Molecular Fractionation in the Organic Materials of Source Rocks

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**ABSTRACT:** Hydrocarbons that are transported in a hierarchal path from the nanoporous constituents of a shale matrix to natural and then hydraulic fractures are subject to continuous fractionation during the journey. The organic nanopores of a source rock matrix known as kerogen have pore sizes on the angstrom scale. At that degree of confinement, pores can act as a selective membrane, preferentially maintaining some components over the others in a continuous fractionation phenomenon that alters the adsorption/desorption isotherm. Several studies have considered the adsorption/desorption behavior of kerogen on the basis of a single component. In reality, methane is associated with other hydrocarbons, making that assumption questionable. The present work investigates the multicomponent gas sorption of kerogen structures via a molecular computational approach. The continuous fractionation results in the accumulation of heavier components. The compositional changes alter the phase behavior, enlarging the anticipated two-phase regime. Additionally, the ability of molecules to diffuse from kerogen was also found to be affected by the fractionation effect. These microscale effects provide some insights into the potential factors that influence the productivity at the reservoir scale.

**INTRODUCTION**

The hydraulic fracturing of source rock formations creates means of hydrocarbon transport from the nanopores of the rock matrix to the wellbore. As the hydrocarbons travel this hierarchal path driven by the augmented pressure gradient, they exhibit different modes of transport, storage mechanisms, and rock–fluid interactions that, in turn, influence their composition.

Source rocks, clastic sedimentary formations consisting of clay-size grain, are rich in organic matter known as kerogen.1 This organic matter forms networks of nanopores where hydrocarbons can be stored.2 Kerogen has a strong affinity for hydrocarbons because of its chemical similarity and hence can store a significant amount in sorbed and compressed forms.3 Fluids confined in nanoporous media behave differently from other types of fluids. Luo et al.4 conducted an experiment to study the phase behavior of an octane–decane binary mixture. The bubble point was found to be lower than the typical value. The extent of the change in phase behavior was found to be proportional to the degree of confinement. Walton and Quirke5 used a grand canonical Monte Carlo simulation (GCMC) to study the condensation of confined fluids, finding that it occurred at a pressure lower than what was expected. Wongkoblap et al.6 followed a similar approach, reporting comparable observations with some pore size-dependent hysteresis in the condensation/evaporation processes. Jiang and Sandler7 studied the phase transitions of hydrocarbons in nanotubes, finding their critical temperature and pressure to be different from their bulk phase values. Singh et al.8 observed a positive deviation of saturation pressure of confined fluid for a 3 nm slit pore and a negative deviation when the pore size was reduced to 1 nm.

The degree of uncertainty is even larger when more than one component is present. Didar and Akkutlu9 and Pitakbunkate et al.10 studied mixtures of hydrocarbons in which one component had a higher relative affinity for the surfaces of nanotubes. The researchers found that the properties of the mixtures were highly correlated with the degree of confinement. Bui and Akkutlu11 conducted a combined molecular dynamics (MD) and GCMC to study the compositional variation of a mixture of hydrocarbons in a nanotube in thermodynamic equilibrium with a bulk phase of constant composition. These researchers found the composition inside the nanotube to be different from that of the bulk phase. Moreover, the variation of composition inside the nanotube was determined to be dependent on the pressure. The fraction of heavier molecules increased as the pressure decreased. Such conclusions have significant implications for the properties of the fluids and hence the recovery from source rock reservoirs.

The build-up of pressure inside kerogen pores during hydrocarbon generation results in the formation of microcracks. These can be seen in various electron microscopy studies of source rock matrices.12–14 These microcracks serve...
as conduits of fluid transport from organic nanopores to larger fractures.\(^\text{15}\) During production, compressed hydrocarbons undergo continuous expansion and depletion through microcracks, shifting the adsorption equilibrium to favor desorption. The walls of the organic nanopores influence transport and storage mechanisms, making the continuum approach to modeling hydrocarbons insufficient.\(^\text{16,17}\) Various studies have considered the occurrence of natural gas in nanopores and adopted modified versions of the classical petrophysical models.\(^\text{18−21}\) Moreover, the surfaces of kerogen can favor one component over another, which makes the composition of a given mixture vulnerable to continuous changes during the production span.

The aforementioned intricacies hinder deriving an analytical solution. Conversely, experimental work is surrounded with a high degree of uncertainty. The extraction and petrophysical analysis of kerogen is quite challenging because of the very fine scale of the constituents.

