2023

Wettability Dynamics of Kerogen: Insights from Molecular Dynamics Simulations on Thermal Maturity and Reservoir Temperature Impact

Wei Liang
UCLA

Xin Chen
CUNY City College

Rajat Sharma
UCLA

Wettability Dynamics of Kerogen: Insights from Molecular Dynamics Simulations on Thermal Maturity and Reservoir Temperature Impact

Wei Liang, Xin Chen and Rajat Sharma

Abstract

This comprehensive review explores the multifaceted role of kerogen in organic-rich mudrock reservoirs, focusing on its impact on porosity, hydrocarbon storage, and transport pathways. The dominance of kerogen-hosted pores is underscored as a critical determinant of reservoir dynamics, with an emphasis on the wettability of kerogen as a pivotal parameter. The intricate relationship between kerogen wettability and petrophysical properties, including water saturation and electromagnetic characteristics, is elucidated, emphasizing the broader implications for reservoir management and hydrocarbon recovery.

The study delves into the thermal maturation of kerogen, unraveling the chemical evolution from hydrogen-rich organic matter to hydrogen-poor residual carbon. The Van Krevelen diagram visually depicts the transformation, highlighting the decreasing oxygen-to-carbon ratio with increasing thermal maturity. Distinct types of kerogen are examined, each exhibiting variable compositions, providing a nuanced understanding of their behavior under different thermal maturation levels.

Temperature emerges as a crucial factor influencing kerogen wettability, drawing parallels with observed shifts in conventional reservoirs during thermal recovery processes. The impact of temperature on kerogen-oil interaction within shale pores is explored, revealing noteworthy variations in the density distribution of adsorbed oil molecules. Linear relationships between temperature and confined oil compounds further emphasize the need to comprehend the interplay between temperature and kerogen wettability for effective thermal recovery mechanisms.

The review concludes by highlighting the necessity of advancing molecular dynamics simulations to capture the complexity of kerogen molecular structures, diverse kerogen types, and temperature variations. By addressing these challenges, future simulations can contribute to a comprehensive understanding of kerogen wettability, offering valuable insights for hydrocarbon reservoir characterization and optimization of recovery strategies.

The Role of Kerogen in Organic-Rich Mudrock Reservoirs

Organic-rich mudrocks serve as hosts to a primary organic matter known as kerogen, a key player in determining porosity and hydrocarbon storage. In numerous instances, the dominance of kerogen-hosted pores over mineral-hosted pores has been established as a critical factor influencing total porosity and hydrocarbon storage in these reservoirs (Lohr et al., 2015). The consequences of this dominance extend to the transport pathways of oil and gas, making the properties of kerogen, particularly its wettability, a significant parameter (Dustin et al., 2018).

Research by Lohr et al. (2015) emphasizes that kerogen-hosted pores play a pivotal role in shaping the porosity landscape, underscoring their supremacy in contributing to hydrocarbon storage. This finding implies that the intricate network of kerogen-hosted pores dictates the behavior of oil and gas within the organic-rich mudrock reservoirs. Furthermore, Dustin et al. (2018) highlights that the transport pathways for these hydrocarbons are intricately tied to the unique properties of kerogen.

The wettability of kerogen emerges as a crucial aspect in understanding the transport dynamics of oil and gas within organic-rich mudrocks. As emphasized by Kethireddy et al. (2014) and Chen and Heidari (2016), the wettability of kerogen has far-reaching implications, not only influencing transport but also impacting the electromagnetic properties of the mudrocks. The interplay between kerogen wettability and electromagnetic properties introduces an additional layer of complexity to the reservoir dynamics.

Kethireddy et al. (2014) and Chen and Heidari (2016) draw attention to the broader implications of kerogen wettability on the reliability of estimating petrophysical properties, such as water saturation. The ability to accurately estimate water saturation is crucial for effective reservoir management and resource recovery planning. Therefore, understanding the role of kerogen wettability becomes instrumental in enhancing the precision of these estimations.

Beyond its impact on transport pathways and electromagnetic properties, the wettability of kerogen introduces a layer of complexity that extends into the realm of petrophysical property estimation. The intricate interplay between kerogen and the surrounding reservoir fluids influences the reliability of estimating key parameters, making it imperative to unravel the nuances of kerogen behavior within organic-rich mudrock systems.

