

ASSESSMENT OF RESERVOIR QUALITY OF SOURCE ROCK

BY

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[To Professor Gabor Korvin]

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TABLE OF CONTENTS

ACKNOWLEDGMENTS	iv
TABLE OF CONTENTS.....	v
LIST OF TABLES	viii
LIST OF FIGURES	ix
LIST OF ABBREVIATIONS.....	xi
ABSTRACT.....	xiii
ملخص الرسالة	xv
CHAPTER 1 INTRODUCTION	1
1.1 Background	1
1.2 Motivation.....	2
1.3 Geological overview of investigated rock samples	3
1.4 Dissertation Outline	5
1.5 References	5
CHAPTER 2	8
2.1 Introduction.....	9
2.2 Theoretical Background.....	17
2.3 Material and methods.....	20
2.3.1 Source Rock sample and characterization	20
2.3.2 Experimental apparatus.....	21
2.4 Results and Discussion	24
2.4.1 Chemical composition	24
2.4.2 Thermogravimetric analysis.....	27
2.4.3 Rate of conversion and maximum temperature	29
2.4.4 Reaction Mechanism.....	31
2.4.5 Effects of catalytic minerals.....	34
2.4.6 Cumulative gas production and implication for maturity	35
2.5 Summary and Conclusions	38
2.6 References	40
CHAPTER 3	48
3.1 Introduction.....	49

3.2 Theoretical Background.....	55
3.3 Experimental apparatus and methods	58
3.3.1 Rock sample description and preparation	58
3.3.2 Experimental apparatus.....	59
3.3.3 Non-isothermal methane sorption measurement	60
3.3.4 Thermogravimetric measurement	60
3.3.5 Mass spectrometric measurement	61
3.4 Results and Discussion	62
3.4.1 Mineralogy and elemental composition.....	62
3.4.2 Effect of grain size	64
3.4.3 Effect of heat-pretreatment on nitrogen sorption.....	65
3.4.4 Intrinsic coupling of thermal maturation and sorption	67
3.4.5 Phase change.....	71
3.4.6 Pore filling	74
3.5 Conclusion	75
3.6 References.....	76
CHAPTER 4	82
4.1 Introduction.....	83
4.1.1 What is Brittleness of rocks?	84
4.2 Theoretical and Mathematical Framework	91
4.2.1 Theoretical Background.....	91
4.2.2 Conceptual Model and Mathematical Formulation	93
4.2.3 Derivation of Dynamic Index of Brittleness.....	95
4.2.4 Derivation of Static Index of Brittleness	97
4.2.5 Implication for Porous Media and Anisotropy	99
4.3 Experimental Measurements.....	100
4.3.1 Shale Description	100
4.3.2 Micro-CT Measurement.....	100
4.3.3 Density and Porosity Measurements.....	101
4.3.4 Geomechanical Measurements	101
4.4 Results and Discussion	103

4.4.1 Cracks Contents, Porosity and Elastic Parameters	103
4.4.2 Dynamic Index of Brittleness	106
4.4.3 Static Index of Brittleness	110
4.4.4 Comparison with other methods	111
4.5 Conclusions	113
4.6 References	115
CHAPTER 5	121
5.1 Introduction	122
5.2 Theoretical Background	127
5.3 Experimental apparatus and methods	131
5.3.1 Preparation of rock cuttings	131
5.3.2 Saturation and Packing	133
5.3.3 NMR Measurements	134
5.3.4 BET Measurement	135
5.4 Results and Discussions	135
5.4.1 NMR T2 and Grain Size	135
5.4.2 Calculation of Bulk Fluid Relaxation Time and Surface Relaxivity	139
5.4.3 Spatial Variation of T2b and ρ_2	141
5.4.4 Effect of T2b on ρ_2	141
5.4.5 Effect of grain shape	144
5.4.6 Surface relaxivity of Source Rocks and Reservoirs Rocks	147
5.4.7 Effect of Potential Determining Minerals	148
5.4.8 Comparison with other methods	151
5.5 Conclusion	154
5.6 References	156
CHAPTER 6	161
References	163
Vitae	164

LIST OF TABLES

Table 2. 1:Chemical Composition of investigated carbonate source rock.....	25
Table 2. 2:Kinetic parameters of first-order reaction.....	34
Table 3. 1: Mineralogical and Elemental Composition of source rock	63
Table 4. 1:Literature Survey of Brittleness Formula (Lawal, 2015).....	89
Table 4. 2:Density and Porosity Data of Qusaiba Shale.....	104
Table 4. 3:Velocity measurements at three orientations	106
Table 4. 4:Linear fit for calculating crack aspect ratio	109
Table 4. 5:Calculation of dynamic index of brittleness γ_d	110
Table 4. 6:Calculation of static index of brittleness γ_s	111
Table 4. 7:Merits and limitations of brittleness prediction	113
Table 5. 1:Surface relaxivity of some selected sedimentary rocks	125
Table 5. 2:Results of T ₂ measurements of bulk water and rock cuttings	137
Table 5. 3:Values of T _{2b} and pH of distilled water	139
Table 5. 4:Values of T _{2b} and ρ_2 based on spherical grain model.....	141
Table 5. 5:Comparison of spherical grain and approximate models	144
Table 5. 6:Comparison of spherical and cubic grain models for estimate of ρ_2	147
Table 5. 7:Chemical Composition of Rock Samples	148
Table 5. 8: Comparison of ρ_2 (μms) Measurements	152

LIST OF FIGURES

Figure 2. 1:A simple model of thermal maturation of carbonate source rock	12
Figure 2. 2:Schematic of thermogravimetric apparatus	24
Figure 2. 3:EDS spectral of elemental composition	26
Figure 2. 4:XRD spectral of mineralogical composition	27
Figure 2. 5:Thermogravimetric decay curves	29
Figure 2. 6:Mass-loss rate curve	31
Figure 2. 7:First-order reaction mechanism for determination of kinetic parameters	33
Figure 2. 8: Bimodal distribution of activation energy	34
Figure 2. 9:Cumulative gas production as function of (a) time and (b) temperature.....	37
Figure 3. 1:Schematic of sorption apparatus	62
Figure 3. 2:XRD spectral of mineralogical composition	63
Figure 3. 3:EDS spectral of elemental composition	64
Figure 3. 4:Isothermal nitrogen sorption	66
Figure 3. 5: Nitrogen sorption hysteresis	67
Figure 3. 6:Non-isothermal Methane Sorption from 40-400°C.....	70
Figure 3. 7:Thermogravimetric analysis of standalone thermal maturation	72
Figure 3. 8:Cumulative gas release during standalone thermal maturation.....	73
Figure 4. 1:Brittleness from stress-strain curves: (a) classical and (b) emergent	87
Figure 4. 2:Crack inclusion cutting through a rock	93
Figure 4. 3: Images of Qusaiba shale plugs (X: xy-axis, Y: yz-axis, Z: xz-axis	105
Figure 4. 4:Confining pressure as function of $\frac{\mu}{1-\nu}$ at 0o orientation.....	108
Figure 4. 5: Confining pressure as function of $\frac{\mu}{1-\nu}$ at 45o orientation	108
Figure 4. 6: Confining pressure as function of $\frac{\mu}{1-\nu}$ at 90o orientation	109
Figure 5. 1:Preparation of rock cuttings	133
Figure 5. 2:Saturation and Packing of rock cuttings.....	134
Figure 5. 3:NMR T_2 distribution-grain size relationship	138
Figure 5. 4: T_2^{-1} versus $\frac{C_{gs}}{W_g}$ for Spherical Grain Model	140
Figure 5. 5: T_2^{-1} versus $\frac{C_{gs}}{W_g}$ for Approximate Model	143
Figure 5. 6: T_2^{-1} versus $\frac{C_{gc}}{W_g}$ for Cubic Grain Model	146
Figure 5. 7:Effect of Mineralogy on 95% Confidence Interval	150

Figure 5. 8:Comparison of ρ_1 values for sandstone (Basan et al., 1997)	154
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LIST OF ABBREVIATIONS

Abbreviations

a: Heating Rate
A: Arrhenius Constant
BET: Brunauer-Emmett-Teller
BSEI: Backscattered Electron Imaging
D: Diffusion Coefficient
E: Activation Energy
IUPAC: International Union of Pure and Applied Chemistry
m: Mass
MICP: Mercury Injection Capillary Pressure
n: Order of reaction
NMR: Nuclear Magnetic Resonance
OIP: Optical Image Analysis
P: Pressure
PFG NMR: Pulse Field Gradient Nuclear Magnetic Resonance
PNM: Pore Network Modeling
t: Time
V: Volume
T: Temperature
TOC: Total Organic Carbon
UCS: uniaxial compressive strength
XRD: X-ray Diffraction
XRF: X-ray Fluorescence

Symbols

$c_{g,c}$: Geometric Constant for a Cubical Grain
 $c_{g,s}$: Geometric Constant for a Spherical Grain
 F_{μ} : Electrical Formation Factor of Micro Grain
 l_p : Pore length
 r_g : Grain radius
 r_p : Pore radius
 $\frac{S}{V}$: Surface-to-Volume Ratio of the Pore Space
 ρ : Surface Relaxivity, density
 ρ_1 : Longitudinal surface relaxivity
 ρ_2 : Transverse Surface Relaxivity
 ρ_{app} : Apparent Surface Relaxivity
 ρ_{int} : Intrinsic Surface Relaxivity
 $\emptyset$: Porosity
 $\emptyset_{\mu}$: Micro- Porosity
 $\emptyset_{NMR}$: NMR Porosity

T : NMR relaxation Time
 T_1 : Longitudinal relaxation time
 T_{1b} : Longitudinal Bulk Fluid Relaxation Time
 T_{1s} : Longitudinal Surface Fluid Relaxation Time
 T_2 : Transverse Relaxation Time
 T_{2b} : Transverse Bulk Fluid Relaxation Time
 T_{2s} : Transverse Surface Fluid Relaxation Time
 $T_{2\mu}$: Transverse Relaxation Time of Micro Grain
 T^{-1} : Relaxation Rate
 V_g : Grain Volume
 V_p : Pore Volume
 $w_{g,s}$: Width of a Sphere-Like Grain
 w_p : Pore Width
 $w_{g,c}$: Cubical Grain Diameter
 $w_{g,s}$: Spherical Grain Diameter
 α : Dimensionless mass, crack aspect ratio
 k : Rate Constant
 λ : Rate Constant
 ρ : Density
 λ : Lamé Parameter; Rate Constant
 μ : Lamé parameter, rigidity, shear modulus
 ν : Poisson ratio; instantaneous Poisson ratio
 γ : Index of brittleness

Subscripts

a : Adsorbed phase
 abs : Absolute
 b : Buoyancy
 $excess$: Excess
 gas : Gas
 o : Initial
 $sorb$: Buoyancy and uptake
 t : Transient
 u : Uptake
 f : Final

ABSTRACT

Full Name : LATEEF OWOLABI LAWAL

Thesis Title : ASSESSMENT OF RESERVOIR QUALITY OF SOURCE ROCK

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Like the conventional reservoirs, the assessment of reservoir quality is of fundamental importance for the formation evaluation of source rocks. However, their geological, physical and chemical characteristics present unique problems to the traditional characterization workflow and hydrocarbon recovery. For example, the unique characteristic of carbonate source rocks makes it difficult to use vitrinite reflectance as thermal maturity indicator. Other source rocks can be very tight, fissile and fragile such that sample preparation and handling makes saturation, porosity and permeability measurements to be of little use in source rock evaluation. In general, commercial production of hydrocarbons from source rocks is highly risky and requires substantial drilling and fracking costs. Based on the above-mentioned challenges, the rationale of this dissertation is to investigate the physics and chemistry of source rock to better understand their reservoir qualities including maturation to assess the hydrocarbon bearing capacity of source rocks; sorption for storage and gas-in-place evaluation and brittleness as an index of hydraulic fracturing potential. The economic and technical benefit of this study is to minimize cost and improve the success rate of fracking operations by identifying the high potential regions of the source rocks that can produce more hydrocarbon. For this purpose, new research ideas on the maturation and non-isothermal sorption kinetics of high-quality, organic-rich carbonate source rock from

Jafurah basin is proposed. In addition, on the basis of crack content and Eshelby's energy partitioning principle, a new quantitative relationship between brittleness and rock properties is developed and demonstrated for the Qusaiba shale. Besides these key rock properties, an analytical method is needed to measure the chemical interaction of the source rocks with fracturing fluids. Using deionized water as an example, the intrinsic surface relaxivity of fluid saturated rocks were derived from their low-field proton relaxation measurements as a measure of rock-fluid interactions. The maturation experiments showed that the volume content of carbon dioxide, methane and water are 2%, 46% and 52% respectively. The laboratory results of non-isothermal sorption suggest that the sorption capacity of methane increases monotonously as a function of temperature. The measurements of Qusaiba shale brittleness show that the directional dependence of brittleness on crack orientation is an imperative guideline to infer the fracturing index of source rocks. Finally, it is demonstrated that the rock-fluid interactions of conventional and unconventional rocks can best be done with NMR surface relaxivity.

ملخص الرسالة

الاسم الكامل: لطيف أولابي لول

عنوان الرسالة: تقييم جودة الخزان من صخور المصدر

التخصص: هندسة البترول

تاريخ الدرجة العلمية: أكتوبر 2021

مثل الخزانات التقليدية ، فإن تقييم جودة الخزان له أهمية أساسية لتقييم صخور المصدر. ومع ذلك ، فإن خصائصها الجيولوجية والفيزيائية والكيميائية تمثل مشاكل فريدة لسير عمل التوصيف التقليدي واستعادة الهيدروكربونات. على سبيل المثال ، يصعب استخدام انعكاس الفيترينيت كمؤشر للنضج الحراري لصخور المصدر الكربوناتها. أيضا يمكن أن تكون صخور المصدر شديدة ضيق المسامات وهشة مما يجعل تحضير العينة والتعامل معها لقياس التشعب والمسامية والنفذية صعبة وقليلة الاستخدام في تقييم صخور المصدر. بشكل عام ، يعتبر الإنتاج التجاري للهيدروكربونات من صخور المصدر محفوقاً بالمخاطر للغاية ويتطلب تكاليف حفر وتكسير كبيرة. بناءً على التحديات المذكورة أعلاه ، فإن الهدف لهذه الرسالة هو التحقيق في فيزياء وكيمياء صخور المصدر لفهم أفضل لصفات مكنها بما في ذلك: النضج لتقييم سعة صخور المصدر لتحمل الهيدروكربون ، الامتصاص للتخزين وتقييم الغاز في مكانه ، وقابلية الكسر كمؤشر لإمكانية التكسير الهيدروليكي. تتمثل الفائدة الاقتصادية والفنية لهذه الدراسة في تقليل التكلفة وتحسين معدل نجاح عمليات التكسير من خلال تحديد المناطق ذات الإمكانيات العالية لصخور المصدر التي يمكن أن تنتج المزيد من الهيدروكربون. لهذا الغرض ، تم اقتراح أفكار بحثية جديدة حول النضج والامتصاص غير متساوي الحرارة لصخور مصدر كربونات غنية عضوية من حوض الجافورة. بالإضافة إلى ذلك ، على أساس محتوى التشقق ومبدأ إيشيلبي لتقسيم الطاقة ، تم تطوير علاقة كمية جديدة بين القابلية للإنكسار وخصائص الصخور في صخر قصيبة. إلى جانب هذه الخصائص الرئيسية للصخور ، هناك حاجة إلى طريقة تحليلية لقياس التفاعل الكيميائي لصخور المصدر مع سوائل التكسير. باستخدام الماء منزوع الأيونات كمثال ، تم اشتقاق ارتخاء السطح الجوهري للصخور المشبعة بالسوائل من قياسات استرخاء البروتون ذات المجال المنخفض كمقياس لتفاعلات السوائل الصخرية. أظهرت تجارب النضج أن المحتوى الحجمي لثاني أكسيد الكربون والميثان والماء هو 2% ، 46% و 52% على التوالي. تشير النتائج المعملية للامتصاص غير المتساوي الحرارة إلى أن قدرة امتصاص الميثان تزداد مع زيادة درجة الحرارة. تظهر قياسات القابلية للانكسار لصخور قصيبة أن الاعتماد الاتجاهي للكسر على اتجاه الشق هو دليل إرشادي ضروري لاستنتاج مؤشر التكسير لصخور المصدر. أخيراً ، تم إثبات أن تفاعلات الموائع مع الصخور للصخور التقليدية وغير التقليدية يمكن أن تتم بشكل أفضل باستخدام استرخاء السطح بالرنين المغناطيسي النووي.

CHAPTER 1

INTRODUCTION

1.1 Background

Shale source rock is a fine grained, nanoporous sedimentary rock of variable mineralogy. In term of mineralogy, it can be classified as a composite of organic and inorganic minerals. The abundance of organic minerals in the form of kerogen can be used to classify shale as organic-rich rock or organic rock. The type of dominating inorganic mineral (clay, quartz, calcite, dolomite), on the other hand, is used to classify shale as carbonate-rich shale, siliceous shale and clayed-rich shale. From the perspective of the petroleum system, the organic-rich shale is usually considered as the source rocks while the organic-lean shale is usually considered the seal of conventional reservoirs (sandstone and carbonate). From maturity standpoint, two sub-categories of shale exist- oil shale and hydrocarbon-bearing shale. Oil shale is an immature shale that does not generate hydrocarbon while hydrocarbon shale can generate oil or gas or both depending on the level of maturity. It is important to note that oil shale is the sedimentary rock while shale oil is the product. From geomechanical perspective, shale can be brittle or ductile. The extent of the degree of brittleness and lamination in shale is now commonly assessed by brittleness index as a measure of the completion quality for the hydraulic fracturing of

shale. Characterization of maturity and brittleness indices are critical to locate the good quality, high productivity shale sections in the shale gas reservoir.

1.2 Motivation

Around the world, including US, Canada, China and Saudi Arabia among others, shale oil and shale gas from hydrocarbon bearing shale are becoming increasingly one of the mainstream sustainable energy resources of the 21st century. Shale gas development has been one of the current research focuses in Saudi Arabia to the rising demand for sustainable energy around the world. The technology limit in the last few decades has been the main challenge to unlock the huge gas reserves in shale. The extensive deployment of horizontal wells coupled with massive hydraulic fracturing significantly facilitate gas production from these formations. However, the rapid decline in recovery factor is now the major research concern. The U.S., in particular, has recently explored different unconventional shale resources with these mainstream technologies. Production analysis from different shale gas reservoirs showed that at the very best, the fast decline rate of not more than 75% of the total production of a specific well gradually bottom out to about 6% in subsequent years (EIA,2011). This is may be due to the inaccurate planning and mischaracterization of shale reservoir in locating high quality reservoir sections.

Similar to the case of conventional reservoirs, the accuracy in shale source characterization is fundamental to the success of shale gas exploration and exploitation projects. Unlike, the conventional reservoir characterization, the conventional porosity

and permeability measurements is difficult and challenging for fine grained fissile shale. Instead, organic content (TOC and kerogen), maturity, and brittleness are more promising parameters to delineate sweep spots which are most favorable for hydraulic fracturing and hydrocarbon recovery in shale reservoirs. However, both in the laboratory and field, the best practice to accurately characterize shale has not been standardized. Therefore, shale characterization presents an interesting study to research workers in academia and industry. The investigation of the shale reservoir quality in terms of maturation, sorption and brittleness characterization is overarching scope of this dissertation.

