

Impact of geochemistry on wettability and electrical properties of kerogen and organic-rich mudrocks

Archana Jagadisan

City College of New York

TABLE OF CONTENTS

1. ABSTRACT.....	3
2. INTRODUCTION.....	4
2.1 ORGANIC-RICH MUDROCK WETTABILITY	4
2.2 KEROGEN WETTABILITY	5
2.3 IMPACT OF WETTABILITY ON RESISTIVITY MEASUREMENTS AND MULTIPHASE FLOW IN ORGANIC-RICH MUDROCKS.....	7
2.4 LIMITATIONS OF EXISTING STUDIES.....	7
3. STATEMENT OF PROBLEM.....	8
4. PROPOSED HYPOTHESES	8
5. RESEARCH OBJECTIVES	8
6. METHOD AND PROPOSED TASKS	9
7. PRELIMINARY RESULTS.....	13
6.1 SAMPLE PREPARATION.....	13
6.2 GEOCHEMICAL ANALYSIS OF KEROGEN.....	14
6.3 WETTABILITY QUANTIFICATION	15
6.4 DEVELOPMENT OF MOLECULAR MODELS FOR KEROGEN.....	16
7 COMPLETION SCHEDULE.....	18
8 REFERENCES.....	17

1. ABSTRACT

The distribution of fluids in the pore space significantly affects the borehole electrical measurements such as resistivity logs, multiphase fluid flow and hydrocarbon recovery. Wettability is therefore an important factor impacting the water production and low resistivity pays in organic-rich mudrocks. Development of reliable models for hydrocarbon-in-place and water saturation estimation requires knowledge about wettability of mudrocks and the factors affecting it. A significant fraction of mudrock is composed of kerogen – insoluble organic matter in mudrocks – and therefore the properties of kerogen can considerably affect the mudrock properties.

Studying rock physics and interfacial properties of kerogen remains an area of active research. Kerogen is often considered as hydrocarbon-wet in reservoir characterization. Despite this, wettability of kerogen is not fully understood and quantified. Assumptions made about the wettability of kerogen affects interpretation of borehole geophysical measurements such as electromagnetic measurements. It is therefore important to quantify wettability of kerogen as a function of relevant factors. For instance, the chemical structure and composition can vary as a function of kerogen type, which affects its surface properties such as wettability. In addition, processes such as thermal maturation induce changes in the chemical composition and structure. Thermal maturation decreases oxygen and hydrogen content and increases aromaticity. Oxygen containing function groups are also altered during thermal maturity. Moreover, changes in temperature and pressure also alter surface properties and affect the wettability of kerogen. However, the impact of different functional groups present in kerogen and reservoir temperature and pressure on kerogen wettability are yet to be quantified through a fundamental study.

Molecular simulation studies can be used to understand the kerogen wettability for a wide range of chemical position of kerogen. In a previous work, molecular dynamics simulation was used to quantify wettability of kerogen. However, simplified kerogen structures were used which does not capture the heterogeneity and complexity of the kerogen structure. Moreover, there have been no studies which consider the impact of functional groups such as carboxyl and hydroxyl groups, and the impact of temperature and pressure conditions on the wettability of kerogen. There has been no previous experimental study to reliably determine wettability of pure kerogen, because of the challenges associated with kerogen isolation and with determining wettability of powders.

I propose to use a combination of experimental and molecular simulation-based approaches to understand wettability of kerogen. First, the impact of composition and thermal maturity of kerogen on wettability of organic-rich mudrock will be studied using experimental and molecular simulation methods. The impact of reservoir temperature and pressure conditions on kerogen wettability would be quantified using molecular dynamics simulations. The methods proposed in the thesis will help in improving the understanding of wettability of organic-rich mudrocks. The sensitivity of wettability of kerogen on the electrical resistivity measurements of organic-rich mudrock will be quantified using a combination of experimental methods and numerical simulation. This study could also provide insight into water production issues in shale and will potentially improve formation evaluation and the understanding of fluid flow mechanisms in organic-rich mudrocks.

2. INTRODUCTION

Successful development of organic-rich mudrocks reservoirs requires reliable characterization of reservoir properties such as wettability, which affects the flow mechanisms in mudrocks. Wettability is the affinity of the rock to a particular fluid and depends on (i) the rock constituents, (ii) the properties of the fluids coating the rock surface, and (iii) temperature and pressure conditions (Anderson 1986; Hjelmeland and Larrondo 1986; Agbalaka et al. 2008). Wettability characterization of reservoirs are important for determining appropriate reservoir simulation models including relative permeability of fluids in the rock, residual phase saturation, capillary pressure, and composition of fracture fluids (Agbalaka et al. 2008). It also affects the distribution of fluids in the pore space, which in turn affects the electromagnetic properties of the rock such as electrical resistivity (Mungan and Moore 1967) and dielectric permittivity (Nguyen et al. 1999). Therefore, uncertainty in wettability of the reservoir can cause irreversible damage to the reservoir during secondary recovery treatments and result in incorrect estimation of petrophysical properties including hydrocarbon in-place.

2.1 ORGANIC-RICH MUDROCK WETTABILITY

Organic-rich mudrock wettability has been reported in the literature has a wide spectrum from water-wet to mixed-wet and oil-wet. Conventional methods for characterizing the wettability (e.g. Amott, USBM wettability indices) are challenging in tight rocks such as organic-rich mudrocks due to their extremely low permeability, porosity and complex pore structure. Moreover, forced imbibition on tight shale rocks requires significant pressure drop which could lead to induced fractures. Spontaneous imbibition and contact angle measurements has therefore been widely used to quantify wettability of shales (Rezaee 2015). Studies on imbibition of liquid on crushed shale packs have been used to determine the wettability of the shales (Lan et al. 2015; Rezaee 2015). Spontaneous imbibition is primarily impacted by the wettability of rock components. Flootation technique is another technique to determine wettability of mudrock samples quantitatively (Fuerstenau et al. 1991). In this technique granulated sample of the organic-rich mudrock is placed inside a separating funnel with equal proportions of water and oil. The funnel is then shaken thoroughly and the particles are allowed to settle. The distribution of particles in the oil and water phases provides a measure of hydrophobicity of shale.

The brine salinity, temperature, pressure, clay content and organic matter have been found to be some of the factors affecting mudrock wettability (Siddiqui et al. 2018). Among these, the total organic content was found to be one of the important factors controlling the wettability of organic-rich mudrocks. The air/water contact angle on mudrocks has been found to increase with increase in Total Organic Carbon (TOC) (Mokhtari et al. 2013; Yassin et al. 2017). Positive correlations between TOC and wettability were also observed in the Eagle Ford, Mancos, and Green River shale samples (Mokhtari et al. 2013). These studies are not tested for a wide range of thermal maturities of organic matter and assume that organic matter is always hydrocarbon-wet. However other studies, such as Engelder et al. (2014), found that a low TOC sample imbibed water much faster when compared to high TOC samples. These observations are inconsistent with the previously mentioned observations and contradict the claim that organic content is always hydrocarbon-wet.

Organic-rich mudrocks have complex mineralogy and can be a mixture of inorganic minerals such as quartz, pyrite, calcite, clays and organic matter such as kerogen, bitumen, and pyrobitumen. The volumetric concentration of kerogen in the rock could be up to 30% or even higher (Passey et al., 2012). Thus, it is an important constituent of organic-rich mudrocks, and can significantly affect their rock physics and fluid-flow properties. Pores hosted by organic matter comprise the dominant or subsidiary pore network of many shale-gas and shale-oil systems (Loucks and Reed, 2014). Secondary porosity is formed in kerogen as it becomes thermally mature (Loucks et al, 2009; Milliken et al, 2013; Löhr et al, 2015), which causes an increase in surface to volume ratio of kerogen. Therefore, surface properties of kerogen including wettability could significantly impact wettability of organic-rich mudrocks and multi-phase fluid flow in these complex formations.