The significance of kerogen in organic-rich mudrock reservoirs extends beyond its role as a primary organic matter. The dominance of kerogen-hosted pores shapes the reservoir's porosity and hydrocarbon storage, with implications for oil and gas transport pathways. The wettability of kerogen, a central player in these processes, further influences electromagnetic properties and the accuracy of estimating essential petrophysical parameters. Acknowledging the multifaceted impact of kerogen enhances our comprehension of organic-rich mudrock reservoir dynamics and aids in devising more accurate reservoir management strategies.

Evolution of Kerogen During Thermal Maturation

Kerogen, as a primary organic matter in organic-rich mudrocks, undergoes significant transformations during thermal maturation, fundamentally altering its chemical composition and structure. This evolution plays a crucial role in shaping the characteristics of organic-rich reservoirs, influencing aspects such as hydrogen-to-carbon (H/C) ratio, aromatic carbon content, and oxygen-to-carbon (O/C) ratio. Understanding these changes is essential for unlocking the intricacies of hydrocarbon reservoir behavior and resource potential.

The thermal maturation of kerogen initiates a profound shift from hydrogen-rich organic matter to hydrogen-poor residual carbon, resulting in a notable decrease in the H/C ratio (Baskin, 1997). This transformation represents a critical phase in the maturation process, marking the evolution of kerogen from its original state toward a more carbonaceous form. The chemical structure undergoes a significant overhaul, with a concurrent increase in aromatic carbon content (Vandenbroucke, 2003). The work of Passey et al. (2012) further elucidates this transformation, highlighting the condensation of kerogen structure into a predominantly graphitic form characterized by sp2 hybridized carbons.

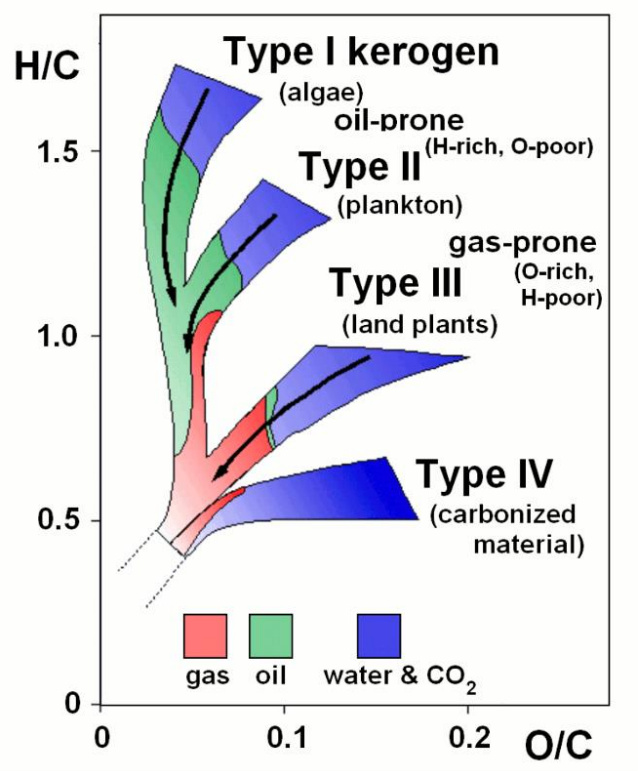

Figure 1. Van krevelen diagram showing the types of kerogen and effect of thermal maturity. The arrows indicate direction of increase in thermal maturity.

The Van Krevelen diagram serves as a valuable tool in visualizing the impact of thermal maturation on kerogen composition. As thermal maturity increases, the diagram indicates a consistent decrease in the O/C ratio (van Krevelen, 1993). This shift reflects the diminishing presence of oxygen-containing functional groups, a hallmark of the thermal evolution process. Examining different types of kerogen unveils the variable relative abundance of hydrogen, carbon, and oxygen content, further emphasizing the diversity of organic matter sources.

Type I Kerogen: Primarily derived from marine organic matter, such as phytoplankton and zooplankton, Type I kerogen is characterized by its hydrogen-rich and oxygen-poor composition (atomic $H/C \approx 1.5$, $O/C < 0.1$).

Type II Kerogen: Formed by a combination of higher plants and marine phytoplankton, Type II kerogen exhibits intermediate hydrogen and oxygen compositions.