1.3 Geological overview of investigated rock samples

The Silurian Qusaiba shale dated at 443.7 to ~428 Ma (Rhuddanian to Late Telychian) (Paris et al. 2015a) of northwest Saudi Arabia was deposited in the Rub' Al-Khali Basin under marine depositional setting of low energy during the Hirnantian glaciation stage of large-scale time transgression (Inan et al., 2016; Lüning et al., 2000). In terms of the Paleozoic Total Petroleum System (PTPS), it serves as the main producer for the heterogeneous reservoirs of the Middle East. The Lower Silurian Qusaiba shale (the basal section), often referred to as “hot shale” (Inan et al., 2016), is believed to be the source of Saudi Arabia’s Ghawar, the largest single collection of crude oil in the world. The Jafurah sub-basin consists of three organic-rich source rocks including Tuwaiq Mountain, Hanifa and Jubaila Formations. These formations are considered by geologists to be the classic Jurassic source rocks for the carbonate reservoirs of the Ghawar Field (Hakami and Inan, 2016). Although significant quantities of shale gas and shale oil is accumulated in these formations, little data have been published. Therefore, the Jafurah formation is

one of the main exploration targets for shale gas and shale oil development in Saudi Arabia. Unlike the Qusaiba shale, the source rocks of the Jafurah basin are mainly carbonate dominated with thin laminations. These unique physical characteristics make core preparations challenging for petrophysical measurements. The Eagle Ford shale is a Cretaceous (Turonian and Cenomanian) organic-rich formation deposited during the marine transgressions of the epeiric (inland) sea in North America (Chalmers and Bustin, 2017; Robison, 1997). The subsurface and outcrops of the Eagle Ford shale is geographically extensive. The subsurface Eagle Ford shale that strike northeast-to-southwest of Texas occurs as siliciclastic and carbonate sediments. The Eagle Ford of East Texas basin consist mainly of calcareous mudstones (brown to bluish-black) and calcareous sandstones (brownish-grey) (Robison, 1997). The southern part of the basin consists of calcareous shale of varying lithology and may contain organic matter in the form of bitumen, inertinite and vitrinite (Chalmers and Bustin, 2017). Berea sandstone, otherwise known as Berea Grit, is a Mississippian-age sandstone that serve as an important oil and gas reservoir in the Michigan Basin. The outcrop analog of the Berea sandstone in Ohio, infilling two channel-fill deposits of Orange Berea Upper Berea respectively. The upper Berea has gained world-wide acceptance as one of rock standards for coreflooding experiments. The mineral content which varies from sample to sample are quartz (85 to 90 %), feldspar (3 to 6 %), dolomite (1 to 2 %), clays (6 to 8 %) and iron sulfide in trace amount (Churcher et al., 1991). The Mississippian age Indiana limestone or Salem limestone, which is comprised mainly of oolites and fossil fragments is deposited in a shallow inland sea environment. It is the calcite cemented grainstone of the Illinois Basin and the carbonate reservoir of the Keenville oil Field. The Indiana

limestone outcrop (Bedford-Bloomington quarry) consists of buff-colored and grey-colored limestone, respectively. The permeability of the basal section is substantially lower than that of the upper section. Mineralogical analysis indicate that Indiana limestone is made up of 99% calcite and 1% quartz (Churcher et al., 1991).

1.4 Dissertation Outline

Chapter one introduces shale source rock and the motivation behind this research. Chapter two is devoted to the artificial maturation of source rock, and give important insights into gas generation kinetics. Chapter three is focused on the experimental investigation of non-isothermal adsorption. Chapter four investigate the kerogen-water interaction. Chapter five describe a new method of characterizing surface relaxivity of conventional and unconventional reservoirs. Chapter six explain a new approach of brittleness evaluation.

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CHAPTER 2

Thermal maturation, mineral catalysis, and gas generation kinetics of carbonate source rock

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Abstract

Source-rock evaluation must start by first characterizing thermal maturity. The concept of thermal maturation or thermal decomposition is a well-defined quantitative modelling of kinetic parameters to explain the generation and expulsion of liquid and gaseous hydrocarbons from sedimentary source rocks. However, unlike coal and shale source rocks, carbonate source rocks are emerging source rocks and no analyses of thermal maturation kinetics have been reported in the literature. Apparently, this study is one of the most recent and first laboratory study of thermal maturation kinetics of carbonate source rock. In this paper, we simulated this process by conducting controlled laboratory experiments under high temperature from 40°C to 450°C using advanced integrated analytical techniques. The dataset is modelled by the solid state kinetics of first order reactions. In addition, the poor knowledge of how catalytic minerals stimulate thermal maturation is investigated; a unique and significant contribution that sets this work apart from previous thermal maturation studies. The result from kinetic modelling showed that the distribution of activation energy in the range of 99-325 KJ/mol is bimodal, reflecting possible peak shift in the thermal decomposition process, reaction mechanism and maturation prediction. The model further suggests that the maturation process of carbonate-rich source rock is very likely to be different from that of clay-rich source

rock. Elemental and mineralogical analyses of investigated sample revealed the presences of catalytic elements such as iron, gypsum, pyrite and kaolinite. The analysis of the generated gases constrained to only three gases showed that the volume content of carbon dioxide, methane and water are 2%, 46% and 52% respectively. The generation of carbon dioxide is constant whereas methane increases and water decreases respectively with thermal maturation. Although, the investigated sample has a high calcite content of 91.9%, the methane content of 46% gives a strong indication of high natural gas generative potential as contrasted with the 2% of carbon dioxide generated. The findings of this study can help to better understand the coupled mechanism controlling thermal maturation of carbonate source rock and also provide useful reference dataset for basin modelling of carbonate source rocks for field studies.

Keyword: Thermal maturation; catalytic mineral; gas generation; carbonate source rock

2.1 Introduction

Organic-rich sedimentary source rocks are accumulation of sediments containing appreciable amount of organic matter and inorganic minerals. These rocks, which serve as the source, reservoir and seal, are of geological and economic importance to the petroleum system and subsurface energy production. The thermal history of the sedimentary basins and the thermal maturation of the source rocks is equally important to the hydrocarbon generation and conversion. Yet, the quantitative evaluation of kinetics of thermal evolution of source rock is complex and remains enigmatic (Ungerer and Pelet,

1987). Source rock geochemists and petroleum geologists have long been concerned with this specific problem and they attributed the physical and chemical processes involved in the complex thermal decomposition of source rocks in sedimentary basin to several interdependent factors such as burial heating, geothermal gradient, time, temperature, pressure, heating rate, mineral catalysis, chemical kinetics, kerogen types and composition (Hood et al., 1975; Luo and Vasseur, 1996; Pepper and Corvit, 1995). Similar to the significant lateral and vertical variations within reservoirs rocks such as sandstone and carbonate (Dakhelpour-Ghoveifel et al., 2018; Olayiwola and Dejam, 2019), these influencing factors can vary substantially from one basin to another or with location within the same basin and even from source rock to source rock within a single basin. For example, the composition and type of organic matter that accumulates in a carbonate source rock can be remarkably different from a siliciclastic source rock. A more specific example is the apparent absence of vitrinite in carbonate source rock and its enrichment in argillaceous source rock.

From a chemical reaction point of view, different mechanisms of phase transformation occurring in series or parallel or both have been proposed in the past to model the generation, cracking and expulsion of hydrocarbon in source rock (Rajeshwar et al., 1979). To predict the rate of hydrocarbon generation in sedimentary systems, it is assumed that the kerogen contained in the source rock consist of reactive and inert components respectively (Luo and Vasseur, 1996; Pepper and Corvit, 1995). The reactive

kerogen is an oil or gas generative kerogen that disintegrates into oil, methane and solid residues as the three main by-products while the inert part generates methane and graphite under high temperature. The combined process can be considered as (1) production of methane, oil and residue; (2) cracking of oil into methane and residue; and (3) cracking of residue into methane and graphite (Luo and Vasseur, 1996). It is important to note that this is one of the simplest transformation scheme among many others. The thermal decomposition of the source rock is represented by solid-state reaction of the general form $AB_{solid} \rightarrow A_{solid} + B_{fluid}$ (Coat and Redfern, 1964; Vyazovkin et al., 2020). It is widely accepted that this reaction can be modeled by first-order irreversible chemical reactions (Coat and Redfern, 1964; Rajeshwar, 1981; Rajeshwar et al., 1979; Ungerer and Pelet, 1987). For simplification, the series of chemical reactions occurring simultaneously is modeled sequentially as a two or three-stage transformation process by first-order kinetic reactions involving conversion of: (1) kerogen to oil; (2) oil to gas; and (3) residue to gas (Luo and Vasseur, 1996; Pepper and Corvit, 1995; Rajeshwar, 1981).

To further simplify the complexity of thermal degradation of source rock, it is generally assumed that the transformation of kerogen is only significant and the effect of thermal alteration of the rock minerals can be disregarded (Pepper and Corvit, 1995). However, in the presence of mineral matter, the thermal transformation process proceeds as follows: (1) evolution of gases and water; (2) kerogen-bitumen conversion; (3) bitumen alteration; (4) conversion of bitumen to other compounds including oils and gases; (5) oil vaporization; (6) combustion of fixed carbon; (7) decomposition of inorganic minerals and organic residues (Rajeshwar et al., 1979). It is important to emphasize that the

decomposition of the mineral matrix or inorganic component of the source rocks cannot be isolated and ignored during thermal maturation, especially: (1) when the relative abundance of the by-products need to be compared and (2) the organic matter is dispersed with the mineral matrix. In addition, the degree of alteration and phase transformation of carbonate and argillaceous shale source rock can be of appreciable difference. For example, during thermal decomposition, it is well-documented that the carbonate minerals dominating the lithology of a carbonate source rock will undergo dissociation whereas the quartz minerals in siliciclastic source rock will undergo crystallographic transformation (Rajeshwar et al., 1979). A simple schematic of the thermal maturation process of carbonate source rock is shown in Figure 2.1.

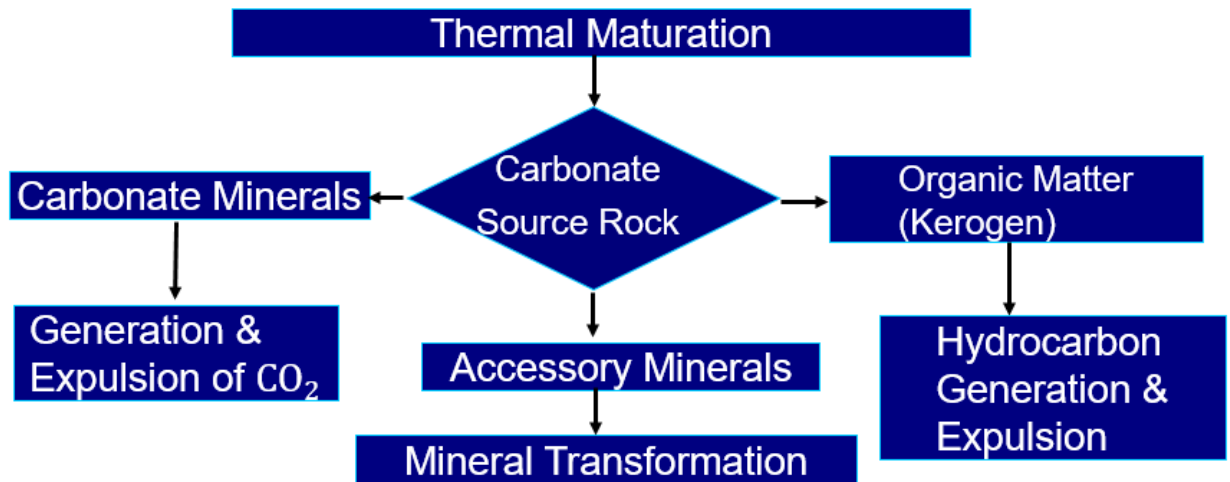


Figure 2. 1: A simple model of thermal maturation of carbonate source rock

The information gained from first-order kinetic is important and useful to capture the possible chemical reaction governing the processes of source rock maturation. However, it is necessary but not sufficient to resolve the thermal evolution of the source rock and predict maturity. To predict the degree of thermal maturity, some early researchers apply

physical variables such as formation age, present day temperature and effective heating time, temperature and pressure while other adopt organic petrology and geochemical analysis by using geochemical parameters such as vitrinite reflectance as maturity indicator (Adegoke et al., 2020; Adeyilola et al., 2020; Hakami et al., 2016; Hood et al., 1975; Lawal et al., 2020b; McCartney and Teichmüller, 1972; Owusu et al., 2019; Pepper and Corvit, 1995; Teichmüller, 1986; Alan and Janell, 1987). The effective heating time is a single parameter introduced to simplify the estimate of the thermal history of the sedimentary basins. It is defined on the assumption of isothermal heating as the time interval that is required to generate hydrocarbon with 15°C increase of the present day temperature (T_{max}) (Hood et al., 1975). While time and temperature are dominant, it has been argued that the effect of pressure is of less importance for the thermal evolution of source rocks (Pepper and Corvit, 1995; Waples, 1980). For this reason, the combined use of time and temperature, the so-called time-temperature index or Lopatin time-temperature index is more appropriate and has been widely used to reconstruct the thermal maturation history of sedimentary basin in the early 80's (Pepper and Corvit, 1995; Wood, 1988). In a more recent study, the effect of pressure is investigated on hydrocarbon generation and expulsion (Wu et al., 2016).

Modern technique of thermal modelling of source rock evolution rely mainly on integrating the physico-chemical processes of thermal reaction. This can be achieved by applying first-order reaction kinetic of solid state thermal decomposition to interpret time-temperature measurements. The possible connection between both approaches is based on the Arrhenius empirical equation which states that the rate of chemical reaction increases exponentially with temperature. However, the main problem associated with

invoking the Arrhenius equation is the empirical value of the rate constant or activation energy distribution as input data for maturity modelling. This data is source rock specific and is not readily available for source rock modelling on a basin-wide scale. To get rid of these empirical constants, it is generally assumed that the reaction rate approximately doubles with ten-fold increase in temperature (Waples, 1980). This simplifying assumption is one of the main uncertainties associated with basin modelling of thermal maturation. Therefore, a representative thermal maturity model of sedimentary basins must be analyzed and interpreted with reliable and accurate data. With this limitation, laboratory studies of source rocks by heating experiments received special consideration for thermal maturity studies.

Laboratory heating experiments can be very sensitive to atmospheric conditions; and are therefore broadly categorized into two: combustion and pyrolysis (Lawal et al., 2019a; Rajeshwar et al., 1979). The former and the latter are conducted under oxygen and oxygen-free atmosphere respectively. Depending on experimental procedures, different forms of source rock pyrolysis such as anhydrous, hydrous, open-system and closed-system pyrolysis are the possible experimental techniques (Lewan and Ruble, 2002; Shao et al., 2018). Pyrolysis and combustion can also be combined in one goal. For example, in the Rock-Eval pyrolysis and its variants, heating experiment is conducted under inert and air atmosphere respectively (Beti et al., 2018; Evenick, 2021; Mukhopadhyay et al., 2021; Scheeder et al., 2020; Wang et al., 2021). With temperature control, lab-scale heating experiments can be further classified as: (1) isothermal when temperature remains constant and (2) non-isothermal when temperature increases linearly in step-wise manner with respect to a specified heating rate. Comparing both conditions of heating,

isothermal approach is at disadvantage by introducing consistent experimental errors in the kinetic data; this is most significant when the heat-up time at higher temperature is an appreciable fraction of the total time for the reaction (Rajeshwar, 1981; Rajeshwar et al., 1979). Also, in geological context, isothermal heating may not be representative for the thermal maturation of subsurface source rocks. Therefore, non-isothermal heating may be more representative of the experimental condition for a lab-scale simulation of thermal maturation of source rocks. It is interesting to note that Rock-Eval pyrolysis combined isothermal technique up to 300 °C and non-isothermal technique up to 650 °C at a predefined heating rate (Beti et al., 2018; Scheeder et al., 2020).

Thermogravimetric, differential thermal and differential scanning calorimetry methods are the three main thermo-analytical techniques for characterizing laboratory heating experiment (Khraisha and Shabib, 2002; Rajeshwar, 1981; Rajeshwar et al., 1979; Rajeshwar and DuBow, 1980). The dataset from these measurements either independently or combined are best interpreted in terms of reaction kinetics to understand the chemistry of solid-state thermal decomposition. For this purpose, thermogravimetric analysis of different geomaterials have been well-reported in the literature (Alade et al., 2019; Elbaz et al., 2015; Khraisha and Shabib, 2002; Murtaza et al., 2020; Niu et al., 2020; Rajeshwar, 1981). Beyond kinetics parameters, thermogravimetric data need to be supported with additional data for compositional and evolved gas analysis. For example, the variants of Rock-Eval pyrolysis are generally equipped with flame ionization and infra-red detectors to calculate Rock-Eval pyrolysis parameters, most importantly, T_{max} and S_2 as indicator of thermal maturity and kerogen content respectively (Beti et al., 2018; Scheeder et al., 2020). Additional complementary data to aid the interpretation of

thermogravimetric data can also be obtained from spectroscopic tools such as mass spectrometry, NMR, FTIR, and gas chromatography/mass spectrometry (GCMS). Solid state ^{13}C NMR-assisted thermogravimetry and pyrolysis gas chromatography have been recently integrated to investigate the molecular signatures of shale source rocks (Johnson et al., 2020; Longbottom et al., 2020). It is important to mention that molecular simulation is also an important tool for kerogen/ inorganic mineral characterization (Lawal et al., 2019b; Wang and Zhao, 2020; Onawole et al., 2021). More recently, molecular modeling of thermogravimetric data is used to propose a new maturity index (Wang and Zhao, 2020).

The research effort of many decades has been devoted to the thermal maturation of oil-prone source rocks. With the promises of natural gas toward sustainable energy production and management, characterization of shale gas reservoirs is currently considered as an interesting and ongoing topic of research. In comparison with gas-bearing shale source rocks, gas-prone carbonate source rocks have only received scanty research attention. Unlike shale source rocks, vitrinite is significantly absent in carbonate source rocks. This unique characteristic of carbonate source rocks makes it difficult to use vitrinite reflectance as a thermal maturity indicator. In this study, we aimed at a more realistic characterization of the thermal maturation, mineral catalysis and gas generation kinetics of carbonate source rock by integrating thermogravimetric, mass spectrometric and mineralogical analyses. This work stands out from other studies in the following aspects: (1) thermal maturation of carbonate source is apparently reported for the first time; (2) the important role of inorganic minerals on the process of thermal maturation which is poorly understood is investigated in this study; (3) the integrated approach of

this study enable the coupled mechanism of thermal maturation, rate of conversion, reaction mechanism and gas generations kinetics to be adequately investigated and understood.

In an effort to gain a fundamental understanding of the mechanism of thermal maturation, the most significant advantages offered by this study are as follows: (1) it provide direct information on the kinetics of thermal maturation; (2) it is not source rock specific; (3) the dataset is a valuable input for further studies on the development of basin and molecular models of carbonate source rock; (4) it is more reliable to overcome the subjective bias and difficulty of identifying vitrinite in source rocks; (5) it provide an opportunity to evaluate the generation and expulsion of non-hydrocarbon constituents (6) it provide a practical approach to examine the effect of inorganic minerals on thermal maturation. For example, in our previous work on the molecular modelling of pure kerogen, we hypothesized the re-interpretation of kerogen maturity in the presence of inorganic mineral matter, particularly, carbonate and clay (Lawal et al., 2019b). In contrast, other surrogate measure of thermal maturation failed to examine the effect of mineralogy on thermal maturity. The limitation of this work are: (1) sophisticated instrumentation; (2) data processing and analysis may be time consuming. In general, the benefits of this work outweigh its drawbacks.

This paper is organized as follows: firstly, the theoretical and mathematical framework to derive kinetic parameters from thermogravimetric measurements is described in section 2; secondly, the workflow of the experiments including sample description, apparatus and experimental procedure of lab measurements is detailed in section 3; thirdly, we

discussed and analyzed our results in section 4 and finally, the summary and the main findings are highlighted in section 5.

2.2 Theoretical Background

The chemical kinetics of hydrocarbon generation from subsurface source rock cannot proceed without burial heating. The source of heat is the heat flux from the core and mantle and the radiogenic heat from the decay of nearby radioactive elements. The radiogenic heat production stems from (1) the lithosphere, (2) the sedimentary rocks within the basin and (3) the basement beneath the basin (Mckenna and Sharp, 1998). In the limit of uncertainty, 80% of the heat lost from the Earth's surface is due to radiogenic heating (Mckenna and Sharp, 1998). For a laboratory equivalent of this geological process, it is well acknowledged that a sedimentary source rock of initial mass m subjected to heating conditions will decay to generate hydrocarbon (Coat and Redfern, 1964; Pepper and Corvit, 1995; Ungerer and Pelet, 1987). The rate of mass change is proportional to the amount $m(t)$ of the source rock remaining after some time t . Mathematically, we write:

$$\frac{dm}{dt} \propto m^n \quad (1)$$

where m is the remaining mass after some time t and n is the order of reaction (e.g. zeroth, first and second order).

If we denote the proportionality constant, rate constant with λ , we write equation 1 as equation 2

$$\frac{dm}{dt} = \lambda m^n \quad (2)$$

The specialized case of temperature independent λ and $n = 1$ is applied in geochronology (radioisotope techniques of dating rocks). For solid state thermal decomposition reaction kinetics, $AB_{solid} \rightarrow A_{solid} + B_{fluid}$, the rate constant λ is said to be temperature dependent and is defined according to the Arrhenius rate constant k expressed by equation 3 (Coat and Redfern, 1964).

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (3)$$

By substituting equation 3 into equation 2, then we have:

$$\frac{dm}{dt} = A \exp\left(-\frac{E}{RT}\right) m^n \quad (4)$$

For a normalized mass, the generalized solid state decomposition reaction is represented by equation 5 (Coat and Redfern, 1964; Khraisha and Shabib, 2002).

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) (1 - \alpha)^n \quad (5)$$

where α , defined by equation 6, is the fraction of m that has been thermally transformed at time t

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \quad (6)$$

where m_o , m_t and m_f are the mass of the source rock before, during and after the thermal maturation process.

For non-isothermal decomposition, the implicit dependence of temperature on time is defined approximately by a linear heating rate according to equation 7.

$$T = T_o + at \quad (7)$$

where T , T_o and a is the temperature, initial temperature and heating rate respectively.