2.2 KERGEN WETTABILITY

Kerogen is often considered to be a fully hydrocarbon-wet constituent of mudrocks (Passey et al. 2010). However, recent studies indicate that kerogen pores are accessible by both water and hydrocarbons (Zhang et al. 2012; Ruppert et al. 2013). The hydrophilic adsorption sites in organic-rich mudrocks, located within their pore structure, are composed of either clays or aliphatic organic matter; and hydrophobic sites are composed of aromatic organic matter (Chalmers and Bustin 2010). Methane adsorption studies on kerogen suggest that methane sorption capacity was higher in thermally mature samples as compared to immature samples (Hu 2014). The measurements of electrical resistivity, dielectric permittivity, and elastic modules by Yang et al. (2016), Jagadisan and Heidari (2017), and Valdes et al. (2017) indirectly showed that the moisture content in kerogen samples under laboratory conditions varies with thermal maturity. These results suggest that (a) the wettability of kerogen samples could vary with thermal maturity of kerogen, and (b) kerogen can be water-wet at low thermal maturities, when it instantly adsorbs water from humid environment.

Three main types of kerogen are described in the literature, namely, type I, type II, and type III (van Krevelen 1961; Tissolt and Welte 1984). Type I kerogen is rare and predominantly composed of hydrogen-rich organic matter. It mainly consists of lacustrine sources. Type II kerogen has predominantly marine depositional origin with some land components. It contains relatively high hydrogen content. Type III kerogen consists of woody terrestrial source and typically contains low hydrogen content. They are mostly prone to gas generation. During thermal maturation of kerogen, it evolves from hydrogen-rich organic matter into hydrogen-poor residual carbon (Baskin 1997). This promotes transformation in the chemical structure of kerogen with a gradual increase in sp^2/sp^3 carbon hybridization ratio, leading to aromatization (Vandenbroucke 2003). At very high thermal maturity, the kerogen structure condenses to mainly aromatic units in sp^2 hybridized graphitic structures (Passey et al. 2010). With increasing thermal maturity, carbonyls and alkyls decrease while aromatics increase (Mao et al. 2010).

Kerogen has been found to have a wide range of composition and chemical structure. Molecular representations of kerogen from Green River shale were first constructed by Yen (1976). The basis of the model was the structure of the chemical degradation compounds of kerogen and

accounted for features observed in X-ray Diffraction (XRD), Infrared (IR), and electron spectroscopy measurements. The model had a bulk formula of $C_{235}H_{397}O_{13}N_3S_5$. Siskin et al (1995) later developed a model for kerogen by incorporating evidence from solid state ^{13}C NMR in addition to mass spectrometry analysis of pyrolysis products of kerogen. Molecular model for kerogen at different stages of thermal maturity was given by Behar and Vandenbrouke (1986) which shows an increase in aromatic chains in later stages of thermal maturity. Kerogen from green river shale was found to contain carboxyl, ester, amide, hydroxyl, aldehyde, and ketone groups (Fester and Robinson 2009). Zhou et al. (2015) suggests that as the metamorphic degree increases, the the carboxyl and hydroxyl functional groups undergo major changes while the carbonyl groups tend to remain the same.

Previous studies on carbon materials have shown that surface functional groups can have critical impacts on their wettability (Deheryan et al. 2014). Therefore, the variation in chemical structure and bonding of kerogen during thermal maturity can modify its wettability characteristics. Wettability studies on coal show that among oxygen-containing functional groups, carboxyl group is shown to increase water-wettability of coal surface (Drake et al. 2013; Zhou et al. 2015). Kerogen composition is also variable between different types of kerogen (van Krevelen 1961), which would have an impact on its wettability. However, the impacts of kerogen type, functional groups and reservoir temperature and pressure on kerogen wettability are still not well understood and need to be quantified. Therefore, experimental wettability studies on pure kerogen are crucial. Experimental measurements alone might not be sufficient for addressing the aforementioned challenges and can hardly cover a wide and continuous range of kerogen and environment properties.

Molecular dynamics simulations can capture the interactions of atoms and molecules with the surrounding environment caused by inter-molecular and intra-molecular forces (Allen 2004) and can be used to understand and quantify the fundamental processes affecting wettability of kerogen. It gives the ability to simulate a wide range of kerogen structures and compositions under a wide range of temperatures/pressures and estimate kerogen wettability for different compositions and reservoir conditions. Experimental work complemented by molecular simulation can provide a more thorough understanding of the underlying processes affecting kerogen wettability.

Molecular simulation studies on kerogen often use a slit graphite model, which consists of stacked sheets of graphene, to represent kerogen pores in organic-rich shale reservoirs (Striolo 2003; Ambrose 2012; Diaz-Campos 2014; Pitakbunkate et al. 2017). However, these models do not capture the complexity of kerogen structure adequately. Moreover, kerogen's crystal structure and oxygen-containing functional groups could have significant impacts on its wettability.

Hu et al. (2014) and Hu et al. (2016) used an inactivated kerogen model, which is composed of graphene sheets to represent highly mature kerogen. In order to simulate the effect of thermal maturity, they embedded varying amounts of carbonyl ($C=O$) functional groups on these graphene sheets to model different oxygen to carbon (O/C) ratios. Wettability studies on these simplified models showed that kerogen is water-wet at low thermal maturities and hydrophobic at high thermal maturity (Hu et al. 2014). However, simplified models for kerogen were used for

this study which does not capture the complexity and heterogeneity adequately. Moreover, this study does not consider the impact of oxygen functional groups such as carboxyl or hydroxyl and sulfur- and nitrogen-based functional groups, which are commonly found to exist in kerogen structure. The effect of temperature and pressure on kerogen wettability is also not considered.

2.3 IMPACT OF WETTABILITY ON RESISTIVITY MEASUREMENTS AND MULTIPHASE FLOW IN ORGANIC-RICH MUDROCKS

Several researchers have documented a consistent trend in the variation of resistivity of organic-rich mudrock reservoirs with thermal maturity (Kreis and Costa 2006; Cumella and Duhailan 2014). For example, in the Niobrara Formation the resistivity of the shale reservoir in low thermal maturity, in the oil generation stage is low at about 20 Ωm ; the resistivity then gradually increases to nearly 100 Ωm at wet gas stage. However, the resistivity trend reverses and drops to around 40 Ωm at even higher thermal maturity at dry gas stage (Cumella and Duhailan 2014). In other highly mature shale-gas reservoirs, the overall electrical resistivity has been found to be 1-2 orders of magnitude less than the measured electrical resistivity in the same formation at relatively lower thermal maturities (Passey et al. 2010). The low resistivity phenomenon is attributed to graphitization of kerogen at high thermal maturities, presence of conductive minerals, clay content, etc. however, distribution of fluids in the pore spaces have significant impact on the resistivity measurements (Mungan and Moore 1967). Therefore, it is critical to understand the factors influencing the wettability of organic-rich mudrocks.

On the other hand, several organic-rich mudrocks plays such as Permian basin and the Bakken, face the challenge of high volumes of water production (Whitfield 2017). The produced water from organic-rich mudrocks (both flowback and produced water) must be stored, transported, and either disposed via injection well or treated for reuse or surface discharge; which results in high cost of water management. However, the mechanism behind the high volumes of water produced or the flowback efficiency of fracturing fluid is poorly understood. The wettability of organic-rich mudrocks strongly impacts the multiphase flow properties and interaction between fracturing fluid and rock. Therefore understanding organic-rich mudrocks microstructure and its wettability is critical for understanding fracturing fluid loss, water production and for optimizing production.

2.4 LIMITATIONS OF EXISTING STUDIES

The main limitations of existing work on kerogen wettability are:

- i. No experimental work to determine the impact of thermal maturity.
- ii. The effect of kerogen type is not clearly understood.
- iii. Previous simulation studies have used simplistic kerogen molecular models.
- iv. Previous simulation work does not consider the effect of functional groups such as carboxyl and hydroxyl present in kerogen.
- v. Previous simulation model does not consider the effect of reservoir temperature on the adsorption characteristics of water and hydrocarbons on kerogen surface.