Type III Kerogen: Predominantly originating from terrestrial organic matter, Type III kerogen is oxygen-rich and deficient in hydrogen ($H/C < 1.0$, $O/C \approx 0.3$).

Type IV Kerogen: Derived from charcoal or fungal bodies, Type IV kerogen mirrors the hydrogen-poor, oxygen-rich characteristics of Type III kerogen.
For each type of kerogen, the H/C, O/C, and aliphatic carbon content exhibit a consistent trend of decrease with increasing thermal maturity (Hunt and Hill, 1996). This convergence toward lower hydrogen and oxygen content, coupled with a decline in aliphatic carbon, underscores the universal impact of thermal maturation on various kerogen types.

The thermal maturation of kerogen represents a pivotal phase in the geological transformation of organic-rich mudrocks. The evolution from hydrogen-rich organic matter to carbonaceous structures significantly alters the chemical composition and structure of kerogen. The Van Krevelen diagram provides a visual representation of these changes, showcasing the decreasing O/C ratio with increasing thermal maturity. Understanding the diverse characteristics of different kerogen types enriches our comprehension of the intricate interplay between organic matter sources and the geological processes that shape hydrocarbon reservoirs.

Understanding the Interplay of Kerogen Wettability and Temperature in Organic-Rich Mudrock Reservoirs

Kerogen, the primary organic matter in organic-rich mudrocks, is a complex entity whose wettability plays a pivotal role in the transport of hydrocarbons within reservoirs. The influence of kerogen type and thermal maturity on its wettability, coupled with the temperature-dependent nature of interfacial interactions, underscores the intricate dynamics at play. This paper delves into the interrelated factors of kerogen type, thermal maturity, and temperature, shedding light on their combined impact on the wettability of kerogen.

Hu et al. (2016) and Jagadisan and Heidari (2019) highlight the importance of recognizing the diverse chemical structures and compositions inherent in different kerogen types. The geochemical changes induced by thermal maturity further contribute to the intricate mosaic of kerogen characteristics. These variances, in turn, have a profound impact on the wettability of kerogen. The transition from hydrogen-rich organic matter to residual carbon during thermal maturation not only alters the H/C ratio but also influences the aromatic carbon content, introducing a myriad of possibilities for changes in wettability.

