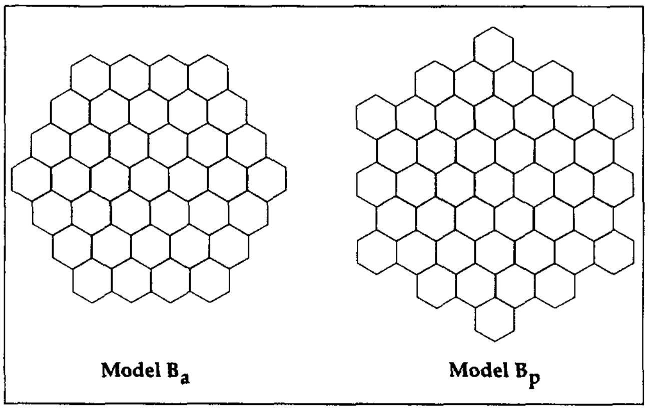

Figure 3. Molecular structure of models B_a (with anthracene-type edges) and B_p (with phenanthrene-type edges).

Table 1. Hypothetical Carbon Crystallite Structures for Gasification Simulation

Model	No. of Rings	No. of Carbon Atoms	L_a (nm)	No. of Zig-Zag Sites	No. of Armchair Sites	No. of Type D Sites	Shape of Carbon Crystallite
A	23	66	1.1	6	12	4	Rectangle, 5 (or 4) × 5 rings
B	39	104	1.4	8	16	4	Rectangle, 6 (or 5) × 7 rings
B_a	37	96	1.4	12	12	0	Anthracene edge type*
B_p	43	114	1.5	0	24	6	Phenanthrene edge type*
C	86	210	2.1	16	20	4	Rectangle, 10 (or 9) × 9 rings
D	1,871	3,916	9.9	84	88	4	Rectangle, 44 (or 43) × 43 rings
D_v	1,856	3,911	9.9	99	88	4	Rectangle, 44 (or 43) × 43 rings**

*see Figure 3
**contains 5 basal-plane vacancies

Table 2. Reaction Probabilities for Three Types of Edge Carbon Sites

Case	Zig-Zag Sites	Armchair Sites	Type *D* Sites
1	0.0217	0.0217	0.0217
2	0.0238	0.0204	0.0217
3	0.0099	0.0083	0.0476
4	0.0163	0.0017	0.0476
5	0.0400	0.0042	0.0217

size, there are five single-lattice vacancies randomly placed on the basal plane of model D_v. Previous experimental work in this laboratory (Lizzio and Radovic, 1989) showed that both the reactivity profiles and the energetic heterogeneities of ordered and disordered carbons (as determined by temperature-programmed desorption) were quite similar, suggesting that this idealized picture is not without basis.

We tested five different reactivity sets for the edge sites, as shown in Table 2. The values listed correspond to reaction probabilities relative to singly bonded edge atoms, which is taken to be unity. In case 1, all three sites have equal reactivity. In cases 2 and 3, the ratio of reactivities of zig-zag and armchair sites is almost the same as the experimental ratio observed by Thomas (1965) in graphite oxidation. Cases 4 and 5 are extreme: the reaction probability at a zig-zag site is about ten times higher than that at an armchair site. Regarding the relative reactivity of type *D* sites, there is little guiding information available. Only the theoretical approach of Stein and Brown (1985, 1987) offers some insights. Using Hückel molecular orbital theory, they calculated π-electron energetic features for polynuclear aromatic molecules with different types of edge atoms. Their calculations confirm that the zig-zag-type molecules are more reactive than the armchair-type ones. The reactivity of a molecule having type *D* edge atoms was found to lie between these two extremes. For this reason, the reactivity of type *D* sites was taken to be intermediate between those of zig-zag and armchair sites in cases 2 and 5. Case 2 is thus likely to represent the most probable set of reactivities in actual carbon samples and we used these site reactivities in most of the simulations. In cases 3 and 4, we assumed high reaction probabilities at type *D* sites. It is reasonable to assume that the reactivity of dangling carbon atoms is much higher than that of other types of edge carbon atoms. For example, if this value is arbitrarily set at 1, the reactivity of the remaining edge atoms should be much less than 1. If these values are too small, however, the computer calculation time becomes impractically long. The chosen order of the values (10^{-2}; see Table 2) is a compromise between these conflicting requirements. The absolute values themselves have no physical meaning, but we set the sum of reaction probabilities in each case to be constant.

