Coarse-grained model of kerogen for the modelling of thermodynamic and transport properties of confined hydrocarbon fluids

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ABSTRACT

Shale formations are recognized as an essential source of unconventional hydrocarbons, with kerogen, being the dominant source of valuable organic components. The unique nanostructure of kerogen, coupled with its inherent complexity, presents a significant challenge to unravelling the behavior of confined fluids and interactions within shale formations. Molecular modelling is the only available tool to explore the properties of kerogen at the atomic level. This work presents our recent advances in utilizing CG models to simulate kerogen structures encountered in shale formations.

OBJECTIVES

Using a mimetic approach and molecular dynamics simulations, we:

- ❑ Adopted the SAFT force field for coarse-grained models of kerogens.
- ❑ Built models of kerogen of different maturities.
- ❑ Validated the bulk density, compressibility, and dynamic swelling of kerogens, as well as the diffusion of confined liquid hydrocarbons.

BACKGROUND

Studying equilibrium adsorption and transport properties of light and heavy hydrocarbon liquids under confinement in shale formations is difficult experimentally due to extreme geological conditions (high pressure, up to 50 MPa).

Atomistic simulations have been the main tool of enquiry to address these challenges. In spite of the progress, these simulations are computationally intensive.

In contrast to fully atomistic simulations, the coarse-grained models enable the exploration of large multicomponent systems for up to several microseconds, hence providing the faithful exploration of equilibrium and transport properties of geofluids.

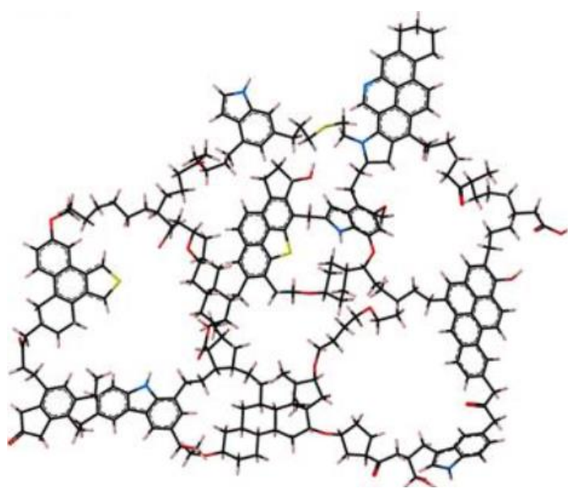


Fig. 1. Molecular model of a kerogen unit, reproduced from Ungerer et al. *Energy Fuels*, 29(1), 91-105, 2015.

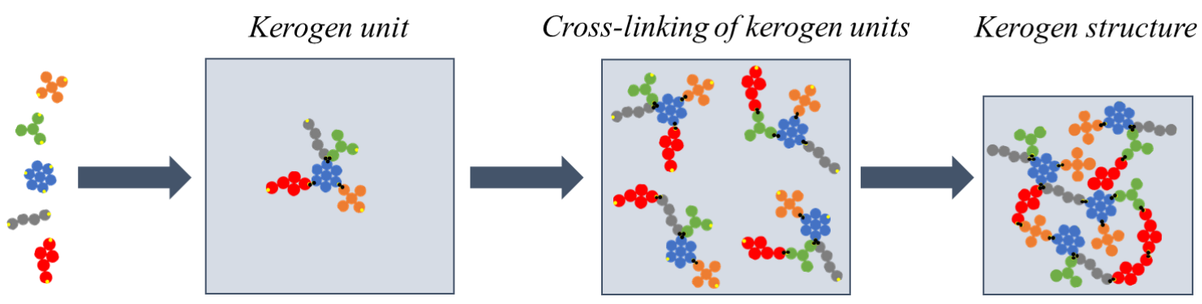
METHODOLOGY

We used the coarse-grained models of molecules with intermolecular interactions described by the Mie potential, which is based on a molecular equation of state, SAFT-γ Mie.

The coarse-grained models of different types of kerogen were constructed in two major steps: the generation of kerogen units and obtaining a kerogen structure from kerogen units.

By combining molecular units (n-dodecane, triphenylene, benzopyrene, perylene, and coronene), we generated kerogen units that reproduce the analytically-determined elemental composition of kerogen.

Kerogen units containing virtual interaction sites stick to each other during molecular dynamics simulations and form a cross-linked kerogen structure.



STRUCTURAL PROPERTIES OF KEROGEN STRUCTURES

Fig. 2 shows that the densities of the designed coarse-grained models are in quantitative agreement with the available experimental and reference theoretical data. Moreover, our models reproduce the isothermal compressibility and reveal a decreasing trend as kerogen matures. In comparison to immature kerogen 1A, mature 2B and over mature 2D and 2D* mostly consist of cross-linked aromatic molecules that lead to formation of a non-flexible structure, hence, reduction of its compressibility.

