STRUCTURE-BASED PREDICTIVE MODEL FOR COAL CHAR COMBUSTION

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EXECUTIVE SUMMARY

Significant progress continued to be made during the past reporting quarter on both major technical tasks.

During the reporting period at OSU, computational investigations were conducted of addition *vs.* abstraction reactions of H, O(³P), and OH with monocyclic aromatic hydrocarbons. The potential energy surface for more than 80 unique reactions of H, O(³P), and OH with aromatic hydrocarbons were determined at the B3LYP/6-31G(d) level of theory. The calculated transition state barriers and reaction free energies indicate that the addition channel is preferred at 298K, but that the abstraction channel becomes dominant at high temperatures. The thermodynamic preference for reactivity with aromatic hydrocarbons increases in the order O(³P) < H < OH. Abstraction from six-membered aromatic rings is more facile than abstraction from five-membered aromatic rings. However, addition to five-membered rings is thermodynamically more favorable than addition to six-membered rings. The free energies for the abstraction and addition reactions of H, O, and OH with aromatic hydrocarbons and the characteristics of the respective transition states can be used to calculate the reaction rate constants for these important combustion reactions.

Experimental work at Brown University on the effect of reaction on the structural evolution of different chars (i.e., phenolic resin char and chars produced from three different coals) have been investigated in a TGA/TPD-MS system. It has been found that samples of different age of these chars appeared to lose their "memory" concerning their initial structures at high burn-offs. During the reporting period, thermal desorption experiments of selected samples were conducted. These spectra show that the population of low temperature oxygen surface complexes, which are primarily responsible for reactivity, are more similar for the high burn-off than for the low burn-off samples of different ages; i.e., the population of active sites are more similar for the "younger" and "older" chars at high burn-offs.

Progress continued on experimental work at OSU. Another furnace run was conducted with a Pittsburgh seam coal. Temperature profiles were obtained, as well as char samples from three sampling ports. Nonisothermal TGA reactivities were also obtained for these samples. Work is continuing on final "fine-tuning" of the gas analysis section.

PROJECT DESCRIPTION

The problem of excessive unburned carbon in fly ash could be better managed if designers and users of combustion systems could determine the reactivity of a given char from basic coal properties, avoiding the need to resort to expensive full-scale testing. Establishing a mechanistic link between coal properties and fuel behavior has long been a goal of the coal research community, as such a capability would find numerous uses in predictive tools and optimization tools for coal technologies. Such a predictive capability will not likely be achieved through incremental improvements to current models — new, more fundamental approaches are needed such as the structure-based approach, which we believe has the long term potential to make the required mechanistic links between coal properties and char behaviors.

The overall objective of this project is to carry out the fundamental research needed to develop a first-generation, structure-based model of coal char combustion. The project involves combustion experimentation at a variety of scales, theoretical treatments of surface chemistry, and the development and refinement of advanced modeling techniques describing solid-state transformations in coal chars. The fundamental modeling approaches taken here may also produce auxiliary benefits for other coal technologies, including cokemaking, liquefaction, activated carbon production and use, and carbon materials manufacture (fibers, composites, graphite, etc.). The crystalline structure of carbons and its evolution during processing plays an important role in each of these diverse applications.

This combined experimental and theoretical approach will result in a first-generation, structure-based model that is a significant improvement over empirical models in its ability to:

- predict, from fundamental principals, the rank-dependence of char reactivity
- predict the dependence of char reactivity on heat treatment conditions
- describe reaction kinetics in a wide variety of combustion / gasification environments

Task Structure

This project consists of the following three interrelated tasks:

Task 1. Project Management

This task involves reporting, documentation, coordination of effort at the two participating universities, and interactions with the advisory board.

Task 2. Development of Structure-Based Models

The objective of this is the development of new models that describe the combustion process on a more fundamental basis. Dynamic models will be formulated that describe the evolution of char crystal structures in flames, and fundamental computational treatments of oxidative attack on model PAH and graphitic structures will be carried out. This task also includes laboratory-scale experiments designed to establish link between char structure and oxidation reactivity, and a direct investigation of carbon crystalline rearrangements by *in-situ*, hot-stage HRTEM.

Task 3. Experiments in Practical Combustion Systems

This represents a parallel effort to investigate and document the importance of thermal history effects on char structure and reactivity in well-controlled and characterized coal flames. Comparative experiments will be carried out on two reactor facilities with widely varying flame type and the properties and reactivities of the chars characterized.

Project Team

The project involves three Universities (Brown, Ohio State, and Boston University), in order to couple engineering expertise in coal combustion and carbon science (at Brown and Ohio State) with research groups in the pure sciences specializing in modern computational chemistry (OSU) and in solid state physics (BU). The multidisciplinary team will apply modern scientific tools to the challenging technological problem of linking char combustion behavior with coal properties and processing conditions.

The project is supported by an advisory panel assembled from industry, academia, and the national laboratories with a wide range of expertise. The panel members are:

Hamid Farzan	Babcock and Wilcox Co.
Alan Kerstein	Sandia National Laboratories
Harry Marsh	University of Alicante
Arun Mehta	Electric Power Research Institute
Richard McCreery	Ohio State University
Nsakala Nsakala	ABB Combustion Engineering
Stuart Daw	Oak Ridge National Labs

DISCUSSION OF PROGRESS THIS PERIOD

Section I. Computational Investigations of Addition vs. Abstraction Reactions of H, O(³P) and OH with Monocyclic Aromatic Hydrocarbons (within Task 2 at OSU)

Elucidating the elementary reactions pathways for hydrocarbon compounds during fuel processing and combustion is of interest not only to understand fundamental combustion chemistry, but also to gain insight into atmospheric reactions that occur following hydrocarbon emission into the environment following fossil fuel consumption.

