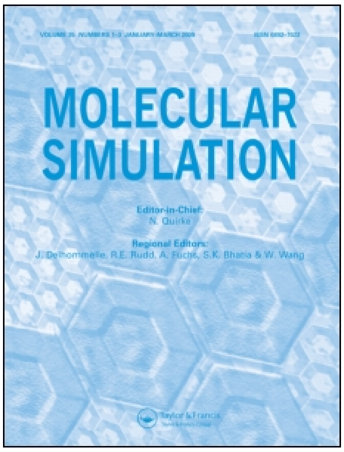

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INVESTIGATION OF LIGNIN–WATER INTERACTIONS BY MOLECULAR SIMULATION

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The results of molecular dynamics simulations of three lignin–water systems are presented. Static and dynamic properties of each system are compared to a benchmark system consisting entirely of water molecules. The significantly reduced mobility of water molecules local to lignin hydroxyl regions is attributed to hydrogen bond formation, while the slightly reduced mobility of water molecules in the vicinity of lignin methoxyl groups results from a hydrophobic effect that causes water molecules to structure themselves around these groups. The average diffusion of water in each system correlates with the number of methoxyl groups present in the system. As the number of methoxyls in the system increases, so too does the average diffusion constant of water in that system. The bulky methoxyl groups obstruct water from accessing lignin hydroxyl regions where hydrogen bond formation is anticipated and the hydrogen-bonded water lowers the average diffusion constant.

Keywords: Coal; Lignite; Lignin; Water interactions; Diffusion; Hydrogen bonding; Molecular modelling

INTRODUCTION

The high moisture content of lignite coal from the Latrobe valley, Victoria, Australia (60–70% wet basis) is a major disadvantage hindering the efficient use of this fuel for power generation. In current practice, lignite is dried evaporatively

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at the intake of the boilers, leading to direct loss of the latent heat of evaporation. This work is directed towards developing an improved understanding of lignite–water interactions, with a view to assisting the development of more efficient drying technologies. An understanding of water adsorption, binding and desorption behaviour in the lignite matrix is sought, together with detailed knowledge of the lignite chemical structure.

Since lignite is an assemblage of fossilized plant materials, it is very complex in both its physical and chemical structure. Naturally, this structure will incorporate many of the characteristics of the dominant precursor plant parts [1,2]. For the purposes of this investigation, this complexity can be substantially reduced if lignite constituents, rather than the entire lignite matrix, are considered.

In some parts of the Victorian lignite deposits, fossil wood is morphologically distinct and can be readily hand-picked from the surrounding coal matrix. Chemical analyses have shown that the cellulose in this fossil material is substantially degraded and that it is mainly the lignin component of the original wood that is preserved, albeit somewhat modified as a result of geochemical transformations [3–6]. Thus, we are using lignin as a model system to investigate lignite–water interactions.

In this preliminary investigation, we have used molecular dynamics (MD) approaches to investigate and compare the interactions between water and three (idealized) lignin polymer constructions.

Molecular modelling (MM) is a valuable tool for studying complex molecular systems at a fundamental level that may be difficult or impossible by other methods. It can be used to create and simulate simplified model systems that are representative of larger, complex systems or their parts. Having built a molecular model, an inter-atomic interaction potential is assumed and the time development of the system is simulated using the classical MD algorithm as described by the Newton's equation of motion. The equilibrium configurations of the molecular systems obtained during the MD can then be analysed in terms of structural, dynamic and thermodynamic properties of the system including molecular geometries, conformations, physico-chemical associations and mobility of components. Structure determination and assessment of mobility are important stages in the course of understanding lignite–water interactions. MM provides a means for investigating the relationship between lignite structure and its molecular interactions with water. MM approaches have been employed to construct and investigate the different conformations of coal precursors [7], coal structure using stochastic approach [8] and the effect of chemical structure on physical density of coal [9]. Other MM studies have also been used for simulating the interactions between coal and various solvents [10].

