

THEORETICAL MODELING OF COLIQUEFACTION REACTIONS OF COAL AND POLYMERS

H.F. Ades and K.R. Subbaswamy,
Department of Physics and Astronomy,
University of Kentucky, Lexington KY 40506-0055

Keywords: coliquefaction, quantum chemical modeling

Differences in the behavior of coliquefaction reactions involving polyethylene/coal and polypropylene/coal have been reported. For instance, conversion and oil yields are higher with the polypropylene/coal system while preasphaltene and asphaltene products are higher in the presence of polyethylene. Also, differences have been observed in the coliquefaction of polystyrene and polyisoprene with coal in the absence of a catalyst, with coal conversion increasing from 38% to 60% with polystyrene and to 80% with polyisoprene. Synergism was observed in the polyisoprene/coal system. In an attempt to explain the differences in coliquefaction behavior of these polymers we have begun quantum chemical studies of these systems, using the Gaussian, MOPAC and TBMD suite of programs, to investigate possible differences in cracking of the polymers, in hydrogen transfer behavior and in addition reactions between polymer fragments and coal. Reaction barrier heights for the possible reaction pathways are being calculated and will be compared in order to build a kinetic model.

I. Introduction

Coliquefaction studies of coal with waste products has focused on certain basic questions: (1) what waste products and in what combinations are the best ones to use in coliquefaction processes; (2) what catalysts are good for coliquefaction and how do they act; and (3) is there synergism involved in coliquefaction? Given the complexity of the systems involved, answering these questions will require a combination of empirical and analytical approaches.

In this report on our preliminary modeling studies pertinent to the coliquefaction of coal and waste polymers we specifically address some of the available experimental results of Huffman, et al. ¹ and Curtis, et al. ²

II. Calculations

A. Polyethylene and Polypropylene

Huffman and coworkers¹ found large differences in the coliquefaction behavior of polyethylene (PE) and polypropylene (PPE) with Black Thunder (BT) coal in the presence of a zeolite catalyst (HZSM-5) and tetralin solvent. The oil yields of PPE with BT coal are higher (71%) than with PE and BT coal (41%). The preasphaltene and asphaltene yields are higher with PE and BT coal (28%) than with PPE and BT (18%). The total conversion for PPE and BT is 93%, while for PE and BT it is 72%. In the presence of the HZSM-5 catalyst and in the absence of the coal, PE and PPE essentially undergo 100% conversion at 430°C. However, with no catalyst present PE undergoes a 65% conversion at 430°C and PPE 88% at 420°C.

In an earlier study we³ addressed the experimental results of Huffman, et al. ¹ by considering several factors that might explain the differences in the coliquefaction of the two polymers with coal, namely: (i) the ease of cracking of PE vs. PPE, (ii) hydrogen transfer reactions from coal fragments to PE+ and PPE+ fragments, and (iii) addition reactions similar to the methylation of benzene found by He et al. ⁴

Zeolites are known to be cracking catalysts of hydrocarbons and these cracking reactions are thought to proceed through carbocation ion intermediates.⁵

Therefore, our starting point was to assume that the zeolite catalyst reacted with the neutral polymer to generate carbocation ions. We then looked at reactions of toluene with PE⁺ and with PPE⁺ in order to try to address the factors listed above. We used the MOPAC 5.0 program of Stewart⁶ and the Tight Binding Molecular Dynamics (TBMD) program developed by Menon and Subbaswamy.⁷ The TBMD method is based on parametrized Hamiltonian band structure methods of solid state physics and ideas from the extended Hückel method. Orbitals are not explicitly introduced at all, and no integrals need be computed. Hence, the method can be used for computing forces for performing molecular dynamics simulations on large systems. Results for structure are at least comparable to the commonly used semi-empirical methods such as MNDO.⁸

We calculated the bond dissociation energies (BDE) for the process

Long [PE⁺ or PPE⁺] fragment → Short [PE⁺ or PPE⁺] fragment + neutral alkene

using the MOPAC suite of programs and found the BDE for the break up of PE⁺ to be 2.10 eV, while that for PPE⁺ is 1.52 eV. The difference in BDE, indicating that PPE⁺ should be easier to crack than PE⁺ is an intrinsic factor that could contribute to the higher coliquefaction yield with PPE than with PE. Our finding is consistent with the observation of Feng, et al.,¹ who find that PPE is more easily liquefied than PE at lower temperatures, with or without a catalyst.

To investigate possible reactions with coal-derived fragments, we considered the interaction of PE and PPE carbocation ion fragments with toluene and with Model I, 4-(1-naphthylmethyl)biphenyl, using the tight-binding molecular dynamics (TBMD) method. The method gives results similar to MOPAC, but can be used to study the "real time" dynamics of processes involving large numbers of atoms. We investigated potential H transfer from the methyl group of toluene to the carbocation ion site of the polymer and found that the H transfer occurs much more readily to PE⁺ than to PPE⁺, suggesting a higher barrier in the latter. In fact, we never observed a complete transfer of the methyl H of toluene to PPE⁺. Such hydrogen transfer processes might provide another pathway for subsequent break-up of the coal fragment. We also investigated the possible transfer of the ring hydrogen from the para position in toluene, since it is known that the methyl group activates the para hydrogen in electrophilic reactions. However, we found no transfer in either PE⁺ or PPE⁺.