Model parameters

The following parameters were determined from the simulation program: carbon conversion (X), reactive surface area (RSA), crystallite width (L_a), and carbon reactivity (R). The first three are defined as follows:

$$X(\%) = \frac{\text{number of gasified carbon atoms}}{\text{total number of initial carbon atoms}} \times 100 \qquad (3)$$

$$RSA = \frac{\text{number of zig-zag} + \text{armchair} + \text{type } D \text{ sites}}{\text{number of that remaining } C \text{ atoms at given } X} \qquad (4)$$

$$L_a\ (\text{nm}) = \sqrt{\text{number of rings} \times 0.0524\ (\text{nm}^2)} \qquad (5)$$

In the calculation of RSA, dangling carbon atoms were not considered. Once these sites are created (Radovic, 1992), they are assumed to be instantly gasified and their relative lifetime is too short for consideration in RSA calculations. The gasification rate was then determined from Eq. 1 in the following way: each plot of conversion vs. time was fitted with a fifth-order polynomial via regression analysis (the correlation coefficients being always close to 1.000) and the slopes of the conversion curves, dX/dt, were calculated from the differential equations of the resulting polynomials.

Results and Discussion

Simulated gasification of model crystallites

Figure 4a presents the RSA vs. conversion plots for the rectangular crystallites of different size, which have the set of reaction probabilities given as case 2 (Table 2). The larger crystallites have smaller RSA values, and in all cases RSA increases with conversion. The effect of varying edge site reac-

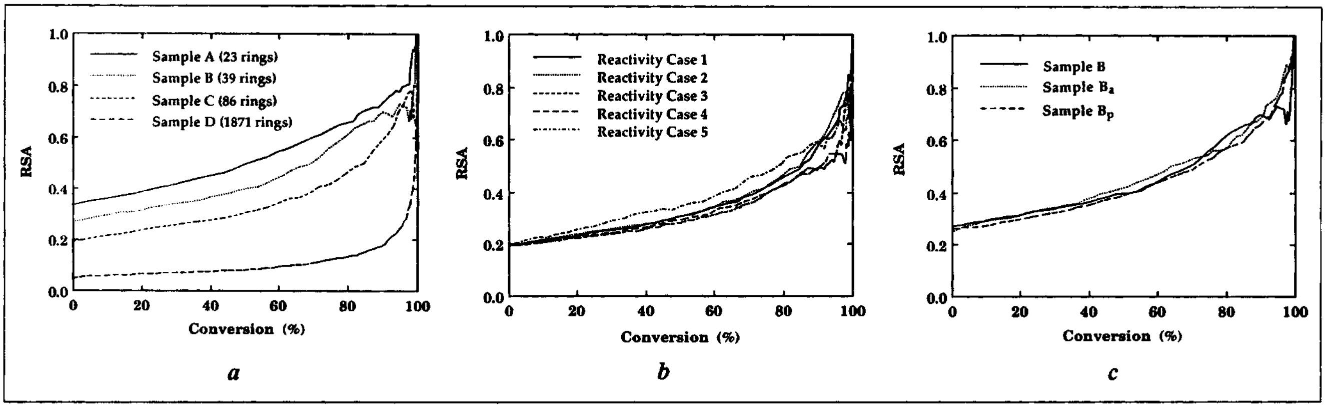

Figure 4. Effects of crystallite size (a), edge site reactivity (b), and crystallite shape (c) on *RSA* vs. conversion plots.
Simulations a and c were done for case 2, Table 2.

