

**STUDY OF MECHANICAL PROPERTIES OF KEROGEN
BY A MOLECULAR SIMULATION APPROACH**

BY

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To my lovely family

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TABLE OF CONTENTS

ACKNOWLEDGMENTS	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	vi
LIST OF FIGURES	vii
NOMENCLATURE.....	viii
ABSTRACT.....	x
ملخص الرسالة	xii
CHAPTER 1 INTRODUCTION	1
1.1 Background	1
1.2 Objectives.....	2
1.3 Deliverables	2
CHAPTER 2 MECHANICAL PROPERTIES OF KEROGEN	3
2.1 Synopsis.....	3
2.2 Basic Rock Mechanics	4
2.3 Kerogen Definition & Classification	6
2.4 Mechanical Properties of Shales	7
2.5 Mechanical Properties of Kerogen from Experimental Approach	7
2.5.1 Nanoindentation Test.....	8
2.5.2 Atomic Force Microscopy (AFM).....	10
2.6 Mechanical Properties of Kerogen from Modelling Approach	12
2.7 Shale Gas Adsorption	14
2.8 Methodology	15
2.8.1 Building Kerogen Models	16
2.8.2 Mechanical Properties from the Elastic Theory	18
2.8.3 Void Space Calculation.....	21
2.9 Results and Discussion.....	22
2.9.1 Density and Porosity of Kerogen Models.....	22
2.9.2 Deformation of Kerogen Models.....	23
2.9.3 Mechanical Properties of Kerogen Models.....	24
2.9.4 Correlation of Mechanical Properties with Porosity	26
2.9.5 Impact of Adsorbate Type on the Mechanical Properties.....	28
2.10 Conclusion Remarks.....	30

CHAPTER 3 MECHANICAL PROPERTIES OF ORGANIC MATTER	31
3.1 Synopsis.....	31
3.2 Literature Review	32
3.3 Molecular Modelling & Methodology	38
3.3.1 Building Organic Matter Models.....	38
3.3.2 Porosity and Pore Size Distribution Calculation.....	40
3.3.3 Mechanical Properties	40
3.4 Results and Discussion.....	41
3.4.1 Porosity & Pore size Distribution	41
3.4.2 Mechanical Properties & Stress-Strain Relationship	42
3.4.3 Effect of Pore Fluid	43
3.5 Conclusion Remarks.....	46
CHAPTER 4 RECOMMENDATIONS	47
REFERENCES.....	48
VITAE.....	54

LIST OF TABLES

Table 1. Comparison of results from different studies.....	11
Table 2. Number of independent elements in stiffness matrix depending on the symmetry type	19
Table 3. Density and Porosity values for kerogen type II at different maturity levels.....	23
Table 4. Mechanical properties, average density, and average porosity values of kerogens	25
Table 5. Mechanical properties of kerogen II-D saturated with different fluids.....	29
Table 6. Quantitive interpretation of TOC (reproduced from Harry Dembicki, Jr. , 2017).....	36
Table 7. Mechanical properties of formations obtained after different studies.....	37
Table 8. Properties of organic matters, kerogen II D, and asphaltene.....	42
Table 9. Mechanical properties of the organic matter after adsorption.....	45

LIST OF FIGURES

Figure 1. Deformation of rock body (reproduced from Economides and Nolte, 2000)	4
Figure 2. Indentation procedure during testing	8
Figure 3. Force-displacement curve (reproduced from Oliver and Pharr, 1992).....	9
Figure 4. Indenter types used during nanoindentation.....	10
Figure 5. Prototypes of kerogen molecules (Ungerer et al., 2015)	13
Figure 6. Typical flow of MD simulation	16
Figure 7. NVT/NPT simulation flowchart (Alafnan, Sultan, et al., 2020).....	18
Figure 8. Stress-strain relationship of kerogens at different maturity levels	24
Figure 9. Moduli versus average density	26
Figure 10. Moduli versus average porosity	26
Figure 11. Moduli versus porosity for the porosity-controlled structure consisting of kerogen II-A as the building block unit.....	27
Figure 12. Moduli versus porosity for the porosity-controlled structure consisting of kerogen II-D as the building block unit.....	28
Figure 13. Stress-strain relationship of kerogen II-D saturated with different fluids	30
Figure 14. Van Krevelen diagram and elemental composition of kerogen types (reproduced from Bend 2007 and Behar & Vandenbroucke 1987)	34
Figure 15. Visual representation of MD protocol used to build organic matters.....	40
Figure 16. Pore size distribution of pure kerogen II D, pure asphaltene A1, and combination of the two at different ratios	41
Figure 17. Stress-strain relationship of organic matters, kerogen II D, and asphaltene	43
Figure 18. Number of adsorbed molecules for pure kerogen, pure asphaltene, and combination of the two	44
Figure 19. Stress-strain relationship of the organic matter before and after adsorption.....	45

NOMENCLATURE

σ_l – stress

F – force

A – cross sectional area

ϵ_l – axial strain

ϵ_r – radial strain

ϵ_v – volumetric strain

L – initial length

R – initial radius

L^* – final length

R^* – final radius

ν – Poisson's ratio

E – Young's modulus

G – shear modulus

K – bulk modulus

H – hardness

P – load

S – initial unloading stiffness

h – depth

E_r – reduced modulus for indenter

β – correction factor

U – total energy change or electrostatic potential

E_0 – energy before distortion

E_t – energy after distortion

V_0 – initial volume

C – Voigt stiffness matrix

e – strain matrix

δ – strain value in the strain matrix

G_R – lower shear modulus limit

G_V – upper shear modulus limit

V_p – pore volume

V_b – bulk volume

r – radius or distance

a, b, c – dimensions

φ – porosity

q – atomic charge

$\epsilon_0; \epsilon$ – dielectric constant; maximum amplitude of potential

σ – distance at which the interaction potential between the two centres is zero

ABSTRACT

Full Name : Elshad Aslanov
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Kerogen petrophysical and mechanical properties are difficult to extract through conventional techniques due to length scale limitations. Characterization of kerogen requires the isolation of organic material from the rock matrix. However, separation methods have a high probability of damaging or chemically altering the properties of kerogen. For these reasons, microscopic methods such as Nano-indentation and Atomic Force Microscopy can be implemented to provide in-situ readings. Alternatively, computational modelling and molecular representation of kerogens can be used to simulate the outcomes of experimental work. Starting from 1960s, several analytical studies have been conducted on kerogen structures to obtain representative models on a computational platform. The literature includes various models varying from basic to most advanced ones that were developed with the advancement in computational power.

This research implements existing 3D kerogen macromolecules to form kerogen structures that can be analysed for the mechanical behaviour of organic material of type II at different maturity levels. Type II kerogen was selected specifically as the most common organic constituent of shales. Additionally, the underlying factors that could control mechanical behaviour such as the density and porosity are to be investigated. The impacts of different types of pore fluids on mechanical properties are to be presented as well, considering

the adsorptive nature of unconventional formations. Finally, the same comprehensive analysis procedure will be applied to the organic matter represented as the mixture of kerogen II-D and asphaltene molecules.

The main objective of the research is to investigate the geomechanical behaviour of kerogens and organic material that exist in shale formations following a complete molecular simulation approach. The results are compared with what have been reported following similar methodology and other advanced fine-scale experimental approaches.

ملخص الرسالة

الاسم الكامل: الشاد اصلانوف

عنوان الرسالة: دراسة الخواص الميكانيكية للكبريتين بأسلوب المحاكاة الجزيئية

التخصص: هندسة البترول

تاريخ الدرجة العلمية: ديسمبر ٢٠٢١

الخواص البتروفيزيائية للمواد العضوية الموجودة داخل الصخور الرسوبية الكثيفة يصعب تحليلها بشكل مباشر من خلال الطرق التقليدية نظرا لصعوبة استخلاصها بكميات مناسبة ، عوضا عن ذلك توفر الطرق الغير تقليدية مثل جهاز قياس الصلابة متناهي الدقة وبرامج المحاكاة الجزيئية وسيلة لمعرفة الخواص المختلفة ، بدأ تطوير برامج المحاكاة الجزيئية للمواد العضوية في عام ١٩٦٠ من خلال اعادة تكوين الحزئيات العضوية واستمر تطويرها خلال السنوات للوصول الى نتائج تعادل ما يتم ملاحظته في التجارب ، هذا البحث يبدأ من خلال إعادة تكوين بعض الحزئيات العضوية للمواد العضوية في المستوى الثاني الحراري ، بعد ذلك يتم التحكم في خصائصها مثل الكثافة والمسامية وربط ذلك بالخصائص الميكانيكية المختلفة لتحقيق هدف البحث وهو فهم الخصائص الجيوميكانيكية تحت الظروف المختلفة من الضغط والحرارة والتكوين الكيميائي ، نتائج البحث ستسمح بتسليط ضوء أكبر على تحسين تحفيز الانتاج من المكامن البترولية غير التقليدية.

CHAPTER 1

INTRODUCTION

1.1 Background

The continuous decline in the proven reserves of hydrocarbons trapped in sandstone and carbonate formations has given the impetus to the development of the unconventional resources. The poor reservoir quality of unconventional resources such as the low permeability and porosity has been overcome by the advanced technologies of lateral drilling and hydraulic fracturing.

The term "unconventional" often refers to the shaly formations, which comprise of organic and inorganic constituents. Typical shale composition includes mostly clay, quartz, feldspar minerals, as well as minor organic content. Hydraulic fracturing is the main stimulation technique applied during the completion of unconventional reservoirs. Therefore, a solid understanding of the formation's mechanical behaviour is important to achieve the targeted design after treatment operations. Attributed to their heterogeneity and mineralogical complexity, determining the mechanical properties of shales is a challenging task. It requires an individual assessment of each component and then tracking the behaviour of the matrix as whole. Kerogen, among these components, is surrounded with high degree of uncertainty due to their characteristically different nature. This research will concentrate on the study of kerogen and its elastic properties. Chapter 2 will cover some fundamental definitions on the rock mechanics and will provide a summary of the approaches followed to investigate the mechanical properties of kerogen, including both experimental and computational methods. The next Chapter 3 will follow the same methodology adopted for the study of organic matter,

which will be represented as the mixture of kerogen II D and asphaltene. The last section of the thesis, Chapter 4, will be dedicated to the recommendations for further analysis.

1.2 Objectives

The objectives of this research are outlined as follows:

- Develop better understanding of kerogen and organic matter mechanical behaviour through an atomistic approach
- Study elastic and plastic deformation of both structures
- Understand factors that influence kerogen's geomechanics
- Delineate kerogen's and organic matter's elastic moduli
- Investigate organic matter's geomechanics honouring kerogen characteristics

1.3 Deliverables

The anticipated deliverables can be outlined as follows:

1. Stress-strain relationship of kerogen and organic matter for both elastic and plastic regimes.
2. Extraction of elastic mechanical properties of kerogen type II and organic matter at some range of maturation.
3. Complete petrophysical analysis of kerogen and organic matter including pore size distribution, density, and porosity.
4. Complete investigation of the impact of pore fluids such as methane, nitrogen, and carbon dioxide on the mechanical and tensile behavior of kerogen and organic matter.

CHAPTER 2¹

MECHANICAL PROPERTIES OF KEROGEN

2.1 Synopsis

Kerogen petrophysical and mechanical properties are difficult to obtain through conventional techniques due to the length scale limitations. Characterization of kerogen requires isolation of organic materials from the rock matrix, which associates a high probability of mechanical damaging or chemical alteration of the properties. Alternatively, computational modelling and molecular representation of kerogens can be used to simulate the outcomes of experimental work. Volumetric and thermodynamics modelling of kerogens have provided means for recreating nano-scale structures virtually. This research implements existing 3D kerogen macromolecules to form kerogen structures that can be analysed for the mechanical behaviour of type II organic matters, mainly found in shales, at different maturity levels. Additionally, the underlying factors that could control the mechanical behaviour, such as density and porosity, were investigated. The results are compared against what have been reported following similar methodology or other advanced fine-scale experimental work. The results revealed elastomer-like mechanical behavior of kerogen with comparable elastic moduli regardless of maturity level. Moreover, the mechanical behaviour of kerogen was sensitive to the type of fluid contained within the structure. Such observations can help shed more light on the macroscopic mechanical properties of shales, especially for formations with high organic contents.

¹ The content of this chapter was submitted for journal publication

2.2 Basic Rock Mechanics

Rock mechanics is the study of the mechanical response of subsurface formations to the applied forces (Economides & Nolte, 2000). Acting forces make the rock body changes its form or shape. These acting forces are usually defined as stresses. Stress (σ_1) is the ratio of a force (F) to the cross-sectional area (A) where the force is applied.

$$\sigma_1 = \frac{F}{A} \quad (1)$$

As compressional force is applied (Figure 1), the cylindrical rock sample shrinks in the axial direction and at the same time expands in the radial direction. These processes result in new dimensions of the rock body. The term strain (ϵ) measures the changes associated with the applied stress and is equal to the amount of deformation divided by the material's initial length. Two types of strain can be distinguished depending on the direction of deformation (B. Guo et al., 2017). Axial and radial strains can be expressed using Equations 2 and 3, respectively. L, R are initial dimensions of the structure while L^* , R^* represent final length and radius after deformation.

