Swelling and maturity effects on adsorption in organic source rocks' organic matter by molecular simulations

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Résumé

The term "kerogen" defines the source rocks' organic matter (OM) that produces oil during the geological process of thermal maturation, in which the OM is progressively exposed to higher temperatures and pressures. Now, kerogen's definition is restricted to the source rocks' OM that is insoluble in the usual organic solvents. The maturity of a kerogen reflects whether it is in a state of oil generation (immature), gas generation (mature), or above its hydrocarbon production stage (overmature). In the so-called van Krevelen diagram, the maturation of kerogen is characterized through a two-dimensional diagram showing the evolution of the atomic H/C and O/C ratios, where three kerogen families are classified according to the origin of the OM: type I kerogen, with the largest H/C and lowest O/C, originates from lacustrine environments, type II kerogen from marine deposits and type III kerogen, with the lowest H/C and largest O/C, from terrestrial plants and animal remains (1). Kerogen has gained a lot of attention due to the emergence of shales gas because it is the key phase impacting the processes of hydrocarbon recovery or carbon sequestration as the fluid molecules are mainly trapped in the vicinity of its amorphous microporosity (pore size $<$ 20). Owing to the inherent complexity, heterogeneity, and diversity of kerogens, predicting their thermodynamic properties remains challenging.
In the past decade, several atomistic models of kerogen have been proposed (2,3,4) in order to study kerogens' properties through molecular simulations (see (5) for a review). Among such models, those of Ungerer *et al.* (3) have been the most widely used. They are built by packing a number of identical kerogen molecules, that respect the OM chemistry, in a periodic simulation box using annealing and cooling Molecular Dynamics (MD) simulations.

More recently, another strategy based on the Replica Exchange Molecular Dynamics (REMD) method was developed to obtain kerogen's models directly related to their organic precursor (4). The thermal decomposition of the latter (lignin, cellulose, etc.) is simulated through the REMD technique with the use of a reactive force field (ReaxFF) to allow for chemical bond breaking and formation. The REMD method accelerates the sampling of the full energy landscape over geological timescales by considering the dynamics of the initial precursor at various temperatures (above the geological one) and by allowing exchanges at a constant time interval between configurations of neighboring temperatures according to a Metropolis criterion. In the end, the resulting kerogen structure depends on the precursor considered (type) and the simulation duration (maturity). Ultimately, the fluid generated durin the degradation process is removed from the simulation box and the resulting kerogen microstructure is equilibrated at a given pressure and temperature.

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Here, based on the REMD technique, we present a new collection of atomistic models of kerogen (REMD models), obtained from a fatty acid precursor (type I), at various maturities (H/C ratio from 1.3 to 0.3). Additionally, the chemical inconsistencies of the obtained models resulting from the inherent approximations in the reactive force field used during the REMD simulations are corrected using a simulated annealing algorithm. Radicals of the kerogen microstructure are first identified, and then a Monte-Carlo method is used to ensure that all atoms satisfy the duet or the octet rules by adding (or removing) hydrogens or transforming a pi (sigma) bond into a sigma (pi) one. A similar procedure can be used to control the quantity of oxygen by functionalizing the microstructure. Once corrected, the kerogens' microstructures can be simulated using the OPLS classical force field, allowing for very efficient molecular simulations. Before turning to their adsorption properties, the evolution of their chemical, structural and mechanical properties (aromatic cluster size, heptagons/pentagons ratio, porosity, bulk modulus, etc...) as function of the H/C ratio is investigated first to notably show that they clearly follow simple trends.

We present a comparative study of CO2 adsorption in some of our models and those of Ungerer *et al.*, which correspond in terms of H/C and O/C ratios, while accounting for the poromechanical coupling between the adsorbed fluid and the kerogen microstructure, i.e., the ability of the structure to deform and swell upon adsorption. This is achieved by alternating between molecular simulations in the grand-canonical (μVT) and the isobaric-isothermal (NPT) ensemble for a large number of cycles, until both, the volume V and the number of adsorbed molecules N fluctuate around equilibrium values, giving thus access to the adsorption isotherm and the volumetric swelling. The imposed chemical potential of the fluid corresponds to a bulk fluid at the same mechanical pressure P that is imposed on the system (unjacketed or drained condition). Strikingly, we find that for pressures above tens of MPa Ungerer's models start to dissolve in CO2, unlike the REMD models (see Fig. 1). This is mainly due to the lack of cross-linking between the molecules used to build the models. Even for the most immature REMD model considered here (H/C = 1.53), the low amount of cross-linking in the model ensures its insolubility at large pressures, even though the volumetric swelling is important (_˜37%). Notably, it is also found that for the slightly more mature case (H/C = 1.12), both models have very similar adsorption isotherms at low pressure, although their accessible porous volumes can differ by 50%. We also note that, with increasing maturity (H/C ratio from 1.53 to 0.59), the porosity of the REMD models at low pressure evolves from roughly 7 to 37%, while it ranges from roughly 1 to 14% for Ungerer's models.
Finally, a study of adsorption for CH4 and CO2 is presented for nine REMD models corresponding to a fatty acid precursor with maturities ranging from very immature to overmature (H/C from 1.3 to 0.3), so as to unveil the effect of the maturity on the adsorption properties while always accounting for the adsorption-induced swelling, which largely prevails when the H/C ratio is greater than 0.7 for both fluids, even though swelling is more important in the case of CO2.