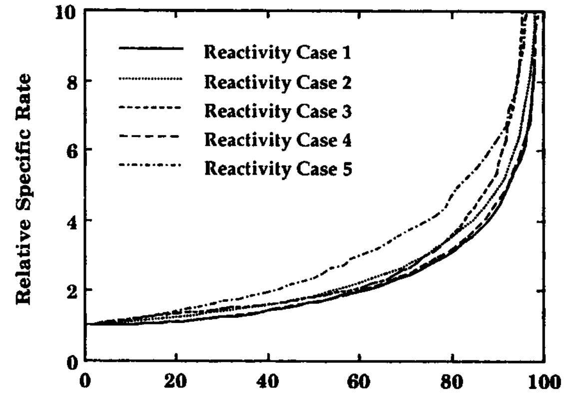

Figure 5. Typical predicted reactivity profiles.

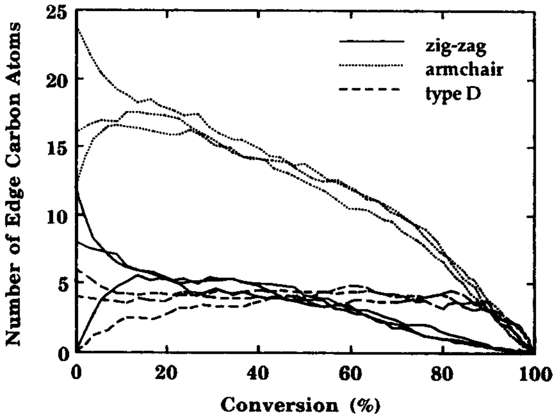

Figure 7. Variation of edge atom types with conversion for models B, B_a and B_p (case 2).

tivity on the *RSA* vs. conversion plot is shown in Figure 4b, where model crystallite *C* is subjected to simulated gasification for five different sets of reactivities (cases 1-5, Table 2). Except for case 5 and in the highest conversion region, the curves are seen to be very similar in spite of large variations in the reaction probabilities at the different sites. When the shape of the crystallite is changed, while keeping its size constant (models *B*, B_a and B_p), there are also almost no differences in the resulting curves, as shown in Figure 4c. Similar simulation experiments (not shown) indicate that in the presence of vacancies (model D_v, Table 2) *RSA* increases more rapidly than that of the corresponding perfect crystallite (model *D*), even though they initially have almost the same *RSA*.

Reactivity profiles were also simulated to investigate the corresponding effects of crystallite size and shape. Figure 5 shows some of the representative results. Reaction rates have been normalized with respect to the initial rate. It is interesting to note the agreement with the commonly observed two-to-fourfold rate increase over the 0-80% conversion range (Lizzio et al., 1990). The following conclusions were drawn from the data: (1) specific reactivity always increases monotonically with increasing conversion; (2) its value depends strongly on the size of the crystallite; (3) reactivity profiles appear to be independent of the shape of the crystallite, except in the high conversion region; and (4) the presence of vacancies results in a faster reactivity increase with conversion. In all cases considered, the specific reactivity exhibits the same tendency as *RSA* (see Eq. 2). To confirm this proportionality, the specific reactivities for the model crystallites of different sizes are plotted against their respective *RSA* values in Figure 6, where the data for the conversion range >95% were omitted (because of large uncertainties associated with division by a very small number; see Eq. 1). As expected, the curves for different models appear to form one smooth curve (except in the higher *RSA* region, that is, higher conversion range). This suggests that the use of an average turnover frequency (site reactivity)—represented by the slope of the curve—is a reasonable assumption (Radovic et al., 1991b) for the chosen range of energetic heterogeneity of the various sites (see Table 2). The slightly concave shape of the curve suggests that the average turnover frequency may increase during reaction, especially at high conversions.

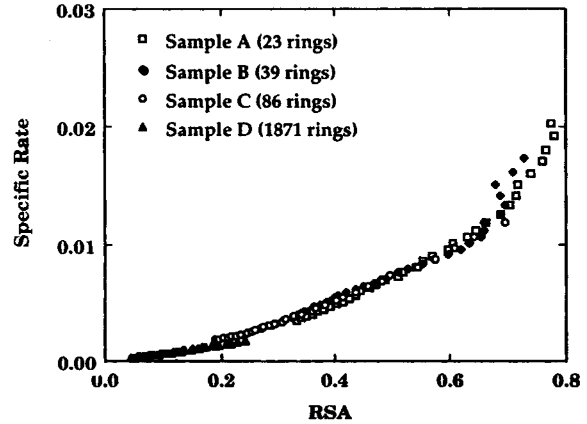

Figure 6. Relationships between reactivity and *RSA* for the model carbon samples of different initial sizes (case 2).