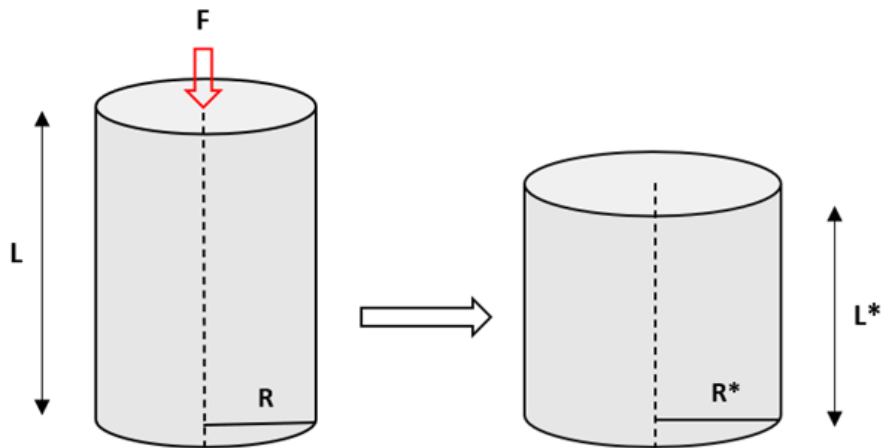


Figure 1. Deformation of rock body (reproduced from Economides and Nolte, 2000)

$$\epsilon_l = \frac{L - L^*}{L} \quad (2)$$

$$\varepsilon_r = \frac{R - R^*}{R} \quad (3)$$

The ratio of radial strain to the axial is known as Poisson's ratio (ν). This parameter can be estimated from laboratory (static) or field (dynamic) measurements. P and S which are the wave propagation velocities from acoustic logging tools are used to determine dynamic Poisson's ratio in the field conditions. Mathematically static Poisson's ratio can be formulated as:

$$\nu = -\frac{\varepsilon_r}{\varepsilon_l} \quad (4)$$

Rock subjected to the compression or tensile stresses may behave in two different manners, elastic or plastic. During elastic deformation, the shape of the rock body recovers to its original shape after releasing the applied stress. However, elastic behaviour may convert to plastic if acting forces exceed the yield point (elastic limit) of the material. Elastic deformation attributed to a linear relationship between stress and strain and governed by Hooke's law (equation 5) (B. Guo et al., 2017).

$$\sigma_l = E\varepsilon_r \quad (5)$$

Parameter E in the equation is Young's modulus, which quantifies the elastic stiffness of the material. Rock fabric and type are key factors that determine Young's coefficient. Generally, the value of E positively correlated with formation depth.

Besides compression and tensile stresses, the rock body exhibits shear forces. Shear stress is defined as the force acting parallel to the cross-section of material. When elastic deformation is valid, there is a proportionality coefficient G, shear modulus, between shear stress and strain. Shear modulus can be directly estimated from Poisson's ratio and Young's modulus values using equation 6.

$$G = \frac{E}{2(1 + \nu)} \quad (6)$$

When a uniform element is subjected to equal stresses in three mutually perpendicular directions, the ratio of direct stress to volumetric strain (ϵ_v) is called "Bulk Modulus". Mathematically this can be represented as:

$$K = \frac{\sigma_1}{\epsilon_v} \quad (7)$$

2.3 Kerogen Definition & Classification

Kerogen is a complex solid material that composed of hydrocarbons. Chemical and physical properties of kerogens are a function of maturation level and origin. That continuous process of maturation controls kerogen characteristics and can be linked to the type of hydrocarbons associated with them. Classification of the organic material (OM) into the four main types according to their origin was firstly proposed by Durand and Espitalie. Organic material could be distinguished according to their depositional environment: land derived (terrestrial) and aquatic.

- **Type I kerogen** - highly aliphatic, immature samples, with an H/C ratio greater than 1.5 and low O/C content. This type of organic matter is associated with the lacustrine depositional environment.
- **Type II kerogen** - contains large number of aromatics and have much more aliphatic in comparison with Type I. Sulphur is always associated with this type of OM, either as pyrite or free sulphur. This type is associated with deep marine depositional environment. Type II comprises primarily of planktons.
- **Type III kerogen** - derived from higher plant debris, and frequently deposited in a shallow marine environment. They are considered as hydrogen poor and oxygen-rich organic material.

- **Type IV kerogen** - hydrogen poor and oxygen-rich. This organic matter is not always distinguished and mainly combined with Type III.

2.4 Mechanical Properties of Shales

In comparison with conventional formations, shales have a complex mineralogical composition. They are composed of two different parts: organic and inorganic materials. The organic matter primarily consists of kerogen, which is not soluble in common polar solvents, while inorganic content comprises of clay, quartz, and calcite minerals.

Mechanical properties of individual minerals and kerogen are not known and create difficulties in modelling the shale matrix as whole. To investigate the effect of inorganic components, Tan et al. (2014) studied the formation from South China and Northern Australia. They found that elastic moduli negatively correlate with the presence of soft compounds like clay, mica, and total organic content (TOC) but positively with harder ones such as feldspars and carbonates. Generally, in shales, increasing content of quartz, pyrite, feldspar, and carbonates would lead to a rise in Young's modulus. In contrast, a reverse trend is observed for an increased contents of clay, mica, and organic composition (Nandi & Conde, 2011; Tan et al., 2014; Wanniarachchi et al., 2017). Rybacki et al. (2015) observed a similar trend for elastic properties in European black shales. Hygroscopic characteristics of clay minerals, which have a tendency to swell, lowers down moduli of the samples (Nandi & Conde, 2011). Ductile behaviour is observed when increasing the percentage of soft components (Rybacki et al., 2015).

2.5 Mechanical Properties of Kerogen from Experimental Approach

As mentioned earlier, determining a kerogen's properties is not an easy task due to its minimal content and fine dispersion in the rock structure. However, some methods allow evaluating the mechanical parameters without the need to isolate the organic material.

2.5.1 Nanoindentation Test

Nanoindentation is the frequently utilized technique for measuring the mechanical properties of thin films, coatings, or even smaller volumes in nano-mechanics to delineate the fine scale heterogeneity of the mechanical behaviour rather than relying only on average bulk properties. The nanoindentation method can evince the contribution of individual phases eliminating errors associated with the influence of nearby parts. The following properties can be calculated from this technique:

- Hardness
- Young's modulus
- Stress-strain relationship
- Fracture toughness

The testing procedure starts with pressing the nano-intender onto the surface of a material (Figure 2). Intender load and displacement are recorded during the loading and unloading steps. Residual depth, after unloading, may vary from nano to micrometers depending on the type of material. The principal mechanical property determined in the indentation tests is hardness (H), which is defined as load (P) divided by the projected area of the contact surface (A).

$$H = \frac{P}{A} \quad (8)$$

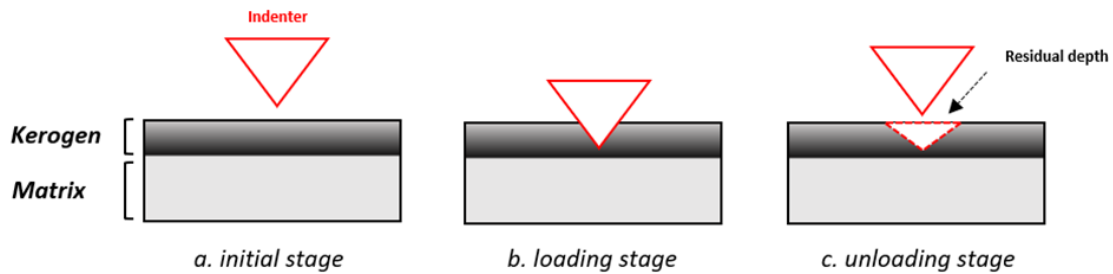


Figure 2. Indentation procedure during testing

Figure 3 illustrates a typical force-displacement curve obtained from the measurements. The parameters shown are $P_{\max}$: peak indentation load; $h_{\max}$: maximum depth of indentation at

P_{max} ; h_f : residual depth after unloading; h : instantaneous depth of loading; and S : the initial unloading stiffness.

$$S = \frac{dP}{dh} \quad (9)$$

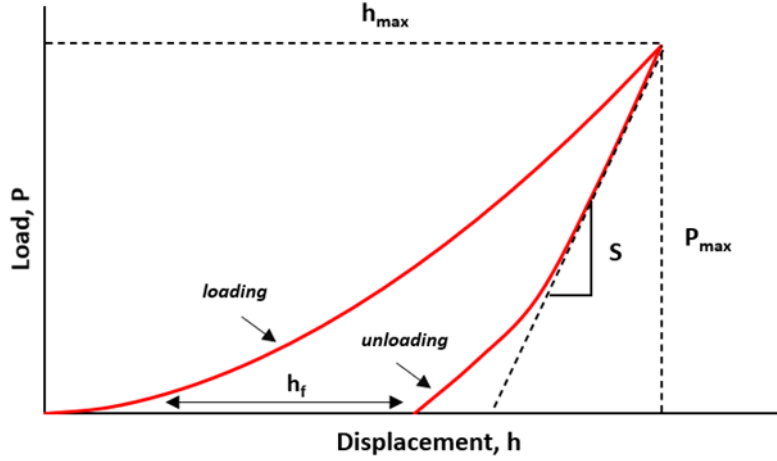


Figure 3. Force-displacement curve (reproduced from Oliver and Pharr, 1992)

Young's modulus of the specimen can be calculated from the reduced modulus (E_r) (Oliver and Pharr, 1992). Parameter β in the equation 9 is a correction factor that takes different values depending on the indenter types and generally varies between 1.01-1.09 according to different researchers (Fischer-Cripps, 2006).

$$E_r = \frac{\sqrt{\pi S}}{2\beta\sqrt{A}} \quad (10)$$

$$E = \frac{1-v^2}{\left[\frac{1}{E_r} - \frac{1-v_i^2}{E_i} \right]} \quad (11)$$

Poisson's ratio of the sample has to be guessed for calculation as this parameter cannot be directly determined (E_i and v_i – indenter parameters). Kumar et al. (2012) report negligible variation in Young's modulus over the range of 0.05-0.3 values for Poisson's ratio. The three-sided Berkovich tip (Figure 4.a) is the most frequently deployed type for nanoindentation. The half-angle face of Berkovich type indenter is equal to 65° . This allows reaching the same

projected area as in four-sided Vickers indenter (Figure 4.b). The main reason that makes Berkovich indenter more useful over others is the possibility of getting a sharper tip after grinding (Fischer-Cripps, 2006).

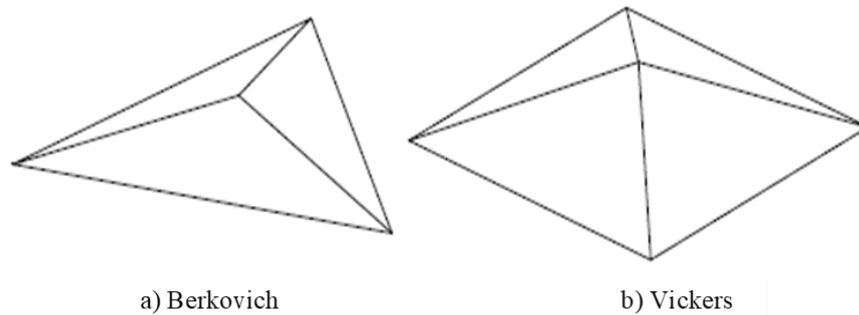


Figure 4. Indenter types used during nanoindentation

2.5.2 Atomic Force Microscopy (AFM)

Zeszotarski et al. (2004) conducted a study on Type II kerogen from Woodford (USA) shale with combined application of nanoindentation and atomic force microscopy. The hardness of organic matter was found to be greater than polymers and close to the soft material like gypsum and lower than inorganic materials. Later Ahmadov et al. (2009,2011) studied in-situ properties of organic-rich Bazhenov formation (Russia) by AFM, coupled with scanning electron microscopy (SEM) and confocal laser-scanning microscopy (CLSM). SEM images were used to identify kerogen regions, and after CLSM was implemented to confirm the existence of organic matter. Measurements confirmed that organic matter in the formation to be softer than other minerals in the matrix. Kumar et al. (2012) conducted similar tests on Woodford and Kimmeridge (USA) formations to determine elastic properties of kerogen. The reported results were in good agreement with previous studies, so Young's modulus values for Woodford shale varied in the range from 6 to 10 GPa. In fact, all aforementioned works followed almost the same methodologies with a minor changes in ultra-high-resolution techniques, which comes from the advancement of technologies. Eliyahu et al. (2015) applied a recently developed “PeakForce” AFM mode to get the nano-mechanical map of organic-rich samples. The

obtained map showed the existence of distinct regions with different elastic properties. As expected, elemental analyses revealed the softest areas to be carbon-rich which corresponds to the organic material. Table 1 summarizes the values of elastic properties obtained from the aforementioned publications.

