Journal of Molecular Graphics and Modelling 62 (2015) 325–341

Contents lists available at ScienceDirect

Journal of Molecular Graphics and Modelling

journal homepage: www.elsevier.com/locate/JMGM

An ab initio molecular dynamics analysis of lignin as a potential antioxidant for hydrocarbons

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ARTICLE INFO

Article history:
Received 16 July 2015
Received in revised form 2 October 2015
Accepted 26 October 2015
Available online 31 October 2015

Keywords:
Lignin
Hydrocarbon oxidation
Ab initio molecular dynamics

ABSTRACT

Lignins are complex phenolic polymers with limited industrial uses. To identify new applications of lignins, this study aims to evaluate the conifer alcohol lignin as a potential antioxidant for hydrocarbons, using the petroleum asphalt as an example. Using the *ab initio* molecular dynamics (AIMD) method, the evaluation is accomplished by tracking the generation of critical species in a lignin-asphalt mixture under a simulated oxidative condition. The generation of new species was detected using nuclear magnetic resonance and four analytical methods including density of states analysis, highest occupied molecular orbital and lowest unoccupied molecular orbital analyses, bonding and energy level analysis, and electrostatic potential energy analysis. Results of the analyses show that the chemical radicals of carbon, nitrogen and sulfur generated in the oxidation process could enhance the agglomeration and/or decomposition tendency of asphalt. The effectiveness of lignins as an antioxidant depends on their chemical compositions. Lignins with a HOMO–LUMO gap larger than the HOMO–LUMO gap of the hydrocarbon system to be protected, such as the conifer alcohol lignin to protect petroleum asphalt as was studied in this work, do not demonstrate beneficial anti-oxidation capacity. Lignins, however, may be effective oxidants for hydrocarbon systems with a larger HOMO–LUMO gap. In addition, lignins may contain more polar sites than the hydrocarbons to be protected; thus the lignins' hydrophobicity and compatibility with the host hydrocarbons need to be well evaluated. The developed AIMD model provides a useful tool for developing antioxidants for generic hydrocarbons.

1. Introduction

Hydrocarbons originated from living organisms on earth are the raw materials for many industrial sectors. To name a few as examples, hydrocarbons have been used to synthesize or make various plastics, textiles, and rubber commonly used in people's daily lives. Hydrocarbons however are prone to degradation in air through a series of exothermic reactions with oxygen. Such oxidative reactions could produce thousands of new species by means of rapid combustion or slow aging at temperature ranging from some hundred to a few thousand K [1–3]. To prevent or minimize the long-term chronic oxidative aging, lignins have been used as antioxidants in different hydrocarbon-based materials such as food [4], paper pulp [5], or in generic hydrocarbons as a radical scavenger [4,6]. Being a waste product from pulp and paper industry, lignins are complex phenolic polymers with limited industrial use and have often been treated as a fuel material in the process of pulping [6]. New and more sustainable applications of the massive lignins produced annually would produce significant economic and environmental benefits.

Research efforts to date have focused on utilizing the anti-oxidation capacity of lignins, leading to two categories of applications of lignins. The first category of applications entails direct blending large amounts of underivatized lignins in the hydrocarbons to be protected [4,7], and the second category uses relatively small amounts of derivatized lignins that have demonstrated capability to prevent or minimize oxidation [8,9]. The first category of applications of lignins could reduce the desirable mechanical properties of the matrix materials being protected [7]. Regarding the second category of applications, lignins are polar polymers with one or two hydroxyl groups per monomer and thus can only dissolve in fairly polar matrix materials. Such low solubility of lignins could limit their contact with the radicals responsible for oxidation and thus limit the effectiveness of lignins as an antioxidant. As such, studies of lignins as an antioxidant have been limited

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http://dx.doi.org/10.1016/j.jmgm.2015.10.013
1093-3263/

to polar hydrocarbons and composite material systems that contain sufficient polar components [9].

Petroleum asphalt is a representative hydrocarbon system with widespread industrial applications, such as for making roof shingles and road pavements. To date, in the United States more than 70% of commercial and residential buildings are cover with shingles made of asphalt mixtures [10] and over 93% of road miles are paved with asphalt concrete [11]. Petroleum asphalt is a balanced system between polar radicals and nonpolar ingredients, composed of saturates, aromatics, resins and asphaltenes based on their polarizability and polarity different solvents [12–14]. The saturate part of asphalt are nonpolar linear, branched and/or cyclic saturated hydrocarbons. The aromatic component of asphalt is more polar than saturates owing to the aromatic rings contained. The resins and asphaltenes of asphalt both are apparent polar radicals, and the resins are soluble with heptane or pentane while asphaltenes are insoluble in heptane. Asphalt mixtures and concrete used for buildings and roads have a service life of 5–10 years under the typical outdoor service conditions due to the chronic oxidative aging of asphalt binder. Such a service life of materials is significantly shorter than the structural life expectances of the buildings and roads which is typically 50 years [11]. Thus, asphalt as a hydrocarbon system needs to be protected against oxidative aging.