In agreement with the definition of *RSA* (Eq. 4), the change in the combined number of zig-zag, armchair and type *D* sites during gasification directly reflects the changes in *RSA*. From this point of view, an analysis of the individual behavior of the three types of reactive sites during gasification is of importance for the understanding of *RSA* vs. *X* and *R* vs. *X* relationships. Figure 7 shows how the concentration of each type of sites varies with conversion for model crystallites *B*, B_a and B_p. Initially, this relationship differs among the models chosen due to differences in crystallite shape (see Table 1). After ~20% conversion, the three curves seem to converge. This explains why *RSA* vs. *X* and *R* vs. *X* curves were independent of crystallite shape.

As gasification proceeds, the crystallite shrinks and the value of L_a decreases. This implies that a large sample (such as crystallite *D*) can become as small in size as crystallites *A*-*C*. If a sample gasified to a given level of conversion has the same reactivity as an unreacted sample of comparable size, the reactivity should be only a function of L_a. Figure 8 shows the reactivity variations with L_a for model crystallites having four different initial sizes. All the data points fall on one continuous curve, indicating that the reactivity during gasification is dictated by the value of L_a, regardless of the initial crystallite size. This fact can be explained by considering the relative changes in the number of different reactive sites during gasification.

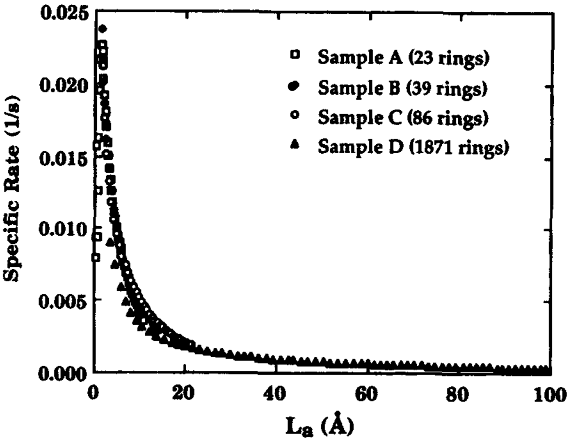

Figure 8. Relationship between reactivity and crystallite size (L_a) for model carbon samples of different initial sizes (case 2).

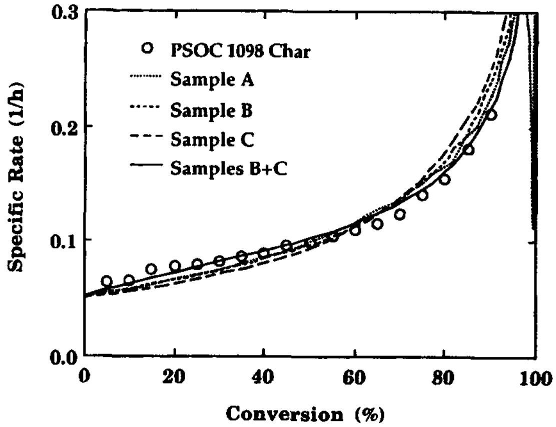

Figure 10. Experimental reactivity profiles for a bituminous coal char (PSOC 1098) predicted by the edge recession models.

Figure 9 shows the relevant plots for models *A-D*. In these plots, gasification starts at a given L_a value and proceeds toward the origin of the graph. (For model *D* only parts of the entire curve are drawn, for clarity.) In agreement with the results shown in Figure 7, the curves corresponding to one type of edge site are practically coincidental in all cases, except in the beginning of the reaction. Therefore, once the reactivities for the postulated sites are fixed, the relative proportion of sites in a given crystallite is only a function of *in situ* crystallite size; it is independent of initial crystallite size and shape.

Comparison with experimental results

Because we found that carbon reactivity is practically independent of crystallite shape and dependent instead on crystallite size, only rectangular crystallites with different sizes (models *A-D*) were considered in the comparisons of simulated reactivity profiles (case 2, Table 2) with their experimentally determined counterparts.