- vi. Dependence of thermal maturity of kerogen on organic-rich mudrock wettability is not understood clearly.

3. STATEMENT OF THE PROBLEM

Wettability and geochemistry of kerogen has a strong impact on the multiphase fluid-flow properties such as relative permeability of organic-rich mudrocks as well as on physical properties of rocks such as resistivity measurements. Therefore, wettability of kerogen could significantly affect water production as well as assessment of hydrocarbon reserves in organic-rich mudrocks. Kerogen is often considered as hydrocarbon-wet in reservoir characterization. However, recent studies indicate that changes in kerogen structure and composition could alter its wettability. Previous molecular simulation studies on kerogen wettability used simplistic models for kerogen structure, which do not capture the complexity and heterogeneity of kerogen. Moreover, there have been no experimental studies to determine the wettability of pure kerogen. Thus, more advanced molecular and experimental studies are required to determine the impact of geochemistry on kerogen wettability.

Wettability and geochemistry of kerogen also significantly affects the fluid distribution within the pore network and impacts the borehole electrical resistivity measurements in organic-rich mudrocks. Low resistivity pays in organic-rich mudrocks have been linked to clay content and graphitization/aromaticity of kerogen at high thermal maturities. However, the impact of kerogen wettability on the resistivity measurements has not yet been studied and quantified. Numerical simulations of effective electrical properties of rocks combined with the outcomes of wettability quantification can be effectively used to quantify the impact of kerogen wettability on electrical resistivity of organic-rich mudrocks. This can potentially (a) improve estimates of hydrocarbon reserves in organic-rich mudrocks and (b) enables reliable prediction of water production.

4. PROPOSED HYPOTHESES

The main hypotheses proposed in this research are:

- i. The geochemistry of kerogen such as its oxygen content and functional groups has considerable impact on its wettability.
- ii. Temperature and pressure conditions affect kerogen wettability.
- iii. Thermal maturity of organic matter impacts the wettability of organic-rich mudrocks.
- iv. Wettability of kerogen significantly impacts the electromagnetic properties of organic-rich mudrocks.

5. RESEARCH OBJECTIVES

The main research objectives are:

- i. Expand existing molecular simulation models of kerogen wettability by using realistic models of kerogen and quantify the impact of oxygen containing functional groups and aromaticity on wettability.

- ii. Quantify the impact of reservoir temperature and pressure on kerogen wettability using molecular simulations.
- iii. Experimentally verify the results of molecular simulations by quantifying wettability of kerogen at different thermal maturity levels using sessile drop method. Experimentally quantify the impact of chemical composition and chemical bonding of kerogen on its wettability.
- iv. Experimentally quantify the influence of geochemistry and kerogen wettability on the wettability of organic-rich mudrocks.
- v. Quantify the impact of wettability on the electromagnetic properties of kerogen and organic-rich mudrocks.

6. METHOD AND PROPOSED TASKS

Molecular dynamics simulation approach models motion at the atomic level caused by inter- and intra-molecular forces by integrating Newton's equations of motion. It involves two basic steps: the determination of interacting forces using potential fields, and the tracing of molecular movements by solving Newton's equations of motion. The models of kerogen, methane, and water molecules are placed in a cubical simulation box as inputs to molecular simulation. Once the initial potential energy of the system is minimized, the system is subjected to temperature and pressure changes. The dynamics simulations are then conducted in isothermal and isobaric conditions. The position and velocities of the molecules present in the system are updated as a function of time. The kerogen molecules are kept stationary and the fluid molecules are allowed to move as the simulation time progresses. Once the kinetic and potential energies are equilibrated, the adsorption behavior of kerogen to water and methane molecules at system equilibrium are then investigated under different temperature and pressure conditions to determine wettability.

TASK 1. DEVELOP REALISTIC MOLECULAR MODELS OF KEROGEN (OBJECTIVE I & II, HYPOTHESIS I&II)

I propose to model a detailed structure of kerogen to be used as input to the molecular simulations. The molecular models of kerogen capture its heterogeneity, functional groups, as well as compositional and structural details as indicated in previously documented experimental data. The model will also consider the effect of kerogen type and maturity on its structure. Finally, the model will account for changes in hydrogen and oxygen content, amount of oxygen containing functional groups, and changes in aromaticity with kerogen of different types and thermal maturity. This task will be used to evaluate objectives I and II and verify hypotheses I and II.

TASK 2. QUANTIFY THE IMPACT OF THERMAL MATURITY ON WATER AND HYDROCARBON ADSORPTION ON KEROGEN SURFACE USING MOLECULAR SIMULATIONS (OBJECTIVE I, HYPOTHESIS I)

Previous publications have shown the importance of considering wettability of kerogen at different thermal maturity levels (Hu et al. 2014). However, simplified models of kerogen were used for these studies. I propose to use realistic models of kerogen to determine water and

hydrocarbon adsorption on kerogen surface. This would be used to complement and reinforce the experimental studies on kerogen wettability. This task will be used to evaluate objective I and verify hypothesis I.

TASK 3. QUANTIFY THE IMPACT OF KEROGEN TYPE ON WATER AND HYDROCARBON ADSORPTION ON KEROGEN SURFACE USING MOLECULAR SIMULATIONS (OBJECTIVE I, HYPOTHESIS I)

Type I kerogen has high H/C ratio and low O/C ratio. The hydrogen to carbon ratio decreases from type I to type III. The aromaticity is also variable between different types of kerogen, with type III being low in aliphatic compounds and high in aromatic compounds. The variations in molecular structure and components among different types of kerogen affect their surface properties such as wettability. I propose to quantify these impacts using molecular simulation method. The effect kerogen type on its wettability has not been quantified in the past. This task will be used to evaluate objective I and verify hypothesis I.

TASK 4. QUANTIFY THE EFFECTS OF TEMPERATURE AND PRESSURE ON KEROGEN WETTABILITY USING MOLECULAR SIMULATIONS (OBJECTIVE II, HYPOTHESIS II)

Temperature changes have been shown to impact the contact angle of various different systems such as molten solder on a copper substrate (Selvaduray and Brindos 1997). The temperature effect is due to the reaction in the liquid/solid interface, which causes alteration of surface tension and thereby alters the equilibrium contact angle and wettability. The methane adsorption capacities of organic matter have been found to reduce with increase in temperature (Chen et al. 2017). Present publications do not quantify the effect of temperature on the wettability of kerogen. Coal was found to have decreasing water-wettability with increase in pressure (Kaveh et al. 2012), however the effects of pressure were found be small for calcite/water/decane system (Hansen et al. 2000). I propose to determine and model the effect of reservoir temperatures and pressure on the wettability of kerogen using molecular simulation. This task will be used to evaluate objective II and verify hypothesis II.

TASK 5. KEROGEN ISOLATION, SYNTHETIC MATURATION AND GEOCHEMICAL ANALYSIS (OBJECTIVE III, HYPOTHESIS I)

Subtask 1. Kerogen Isolation. Several studies in the past have isolated kerogen from organic-rich mudrocks in order to to characterize its chemical and physical properties. There exist two basic methods to extract kerogen: (1) physical and (2) chemical methods (Saxby 1970). The physical methods of separation are mostly based on specific gravity difference between kerogen and other minerals and use centrifugation and gravity segregation (Hubbard et al. 1952; Robinson 1969; Durand and Nicaise 1980). Chemical separation methods for isolating kerogen involve demineralization of organic-rich mudrocks using hydrochloric acid (HCl) and hydrofluoric acid (HF) (Forsman and Hunt 1958; Saxby 1970; Durand and Nicaise 1980; Vandenbroucke and Largeau 2007). Chemical separation methods are more efficient and yield higher kerogen recovery rates as compared to physical separation process. Moreover, the acids treatments do not alter the kerogen structure significantly (Vandenbroucke and Largeau 2007).