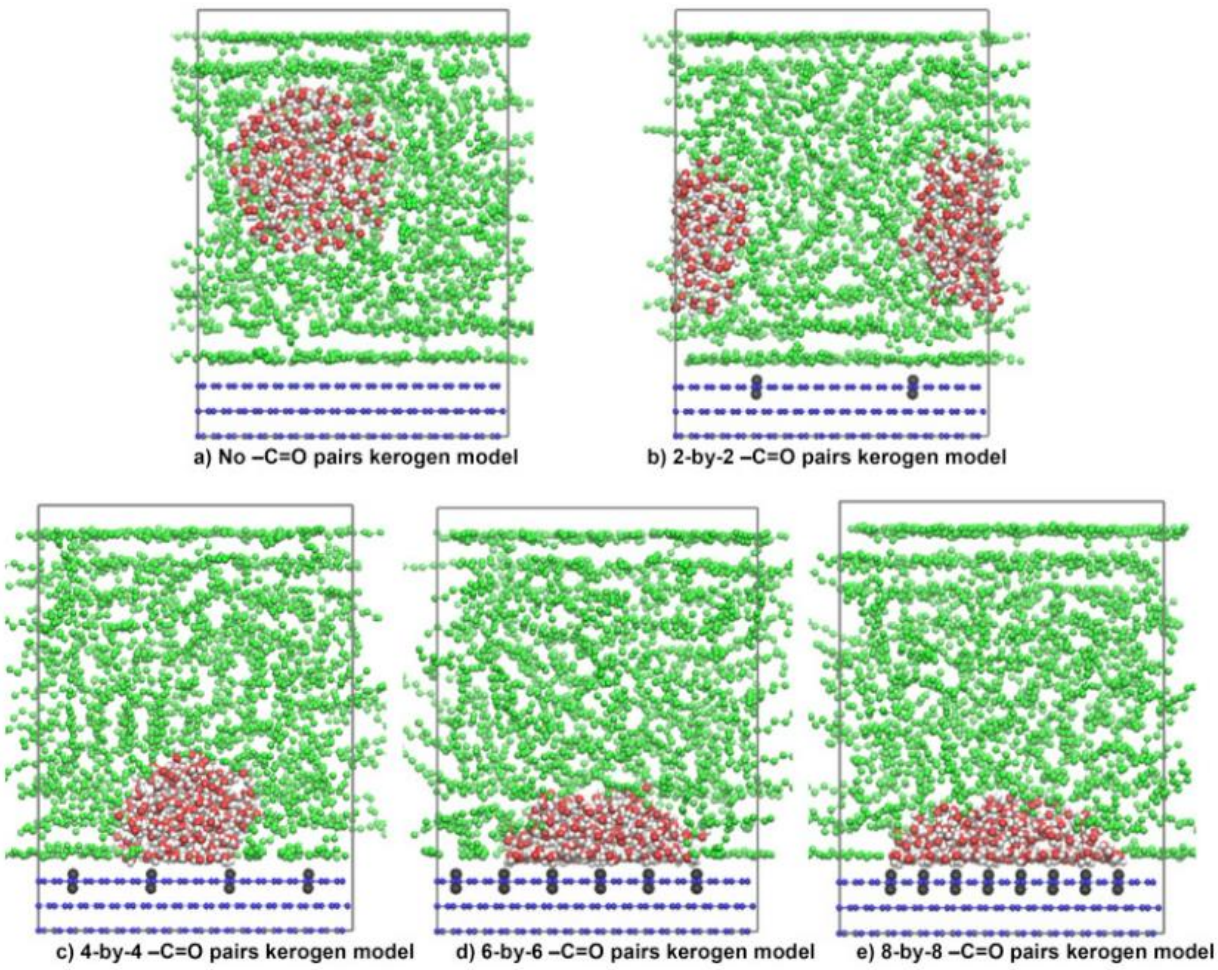

Figure 2. Representative snapshot of equilibrium states for kerogen surfaces of different degrees of activation. Adapted from Hu et al. (2016)

Elevated temperatures have been observed to induce alterations in wettability, particularly in conventional reservoirs during thermal recovery processes. Studies by Hjelmeland et al. (1986), Wang et al. (1995), Al-Hadhrami and Blunt (2001), and Mahani et al. (2017) underscore the shift towards water-wet conditions at higher temperatures. This observed phenomenon carries significant implications for recovery mechanisms in reservoirs subjected to thermal processes.

In the realm of shale pores, the influence of temperature on kerogen-oil interaction gains prominence. Wang et al. (2015) provide evidence of the temperature-dependent density distribution of octane molecules on a kerogen slit modeled as a graphene surface. The study reveals a 2% reduction in the number of adsorbed octane molecules at higher temperatures (393 K) compared to lower temperatures (333 K). Additionally, the work of Yang et al. (2020) establishes linear relationships between temperature and the number of oil compounds confined within the kerogen slit. These findings emphasize the necessity of comprehending the nuanced relationship between temperature and kerogen wettability for effective thermal recovery in organic-rich mudrocks.

To leverage thermal processes effectively for recovery mechanisms in organic-rich mudrocks, a nuanced understanding of the temperature-driven changes in kerogen wettability becomes imperative. The intricate interplay between kerogen type, thermal maturity, and temperature necessitates a comprehensive approach for reservoir management. Tailoring thermal recovery strategies to accommodate these factors can significantly enhance the efficiency of hydrocarbon recovery processes.

In conclusion, the wettability of kerogen in organic-rich mudrock reservoirs is a multifaceted phenomenon influenced by the intricate interplay of kerogen type, thermal maturity, and temperature. The diverse chemical structures of different kerogen types, coupled with geochemical changes due to thermal maturity, create a dynamic landscape for wettability alterations. Temperature, acting as a critical factor in interfacial interactions, further complicates this scenario. Recognizing and understanding these complexities are essential for optimizing thermal processes in organic-rich mudrocks and maximizing the recovery of valuable hydrocarbon resources.