Within the TBMD calculation we also investigated the possibility of an electrophilic addition reaction in which the PE⁺ or PPE⁺ carbocation ion fragment adds to the toluene molecule (leading to carbon-carbon bond formation). This addition reaction was found to occur from an initial C-C distance of 2.5 Å with both PE⁺ and PPE⁺. The hydrogen transfer reaction should compete with this addition reaction in the case of PE⁺. However, we find the addition reaction to be lower in energy than the hydrogen transfer reaction and so the addition reaction should be favored. This latter reaction would lead to higher molecular weight products, *i.e.*, a retrograde process.

In trying to explain why in the PPE coliquefaction scheme there are fewer preasphaltenes and asphaltenes than with PE, we noted the following qualitative differences in the reactions and reaction products in our simulations.

1. We find that with TBMD the C-C bond of the addition product is longer in PPE⁺ than in PE⁺. In general the longer the bond, the smaller the overlap between the orbitals of the atoms in the bond, which thus leads to weaker bonds. Therefore, the addition product formed with PPE⁺ should have a weaker bond compared to the PE⁺ addition product and the reaction could be relatively more reversible under liquefaction conditions.

2. Primary carbocation ions are much higher in energy than secondary, which are higher in energy than tertiary. Therefore, the primary carbocation should

be much more reactive and undergo faster reactions. Using the MOPAC 5.0/PM3 computational scheme, we find with PE+ that the addition products are more stable than the starting reactants by 2.2 eV; for PPE+ the corresponding stabilization energy is only 1.2 eV. Therefore, the PE+ addition is more exothermic than PPE+. In an attempt to quantify the energy differences between PE+ and PPE+ for the addition reaction we compared the MOPAC calculated energies of the starting MOPAC minimized toluene and PE+ or PPE+ to the configuration that the toluene, PE+ and PPE+ took after addition but with removing the other species (a 1-SCF calculation) and found it takes 1.4 eV for PE+ to move to the configuration after addition and 1.65 eV for PPE+ to move. Including the rearrangement of the toluene, a first approximation to the "barrier" for molecular adjustment is 3.28 eV for PE+ and 3.43 eV for PPE+. Therefore, it appears that the PPE+ reaction has a higher activation energy for addition and is, therefore, slower than the PE+ addition reaction.

In our latest series of calculations we have been investigating possible hydrogen transfer reactions from solvent to the two polymeric cation fragments. It has also been found that good hydrogen donor solvents, such as tetralin, the solvent used by Huffman, et al.¹, act as chain terminators in the chain depolymerization schemes of polymers. This, in turn, will lead to lower conversion.⁸ Therefore, we investigated potential hydrogen transfer from tetralin to PE+ and PPE+ using the TBMD method. (See Figure 1.) We have found that hydrogen transfer readily occurs from tetralin to PE+ at PE+... (H-tetralin) distances up to 2.5 Å. The transfer from tetralin to PPE+ was found to occur only when the PPE+... (H-tetralin) distance was 1.9 Å. Therefore, the depolymerization of PE+ is much more readily terminated in the tetralin solvent than the depolymerization of PPE+, which would lead to lower conversions for PE. We are now quantifying the barriers for the H transfer from tetralin and for H transfer from the aliphatic carbon atoms of Model I to the two polymers, as well as the barrier for C bond formation in order to construct an overall kinetic scheme.

B. Polystyrene and Polyisoprene

Curtis, et al.² have observed differences in the coliquefaction behavior of polystyrene (PS) and polyisoprene (PI) with Illinois No. 6 coal. When liquefied alone, polystyrene and polyisoprene liquefied readily, while coal underwent a 38% conversion. No solvent or catalyst was used. In coliquefaction with coal, and in the absence of either catalyst or solvent, conversion increased to 60% with coal/polystyrene and 80% with coal/polyisoprene. A synergistic effect was observed in the coal/isoprene system. The experiments were carried out at 400°C.

Synergism was also observed for the PI/coal system when a Mo naphthenate plus sulfur or Fe naphthenate plus sulfur catalyst was used. However, for the PS/coal system a slight synergism was observed with the Mo naphthenate plus sulfur catalyst but not with the Fe naphthenate plus sulfur catalyst.

We have begun our modeling of the PI/coal and PS/coal systems by considering the experiments in which there were no catalysts or solvents present. We are using the PM3 option in the MOPAC computational scheme and, in the absence of any catalyst, we are assuming that free radical decomposition of the two polymers would occur. By comparing the energies of the two free radicals formed on bond cleavage to the energy of the whole polymer fragment, we calculate the BDE of PS to be 2.54 eV while that of PI is 2.42 eV. For comparison, the PM3 BDE of the bibenzyl bond of Model I is 2.96 eV. Therefore, PI should be slightly easier to liquefy than PS and both decompose more readily than Model I.