The chemistry of the combustion of fossil fuels such as coal is further complicated by the large fraction of aromatic compounds in the fuel. Benzene provides the simplest model with which to study the combustion of aromatic molecules. The reactions of benzene with H, ³O, and OH have been studied experimentally³⁻⁶ and much controversy exists over the chemistry that occurs during these reactions. The functional groups present in the aromatic network of coal add greater complexity to the reactions with H, ³O, and OH that occur during combustion.

H Atom Reactions

The simplest free radical attack on an aromatic molecules is the reaction of a hydrogen atom with benzene. The possible reactions that can occur include both abstraction and addition reactions. Several measurements have been made of the kinetics of these reactions via shock tube,⁸⁻¹⁰ FTIR/MS¹¹ experiments, radiolysis,¹²⁻¹⁴ discharge flow tube ESR/MS,^{15,16} and flash photolysis-resonance fluorescence.¹⁷ The conclusion of several of these studies was that abstraction of a hydrogen atom does not occur but that H atom undergoes electrophilic addition to the ring to form the cyclohexadienyl radical at temperatures up to 1000 K.^{13,15-17} However, very little effort has been made to bridge the gap between these kinetic studies and the chemistry that occurs under combustion conditions.

Recently *ab initio* studies of the reaction C₆H₆ + H have been performed at various levels of theory by Lin and coworkers that seemingly confirm the experimental results.¹⁸ The room temperature barrier for abstraction of a H atom to form C₆H₅ + H₂ was calculated to be higher than that for H atom addition to benzene. In addition, the abstraction path was determined to be

an endothermic process whereas the addition of H atom to C_6H_6 to form C_6H_7 , was calculated to be exothermic.

O (3P) Atom Reactions

More controversy exists over the preferred pathway for the reaction of the oxygen atom with benzene than from the analogous reaction with the hydrogen atom. Addition of atomic oxygen to the benzene ring occurs by formation of a long-lived triplet biradical.¹⁹ Alternatively, hydrogen abstraction can occur via oxygen atom to produce the phenyl and hydroxyl radicals.

A few kinetic measurements of the reaction of oxygen atoms with benzene have been reported,²⁰⁻²⁶ but very few experiments have been able to elucidate the mechanism for this reaction.^{19,23,24,27} Most studies conclude that the reaction of oxygen atoms with benzene proceed via addition to the ring.^{19,23,24} However, OH formation has been observed²⁷ in crossed beam experiments at high collision energy that correspond to a temperature high enough to overcome the endothermicity of the reaction.

It is also important to study the reactions of other heteroatomic aromatic hydrocarbons with atomic oxygen to understand the chemistry that occurs in more complex fuels such as coal. A kinetic measurement of the reaction of O (3P) with pyridine²⁸ determined that the addition reaction occurred with a lower activation barrier than for the analogous reaction with benzene. In addition, it was deduced from the product distribution that there was a preference for electrophilic addition to pyridine at the *meta* position. There are a few reports of the reactions of O (3P) with the five-membered aromatic rings: furan,²⁹ thiophene,²⁹⁻³¹ and pyrrole.²⁹ There is disagreement in the kinetic results from these experiments; however, evidence was found only for addition to the aromatic ring. Only in the reaction of atomic oxygen with furan was addition to the double bond considered to be the most likely path.²⁹ Addition of O (3P) to thiophene^{29,30} and pyrrole²⁹ was interpreted to proceed by addition to the heteroatom. However, the results of a scattering experiment indicated that the reaction of O (3P) with thiophene may proceed by O atom addition to a carbon followed by H atom elimination.³¹

OH Radical Reactions

A relatively large number of kinetic studies have been reported for the reaction of the hydroxyl radical with benzene, and the results of these studies are summarized as part of a lengthy review on the chemistry of hydroxyl radicals under atmospheric conditions.³ The prevalent thought is that two reaction channels for the reaction of OH with benzene are available that dominate in different temperature regimes. The first is the electrophilic addition to the benzene ring³² to form the hydroxycyclohexadienyl radical that is collisionally stabilized but will decompose back to reactants at moderate temperatures ($T > 325$ K).³³⁻³⁵ The abstraction channel is thought to be a minor channel at low temperatures and only becomes significant at temperatures greater than 500 K.^{33,35,36}

However, the preference for abstraction at high temperatures has been questioned in favor of the addition-elimination path.³⁷ The uncertainty in reaction products warrant further study of the attack of the hydroxyl radical on benzene.