In the absence of analytical and experimental means of studying multicomponent depletion from organic nanopores, computational approaches such as molecular modeling can offer insights. Bui and Akkutlu\(^\text{11}\) studied recovery from a single organic nanopore a few nanometers in size that contained some light hydrocarbons, reporting some dependency of the fluid composition on the degree of confinement. The present work investigates the depletion of a multicomponent gas mixture from nanoporous materials, considering more representative kerogen structures rather than straight nanopores.

We based our conceptual model on repeated observations of the close association of organic materials with microcracks. Examples can be found in the scanning electron microscopy (SEM) images shown in Figure 1. Hydrocarbons stored in the kerogen were subject to a pressure gradient when the formation was hydraulically fractured. During their continuous migration to the microcracks, the hydrocarbons were subject to chemical and physical interactions with the kerogen surfaces. A molecular replication of the kerogen was then obtained, loaded with some arbitrary multicomponent gas mixture. After that, desorption simulations were performed to mimic the depletion process, as shown in Figure 2. The goal was to closely monitor the compositional variations during the depletion of the source rock matrix, providing some insight into the factors influencing flow properties and phase behavior and hence understanding how the productivity of source rock formations can be improved.

### KEROGEN STRUCTURES IN MOLECULAR SIMULATIONS

Ungerer et al.\(^\text{22}\) created six kerogen molecules corresponding to different types at some levels of maturity. These serve as building blocks of nanoporous organic materials. In that study, type I was built for immature kerogen. Four versions of type II were created with some variations in their origin. Type III was represented by one version corresponding to coal. The degree of aromaticity was linked with maturity, as can be inferred from Figure 3. Those porotypes, which were created on a computational platform, were found to be within acceptable compositional agreement with the experimental work.

Kerogen I-A is an immature of type I with 251 carbon, 385 hydrogen, 13 oxygen, and three sulfur atoms \(\text{C}_{251}\text{H}_{385}\text{O}_{13}\text{S}_3\). It has the highest degree of aliphatic structures among the others. Kerogen II-A is immature organic matter with 252 carbon atoms, and its chemical formula is \(\text{C}_{252}\text{H}_{294}\text{O}_{24}\text{N}_6\text{S}_3\). It has two polycyclic saturated structures. The oxygen atoms are

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Figure 1. SEM images of source rock matrices showing organic matter (in dark gray). Images (A,B) are from Curtis et al.\(^\text{12}\)

Figure 2. Conceptual model for studying multicomponent hydrocarbon transport in an organic material-microcrack system. The SEM on the left is from Curtis et al.\(^\text{12}\)
associated with ether, carbonyl, hydroxyl, and carboxylic groups in ratios of 9:7:4:2, respectively. Three of the nitrogen atoms are present in thiophenic rings and one in a pyridinic ring. The sulfur is present in two thiophenic rings and one sulfide bridge. The fraction of carbons atoms in aromatic substructures is 41%.

Kerogen II-B has a formula of \( \text{C}_{234}\text{H}_{263}\text{O}_{14}\text{N}_{5}\text{S}_{2} \), with 45% of its carbon atoms being part of an aromatic system. More oxygen atoms form single bonds with carbon than double bonds compared to type II-A. Nitrogen and sulfur are associated with thiophenic and pyridinic rings.

Kerogen II-C is taken to represent a more mature unit. Its formula is \( \text{C}_{242}\text{H}_{219}\text{O}_{13}\text{N}_{5}\text{S}_{2} \). It is very similar to type II-B but with less alkyl chains to achieve a higher maturity level. That is reflected by the percentage of aromatic carbon, which is 58%. Similarly, kerogen II-D is the most mature kerogen type with a formula of \( \text{C}_{175}\text{H}_{102}\text{O}_{9}\text{N}_{4}\text{S}_{2} \) and 79% as the percentage of aromatic carbon. Kerogen III-A is an immature type III with its formula of \( \text{C}_{233}\text{H}_{204}\text{O}_{27}\text{N}_{4} \). It is mostly found in coal seam formations. Type II-D, which corresponds to shale gas, was recreated and used in our study.