The substitution of equations 7 into equation 5 leads to equation 8.

$$(1 - \alpha)^{-n} \frac{d\alpha}{dT} = \frac{A}{a} \exp\left(-\frac{E}{RT}\right) \quad (8)$$

The n th-order differential equation in equation 8 does not have exact analytical solution but can be computed approximately by different graphical models. Two notable examples include the direct Arrhenius and the Coats-Redfern techniques (Braun and Burnham, 1987; Rajeshwar, 1981; Vyazovkin et al., 2020; Wood, 2017). Using the direct Arrhenius technique, equation 8 is transform to logarithmic scale according to equation 9.

$$\ln\left[a(1 - \alpha)^{-n} \frac{d\alpha}{dT}\right] = \ln A - \frac{E}{RT} \quad (9)$$

We follow the solution of Coats and Redfern (Coat and Redfern, 1964) given by equation (10).

$$\ln\left(\frac{AR}{aE}\right) - \frac{E}{RT} = \begin{cases} \ln\frac{-\ln(1 - \alpha)}{T^2}, & n = 1 \\ \ln\frac{1 - (1 - \alpha)^{1-n}}{(1 - n)T^2}, & n \neq 1 \end{cases} \quad (10)$$

The derivation of the kinetic parameter based on the direct Arrhenius method may seems unfavorable because numerical differential of the thermogravimetric data will

significantly reduce the signal-to-noise ratio. For this reason, we adopt the Coats-Redfern method as the working model in this study. Assuming a first-order reaction, kinetics parameters can be derived from the plot of $\ln \frac{-\ln(1-\alpha)}{T^2}$ denoted as Y thereafter against $\frac{1}{T}$.

2.3 Material and methods

2.3.1 Source Rock sample and characterization

The carbonate source rock samples investigated in this study were collected from subsurface basin of Saudi Arabia- the Jafurah sub-basin. It is Jurassic-age source rock which comprises of Tuwaiq Mountain, Hanifa and Jubaila Formations as the three major organic-rich source rocks. The source rock contains at least 90 wt.% carbonate mineral and as a result it represents excellent model of carbonate source rock with prolific natural gas generating potential. However, this prospective carbonate source rock has not been fully characterized and few studies have been published for comprehensive source-rock evaluation. For this work, millimeter-sized and pulverized samples were prepared for thermogravimetric and mineralogical analysis respectively. XRF and XRD was used for the semi-quantitative analysis of the elemental and mineralogical composition of the sample. The total organic carbon (TOC) was measured based on the experimental protocol of Leco analysis. The details of the experimental procedures have been discussed elsewhere (Lawal et al., 2020a, 2019a).

2.3.2 Experimental apparatus

An experimental apparatus consisting of a heater, a microbalance and a mass spectrometer was used for thermogravimetric-mass spectrometric analyses of carbonate source rock. The schematic of the setup is shown in Figure 2.2.

2.3.2.1 Pyrolysis

The pyrolysis of the sample can be performed with a heater, a water bath or stainless steel reactor chamber. The choice of the heater depends on the temperature range of the experiment, maximum of 85°C and 500°C for water bath and reactor respectively. For this experiment, the reactor chamber is used for the stepwise heating of the carbonate source rock sample from ambient condition to 450°C . The samples were crushed to about 3-4 mm grain size, weighed and placed in an aluminum crucible and then suspended in the reactor by a tungsten wire. The top of the wire is replaced by a chrome wire connected to the microbalance. The same procedure is followed for the counter weight, except that the reactor contains no heating element. Before the reactor is switched-on, vacuum is applied to remove adsorbed moisture or gases on the carbonate source rock sample. Afterwards, the sample is then pyrolyzed under inert atmosphere using nitrogen of high purity. The furnace is programmed to warm-up the sample from ambient condition to 40°C and then pyrolysis of the sample under non-isothermal condition begins from 40°C to 450°C at a heating rate of $5^{\circ}\text{C}/\text{min}$. The temperature

program is as follows: hold for minimum of 60 min and maximum of 300 minutes until the temperature of the sample is constant before proceeding to the next temperature.

2.3.2.2 Thermogravimetric measurement

A microbalance with a mass resolution of about $0.1\mu g$ was used to capture the small change difference of the sample during the heating experiment. With the support of a sensitive thermocouple, the main real-time measurement data acquired during the heating experiment include, differential mass of carbonate source rock sample, temperature of the furnace and temperature of the sample, respectively.

2.3.2.3 Mass spectrometric measurement

An online- mass spectrometer was coupled with the TGA to continuously detect gas generated during the pyrolysis process. The gas of interest for maturation studies are water vapor, methane, and carbon dioxide. Each of the evolved gases has a unique spectral which are detected as charge ions. The relative sensitivity of the gases is measured for more reliable and accurate estimate of the gases with an internal ion source. For quantitative analysis, the detected ions are converted into partial pressure using a Faraday bucket.

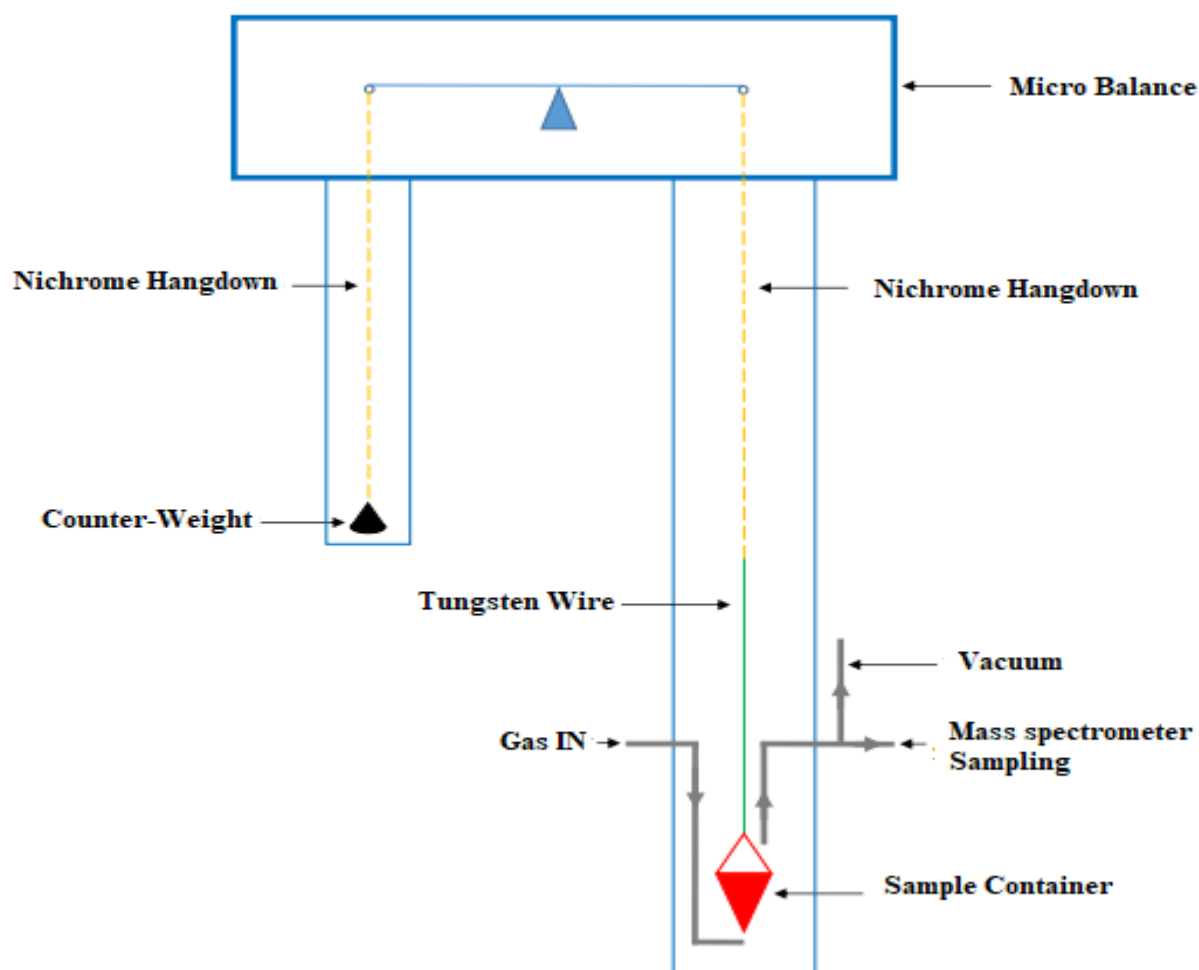


Figure 2.2: Schematic of thermogravimetric apparatus

2.4 Results and Discussion

2.4.1 Chemical composition

Seven representative inorganic elements as shown in Table 2.1 and Figure 2.3 were identified by Energy Dispersive X-ray Spectroscopy (EDX) analysis to reveal the chemical composition of mineral content of the carbonate source rock. The presence of these elements is well correlated with the mineral constituents measured from the X-ray

Diffraction (XRD) analysis of Figure 2.4 in the order of abundance as calcite, quartz, clay and pyrite respectively. The high weight percent of calcium give further evidence that lithology of the source is dominated by calcite. The weight percent of the TOC as measured by Leco analysis also suggest that the source rock is rich in organic content.

Table 2. 1:Chemical Composition of investigated carbonate source rock

Elements	(wt.%)	Mineralogy	(wt.%)	Organic content	(wt.%)
O	48.5	Calcite	91.9	TOC	12
Al	3.6	Quartz	3.5		
Si	7.6	Kaolinite	1.8		
S	3.2	Gypsum	1.7		
K	0.8	Pyrite	1.1		
Ca	34.7				
Fe	1.6				

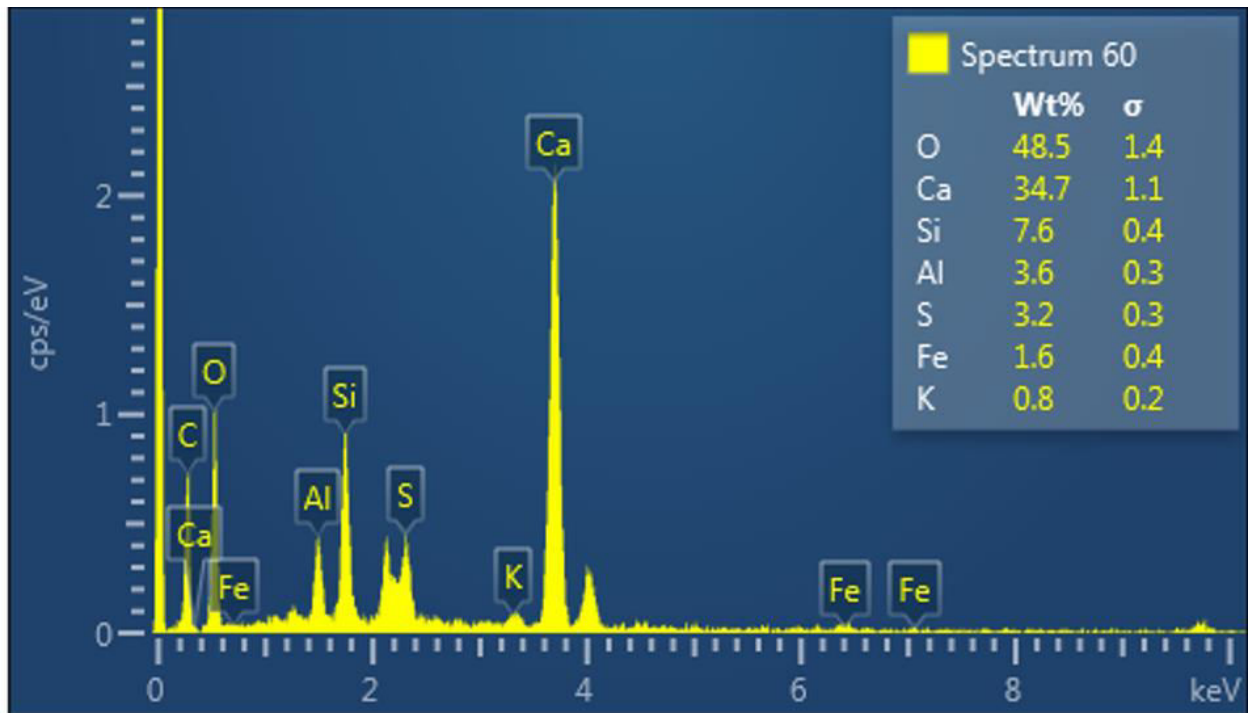


Figure 2.3:EDS spectral of elemental composition

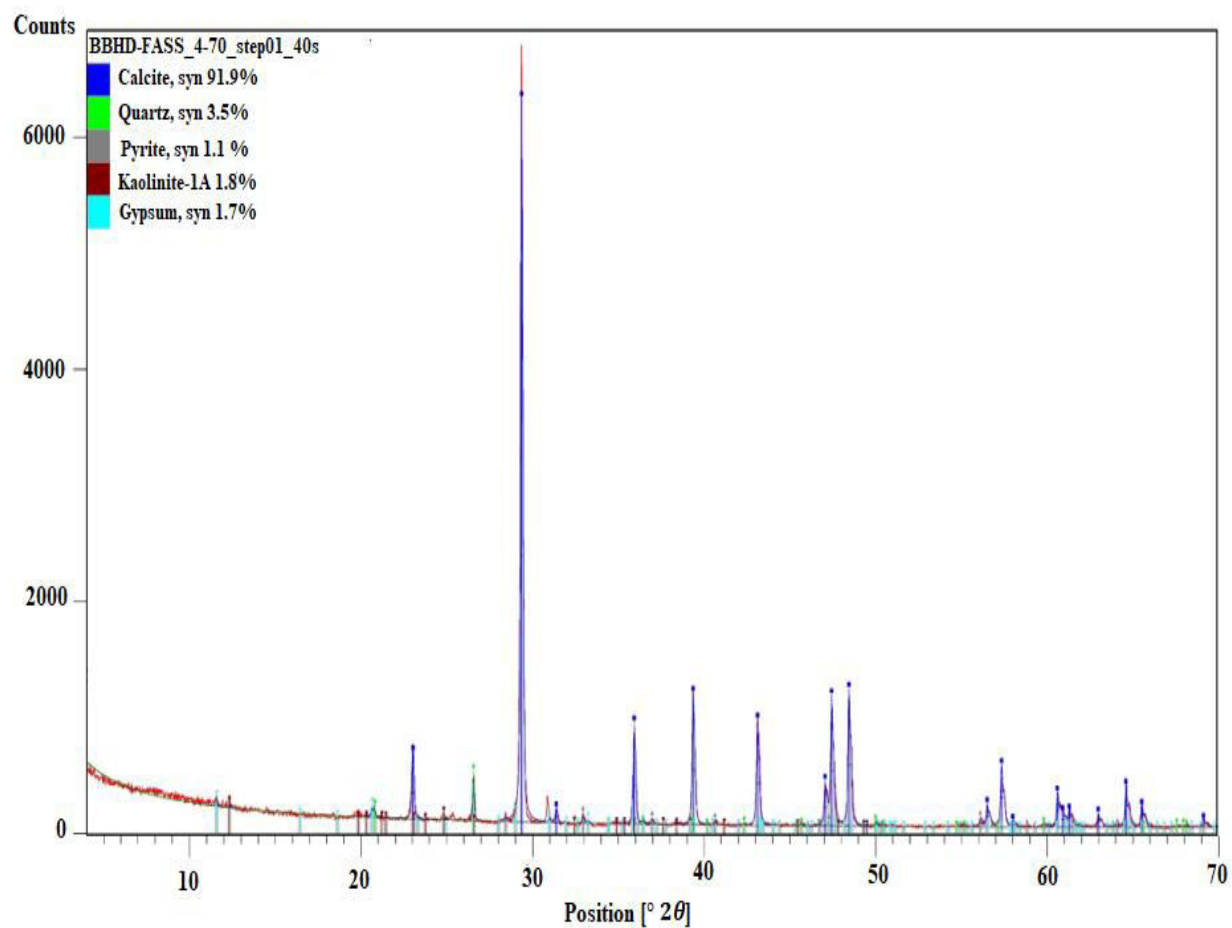


Figure 2.4:XRD spectral of mineralogical composition

2.4.2 Thermogravimetric analysis

The laboratory recreation of the geological condition of thermal maturation under a pyrolytic nitrogen atmosphere is demonstrated for a carbonate source sample at heating rate of $5^{\circ}\text{C}/\text{min}$. A superimposed time-mass-temperature plot is shown in Figure 2.5 to describe the relationship between time, mass, and temperature as a result of the thermal decomposition due to pyrolysis. In Figure 2.5, the thermogravimetric decay curve (the relationship between mass and time) is represented on the primary axis to the left while the temperature profile (the relationship between temperature and time) is represented on the secondary axis to the right. The thermal decomposition of the source rock is reflected by the gradual decrease in mass during the different temperature regimes from 40°C to 450°C . The thermogravimetric decay curve showed that the cumulative decrease in mass at the end of the thermal decomposition of the source rock at 450°C and about 1400 minutes is from 285 mg to 278.3528 mg. Given that the heating rate remain the same, the comparison of the thermogravimetric decay curve with temperature profile showed that the step-wise pattern of these plots is exactly the same until a significant deviation after 200°C . The fact thermogravimetric decay curve of the source rock does not completely follow the prescribed heating program suggest the possibility of some other significant reactions apart from the thermal decomposition. The subsequent discussions will look into this interesting observation.

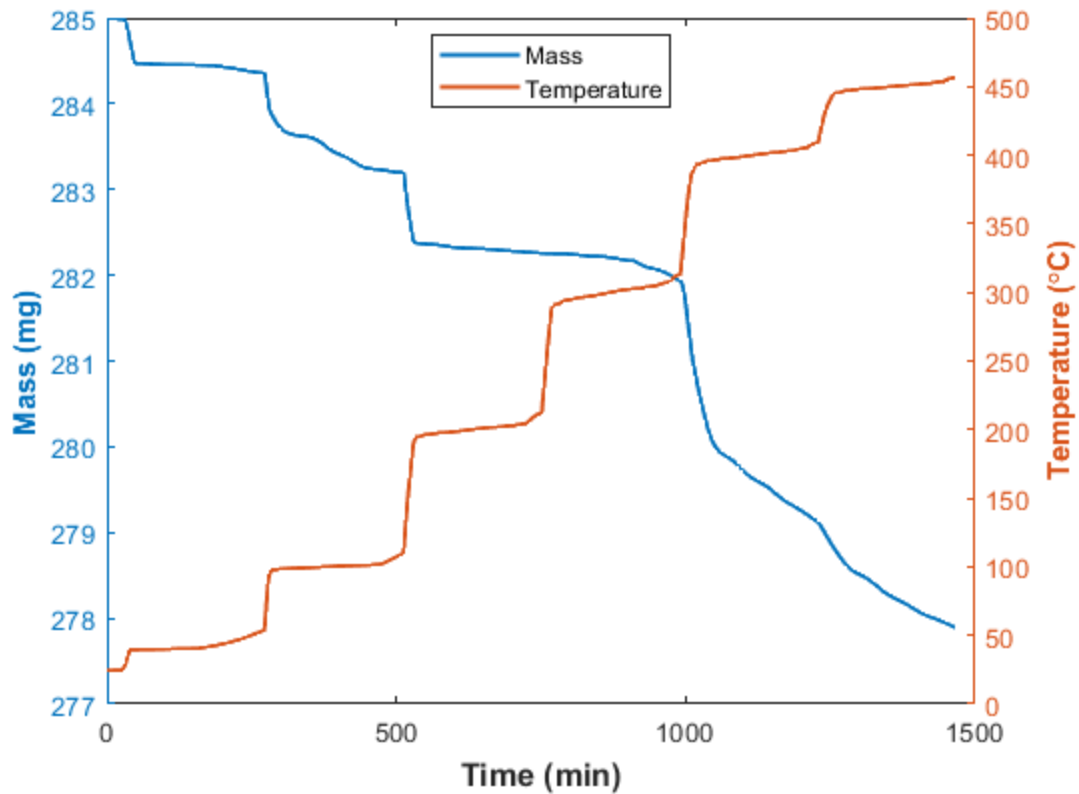


Figure 2.5: Thermogravimetric decay curves

2.4.3 Rate of conversion and maximum temperature

Before detailed analysis, the thermogravimetric decay curve as shown in Figure 2.5 is the preliminary first step of demonstrating mass-time-temperature relationship. However, the thermogravimetric decay curve has lower sensitivity to the conversion of the source rock to byproducts. A better sensitivity of the source rock to thermal decomposition can be obtained from the mass-loss rate curve plotting the rate of conversion against temperature. On the other hand, the mass loss rate of conversion-temperature plots (differentiation of the thermogravimetric data with respect to time) as shown in Figure 2.6 is obtained by applying the Savitzky-Golay smoothing filters (Press and Teukolsky, 1990) to get rid of random noise due to numerical differentiation. It is important to

mention that the raw thermogravimetric data has been used for the rest of the analyses without applying smoothing algorithm. The relationship between the rate of mass loss and temperature as shown in Figure 2.6 generally has six distinct temperature regimes: (1) 40°C ; (2) $60 - 100^{\circ}\text{C}$; (3) $100 - 200^{\circ}\text{C}$; (4) $200 - 300^{\circ}\text{C}$; (5) $300 - 400^{\circ}\text{C}$; (6) $400 - 450^{\circ}\text{C}$ respectively. The peak height is the response of the rate of mass loss and the corresponding peak width or peak area is related to the extent at which the rate of mass loss is observed. The temperature corresponding to the peak height is the peak temperature or the maximum temperature T_{max} . An important observation is that the peak height increased relatively from the temperature regime of 40°C until 200°C , then it is relatively zero from $200 - 300^{\circ}\text{C}$, afterwards, the peak height increased from $300 - 400^{\circ}\text{C}$ and finally decreased rapidly from $400 - 450^{\circ}\text{C}$. While the heating rate remain the same throughout the thermal maturation process, the relatively near zero rate of mass loss after 200°C is somewhat unexpected. Published research explained that this phenomenon is due to the occurrence of different simultaneous reactions. Perhaps, the thermal decomposition is less dominant in this regime or thermal decomposition at other temperatures have been activated by catalytic minerals.