Table 1. Comparison of results from different studies

Zeszotarski et al., 2004				
Formation type	TOC wt.(%)	v	E (GPa)	H (GPa)
Woodford shale (USA)	0.22	0.1	10.4	0.57
		0.2	10.1	
		0.3	9.6	
		0.4	8.8	
Ahmadov et al., 2011				
Lockatong (USA)	2.84	0.07	13	n/a
		0.15	11.9	
		0.35	11	
		0.45	10.1	
Bazhenov (Russia)	0.03	0.02	5.9	n/a
		0.15	5.5	
		0.35	5.2	
		0.45	4.7	
Kumar et al., 2012				
Woodford shale (USA)	0.13	0.3	6.2	0.2
Kimmeridge (USA)	0.49	0.3	5	0.2
Eliyahu et al., 2014				
Upper Jurassic source rock (USA)	0.5-4.50	0.3	0-25	n/a

Kerogen exposed to high temperature and pressure within a considerable time turns into hydrocarbon through maturation stages. The degree of maturation in unconventional resources determines the end products of the generation process. Valdes et al. (2017) investigated the relation between thermal maturity and elastic properties by extraction of organic material from the sample. The isolated matter was then synthetically heated to obtain structures of kerogen at different maturity levels. Elastic moduli of samples drop at relatively small temperatures (150°C) and rise after the further increase of temperature. It was observed that elastic moduli of the samples have a higher value at the high maturity levels. This behaviour was attributed to

the graphitization of kerogen at higher temperatures and followed by an increase of cyclical molecules, which are more structurally stable compared to simple ones. A similar tendency was observed with naturally mature shale (Young's modulus increase) in the Bakken formation (Zargari et al., 2013). It was explained by the reduction of organic content with increasing maturity. However, after hydro-pyrolysis of the same samples, elastic properties were found to reverse this trend. Heating of kerogen drives bitumen generation at high temperatures, which is softer than organic matter (2 GPa) and causes a reduction in modulus.

2.6 Mechanical Properties of Kerogen from Modelling Approach

One of the main drawbacks of experimental measurements is that they could only determine reduced parameters used to calculate Young's modulus. The value of Poisson's ratio should be known in advance, but in most cases, it is assumed to be in the range from 0.2-0.3. Therefore, the lack of exact data may lead to wrong estimations. Secondly, kerogen isolation from the matrix for testing purposes introduces risks associated with alteration of original properties. Hence, complexities and uncertainties associated with those processes limit the efficient characterization of such systems. Alternatively, computational modelling and molecular representation of kerogens can be used to mimic outcomes of experimental work.

During the 1960s, several analytical studies have been conducted on kerogen structures. Burlingame et al. (1968) proposed the first kerogen model, although this model did not represent a full chemical structure of kerogen. The first detailed representation of kerogen has been described by Yen et al. (1976). The published model was developed through studies of asphaltene structure. But this model was found to underestimate the measured density of organic material. Later, Shiskin et al. (1995) published a new model of Green River Shale. His model was successful to capture various structural constituents in these oil shales compared to the previous studies. One of the first applications of computers to the structural elucidation of moieties from sedimentary OM was published by Oka et al. (1977). Because of the lack of

computational power available at that time, such modelling was limited to low molecular weight compounds. Fortunately, the advancements in computational tools allowed scientists to develop more representative 3D structures. Hence, Ungerer et al. (2015) generated six prototypes of kerogen structures (Figure 5) at a different range of maturity levels ranging from type I to type III.

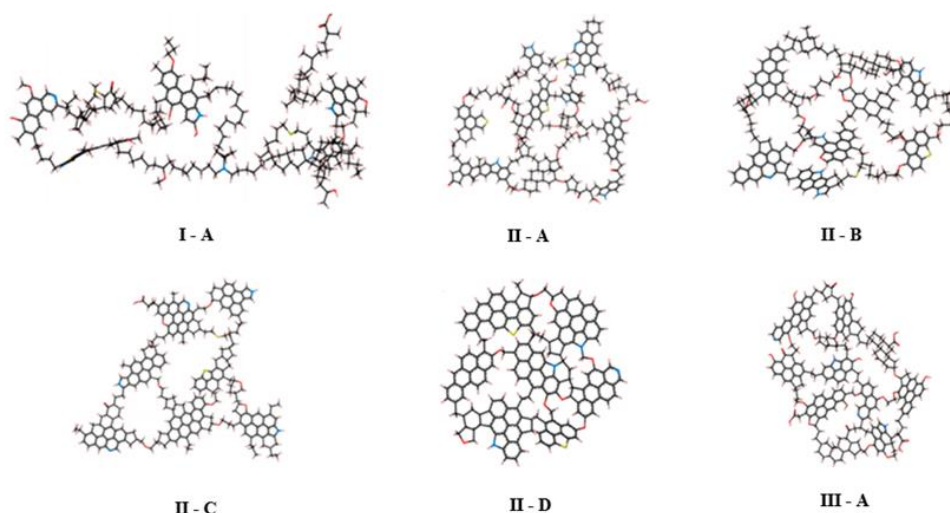


Figure 5. Prototypes of kerogen molecules (Ungerer et al., 2015)

Based on the available kerogen models, Zhang & Jamili (2015) build a solid-state model of kerogen from Green River formation to examine elastic properties, and reported results ($E=3.5$ GPa, $\nu=0.25$) were close to the previous studies conducted on the same formation by Yan & Han (2013). Kashinath et al. (2019) studied the evolution of mechanical properties with changing maturity. They construct atomistic models of type II kerogen at four different maturation stages and run the simulation at different density values. Less mature samples were observed to have less density and, respectively, less hardness. Values of Poisson's ratio were in line with experimentally obtained results and varied between 0.2 and 0.35 (Ahmadov et al., 2009; Bousige et al., 2016; Eliyahu et al., 2015; Kumar et al., 2012).

This approach has been widely adopted in material science applications. Literature includes similar studies on silica, graphene-polythiophene, carbon nanotubes, and nanofibers (Buell et

al., 2009; Chowdhury et al., 2016; Nayebi & Zaminpayma, 2016; Sheikhnejad, 2018). The number of foregoing examples may be extended further however, the main target was to show the applicability of the atomistic approach.

2.7 Shale Gas Adsorption

In an attempt to explain the influence of the adsorption process on shales, several scholars did useful studies through an experimental approach over the last three decades. Comprehensive works trying to link organic content, mineralogy, and pore structures with the adsorption capacity of shales are available in the literature. Schettler et al. (1991) carried study on separate components of shale like quartz, clay, and carbon minerals as well as shale samples from the Devonian basin to understand the parameters controlling the adsorption. All minerals were found to have a significant ability to retain gas molecules on the surface while testing individually. Additionally, the capacity of shale to adsorb gas was explained by the dominance of organic carbon while in the absence of organic content by illite mineral. In the same manner, Lu et al. (1995) examined the absorptive capacity of shale samples from the same formation. The results reveal the strong correlation between total organic content (TOC) and adsorptive capacity in shale samples. The illite minerals were also observed to have a considerable contribution to gas storage, especially in samples with low organic content. The most recent attempts concluded quite analogous results to the aforementioned studies. Chalmers & Bustin (2008) elucidate the relationship of methane sorption capacity with TOC, kerogen type, maturity, and other geochemical properties. They deduced that while TOC was the main factor controlling the adsorption capacity, maturity was negatively correlated with methane adsorption because of decreasing TOC with maturity. At the same time, they showed that all kerogen types share nearly similar adsorption capacities. Luo et al. (2015) highlighted the effect of mineralogy on adsorption, particularly emphasizing the role of illite and kaolinite. Moreover, they observed an increasing trend of adsorption with the growth of micropores. Besides

methane, several studies were underlying carbon dioxide adsorption in shales (Ravikovitch et al., 2005). Kang et al. (2011) and Nuttall et al. (2005), in two different studies, showed that carbon dioxide has greater adsorption potential than methane at least five times. Although this study will not consider adsorption-related concerns in detail, it will be worthy of highlighting the impact of fluids contained in kerogen micropores on mechanical properties of organic matters.

2.8 Methodology

Molecular Dynamics is a powerful tool to study the properties of materials and to see how molecules move and interact at the atomistic levels. MD simulations are frequently utilized in material science to obtain different properties. It is usually used when experimental approaches are inaccessible or time-consuming. To run the MD simulations, typically, three steps should be followed (Figure 6):

1. **Create an initial state:** It is necessary to define particles' initial position inside the simulation box.
2. **Define interaction potentials:** To introduce the interaction potentials, we can use available force fields. These force fields are mathematical expressions that described the interaction between molecules.
3. **Predict particle movement:** After defining force fields, the next step is to integrate Newton's equation of motions to predict the movement trajectories of the particles. There are many algorithms that are used to execute this step. However, the simplest and most commonly used is the Verlet algorithm which provides desired numerical stability.

While repeating these steps, we calculate the trajectory of each particle in the system during the simulation. Based on that, we can infer how the whole system behaves under specific controlled condition like fixed temperature or pressure.

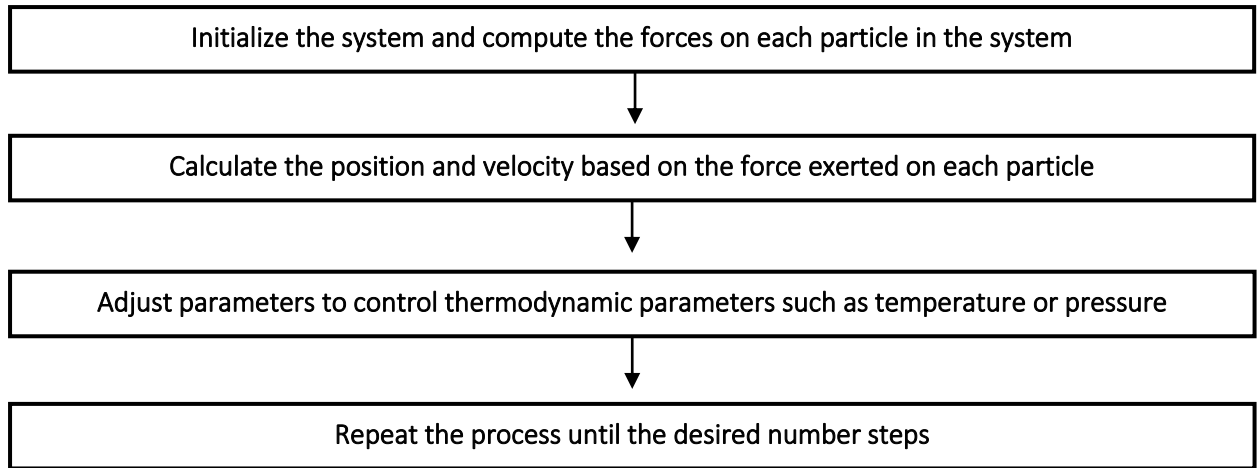


Figure 6. Typical flow of MD simulation

2.8.1 Building Kerogen Models

All necessary procedures were performed using the MedeA environment, including molecular dynamics (MD) modelling (MedeA LAMMPS). The PCFF+ forcefield was selected to simulate atomic interaction during MD simulations, which showed prominent performance in the past studies (Afagwu et al., 2021a; Alafnan, 2021a; Alafnan, Falola, et al., 2020; Alafnan, Solling, et al., 2020; Alafnan, Sultan, et al., 2020; Ungerer et al., 2015). The individual kerogen units were parameterized by PCFF++ forcefield with the molecular interactions between two force centers i , and j being described by 6-9 Lennard Jones with the electrostatic potential term:

$$U_{LJ} = \epsilon \left[2 \left(\frac{\sigma}{r_{ij}} \right)^9 - 3 \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (12)$$

$$\sigma = \left(\frac{\sigma_i^6 + \sigma_j^6}{2} \right)^{1/6} \quad (13)$$

$$\epsilon = 2\sqrt{\epsilon_i \epsilon_j} \frac{\sigma_i^3 \sigma_j^3}{\sigma_i^6 + \sigma_j^6} \quad (14)$$

Where r_{ij} is the separation distance between the two forces centres of charges q_i and q_j , ϵ_0 is the dielectric constant, σ is the distance at which the interaction potential between the two centres is zero, and ϵ is the maximum amplitude of the potential well. σ and ϵ are both approximated using the sixth power combination rule as given by equations 13 and 14 (Waldman & Hagler, 1993).