Advancements in Understanding Kerogen Wettability

Kerogen wettability in organic-rich mudrocks is a critical parameter influencing hydrocarbon recovery, with thermal maturity being a key factor. Recent studies by Jagadisan and Heidari shed light on this relationship, both experimentally and through molecular dynamics simulations. While their experimental work (2019) demonstrates significant variations in kerogen wettability with thermal maturity, it falls short in capturing a broad spectrum of kerogen types and reservoir temperatures. A subsequent study (2020) utilizes molecular dynamics simulations to explore water adsorption capacities, providing valuable insights but raising questions about the direct comparison of simulation results with experimentally measured wettability.

Jagadisan and Heidari (2019) undertook experimental endeavors to elucidate the relationship between kerogen wettability and thermal maturity. The study convincingly showed that kerogen wettability exhibits substantial variability with thermal maturity, notably manifesting as water-wet characteristics at lower thermal maturities. This experimental evidence contributes significantly to our understanding of kerogen behavior, emphasizing the dynamic nature of wettability in response to thermal evolution. However, the scope of the experiments was limited, lacking representation across a diverse range of kerogen types and reservoir temperature conditions.

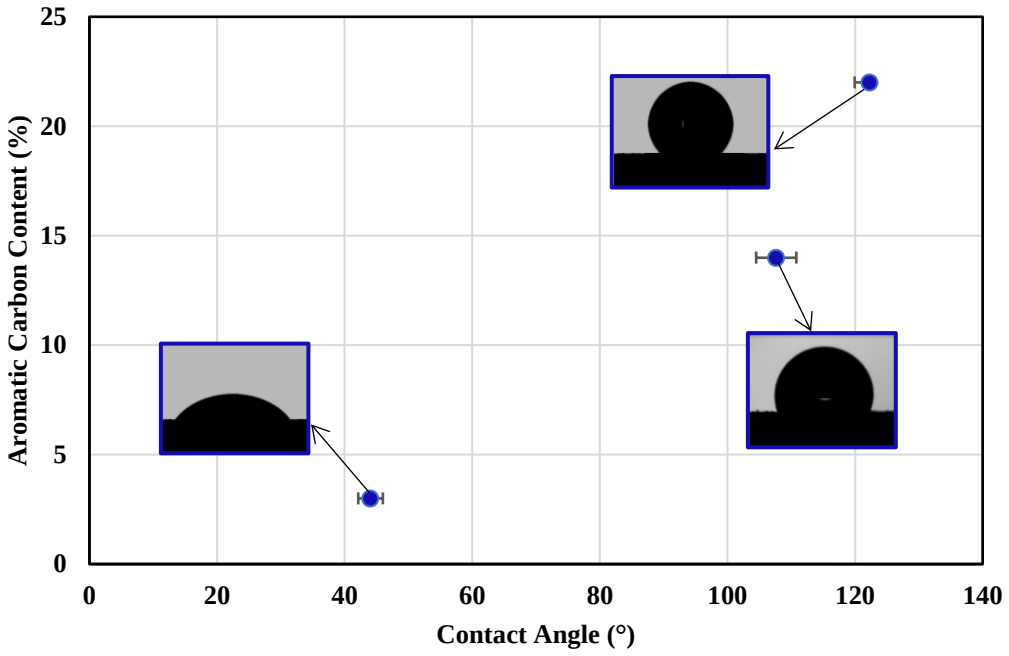

Figure 3: Contact angle formed by water droplets on the surface of kerogen samples from formation A at different aromatic carbon concentrations. The bar on each data point represents the range of multiple measurements performed on each sample. The dots represent the average values for the contact angle measurements at each data point. Adapted from Jagadisan and Heidari (2019)

In an attempt to bridge these gaps, Jagadisan and Heidari (2020) employed molecular dynamics simulations to investigate the water adsorption capacities of kerogen. This approach provides a complementary perspective, enabling a more comprehensive exploration of thermal effects on kerogen behavior. The simulations, while offering valuable insights, introduce a nuanced challenge – the direct comparison of water adsorption capacities with experimentally measured wettability. This discrepancy prompts a closer examination of the relationship between simulation outcomes and real-world wettability.

The complexity of the kerogen-water interaction poses challenges in directly comparing simulation results with experimentally measured wettability. While molecular dynamics simulations offer atomic-level insights into water adsorption capacities, translating these quantities into macroscopic wettability observations requires careful consideration of numerous factors. The intricacies of the simulation environment, the choice of force fields, and the accuracy of modeling thermal effects all contribute to the disparity between simulated and experimentally observed wettability.