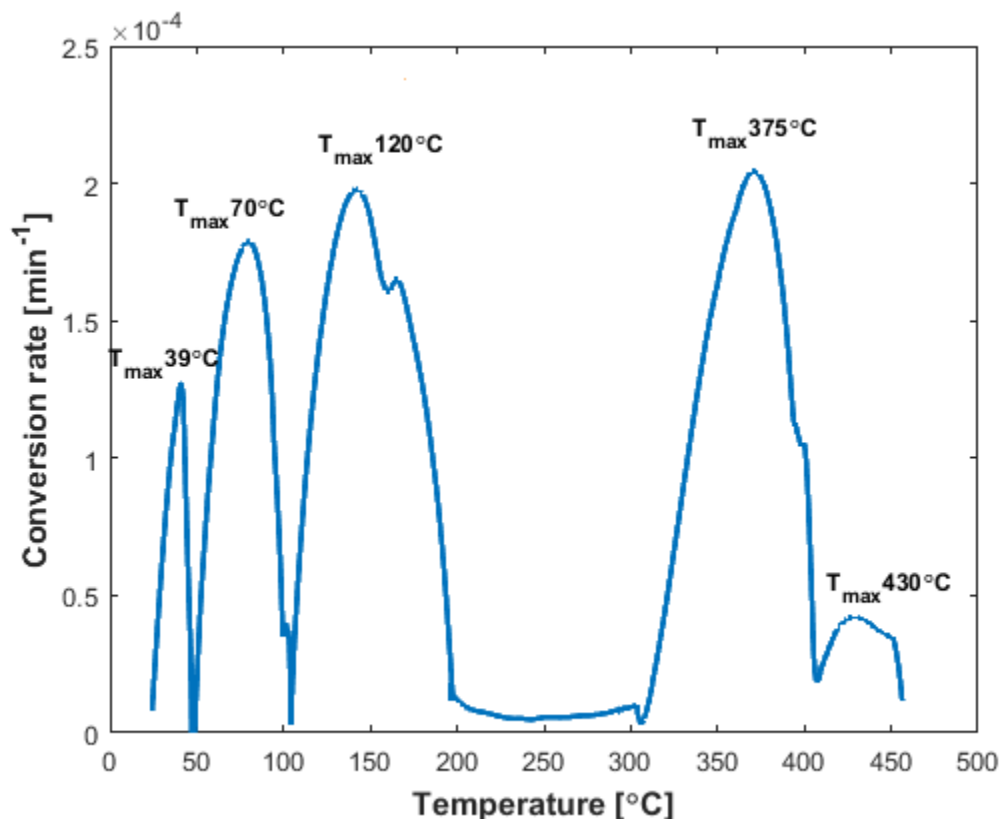


Figure 2.6: Mass-loss rate curve

2.4.4 Reaction Mechanism

The different segments on the mass-loss rate curve indicate that a one-step fit-for-all kinetic model may be insufficient to describe the mechanism of thermal maturation of the source rock. Thus, the overall rate of mass loss can be described as a linear combination of different independent reactions for each temperature regime. In order to further investigate the possible mechanism of reaction, a first-order model was applied on the basis of Coats-Redfern method (Coat and Redfern, 1964). With the assumption that the order of reaction is constant throughout the reaction, the thermogravimetric decay curve were converted to kinetic parameters by least squares regression fit shown in Figure 2.7. It is interesting to observe that the peak height of the rate of mass loss curve in Figure 2.6

is well correlated with the coefficient of determination for the kinetic parameters. Specifically, at 250°C and 450°C the coefficient of determinations is relatively lower and the corresponding peak height is relatively lower as well. The corresponding kinetic parameters including activation energy, pre-exponential factor and rate constant respectively were listed in Table 2.2. An observation of Table 2.2 showed that from the onset of the thermal maturation at 40°C , the kinetic parameters were not constant; the continuous variation of kinetic parameters (activation energy, pre-exponential factor and rate constants) in the same manner of decrement and increment respectively were observed. For example, the plot of activation energy against temperature in Figure 2.8 clearly showed that the activation energy distribution obeys a bimodal distribution. The two inflection points of the bimodal distribution are possible indications of the shift in reaction mechanism. This further suggest the possibility of other concurrent reactions taking place during the thermal maturation of sample.

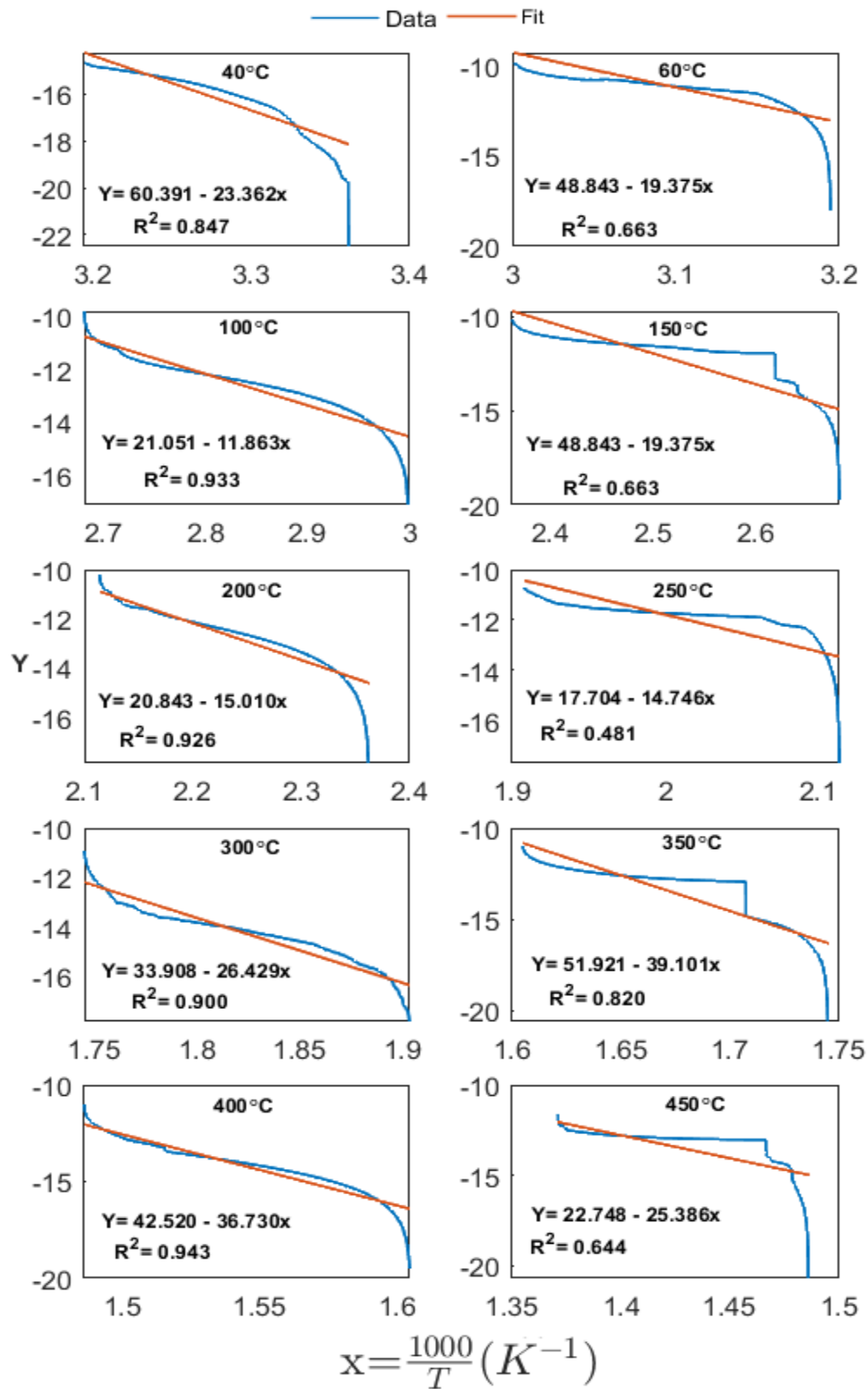


Figure 2.7: First-order reaction mechanism for determination of kinetic parameters

Table 2. 3: Kinetic parameters of first-order reaction

T °C	E(kJ/mol)	A(min ⁻¹)	k(min ⁻¹)
40	194.23	1.97x10 ²⁸	1.83x10 ²⁸
60	161.09	1.58x10 ²³	1.49x10 ²³
100	98.631	8.23x10 ¹⁰	7.97x10 ¹⁰
150	136.77	3.39x10 ¹⁴	3.64x10 ¹⁴
200	124.80	8.46x10 ¹⁰	8.19x10 ¹⁰
250	122.60	3.60x10 ⁹	3.50x10 ⁹
300	219.73	7.03x10 ¹⁶	6.72x10 ¹⁶
350	325.09	6.92x10 ²⁴	6.50x10 ²⁴
400	305.38	5.37x10 ²⁰	5.09x10 ²⁰
450	211.06	9.91x10 ¹¹	9.28x10 ¹¹

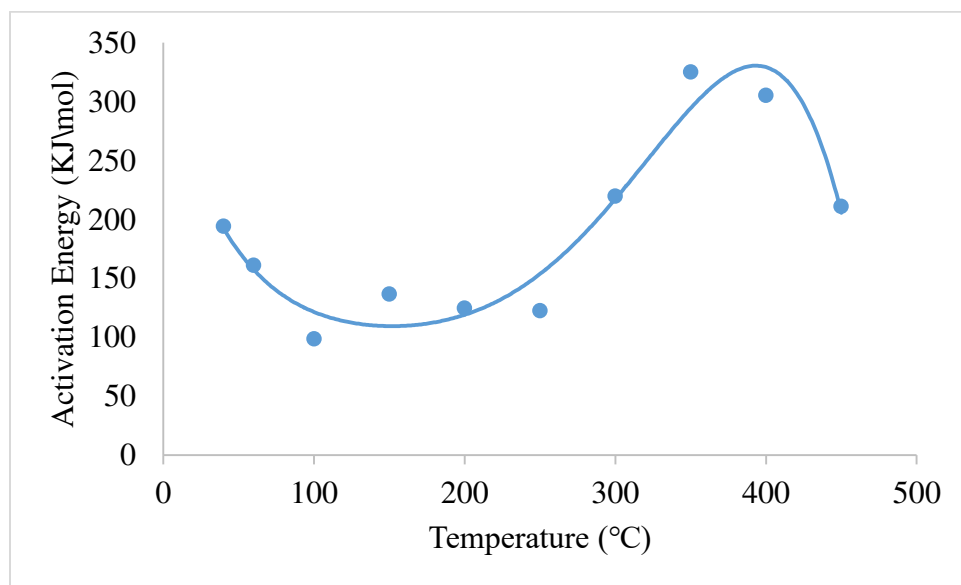


Figure 2.8: Bimodal distribution of activation energy

2.4.5 Effects of catalytic minerals

Catalytic materials are well-known to undoubtedly improve reaction kinetics by lowering the energy barriers of chemical reactions. However, the role of the mineral constituents of source rocks as possible sources of natural catalyst that could influence the thermal

maturation of source rocks has been questionable and rarely investigated in the past (Jacques Connan (2), 1976; Pepper and Corvit, 1995). Possible catalytic elements and minerals to activate thermal decomposition of source rocks include sulphur, iron, cobalt, nickel, carbonate, clay and iron-bearing minerals respectively (Hu et al., 2014; Ma et al., 2018; Pan et al., 2008). Carbonate minerals such as calcite and dolomite may inhibit the generation of methane (Pan et al., 2008). Laboratory investigation suggests that pyrolysis in the presence of minerals show decreasing gaseous hydrocarbon generated in order of montmorillonite, gypsum, kaolinite and calcite respectively (Hu et al., 2014). A more recent study show decreasing gaseous hydrocarbon generation during pyrolysis in the following minerals iron, smectite, pyrite and mixed mineral (0.5% iron +10% iron sulphide+30% smectite) (Ma et al., 2018). For the present study, the occurrence of iron, sulphur, calcite, clay (kaolinite), pyrite and sulphur as revealed by EDX and XRD analysis is a reassuring evidence that the catalytic effect of inorganic constituent of the investigated source rock may likely influenced the thermal maturation process.

2.4.6 Cumulative gas production and implication for maturity

The monitoring and analysis of hydrocarbon generation from source rocks cannot be predicted completely from thermogravimetric measurements. The coupling of mass spectrometer during the stage heating of the carbonate source rock gives room for the quantitative analysis of the gaseous by-products of thermal decomposition. It is beyond the scope of this work to go into the detailed analysis of all the evolved gases. The three main gassy by-products of interest to maturation studies are the produced water vapor, methane and carbon dioxide as shown in Figure 2.9. Based on the well accepted concept theory of hydrocarbon generation upon thermal maturation, it is expected that the release

of methane is due to the thermal decomposition of kerogen, the release of carbon dioxide may be due to the thermal degradation of calcium carbonate and the water vapor is due to the clay bound water or as a results clay mineral transformation from one type to other due to the heating effect. As shown in Figure 2.9, it is clearly seen that that the produced carbon dioxide is the least and remains relatively constant with time and temperature throughout the thermal reaction. This may indicate that the carbon dioxide is mainly produced from carbonate mineral and not from the reaction of water and methane. The high calcite content of 91.1% based on mineralogical analysis provide further supporting evidence to reach this conclusion and validate the reliability of this interpretation. Conversely, with increasing thermal maturation, water production depletes with time and temperature. The opposite trend is observed for methane production, that is, methane continues to increase with time and temperature. This give a clear indication of the generative potential of methane gas for the investigated source rock. The comparison of the relative proportion of produced carbon dioxide, methane and water offers one possibility of interpreting maturity.

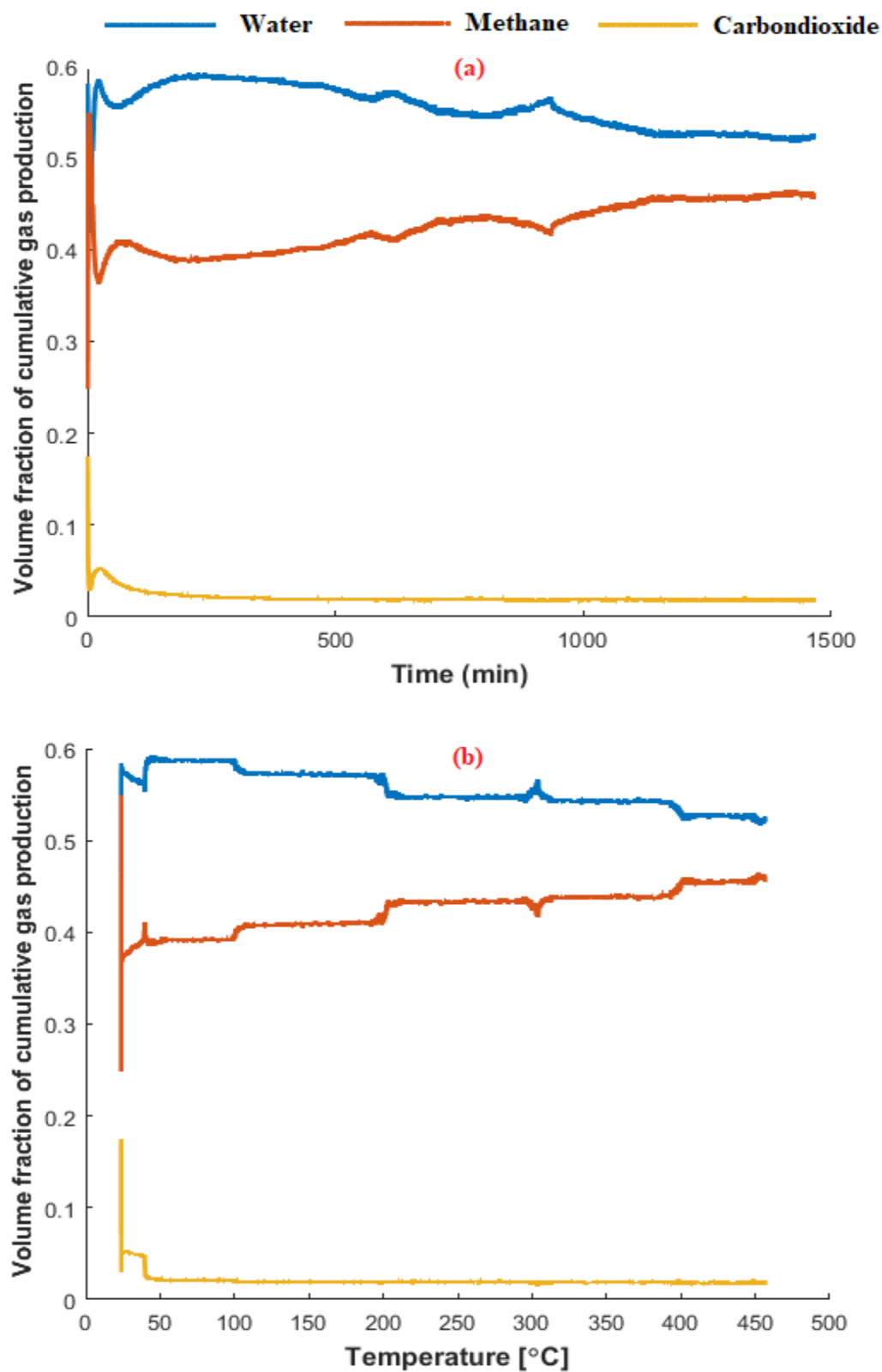


Figure 2.9: Cumulative gas production as function of (a) time and (b) temperature

2.5 Summary and Conclusions

An integrated approach of four experimental techniques including thermogravimetric, mass spectrometric, elemental and mineralogical analyses have been adopted to characterize the complex mechanism of the fluid-release-kerogen-mineral thermal maturation of carbonate source rock. The thermal maturation of the carbonate source rock to gaseous hydrocarbon is conducted under a nitrogen atmosphere and the following conclusions can be drawn:

- The trend in the variation of mass decay upon pyrolysis deviate from the prescribed temperature profile after 200 °C. The rate of mass loss plot showed six distinct temperature regimes and further suggest that the temperature regime from 200-250 °C is thermally insensitive to rate of conversion. Both the thermogravimetric and mass-loss rate curves are indicative of mineral catalysis influencing thermal decomposition at different temperature.
- First-order reaction kinetics suggest that the activation energies are different and dependent on the rate of conversion. Specifically, the low coefficient of determination of activation energies at 250 °C and 450 °C are well correlated with their relatively small peak height from the rate of mass plot curve are 0.481 and 0.644 respectively. The bimodal distribution of activation energy provides a mechanistic explanation for the possible shift in reaction mechanisms.
- EDS and XRD analyses further provide reassuring evidence for the presence of the catalytic mineral and element such as gypsum, pyrite, kaolinite and iron respectively. Mass spectrometric analysis supported that thermogenic generation

of carbon dioxide, methane and water is feasible for the investigated carbonate source rock.

- The water and methane generated decreases and increases respectively with thermal maturation whereas carbon dioxide remain fairly constant. This further suggest that the evolution of carbon dioxide is probably attributed to the carbonate content of the source rock and it is not due to reaction of water and methane.
- The increasing volume fraction of methane is an indication of thermal maturity and gas generative potential of the source rock. The volume content of carbon dioxide, methane and water are 2%, 46% and 52% respectively.