Pyrite can be one of the major constituents of organic-rich mudrocks with its weight concentrations as high as 40 wt% (Vandenbroucke and Largeau 2007). Pyrite still remains embedded in the demineralized sample after successive physical and chemical treatments of the organic-rich mudrocks (Vandenbroucke 2003). One of the effective methods to eliminate pyrite is to use acidic CrCl₂ solution (Acholla and Orr 1993). However, this procedure produces toxic H₂S. Kinghorn and Rehman (1980) propose a safer density separation method using ZnBr₂ solution to eliminate pyrite.

I propose to use a combination of chemical and physical separation method to isolate kerogen from organic-rich mudrocks covering a range of kerogen types. This would be a preparatory step for geochemical analysis and wettability assessment methods discussed later.

Subtask 2. Synthetic Maturation. Studies on kerogen often employ laboratory simulations of maturation, such as hydrous and anhydrous pyrolysis, as a means to study properties of kerogen with variations in thermal maturity (Tissot and Espitalie 1978; Ungerer 1990; Behar et al. 2010). These studies are based on the theory that organic matter exposed to higher temperature for a shorter period of time has the same maturity as organic matter exposed to lower temperature for a longer period of time (Stach et al. 1982).

I plan to artificially mature kerogen to different thermal maturity levels to generate samples covering a wide range of maturity levels. For the current study, I propose to use anhydrous pyrolysis which is performed by systematically heating the kerogen sample in a closed system in the absence of oxygen. The advantage of anhydrous pyrolysis is that large sample sizes can be pyrolyzed reactively to simulate natural maturation process (Macko and Engel 1993).

Subtask 3. Geochemical Analysis. Pyrolysis, solid-state ¹³C nuclear magnetic resonance (¹³C SSNMR), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) are examples of measurement methods used for geochemical characterization and quantification of thermal maturity of kerogen (Kelemen et al. 2007; Tong et al. 2011; Duan et al. 2016). Among these, XPS is widely used in chemical structure analysis for its ability to efficiently observe elemental composition and functional group information on the surface within 10 nm and is one of the most effective methods for element investigation (Kelemen et al. 2002; Zhou et al. 2015). Kelemen et al. (2002) used XPS for geochemical characterization of kerogen and showed that organic oxygen content in kerogen decreases as it becomes more thermally mature. Pyrolysis is the process of decomposition of organic matter by heating and is regularly used in petroleum geochemistry to measure total organic carbon content (TOC) and other properties such as hydrogen index (HI) and T_{max} for characterization of thermal maturity of organic matter.

I propose to use pyrolysis and XPF for thermal maturity assessment and molecular characterization of kerogen. The relationship between molecular characteristics and the level of maturation will be established through indicators of thermal maturation including hydrogen, oxygen indices and aromaticity. This task will be used to evaluate objective III and verify hypothesis I.

TASK 6. EXPERIMENTALLY QUANTIFY KEROGEN WETTABILITY USING SESSILE DROP TEST AND CROSS VALIDATE THE RESULTS OF MOLECULAR SIMULATION (OBJECTIVE III, HYPOTHESIS I)

There exists several methods for wettability quantification including wilhelmy balance method (Wilhelmy 1863), tilting plate method (Adam and Jessop 1925), capillary bridge method (Restango et al. 2009), and sessile drop method (Bigelow et al. 1946; Krishnan et al. 2005; Yuan and Lee 2013). Among these methods, sessile drop method has become one of the standard and commonly used methods, which we considered as the best option for the kerogen samples in this study. In the sessile drop method contact angle measurement is achieved by measuring the tangent angle at the three phase contact point on a drop profile. The shape of a droplet and contact angle is determined by the intermolecular forces and the surface tensions between the phases involved. The mechanical equilibrium of a drop of fluid on a solid surface is achieved as a result of three surface tensions given via,

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (1)$$

where, γ_{LV} , γ_{SL} , and γ_{SV} are the surface tensions at the interface of liquid and vapor, solid and liquid, and solid and vapor phases, respectively, and θ is the Young's contact angle (Young, 1805).

I propose to use sessile drop method to experimentally quantify the wettability of kerogen. Experimental wettability on isolated kerogen has not been done previously. The experiments would be performed on kerogen samples covering a range of kerogen types and natural and synthetic kerogen thermal maturity states. The novel aspect of the experimental part of this proposal is to integrate the chemical alterations in kerogen to its wettability characteristics using a suite of pure isolated kerogen. This task will be used to evaluate objective III and verify hypothesis I.

TASK 7. EXPERIMENTALLY QUANTIFY THE IMPACT OF THERMAL MATURITY OF KEROGEN ON WETTABILITY OF ORGANIC-RICH MUDROCKS (OBJECTIVE IV, HYPOTHESIS III)

I propose to test the impact of kerogen wettability at different levels of thermal maturity on the wettability of organic-rich mudrock experimentally using (i) sessile drop test on organic-rich mudrock core samples, (ii) spontaneous imbibition test on crushed mudrock samples, and (iii) floatation technique. This study will be conducted on mudrock samples with different natural and artificial thermal maturity levels of organic matter present in it. This task will be used to evaluate objective IV and verify hypothesis III.

TASK 8. QUANTIFY THE SENSITIVITY OF KEROGEN WETTABILITY ON RESISTIVITY MEASUREMENTS OF ORGANIC-RICH MUDROCKS USING NUMERICAL SIMULATIONS AND EXPERIMENTAL MEASUREMENTS (OBJECTIVE V, HYPOTHESIS IV)

I propose experimentally quantify the impact of thermal maturity on the measurements of dielectric constant of kerogen. I would use a previously developed numerical simulator to evaluate the sensitivity of kerogen wettability on the electrical measurements (electrical resistivity and dielectric constant) of organic-rich mudrocks. The synthetic pore scale rock in numerical simulation is synthetically saturated by assigning different wettability conditions to kerogen at different thermal maturities. The sensitivity of resistivity measurements to wettability of kerogen is then quantified. The model also takes into account the variation in resistivity of pure kerogen with change in thermal maturity. This task will be used to evaluate objective V and verify hypothesis IV.

7. PRELIMINARY RESULTS

6.1 SAMPLE PREPARATION

6.1.1 KEROGEN ISOLATION

I use the chemical isolation technique proposed by Durand and Naicase (1980) method for isolating kerogen from two formations (named A and B). **Figure 1** shows examples of isolated kerogen powder and a kerogen pellet.

6.1.2 SYNTHETIC MATURATION

I perform synthetic thermal maturation of organic matter by heat-treating mudrock samples (i.e., core and crushed samples) and isolated kerogen samples. The steps followed in the procedure are as follows,

1. The samples are heated in the oven at 4°C/min to the required heat-treatment temperature under the flow of nitrogen
2. The samples are then isothermally heated at that heat-treatment temperature for an hour to endure that all the particles are uniformly heated at that temperature.
3. The samples are then cooled at 25°C/min till it reaches the the room temperature.



(a)



(b)

Fig 1. Examples of (a) isolated kerogen powder and (b) kerogen pellet used for contact angle measurements.

6.2 GEOCHEMICAL ANALYSIS OF KEROGEN

6.2.1 IMPACT OF SYNTHETIC MATURITY OF KEROGEN SAMPLES ON ITS THERMAL MATURITY AND CHEMICAL COMPOSITION

We used the pyrolysis parameter HI as a thermal maturation proxy to qualitatively confirm the synthetic maturation of kerogen samples from formations A and B. **Figure 2** shows the variation of HI as a function of heat-treatment temperature. It is observed that the hydrogen index of kerogen samples decreases as the heat-treatment temperature increases in both formations A and B confirming that synthetic maturation increases the thermal maturity of the kerogen samples.