### MOLECULAR APPROACH

This section presents the molecular modeling approach used in this work. The first subsection details the building of the type II-D kerogen structures. The second considers the methodology for estimating sorption of the multicomponent system into the kerogen structure. All were performed using the MedeA environment, while MD calculations used a large-scale atomic/molecular massively parallel simulator (LAMMPS).\(^{23}\)

**Construction of Kerogen as a Nanoporous Medium.** The condensed bulk kerogen for type II-D was performed following Ungerer et al.\(^{22}\) A Nosé–Hoover thermostat and barostat were used for the temperature and pressure, respectively.\(^{24,25}\) A polymer-consistent force field (PCFF)+ was utilized for the MD calculations.\(^{26}\) The PCFF+ was shown to have an excellent capacity to describe the different kinds of interactions, including dispersion and repulsion (i.e., as described by the Lennard-Jones 6−9 potential), and Columbic interactions in classic bond terms (e.g., stretching, bending, torsion) for different systems.\(^{27,28}\) A cutoff at 1.2 nm was utilized for the electrostatic interactions during the equilibration calculations. The average was obtained by the particle−particle−particle−mesh method at the final temperature of the calculation.\(^{23,26,29}\)

Initially, 5 kerogen units were placed inside the simulation box; the initial average density was approximately 0.1 g/cm\(^3\) (i.e., initiation at low density was followed to ensure system stability prior to further MD stages). The selected number of kerogen macromolecules should reproduce some of the macroscopic properties such as the density.\(^{23,26}\) Several consecutive relaxations were performed to build the dense kerogen structure, starting with an NVT simulation in which the amount of substance (\(N\)), volume (\(V\)), and temperature (\(T\)) are conserved, at a temperature of 900 K for 250 ps, followed by four NPT simulations; in each simulation the amount of substance (\(N\)), pressure (\(P\)), and temperature (\(T\))
are conserved, with stepwise decreases in temperature from 900 to 300 K at a constant pressure of 20 MPa, as shown in Figure 4. The time step used in all calculations was 1 fs. The final density of the kerogen structure was found to be approximately 1.1 g/cm³ with a cubical dimension of 2.68 nm. The obtained density of the final structure was consistent with what is anticipated for real kerogens (Figure 5).22

Gibbs–Monte Carlo Adsorption Calculations. The nanoporous material was loaded with a mixture of C₁ to C₄ at a pressure of 2500 psi and temperature equal to 194 °F (i.e., a typical reservoir temperature). The bulk phase composition was arbitrarily selected to be 0.3, 0.15, 0.2, and 0.35 for the four alkanes, respectively. Gibbs–Monte Carlo calculations were performed. The parameters of such an ensemble are the adsorbed molecule’s chemical potential, volume, and temperature. The fugacities were imposed for each component (as they were gas mixtures with relatively high pressures), which was the equivalent of using the chemical potential, as follows

\[
\mu_i = \mu_{i0} + RT \ln \left( \frac{f_i}{f_{i0}} \right)
\]

where \(\mu_i\), \(\mu_{i0}\), \(R\), \(T\), \(f_i\) and \(f_{i0}\) are the chemical potential for component \(i\), ideal chemical potential for component \(i\), gas constant, temperature, fugacity of component \(i\), and ideal fugacity of component \(i\), respectively (see Table 1). The initial composition of the loaded mixture on the kerogen structure was 0.673, 0.255, 0.0073, and 0.065, respectively, as given in Table 2.

When the kerogen structure adsorbs molecules, its volume could change depending on its molecular-level elasticity. This is referred to as the swelling effect. In the adsorption calculations, we followed an iterative approach where initial adsorption calculations were carried out. Then, MD simulation LAMMPS was performed on the structure along with its adsorbed molecules. The new equilibrated structure was obtained and kerogen (host) was extracted. Gibbs adsorption calculations were performed again. The iterations were terminated once kerogen volume changes became insignificant. In our case, we noticed that the changes in kerogen volume through iterations were minimal. That could be explained by the type of kerogen used, which was a mature one with a high degree of aromaticity (i.e., the aromatic structure has lesser flexibility to move compared to the aliphatic structure).

### RESULTS AND DISCUSSION

After obtaining the initial structure of the gas and sorbed gases, the pressure of the system was dropped to allow for gas release. This approach mimicked the depletion process for reservoirs. During the depletion process, compositional variations and the total number of molecules were monitored for further analysis.

The total number of moles per unit mass of kerogen at a given pressure is shown in Figure 6. The saturated pressure was around 1500 psi (corresponds to the maximum capacity of molecules contained within a given structure). Below that value, the rapid desorption of molecules could be observed. This portion of the data was anticipated to be where fractionation would occur. Heavier molecules were trapped as lighter ones were released. At 300 psi, less than 40% of the initial gases remained in the kerogen.

Table 1. Bulk Phase Composition To Load Kerogen with Molecules

| component | composition (%) | fugacity (psi) |
|-----------|-----------------|---------------|
| CH₄       | 30              | 1061.1        |
| C₂H₆      | 15              | 195.7         |
| C₃H₈      | 20              | 123.4         |
| n-C₄H₁₀   | 35              | 106.2         |

Table 2. Initial Composition of the Loaded Kerogen at 2500 psi

| component | composition (%) |
|-----------|-----------------|
| CH₄       | 67.30%          |
| C₂H₆      | 25.50%          |
| C₃H₈      | 0.73%           |
| n-C₄H₁₀   | 6.50%           |

Figure 4. NVT/NPT simulation parameters.