2.6 References

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CHAPTER 3

Non-isothermal sorption of gas-rich source rock at elevated temperature and pressure

To be submitted Published Paper in Journal of Natural Gas and Engineering

Abstract

Sorption is a well-established technique for gas shale characterization and evaluation. However, laboratory measurement is currently limited to rock powders and isothermal condition; both of which do not reflect the subsurface settings of source rocks. For example, at a temperature well above that at which gas evolution occurs, isothermal sorption experiment is inadequate to capture the dependence of both maturation and sorption on temperature. As far as is known, non-isothermal sorption experiment of gas shale has not been attempted previously although it is ideally suited to investigate the temperature-dependent behavior of maturation and sorption over geological time. We present for the first time, temperature programmed methane sorption experiments on millimeter-sized core plugs under non-isothermal condition at a rate determining step of 5 °C/min at temperatures between 40 and 400°C and pressures up to ~80 bar. For comprehensive characterization, mineralogy, low-pressure isothermal Nitrogen adsorption, thermogravimetric and gas evolution by mass spectrometer are also measured. The more representative data derived from non-isothermal heating cycle show that sorption capacity of methane increases monotonously as a function of temperature. This new experimental finding is explained by three mechanisms: intrinsic coupling of maturation and sorption, phase change and pore filling. The findings from this work

provide new perspective to better understand and predict high temperature sorption property of gas shale which can also be extended to coal. In addition, this study offer promise for field application of sorption measurement on drill cuttings which are more representative than rock powders.

3.1 Introduction

Temperature dependent behavior is well-known to be exhibited by many materials and the understanding of this phenomenon is important in many natural and technological processes. In the field of geology, for example, an important thermal effect of interest is the ability of some rocks to generate liquid and gaseous hydrocarbon upon heating. The rocks which exhibit this characteristic are referred to as source rocks. Uniquely among the sedimentary rocks of the petroleum system, organic- and gas-rich shales and mudrocks have been proven to be geologically satisfactory as source rocks. One of the key defining differences between the source and reservoir rock is attributed to the kerogen and bitumen composing the organic matter fraction of the source rocks. The kerogen component can be classified as reactive when oil, methane and solid residues are the three by-products or inert when graphite and methane are the two by-products at high temperature (Pepper and Corvit, 1995). In contrast to the characterization of reservoir rocks, there has been emerging interest in understanding brittleness, TOC, rock-fluid interactions, thermal maturation, sorption capacity of organic- and gas-rich source rocks (Adeyilola et al., 2020; Afagwu et al., 2021; He et al., 2021; Kim et al., 2021; Lawal et al., 2021, 2020b, 2020a, 2019b, 2019a; Lawal and Mahmoud, 2020; Liu et al., 2021; Onawole et al., 2021; Xie et al., 2021; Xu, 2020; Xu et al., 2021; Zhao et al., 2017).

Unlike other rocks properties of source rocks, maturation and sorption are highly temperature sensitive.

Thermal maturation controls the rate of hydrocarbon generation; a complex geological process (Ungerer and Pelet, 1987). For simplicity, it is generally modelled from reaction point of view as solid-state irreversible decomposition reaction that conform to: $AB_{solid} \rightarrow A_{solid} + B_{fluid}$ (Coat and Redfern, 1964). Further simplification is imposed by assuming that thermal maturation is a first-order chemical reaction (Coat and Redfern, 1964; Rajeshwar, 1981; Rajeshwar et al., 1979; Ungerer and Pelet, 1987). According to petroleum geoscientists, previous research efforts revealed that the mechanism of thermal maturation is controlled by the synergy of different factors such as burial heating, geothermal gradient, time, temperature, pressure, heating rate, mineral catalysis, chemical kinetics, kerogen types and composition (Hood et al., 1975; Luo and Vasseur, 1996; Pepper and Corvit, 1995). On a temporal and spatial scale, the aforementioned factors can be highly variable on a basin-wide scale or from one source rock to another for a specific basin. This is because, over geological time, the sedimentary basins that serve as the repository of the source rocks are formed differently. From mechanistic point of view, the dependence of thermal maturity on pressure is assumed to be negligible and the prediction of the maturity of the source rock is mainly constrained to time and temperature (Pepper and Corvit, 1995; Waples, 1980). Accordingly, the concept of time and temperature can be used to lab or field evaluation of thermal maturity. On a field scale, the concept of formation age, present day temperature and effective heating time has been used to interpret the thermal maturity of source rocks (Hood et al., 1975; McCartney and Teichmüller, 1972; Pepper and Corvit, 1995; Teichmüller, 1986).

Alternatively, petrographic analysis of maceral group has established reflectance measurement of vitrinite as the standard measure of thermal maturity (Bernard et al., 2012).

In addition to the organic matter enrichment, source rocks can be further characterized as fine-grained rocks, the unique geological feature that reflects their low porosity and nano-Darcy permeability. The resulting pore space of source rocks is said to be dominated by micrometer-to-nanometer-scaled pores (Bahadur et al., 2018; Clarkson et al., 2013; Curtis et al., 2012; Goral et al., 2019; Wang et al., 2016; Zhang et al., 2012). In line with sized-based nomenclature of IUPAC (International Union of Pure and Applied Chemistry), the subdivision of pores with respect to diameter is necessary and the generally accepted types are: macro (>50 nm), meso (2-50 nm) and micro (< 2 nm) respectively (Thommes et al., 2015a). In the context of source rock geology, the pores are randomly distributed and concentrated in the mineral and organic matter fractions (Bahadur et al., 2018; Clarkson et al., 2013; Curtis et al., 2012; Goral et al., 2019; Wang et al., 2016; Zhang et al., 2012). Thus, it is more practical and convenient to classify pores with respect to their mineral fractions as mineral and organic hosted pores respectively (Loucks et al., 2010). With these essential characteristic properties, source rocks would not be able to sustain the predominantly pore storage mechanism found in conventional reservoir rocks such as sandstone and carbonate. Consequently, the fluid trapping mechanism is primarily accomplished through sorption in which hydrocarbon can be stored as liquids or gases in condensed phase (Heller and Zoback, 2014; Lu et al., 1995). In contrast to conventional reservoirs with relatively high porosity, the classical equation of hydrocarbon volume estimation based on the effective porosity of the connected pore space is no longer valid

for source rocks. Instead, the concept of sorption has been widely applied to account for the formation evaluation of the gas-in-place (Curtis et al., 2012; Lu et al., 1995). It is noteworthy that the unique sorption capacity varies with source rocks such as coal, shale and mudrocks. For example, the contribution of sorbed gas to the original-gas-in-place is at least 60-80%, 50% and 20% for the Lewis, Devonian and Barnett shale respectively (Lu et al., 1995; Tian et al., 2016; Xiong et al., 2017).

In studying the sorption mechanism of shale source rocks, some previous experiments established that, statistically significant positive correlation exist between sorption capacity and organic matter measured in the form of total organic carbon (Guo et al., 2015; Ji et al., 2015; Löhr et al., 2015; Lu et al., 1995; Zhang et al., 2012). On the basis of kerogen types, it is reported that sorption capacity showed decreasing trend with organic matter in order of type III, type II and type I kerogen respectively (Zhang et al., 2012). The possible explanation of this effect have been attributed to different factors among researchers. Based on the maceral group, this effect has been attributed to the relative abundance of vitrinite (Zhang et al., 2012). Some other authors provide the alternative explanation that the chemistry of the organic matter such as maturation, types and TOC is not responsible for this effect but the geometrical characteristics of the pore size (Gasparik et al., 2014; Li et al., 2017). Furthermore, aromaticity indicates high maturity, suggesting that it account for the increase in sorption capacity (Bernard et al., 2012). The phenomenon of gas sorption is not only restricted to the organic matter fraction of the source rocks. Further experimental studies revealed that the inorganic minerals, particularly clay minerals also play critical role in the gas sorption mechanism of clay rich organic shales. Experimental information on methane sorption capacity for

different clay types suggests an increasing trend in the order of illite, chlorite, kaolinite, illite/smectite and montmorillonite (Ji et al., 2012). In general, the relative experimental comparison of methane sorption is highest for kerogen followed by shale and clay respectively (Ji et al., 2012; Lu et al., 1995; Zhang et al., 2012).

Besides mineralogical constituents, e.g. kerogen and clay, the moisture state of the source rock usually plays significant role with regards to the overall sorption capacity. It is well reported that some amount of moisture can significantly affect the total sorption capacity (Ji et al., 2012; Lawal et al., 2019b; Ross and Marc Bustin, 2009). This phenomenon is normally understood as moisture effect, in which the moisture adhering to the surface of the sample, particularly for the inorganic minerals, may further limit gas sorption capacity (Ji et al., 2012; Lawal et al., 2019b; Ross and Marc Bustin, 2009). Molecular modelling studies revealed that the adsorption of water on pure aromatic kerogen surface is not a favorable thermodynamic process (Lawal et al., 2019b). Experimentally, the significance of pre-adsorbed water on methane sorption has been demonstrated for Haynesville and Bossier at 32 and 50% water saturation respectively (Merkel et al., 2015). In that study, it is stated that weak methane sorption of illite may be attributed to the increase in moisture content. Under the dry state condition of the sample, the sorption capacity of kaolinite has been reported to be less than that of illite and montmorillonite (Ross and Marc Bustin, 2009).

Considering the wide range of geological and environmental conditions at which different source rocks are encountered in the sedimentary basin, the mechanism of sorption can be further dictated by the physical state of pressure (P) and temperature (T). In general, sorption experiments can be reported in principle with reference to pressure as

isobar or with respect to temperature as isotherm (Ranke and Joseph, 2002). However, in practice, sorption experiments are usually reported as isotherm. To study this effect, P–T characteristics of gas sorption can be conducted on source rocks in the lab under low P-T and high P-T condition respectively. Two illustrative examples are the low pressure nitrogen sorption below room temperature (Liu et al., 2021; Mastalerz et al., 2017) and high pressure sorption of CO₂ and CH₄ at or above room temperature (Gasparik et al., 2014, 2013; Heller and Zoback, 2014; Ji et al., 2012; Khosrokhavar et al., 2014; Liu et al., 2013; Lu et al., 1995; Rexer et al., 2013; Zhang et al., 2012). Similar to thermal maturation experiments, the effect of temperature on gas sorption can be investigated under isothermal and non-isothermal heating experiment respectively. The former is independent of time and the latter is dynamically controlled by a rate-determining step. For isothermal sorption, a constant temperature is applied for each measurement whereas non-isothermal sorption is the special name for sorption measurement carried out on the same sample such that temperature is not constant but increases linearly according to a specific heating rate. Perhaps for experimental convenience, isothermal condition is generally considered as evidenced in the literature. With respect to thermal maturation, the non-isothermal technique is said to be geologically significant to approximate the condition of thermal maturation processes of active sedimentary shale basins (Rajeshwar et al., 1979; Rajeshwar and DuBow, 1980). On the other hand, the isothermal approach is prone to significant error that need to corrected especially during the final stage of the heating experiment (Rajeshwar et al., 1979; Rajeshwar and DuBow, 1980). Using isothermal sorption measurements, the early and recent experimental works suggest that the methane sorption capacity of the investigated source rocks in powdery form decreases

with temperature (Gasparik et al., 2014, 2013; Heller and Zoback, 2014; Ji et al., 2012; Khosrokhavar et al., 2014; Liu et al., 2013; Lu et al., 1995; Rexer et al., 2013; Zhang et al., 2012). Seldom research works considered non-isothermal sorption, which is, however, very important for understanding the sorption mechanism of highly temperature-dependent geological adsorbents such coal and shale source rocks.

The distinction between thermal maturation and sorption may appear to be well defined, but as no sorption can occur without hydrocarbon generation through thermal maturation. The fundamental research question is that are both processes somewhat coupled. This study unravels this question using non-isothermal laboratory heating technique, a laboratory condition which better simulate subsurface settings of sedimentary basins. Accordingly, methane sorption on shale gas source rock under high temperature and pressure conditions is investigated. In addition, mineralogy, low-pressure Nitrogen adsorption, thermogravimetric and gas evolution by mass spectrometer are conducted for comprehensive characterization. This study will provide new insights into sorption capacity of gas shale as well as to establish a framework for future work on non-isothermal sorption of other geomaterials such as coal.

3.2 Theoretical Background

Sorption is a generic term embracing absorption and adsorption as a measure of uptake (Sing et al., 1985; Thommes et al., 2015b). The phenomenon of sorption arises from the uptake of molecules or atoms accumulating in one or more layers on a solid (adsorbent) in contact with a fluid (adsorbate). When the molecules dissolved in the solid, the process of sorption is referred to as absorption, otherwise, it is called adsorption. The term

sorption is commonly used when it is difficult to distinguish between absorption and adsorption. Experimentally, the phenomenon of sorption can be conveniently studied by measuring two related quantities: adsorption and desorption. The latter can be readily understood as the reverse process of the former. The strength of adsorption can be further classified as physical and chemical sorption respectively depending on the energy of interaction.

From measurement point of view, the amount of sorption or uptake cannot be measured directly. Instead, it is computed from the experimental results determined in terms of two physical variables: volume, pressure and mass. For the former, the corresponding measurement technique is referred to as volumetric method and for the latter two, they are called manometric and gravimetric method respectively (Busch and Gensterblum, 2011). Because thermal decomposition and uptake can be “measure” gravimetrically by change in mass, gravimetric technique provides a sensitive and convenient means for temperature-controlled sorption experiments under isothermal and non-isothermal conditions. The dual purpose of gravimetric method is an obvious advantage of gravimetric sorption analyzer for non-isothermal studies over volumetric and manometric methods. The details of comparison of these methods is beyond the scope of this study, emphasis is only given with respect to non-isothermal condition. In what follows, the governing equation of gravimetric method is presented.

By convention, the amount of sorption can be generally computed as excess or absolute sorption (Rexer et al., 2013). For gravimetric method, buoyancy effect arising from the apparent mass loss of the sample as a function of pressure and temperature is usually considered as non-sorption case and it is computed according to equation 1 (Busch and

Gensterblum, 2011; Khosrokhavar et al., 2014). Similarly, the mass change due to uptake can be expressed by equation 2. The additive effect of buoyancy and uptake is referred to as the sorption case and it is expressed by equation 3. The overall sorption expressed in excess mass is given by equation 4. According to the Gibb's definition, the relationship between the excess and absolute sorption is given by equation 5. Accordingly, the absolute sorption can be approximated by the excess sorption if the last term of equation 5 can be reasonably assumed to be negligible (Busch and Gensterblum, 2011).

$$\Delta m_b = m_s - V_s \rho_{gas}(P, T) = m_s - \frac{m_s}{\rho_s} \rho_{gas}(P, T) = m_s \left(1 - \frac{\rho_{gas}(P, T)}{\rho_s} \right) \quad (1)$$

$$\Delta m_u = m_a - V_a \rho_{gas}(P, T) = m_a - \frac{m_a}{\rho_a} \rho_{gas}(P, T) = m_a \left(1 - \frac{\rho_{gas}(P, T)}{\rho_a} \right) \quad (2)$$

$$\Delta m_{sorb} = m_s \left(1 - \frac{\rho_{gas}(P, T)}{\rho_s} \right) + m_a \left(1 - \frac{\rho_{gas}(P, T)}{\rho_a} \right) \quad (3)$$

$$m_{excess} = \Delta m_{sorb} - \Delta m_b = m_a \left(1 - \frac{\rho_{gas}(P, T)}{\rho_a} \right) \quad (4)$$

$$m_{abs} = m_{excess} + V_a \rho_{gas}(P, T) \quad (5)$$

where Δm_b , Δm_u , Δm_{sorb} , is change in mass during buoyancy, uptake and the combined effects of buoyancy and uptake respectively; The letter m, V, and ρ denotes mass, volume and density respectively, while the subscript a, s, abs, excess, gas, denote the adsorbed phase, sample, absolute, excess and gas respectively.

For thermal maturation, the mass loss during thermal decomposition is typically referred to as thermogravimetric data and can be modeled by equation 6 (Atiqullah et al., 2014; Coat and Redfern, 1964). With respect to the operating environment, laboratory heating

experiment can be further subdivided into two categories as: (1) combustion, in the presence of air and (2) pyrolysis in the absence of air. The commercially available Rock-Eval pyrolysis for source rock evaluation is a thermogravimetric technique that combine combustion and pyrolysis (Lawal et al., 2019a) .

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right)(1 - \alpha)^n \quad (6)$$

where t , T , R , A , E_a α are time, temperature, gas constant, Arrhenius factor, activation energy and fraction of mass loss. The fraction of mass loss is defined by equation 7.

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \quad (7)$$

where m_o , m_t and m_f is the mass before, during and after the thermal decomposition process.

3.3 Experimental apparatus and methods

In this section, the laboratory apparatus and experimental protocol conducted on the investigated sample is described. The subdivisions of the experiment are as follow: rock sample description and preparation; experimental apparatus; isothermal nitrogen sorption measurement; non-isothermal methane sorption measurement; thermogravimetric measurement and mass spectrometric measurement.

3.3.1 Rock sample description and preparation

The sedimentary source rock is of Jurassic-age and represent an important gas producing formation in the Jafurah basin of Saudi Arabia. Representative samples of the source

rock have been collected at reservoir condition and have been previously described as part of a comprehensive NMR study for surface relaxivity measurement. By visual inspection, sample is fissile, black in color and clearly stains one's hand or white paper towel upon touching. The very black color of the sample reflects the potential for high organic matter content.

The black fissile subsurface sample is firstly crushed in a grinding machine into cm-size fragments. Then, intact miniaturized core plugs of mm-size (3-4mm) is prepared by successive sieving and hammering for gas sorption and thermogravimetric measurements. Some duplicate of the crushed sample was further finely-powdered for composition analyses. The composition of the sample is characterized on elemental and mineralogical basis using semi-quantitative analysis from XRF and XRD respectively. The organic matter content is characterized in term of total organic content (TOC) derived from Rock-Eval pyrolysis. The step-by-step experimental procedures have been discussed elsewhere (Lawal et al., 2020a, 2019a).

3.3.2 Experimental apparatus

A pressure and temperature controlled apparatus as shown in Figure 3.1 is equipped with heater (water bath and furnace), microbalance and mass spectrometer. The water bath and furnace can heat up the reaction chamber up to 85 and 500°C respectively. In this apparatus, the experiments can be carried out at a specified rate determining step for non-isothermal sorption and thermogravimetric studies based on the governing principles earlier discussed. A block of mm-sized intact rock sample can be pre-weighted into sample container and suspended by Nichrome hang-down and Tungsten wire inside the

right-hand side reactor containing the heating element. The left-hand reaction chamber contains a counter weight without the furnace. The initial condition of the experimental set up is to eliminate the effect of moisture or gases that could have adsorbed on the sample.

3.3.3 Isothermal nitrogen sorption measurement

For isothermal experiment, sorption experiments are performed on different samples, that is, one sample for each temperature step. Isothermal nitrogen sorption experiment is typically conducted under low pressure and temperature condition. In order to study the effect of temperature, two different intact source rock samples of 3-4mm in size are further pre-heated as part of the pretreatment protocols at two different temperatures, below and above 100°C before sorption measurement. Duplicates of the samples for nitrogen sorption is used for non-isothermal methane sorption and thermogravimetric analysis.

3.3.3 Non-isothermal methane sorption measurement

Unlike the routine isothermal methane sorption experiments in which temperature is maintained constant, non-isothermal methane sorption under high pressure and temperature setup is close to the natural condition of sedimentary source rocks. For this experiment, the sample is heated at rate of 5°C/min for the temperature steps between 40 and 400°C, simultaneously the sorption of methane on the sample is measured. The sample is properly pretreated to ensure that possible gases and/or water sorbed on the sample is not measured.

3.3.4 Thermogravimetric measurement

To decouple the effect on sorption, non-isothermal heating experiment at the rate of 5°C/min for the temperature steps between 40 and 450°C is also conducted on another duplicate sample. The very small change in mass of the rock sample was determined by a microbalance with detection limit of 0.1 μ g.

3.3.5 Mass spectrometric measurement

In combination with the mass balance, we also used a mass spectrometer to continuously monitor and detect the evolution of gases during the non-isothermal heating experiment. In principle, the gas to be detected will correspond to specific spectrum that will be captured as charge ions and computed as partial pressure with the use of Faraday bucket.