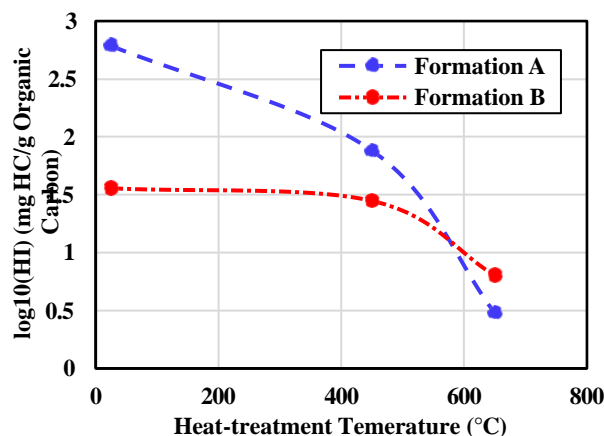


Fig. 2 The effect of heat-treatment temperature on Hydrogen Index of kerogen samples from formations A and B.

We performed XPS measurements on the kerogen samples from Formations A and B at different thermal maturities. **Figure 3** shows an example of XPS measurements, obtained for a non-heated kerogen sample from Formation A. Similar results were obtained for samples prepared at different thermal maturity levels for both formations. The XPS measurements confirmed the presence of carbon, oxygen, nitrogen, sulfur and traces of fluorine in Formations A and B.

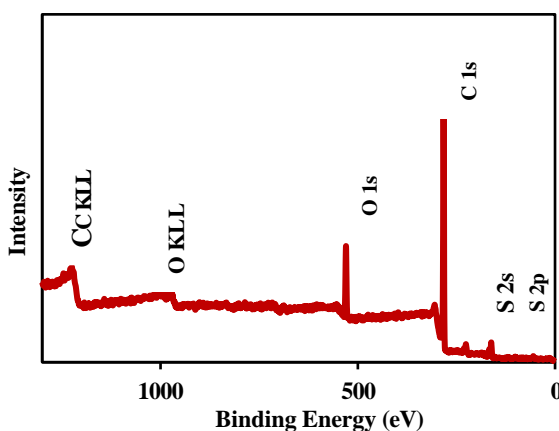


Fig. 3 XPS Spectrum of a non-heated kerogen sample from formation A.

The results of XPS measurements were used to estimate oxygen to carbon (O/C) ratio. **Figure 4** shows the variation in O/C ratio with heat-treatment temperature. Formation B (i.e., type II/III kerogen) has higher O/C ratio than Formation A, which contains type II kerogen. We observe that the O/C ratio decreases as heat-treatment temperature increases in both formations A and B. This observation can be explained by the decrease in O/C ratio during catagenesis of kerogen samples as they become thermally mature.

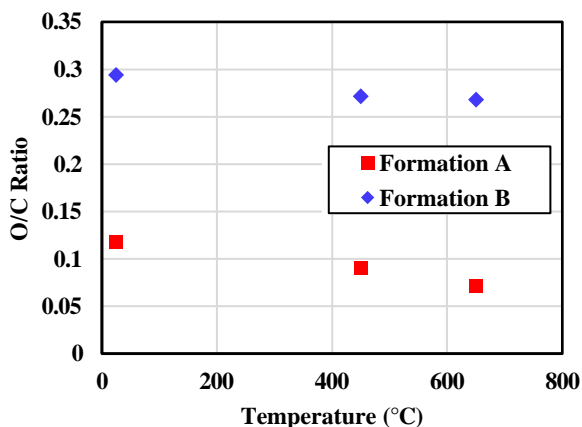


Fig. 4 Oxygen to carbon ratio vs heat-treatment temperature for formations A and B.

6.3 WETTABILITY QUANTIFICATION

6.3.1 IMPACT OF THERMAL MATURITY OF KEROGEN ON CONTACT ANGLE MEASUREMENTS

The contact angle formed by water droplet on the kerogen surface is recorded for two formations at different thermal maturity levels. The contact angles were averaged over 5 measurements on different locations of the kerogen sample. The angles at the left and right side of the droplet were also averaged at each location. The measurements were made using ImageJ software (Rueden et al., 2017) which uses a spherical approximation of the droplet. The angle is then calculated via

$$\theta = 2 \tan^{-1}(h / d) , \quad (2)$$

where d is the drop diameter and h is the height of the apex. The error in contact angle measurements is also recorded and was found to be within $\pm 2.8^\circ$.

Figures 5a, 5b, and 5c show the contact angle for samples from formation A, non-heated and heat-treated at 450°C and 650°C , respectively. The results suggest that non-heated kerogen sample from formation A is hydrophilic with a low contact angle of 44° . As the heat-treatment temperature increases to 450°C , the contact angle of kerogen increases to 107° . Furthermore, as the heat-treatment temperature increases to 650°C , the water droplet forms a sharp kerogen/water/air contact angle of 122° indicating that the kerogen surface is hydrophobic.

Similar measurements were performed on kerogen samples isolated from formation B. The results of measurements in formation B indicate that non-heated kerogen from formation B is neutral-wetting with a contact angle of 111° . As the heat-treatment temperature of kerogen increases to 450°C , the contact angle of kerogen increases to 116° . As the heat-treatment

temperature increases to 650°C, the contact angle further increases to 140°, indicating that the kerogen surface is hydrophobic.

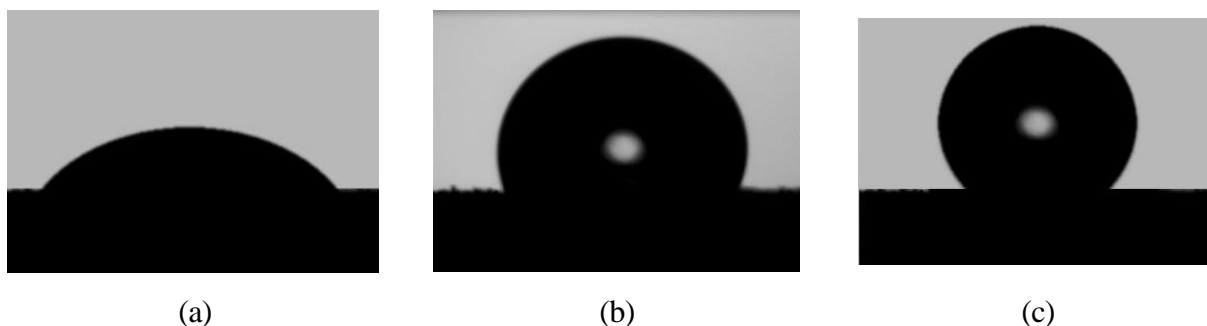


Fig. 5 Contact angle formed by a water droplet on kerogen surface from formation A at (a) room temperature, (b) heat-treated at 450°C and, (c) heat-treated at 650°C.

Figure 6 summarizes the results of contact angle measurements as a function of oxygen to carbon ratio for kerogen samples from formations A and B. The results show that the contact angle increases from 44° to 122° in formation A as the O/C decreases from 11% to 7%. In formation B, the contact angle increases from 111° to 140° as the O/C decreases from 29% to 26%. The results indicate that at higher O/C ratio the contact angle is smaller and as the O/C ratio decreases, the contact angle increases. This indicates that kerogen is water wet at low thermal maturities and becomes hydrophobic as it thermally matures.