MM can be extended to the investigation of systematic changes in chemical structure which may or may not be real, but which can assist chemists in the rationalisation and understanding of observed behaviour. The long-term goal of this work is to discriminate the effects of changes in chemical structure upon lignite–water interactions, in particular the equilibrium moisture content (EMC). With this kind of knowledge, it may be possible to control and modify both the lignite structure and lignite–water behaviour to assist dewatering. It has been claimed that the percentage of elemental oxygen, the oxygen functional group distribution and the extent of cations exchanged at acid sites in the lignite structure may influence the EMC of lignite [11]. It has also been observed that the EMC of lignite is irreversibly altered following drying [12,13]. Discriminating the relative importance of organic structure versus physical structure (e.g. the micropore size distribution) is also a target of this investigation.

Using MM, basic models of lignite–water systems can be constructed and simulated such that each of these factors can be investigated independently. The strategy is to gradually improve and expand the models to better represent real

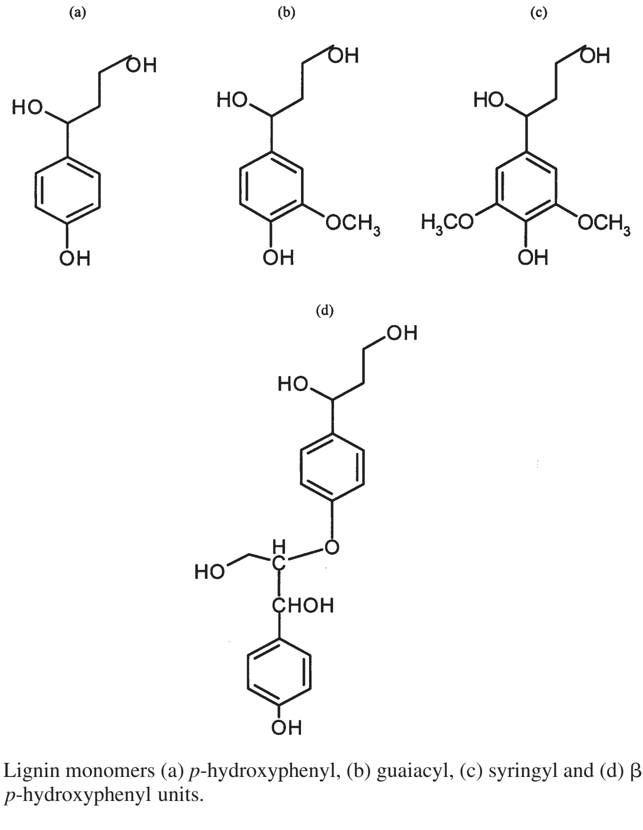

FIGURE 1 Lignin monomers (a) *p*-hydroxyphenyl, (b) guaiacyl, (c) syringyl and (d) β-*O*-4 linkage between two *p*-hydroxyphenyl units.

systems and allow the combined effects of variations in organic and physical structure to be evaluated. Through this approach it is anticipated that MM results will help us interpret the experimental observations in terms of fundamental molecular interactions.

MODEL SYSTEMS

It is well known that lignite is derived largely from plant materials (with wood making up a large bulk of lignite) and that lignin is the main surviving component of coalified wood [3–6,14,15]. The presence of lignin-derived molecules in lignite has been confirmed through carbon nuclear magnetic resonance (^{13}C NMR) and pyrolysis–gas chromatography–mass spectrometry [3–5,14,16]. Lignin is a biopolymer of propylphenyl units linked through various types of linkages but, of all the linkage types, the β-*O*-4 is by far the most abundant [17,18]. The common lignin monomers are *p*-hydroxyphenyl (Fig. 1a), guaiacyl (Fig. 1b) and syringyl (Fig. 1c). Figure 1d depicts a β-*O*-4 linkage between two *p*-hydroxyphenyl units.

Ten monomers of *p*-hydroxyphenyl were linked in a linear fashion through the β-*O*-4 linkage to produce a decamer of *p*-hydroxyphenyl. Decamers of guaiacyl and syringyl were constructed in same manner described.

Three lignin–water molecular systems were constructed for the modelling studies, each containing three decamers (of the same type) of lignin and water. The amount of water was determined experimentally by oven-drying a fossil wood sample (recovered from the Latrobe Valley) at 105°C for 4 h under nitrogen atmosphere. The moisture content of the wood was found to be 62% of the wet wood. Water was added to each of the three model systems so that the ratio of lignin to water corresponded to 38:62 by weight. For the purposes of benchmarking, a fourth model system, consisting purely of water molecules, was simulated. Table I summarizes the composition of these model systems. The density assigned to the model system was determined experimentally by helium pycnometry, using the same fossil wood sample referred to previously.