Figure 5. NVT/NPT from a single kerogen molecule to the final kerogen structure. The final structure has a cubical shape with a dimension of 2.683 nm and a density of 1.1 g/cm³.
At pressures equal to or higher than the saturated pressure, the composition of the gases in the kerogen stayed almost constant, with a slight decrease in the methane fraction as shown in Figure 7. Methane, which has the highest vapor pressure, tends to shift the $P−T$ diagram to the left, while $n$-butane has the opposite effect. Vapor pressure, which is the pressure at which liquid forms, is 175 psi for pure $n$-butane under typical reservoir conditions, while pure methane can never form a liquid because reservoir temperatures are always above its critical temperature. As the pressure continued to drop below the saturation pressure, more methane molecules were released relative to other components. The mole fraction of methane dropped from 0.65 at 1500 psi to 0.42 at 1000 psi (see Figure 7). This is clearly reflected in the $P−T$ diagram (as shown in Figure 8), where the area of the two-phase envelope expanded significantly. As the pressure continued to drop, most of the methane molecules were desorbed, while other gases occupied the kerogen.

The kerogen structure being depleted under decreasing pressure enabled our capturing of the fractionation behavior. Next, we considered how fractionation might influence the transport properties. We analyzed two essential transport parameters: the viscosity and diffusivity coefficients. Viscosity, which is a macroscopic flow parameter, is defined for fluid particles. In our observation of the molecules trapped in the kerogen structures, it appeared that they became scattered rather than forming fluid particles, making defining viscosity meaningless. For that reason, the viscosity estimation was performed after eliminating the kerogen structure. This represented the viscosity of the fluid in the microcracks (i.e., after being expelled from the kerogen during migration to the larger pore spaces). The computations were performed considering the composition extracted from the kerogen at the same conditions of pressure, temperature, and volume via the Green–Kubo method. An example of such a system is given in Figure 9, where kerogen and its contained gas mixture at 2500 psi is shown. The same procedure was repeated for the remaining depletion stages. The results given in Figure 10 show a decent match with what was obtained from the CPA (Cubic-Plus-Association) equation of state (EOS). The calculations of viscosity were performed using the thermodynamic kit of an ASPEN Plus simulator. Using the same scheme created for viscosity, diffusivity calculations were performed separately for the kerogen structure and extracted gas molecules. The former reflected the actual diffusivity coefficient, accounting for the degree of heterogeneity experienced by the gas molecules; the latter defined the diffusivity in nonporous media. In both cases, the...
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NOMENCLATURE

- $P$, pressure (psi)
- $T$, temperature (F)
- $f$, fugacity (MPa)
- $\mu$, fluid viscosity (cp)
- $\epsilon_p$, relative pore volume
- $\tau$, tortuosity

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Figure 10. Viscosity of the gas mixture as obtained by MD simulation and CPA EOS for the given composition at each sorption stage.

Figure 11. $\tau^2/\epsilon_p$ ratio as a function of pressure. Each pressure value represents a sorption stage of the composition given in Figure 6.

The results show that the tortuosity factor was proportional to the pressure. Larger molecules accumulating as pressure decreases might experience more tortuous pathways to diffuse out of a kerogen structure.

The fractionation behavior observed in our study of multicomponent gases in kerogen clearly deviated from the extended Langmuir isotherm for multicomponents, as the composition kept changing during molecular desorption (i.e., the extended Langmuir isotherm is obtained based on the individual component isotherms and partial pressures). The data presented correspond to some arbitrarily predefined gases. Different behaviors would be seen for different combinations of gas composition, kerogen porosity, temperature, and pressure.

CONCLUSIONS

In this study, the fractionation effect of multicomponent desorption from kerogen was investigated through molecular simulations. Molecular desorption from a nanoporous kerogen structure was found to exhibit the preferential release of lighter over heavier components. This compositional variation can influence fluid properties, which in turn can affect a reservoir’s productivity. The accumulation of heavier hydrocarbons altered the $P$–$T$ diagram, enlarging the two-phase envelope gradually. Additionally, the degree of tortuosity experienced by the sorbed molecules was found to be increasing as fractionation effect becomes more pronounced at a lower pressure range by a factor of 3 in a specific case that was conducted in this paper. A similar molecular approach can be followed for other specific reservoir cases for more accurate modeling and reservoir management of shale resources.

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Notes

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