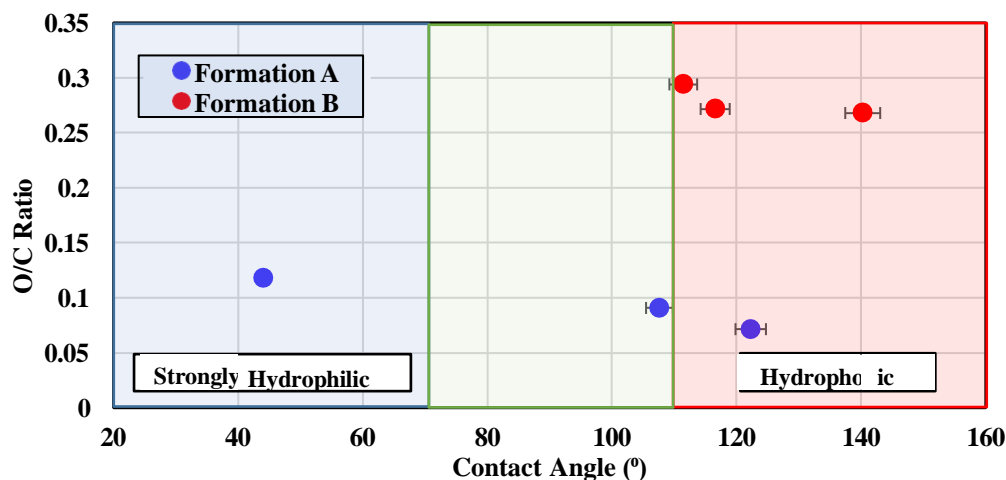


Fig. 6 Contact angle formed by water droplet on kerogen samples from formations A and B at different oxygen to carbon ratios. Shaded regions blue, green and orange denote strongly hydrophilic, moderately hydrophilic and hydrophobic regions, respectively.

Increase in thermal maturity of kerogen leads to chemical restructuring and loss of hydrogen, which results in increase in aromaticity and transformation of kerogen into graphene sheets (Welte, 1973; Harrison, 1979; Baskin, 1997; Vandenbroucke, 2003; Passey et al., 2010). Aromatic rings of carbon are composed of relatively non-polar C-C and C-H bonds, which do not have affinity to water molecules and makes aromatic carbon and graphite hydrophobic (Li et al., 2013). On the other hand, aliphatic carbons with the high concentration of oxygen

functionalized groups in kerogen makes kerogen polar and therefore hydrophilic in nature. This theory is consistent with our observations that kerogen samples at high thermal maturity (low O/C ratio) are hydrophobic and that kerogen samples at low thermal maturity (high O/C ratio) are hydrophilic.

6.4 DEVELOPMENT OF MOLECULAR MODELS FOR KEROGEN

Figures 7a, 7b and 7c show the molecular representations of type I, II and type III kerogen, respectively. Type I kerogen (originated from anoxic lacustrine environment) is characterized by high aliphatic carbon content and low oxygen and high hydrogen contents. Type I kerogen model is developed with an assumption of H/C ratio of 1.3, and O/C ratio of 0.07. Type II kerogen (originated from marine anoxic environments) is characterized by the presence of higher aromatic carbon content, lower hydrogen content, and higher oxygen content as compared to type I kerogen. The kerogen type II model contains H/C ratio of 0.92 and O/C ratio of 0.09. Type III kerogen (originated from terrestrial plants) is characterized by a larger oxygen content and lower hydrogen content compared to type I and type II kerogen samples. This type of kerogen has greater potential for generating liquid hydrocarbons and has higher aromaticity. The kerogen type III model contains H/C ratio of 0.70 and O/C ratio of 0.14. The kerogen models include the typical functional groups of oxygen and carbon found in kerogen structure, such as C-O, C=O, COOH and OH.

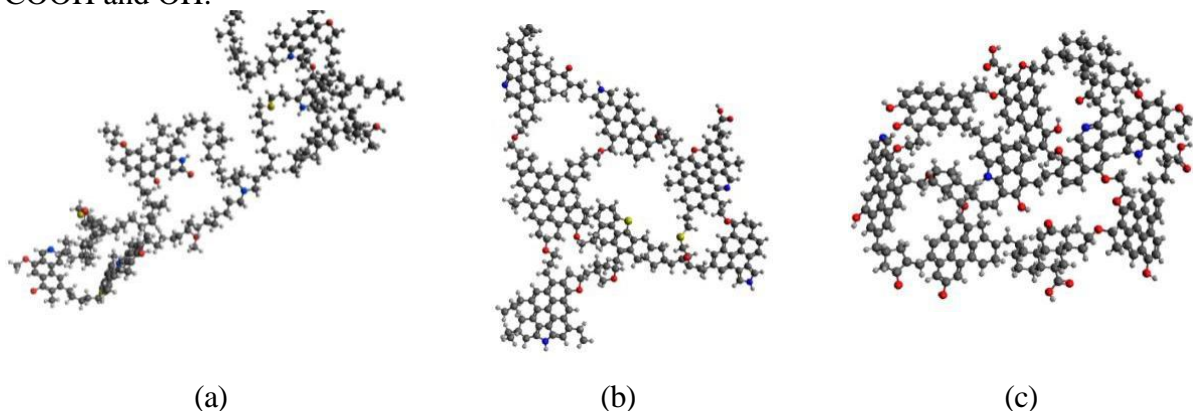


Fig 7 Molecular models representative of (a) type I, (b) type II, and (c) type III kerogen samples.

7 REFERENCES

1. Acholla, F.V. and Orr, W.L., 1993. Pyrite removal from kerogen without altering organic matter: the chromous chloride method. *Energy & fuels*, 7(3): 406-410.
2. Adam, N.K. and Jessop, G., 1925. CCL.—Angles of contact and polarity of solid surfaces. *Journal of the Chemical Society*, 127: 1863–1868.
3. Ambrose, R.J., Hartman, R.C., Diaz-Campos, M., Akkutlu, I.Y. and Sondergeld, C.H., 2012. Shale gas-in-place calculations part I: new pore-scale considerations. *Spe Journal*, 17(01): 219-229.
4. Amott, E. 1959. Observations relating to the wettability of porous rock. *Petroleum Transactions AIME*, 216: 156-162.
5. Anderson, W., 1986. Wettability literature survey-part 2: Wettability measurement. *Journal of petroleum technology*, 38(11): 1–246.
6. Baskin, D.K., 1997. Atomic H/C ratio of kerogen as an estimate of thermal maturity and organic matter conversion. *AAPG bulletin*, 81(9): 1437–1450.

