A NEW APPROACH TO MODELLING CARBON REACTIVITY

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Introduction

Modelling of the reactivity of chars and carbons, and understanding the factors affecting this, has long been a subject of intense investigation because of the relevance to a growing list of many traditional and modern applications. Among these are gasification processes, the activation of chars and other carbonaceous materials, and the integrity of structural carbons and composites, which are often required to withstand adverse environments without failure. However, despite decades of research the key goals have not been achieved, predominantly due to the complexity of the structure and chemistry of carbons.

Several reactivity models have been proposed in the literature, of which those that incorporate the competing mechanism of pore growth and intersection [1-3] have been most successful. Such models can predict observed trends, such as the existence of a rate maximum with respect to conversion; however, there is often a discrepancy obtained between parameters obtained by fitting of rate data and their values obtained from structural characterization [4]. In addition, in their current form these models cannot predict the recently reported shrinkage [5] of various chars and carbons when gasified in the chemically controlled regime. Another important feature, which is not treated by the existing models, is that of initial surface chemistry. The latter is now known to be at least as important as the bulk composition in influencing the reactivity.

In addition, these models also do not adequately represent the true underlying nanoscale structure of carbons, which is known to be turbostratic and comprising of crystallites having stacked aromatic sheets [6, 7]. In the project work a new approach has been developed which accounts for the features of surface chemistry as well as turbostratic structure, while predicting the observed shrinkage.

Mathematical Modelling

The mathematical model considers the reaction of agglomerates of crystallites, and develops a probabilistic model of the recession of the edges of the aromatic sheets, and the slower reaction on the exposed basal sites. The model is developed under the following assumptions:

1. The char or carbon particles comprise an aggregate of spherical grains, which themselves comprise an agglomerate of crystallites.
2. Each crystallite consists of a stack of H planes spaced 0.34 nm apart.
3. Each plane comprises an aromatic sheet with functional groups at the edge sites. In addition the two exposed bounding sheets of the crystallites have functional groups at the planar sites.
4. It is assumed the gasifying agent cannot penetrate the interplanar space.
5. The ratio of the reactivity of new edge sites to new internal sites has the value of 3, which is a good representation of the results of Kyotani et al. [8].
6. When an exposed planar surface reacts, the entire exposed part is instantly gasified.
7. Shrinkage of the crystallite agglomerate occurs when a complete plane has been gasified away.
8. Crystallites are randomly overlapping, which simulates angular boundaries and defects.

Details of the model are presented elsewhere [9].

Results and Discussion

One of the important features of the new model is the role of surface chemistry, as represented by the inverse of the ratio of relative initial reactivity, A. Figure 1 depicts the effect of this parameter A on the dimensionless rate for a carbon having microporosity of 0.2, with the number of planes in a crystallite equalling 4, and 8 rings of carbon atoms per plane. In addition the ratio of edge site to basal site reactivity is 3. With an increase in A the position of the maximum increases strongly, demonstrating the effect of initial surface chemistry. This position is also sensitive to the number of planes in a crystallite. However, the shrinkage is most sensitive to this variable, the results for which are given in Figure 2.

The model has been found to fit the data of Hurt et al. [10] for the air-oxidation of spherocarb, using only the position and rate value at the rate maximum in the fitting. The

value of A for the fits was found to be approximately 2, implying that the initial reactivity is half that of the freshly exposed carbon surface. The model also accurately predicted shrinkage of the carbon, as shown in Figure 3, using only parameter values from the fit of the rate maximum.

Conclusions

The new approach of modelling carbon reactivity based on crystallite structure is more realistic than earlier ones, and offers a convenient framework for incorporating surface chemistry as well as the turbostratic structure. It can also predict observed shrinkage, and needs to be pursued and further developed.

References

[1] Bhatia, S. K., Perlmutter, D.D. A random pore model for fluid-solid reactions: I. isothermal, kinetic control. AIChE J. 1980; 26: 379-386.

[2] Gavalas, G. R. A random capillary model with application to char gasification at chemically controlled rates. AIChE J. 1980; 26: 577-585.

[3] Petersen, E. E. Reaction of porous solids. AIChE J 1957; 3: 443-448.

[4] Miura, K., Makino, M., Silveston, P. L. Correlation of gasification reactivities with char properties and pyrolysis conditions using low rank Canadian coals. Fuel 1990; 69: 580-589.

[5] Hurt, R. H., Sarofim, A. F., Longwell, J. P. Gasification-induced densification of carbons: from soot to form coke. Comb. Flame 1993; 95: 430-432..

[6] Davis, K. A., Hurt, R. H., Yang, Y. C., Headley, T. Evolution of char chemistry, crystallinity, and ultrafine structure during pulverised coal combustion. Proc. Int. Symp. on Combustion. 1994; Los Angeles.

[7] Babu, V. S., Seehra, M. S. Modelling of disorder and X-Ray diffraction in coal-based graphitic carbons. Carbon 1996; 34: 1259-1265.

[8] Kyotani, T., Ito, K. C., Tomita, A., Radovic, L. R. Monte Carlo simulation of carbon gasification using molecular orbital theory. AIChE J. 1996; 42: 2303-2307.

[9] Bhatia, S. K. Reactivity of chars and carbons: new insights through molecular modelling. AIChE J. 1998; 44: 2478-2493.

[10] Hurt, R. H., Dudek, D. R., Longwell, J.P., Sarofim, A. F. The phenomenon of gasification-induced carbon densification and its influence on pore structure evolution. Carbon 1988; 26: 433-449.
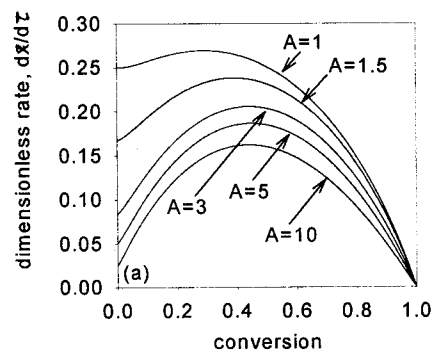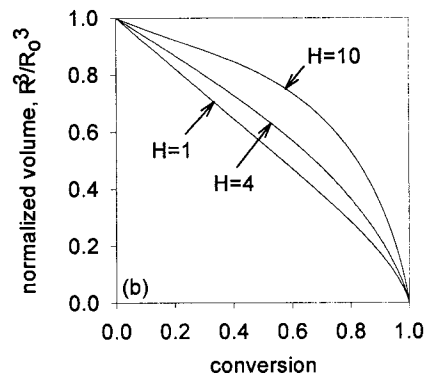
Figure 1. Effect of reactivity ratio A on reaction rate

Figure 2. Effect of number of crystallite planes, H, on shrinkage
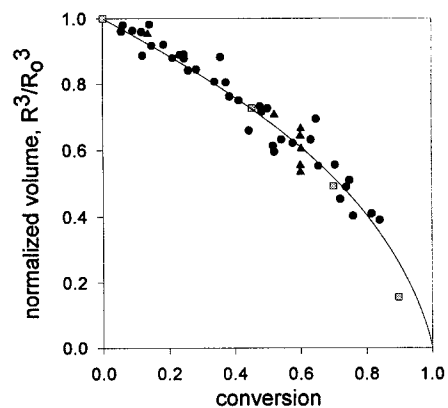

Figure 3 Variation of particle size with conversion in the chemically controlled regime. Symbols represent data from various sources and the line represents current model predictions

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