In the initial stage, kerogen units of type II, introduced by Ungerer et al. (2015), were placed into the simulation box for each maturity level. The number of kerogen units placed in a periodic boundary box (i.e. 8-12 units). The density of the cubic cell before running the simulation was set to be 0.2 g/cm³. This step was done to eliminate instability issues that may arise in the subsequent simulation steps. After building the simulation box, an isochoric-isothermal NVT simulation at temperature 900 °K for 250 ps was performed. NVT is the constant volume and temperature molecular dynamics in which amount of matter (N), volume (V) and temperature (T) are kept constant after exothermic and endothermic exchanges with Nose-Hoover thermostat (in our case). Then, the structure was relaxed through four consecutive isobaric-isothermal NPT stages in a decreasing temperature from 900 K to 350 K at a constant pressure of 20 MPa with a timestep of 1 fs (i.e. 350 K and 20 MPa are deemed to be representative of typical reservoir conditions). NPT is the constant pressure and temperature ensemble where amount of matter (N), volume (V) and temperature (T) are maintained using Nose-Hoover barostat (in our case). The aforementioned procedures were repeated different initial density values (0.3 g/cm³, 0.4 g/cm³, 0.5 g/cm³) as well to ensure validity of outcomes. Figure 7 summarizes all described steps in one flow chart.

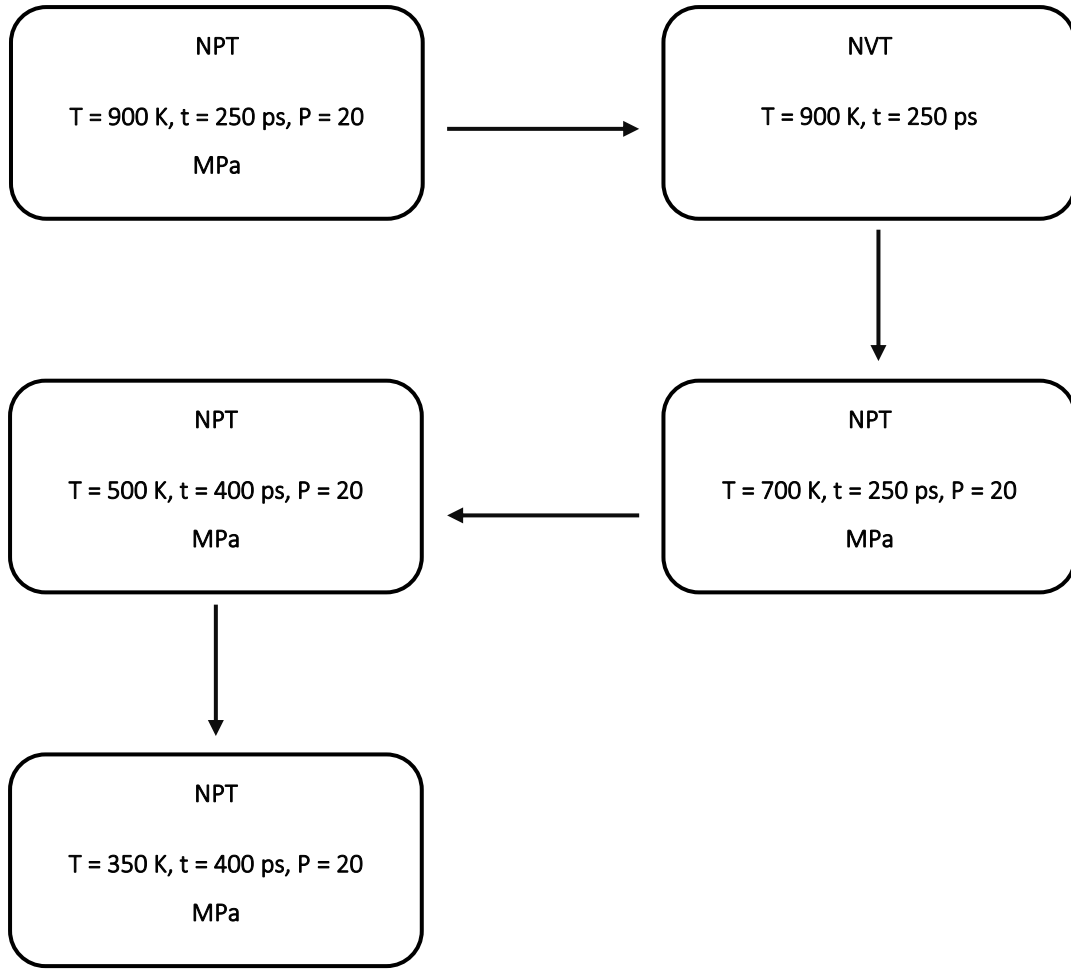


Figure 7. NVT/NPT simulation flowchart (Alafnan, Sultan, et al., 2020)

2.8.2 Mechanical Properties from the Elastic Theory

The elastic behaviour and parameters of a structure can be found by deforming Bravais lattice vectors of the unit structure applying engineering strain. Created distortion produces the changes in the total energy of the system (Y. Le Page & Saxe, 2001; Yvon Le Page & Saxe, 2002). Mathematically this process can be expressed as:

$$U = \frac{E_t - E_0}{V_0} = \frac{1}{2} \sum_{i=1}^6 \sum_{j=1}^6 C_{ij} e_i e_j \quad (13)$$

Where U is the total energy change during distortion process; E_0 and E_t are energies before and after distortion respectively; V_0 is the original volume of the unit cell; e_i and e_j are components

of the strain matrix; and C is the Voigt stiffness matrix, which comprised of 36 elements and can be represented as:

$$C = \begin{bmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ c_{21} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ c_{31} & c_{32} & c_{33} & c_{34} & c_{35} & c_{36} \\ c_{41} & c_{42} & c_{43} & c_{44} & c_{45} & c_{46} \\ c_{51} & c_{52} & c_{53} & c_{54} & c_{55} & c_{56} \\ c_{61} & c_{62} & c_{63} & c_{64} & c_{65} & c_{66} \end{bmatrix}$$

However, it is possible to reduce the matrix to a more simple form. The number of unknown elements depends on the symmetry of the structure. Table 2 summarizes the number of linearly independent elements for different symmetries.

Table 2. Number of independent elements in stiffness matrix depending on the symmetry type

Symmetry Type	Independent Elements in Matrix
Cubic	3
Hexagonal	5
Orthorhombic	9
Monoclinic	13
Triclinic	21

Kerogen models analysed in our study were initially placed in a cubic shape simulation box; therefore, the stiffness matrix is anticipated to have cubic symmetry. Consequently, the number of independent elements will be reduced to 3, and the matrix will become as follow:

$$C = \begin{bmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{bmatrix}$$

The following steps will describe the required procedure to find unknown elements C_{11} , C_{12} and C_{44} implementing strain field equation (Jiang et al., 2019).

STEP 1:

Define strain array as $e = (0,0,0,\delta,\delta,\delta)$, where δ is the strain value. This step will allow unique determination of C_{44} . As a result, equation 11 will become:

$$U = \frac{3}{2} C_{44} \delta^2 \rightarrow C_{44} = \frac{2U}{3\delta^2} \quad (15)$$

STEP 2:

Define strain array as $e = (\delta,\delta,0,0,0,0)$, where δ is the strain value. This step will reduce equation 12 to the following form:

$$U = (C_{11} + C_{12})\delta^2 \quad (16)$$

STEP 3:

Define strain array as $e = (\delta,\delta,\delta,0,0,0)$, where δ is the strain value. This step will reduce equation 12 to the following form:

$$U = \frac{3}{2} (C_{11} + C_{12})\delta^2 \quad (17)$$

By solving equations 13 and 14 simultaneously, we can quantify C_{11} and C_{12} .

Mechanical properties of the kerogen structure can be calculated from the single crystal data by following the Voigt-Reuss-Hill method (Hill, 1963). This method predicts lower (G_R) and upper (G_V) bounds based on the constituent's moduli for disordered structures. Based on the Voigt-Reuss-Hill method, for the cubic lattice shear modulus (G), bulk modulus (K), Young's modulus (E) and Poisson's ratio (ν) can be determined utilizing C_{11} , C_{12} and C_{44} .

$$G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})} \quad (18)$$

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5} \quad (19)$$

$$G = \frac{G_R + G_V}{2} \quad (20)$$

$$K = \frac{C_{11} + 2C_{12}}{3} \quad (21)$$

$$E = \frac{9KG}{3K + G} \quad (22)$$

$$\nu = \frac{3K - 2G}{2(3K + G)} \quad (23)$$

After constructing kerogen models at the proper densities deforming the structure by subjecting it to strain with a stepwise increase in strain from 0.02 to 0.4 with an increment of 0.02 to obtain a stress-strain relationship was followed. After obtaining stress-strain curves, we select the appropriate strain values from the elastic region of the graph.

2.8.3 Void Space Calculation

Void spaces in the structure can be found using a built-in feature of Medea software. This function inserts non-overlapping spheres into the available spaces inside of kerogen unit with a minimum radius (r) of 0.2 nm. After obtaining all inserted spheres, the total pore volume (V_p) was determined by calculating each sphere's volume and adding them up. The bulk volume (V_b) was computed using lattice dimensions (a , b , c) of the kerogen units. The porosity (ϕ) was calculated using a ratio of total void space in structure to the structure's bulk volume. All equations implemented during porosity finding are listed below:

$$V_p = \sum_{i=1}^n \frac{4}{3} \pi r_i^3 \quad (24)$$

$$V_b = a \times b \times c \quad (25)$$

$$\varphi = \frac{V_p}{V_b} \quad (26)$$

2.9 Results and Discussion

2.9.1 Density and Porosity of Kerogen Models

As mentioned in the methodology section, kerogen structures were built by starting from less dense structures and running the stated MD protocol. Different independent configurations for each kerogen type were obtained to assess the robustness of the followed approach and its reproducibility. After MD simulations, the densities of kerogen structures were found to be in the range from 1.11 to 1.29. These values were in good agreement with previous studies conducted on an experimental and computational basis (Ungerer et al., 2015; Xie et al., 2019). Calculated porosities of the kerogens were between 0.13 - 0.15, and the highest corresponded to the most mature one (II – D).

It should be pointed out that there was no clear relation between maturity level and density based on the simulation data. The same conclusion can be made for the maturity-porosity relation. Nevertheless, the most mature kerogen was found to have highest density and porosity. Table 3 shows densities and porosities for each configuration. For brevity and clarity of information in coming sections, we will average densities and porosities for every kerogen type. This step will not introduce errors associated with averaging since all results lay close to each other.

Table 3. Density and Porosity values for kerogen type II at different maturity levels

Type	Configuration	Density (g/cm ³)	ϕ
II - A	1	1.13	0.141
	2	1.12	0.142
	3	1.13	0.130
	4	1.13	0.141
II - B	1	1.10	0.139
	2	1.11	0.146
	3	1.12	0.153
	4	1.11	0.152
II - C	1	1.17	0.142
	2	1.19	0.134
	3	1.17	0.150
	4	1.16	0.153
II - D	1	1.28	0.152
	2	1.29	0.140
	3	1.24	0.147
	4	1.26	0.156

2.9.2 Deformation of Kerogen Models

The kerogen's stress-strain behaviour was created by applying strain from 0.02 to 0.4 with an increment of 0.02. Generally, graphs follow the same trend in all cases with slight deviations. The elastic region for all kerogen types was falling in the strain range between 0.04-0.15.

Hence, based on the deformation behaviour, we can deduce that the thermal maturity does not significantly impact the mechanical properties. This observation may be considered while modelling the mechanical properties of shale. We may take the average for the moduli value that we can regard as representative for the whole range. Figure 8 illustrates the deformation behaviour of selected two sets of configurations.