7. Bigelow, W.C., Pickett, D.L. and Zisman, W.A., 1946. Oleophobic monolayers: I. Films adsorbed from solution in non-polar liquids. *Journal of Colloid Science*, 1(6): 513–538.
8. Chalmers, G.R. and Bustin, M.R., 2010. The Effects and Distribution of Moisture in Gas Shale Reservoir Systems: AAPG Annual Convention and Exhibition, New Orleans, Louisiana, 11–14 April.
9. Cumella, S. and Al Duhailan, M., 2014. Niobrara Maturity Goes Up, Resistivity Goes Down; What's Going On?: Unconventional Resources Technology Conference, Denver, Colorado, 25–27 August.
10. De Ruijter, M.J., Blake, T.D. and De Coninck, J. 1999. Dynamic wetting studied by molecular modeling simulations of droplet spreading. *Langmuir*, 15(22): 7836–7847.
11. Donaldson, E.C., Thomas, R.D. and Lorenz, P.B., 1969. Wettability determination and its effect on recovery efficiency. *Society of Petroleum Engineers Journal*, 9(1): 13–20.
12. Durand, B., and Nicaise, G., 1980, *Kerogen: Insoluble Organic Matter from Sedimentary Rocks*: Éditions Technip, 35–52, Paris.
13. Er, C., Li, Y., Zhao, J., Wang, R., Bai, Z. and Han, Q., 2016. Pore formation and occurrence in the organic-rich shales of the Triassic Chang-7 Member, Yanchang Formation, Ordos Basin, China. *Journal of Natural Gas Geoscience*, 1(6): 435–444.
14. Engelder, T., Cathles, L.M. and Bryndzia, L.T., 2014. The fate of residual treatment water in gas shale. *Journal of Unconventional Oil and Gas Resources*, 7: 33–48.
15. Dayal, A.M., Mani, D., Mishra, S. and Patil, D.J., 2013. Shale gas prospects of the Cambay Basin, western India. *Geohorizon*, 18(1): 26–31.
16. Giro, R., Bryant, P.W., Engel, M., Neumann, R.F. and Steiner, M.B., 2017. Adsorption energy as a metric for wettability at the nanoscale. *Scientific Reports*, 7: 46317.
17. Hansen, G., Hamouda, A.A. and Denoyel, R., 2000. The effect of pressure on contact angles and wettability in the mica/water/n-decane system and the calcite+ stearic acid/water/n-decane system. *Colloids and Surfaces A. Physicochemical and Engineering Aspects*, 172(1–3): 7–16.
18. Harrison, W.E., 1979. Levels of graphitization of kerogen as a potentially useful method of assessing paleotemperatures. *Special Publications of SEPM*.
19. Hu, Y., Devegowda, D. and Sigal, R., 2016. A microscopic characterization of wettability in shale kerogen with varying maturity levels. *Journal of Natural Gas Science and Engineering*, 33: 1078–1086.
20. Jagadisan, A. and Heidari, Z., 2017, Application of X-Ray Photoelectron Spectroscopy in Connecting Thermal Maturity of Kerogen to Its Dielectric Constant in Organic-Rich Mudrocks: SPWLA 58th Annual Logging Symposium. Society of Petrophysicists and Well-Log Analysts, Oklahoma City, Oklahoma, USA, 17–21 June.
21. Jones, S.C. and Roszelle, W.O. 1978. Graphical techniques for determining relative permeability from displacement experiments. *Journal of Petroleum Technology*, 30(05): 807–817.
22. Kaveh, N.S., Wolf, K.H., Ashrafizadeh, S.N. and Rudolph, E.S.J., 2012. Effect of coal petrology and pressure on wetting properties of wet coal for CO₂ and flue gas storage. *International Journal of Greenhouse Gas Control*, 11: S91–S101.
23. Kelemen, S.R., Afeworki, M., Gorbaty, M.L., Kwiatek, P.J., Solum, M.S., Hu, J.Z. and Pugmire, R.J., 2002. XPS and ¹⁵N NMR study of nitrogen forms in carbonaceous solids. *Energy & fuels*, 16(6): 1507–1515.
24. Kelemen, S.R., Afeworki, M., Gorbaty, M.L., Sansone, M., Kwiatek, P.J., Walters, C.C., Freund, H., Siskin, M., Bence, A.E., Curry, D.J. and Solum, M., 2007. Direct characterization of kerogen by X-ray and solid-state ¹³C nuclear magnetic resonance methods. *Energy & Fuels*, 21(3): 1548–1561.
25. Kinghorn, R.R.F., and Rahman, M., 1980. The Density Separation of Different Maceral Groups of Organic Matter Dispersed in Sedimentary Rocks. *Journal of Petroleum Geology*, 2(4): 449–454.
26. Kreis, K., Costa, A. and Osadetz, K., 2006. Hydrocarbon potential of Bakken and Torquay formations. Summary of investigations, Saskatchewan Geological Survey, 1: 1–10.
27. Krishnan, A., Liu, Y.H., Cha, P., Woodward, R., Allara, D. and Vogler, E.A., 2005. An evaluation of methods for contact angle measurement: *Colloids and Surfaces B. Biointerfaces*, 43(2): 95–98.
28. Li, Z., Wang, Y., Kozbial, A., Shenoy, G., Zhou, F., McGinley, R., Ireland, P., Morganstein, B., Kunkel, A., Surwade, S.P. and Li, L., 2013. Effect of airborne contaminants on the wettability of supported graphene and graphite. *Nature materials*, 12(10): 925.

29. Lutz, B. D.; Lewis, A. N.; Doyle, M. W. 2013. Generation, Transport, and Disposal of Wastewater Associated with Marcellus Shale Gas Development. *Water Resources*, 49(2): 647.
30. Macko, S.A., Engel, M.H. and Parker, P.L., 1993. Early diagenesis of organic matter in sediments. *Organic geochemistry*, Springer, Boston, MA.
31. Mokhtari, M., Alqahtani, A.A., Tutuncu, A.N. and Yin, X., 2013, August. Stress-dependent permeability anisotropy and wettability of shale resources. Presented in Unconventional Resources Technology Conference, Society of Petroleum Engineers.
32. Mungan, N. and Moore, E.J. 1968. Certain wettability effects on electrical resistivity in porous media. *Journal of Canadian Petroleum Technology*, 7(01): 20-25.
33. Nguyen, B.L., Bruining, J. and Slob, E.C. 1999. Effects of wettability on dielectric properties of porous media. Presented at the SPE Annual Technical Conference and Exhibition, Society of Petroleum Engineers.
34. Olson, J.E., 2008, January. Multi-fracture propagation modeling: Applications to hydraulic fracturing in shales and tight gas sands. In *The 42nd US rock mechanics symposium (USRMS)*. American Rock Mechanics Association.
35. 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: International Oil and Gas Conference and Exhibition, Beijing, China, 8–10 June.
36. Pitakbunkate, T., Blasingame, T.A., Moridis, G.J. and Balbuena, P.B., 2017. Phase Behavior of Methane–Ethane Mixtures in Nanopores. *Industrial & Engineering Chemistry Research*, 56(40), pp.11634-11643.
37. Jagadisan, A. and Heidari, Z. (2019). Experimental quantification of the effect of thermal maturity of kerogen on its wettability. *SPE Reservoir Evaluation & Engineering*, 22(04), pp. 1323-1333.
38. Jagadisan, A. and 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, p. 122039.
39. Jagadisan, A. and Heidari, Z. (2020). Impact of geochemical properties on wettability of kerogen and organic-rich mudrocks. *SPE Reservoir Evaluation & Engineering*, 23(02), pp. 758-771.
40. Jagadisan, A., Yang, A., and Heidari, Z. (2017). Experimental quantification of the impact of thermal maturity on kerogen density. *Petrophysics*, 58(06), pp. 603-612.
41. Jagadisan, A. and 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), pp. 1180-1189.
42. Jagadisan, A. and Heidari, Z. (2020). Effects of thermal maturity and chemical composition of kerogen on its dielectric constant. *Geophysics*, 85(1), pp. D53-D64.
43. Jagadisan, A. and Banerjee, S. (2024). Asphaltene adsorption on solid surfaces investigated using Quartz Crystal Microbalance with Dissipation under flow conditions. *ACS Omega*, 9(14), pp. 15982-15995.
44. Jagadisan, A., Chen, J.H., and Althaus, S.M. (2022). Improved methods for determination of petrophysical properties of unconventional tight rocks using particulate samples. *ACS Omega*, 7(11), pp. 9636-9641.
45. de Araujo, I.S., Jagadisan, A., and Heidari, Z. (2023). Impacts of kerogen type and thermal maturity on methane and water adsorption isotherms: A molecular simulation approach. *Fuel*, 352, p. 128944.
46. Garcia, A.P., Jagadisan, A., Hernandez, L.M., Heidari, Z., Casey, B., and Williams, R. (2020). Enhanced formation evaluation in the Permian Basin using a novel field-scale workflow including wells with missing data. *SPE Reservoir Evaluation & Engineering*, 23(03), pp. 865-878.
47. Darjani, S., Jagadisan, A., Koplik, J., and Banerjee, S. (2022). Lattice-Gas Model for Asphaltene Interactions Observed at Interfaces in the Context of the Yen-Mullins Model. *Energy & Fuels*, 36(16), pp. 8778-8785.
48. Garcia, A.P., Jagadisan, A., Rostami, A., and Heidari, Z. (2018). A new resistivity-based model for improved hydrocarbon saturation assessment in clay-rich formations using quantitative geometry of the clay network. *Petrophysics*, 59(03), pp. 318-333.
49. Invited Talks/Presentations