Figure 10 presents the reactivity profiles for a char derived from a bituminous coal (PSOC 1098) gasified in 0.1 MPa CO_2 at 1,093 K (Jiang, 1989) together with the simulated profiles for models *A*, *B*, and *C*. For every model crystallite, the simulated reactivity profiles agree quite well with the experimental trend of monotonically increasing rate. Below 50% conversion, the experimental profiles are slightly underestimated; above 60% conversion, they are somewhat overestimated. A typical char consists of many carbon crystallites, probably with a wide distribution of sizes. Therefore, the actual reactivity profile is not expected to be exactly reproduced by either one of these simple models. With this in mind, the simultaneous gasification of two or three model crystallites was examined (combined models *A* and *B*; *B* and *C*; *A* and *C*; and *A*, *B* and *C*). As also shown in Figure 10, a better prediction of the experimental data was obtained, for example, with combined models *B* and *C*.

The reactivity profile of Carbosieve, a commercial molecular-sieve carbon, gasified with CO_2 at 1,133 K (Lizzio et al., 1990) was also tested using this edge recession model (Figure 11). Again, simulation results for simultaneous gasification (models *A* and *B*) give a better prediction than those from the gasification of single model crystallites, although deviations are still observed below 20% conversion. It is perhaps somewhat surprising that the reactivity profiles of these disordered carbons, which are thought to have a wide distribution of

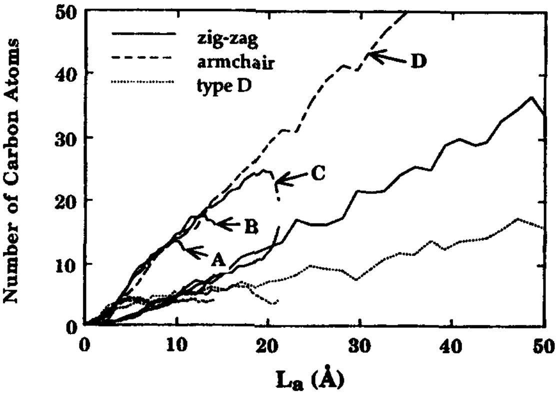

Figure 9. Variation of edge atom types with crystallite size (L_a) for model carbon samples of different initial sizes (case 2).

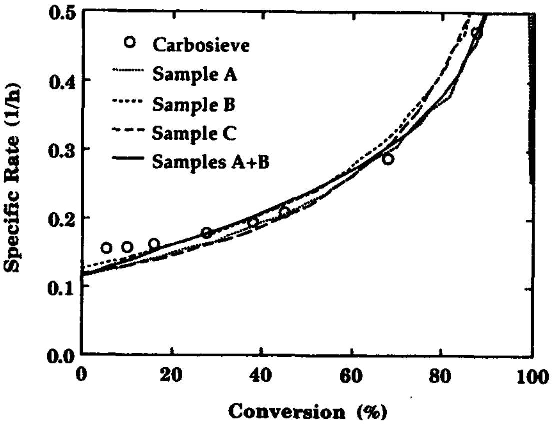

Figure 11. Experimental reactivity profiles for Carbosieve carbon predicted by the edge recession models.

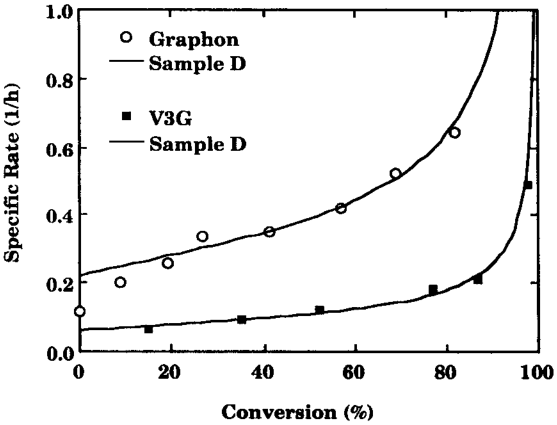

Figure 12. Comparison of experimental reactivity profiles for Graphon and V3G with the simulated profiles using model *D* carbon (see Table 1).

crystallite sizes, can be predicted in the straightforward manner discussed above. This implies that their "average" structure can be represented, as far as gasification is concerned, by a mixture of a few simple model crystallites.