A few investigations of the reaction of hydroxyl radicals with five-membered aromatic rings have been performed to investigate the probable reaction channel. There is general agreement that reaction of OH with furan proceeds via addition to the carbon-carbon double bond,^{38,39} similar to furan's reaction with oxygen atoms. It was later proposed that addition to the *ortho* position in furan would be preferred over addition at the *meta* position due to the existence of an additional resonance structure in the addition product.^{40,41} Addition is also thought to be the preferred mechanism for the OH reaction with thiophene, although there is disagreement over whether OH adds to the double bond or to the heteroatom. However, most experiments to date have been inconclusive about the actual addition mechanism.^{38,39,42} The barrier height for the reaction of the hydroxyl radical with thiophene is lower than that for furan, based on the recommended Arrhenius rate expression for these five-membered aromatic rings.³

Reaction of Benzene with H, O (³P), and OH: Net reaction

The potential energy surface for the abstraction of a hydrogen atom from benzene by molecular oxygen is quite similar to the surface for the analogous reaction for methane.¹ Because H-atom abstraction by O₂ is so endothermic, reactions of benzene with H, O, and OH will gain in importance once the radical pool is established. Reactants, products, and transition state

structures for the abstraction reactions by H, O (^3P) and OH have been characterized at the B3LYP/6-31G(d) level of theory. Abstraction by OH is thermodynamically favored over abstraction by H or O atom because the overall reaction to form the phenyl radical and water is slightly exoergic at 298 K.

There are no experimental data for the reaction energies for the abstraction of a hydrogen atom from benzene by H, O (^3P), and OH. However, the reaction enthalpy can be estimated from the relevant bond dissociation energies (Table I.1). As a result of the deviation between the BDEs calculated by the B3LYP/6-31G(d) level of theory and the experimental values, the reaction enthalpies calculated by the B3LYP method can not be expected to have better agreement with experiment than the differences listed in the “expected” column of Table I.2. Therefore, the deviation in the reaction enthalpy for abstraction by H atom can be attributed to the underestimation of the C-H BDE in benzene by the B3LYP/6-31G(d) method. The reaction enthalpy for the abstraction by O atom is actually calculated to be 1.7 kcal-mol $^{-1}$ higher than the experimental estimate. This positive deviation occurs because the B3LYP method also underestimates the O-H BDE by 4.4 kcal-mol $^{-1}$. Finally, the calculated reaction enthalpy for the abstraction channel of the reaction of benzene with the hydroxyl radical is 1.3 kcal-mol $^{-1}$. This is 6.8 kcal-mol $^{-1}$ higher than the experimental estimate primarily due to the drastic underestimation of the H-OH bond strength in water by 9.5 kcal-mol $^{-1}$.

Table I.1. Bond dissociation enthalpies at 298K (kcal-mol $^{-1}$).

H₂₉₈ (R–X)	experiment	B3LYP/6-31G(d)	
C₆H₅–H	113.5 ⁴⁴	110.8	– 2.7
H–H	104.2 ⁴⁵	104.4	+ 0.2
H–O	102.2 ⁴⁵	97.8	– 4.4
H–OH	119.0 ⁴⁵	109.5	– 9.5

Table I.2. Reaction enthalpies for H atom abstraction reactions at 298K (kcal-mol $^{-1}$).

H_{rxn} (298 K)		experiment	B3LYP/6-31G(d)		expected
C₆H₆ + H	C₆H₅ + H₂	+ 9.3	+ 6.4	– 2.9	– 2.5
C₆H₆ + O	C₆H₅ + OH	+ 11.3	+ 13.0	+ 1.7	+ 1.7
C₆H₆ + OH	C₆H₅ + H₂O	– 5.5	+ 1.3	– 4.2	– 6.8

Reaction of Benzene with H, O (³P), and OH: Transition States

Benzene is more reactive with the hydroxyl radical than with hydrogen and oxygen atoms because the reaction is more thermodynamically favorable and because the barrier for abstraction by OH is several kcal-mol⁻¹ lower than abstraction by H and O. Comparison of the C-H bond length in the transition state structure for these abstraction processes can be used to determine the approximate location of the transition state along the reaction coordinate. As expected, the transition state for the C₆H₆ + OH reaction occurs “earlier” ($r_{\text{CH}} = 1.313 \text{ \AA}$) than those for the C₆H₆ + H and C₆H₆ + O reactions ($r_{\text{CH}} = 1.464 \text{ \AA}$ and $r_{\text{CH}} = 1.484 \text{ \AA}$, respectively). Similar to the analogous reaction with methane,² Hammond’s postulate is not obeyed for the hydrogen atom abstraction reactions from benzene. The reaction to form the phenyl radical and H₂ is lower in energy than the reaction to form the phenyl radical and OH radical, although the barrier for abstraction via H atom is higher.

Heteroatomic Aromatic Hydrocarbons Reactions with H, O (³P), and OH

A complete summary of the calculated transition state and reaction free energies for the reaction of H, O, and OH with several heteroatomic aromatic hydrocarbons as well as benzene are given in Table I.3. Reaction with the hydroxyl radical is the thermodynamically preferred reaction that also has the lowest barrier height. In general, Hammond’s postulate is not obeyed for the reactions of aromatic hydrocarbons with hydrogen and oxygen atoms because the formation of OH radical via O (³P) abstraction of the hydrogen atom is the least favorable process, although the barrier to abstraction by hydrogen atom is most often the highest.