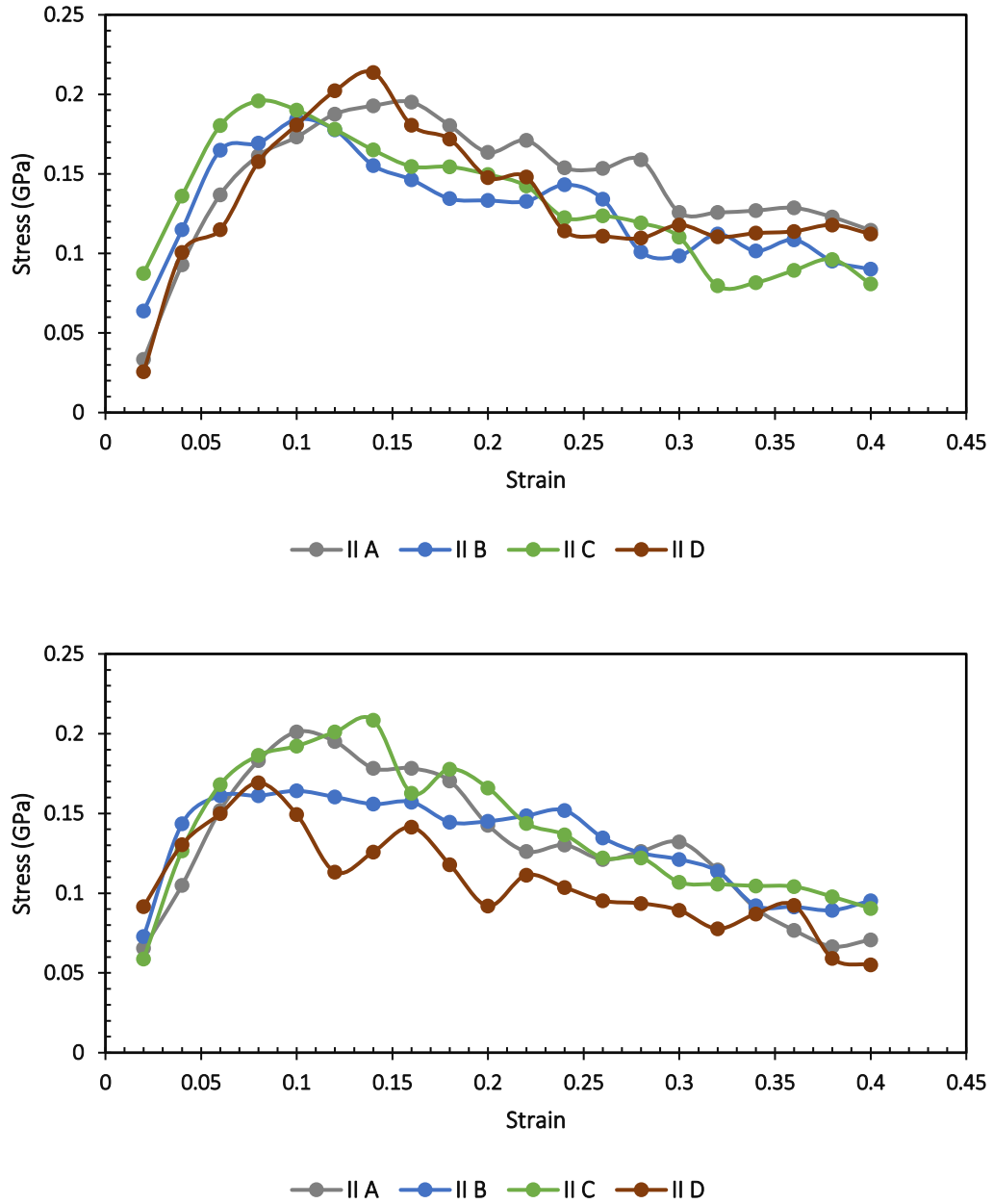


Figure 8. Stress-strain relationship of kerogens at different maturity levels

2.9.3 Mechanical Properties of Kerogen Models

Mechanical properties of kerogen were determined after applying the strain within the elastic interval of structures. For the sake of simplicity in analysis, we decide to take an average for each configuration at each maturity level. It will reduce the data size without introducing errors as all results were in the same range. Table 4 illustrates the results of simulations combined with average values for density and porosity. The most mature kerogen type was

observed to have the lowest moduli values compared to other types. On the contrary, type II-B was found to have the highest shear and Young's moduli. Poisson's ratio values were in the range between 0.39 to 0.42, and the maximum and minimum correspond to the type II-D and II-B, respectively.

Table 4. Mechanical properties, average density, and average porosity values of kerogens

Type	K (GPa)	G (GPa)	E (GPa)	Poisson's Ratio	Density (g/cm ³)	ϕ
II - A	3.71	0.79	2.20	0.401	1.13	0.138
II - B	3.57	0.87	2.42	0.386	1.11	0.147
II - C	3.62	0.81	2.27	0.395	1.18	0.144
II - D	3.39	0.60	1.70	0.418	1.26	0.149

The moduli were plotted versus average densities to establish the relation between parameters as illustrated in Figure 9. Generally, increasing density is associated with a decrease in moduli values. However, type II-A kerogen appears to deviate from the general trend in all three cases. The same plot was generated between porosity and mechanical properties (Figure 10). Again, no significant connection between these parameters was observed.

The porosity obtained in all cases is attributed to the intermolecular spaces between macromolecule units. Porosity values, as reported in Table 3, were in the narrow range such that no clear correlation between porosity and mechanical properties could be observed. In the reality, however, pressure build-up during catagenesis can induce some micropores which in turn increases the porosity and alter the mechanical behavior (X. Guo et al., 2018; Tang et al., 2016; Y. Zhang et al., 2018).

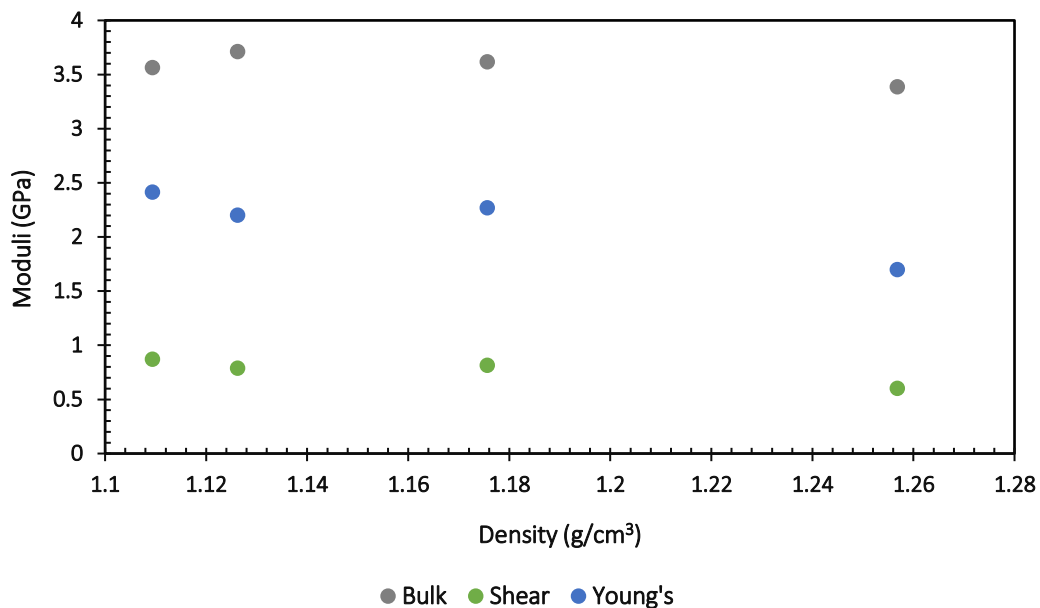


Figure 9. Moduli versus average density

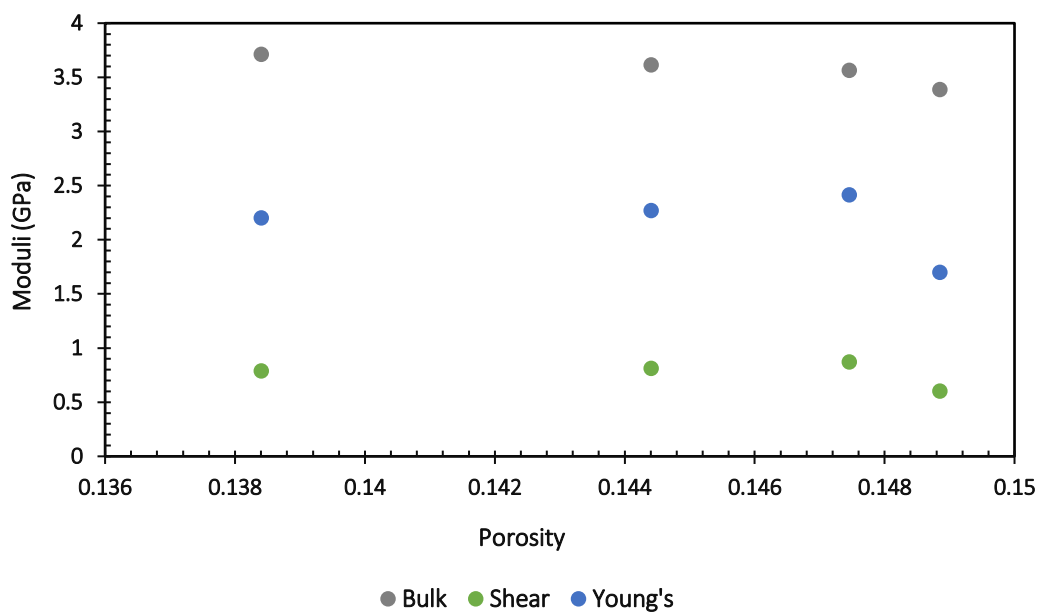


Figure 10. Moduli versus average porosity

2.9.4 Correlation of Mechanical Properties with Porosity

To further delineate the impact of porosity on the mechanical properties, porosity-controlled kerogen structures were generated following the previously outlined molecular dynamics construction protocol. To control the porosity a specified number of director

molecules (0, 10 and 25) were inserted in the initialization stage and then removed upon final convergence to the targeted pressure and temperature (i.e., heptane was used as the choice of director in our case). The broader range of porosity can help establishing better understanding of how mechanical properties vary with porosity. A kerogen type II-A and II-D was used for this purpose. The results indicated strong correlation with porosity in which all the mechanical constants had negative relationships with porosity as shown in Figure 11 and Figure 12.

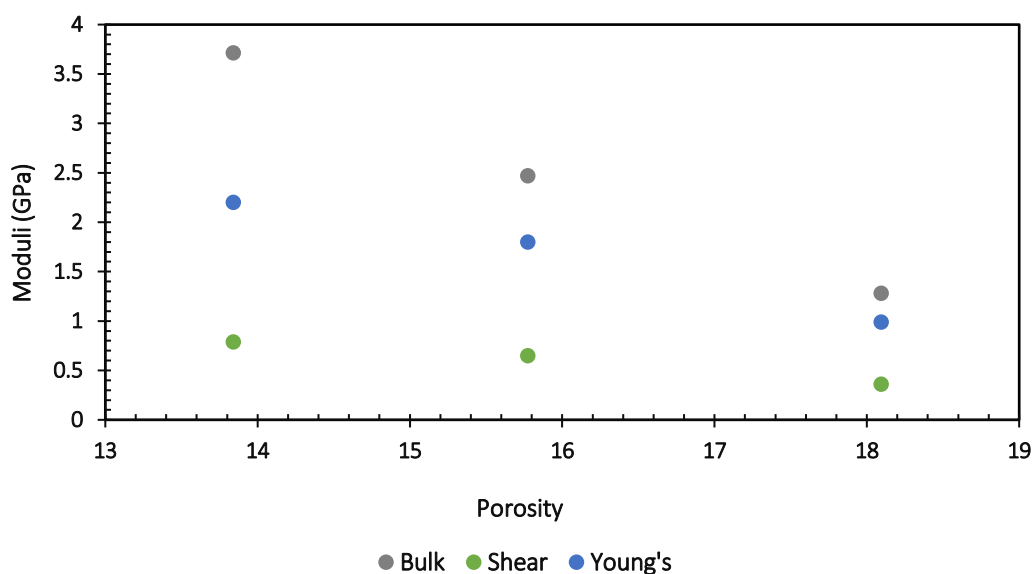


Figure 11. Moduli versus porosity for the porosity-controlled structure consisting of kerogen II-A as the building block unit

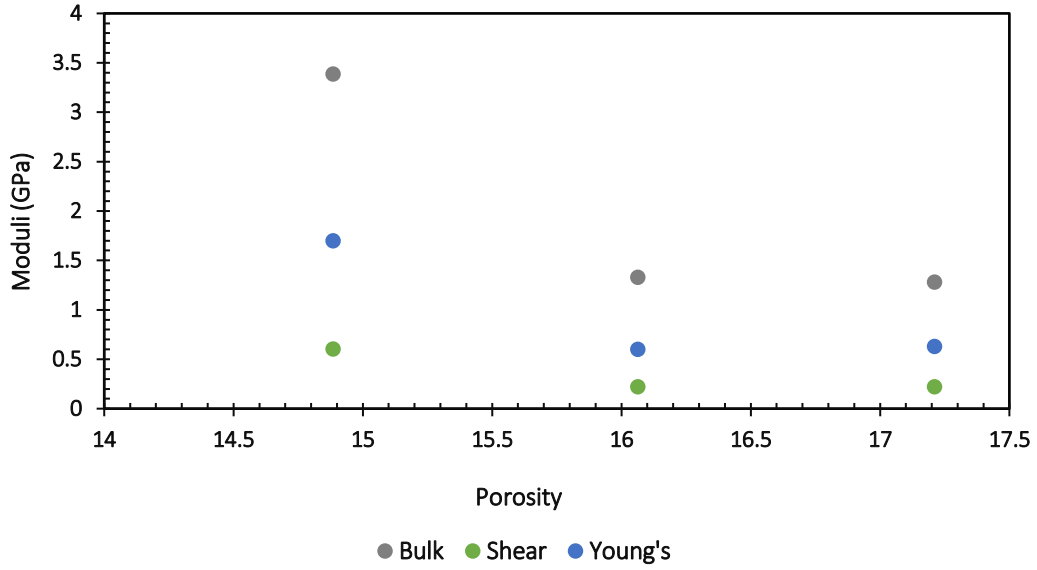


Figure 12. Moduli versus porosity for the porosity-controlled structure consisting of kerogen II-D as the building block unit

2.9.5 Impact of Adsorbate Type on the Mechanical Properties

Kerogens, at subsurface conditions, are saturated with natural gas. The gas contained in the organic materials of shales is primarily consisted of methane with smaller fractions of other light and intermediate hydrocarbons. Carbon dioxide can also exists either naturally, as nitrogen, or injected for sequestration or hydraulic fracturing purposes (Dasani et al., 2017). In this section, the impact of fluid type is investigated. Kerogen II-D is subjected to adsorption considering three cases of pure methane, nitrogen, and carbon dioxide. Gibbs ensemble Monte Carlo simulation of the methane-kerogen, nitrogen-kerogen, and carbon dioxide-kerogen interactions can be interpreted as amount of gas phase. The sorption calculations were carried out at typical reservoir conditions (350 K, and 41.34 MPa). At these conditions, Peng-Robinson equation of state was used to approximate the fugacity of all fluid types. The fugacity of methane and nitrogen was 35.84 MPa and 16.3 MPa, respectively, while that of carbon dioxide was 31.18 MPa. After saturation stage, kerogen structures with methane, nitrogen and carbon dioxide were analyzed for the mechanical behavior following the previously outlined molecular calculations.