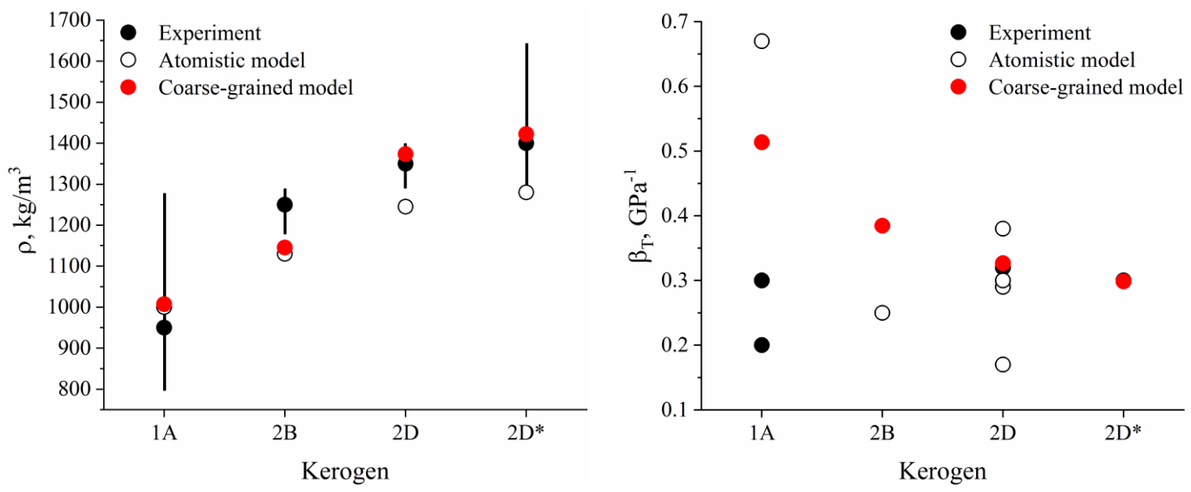


Fig. 2. Density (LEFT) and isothermal compressibility (RIGHT) of kerogens of different types

DIFFUSION OF CONFINED HYDROCARBON LIQUIDS

According to our studies presented in Fig. 3, the confined hydrocarbon liquids, such as toluene and cyclohexane, experience reduced mobility in immature 1A kerogen in comparison to bulk solvents. The confined liquid can move freely in the confined space due to the swelling of the kerogen. As kerogen matures and its structure becomes stiffer, the mobility of solvents significantly reduces.

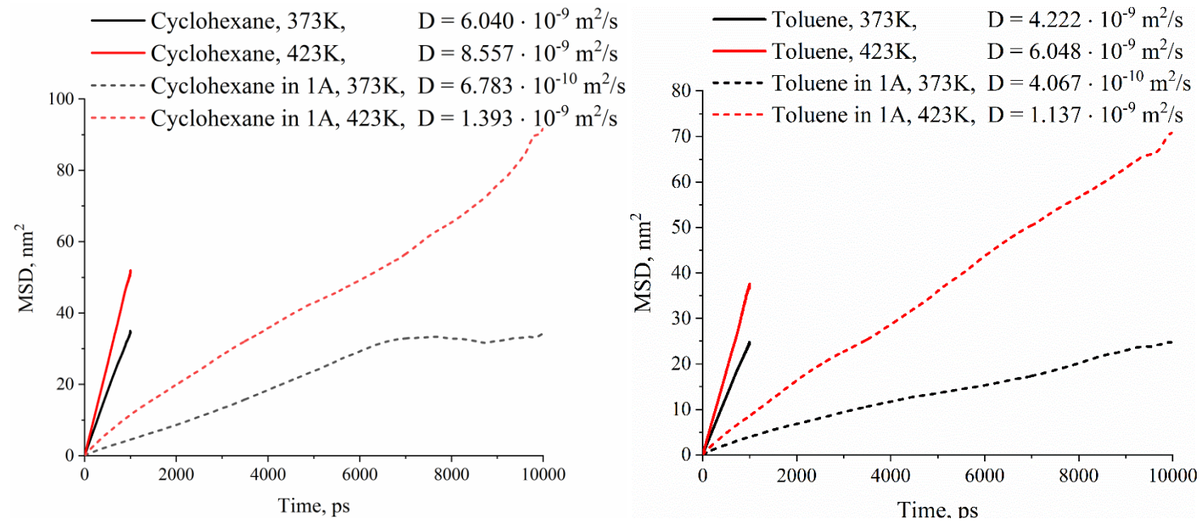


Fig. 3. Mean squire displacement of supercritical confined solvents in 1A kerogen structure at 30 MPa.

SUMMARY

- ❑ Coarse-grained simulations provide a suitable approach to study the behavior of hydrocarbon liquids confined in kerogen structures.
- ❑ The coarse-grained models reproduce the key bulk properties of kerogens, particularly density and isothermal compressibility.
- ❑ The obtained models also reveal transport properties of the confined heavy oil components, such as toluene and cyclohexane.
- ❑ The confined fluid swells kerogen structures to different extent depending on the maturity of kerogen and the nature of the fluid.
- ❑ The coarse-grained simulations based on the SAFT EOS provide a promising approach to study large scale systems at extreme conditions not attainable in experiments.