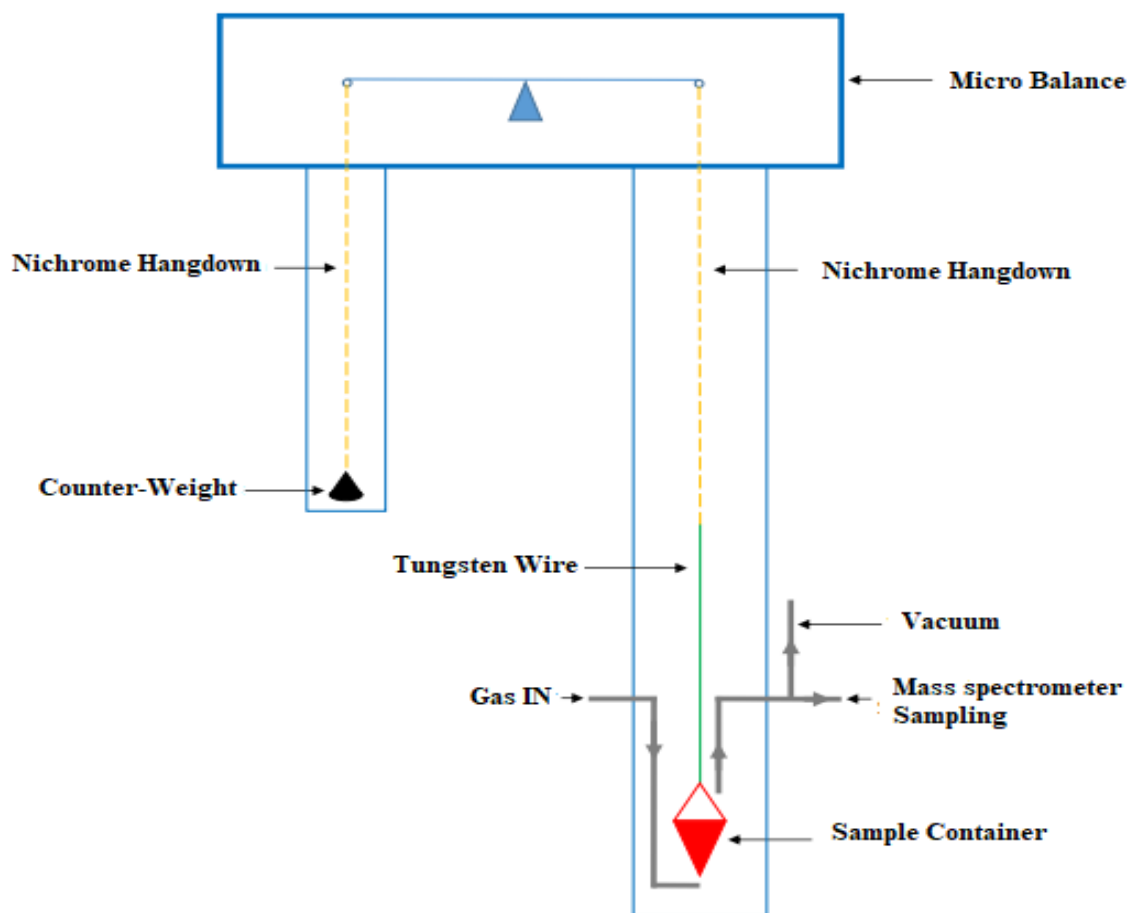


Figure 3.1: Schematic of apparatus for sorption measurement

3.4 Results and Discussion

3.4.1 Mineralogy and elemental composition

The geochemical data from the results of XRD analyses revealed that the highest fraction of the inorganic mineral content is calcite. The other main minerals include: quartz, clay and pyrite. Leco analysis further showed that the organic matter content predicted by TOC is high. The source rock composition is given in Table 3.1 and also in Figures 3.2 and 3.3 respectively.

Table 3. 1: Mineralogical and Elemental Composition of source rock

Mineralogy	(wt.%)	Elements	(wt.%)	Organic content	(wt.%)
Calcite	91.9	O	48.5	TOC	12
Quartz	3.5	Al	3.6		
Kaolinite	1.8	Si	7.6		
Gypsum	1.7	S	3.2		
Pyrite	1.1	K	0.8		
		Ca	34.7		
		Fe	1.6		

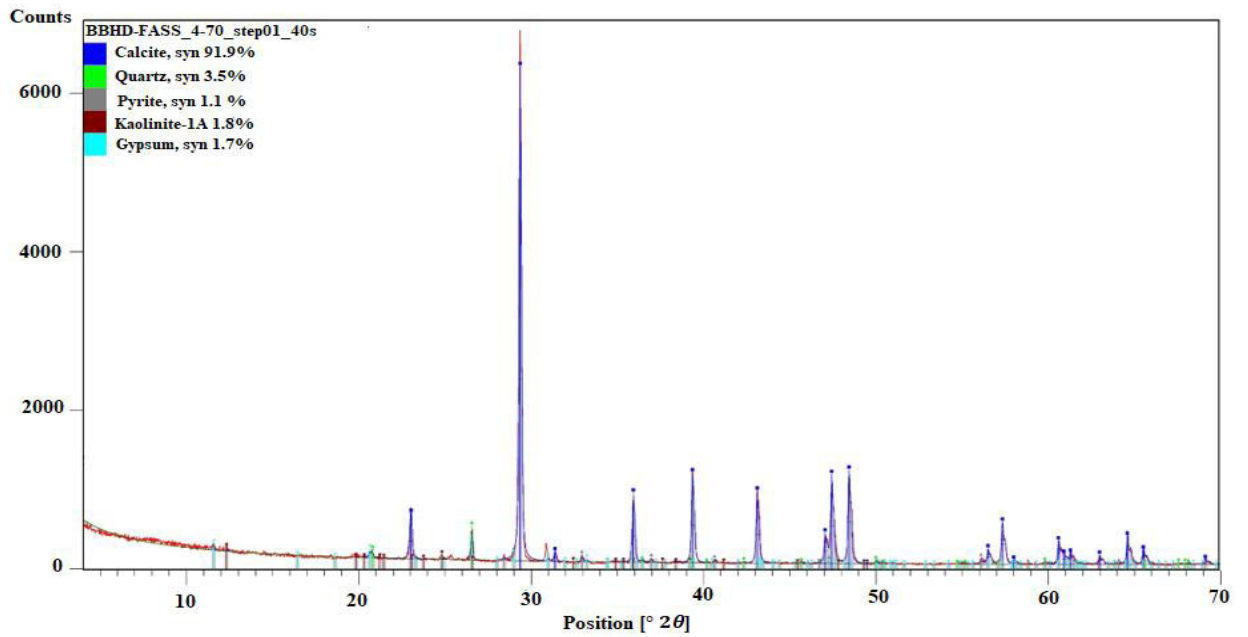


Figure 3.2:XRD spectral of mineralogical composition

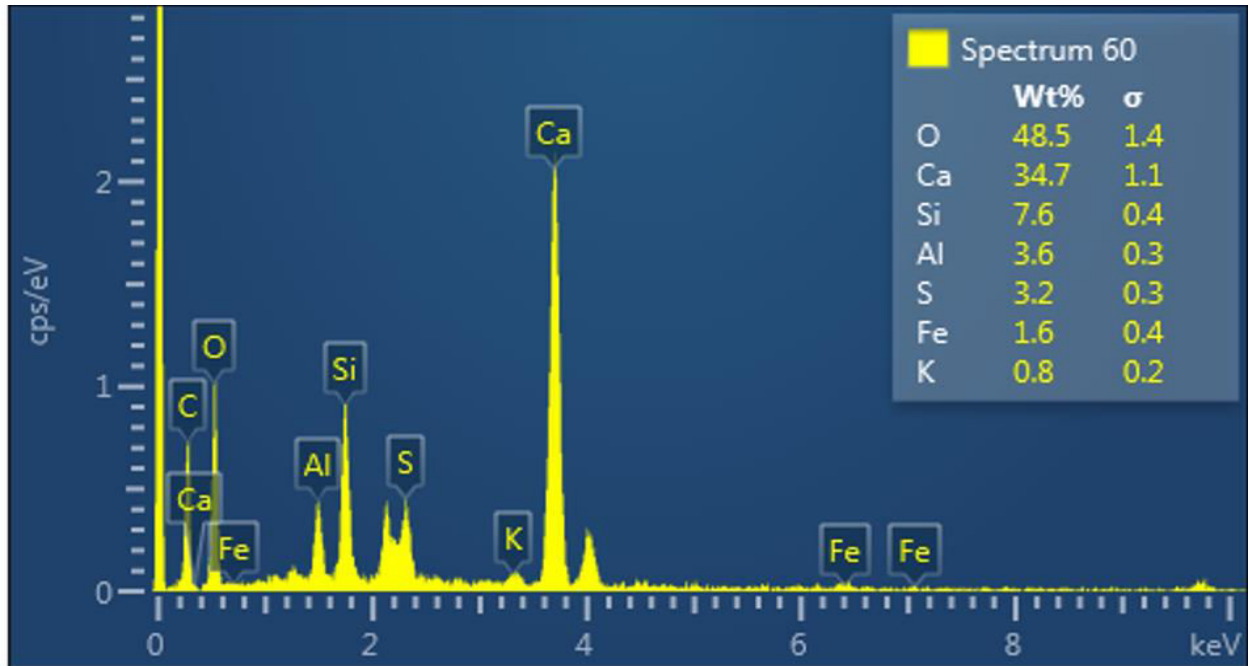


Figure 3.3:EDS spectral of elemental composition

3.4.2 Effect of grain size

In principle, grain size is inversely related to surface area. Since sorption is a manifestation of surface effect (Xiong et al., 2021), careful attention must be given to the grain size effect. For a wide range of grain size fractions, ~ 7mm to <0.063mm or chunk to 230 mesh, the volumetric measurement of low pressure N₂ and CO₂ isotherm under isothermal condition increases with a decrease in grain size for coal and shale respectively (Liu et al., 2021; Mastalerz et al., 2017). That is, the sorption capacity is higher in the finer grains than the in the coarse grain samples of the same rock. On the contrary, there is no size effect on the isothermal volumetric sorption measurement of methane on coal grain fractions (6 to 325 mesh) at elevated pressure (~ 15MPa to ~24MPa) (Ruppel et al., 1974; Zhao et al., 2021). Because powder sample is more representative for soil and sediment but not rock formations, the use of drill cuttings for

sorption measurement may be more appropriate for petrophysical studies of gas shale. As an important consequence of size effect, sorption capacity should not be reported without referencing the grain size and experimental condition. In addition, unlike powder sample, drilling cuttings which are rigid and compact may be more appropriate to study pore structure alterations by heat treatment. For example, a more realistic theoretical pore model that will account for structural deformation of non-rigid adsorbent materials has been emphasized (Thommes et al., 2015a).

3.4.3 Effect of heat-pretreatment on nitrogen sorption

As shown in Figure 3.4, the adsorption and desorption characteristic of the low-pressure nitrogen sorption measurements for the investigated samples is affected by temperature in the process of heat pretreatment. The sorption capacity to nitrogen increases with the preheating temperature because the adsorption capacity of the sample preheated at 110 °C is higher than the sample preheated at 50 °C. Based on the gravimetric sorption analysis, the adsorption capacity for the sample with the higher temperature pretreatment is in the range of 0.05-0.30 mmol/g while that of the lower temperature pretreatment is in range of 0.0099-0.125 mmol/g. Similarly, the desorption capacity of the sample preheated at 110 °C is greater than the sample preheated at 50 °C. The much larger increase in nitrogen uptake is attributed to the preheating temperature at which the sample had been preconditioned to get rid of moisture. Such an increase demonstrates the significant effect of environmental moisture and volatiles uptake by hygroscopic materials like shale and coal. The nitrogen sorption isotherms can also be represented by superimposing the corresponding adsorption and desorption curves, as illustrated in Figure 3.5. In this plot,

the low-pressure nitrogen sorption isotherms exhibit hysteresis. Interestingly, similar hysteresis loop is observed for all the samples. This observation revealed that the hysteresis effects do not depend on the preheating temperature but only on the history of the adsorption/desorption characteristics. In reference to the IUPAC nomenclature, the shape of the hysteresis loop is referred to as type 2 and is typical for that found in slit pore (Liu et al., 2021).

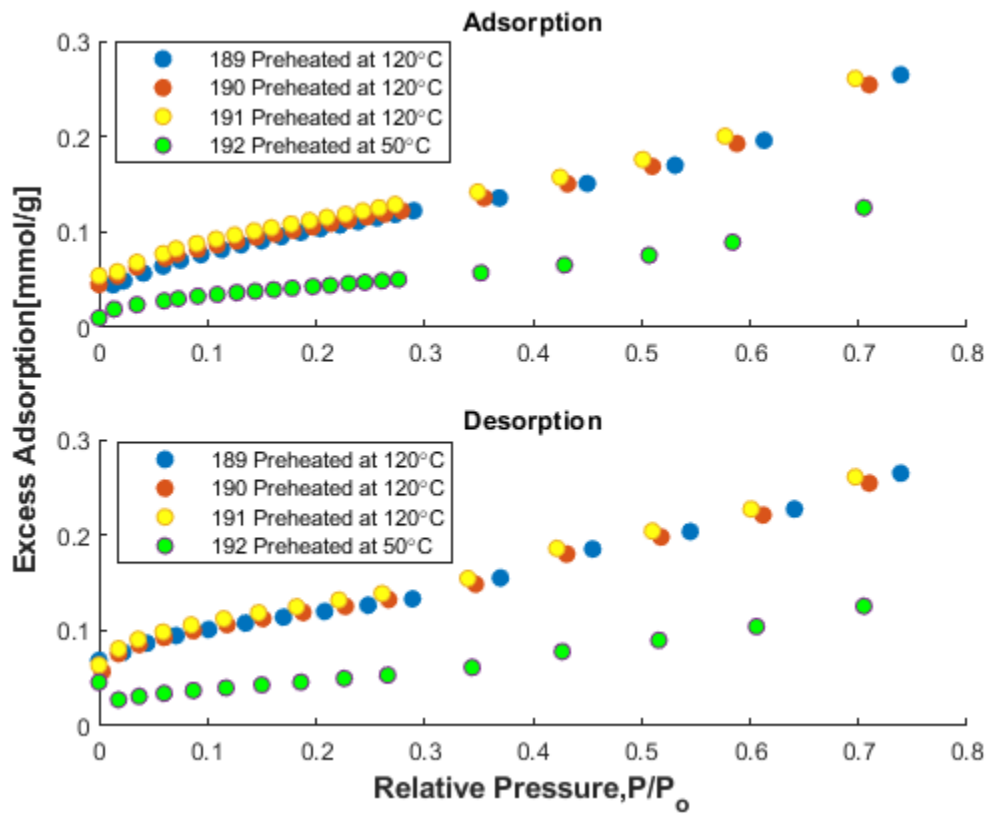


Figure 3.4: Isothermal nitrogen sorption

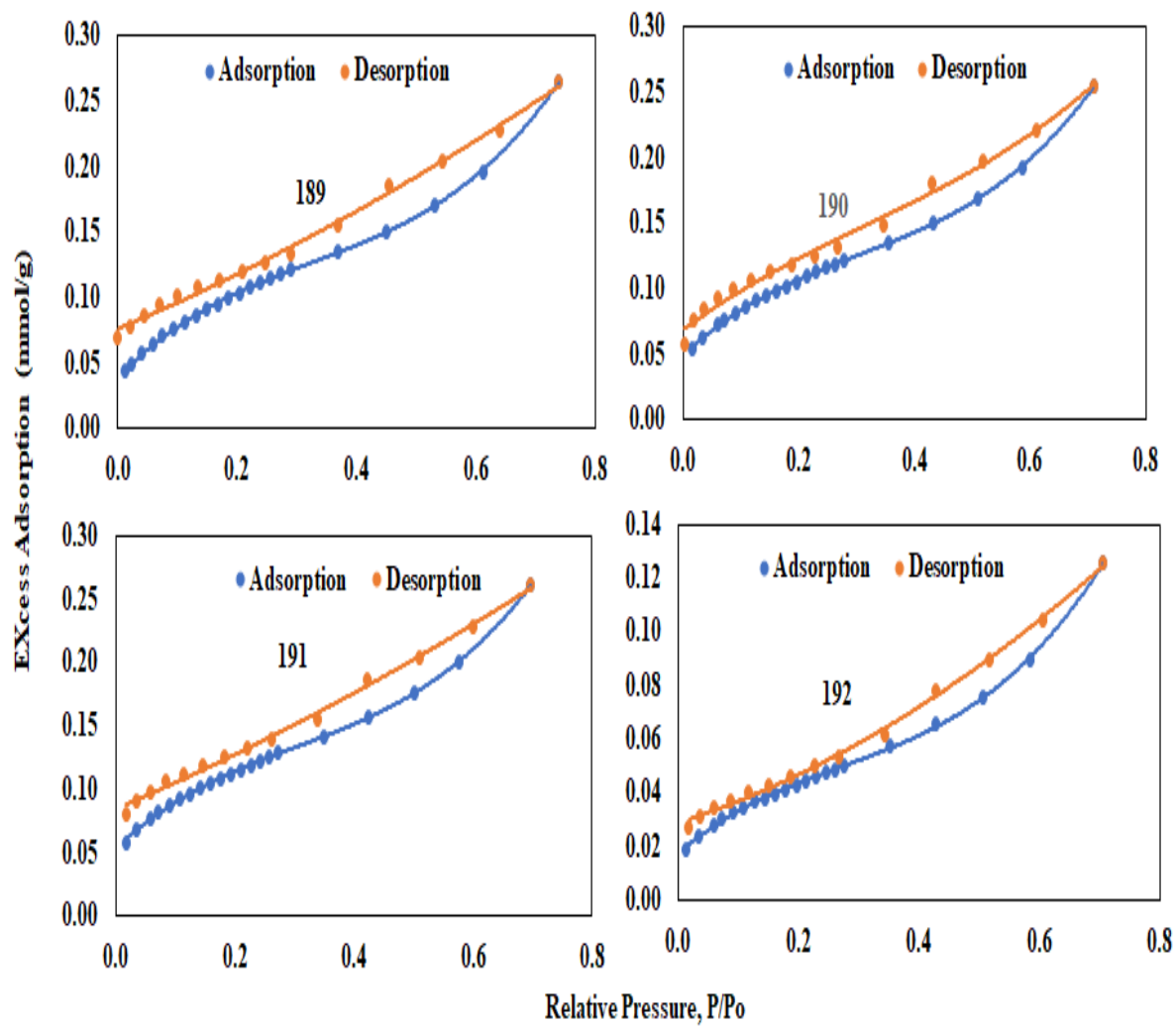


Figure 3.5: Nitrogen sorption hysteresis

3.4.4 Intrinsic coupling of thermal maturation and sorption

Some notable papers (Gasparik et al., 2014, 2013; Heller and Zoback, 2014; Ji et al., 2012; Khosrokhavar et al., 2014; Liu et al., 2013; Lu et al., 1995; Rexer et al., 2013; Zhang et al., 2012) have attempted to experimentally investigate the effect of temperature on methane sorption in shale. In these studies, the experiments were designed for carefully sieved powdered sample aliquot under constant temperature (isothermal) condition. That is, sorption measurement is carried out sequentially at different temperature for different aliquots of the sample. It is commonly observed by these authors that the sorption capacity of shale for methane increases with decreasing temperature. This observation is explained on the basis that heat transfer during adsorption is exothermic (Lu et al., 1995). Temperature is an important parameter of thermal maturation and sorption processes in shale; impacting both gas generation and gas sorption. As a result of the synergetic effect of thermal maturation and sorption, the effect of temperature on sorption mechanism of shale on the basis of isothermal condition may not be representative. Thus, isothermal sorption experiment may not capture both heat and mass transfers, compositional change and changes in pore structure.

Since maturation and sorption both dependent on temperature, we considered two separate experimental analyses of the source rock sample to clearly understand the effect of temperature on the mixed-mechanisms of thermal maturation and sorption. Methane sorption measurement were conducted under more representative non-isothermal condition on one aliquot of the sample, while thermal maturation aided by mass spectrometry but without sorption is conducted on another aliquot. The characteristic non-isothermal methane sorption isotherm is shown in Figure 3.6a. As temperature is

increased from 40-400°C according to predefined heating rate, methane sorption capacity generally increases with temperature as shown in Figure 3.6a. In the temperature range from 40-200°C, as illustrated by Figure 3.6b, it is clear that non-isothermal sorption increase with temperature. As further illustrated in Figure 3.6c, from 100-400°C, increase in sorption proceed from 100-300°C. In this plot, there is overlap between the methane sorption at 200°C and 300°C correspond to the plateau. At a sufficiently high temperature, the transition from 300 to 400 °C shows a decrease in methane sorption as shown in Figure 3.6d. As a result of the decrease at the stage, the non-isothermal sorption effect from 200-300°C can be said to correspond to the plateau region.

These observations can be explained with respect to the experimental variables such as temperature, heating rate and flow rate. Because the geological processes of maturation and sorption co-vary with temperature, there is competing effect on which mechanism dominant at a given temperature, heating rate and gas flow rate. For example, during the increase in methane sorption, sorption mechanism dominant over maturation. In this case, the fraction of methane gas generated during maturation is insufficient to maintain the amount of sorbed methane. Conversely, during the drop in methane sorption, the methane generated from maturation supersede that due to sorption. This is expected at sufficiently high temperature, and the possible reason for the drop in sorption capacity at 400°C. As shown in Figure 3.6d, the sorption capacity at 400°C is less compare than that at 300°C. Also, in Figure 3.6a, the sorption capacity at 400°C begin to approach that at 100°C. At the plateau region of maximum methane sorption, the sorption capacity at 200°C and 300°C is approximately equal as shown in Figure 3.6a and 3.6d respectively. This

observation can be explained as follows: apparently, the net effect of changes in generated and sorbed methane at 200 °C and 300 °C respectively is negligible.