The mechanical tensile test revealed some sensitivity to the presence of fluid (Figure 13) where the stress-strain curve was shifted downward suggesting a slight reduction in the yield strength. Interestingly, the stress-strain shift was more pronounced in the case of nitrogen.

Table 5. Mechanical properties of kerogen II-D saturated with different fluids

Property	No fluid	CH ₄	CO ₂	N ₂
Bulk (GPa)	3.99	5.31	5.95	4.2
Shear (GPa)	0.88	0.94	1.06	0.52
Young's (GPa)	2.46	2.67	3.01	1.49
Poisson's ratio	0.3972	0.4167	0.4156	0.44

The elastic moduli were calculated as shown in Table 5. The bulk modulus showed an increase by 5%, 33% and 50% when the structure was saturated with nitrogen, methane and carbon dioxide respectively. Similarly, Young's moduli values increased once saturated with methane and carbon dioxide by 8.5% and 22% correspondingly, while nitrogen was found to reduce moduli by around 40%. Although shear modulus increased from 0.88 GPa to 0.94 GPa and 1.06 GPa after saturation with methane and carbon dioxide, respectively, it decreased again by 41% to 0.52 GPa after saturation with nitrogen. The sensitivity of mechanical behavior on the fluid type might be attributed to the intermolecular interactions between adsorbent (kerogen) and adsorbate (methane, nitrogen, carbon dioxide) where Gibbs calculations revealed lower electrostatic potential for the nitrogen case compared to the methane and carbon dioxide.

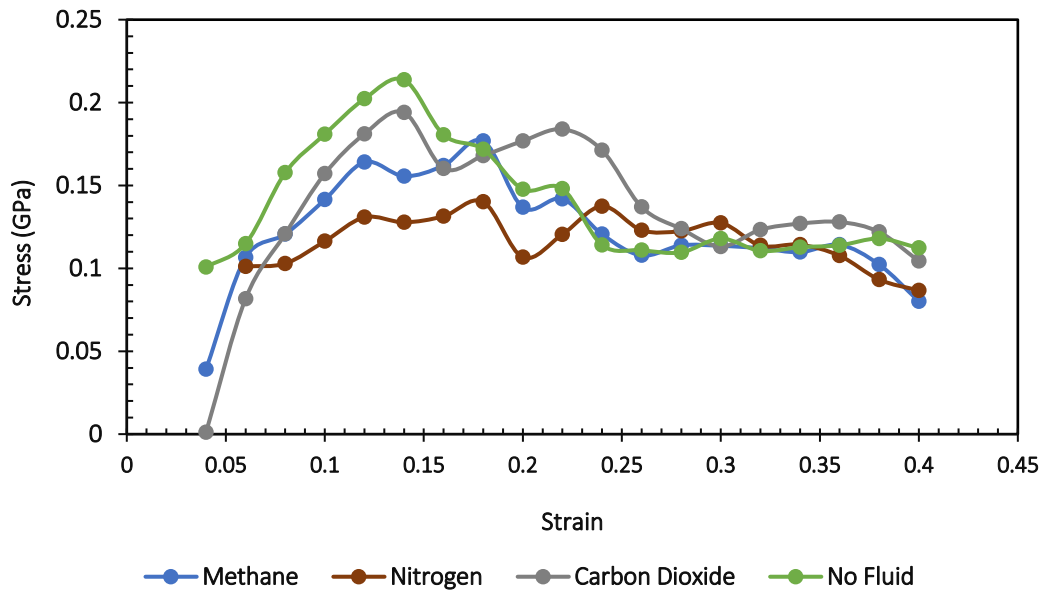


Figure 13. Stress-strain relationship of kerogen II-D saturated with different fluids

2.10 Conclusion Remarks

- Kerogen structures, regardless of thermal maturity, exhibited elastomer-like behaviour which is characteristically different than the other shale matrix constituents. Such behaviour is anticipated to severely impact the macroscopic geomechanics of shales especially for high organic contents formations.
- Thermal maturity was not found to influence the mechanical properties of kerogen significantly.
- Kerogen II-D, which was the most mature one, had the lowest elastic moduli. That might be explained by its relatively higher intermolecular porosity.
- Porosity can be formed as a result of pressure build-up during oil and gas generation windows. To investigate the impact of that induced porosity on mechanical behaviour, porosity-controlled structures were used. The results revealed a negative correlation between mechanical properties and porosity.
- The fluid contained within kerogen structure was found to have an influence on the mechanical behaviour.

CHAPTER 3²

MECHANICAL PROPERTIES OF ORGANIC MATTER

3.1 Synopsis

Assessment of mechanical properties of organic matters contained in unconventional formations is needed to understand the geomechanics of source rocks. The organic matters are part of the source rocks matrix and they are made of kerogen and bitumen. Although the literature has some studies addressing the properties of kerogen and bitumen, no apparent attempts were made to address the mechanical behavior of organic matters as a combination of both. Isolation of organic matters from the rocks for experimental assessments has some risks of altering the original properties because of their delicate nature and their existence as micro and nano constituents. Some computational approaches such as molecular simulation can serve as an alternative platform for the purpose of delineating organic matters properties including the mechanical ones. This work implements available 3D molecular modelling of kerogen and bitumen with different ratios to mimic organic matters that can be investigated for the mechanical properties. Upon the recreation of different configurations of organic matters molecularly, mechanical parameters such Young's, bulk, and shear constants, as well as the stress-strain relationship for the elastic and plastic deformations were extracted. The mechanical behavior was closely monitored before and after saturation with a number of gases that are commonly found in subsurface formations such as methane, carbon dioxide, and nitrogen.

² The content of this chapter was submitted for journal publication

The results revealed that the organic matters had a mechanical behavior envelope similar to what were reported for organic-based materials such as polymers. Moreover, the structures containing bitumen exhibited larger values of Poisson's ratio indicating less likelihood of them to degrade upon applied stresses. The presented data substantiate the importance of accounting for both bitumen and kerogen in modelling the petrophysics and the mechanical behavior of the organic matters.

3.2 Literature Review

The increasing demand for energy and the declining rate of production from conventional reserves necessitates the need for exploiting unconventional formations, commonly known as source rocks. Such formations require sophisticated drilling and stimulation technologies. "Unconventional" formations (self-sourcing) often refer but not limited to the shaly formations, which contain organic and inorganic constituents. The shaly formations, possessing a significant amount of natural gas, associate poor reservoir quality, such as permeability. Hence, commercial production requires stimulation techniques such as hydraulic fracturing to enhance the reservoir quality by creating conductive pathways inside the rock matrix with the mechanical properties of shales being an input in the design of the fracturing process. It is difficult to determine the mechanical properties of shales due to their heterogeneity and the complex mineralogy. The current practice relies on individual assessment of all inclusions, and then the matrix could be modelled as a whole.

The mechanical behavior of shales was investigated extensively. It was observed that the higher content of inorganic minerals associates a higher degree of brittleness and values elastic moduli. The increasing percentage of clay, mica, and organic matters, on the other hand, had the opposite effect (Nandi & Conde, 2011; Rybacki et al., 2015; Tan et al., 2014; Wanniarachchi et al., 2017). Organic matters are inclusions existing at the micro level and they are finely dispersed in the source rocks. They are generated from cells and tissues of biological

substances such as plants, planktons, algae, and animals. The organic matters, exposed to the right conditions of pressure and temperature, are the source of hydrocarbons produced over the period of millions of years. There are various factors such as deposition, preservation, and maturation of organic matter that influence the quantity and quality of end products (Mani et al., n.d.; Petsch & Amherst, 2014). The generation capacity is ultimately determined by the amount and the type of the organic matters during diagenesis, metagenesis, and catagenesis processes (Loucks & Ruppel, 2007; Romero & Philp, 2012; Seifert and Moldowan, 1986). Continuous supply of organic remaining carried by rivers, oxygen level, water circulation, disturbance by living organisms, sediment particles of fine-scale, and sedimentation rate are the conditions controlling the preservation of the organic matters (Tissot and Welte, 1984). Hydrocarbons, mainly lipids origin, form a small percentage of petroleum (10% - 20%). The lipid content consists of carbon homologous compounds that undergo minor structural changes during the maturation stages. This part of organic matters is more often referred to as bitumen. Bitumen is adhesive material composed of complex hydrocarbons. Calcium, iron, sulphur, and oxygen are among the elements found in this waxy material. The properties of bitumen change with the temperature. Bitumen is rigid and brittle in low temperatures, flexible in room temperatures, and flowable in high temperatures. Consequently, bitumen tends to be mobile under the reservoir conditions of high temperature.

The second and more important component of organic matters is kerogen which hosts significant amount hydrocarbons attributed to its large surface area. Kerogen serves as meso- or microporous media (Tegelaar et al., 1989). Based on the evolution of organic matters and elemental content (carbon, hydrogen, oxygen), kerogens are classified into four groups: I, II, III, and IV. Type I kerogen is primarily originated from the algae and planktons that are usually deposited in lacustrine environments. This type of kerogen is immature with high hydrogen and low oxygen contents at its initial condition. The maturation of type I kerogen usually leads

to the generation of waxy oils. Similarly, type II kerogen is capable of generating oil and gas under favourable subsurface conditions. This type of kerogen is rich in hydrogen and has a low concentration of oxygen. In contrast, type III kerogen has a low hydrogen and high oxygen contents which influences its hydrocarbon generation potential. Type III kerogen is prone to produce dry gas. Kerogens of type IV are derived mainly from organic matters surviving after erosion and are present in older sediments. Weathering, combustion, and biological oxidation all play a significant role in altering kerogen content. The remaining carbon in this type of kerogen is almost entirely inert and low in hydrogen. This results in no oil or gas potential (B. Tissot (2), B. Durand (2), J. Es, 1974; Behar & Vandenbroucke, 1987; Geological & Organisation, 1995). Figure 14 provides information about the evolution of kerogen through diagenesis, catagenesis, and metagenesis, along with the elemental composition of each kerogen type.

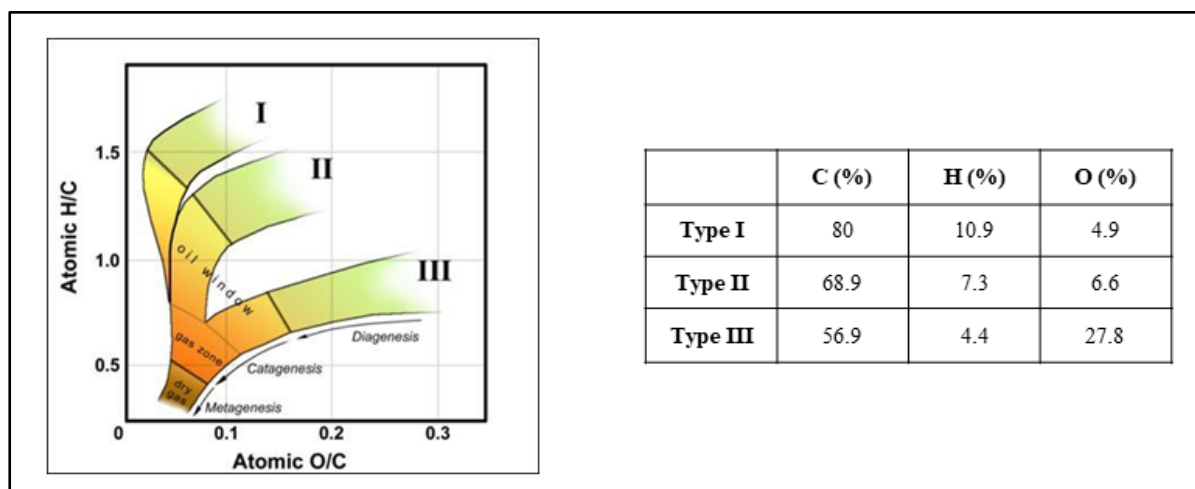


Figure 14. Van Krevelen diagram and elemental composition of kerogen types (reproduced from Bend 2007 and Behar & Vandenbroucke 1987)

The diagenesis stage occurs in the relatively shallow depth at the temperatures and pressures close to the atmospheric condition. Although this stage is not accompanied by significant alteration of organic matter, different compounds like water, carbon dioxide, and water are expelled off during diagenesis to leave kerogen. Kerogen is already defined as an insoluble

structure in organic solvents that emits petroleum when heated. For more detailed information about kerogen types, it is recommended to refer to Chapter 1. Further sedimentation and burial in the subsequent stage of catagenesis expose deposited beds to higher temperatures (60-150 C) and pressures (300-1000 bars). The catagenesis stage is attributed to the formation of oil, gas condensates, and wet gases due to the thermal degradation of kerogen. In the last stage of the evolution chain, known as metagenesis, exposure to the extremely high-temperature range of about 150-200 C leads to dry gas production (Petrov, 1987; Speight, 2007; Peters and Moldowan, 1993; Peters et al., 2005).