Addition to Aromatic Hydrocarbons

H, O (³P), and OH Addition to Benzene: Net reaction

The aromatic ring provides a site for electrophilic addition to occur that can compete with the abstraction of a hydrogen atom from the aromatic ring. Kinetic data suggests that radical addition is the dominant pathway at low temperatures ($T < 325 \text{ K}$).³ All of these addition reactions are exoergic; however, the addition of atomic hydrogen to benzene is thermodynamically favored by $\sim 10 \text{ kcal-mol}^{-1}$.

Table I.3. B3LYP/6-31G(d) free energies (298 K) for the transition structures and products for the abstraction reactions: $\text{Ar-H} + \text{X} \rightarrow \text{Ar} + \text{HX}$ ($\text{X} = \text{H}, {}^3\text{O}, \text{and OH}$). Energies are relative to reactants in $\text{kcal}\cdot\text{mol}^{-1}$.

	Site	H Atom		O (${}^3\text{P}$) Atom		OH Radical	
		TS	Product	TS	Product	TS	Product
Furan	2	21.7	11.6	22.1	18.2	14.0	7.6
	3	21.3	11.6	21.9	18.2	13.7	7.5
Thiophene	2	19.9	9.8	20.5	16.4	12.7	5.8
	3	17.9	7.1	17.1	13.6	11.1	3.0
Pyrrole	2	20.9	11.1	19.6	17.6	12.2	7.0
	3	20.6	10.9	^a	17.4	12.5	6.8
	n	25.9	-16.5	^a	-9.9	^a	-20.6
Benzene	1	13.3	3.4	12.9	10.0	8.3	-0.6
Pyridine	2	13.0	-1.2	10.0	5.4	6.3	-5.2
	3	16.3	4.6	14.6	11.1	9.5	0.5
	4	16.0	3.7	13.8	10.2	9.2	-0.4
Pyridazine	3	14.4	0.3	12.4	6.8	7.7	-3.8
	4	15.1	2.2	12.6	8.7	8.1	-1.9
Pyrimidine	2	14.8	0.9	13.4	7.4	8.4	-3.2
	4	12.9	-2.0	10.4	4.6	6.3	-6.0
	5	17.5	6.0	16.1	12.5	10.3	1.9
Pyrazine	1	13.0	-1.4	10.3	5.1	6.0	-5.5

^a A transition structure was not located for this reaction.

H, O (³P), and OH Addition to Benzene: Transition States

Although the reaction free energies for the addition of H, O (³P), and OH vary by ~ 13 kcal-mol⁻¹, the barriers to the addition reactions are within ~ 2 kcal-mol⁻¹ of each other. Table I.4 presents a comparison between the Arrhenius activation energies calculated by the B3LYP/6-31G(d) method and those determined by experiment. Although the values are not in quantitative agreement, it is evident that the B3LYP/6-31G(d) qualitatively reproduces the experimental barriers.

Table I.4. Calculated and experimental activation barriers at 298K (in kcal-mol⁻¹).

	n	H [‡]	H [‡] + nRT	E _a (exp)
C ₆ H ₆ + H C ₆ H ₇	2	+ 2.5	+ 3.7	4.3 ^{13,17}
C ₆ H ₆ + O C ₆ H ₆ O	2	- 0.7	+ 0.5	4.0 ²⁶ , 4.8 ²⁴
C ₆ H ₆ + OH C ₆ H ₆ OH	2	- 2.3	- 1.1	0.9 ³³
C ₆ H ₆ OH C ₆ H ₆ + OH	1	+ 14.7	+ 15.3	17.8 ³⁴ , 18.7 ³³

H, O (³P), and OH Addition to Heteroatomic Aromatic Hydrocarbons

Although all of the addition reactions are exoergic, it is evident that addition to the five-membered aromatic rings is thermodynamically preferred. A summary of the reactions of H, O, and OH that proceed via the addition channel is presented in Table I.5. Addition of these radicals at each carbon site in every aromatic hydrocarbon is exoergic

Addition of O and OH to the heteroatoms in thiophene and pyrrole has been postulated as a mechanism by which these radicals react with the five-membered heteroatomic rings to explain kinetic measurements that are not in agreement with radical addition to furan.^{29-31,38,39,42} However, it is evident from the calculations presented in Table I.5, that addition to the heteroatoms in pyrrole and thiophene is not a likely pathway. For example, addition of O (³P) to the nitrogen atom in pyrrole is an endoergic step and is ~ 40 kcal-mol⁻¹ less favorable than addition to the *ortho* carbon atom. The barrier to addition directly to the heteroatom is also at least 30 kcal-mol⁻¹ higher than addition to the carbon atoms in pyrrole. In addition, a minimum that represented the addition of the OH radical directly to the nitrogen atom in pyrrole could not be found on the potential energy surface for the pyrrole + O (³P) reaction. Similarly, it is not thermodynamically favorable for the reaction of thiophene with O or OH to proceed via addition to the sulfur atom.

Table I.5. B3LYP/6-31G(d) free energies (298 K) for the transition structures and products for the addition reactions: Ar + X → ArX (X = H, ³O, OH). Energies are relative to reactants in kcal-mol⁻¹.