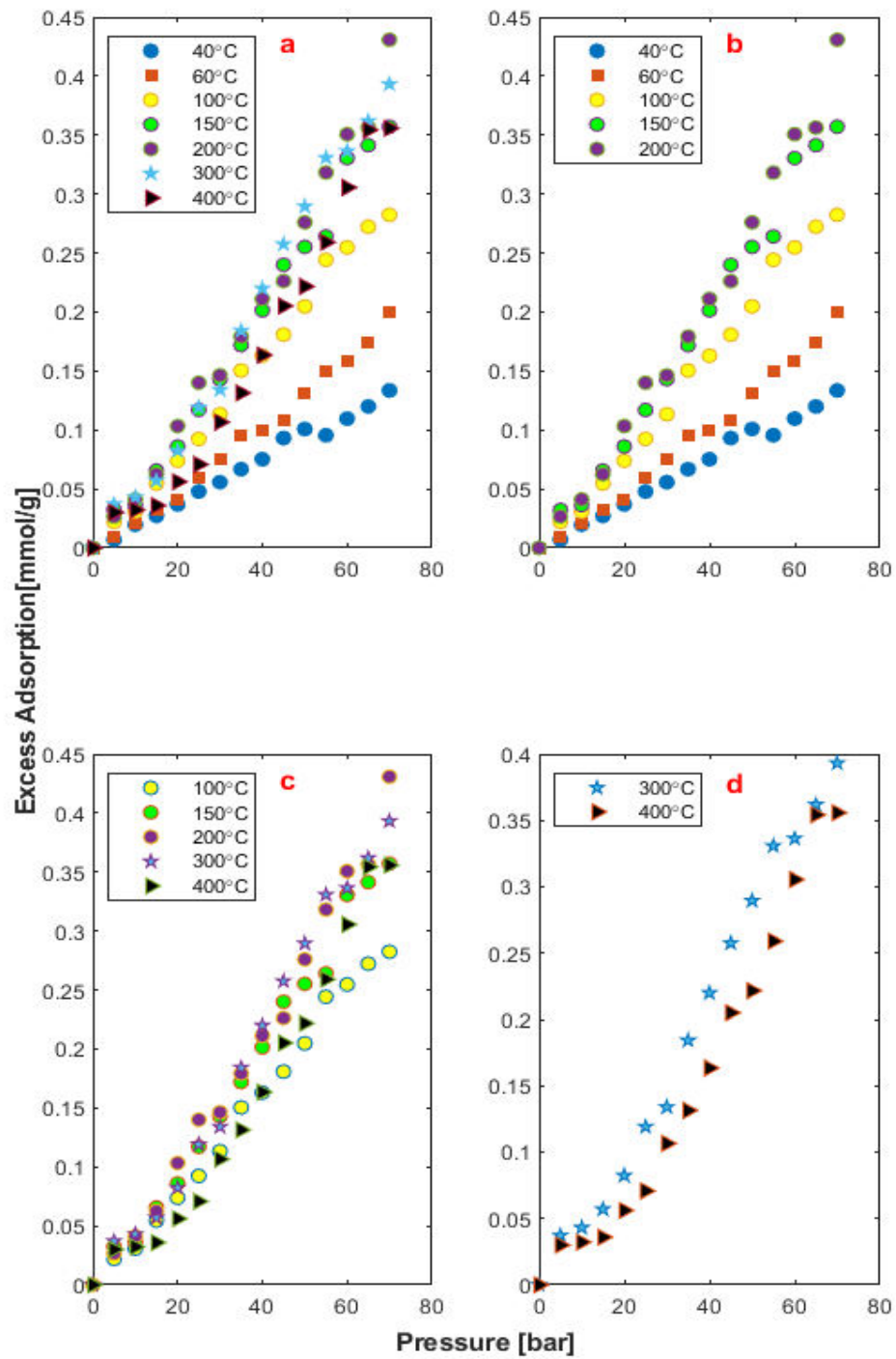


Figure 3.6: Non-isothermal Methane Sorption from 40-400°C

3.4.5 Phase change

Phase change can be characterized in term of mass change, compositional change and gas evolution. Because of the multi-component as well as multi-mineral nature of source rocks, significant phase change can be driven by rate-dependent high temperature variation. To better understand the effect of phase change on sorption mechanism of gas shale, a standalone measurement of thermal maturation, that is, without sorption measurement, is conducted on another aliquot of sample under the same experimental condition. The phase change of primary interest is: mass change and gas evolution. As shown in Figure 3.7, the thermogravimetric analysis showed that the mass of sample decreases with an increase in temperature. Similarly, the phase change associated with gas evolution is quantified by mass spectrometer with gases which are rich in water vapor, methane and carbon dioxide respectively. The evolve gas analysis of Figure 3.8 firmly establish that the release of gases is very much in evidence during thermal maturation. The important implication of phase change is that, at a temperature well above that at which gas evolution occurs, isothermal sorption experiment is inadequate to capture the dependence of both maturation and sorption on temperature. The effect of phase change further substantiates our understanding of the dynamic coupling between maturation and sorption.

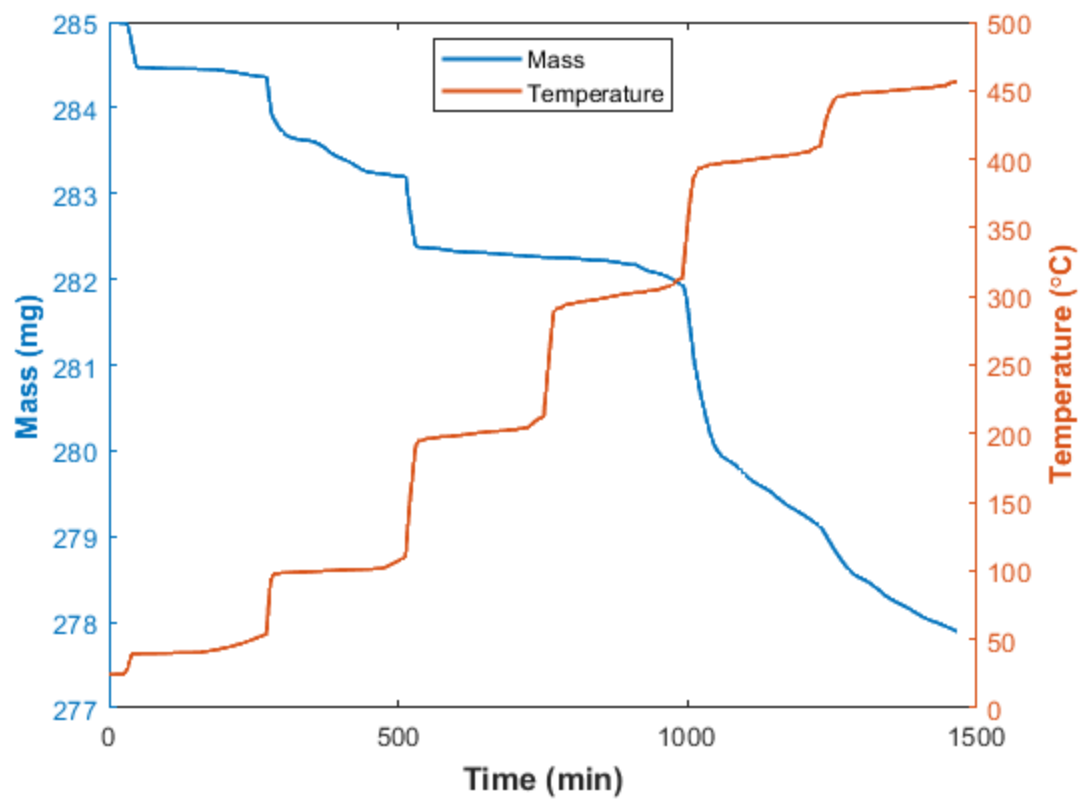


Figure 3.7: Thermogravimetric analysis of standalone thermal maturation

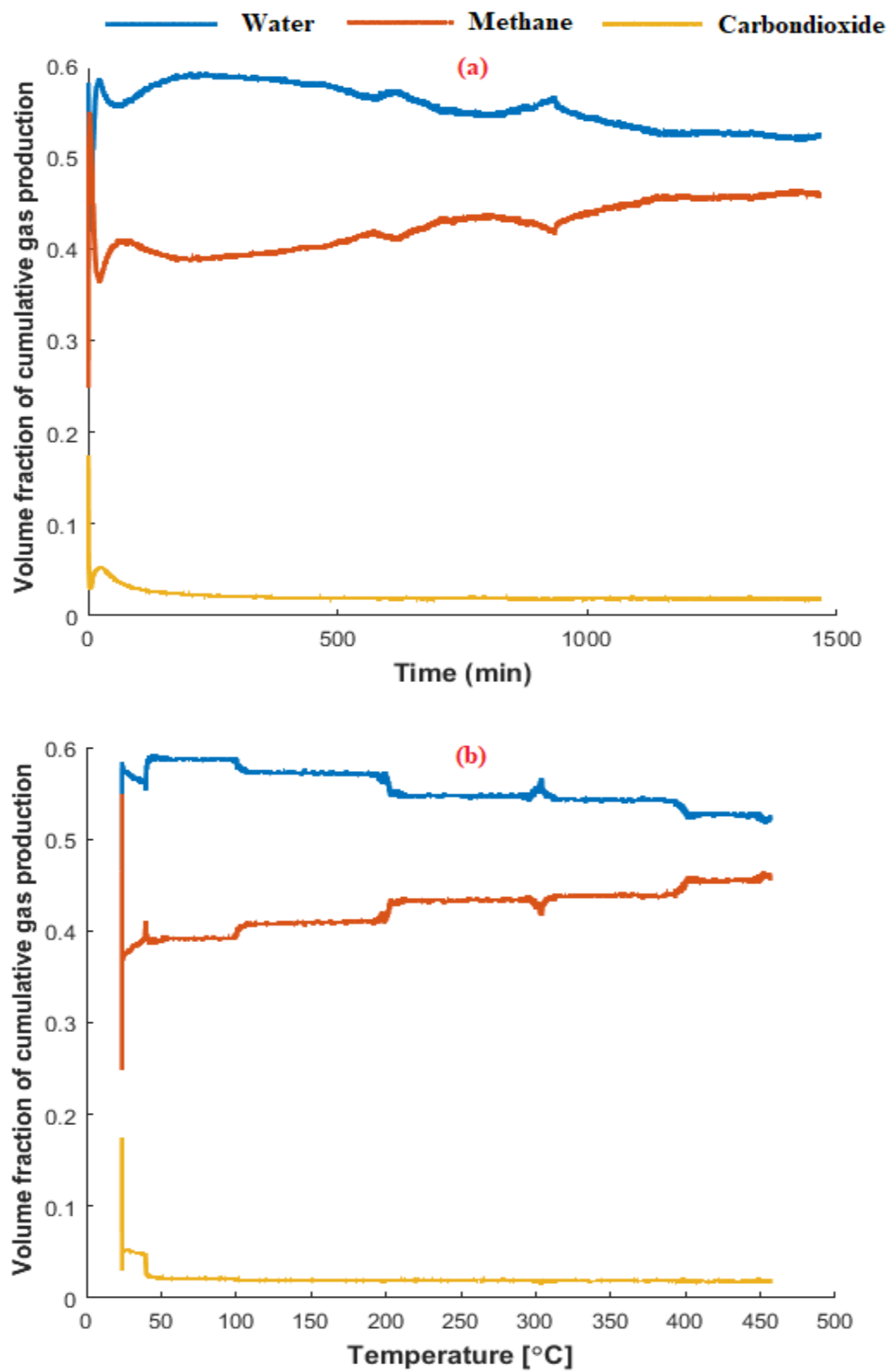


Figure 3 8: Cumulative gas release during standalone thermal maturation

3.4.6 Pore filling

Physisorption is controlled by number of pore filling processes which are dependent on the molecular dimension of pores, characteristics of the adsorptive, and the adsorbent-adsorptive interactions (Sing et al., 1985; Thommes et al., 2015b). Based on the well-adopted IUPAC classification scheme, the wide range of pores of different size can be classify as micropore (2nm), mesopore (2-50 nm) and macropore (>50nm). Accordingly, it is more simplifying to classify pore filling mechanisms according to the adsorption space corresponding to the different pore sizes as: micropore filling for micropore; surface coverage for the walls of the meso-or macro-pores and monolayer-multilayer adsorption for mesopore (Sing et al., 1985; Thommes et al., 2015b). In the mesopore, the adsorption space is one for monolayer adsorption and at least two for multilayer adsorption. It is well-known that the gas shale has hierarchical pore structure with nm to micron-scale pores which are dominated by organic matter and minerals (Curtis et al., 2012; Löhr et al., 2015; Loucks et al., 2010; Zhang et al., 2012). As discussed in the previous section, for the conservation of mass to hold, the phase change resulting from mass loss and gas evolution will be compensated by changes in pore structure. The evolution of the pore structure can be altered quite markedly depending on the heat treatment: isothermal or non-isothermal. The extent and degree of pore structure alteration with rate-dependent high-temperature variation from 40-400 has important implication to promote layer-by-layer adsorption of methane in the generated micro and meso pores. A related discussion on the “adsorption-induced structural transformations between large pore and narrow pore” has been investigated for zeolites and metal-organic frameworks (Kaneko et al., 2012; Thommes et al., 2015a; Triguero et al., 2019).

3.5 Conclusion

Gas sorption of shale source rock is a complex and dynamic process that is dependent on temperature, composition and grain size. These multi-factor effects are multi-physics in nature, and their role on gas sorption cannot be investigated using simple experiment that assume constant temperature. A more realistic experimental condition must take rate dependent temperature into account to better understand the dynamic behavior of gas sorption. Temperature dependent methane sorption is conducted under non-isothermal condition and the important conclusions of this study can be summarized as follows:

- 1.) Because of temperature dependency, the geological processes of thermal maturation and sorption are more-or-less interacting, so that organic-rich shale and mudrock can generate and store liquid and gaseous hydrocarbon.
- 2.) Compositional change in terms of mass loss and gas evolution which is characterized by standalone non-isothermal maturation, thermogravimetric and mass spectrometric analyses further suggest the coupling of maturation and sorption.
- 3.) Non-isothermal methane sorption on gas shale at elevated temperature and pressure generally increase with temperature.
- 4.) The observed increase in methane sorption is explained in terms of the layer-by-layer filling of generated pores.

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CHAPTER 4

Brittleness and Microcracks

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Abstract

With the recent global development of shale gas, geomechanical characterization of shale plays is now at a critical point, for which brittleness prediction is a key element. Since brittleness cannot be measured directly, it needs to be estimated from measurable rock properties. However, there is no unique quantitative theory to relate brittleness to rock properties. Therefore, different heuristic arguments linking elastic constants and mineralogy to brittleness have been proposed. Although, the dependence of brittleness on microcracks is experimentally and theoretically established in rock mechanics, quantitative evaluation of brittleness is not yet satisfying. In this study we investigated the hypothesis that brittleness of shale is proportional to its crack distributions. By this means, equations relating brittleness to other measurable properties of solids and natural rocks is proposed. Theoretically, the mathematical-physical derivation of this equation is based on the energy partitioning between the crack inclusion and the rock body. Experimentally, micro-CT imaging, ultrasonic velocity measurement and uniaxial compression tests were measured on shale samples in their native state as received from subsurface shale reservoir. The experimental data is used to calculate the newly proposed index of brittleness and these new results indicate that the orientation of crack distribution is one of the most critical property controlling the anomalous brittle behavior

of the investigated rocks. Our calculation of the brittleness index and the visual examination of the crack distributions aided by micro-CT imaging shows that the shale samples oriented horizontally to the bedding plane are more brittle compared with the one that is oriented vertically to the bedding plane.

4.1 Introduction

Around the world, including US, Canada, China and Saudi Arabia among others, shale oil and shale gas from hydrocarbon bearing shale are becoming increasingly one of the mainstream sustainable energy projects of the 21st century. Initially, technology has been the major limitation of gas production from these vast shale formations. With the successful application of horizontal drilling and multistage hydraulic fracturing as the two key techniques to unlock these formations, the amount of hydrocarbon in shale reservoirs is yet to be fully harnessed for sustainable energy. This is mainly attributed to the rapid decline in recovery. As a consequence, one can state that hydraulic fracturing is not an efficient recovery method for shale gas production. Hydraulic fracturing can be very efficient but mischaracterization of shale reservoirs in identifying appropriate zone is the main challenge and current limitation.

This technical task requires the understanding of the geological, geochemical and geomechanical characteristics that is favorable to unconventional shale development. As a first step, petrophysical, petrographic and geochemical analyses e.g. measurement of total organic content and vitrinite reflectance are made as an indication of hydrocarbon potential and maturity of shale plays. Significant progress has been put forward in this regard (Adeyilola et al., 2020; Kenomore et al., 2017; Lawal and Mahmoud, 2020; Lawal

et al., 2019; Lawal et al., 2019a, 2019b; Lawal et al., 2020; Wang et al., 2015; Zhang et al., 2019). If the geology is favorable for shale gas accumulation, the second phase of the workflow is to increase the intrinsically low permeability of shale plays via fracking. In this case, brittleness analysis is performed to spot brittle shale. This is important to enhance and improve the success of hydraulic fracturing treatment. However, unlike TOC, “measurement” of brittleness is not yet covered by measurement standards. This difficulty has certainly led to the new and interesting study of brittleness among rock mechanists, geophysicists and geochemists (e.g. Kumar et al., 2018; Li et al., 2020; Liu et al., 2020; Nygård et al., 2006; Kivi et al., 2018; Tarasov and Potvin, 2013 among others). A short overview of these different specialized methods of defining and calculating brittleness follows.

4.1.1 What is Brittleness of rocks?

The discussion of brittleness should begin with its definition. Unfortunately, brittleness is an intrinsic fracture or failure parameter which is not only ill-defined but also controversial. This is partly due to the fact that the concept of brittleness or brittle fracturing of rocks and solids is an interdisciplinary topic that cut across many fields of earth sciences and engineering such as earth quake mechanics, geophysics and petroleum engineering. The common goal of engineering design analysis among these different disciplines is to identify weak or incompetent zones of interest. While the study of brittleness for catastrophic damage prevention has been focus of applied earth sciences for many years, it appears recently in petroleum engineering for efficient placement of hydraulic fractures in shale reservoirs. Thus, no generally accepted definition or

mathematical formula exist for qualitative and quantitative interpretation of brittleness (Hucka and Das, 1974; Lawal and Mahmoud, 2020; Tarasov and Potvin, 2013). How then do we quantify what we cannot precisely define? References to previous studies show that there are three main concepts of estimating brittleness with respect to the following subject areas: rock mechanics, geophysics and mineralogy.

4.1.1.1 Rock Mechanic Aspects of Brittleness

The constitutive law linearly connecting stress to strain and vis-versa is the famous Hooke's law. Rock as linear elastic material would exhibit behavior characteristics of Hookean solid and its elastic properties can be conveniently derived from stress-strain measurement. These elastic constants can be considered as compliance parameters when stress is a function of strain, otherwise they are called stiffness elastics parameters. The simplest approximation is when the stress and strain is a zero-order tensor and of course the elastic constants would not depend on orientation. From the general rock mechanics standpoint, "a material is brittle if it retains its linear elasticity up to the point of fracture" (Cherepanov, 1979). As Zhang et al., (2015) stated: (1) "A material is brittle if, when subjected to stress, it breaks with little elastic deformation and without significant plastic deformation"; (2) "Brittle materials absorb relatively little energy prior to fracture, even those of high strength". Based on this concept, the stress-strain curve shown in Figure 6.1 would be the baseline for predicting brittleness. However, the prediction of brittleness from stress-strain curve is a qualitative graphical method which is not straightforward and may lead to ambiguous interpretations. This is because laboratory experiments show that rock of the same mineralogy would deviate anomalously from this theoretical stress-strain curve. Such a behaviour suggests that the deformation of rock under a given

experimental condition is controlled by the internal structure of the rocks. This phenomenon is said to be related to the weakening and embrittlement of intact rocks (Tarasov, 2019).

To measure the brittleness of rocks from stress-strain curve, the recent paper by Tarasova and Potvin (Tarasov and Potvin, 2013) illustrate the present state of knowledge. Since brittleness is an intrinsic deformation parameter which cannot be measured or quantified directly but inferred from measurable properties such as energy ratio, uniaxial compressive strength, tensile strength, angle of internal friction, peak and residual strain, fracture toughness, micro indentation and macro indentation hardness. The comparative study of Hucka and Das showed that it becomes challenging to achieve reliable and consistent estimates of brittleness. From the perspective of different researchers (Hucka and Das, 1974), “reliable” physical attribute for measuring and interpreting brittleness are the following: low values of elongation; fracture failure; formation of fines; higher ratio of compressive to tensile strength; higher resilience; higher angle of internal friction; formation of cracks in indentation. Chen et al., (Chen et al., 2017) re-introduced the concept of mode II crack and also proposed fracture density derived from fractal dimension for estimating brittleness. Tao et al., (Tao et al., 2020) adopt the graphical analysis of stress-strain curve for brittleness study, an approach similar to Tarasov and Potvin method (Tarasov and Potvin, 2013) , by considering the dissipation and elastic strain energy before and after peak strength. The classical versus emergent approach of brittleness analysis from stress-strain curve is depicted in Figure 4.1. Yet, there exists a gap to validate both the typical and refined stress-strain curve characterization methods of

brittleness and their restriction to laboratory experiments further have significant limitations with respect to field implementations.