Total organic carbon content (TOC) (comprised of organic material) is an indicator used to define the potential of formation to generate petroleum. The hydrocarbon potential of the source rock is positively correlated with high TOC values. The TOC of a sample is determined by grinding a sample of the source rock to a fine powder and weighing the powder. A solution of acid is then applied to the sample to eliminate any carbonate minerals before analysis. To analyse the sediment, a very high temperature is applied to the carbonate-free sample in an oxygenated atmosphere to convert the carbon into carbon dioxide. Once the carbon dioxide content is calculated, the TOC content is determined. A more detailed description of TOC measurements is available in Carvajal-Ortiz & Gentzis (2015). Although there are other indirect techniques based on pyrolysis available as well, the combustion method is the more preferred measurement. Usually, a value of 0.5% TOC by weight percent is needed to be considered a reliable source rock. **Table 6** summarizes the classification of sources rocks based on the TOC percentage (Peters, 1986; Jarvie, 1991).

Table 6. Quantitive interpretation of TOC (reproduced from Harry Dembicki, Jr. , 2017)

Total Organic Carbon Content Weight (%)	Hydrocarbon Generation Potential
< 0.5	Very Poor
0.5 - 1	Poor
1 - 2	Fair
2 - 4	Good
4 - 12	Very Good
> 12	Excellent

As stated above, organic matters are the combination of kerogen and bitumen in different concentrations. Usually, the latter's concentration does not exceed 20% by weight in the organic matters, while the former is considered a major source of hydrocarbons existence. Up to our knowledge, there are no existing literature considering the mechanical behavior of the organic matters considering both kerogen and bitumen either experimentally or analytically. The available literature primarily focused on the properties of shale without much insights into its individual constituents, which leaves some gap in modelling the behavior as the mineralogy changes. This study investigates the mechanical properties of organic matters, represented by forming different kerogen-bitumen configurations. The kerogen type II, commonly found in shales, and asphaltene were used as representatives of kerogen and bitumen. Asphaltene is one of the major components forming bitumen (Béhar & Pelet, 1985). Asphaltenes are high molecular weight substances found in crude oils and bitumen. Even though the exact composition of asphaltene molecules varies, the asphaltene molecule of a particular crude oil or bitumen is quite similar in its molecular structure. It appears in the core as a dark brown to black material that coats grains, filling pore spaces and voids. Originally, asphaltenes were thought to be fragments of kerogen that had been degraded by heat (Louis and Tissot, 1967).

Nevertheless, Pelet et al. (1986) reported that asphaltenes might also be formed through condensation processes similar to those leading to kerogen.

The low content of kerogen and its fine dispersion in the rock structure make experimental determination of its mechanical properties difficult. However, nanoindentation and atomic force microscopy techniques allow the evaluation of rocks without the need for isolation. Table 7 shows information from some studies conducted for the organic matters found in different types of formations (Ahmadov et al., 2009 and 2011; Eliyahu et al., 2015; Kumar et al., 2012; Zeszotarski et al., 2004).

Table 7. Mechanical properties of formations obtained after different studies

Study	Formation	Young's coefficient (GPa)	Poisson's ratio
<i>Zeszotarski et al., 2004</i>	Woodford shale (USA)	8.8 - 10.4	0.1 - 0.4
<i>Kumar et al., 2012</i>			
<i>Ahmadov et al., 2009 and 2011</i>	Lockatong (USA)	10.1 – 13	up to 0.45
	Bazhenov (Russia)	4.7 - 5.9	up to 0.45
<i>Kumar et al., 2012</i>	Kimmeridge (USA)	5	0.3
<i>Eliyahu et al., 2015</i>	Upper Jurassic source rock (USA)	up to 25	0.3

On the other hand, the advancement in computational power enabled researchers to mimic the experimental processes and provides in depth insights into some nano-scale intricacies. Molecular dynamics MD approach has broad applications in different branches of engineering to study materials such as silica, carbon nanotubes and others (Buell et al., 2009; Chowdhury et al., 2016; Nayeibi & Zaminpayma, 2016; Sheikhnjad, 2018). This method is particularly advantageous in the case of organic matters, which are very sensitive and associate a risk of altering their original properties while testing them experimentally. The first molecular representation of kerogen was introduced by Burlingame et al. (1969), but the model failed to capture the full the chemical structure. More advanced molecular models came after (Yen et

al. 1976; Oka et al. 1977). Although the proposed models performed well in application to bitumen structures, they were found to underestimate properties of kerogen. They were restricted to the low molecular weight compounds due to technical limitations. In recent years, a greater variety of 3D structures have been developed. Studies of mechanical properties based on the available models revealed a high degree of consistency with the reported values experimentally. For instance, the outcomes of Green River shale's mechanical properties investigated by Zhang & Jamili (2015) were in alignment with the experimental findings of (Yan & Han, 2013). Moreover, observations made by Kashinath et al. (2019) on Poisson's coefficients matched decently the experimental ones.

In this study, the organic matters of different kerogen to bitumen ratios are formed in a molecular simulation platform. The structures were saturated with different gases that are typically exist in the reservoir and the mechanical behavior was thoroughly assessed before and after saturation with gases. The reminder of the paper is organized as follows: the molecular methodology including the creation of the structures, the characterization, and mechanical workflows are outlined in section 3.3. That is followed by the results and discussion in section 3.4. Some concluding remarks are drawn in section 3.5.

3.3 Molecular Modelling & Methodology

3.3.1 Building Organic Matter Models

Molecular simulation is an efficient tool that has been frequently utilized in different engineering applications to infer the system's behavior under certain conditions. The basic idea behind the molecular simulation concept consists of three steps. In the first step, the molecules of the structure are positioned in the simulation box to create an initial state. This is followed by defining interactions forces, which describe repulsive and attractive forces between molecules. PCFF+ forcefield (polymer consistent forcefield plus) was used to simulate atomic

interactions in this work. PCFF+ has shown an ability to reproduce properties of organic-based materials as reported by different scholars in recent studies (Afagwu et al., 2021b; Alafnan, 2021a, 2021b; Alafnan, Falola, et al., 2020; Alafnan, Solling, et al., 2020; Alafnan, Sultan, et al., 2020; Ungerer et al., 2015). Having the force field defined, the final step is to integrate Newton's equations of motion to predict particle trajectories inside the box during simulation.

MedeA software was used to conduct the molecular dynamics protocol, shown in Figure 15. This protocol allows forming the final condensed structure starting from given set of macromolecules. The structures of the organic matters were built by initializing the simulation box with twelve units of type II D kerogen, introduced by Ungerer et al. (2015), and later adding asphaltene molecules, known as A1, as a representative of bitumen. The asphaltene macromolecule unit used in this study was derived by Alqam, et al. 2021. Both asphaltene and kerogen units were derived from actual samples. The molar weight of every structure was taken as a base to ensure a proper mixing ratio. The chemical formula of kerogen II D and asphaltene A1 used in this study is $S_2C_{175}N_4O_9H_{102}$ (2466 g/mol) and $C_{37}H_{33}$ (477 g/mol), respectively. Considering the molar weights of the structures, organic matters with three different kerogen to asphaltene ratios were created. It was achieved by maintaining the same number of twelve kerogen units and keep adding 62, 92, and 122 units of asphaltene for each calculation cycle. To avoid issues of instability that may arise in subsequent simulation steps, initialization at low density was done. As part of the molecular dynamics procedure, a 9.5 cut-off value along with a 2.0 skin is applied to the cell. An isochoric-isothermal NVT stage was conducted at the temperature of 900 °K for 250 ps. Starting the simulation at high temperature would help speeding up the relaxation of the cell. Finally, three stages of NPT were performed to relax the structure by gradually reducing the temperature from 900 K to 350 K isobarically at 20 MPa with the 1 fs time step (i.e., 350 K and 20 MPa are deemed to be representative of typical reservoir conditions).

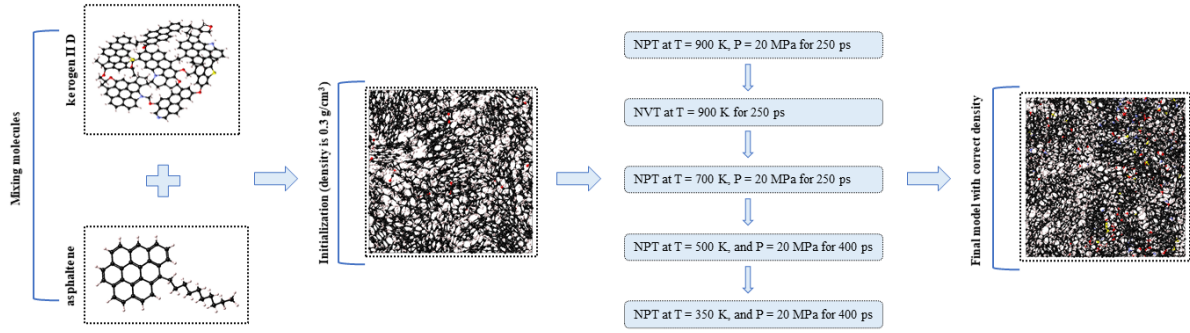


Figure 15. Visual representation of MD protocol used to build organic matters

3.3.2 Porosity and Pore Size Distribution Calculation

In order to discern the degree of confinement, a detailed petrophysical characterization of the obtained structures was necessary. This was accomplished by inserting non-overlapping spheres of a predefined threshold radius (r_i) into the void spaces within the nanoporous matrix (C Bradford et al. 1996). After retrieval of each sphere (n) dimensions, total pore volume (V_{pore}) is determined by summing them all.

$$V_{\text{pore}} = \sum_{i=1}^n \frac{4}{3} \pi r_i^3 \quad (27)$$

The minimum sphere radius was set to be 0.2 nm, and the frequency of radii was normalized with respect to the total number of pores obtained for each structure to extract the information about the pore size distribution. The normalization stage was necessary to establish a meaningful comparison between different structures and eliminate the size dependency because every addition of asphaltene causes an increase in size of the cubic cell.

3.3.3 Mechanical Properties

The same procedure described in section 2.8.2 of Chapter 2 was followed to analyse the mechanical behaviour of organic matter.

3.4 Results and Discussion

3.4.1 Porosity & Pore size Distribution

Kerogen II D was found to have the highest porosity with 14.885% among all structures. Interestingly the void fraction of organic matters decreased with the addition of new asphaltene molecules. Although the porosity of pure asphaltene (11.207%) was slightly lower compared to the initial model of organic matter (11.387%), the continuous addition of asphaltene led to porosity reduction in remaining cases. This behavior can be explained by the pore-filling effect on kerogen by asphaltene attributed to the difference in their molecular sizes. Based on the pore size distribution data given in the Figure 16, it can be deduced that pores with a radius of 0.2 to 0.25 nm were the most frequent. A similar observation can be made regarding asphaltene. On the contrary, kerogen revealed the predominance of two pore size ranges: between 0.2 nm. and 0.24 nm. ; between 0.24 nm. and 0.29 nm. This may indicate the presence of the dual pore system of the kerogen matrix.

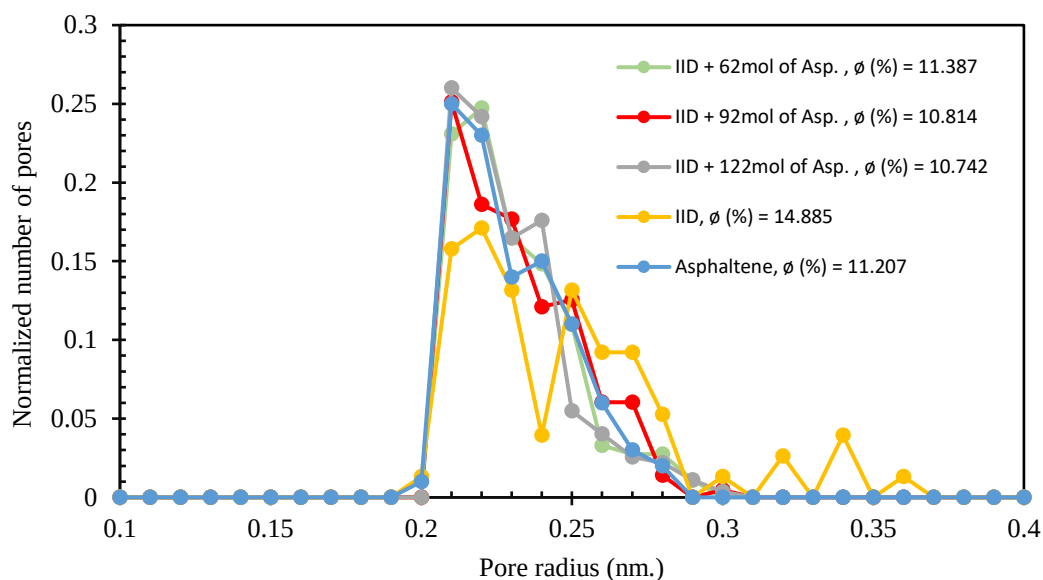


Figure 16. Pore size distribution of pure kerogen II D, pure asphaltene A1, and combination of the two at different ratios

3.4.2 Mechanical Properties & Stress-Strain Relationship

As described in the earlier section, the models of the organic matters, kerogen II D, and asphaltene A1 were formed from their respective units using the described MD protocol. The final values of density for kerogen II D (1.26 g/cm³) and asphaltene A1 (1.14 g/cm³) were in alignment with the values measured experimentally for the same types.