Numerous chemical agents have been proposed as potential antioxidants for hydrocarbon systems, such as the dibutyldithiocarbamates and naphthenic oil for general organic polymers and styrene-butadiene-styrene and styrene-b-butadiene for petroleum asphalt in specific [15,16]. Considering the scavenging capability of lignins on the radicals of a hydrocarbon system, this study aims to explore the potential application of lignins as an antioxidant for asphalt binder. This study takes the approach of numerical analysis towards this goal to avoid the expensive and laborious experimental endeavors. Moreover, since the study of the effectiveness of antioxidants for hydrocarbons is constantly challenged by the complexities of organic chemistry and the slow process of oxidative aging at service temperature, a clear understanding of the anti-aging mechanisms of lignins has not been adequately addressed experimentally although many antioxidants have been proposed for hydrocarbons. The numerical approach can hopefully circumvent these challenges by accurately tracking new species generated in oxidation.

2. Ab initio molecular dynamics

Generic atomistic modeling approaches enable the calculation for molecular geometries, structures, reactivities, spectra, and other properties. There are five major types of atomistic modeling approaches that have been developed and used for modeling materials, which are listed as follows in the order of their development time. (1) Molecular mechanics based on a ball-and-springs type of analogy of motion of molecules, (2)Ab initio methods based on theoretical solutions of Schrödinger equation without fitting to experiment, (3) Semiempirical methods based on approximate solutions of Schrödinger equation with appeal to fitting to experiment using parameterization, (4) Density functional theory (DFT) method that solves Schrödinger equation by means of electron density instead of wavefunctions as used in ab initio methods, (5) Molecular dynamics methods that simulate motion atoms of a molecular system based on classical Newtonian or Hamiltonian mechanics while meeting the thermodynamic equilibrium at the same time [17].

The method of molecular mechanics can be used to determine the geometries, structures and energies of large hydrocarbon molecules such as proteins and nucleic acids. Molecular mechanics however does not give information on electronic structures and therefore cannot simulate new bonding or de-bonding that is not pre-defined in the interatomic potentials [18]. The method of molecular dynamics based on classical Newtonian or Hamiltonian mechanics in general does not give electronic information either and therefore does not simulate chemical reactions that are not predefined. Ab initio and DFT methods enable generating new species by solving the Schrödinger equation; however, these two methods do not allow computing big systems that exceed a few hundred atoms [19]. The semiempirical methods, which are much faster than ab initio and DFT methods, can be applied to much larger molecular system. The semiempirical methods however involve more approximations in solving the Schrödinger equation. The very complicated integrals that must be calculated in the ab initio method are not evaluated but fitted to the experimental values [17]. This plugging of experimental values into a mathematical procedure to get the best calculated values is known as parameterization. The semiempirical methods therefore are the mixing of theory and experiment based on the Schrödinger equation but parameterized with experimental values. As such, a semiempirical method cannot give good answers for molecules or molecular systems for which the method has not been parameterized. Semiempirical calculations in general are about 100 times slower than molecular mechanics, but can be 1000 times faster than the DFT or ab initio calculations [20].

Aiming at predicting the unknown species and particularly the radicals that are responsible for the oxidative aging of petroleum asphalt and those that are responsible for the anti-oxidation capacity of lignins, this study adopts the ab initio molecular dynamics (AIMD) method for numerical simulation. The hybrid ab initio and

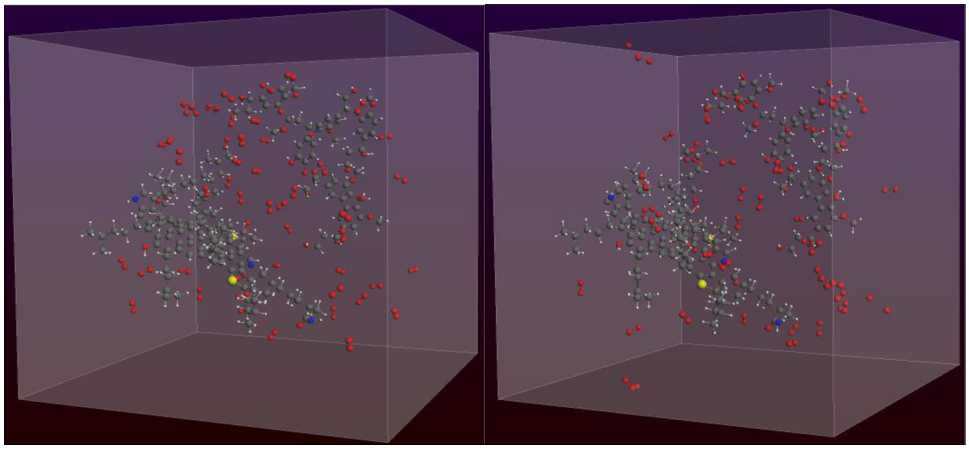

Fig. 1. Asphalt-lignin-oxygen system before (left) and during (right) oxidation simulation.