We are now investigating hydrogen transfer barriers for transfer of hydrogen between toluene (our initial model for coal derived fragments) and the two free radical fragments formed in the thermal decomposition of PI and PS. (See Figure 2.) A lower hydrogen transfer barrier in the PI/coal system, which would aid in the decomposition of coal, than in the PS/coal system might explain the synergism observed in one system and not the other. We will also consider radical hydrogen

transfer reactions and hope to extend our studies to the catalyst systems in the future.

Acknowledgements: This research was supported by USDOE contract DE-FC22-93PC93053 to the Consortium on Fossil Fuel Liquefaction Science.

References

1. Feng, Z.; Zhao, J.; Rockwell, J.; Bailey, D.; Huffman, G. *Prepr., Div. Fuel Chem., Am. Chem. Soc.*, **1995**, *40*, 34.; *Fuel Proc Tech*, **1996**, in press.
2. Curtis, C.; Tang, Y.; Luo, M. Presented at 8th Annual Technical Meeting, CFFLS, **1994**.
3. Ades, H.F.; Subbaswamy, K.R. *Fuel Proc Tech*, **1996**, in press.
4. He, S.J.X.; Long, M.A.; Wilson, M.A.; Gorbaty, M.L.; Maa, P.S. *Energy Fuels*, **1995**, *9*, 616.
5. Bhatia, S. *Zeolite Catalysis: Principles and Applications*; CRC Press, **1990**.
6. Dewar, M.J.S.; Stewart, J.J.P. *Quantum Chemistry Program Exchange No. 58 vers. 5.0*, Indiana University (Bloomington).
7. Menon, M.; Subbaswamy, K.R. *Phys. Rev. Lett.*, **1991**, *67*, 3487; Menon, M.; Richter, E.; Subbaswamy, K.R. *J.Chem.Phys.* **1996**, *104*, 5875.
8. Sato, S.; Murakata, T.; Baba, S.; Saito, Y.; Watanabe, S. *J. Appl. Polym. Sci.*, **1990**, *40*, 2065.

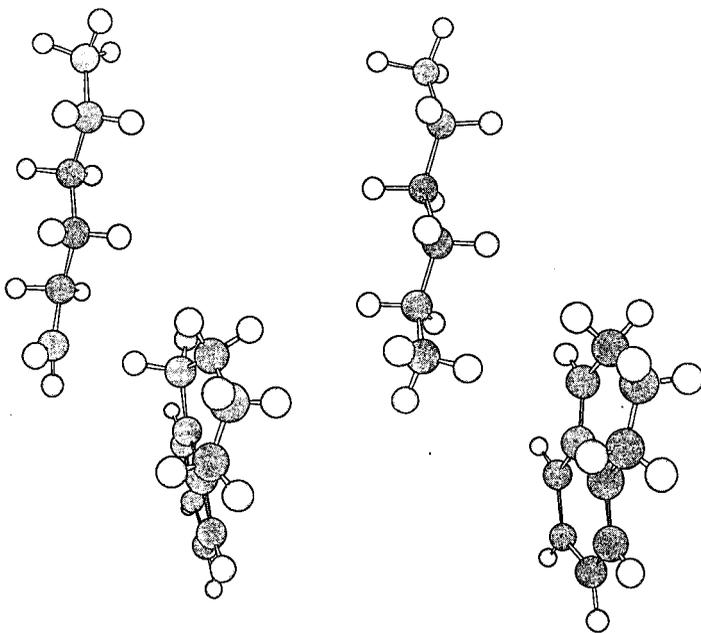


Fig. 1. Tetralin-PE⁺ before and after H transfer from tetralin to PE⁺.

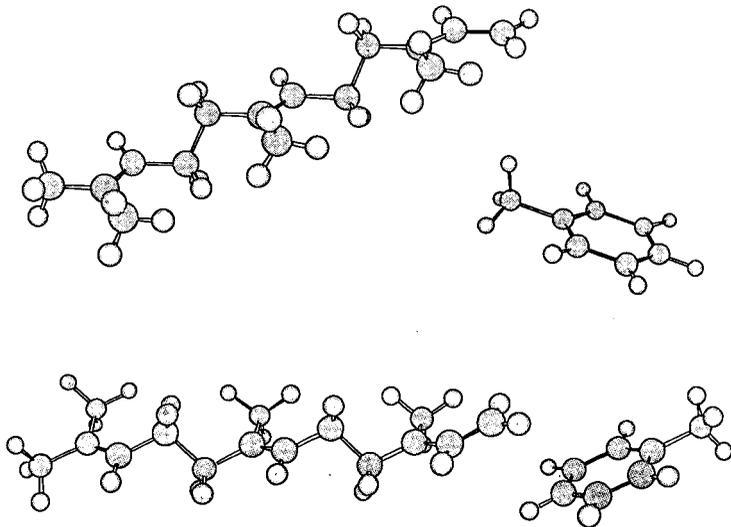


Fig. 2. Typical initial configurations considered for H atom transfer from toluene to a PI free radical fragment.