		H Atom		O (³ P) Atom		OH Radical	
	Site	TS	Product	TS	Product	TS	Product
Furan	2	6.1	– 28.7	^a	– 29.0	^a	– 25.5
	3	8.8	– 16.8	5.4	– 9.2	6.2	– 7.6
Thiophene	2	6.9	– 31.1	3.1	– 23.1	3.9	– 22.0
	3	8.2	– 19.7	5.5	– 11.2	6.0	– 9.3
	S				2.4		
Pyrrole	2	5.5	– 22.9	^a	– 22.2	^a	– 18.8
	3	8.2	– 13.8	4.3	– 8.4	5.3	– 5.8
	N	26.1	24.5	37.7	37.3	^b	^b
Benzene	1	7.6	– 18.4	6.3	– 4.8	5.7	– 8.3
Pyridine	2	9.2	– 17.9	8.5	– 11.2	8.6	– 9.5
	3	8.9	– 18.5	7.1	– 10.6	7.1	– 7.3
	4	9.4	– 16.9	9.3	– 7.3	8.6	– 5.2

^a Barrierless reaction.

^b Transition state and product were not located for this reaction.

The B3LYP/6-31G(d) calculations suggest that transition states structures do not exist for several of the addition products. There is an asymptotic addition channel that is barrierless for the reaction of the atomic oxygen and the hydroxyl radical to furan and pyrrole at the *ortho* position. In general, the barrier for addition of H, O, and OH to the five-membered aromatic rings is ~ 2 kcal-mol⁻¹ lower than addition to the six-membered aromatic rings. Although calculation of Arrhenius activation energies facilitates comparison of computational energies to experimental values, the comparison is not straightforward for the addition reactions to the heteroatomic aromatic rings. The available kinetic data do not distinguish between addition and abstraction pathways. The experiments have not discerned the addition mechanism, i.e. to which unique

carbon the radical is being added or whether the radical adds directly to the heteroatom.^{3,29-31,38,42}

Addition vs. Abstraction for Small Aromatic Hydrocarbons

The reaction of H, O (³P), and OH with aromatic hydrocarbons can proceed by two mechanisms: hydrogen atom abstraction or addition of the attacking radical. It is evident that the thermodynamically preferred site for addition is the site from which abstraction of a hydrogen atom requires the most energy, i.e. the site of the strongest C-H bond. For example, there are three unique sites for atomic hydrogen to attack pyridine. Hydrogen atom abstraction is the most facile at the *ortho* position, which corresponds to the site of the weakest C-H bond. The strongest C-H bond in pyridine is at the *meta* position. However, the *meta* position is the thermodynamically preferred site for addition to pyridine. A comparison of the energetics of these reactions is illustrated in Figure I.1 for hydrogen atom reaction with pyridine at the *ortho* and *meta* positions.

In general, the room temperature barrier height for the addition channel is lower than that for the abstraction channel. Several experiments, however, have shown that the abstraction channel becomes the dominant pathway at high temperatures.^{17,27,33,35,36}

Benzene + H, O (³P) and OH as a Function of Temperature

The free energy barrier height and the reaction free energy for both the abstraction and addition channel for the reaction of hydrogen atoms with benzene over the temperature range 298 to 2000 K are shown in Figure I.2. Throughout the temperature range the difference in the barrier heights remains less than 6 kcal·mol⁻¹, although at ~1200 K, the barrier for abstraction becomes lower than the barrier for addition. The abstraction channel becomes thermodynamically favored at temperatures > 1050 K. This supports the kinetic determination that the abstraction channel is negligible at temperatures less than 1000 K.¹⁷

Figure I.1. Hydrogen atom addition and abstraction on pyridine (G_{298} , kcal-mol⁻¹).

Figure I.2. Addition and abstraction on benzene vs temperature (ΔG , kcal·mol⁻¹).

For O atom, at ~ 1550 K the transition state energy for abstraction actually becomes lower than that for addition, although throughout the temperature range investigated here (298 to 2000 K) the energy difference is small enough that both reactions are likely to occur. Thermodynamically, the preference for the abstraction channel over the addition channel occurs at a lower temperature (~ 725 K) than the crossover for the reaction of benzene with atomic hydrogen. In addition, at 2000 K there is > 40 kcal-mol⁻¹ preference for atomic oxygen to react with benzene by abstracting a hydrogen atom instead of by electrophilic addition.

The barrier for the OH abstraction channel becomes lower than the barrier for the OH addition channel at an even lower temperature than for the analogous reactions with hydrogen and oxygen atoms, ~ 1025 K,. More significantly, the thermodynamic preference for the abstraction channel over the addition channel is calculated to occur at temperatures higher than only ~ 515 K. This will have a very important impact on NO_x staging conditions.

Conclusions

The potential energy surface for greater than 80 unique reactions of H, O (³P), and OH with aromatic hydrocarbons has been calculated at the B3LYP/6-31G(d) level of theory. The calculated transition state barriers and reaction free energies suggest that the addition channel is preferred at 298 K, but abstraction channel becomes dominant at high temperatures. The thermodynamic preference for reactivity with aromatic hydrocarbons increases in the order O(³P) < H < OH. Abstraction from six-membered aromatic rings is more facile than abstraction from five-membered aromatic rings. In general, barrier height and preference for abstraction from sites within the aromatic hydrocarbon is directly correlated with C-H BDE. However, addition to five-membered rings is thermodynamically more favorable than addition to six-membered rings. The free energies for the abstraction and addition reactions of H, O, and OH with aromatic hydrocarbons and the characteristics of the respective transition states can be used to calculate the reaction rate constants for these important combustion reactions.