The divergence between experimental and simulation results underscores the need for a comprehensive approach that integrates both methodologies. Future studies could benefit from a synergy between experimental investigations and molecular dynamics simulations, leveraging the strengths of each. Experimental work provides real-world validation and a broad spectrum of conditions, while simulations offer a detailed molecular understanding of the underlying processes. The amalgamation of these approaches could yield a more robust and nuanced comprehension of kerogen wettability across diverse scenarios.

Jagadisan and Heidari's studies contribute significantly to our understanding of kerogen wettability, emphasizing its variability with thermal maturity. The experimental insights and molecular dynamics simulations, though offering distinct advantages, present challenges in direct comparison. The nuanced nature of kerogen-water interactions and the complexities of simulation environments highlight the importance of a holistic approach. Future research endeavors should aim for a synergistic integration of experimental and simulation methodologies to unravel the intricacies of kerogen wettability comprehensively.

Molecular Dynamics Simulation in Unraveling Kerogen Wettability

Molecular dynamics (MD) simulation has emerged as a powerful tool for investigating atomic-level interactions in multi-scale systems, offering valuable insights into complex phenomena. Various studies (Yan and Yuan 2016; Zhang et al. 2016; Zhao et al. 2018; Li et al. 2017) have successfully utilized MD simulation to explore contact angles on mineral and metal surfaces by water, demonstrating consistency with experimental values. This approach extends to three-phase systems, as evidenced by the study of water/decane/silica interfaces (Xu et al. 2018), providing in-depth understanding at the atomic level. However, the application of MD simulation to kerogen wettability introduces unique challenges, especially in capturing the complexity of molecular structures and considering diverse kerogen types and temperature conditions.

Previous MD simulations on kerogen wettability, such as those by Diaz Campos et al. (2014) and Hu et al. (2016), utilized a simplified kerogen model composed of graphene sheets to represent highly mature kerogen. While this approach allowed for the exploration of wettability trends with thermal maturity, it falls short in capturing the intricate molecular structure of kerogen. The oversimplified model limits the applicability of simulation results to real-world scenarios, particularly in understanding the behavior of different kerogen types and the influence of temperature variations.

In an attempt to simulate different thermal maturity levels of kerogen, Hu et al. (2015) introduced variable amounts of carbonyl (C=O) functional groups onto the graphene sheets. The study concluded that kerogen exhibits water-wet characteristics at low thermal maturity and becomes hydrophobic at high thermal maturity. While providing valuable insights into the broad trends of kerogen wettability, this approach lacks the capability to fully capture the diverse range of kerogen types and temperature conditions prevalent in natural reservoirs.

A notable limitation of the existing MD simulations on kerogen wettability is the neglect of diverse kerogen types and temperature variations. The natural heterogeneity of kerogen types, as classified into Type I to IV, brings forth distinct compositional differences that can influence wettability. Additionally, the impact of temperature on kerogen-oil interactions, observed in real-world shale pores, remains unexplored in these simplified simulations.

Addressing the complexity of kerogen molecular structure requires a departure from simplistic models. Future MD simulations can benefit from incorporating realistic molecular models of different kerogen types, as proposed by Ungerer et al. (2015), enabling a more accurate representation of natural conditions. Furthermore, the inclusion of temperature variations and a broader spectrum of thermal maturities will enhance the applicability of simulation results to a wider range of reservoir scenarios.

While MD simulation has proven effective in elucidating interfacial interactions in various systems, its application to kerogen wettability necessitates a more nuanced approach. The challenges posed by oversimplified models, neglect of diverse kerogen types, and lack of consideration for temperature variations underscore the need for advancements in simulation methodologies. By addressing these limitations, future MD simulations can provide a more comprehensive understanding of kerogen wettability, contributing valuable insights to the field of hydrocarbon reservoir characterization and recovery strategies.

The study conducted by Jagadisan and Heidari in 2019 addresses critical gaps in understanding kerogen wettability by employing Molecular Dynamics (MD) simulations. This research delves into the complexities of different kerogen types (I, II, and III), exploring their behavior at various thermal maturity levels and within a temperature range of 300 to 360 K. The results provide crucial insights into air/water/kerogen and methane/water/kerogen contact angles, shedding light on the intricate relationship between kerogen properties, thermal maturity, and temperature.