The stress-strain relationship behavior was obtained following the methodology covered in section 2.3. An incremental strain of 0.02 was exerted on all units to investigate both elastic and plastic deformations. The elastic region was used to evaluate the mechanical constants. The results revealed that while shear and Young's moduli values of kerogen were almost three times higher than asphaltene, the latter was more resistant to compression, as inferred from the value of Bulk moduli. Similarly, asphaltene was more prone to elongate in the direction perpendicular to the direction of the applied force, which was deduced based on Poisson's ratio. On the other hand, when it comes to the mechanical properties of the organic matters, the influence of increasing concentration of asphaltene negatively correlated with all elastic coefficients. However, this number was still higher compared to the pure state of kerogen and asphaltene. Poisson's ratio of the organic matters wasn't sensitive to the proportion of compounds as changes were negligible. Table 8 summarizes all findings.

Table 8. Properties of organic matters, kerogen II D, and asphaltene

Structure	Density (g/cm ³)	ν (%)	Bulk (GPa)	Shear (GPa)	Young's (GPa)	Poisson's (GPa)
II D + 62 mol Asp.	1.25	11.3870	4.41	0.65	1.85	0.43
II D + 92 mol Asp.	1.23	10.8140	4.4	0.5	1.46	0.45
II D + 122 mol Asp.	1.21	10.7420	4.29	0.47	1.37	0.45
II D	1.26	14.8850	3.39	0.6	1.7	0.42
Asphaltene	1.14	11.2070	3.5	0.2	0.59	0.47

The tensile deformation trend was observed to move downward, indicating a softening effect in the asphaltene (see Figure 17). The stress value for the given kerogen peaked at nearly 0.27 GPa, while asphaltene was just under 0.15 GPa for the same applied strain of 0.15. At the same time, the presence of asphaltene content with 62 molecules (the ratio is 1:1) in the matrix was found to shrink the elastic region of the structure by almost 70 % compared to the kerogen. Moreover, further addition of molecules shifts the stress-strain curves of organic matters downwards towards the pure asphaltene line.

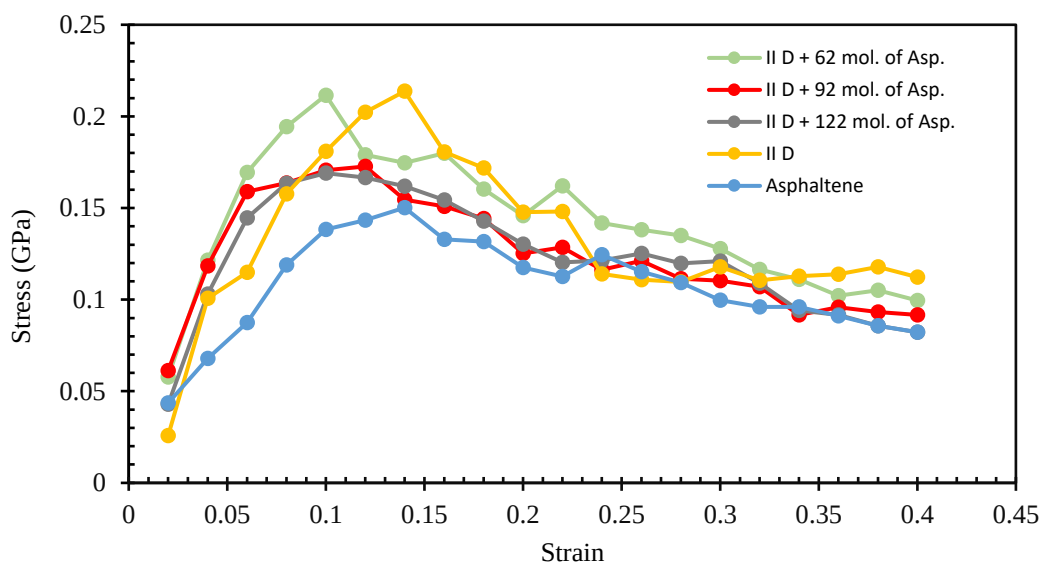


Figure 17. Stress-strain relationship of organic matters, kerogen II D, and asphaltene

3.4.3 Effect of Pore Fluid

The organic matters that exist at subsurface conditions are usually saturated with gas. Although methane is the most common gas in the rock matrix, carbon dioxide and nitrogen can also be present naturally or as a result of an injection process for sequestration purposes. The condensed structure of asphaltene A1 and kerogen type II D in 1:1 (kerogen II D with 62mol. of asphaltene) was saturated with methane, carbon dioxide, and nitrogen using Gibbs Monte Carlo simulation to investigate the influence of different fluid types adsorbed in the organic matter. The required fugacity inputs were computed through Peng-Robinson EOS with values

of 35.84 MPa for methane, 16.3 MPa for carbon dioxide, and 48.94 MPa for nitrogen gas. The simulation job was performed at 350 K and 3000 psi which was taken as a representative of the typical reservoir condition. The calculations were assisted by the Gibbs Module of MedeA environment.

It can be observed from the Figure 18 that the kerogen structure tends to show a higher adsorption capacity as the number of gas molecules in all three categories was significantly higher compared to the asphaltene and the organic matter. The adsorption capacity is in alignment with the characterized porosity for all structures. The finely dispersed particles of asphaltene reduced the void spaces available in the kerogen matrix.

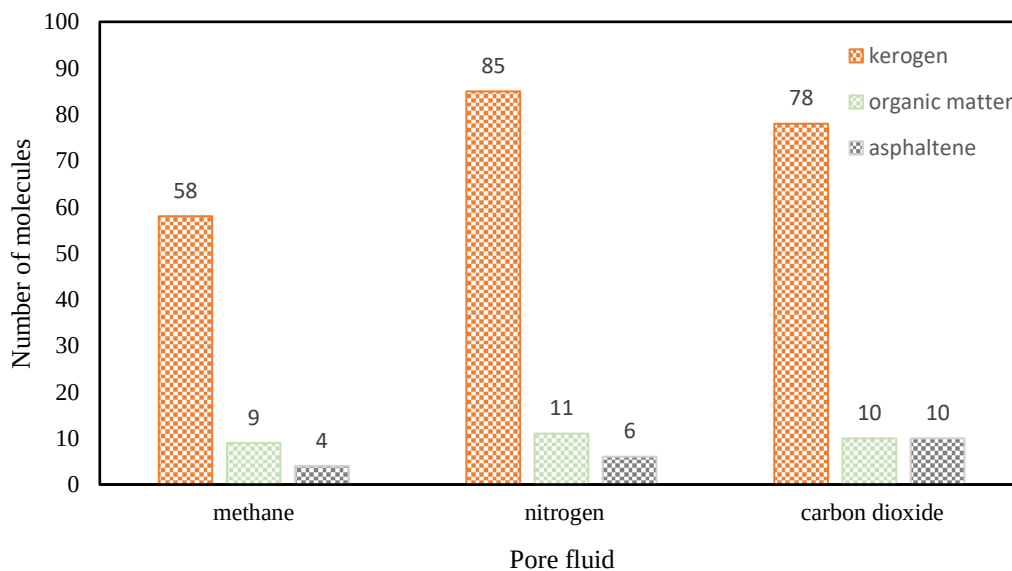


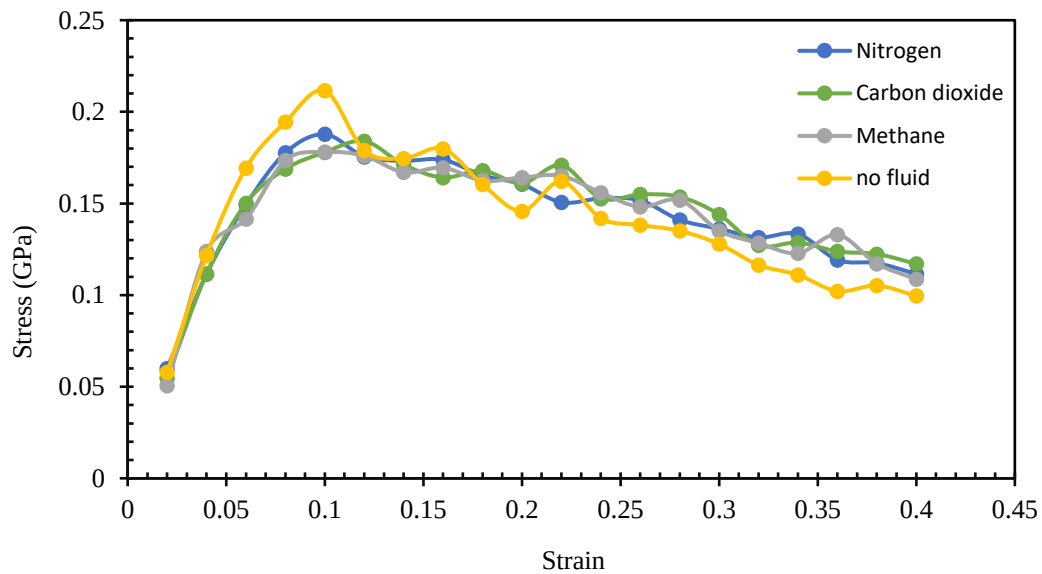
Figure 18. Number of adsorbed molecules for pure kerogen, pure asphaltene, and combination of the two

On the other hand, the mechanical properties of the organic matters were altered after saturation with different gases. Although Poisson's ratios remained almost the same, bulk moduli coefficients of the matrix increased following adsorption. Shear coefficients increased slightly after saturation with N_2 and CH_4 but decreased after CO_2 . Young's moduli changed in the exact same manner as in the previous case (see Table 9).

Table 9. Mechanical properties of the organic matter after adsorption

Property	No fluid	CH ₄	CO ₂	N ₂
Bulk (GPa)	4.41	4.68	4.62	4.6
Shear (GPa)	0.65	0.68	0.59	0.7
Young's (GPa)	1.85	1.95	1.69	1.99
Poisson's ratio	0.43	0.43	0.44	0.43

Finally, the visual representation reflecting the stress-strain relationship of the organic matter saturated with fluids was shifted downward compared to the one empty of gas. The first failure point of all structures happens at 0.1 strain, but more stress corresponds to pure organic matter. However, further propagation to the failure point continues to follow a similar path for all cases as shown in Figure 19.

**Figure 19.** Stress-strain relationship of the organic matter before and after adsorption

3.5 Conclusion Remarks

- The density of the organic matters represented as the mixture of asphaltene A1, and kerogen II D was close to the kerogen one's. Moreover, the porosity of kerogen II D was higher compared to the organic matters and pure asphaltene.
- The presence of asphaltene as part of the organic matters had a negative effect on the porosity due to the fine dispersion of asphaltene particles in the matrix.
- Organic matters, in a general sense, exhibited both plastic and elastic deformations. The mechanical properties negatively correlated with the increasing presence of asphaltene.
- The adsorption capacity of organic matters reduced with increasing asphaltene contents which altered the impact of pore fluid on the mechanical behavior.
- It is recommended that the methodology outlined in this paper is repeated for other types of kerogen and bitumen. It is also recommended to verify the reported findings experimentally.

CHAPTER 4

RECOMMENDATIONS

An investigation of kerogen and organic matter geomechanics, including tensile behavior, is presented in this study through a computational approach. The following suggestion can be made for further analysis:

- It is recommended that the outcomes of this study are validated experimentally, and fluid type effect extended to other kerogen models.
- The current study utilizes specific organic matter comprised of kerogen II D and sulphurless asphaltene. Considering the versatility of organic material composition, it is suggested to use different structures of asphaltene available in the literature in combination with other types of kerogen.
- The swelling nature of kerogen and organic matter was not captured as part of adsorption calculations. It would be worth examining mentioned effect as the inevitable volumetric strain after the adsorption stage is sought to impact the mechanical properties.
- Organic compounds within rocks may negatively affect stimulation performance. This occurrence is attributed to the plastic deformation of organic compounds under applied stress, leading to the closure of fractures created in the contact region with minerals. Therefore, studying the interface between minerals (calcite, quartz) and organic compounds is recommended.

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