TABLE I Composition of model systems

System	*Lignin decamers*	*Lignin/water* (% weight)	*System density* (g cm^{-3})	*Cell dimensions* (Å^3)
Benchmark	–	0:100	1.000	28 × 28 × 28
1	*p*-Hydroxyphenyl	38:62	1.117	28 × 28 × 24
2	Guaiacyl	38:62	1.117	28 × 28 × 28
3	Syringyl	38:62	1.117	28 × 28 × 33

Prior to helium density measurement, the wood was dried. Thus, the density measured was that of the dry wood. Since shrinkage occurs on drying, it is necessary to correct the measured density to reflect that of the "as-recovered" wood using the following equation:

$$D_{\mathrm{r}} = \frac{D_{\mathrm{He}}}{1 + \frac{W}{100}(D_{\mathrm{He}} - 1)}$$

(Ref. [19]) where D_{r} is the raw density, D_{He} is the Helium density and W is the weight of the wet wood.

The corrected values have been assumed for the model systems.

SIMULATION PROCEDURE

The Amorphous Cell software (Accelrys Inc.) was employed to construct the initial configurations of the lignin decamers and water molecules in three-dimensional unit cells at the specified density (Table I). Details of the packing procedure can be found in Theodorou and Suter [20]. The time developments of these model systems were then simulated under constant temperature and volume conditions (thermodynamic NVT ensemble), using the classical MD algorithm with 1 fs time-steps. A thorough description of this algorithm can be found, for example, in Yarovsky [21]. The PCFF forcefield (Accelrys Inc.) was used to specify the potential energy functions. The simulation temperature was 300 K and the volume of the unit cell was maintained according to the defined density. Three-dimensional periodic boundary conditions were imposed on all systems during simulation with non-bonded Van der Waals and electrostatic interactions calculated using the cell multipole algorithm [22–24]. The systems were allowed to equilibrate for 100 ps, after which every 500th equilibrium configuration was collected for the next 100 ps. These configurations were used for subsequent analyses of static and dynamic properties of the molecular systems.

RESULTS AND DISCUSSION

In system 1, the lignin decamers are arranged in a layered manner, i.e. all three polymers are parallel to each other. In the other lignin–water systems (systems 2 and 3), pore-like features are observed. These pores are roughly estimated as 14 Å × 14 Å × 14 Å (system 2) and 14 Å × 22 Å × 14 Å (system 3).

Structural Properties: Hydrogen Bond Structure

The radial distribution function (RDF) is a measure of the probability of finding atom B within a specified distance of atom A [25] and hence is a valuable tool for identifying the hydrogen bond structure, i.e. sites where potential hydrogen bond donor and acceptor are within the hydrogen bonding distance.

To identify potential hydrogen bond pairs, we have adopted Luzar and Chandler's [26] distance criteria for hydrogen bonding in water–dimethyl sulfoxide systems. The cutoff distances were obtained from the first minimum in the RDFs, which were comparable to the RDFs determined from neutron diffraction data [27]. The cutoff distance between intermolecular oxygen and hydrogen was specified as 2.45 Å while the cutoff distance for hydrogen bonding between two oxygen atoms was 3.6 Å.

Figure 2 shows the RDFs between various lignin–water atomic pairs. In the benchmark system, the average O–H intermolecular distance between water molecules is 1.95 Å while the O–O intermolecular distance is 2.95 Å. Not surprisingly, these distances fall within the cutoff range for hydrogen bonding. It is well documented that water molecules in a bulk water system hydrogen bond with one another [28,29].

It can be inferred that hydrogen bonds form between lignin hydroxyl groups and water molecules since these atoms are located within the cutoff range, as demonstrated by peaks at 1.95 Å between hydroxyl oxygens and water hydrogens (and vice versa) in the RDF presented in Fig. 2a and b.

Methoxyl hydrogen atoms and water oxygen atoms do not come close enough to form hydrogen bonds (peaks at 3.05 Å, Fig. 2c). Methoxyl oxygens are physically shielded by adjacent methoxyl carbons (Fig. 2d) and hydrogens, consequently the hydrogen of water molecules cannot access the vicinity of methoxyl oxygens (4.75 Å separation as shown by RDF, Fig. 2e). Furthermore, methoxyls are considered hydrophobic compared to hydroxyls. The high probability of finding water at 3.05 Å form methoxyl hydrogens and 5.45 Å from ether oxygens implies a preferred distance or a hydration shell around these less-hydrophilic sites (Fig. 2f). Around the ether oxygen, water molecules are not found within the cutoff distance for hydrogen bond formation.