The findings reveal intriguing trends in air/water/kerogen contact angles. Type III kerogen exhibited the highest contact angle at 45.5°, while type II kerogen displayed the lowest at 20°. Furthermore, as thermal maturity progressed from immature to over-matured stages for type II kerogen, the contact angle increased substantially, reaching 75.5°. The impact of temperature was also notable, with an increase from 300 to 380 K leading to a significant 62% decrease in contact angle measurements.

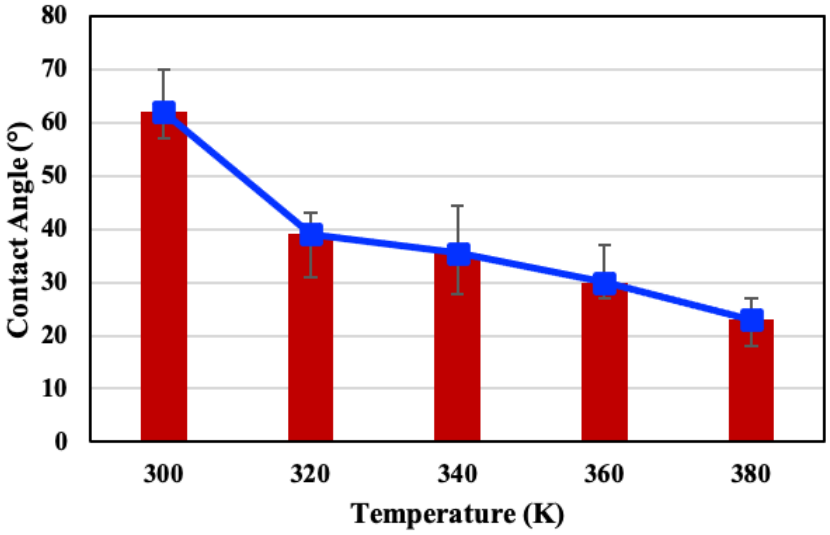

Figure 4: Contact angle of water droplet on type I kerogen surface at 300K, 320K, 340K, and 360K, respectively. The error bars show the range of contact angles measured for each kerogen sample. Adapted from Jagadisan and Heidari (2019).

The methane/water/kerogen contact angles mirrored the trends observed in air/water/kerogen interactions. Type III kerogen exhibited the highest contact angle at 58°, with consistent observations across both systems. The influence of thermal maturity on methane/water/kerogen contact angles showed a progressive increase from 25.5° to 88.5° as thermal maturity advanced from kerogen II-A to kerogen II-D. This alignment with air/water/kerogen contact angles underlines the consistency in wettability behavior across different kerogen types.

References

1. Passey, Q.R., Bohacs, K., Esch, W.L., Klimentidis, R. and Sinha, S, 2010. From oil-prone source rock to gas-producing shale reservoir-geologic and petrophysical characterization of unconventional shale gas reservoirs. Presented at the International oil and gas conference and exhibition in China, Beijing, China, 8-10 June.
2. Passey, Q.R., Bohacs, K.M., Esch, W.L., Klimentidis, R. and Sinha, S. 2012. My source rock is now my reservoir: Geologic and petrophysical characterization of shale-gas reservoirs. AAPG Search and Discovery Article, 90124.