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Section II. Structure-Based Predictive Models for Coal Char Combustion - Experimental Program (within Task 2 at Brown University).

The "Loss of Memory" Effect on Char Reactivity.

One of the fundamental premises of the current project is that char reactivity is significantly affected by structural changes in the carbon structure as a consequence of heat treatment and annealing. It is also suspected, however, that reaction itself can also play a role in determining the structure of the carbon. For example, it has been well established that kinetically-limited gasification does not always occur at constant particle diameter, but rather may be accompanied by gasification-induced atomic rearrangements, which in some chars result in loss of pore volume and carbon particle shrinkage [1,2]. Breaking bonds, removing cross links, and removing carbon atoms, increases the driving force for, and facilitates char *densification via* rearrangements analogous to those occurring spontaneously at somewhat higher temperatures *via* thermal annealing. If the net effect of this mechanism is significant enough, it can cause the reactivity of carbon materials which initially may be considerably different to ultimately be quite similarly; that is, they can lose the memory of their precursor state.

Experimental

Coal samples were obtained from the Penn State Coal Sample Bank, and the phenol-formaldehyde resin was synthesized in our laboratory [3]. Chars were prepared in a tube furnace in flowing ultra-high purity helium at 900°C and 1300°C for 1.5 and 4 hours, respectively, for each material. The final particles used were 30-100 Tyler mesh. Gasification was performed in a TGA in one atmosphere of pure O₂ at the indicated temperatures. The samples were burned out completely, and the amount of residual ash (for the coal chars) was used to determine fractional conversion on a carbon basis. Samples were characterized for pore size distributions and surface areas from 77K nitrogen isotherms.

Selected samples were subjected to thermal desorption following reaction in order to investigate the behavior of the population of intermediate oxygen surface complexes with respect to elucidating the mechanisms responsible for the observed reactivity behavior. These experiments were performed in the same apparatus at a heating rate of 50K/min following a

reactivity determination. The evolution rates of CO and CO₂ upon thermal desorption were recorded with a quadrupole mass spectrometer.

Results

Figure II.1 presents the reactivity and reaction rate behavior of the two Pocahontas #3 coal char (POC) samples. As shown, both rate measures approach one another asymptotically at high burn-offs. Pocahontas #3 (DECS-19), is a low volatile bituminous coal with about 4.55% ash (AR basis). Consequently, it is possible that the approach of the rate curves to one another may be due to improvement in the carbon-mineral matter interfacial contact due to progressive concentration of mineral matter with burn-off, and eventual domination of catalytic effects in controlling sample reactivity. As shown in Figure II.2, however, the phenolic resin char (PRC) samples exhibit the same qualitative behavior as the POC samples. In this latter case, however, the behavior cannot be ascribed to catalysis, since the mineral matter content of this material is insignificant.

Figure II.3 also shows the same qualitative trend for Beulah coal char (BEU) samples. Beulah (DECS-11) is a lignite coal with about 6.37% ash (AR basis). Although Figures 2 and 3 are qualitatively similar, the rate curves for the BEU char do not merge as rapidly as for the PRC at high burn-offs. Figure II.4 presents similar results for Pittsburgh coal char. Pittsburgh coal (DECS-23) is a high volatile bituminous coal with about 9.25% mineral matter (AR basis). Just as for the BEU char, the rate curves do not merge as rapidly as for the PRC and POC chars. Pittsburgh coal undergoes a fluid phase upon slow pyrolysis such that most of the porosity of the original coal is lost, which explains the very similar reactivities at low-burn-offs. As shown, the reactivity curves subsequently diverge quite considerably, however, due to different rates of porosity evolution, presumably controlled by the different morphologies of the two samples.

Post-reaction, CO thermal desorption spectra are presented in Figure II.5 for selected PRC samples, and Figure II.6 for selected POC samples. These reveal some interesting trends. For both types of chars, the oxygen surface coverage is considerably greater for the 900°C (“younger”) samples than for the 1300°C (“older”) samples. This is consistent with other indications that the “younger” chars have more disordered carbon associated with them, and, consequently, a greater number of sites for oxygen chemisorption. However, it is well-known [15] that the overwhelming majority of these oxygen surface complexes are not active in the

gasification reaction; rather it is only a small fraction of the lowest temperature complexes with the lowest desorption activation energies that effectively contribute to reactivity. In this regard, it is noted that the desorption spectra for the high burn-off cases for both chars appear to converge more closely at low temperatures than the low burn-off samples. This is evident in the “blow-up” of the low temperature region in Figure II.5 and is also in Figure II.6. This is consistent with the reactivities being more similar at high burn-offs than at low burn-offs..

Potentially, there are at least three major mechanisms that may be involved in determining the observed behavior; i.e., the effects of (1) porosity and surface area evolution; (2) degree of carbon ordering; and (3) mineral matter impurities. As already indicated, in the case of the PRC and POC samples, catalytic effects do not provide a suitable explanation. Normalization of the reactivities for surface area also does not account for the observed differences at low to moderate burn-offs. For example, the surface areas for the two POC samples are practically the same at low burn-offs and yet the reactivity of the 900°C sample is about five times that of the 1300°C sample. The surface areas of the two PRC samples are almost the same throughout the entire burn-off history, yet the reactivity of the 900°C sample is as much as an order of magnitude greater than that of the 1300°C at low burn-offs. And finally, the surface areas of the 1300°C BEU char are about *twice as large* as those of the 900°C sample over most of the burn-off range, and yet the reactivity of the 900°C sample is considerably greater.