Dynamic Properties: Mobility of Water

To approximate the dynamic properties of the studied systems, diffusion constants of water have been calculated. The diffusion constant can be calculated from the Einstein equation or the slope of the mean squared displacements

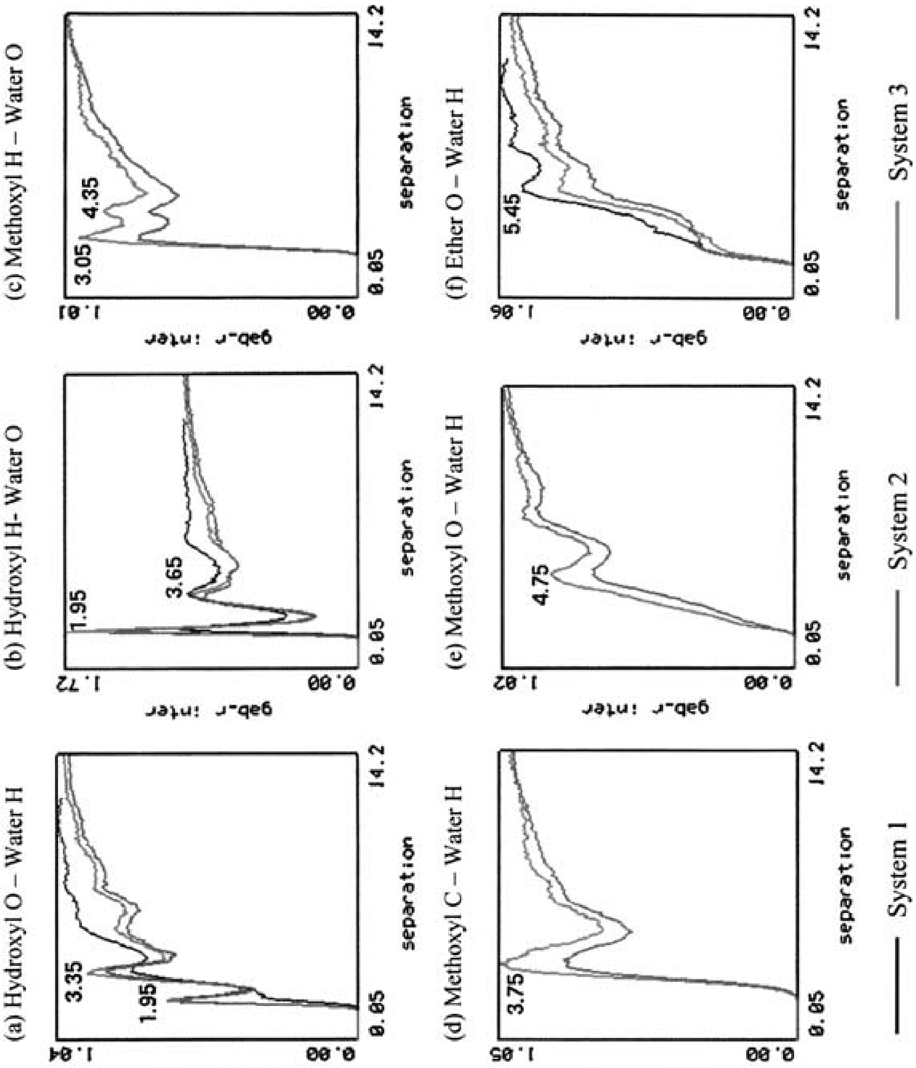

FIGURE 2 Radial distribution functions (first hydration shell).

(MSD) versus time plot [30], i.e.

$$D = \frac{1}{6N} \lim_{t \to \infty} \frac{\mathrm{d}}{\mathrm{d}t} \sum_{i}^{N} [r_i(t) - r_i(0)]^2$$

(Ref. [25]) where D is the diffusion constant, N is the total number of atoms, r_i is the position of atom i and t is time.