50. Jagadisan, A. and Heidari, Z. (2018, June). Experimental quantification of kerogen wettability as a function of thermal maturity. In SPWLA Annual Logging Symposium (p. D043S010R004).
51. Jagadisan, A. and 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 Annual Logging Symposium (p. D053S016R005).
52. Jagadisan, A., Silveira de Araujo, I., and Heidari, Z. (2021, December). Impact of kerogen geochemistry on methane and water adsorption using molecular simulations. In URTeC 2021 (pp. 2506-2519).
53. Jagadisan, A., Hernandez, L.M., and Heidari, Z. (2019, October). Impact of thermal maturity on water production in organic-rich mudrocks. In Unconventional Resources Technology Conference (URTeC), Denver, Colorado, 22-24 July 2019 (pp. 2655-2671).
54. Jagadisan, A. and Heidari, Z. (2019, October). Quantifying the impacts of competitive water adsorption of kerogen and clay minerals on wettability of organic-rich mudrocks. In URTeC, Denver, Colorado (pp. 3038-3052).
55. Jagadisan, A. and Heidari, Z. (2022, October). Quantifying the impact of geochemistry on the interfacial interactions of kerogen and water and its impact on fluid mobility. In Unconventional Resources Technology Conference (URTeC), 20–22 June 2022 (pp. 3079-3091).
56. Jagadisan, A. and 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 (p. D021S032R006).
57. Jagadisan, A. and Heidari, Z. (2020, June). Impact of kerogen geochemistry and reservoir temperature on contact angle and wettability of kerogen. In SPWLA Annual Logging Symposium (p. D223S013R002). SPWLA.
58. Tandon, S., Heidari, Z., and Jagadisan, A. (2018, July). Quantifying the mechanisms contributing to surface relaxation of protons in kerogen pores of organic-rich mudrocks. In SPE/AAPG/SEG Unconventional Resources Technology Conference (URTeC) (p. D013S012R007).
59. Jagadisan, A., Silveira de Araujo, I., and Heidari, Z. (2021, December). Impact of kerogen geochemistry on methane and water adsorption using molecular simulations. In Unconventional Resources Technology Conference (URTeC), 26–28 July 2021 (pp. 2506-2519).
60. Garcia, A.P., Jagadisan, A., Hernandez, L.M., Heidari, Z., Casey, B., and Williams, R. (2020). Enhanced formation evaluation in the Permian Basin using a novel field-scale workflow including wells with missing data. SPE Reservoir Evaluation & Engineering, 23(03), pp. 865-878.
61. Rostami, A., Jagadisan, A., Hernandez, L.M., Heidari, Z., Fairhurst, B., Yurchenko, I., Ikonnikova, S., and Hamlin, S. (2019, July). Advanced simultaneous formation evaluation and completion-oriented rock classification in the Midland Basin using integrated analysis of well logs, core measurements, and geostatistical data. In SPE/AAPG/SEG Unconventional Resources Technology Conference (URTeC) (p. D013S002R003).
62. de Araujo, I.S., Jagadisan, A., and Heidari, Z. (2021, May). A geochemistry-oriented workflow for wettability assessment at reservoir condition using molecular dynamics simulations. In SPWLA Annual Logging Symposium (p. D031S025R003). SPWLA.
63. Rezaee, R., 2015. Fundamentals of gas shale reservoirs. John Wiley & Sons.
64. Rueden, C.T., Schindelin, J., Hiner, M.C., DeZonia, B.E., Walter, A.E., Arena, E.T. and Eliceiri, K.W., 2017. ImageJ2: ImageJ for the next generation of scientific image data. BMC bioinformatics, 18(1): 529.
65. Ruppert, L.F., Sakurovs, R., Blach, T.P., He, L., Melnichenko, Y.B., Mildner, D.F. and Alcantar-Lopez, L., 2013. A USANS/SANS study of the accessibility of pores in the Barnett Shale to methane and water. Energy & Fuels, 27(2): 772–779.
66. Selvaduray, G.S. and Brindos, R., 1997. Effect of Temperature on Wetting Angle. In National Educators' Workshop: Update 96-Standard Experiments in Engineering Materials Science and Technology. NASA Publication, 3354: 137.
67. Siddiqui, M.A.Q., Ali, S., Fei, H. and Roshan, H. 2018. Current understanding of shale wettability: A review on contact angle measurements. Earth-Science Reviews.

68. Stach, E, M-Th. Mackowsky, M. Teichmüller, G.F. Taylor, G. Chandra, R. Teichmüller, Stach's Textbook of Coal Petrology, 1982.
69. Striolo, A., Chialvo, A.A., Cummings, P.T. and Gubbins, K.E., 2003. Water adsorption in carbon-slit nanopores. *Langmuir*, 19(20): 8583-8591.
70. S. S. Drake, D. M. O'Carroll, and J. I. Gerhard. 2013. Wettability contrasts between fresh and weathered diesel fuels. *Journal of Contaminant Hydrology*, 144 (1): 46–57.
71. Tissot, B. and D.H. Welte. 1978. Petroleum occurrence and formation: A New Approach to Oil and Gas Exploration
72. Tong, J., Han, X., Wang, S. and Jiang, X., 2011. Evaluation of structural characteristics of Huadian oil shale kerogen using direct techniques (solid-state ¹³C NMR, XPS, FT-IR, and XRD). *Energy & fuels*, 25(9): 4006–4013.
73. Valdes, C.C., Heidari, Z. and Gonzalez, A., 2017. Quantifying the Impacts of Thermal Maturity on Elastic Properties of Kerogen: SPWLA 58th Annual Logging Symposium. Society of Petrophysicists and Well-Log Analysts, Oklahoma city, Oklahoma, USA, 17–21 June.
74. Van Krevelen, D.W. 1961. Coal, Elsevier, New York.
75. Vandenbroucke, M., 2003. Kerogen: from types to models of chemical structure. *Oil & gas science and technology*. 58(2): 243–269.
76. Vandenbroucke, M., and Largeau, C., 2007. Kerogen Origin, Evolution and Structure. *Organic Geochemistry*. 38(5): 719–833.
77. Welte, D., 1973. Recent advances in organic geochemistry of humic substances and kerogen. A review. *Advances in organic geochemistry*: 10–13.
78. Werder, T., Walther, J.H., Jaffe, R.L., Halicioglu, T., Noca, F. and Koumoutsakos, P. 2001. Molecular dynamics simulation of contact angles of water droplets in carbon nanotubes. *Nano Letters*, 1(12): 697-702.
79. Wilhelm, 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.
80. Whitefield. S. 2017. Permian, Bakken Operators Face Produced Water Challenges: *Journal of petroleum technology*.
81. Yang, A., Firdaus, G. and Heidari, Z., 2016. Electrical resistivity and chemical properties of kerogen isolated from organic-rich mudrocks: *Geophysics*. 81(6): D643–D655.
82. Yassin, M.R., Begum, M. and Dehghanpour, H., 2017. Organic shale wettability and its relationship to other petrophysical properties: A Duvernay case study. *International Journal of Coal Geology*, 169: 74-91.
83. Yuan, Y. and Lee, T.R., 2013, Contact angle and wetting properties: In *Surface science techniques*, Springer Berlin Heidelberg: 3–34.
84. Young, T., 1805, III. An essay on the cohesion of fluids. *Philosophical transactions of the royal society of London*. 95: 65–87.
85. Zhang, T., Ellis, G.S., Ruppel, S.C., Milliken, K. and Yang, R., 2012, Effect of organic-matter type and thermal maturity on methane adsorption in shale-gas systems. *Organic geochemistry*, 47: 120–131.
86. Zhou, G., Xu, C., Cheng, W., Zhang, Q. and Nie, W., 2015. Effects of oxygen element and oxygen-containing functional groups on surface wettability of coal dust with various metamorphic degrees based on XPS experiment. *Journal of analytical methods in chemistry*.