In view of the preceding, it is proposed that the observed behavior is largely attributable to the evolution of the structural morphology of the samples. HRTEM fringe image analysis [4] indicates that although in each case the samples are quite different at low burn-offs, they become more similar at high burn-offs. Although this is a complex process, it appears that a major factor is selective burn-off of less ordered material at the expense of more highly ordered structures [5], such that eventually the morphology becomes similar enough that reactivity differences are minimized. This is supported by the thermal desorption data which indicate that the portion of the active sites responsible for reactivity appear to become more similar at high burn-offs for both the “younger”: and “older” char samples. These effects may also be related to recent observations of Salatino and co-workers [6] at higher temperatures where continued growth of ordered regions may also contribute to this effect.

References: Section II.

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Figure II.1. Reactivities of 900°C and 1300°C Pocahontas coal char samples in O_2 at 650°C.

Figure II.2. Reactivities of 900°C and 1300°C phenolic resin char samples in O_2 at 500°C.

Figure II.3. Reactivities of 900°C and 1300°C Beulah lignite char in O_2 at 525°C.

Figure II.4. Reactivities of 900°C and 1300°C Pittsburgh coal char in O_2 at 700°C.

Figure II.5(a). CO desorption spectra (50K/min) of selected phenolic resin char samples. The corresponding pyrolysis temperatures (900°C/1.5h; 1300°C/4h) and burn-off at 500°C in oxygen are indicated in the legend.

Figure II.5(b). Blow-up of low temperature region of Figure 5(a).

Figure II.6. CO desorption spectra (50K/min) of selected Pocahontas coal char samples. The corresponding pyrolysis temperatures (900°C/1.5h; 1300°C/4h) and burn-off at 500°C in oxygen are indicated in the legend.

**Section III. Experiments in Practical Combustion Systems -
Combustion Laboratory Activities (within Task 3 at OSU).**

Experimental Development.

The experimental aspects of the project continue to evolve. The second run of the furnace, utilizing Coal #1, has been successfully completed. Coal #1, hereafter referred to as C1, has been identified as a Pittsburgh seam coal and was analyzed by Commercial Testing and Engineering Company. The results are presented below in Table III.1.

Table III.1: Analysis of Coal #1.

<u>PROXIMATE ANALYSIS</u>			<u>ULTIMATE ANALYSIS</u>		
	<u>As Received</u>	<u>Dry Basis</u>		<u>As Received</u>	<u>Dry Basis</u>
% moisture	1.65	xxxx	% moisture	1.65	xxxx
% ash	3.61	3.67	% carbon	80.54	81.89
% volatile	37.09	37.71	% hydrogen	4.95	5.03
% fixed carbon	<u>57.65</u>	<u>58.62</u>	% nitrogen	1.50	1.53
	100.00	100.00	% sulfur	1.97	2.00
			% ash	3.61	3.67
Btu/lb	14226	14465	% oxygen (diff)	<u>5.78</u>	<u>5.88</u>
% sulfur	1.97	2.00		100.00	100.00
MAF FTU		15016			

The coal feed rate for Run #2 was 8 kg/hr; the air rate was 63 kg/hr. This yields an equivalence ratio of 1.6.

Based on the data available we estimate the combustion efficiency to be approximately 75%.

Wall temperatures were measured using thermocouples embedded in one wall of the furnace at 11.4 cm intervals. The profile obtained from Run #2 is shown in Figure III.1. The two measurements were taken about an hour apart and exhibit good agreement, showing that steady-state operation was probably attained at that time.

Solid samples were collected from the Ports 1, 2 and 3. These ports are located 25.40 cm, 36.83 cm, and 48.26 cm from the top of the furnace, respectively. Particle size distributions (PSD)

were determined for each of these char samples, as well as for the raw coal and the ash. Three separate distributions were gathered from each port and averaged. The results are presented in Figure III.2.

The gas analysis system is undergoing the final fine-tuning. The carbon monoxide analyzer (ordered in July) has finally been delivered and is currently being installed and integrated into the existing system. Preliminary analysis on Run #2 showed the carbon dioxide concentration in the upper section of the furnace to be approximately 7%. At an equivalence ratio of 1.6 there should be a corresponding carbon monoxide concentration of 16%. These results are subject to correlation with future findings. The CO analyzer will provide the necessary closure needed to determine the accuracy of the readings.

Experimental Results.

Thermogravimetric analyses (TGA) were performed on all of the char samples. A typical profile is shown in Figure III.3. The results are substantially similar to those previously reported except for the evident appearance of a double-sigmoid structure. The TGA procedure was to hold the sample at ambient (25°C) for five minutes. The temperature was then ramped 30°C/minute to 900°C, where it was held for five minutes. A MATLAB code has been written to analyze the TGA results, and to calculate the reaction rate. Although it is undergoing final refinements, preliminary results are shown in Figure III.4.

Other Work.

Additionally, we have submitted two short communications to *Energy and Fuels*: “Combustion Characteristics of Carbon: Dependence of the Zone I - Zone II Transition Temperature (T_c) on Particle Radius” and “Combustion Characteristics of Carbon: Influence of the Zone I - Zone II Transition on Particle Burn-Out in PC Flames.” These papers are co-authored with Dieter Fortsch of the University of Stuttgart. One of these papers has been reviewed. A third paper addressing the same issues as the others, should be complete within the next several weeks.