3. Wilhelmy, L. (1863). "On the dependence of the capillarity constants of the alcohol on the substance and form of the wetted solid body." Annalen der Physik, 195(6), 177–217.
4. Rickard, T. A. (1916). "The Floatation Process." Mining & Scientific Press, San Francisco.
5. Stokes, R. H., & Robinson, R. A. (1949). "Standard Solutions for Humidity Control at 25° C." Industrial & Engineering Chemistry, 41(9), 2013-2013.
6. van Krevelen, D. W. (1961). "Coal: Typology-Chemistry-Physics-Constitution." Elsevier.
7. van Duin, A. C., Dasgupta, S., Lorant, F., & Goddard, W. A. (2001). "ReaxFF: a reactive force field for hydrocarbons." The Journal of Physical Chemistry A, 105(41), 9396-9409.
8. van Krevelen, D. W. (1993). "Coal: typology-physics-chemistry-constitution."
9. Washburn, E. W. (1921). "The Dynamics of Capillary Flow." The Physical Review, 17(3), 273-283.
10. Young, T. (1805). "III. An essay on the cohesion of fluids." Philosophical Transactions of the Royal Society of London, 95, 65–87.
11. Jagadisan, A., & Heidari, Z. (2019). Experimental quantification of the effect of thermal maturity of kerogen on its wettability. SPE Reservoir Evaluation & Engineering, 22(04), 1323-1333.
12. Jagadisan, A., Yang, A., & Heidari, Z. (2017). Experimental quantification of the impact of thermal maturity on kerogen density. Petrophysics, 58(06), 603-612.
13. Jagadisan, A., & Heidari, Z. (2018, June). Experimental quantification of kerogen wettability as a function of thermal maturity. In SPWLA 59th Annual Logging Symposium. OnePetro.
14. Jagadisan, A., & Heidari, Z. (2022). Molecular dynamic simulation of the impact of thermal maturity and reservoir temperature on the contact angle and wettability of kerogen. Fuel, 309, 122039.
15. Jagadisan, A., & Heidari, Z. (2018, July). Impacts of geochemical Properties on wettability of kerogen and organic-rich mudrocks. In SPE/AAPG/SEG Unconventional Resources Technology Conference. OnePetro.
16. Jagadisan, A., & Heidari, Z. (2020). Impact of geochemical properties on wettability of kerogen and organic-rich mudrocks. SPE Reservoir Evaluation & Engineering, 23(02), 758-771.
17. Jagadisan, A., & Heidari, Z. (2019, September). Demystifying wettability alteration in kerogen as a function of its geochemistry and reservoir temperature and pressure using molecular dynamics simulations. In SPE annual technical conference and exhibition. OnePetro.
18. Jagadisan, A., & Heidari, Z. (2017, June). Application of X-ray photoelectron spectroscopy in connecting thermal maturity of kerogen to its dielectric constant in organic-rich mudrocks. In SPWLA 58th Annual Logging Symposium. OnePetro.

19. Jagadisan, A., & Heidari, Z. (2020). Impacts of competitive water adsorption of kerogen and clay minerals on wettability of organic-rich mudrocks. SPE Reservoir Evaluation & Engineering, 23(04), 1180-1189.
20. Jagadisan, A., & Heidari, Z. (2020, June). Impact of kerogen geochemistry and reservoir temperature on contact angle and wettability of kerogen. In SPWLA 61st Annual Logging Symposium. OnePetro.
21. Jagadisan, A., Silveira de Araujo, I., & Heidari, Z. (2021, December). Impact of Kerogen Geochemistry on Methane and Water Adsorption Using Molecular Simulations.In Unconventional Resources Technology Conference, 26–28 July 2021 (pp. 2506-2519). Unconventional Resources Technology Conference (URTeC).
22. Jagadisan, A., & Heidari, Z. (2020). Effects of thermal maturity and chemical composition of kerogen on its dielectric constant. Geophysics, 85(1), D53-D64.
23. Jagadisan, A., & Heidari, Z. (2019, October). Quantifying the impacts of competitive water adsorption of kerogen and clay minerals on wettability of organic-rich mudrocks. In Unconventional Resources Technology Conference, Denver, Colorado, 22-24 July 2019 (pp. 3038-3052). Unconventional Resources Technology Conference (URTeC); Society of Exploration Geophysicists.
24. Jagadisan, A., & Heidari, Z. (2020). Impacts of competitive water adsorption of kerogen and clay minerals on wettability of organic-rich mudrocks. SPE Reservoir Evaluation & Engineering, 23(04), 1180-1189.
25. Jagadisan*, A., Hernandez, L. M., & Heidari, Z. (2019, October). Impact of thermal maturity on water production in organic-rich mudrocks. In Unconventional Resources Technology Conference, Denver, Colorado, 22-24 July 2019 (pp. 2655-2671). Unconventional Resources Technology Conference (URTeC); Society of Exploration Geophysicists.
26. Jagadisan, A., & Heidari, Z. (2022, June). Quantifying the impact of geochemistry on the interfacial interactions of kerogen and water and its impact on fluid mobility. In SPE/AAPG/SEG Unconventional Resources Technology Conference. OnePetro.