Figure 12 shows the reactivity profiles predicted by model *D* for two "graphitized" carbon blacks (Graphon and V3G) gasified in 0.1 MPa air at 863 and 873 K, respectively (Leon y Leon, 1993). The simulated curves display good agreement with experimental data, except in the low conversion region for Graphon. In both cases, a single model crystallite was sufficient to get good prediction. This seems reasonable, because the high-temperature carbon blacks are thought to have a more homogeneous structure (a narrower crystallite size distribution due to their more ordered polygon structure) than the Carbosieve and coal char, which were exposed to much lower temperatures. It is interesting to note that the model with vacancies (model D_v) did not fit the actual data points of either one of the two samples. The calculated density of defects in model D_v is $5\times10^{12}/\text{cm}^2$, which is much higher than that of graphite [10^7-$10^{10}/\text{cm}^2$ (Henning, 1966)]. The above results thus imply that even a "graphitized" carbon black does not have as many vacancies as model D_v has.

The trend of increasing *RSA* with conversion was established experimentally (Lizzio et al., 1990; Radovic et al., 1991b). Nevertheless, the experimental *RSA* values were found to be lower than these "theoretical" ones. Two reasons for this discrepancy can be considered (Radovic et al., 1991a): (1) a significant number of edge atoms may be physically inaccessible to the reactant gas, because of the complex three-dimensional (for example, microporous) structure of carbon; (2) the formation of stable carbon-oxygen complexes at some of the edge sites makes a certain number of these carbon atoms temporarily unreactive.

We have thus established that the "theoretical" reactivity is only a function of crystallite size, L_a (if the contribution by vacancies can be neglected). This relationship is often corroborated by experimental results: the more crystalline the carbon (the larger the L_a), the less reactive it is. For example, graphite is much less reactive (per unit of total surface area) than coal char. For chars obtained from the same coal, the ones heat-treated at higher temperature are less reactive than the ones exposed to lower temperature (Smith, 1978). Nevertheless, during gasification of a given carbon, experimentally determined L_a values often do not change up to high conversion levels (Kotlensky and Walker, 1960; Leon y Leon, 1992; Walker et al., 1954). This fact is in conflict with the "theoretical" results shown in Figure 9. There are two possibilities for reconciling this apparent contradiction. One is related to the gasification of nonporous carbon. Because such a sample is gasified primarily from the outside, the crystallites inside the particle remain unreacted even at high conversion. The other reason is that there may exist a difference between the actual and experimentally determined L_a values (Walker et al., 1954). The crystallite width is determined using an X-ray diffractometer, which is sensitive only to the ordered structure (large L_a portion) of a given sample. Thus, when a carbon sample contains a highly crystallized region (even if it is a small fraction of the total carbon), the experimentally observed L_a may not correspond to the average crystallite size, but to the average size of the ordered crystalline portion. As gasification proceeds, the less crystalline portion of a carbon sample (which is the most reactive) is preferentially consumed; at the same time, the more crystalline portion is consumed very slowly. As a result, the actual average size decreases, but the experimentally determined L_a does not change, or even increases, with conversion.

Conclusions

In the proposed edge recession model of carbon gasification, the simulated plots of reactivity vs. conversion and reactive surface area vs. conversion are found to be insensitive to variations in crystallite shape. They are also largely independent of the relative reactivities of the different types of reactive sites. The absolute values of reactivity and *RSA* strongly depend on carbon crystallite size. The fraction of the total edge sites that are reactive changes with conversion and is somewhat dependent on the initial crystallite size. Although many simplifying assumptions were made, very good agreement between model results and experimental data was obtained when realistic model parameters were used.

The edge recession modeling of carbon gasification is thus proposed as an alternative, or at least complementary, approach to the more conventional (and less physically meaningful) pore structure development models. The complementary nature of the two approaches can be explored, as Eq. 2 suggests, by: (a) simulating the *RSA/TSA* development using the two-dimensional edge recession model described here; (b) simulating the development of *TSA* using, for example, a random pore model.

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