Figure III.1. Temperature profile of furnace wall (Run #2).

Figure III.2. Particle size distributions (PSD) for coal char, raw coal and ash.

Figure III.3. TGA profile for coal char sample collected from the top sampling port.

Figure III.4. Arrhenius plot for char collected from the top sampling port.

U.S. DEPARTMENT OF ENERGY

1 Program: DE -FC22-96PC96249

2. Program/Project Title: Structure-Based Model of Coal Char Combustion

3. Performers: Robert Hurt, Division of Engineering, Brown University

Project start date: 9/30/96

182 Hope Street,
Providence, RI 02912

Project completion date: 9/30/99

Number	Task/ Subtask	Activity	Project Duration												Comments / notes / performer
			<div> <div>1996</div> <div>1997</div> <div>1998</div> </div> <div> <div>ONDJFMAMJJASONDJFMAMJJAS</div> </div>												
1.	general	selection of test coals	<div> <div>1</div> </div>												Brown / OSU
2.	2.1	development of dynamic structural models													
2a.		<i>nonbonded graphene layers</i>	<div> <div>2</div> </div>												BU / Brown
2b.		<i>linked networks</i>	<div> <div>3</div> <div>4</div> </div>												BU / Brown
2c.		<i>model synthesis</i>													Brown
3.	2.	<i>in-situ, hot-stage fringe imaging</i>	<div> <div>5</div> </div>												Brown
4.	2.2	computational chemistry of surface oxidation	<div> <div>6</div> </div>												OSU
5.	3	experiments in contrasting flame types	<div> <div>7</div> <div>8</div> </div>												OSU
6.	3	analyses of char samples from part 5.	<div> <div>9</div> </div>												OSU
7.	2.1	establishment of secondary correlations:													
7a.		<i>structure / reactivity</i>	<div> <div>10</div> </div>												Brown
7b.		<i>structure / fluidity</i>	<div> <div>11</div> </div>												Brown

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Number	Task / Subtask	Activity	Project Duration												Comments / notes / performer	
			1998	1999												
			O	N	D	J	F	M	A	M	J	J	A	S		
1.	general	selection of test coals	complete												Brown / OSU	
2.	2.1	development of dynamic structural models														
2a.		<i>nonbonded graphene layers</i>													12	BU / Brown
2b.		<i>linked networks</i>													13	BU / Brown
2c.		<i>model synthesis</i>													14	Brown
3.	2.	<i>in-situ, hot-stage fringe imaging</i>													15	Brown
4.	2.2	<i>computational chemistry of surface oxidation</i>													16	OSU
5.	3	<i>experiments in contrasting flame types</i>													17	OSU
6.	3	<i>analyses of char samples from part 5.</i>													18	OSU
7.	2.1	<i>establishment of secondary correlations:</i>														
7a.		<i>structure / reactivity</i>													19	Brown
7b.		<i>structure / fluidity</i>	complete													Brown

U.S. Department of Energy
Milestone Log

Project title: Structure-based models for char combustion

Milestone Number	Description	Planned Completion Date	Actual Completion Date	Comments
1	Coals selected for laboratory and OSU furnace testing	April, 1997	June, 1997	coals also selected for laboratory testing at Brown, AFR, and BYU
2	First successful simulation of structural ordering in nonbonded graphene layers	Sept., 1997	June, 1997	
3	Completed set of simulations of growth and hindered motion based on hard lines	Sept. 1997	Sept. 1997	
4	Enhancement of algorithm in 3 to produce simulated structures comparable to HRTEM fringe images.	May., 1998	May., 1998	
5	First successful demonstration of in-situ, hot-stage fringe imaging	Sept. 1997	July 1997	
6	First set of thermochemical computations complete for model organic structures	Dec. 1997	Oct. 1997	
7	Shakedown / testing of OSU furnace facilities complete	Oct. 1997	Jan 98	
8	First set of char generation experiments complete on OSU furnaces	Apr. 1998	May 1998	
9	First set of char samples characterized -- major differences in flame types identified	Sept. 1998	Sept. 1998	
10	Structure-based prediction concept developed for fluidity and char macromorphology	Sept. 1998	still pending	
11	Reactivity / structure link assessed for mineral-free model carbon	Sept. 1998	still pending	

**U.S. Department of Energy
Milestone Log (page 2)**

Project title: Structure-based models for char combustion

Milestone Number	Description	Planned Completion Date	Actual Completion Date	Comments
12	Modeling activities on non-crosslinked networks complete	Dec. 1998		
13	Modeling activities on cross-linked networks complete	Dec. 1998		
14	Unified model developed from parallel modeling efforts in 12, 13	Sept. 1999		
15	Completion of in-situ HRTEM studies - insights into structural dynamics included in models	Dec. 1998		
16	Thermochemical computations complete, likely oxidation pathways identified. Implications for modeling identified.	April. 1999		
17	Flame experiments complete	Jul. 1999		
18	Char analyses complete. Impact of annealing and heating rate on burnout from various flame types identified and quantified.	Jul. 1999		
19	Auxilliary correlations complete	Dec. 1998		