The term "diffusion", as used in this paper, refers to the self-diffusion of water. The diffusion constants obtained from these simulations are useful parameters for studying the dynamic behaviour of water in the lignin matrix, as a function of the polymer composition [31].

The diffusion constants, averaged for all water molecules in each system, have been calculated (see Table II). In addition, "subsets" of water molecules in the vicinity of lignin functional groups have been specified and their diffusion constants calculated (Table III).

It has been observed that the mobility of water can be correlated with the number of methoxyls in the systems. Methoxyls are rather bulky and hydrophobic compared to hydroxyls. Their presence seems to physically obstruct water molecules from accessing the vicinity of hydroxyls, where formation of hydrogen bonds is anticipated. Formation of hydrogen bonds will result in reduced mobility since the hydrogen-bonded water molecules become temporarily suspended at that position [31].

The local diffusion constants (Table III) show that the mobility of water molecules near hydroxyl groups is significantly reduced compared to the mobility of water molecules near methoxyl groups.

Water molecules located further than 6 Å away from lignin molecules are termed bulk water. Beyond this distance, the likelihood of any specific water–polymer interaction is doubtful so these water molecules might be expected to have properties similar to water in the absence of lignin, such as those in the benchmark system. However, compared to water molecules in the benchmark system, somewhat lower diffusion constants of bulk water molecules in the lignin–water systems were observed. This can be ascribed to the fact that the lignin–water systems have higher average densities than the benchmark system, resulting in slower diffusion. Realistically, there are two discrete densities in a lignin–water system: one of the lignin matrix and one of the water. The density measured by helium pycnometry is that of the dry lignin which was then corrected for the wet state. This density of the wet lignin takes into account the volume occupied by water in the lignin matrix. In the model systems, however, there is only one density value, with both lignin and water molecules sharing the same density. Hence, water molecules in the lignin–water model systems have a

TABLE II Global diffusion constants

System	*Diffusion constants* ($\times 10^{-5}\,g\,cm^{-2}\,s^{-1}$)
Benchmark	3.31
1	1.44
2	1.71
3	1.93

higher density than those of the benchmark system ($1{:}117\,g\,cm^{-3}$ cf. $1.000\,g\,cm^{-3}$). The "artifact" of the modelling protocol will require attention in future work.

CONCLUSIONS AND FUTURE WORK

Three lignin–water model systems and a pure water benchmark system were constructed and their structural and dynamic properties were simulated using the MD method. In system 1, the decamers are arranged in a layered fashion where all three decamers are parallel to one another. Pore-like features are observed in the other lignin–water systems. Compared to the benchmark system, on average, water molecules in the lignin–water systems exhibit slower diffusion. In particular, the diffusion constants of water molecules near lignin hydroxyl regions are significantly reduced, due to formation of hydrogen bonds as indicated by the preferred interatomic distance of 1.95 Å. The slightly reduced diffusion constant of water near methoxyl groups is attributed to the structuring of water around these groups, as a result of hydrophobic interactions. There is a preferred distance of 3.05 Å between methoxyl hydrogens and water oxygens. Water molecules that are further than 6 Å away from lignin molecules exhibit diffusion constants that are closer to those of the benchmark system. The differences that remain may be the result of the different densities ascribed to water in the benchmark system versus lignin systems, the latter being denser. Finally, the overall diffusion constant of water in the lignin–water systems

TABLE III Local diffusion constants (system 2)

Local water group	*Diffusion constants* ($\times 10^{-5}\,cm^{-2}\,s^{-1}$)
Within 2.85 Å of OH	0.83
Within 4.65 Å of OCH_3	1.34
Bulk water*	1.77
All water	1.71

* Water molecules located further than 6 Å away from lignin polymers.

increases with the number of methoxyl groups present in the system. This appears to be a consequence of the bulky methoxyl group hindering the access of water molecules to lignin hydroxyl regions, where hydrogen bonds would otherwise form.

This is a preliminary investigation into the structure of lignite. It is anticipated that future work will include the introduction of cross-linking between lignin polymers and inclusion of other oxygen functional groups such as carboxyls. This represents the condensation and oxidation processes that are observed during the transformation of fresh wood into fossilized wood (and hence to lignite). In addition, the three types of lignin polymers will be combined in the appropriate ratio for a better representation of wood. Further studies will also involve simulations of the effects of temperature and pressure on lignin–water interactions.

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