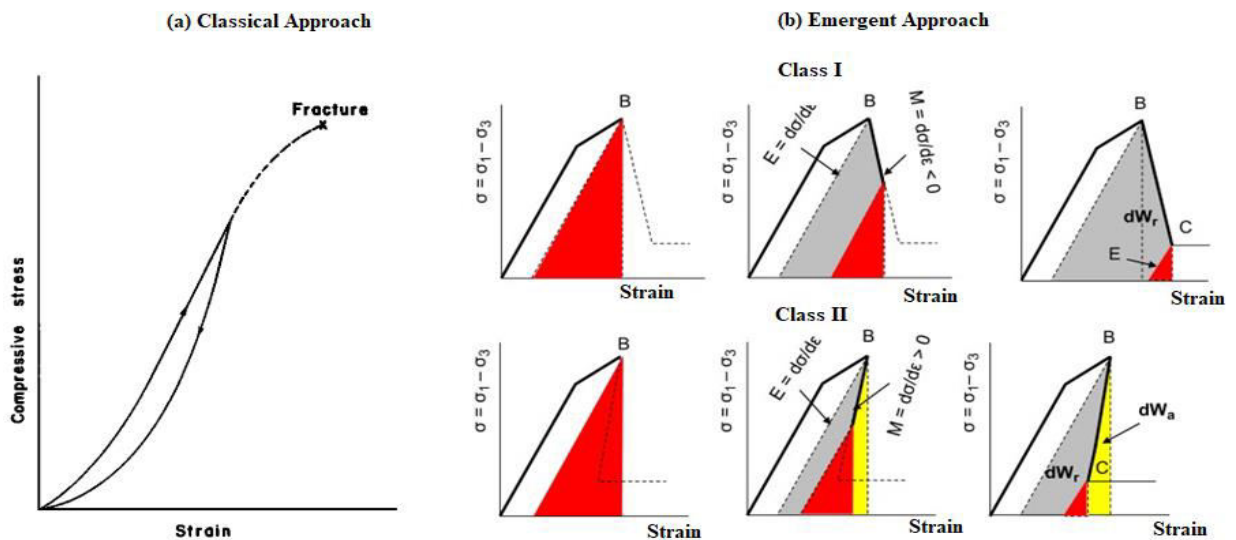


Figure 4.1: Brittleness from stress-strain curves: (a) classical and (b) emergent

4.1.1.2 Geophysical Aspects of Brittleness

Perhaps, the early ideas of brittleness prediction from rock mechanics cannot be implemented with geophysical data obtained from well logs and core analysis. Thus, the concept of brittleness in geophysics assumes that ratio of isotropic elastic constants serves as a reasonable indication of brittleness. Grieser and Bray (Grieser and Bray, 2007) introduced this concept using the cross plot of Young's modulus and Poisson ratio for interpreting brittleness of shale. They claim that brittleness of rock is inversely proportional to Poisson ratio but directly proportional to Young's modulus. Since this pioneering work, several studies argued that other elastic constants ratio are possible indicators of brittleness. This becomes ambiguous since only two out of the five possible elastic constants are required to characterize linearly isotropic rocks. When the two

isotropic elastic constants are selected from the 5 possible isotropic elastic constants, the number of combinations that results are ten, so there are 20 possibilities of forming their ratio. This approach presents a significant pitfall which makes brittleness interpretation from elastic constants inherently non-unique. A quick survey of the various attempts of brittleness prediction particularly from elasticity-based approach can be found from the work of Herwanger et al. (2015) and Zhang et al. (2016). Brittleness estimation from the ratio of elastic constants has been extensively pursued because the geophysical measurement of elastic constants of rock can be readily available on lab and field basis. However, this method is limited in that the exact or unique functional relationship of elastic constants for brittleness prediction is still missing and subject to validation.

4.1.1.3 Mineralogy (Geology & Geochemistry) Aspects of Brittleness

From mineralogical viewpoint, the ratio of mineral composition of shale is accepted for predicting brittleness. This is based on the simple metric that quartz is brittle. This idea is based on the original work led by Jarvie (Jarvie et al., 2007). Although these assumptions are widely cited, it has also been criticized. Brittleness has been argued to be attributed to the following mineral(s): (1) quartz; (2) quartz, dolomite, and pyrite; (3) quartz, feldspar, and dolomite; (4) carbonate minerals and quartz; (5) carbonate and quartz and (6) all the minerals in shale except clay (Huo et al., 2018). For brittle shale spot, the maximum clay and minimum quartz contents should be 20% and 60% respectively (Moghadam et al., 2019). In a recent study, specific weight fraction is specified for quartz, feldspar, calcite, and dolomite respectively (Kang et al., 2020). Like the other aspects of brittleness evaluation, the interpretation of brittleness in terms of mineralogy is also not conclusive. The extensive literature searches of *brittleness* in petroleum geoscience literature showed

that numerous attempts for new or modified equations exist without much success. A literature survey of these existing methods of brittleness quantification has been reported in Table 4.1 (Lawal, 2015), see also references (Hucka and Das, 1974; Zhang et al., 2016) for discussion of these formulas. Mineralogical prediction of brittleness is equally yet to be verified and different methods of prediction lead to ambiguities and uncertainties. The need for powdered rocks sample is a notable disadvantage for practical reliability and comparison with other methods predicted on intact core plugs.

Table 4. 1:Literature Survey of Brittleness Formula (Lawal, 2015)

Brittleness Equation B	Parameters
$B_1 = \frac{W_r}{W_t}$	W_r :reversible energy, W_t : total energy
$B_2 = q\sigma_c$	σ_c : uniaxial compressive strength q :percentage of fines
$B_3 = \frac{\varepsilon_r}{\varepsilon_t}$	ε_r : reversible strain ε_t : total strain
$B_4 = \frac{\tau_P - \tau_R}{\tau_P}$	τ_P : peak strength τ_R :residual strength
$B_5 = \sin \theta$	θ : angle of internal friction
$B_6 = \frac{\sigma_c - \sigma_t}{\sigma_c + \sigma_t}$	σ_c : Uniaxial compressive strength σ_t :tensile strength
$B_7 = \frac{H_\mu - H}{K}$	H_μ : micro-indentation hardness, H :macro-indentation hardness, K : constant
$B_8 = \frac{\sigma_c}{\sigma_{NC}}$	σ_c : Uniaxial compressive strength, σ_{NC} : Uniaxial compressive strength at normal consolidation

4.1.1.4 Knowledge Gap and Objectives

The concept of brittleness as defined and quantified from the stress-strain curve, elastic constants and rock minerals respectively is still not clear and also controversial. To predict and interpret brittleness from the stress-strain curve is not straight-forward, the ratio of elastic constants gives different possibility of interpreting brittleness and so is the ratio of rock minerals. For example, the elastic constants and rock minerals that control the brittle behavior of shale has been controversial among researchers. Consequently, the different interpretation of brittleness will introduce ambiguity on how to infer the fracturing index of shale. A more generalized form of brittleness which is yet to exist would make possible the comparison of conflicting ideas among researchers. In this paper, we aim to address the above-mentioned limitations of previous works by investigating the relationship between brittleness and microcracks. Recognizing this need, we seek to develop simple and reliable methods that quantify brittleness on the basis of energy partitioning. We suppose that different geomaterials would exhibit different cracking conditions; therefore, the brittleness of rock of a given mineralogy is tied to its crack distributions. Theoretical and experimental efforts were made in this direction.

As far as the authors are informed, there is yet any attempt to establish a quantitative relationship between brittleness and crack distribution even though it has long been hypothesized that there is a causal relationship between the mechanical behavior of brittle solids and the pre-existing cracks. The validity of this approach is that, it is based on well-established theoretical concept and not solely due to heuristic argument. In addition, our methodology takes into importance the effect of microstructural properties on the

mechanical response of the rock. To be more specific, P- and S- wave velocities as well as the associated elastic constant are very sensitive to crack distribution, this is also true with the static elastic parameters measured from compression test. This is an added advantage over other methods because of the relevance and breadth of this new approach to be implemented easily with data from well logging, seismic and geomechanical measurements. In addition, the preliminary data from micro-CT imaging helps to validate this methodology.

The main objectives of this paper are: (1) to provide the theoretical and mathematical framework to derive a dimensionless index of brittleness based on the energy partitioning between the microcrack and the rock matrix; (2) to provide experimental measurements to illustrate proposed concept; (3) evaluate dynamic index of brittleness nondestructively based on the concept of rock physics (geophysics) and (4) evaluate static index of brittleness destructively based on the concept of rock mechanics;(5) validate the approach with micro-CT imaging of microcracks .

4.2 Theoretical and Mathematical Framework

4.2.1 Theoretical Background

Although, the classical Griffith's crack theory does not lend itself to a deterministic equation for predicting brittleness, it is well-known for understanding the compressive failure of brittle rocks. This theory established that the characteristic length of cracks in solids is a major contributing factor for brittle failure. In other words, the equilibrium between the elastic (stored) and surface (fracture) energy in the presence of cracks is

considered as the criterion of brittle fracture (Cherepanov, 1979; Griffith, 1921). For example, the stored strain energy what is released will have to overcome the cohesive energy of the molecules to create a new fracture surface in the form of cracks (Griffith 1920; Cherepanov, 1979). Both kinds of energy which are generally not known depends on some material constants which are in turn unknowns. This concept informed the use of energy ratio in the old literature of rock mechanics and later simplified in geophysics with the use of ratio of elastic constants (see Table 6.1). This is because the energy parameters are difficult to quantify. Secondly, one of the criteria of brittleness as mentioned in Hucka and Das (1979) is: “formation of cracks in indentation”. On this premise, we considered the following definitions: (1) cracks are the intrinsic mechanical discontinuities that separate a solid material into two or more parts; (2) a solid in the presence of pre-existing crack will tend to be more brittle than the one without cracks. For example, a crack-filled glass will have greater tendency to brittle mechanical behavior than crack-free glass. (3) from a mathematical point of view, brittleness is defined as the ratio of crack surface energy to the total elastic energy.

Experimental measurement of the parameters of these energy equations such as the crack length, tensile strength and thermodynamic surface energy are inherently difficult. In the course of quantitative analysis of brittleness as ratio of energy, we circumvent this difficulty by considering the partitioning of elastic energy between the cracks and matrix. The Eshelby's techniques (Eshelby, 1957) showed that the relation between the crack energy and that of the matrix is expressed by equation 1. In agreement with the concept of brittleness as energy ratio, we use the Eshelby's energy partitioning formula (equation 1) to derive a new index of brittleness. For this purpose, energy or work done associated

with the crack and matrix is defined in terms of a volume-pressure relationship or volume-compressibility ratio. Given that that the rock body will be acted upon by compressive stress, the volume-compressibility ratio is preferred. This offers a simple approach to recast brittleness as the ratio of energy.

The mathematical illustration is given next and the proof of concept will be demonstrated by micro-CT imaging, ultrasonic velocity and uniaxial compression measurements on real subsurface shale samples in subsequent sections.

4.2.2 Conceptual Model and Mathematical Formulation

Let's suppose a crack inclusion of crack volume V_c and compressibility C_c is cut through a homogeneous isotropic elastic rock of volume V_b and compressibility C_b as shown in Figure 4.2.

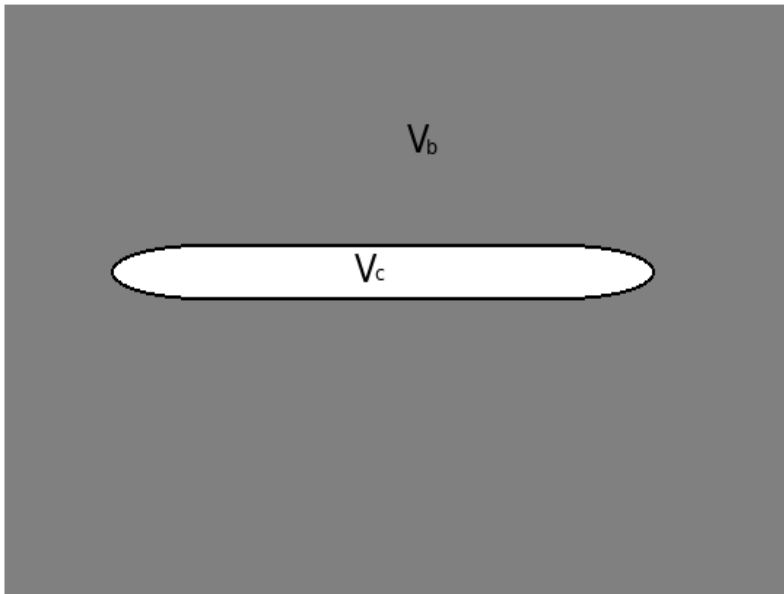


Figure 4.2: Crack inclusion cutting through a rock

Using Elsheby's original notation, the symbol γ is the energy partitioning parameter between the matrix and crack according to equation 1.

$$\frac{1 - \gamma}{\gamma} = \frac{\text{energy in matrix}}{\text{energy in crack inclusion}} \quad (1)$$

Considering the analogy between the Griffith's crack theory and Elsheby's solution, we accept γ as defined by equation 2 as the index of brittleness. To avoid confusion, we shall adopt the Elsheby's symbol of energy partitioning γ to represent the index of brittleness. Please note that γ is a symbolic representation as B is used for representing brittleness index in Table 6.1.

$$\gamma = \frac{\text{energy in crack inclusion}}{\text{energy in matrix} + \text{energy in crack inclusion}} \quad (2)$$

The physical interpretation of equation 2 implies that γ needs to be very small in order to accommodate more cracks. However, the estimate of the crack and matrix energy is the major setback. This limitation can be overcome by rewriting the energy term as pressure-volume product. Suppose the idealized crack model shown in Figure 6.2 is subjected to uniform hydrostatic compression, Zimmermann (1991) state that the associated energy is proportional to volume-compressibility product. Instead of defining energy in terms of pressure-volume product we used the volume-compressibility ratio to express equation 2 as 3.

$$\gamma = \frac{C_b V_c}{C_c V_b + C_b V_c} \quad (3)$$

where γ is the dimensionless index of brittleness, C_b is the compressibility of rock matrix, C_c is the compressibility of the crack inclusion, V_b is the volume of the rock matrix and V_c is the volume of the crack inclusion.

For penny-shaped crack, the volume of crack is defined as $V_c = \frac{4}{3}N\pi a^3\alpha$, where N is the number of cracks of aspect ratio α and semi-major axis of length a and the porosity ϕ due to the cracks is $\frac{4N\pi a^3\alpha}{3V_b}$ (Zimmerman, 1991). Assuming a penny-shaped crack, substituting for the bulk volume V_b and crack volume V_c , equation (3) becomes (4).

$$\gamma = \frac{\phi C_b}{C_c + \phi C_b} \quad (4)$$

According to Zimmerman (1991), the compressibility of the crack is given by equation 5.

$$C_c = \frac{2(1 - \nu)}{\pi\alpha\mu} \quad (5)$$

μ is the shear modulus, ν is Poisson ratio, α is crack aspect ratio

Replacing the compressibility of the rock with bulk modulus and substituting equation 5 into 4 we have the generalized index of brittleness has equation 6.

$$\gamma = \frac{\pi\alpha\mu\phi}{2K(1 - \nu) + \pi\alpha\mu\phi} \quad (6)$$

where γ is the dimensionless index of brittleness, α is the crack aspect ratio, μ is the shear modulus, K is the bulk modulus, ν is the Poisson's ratio and ϕ is the porosity.

4.2.3 Derivation of Dynamic Index of Brittleness

In geophysics, rock physics and well logging, the elastic parameters in equation 6 can be measured dynamically from non-destructive ultrasonic pulse technique (acoustic velocities); whereas, in rock mechanics they can be measured independent of time from destructive static-compression experiment. Therefore, the subdivision of index of brittleness into dynamic and static index of brittleness is necessary and the separate derivation of the corresponding index of brittleness is useful.

To measure brittleness non-destructively from acoustic velocities measured in rock physics and well logging, we introduce the dynamic brittleness index denoted as γ_d . In geophysics, rock physics and well logging, the response of a rock to the dynamic stress in form of acoustic velocity is commonly used to extract the elastic rock constants. The velocity and elastic constants are directly related as follows (Fung, 1965):

$$\lambda + 2\mu = V_p^2 \rho_b \quad (7)$$

$$\mu = V_s^2 \rho_b \quad (8)$$

$$v = \frac{V_p^2 - 2V_s^2}{2(V_p^2 - V_s^2)} \quad (9)$$

$$K = \frac{3\lambda + 2\mu}{3} \quad (10)$$

λ and μ are Lamé's elastic constants, v is Poisson's ratio, V_p is P-wave velocity, V_s is the S-wave velocity, ρ_b is the bulk density.

Using equation 7,8 and 9 we express K and $(1 - \nu)$ in equation 6 in terms of elastic wave velocities as:

$$K = \frac{(3V_p^2 - 4V_s^2)\rho_b}{3} \quad (11)$$

$$1 - \nu = \frac{V_p^2}{2(V_p^2 - V_s^2)} \quad (12)$$

Substituting (8), (11) and (12) into equation (6), we arrived at equation (13) after simple algebra

$$\gamma_d = \frac{3\pi\alpha\phi(V_p^2 - V_s^2)V_s^2}{(3V_p^2 - 4V_s^2)V_p^2 + 3\pi\alpha\phi(V_p^2 - V_s^2)V_s^2} \quad (13)$$

To expressed the dynamic index of brittleness γ_d as velocity ratio, we factored out $3V_p^2V_s^2$ to arrive at the final form:

$$\gamma_d = \frac{\pi\alpha\phi \left[1 - \left(\frac{V_s}{V_p} \right)^2 \right]}{\left[\left(\frac{V_p}{V_s} \right)^2 - \frac{4}{3} \right] + \pi\alpha\phi \left[1 - \left(\frac{V_s}{V_p} \right)^2 \right]} \quad (14)$$

Under dynamic condition, the applied pressure in the form of confining pressure P_c is related to the crack aspect ratio according to equation 15 (Gueguen and Palciauskas, 1994)

$$P_c = \left(1 - \frac{b}{b_o} \right) \frac{\alpha\mu}{1 - \nu} \quad (15)$$

Where P_c is the confining pressure, b is the crack aperture, b_o is the initial crack aperture, α is the crack aspect ratio, μ is the shear modulus and ν is the Poisson ratio. The crack aspect ratio can be obtained from the plot of confining pressure P_c versus $\frac{\mu}{1-\nu}$. We can compute the values of $\frac{\mu}{1-\nu}$ expressible in terms of velocity and density using the formula:

$$\frac{\mu}{1-\nu} = 2\rho_b V_s^2 \left[1 - \left(\frac{V_s}{V_p} \right)^2 \right] \quad (16)$$

4.2.4 Derivation of Static Index of Brittleness

We now introduce the static index of brittleness, γ_s , which corresponds to the parameters of equation 6 measured from the destructive static-compression test commonly used in rock mechanics. The shear modulus μ and bulk modulus K are related according to equation 17 (Fung, 1965).

$$\frac{\mu}{K} = \frac{3(1-2\nu)}{2(1+\nu)} \quad (17)$$

By substituting equation 17 into 6, we have:

$$\gamma = \frac{3\pi\alpha\phi(1-2\nu)}{4(1-\nu^2) + 3\pi\alpha\phi(1-2\nu)} \quad (18)$$

The equivalent form of 15 under static condition in which the applied pressure P_c is the crack closure pressure is given by equation 19 (see reference (Zimmerman, 1991)).

$$P_c = \frac{\alpha\mu}{1-\nu} \quad (19)$$

where P_c is the crack closure pressure.

Substituting, equation 19 into 18 we have:

$$\gamma = \frac{3\pi\phi P_c(1-2\nu)}{4\mu(1+\nu) + 3\pi\phi P_c(1-2\nu)} \quad (20)$$

It is important to express equation 20 in terms of Young's modulus and Poisson's ratio; the two elastic parameters commonly obtain from the destructive rock mechanic testing.

To do so, we recall the constitutive equation (Fung, 1965):

$$4\mu = \frac{2E}{1+\nu} \quad (21)$$

Substituting equation 21 into 20, we have:

$$\gamma = \frac{3\pi\phi P_c(1-2\nu)}{2E + 3\pi\phi P_c(1-2\nu)} \quad (22)$$

It would be experimentally challenging to make measurement of the crack closure pressure P_c . To avoid this difficulty, we make a reasonable assumption by replacing P_c with the uniaxial compressive strength UCS . Since UCS is greater than P_c , the numerical value of brittleness would be an upper limit. This assumption leads to the final formula of γ_s as equation 23.

$$\gamma_s = \frac{3\pi\phi UCS(1-2\nu)}{2E + 3\pi\phi UCS(1-2\nu)} \quad (23)$$

4.2.5 Implication for Porous Media and Anisotropy

The derivation of the dynamic and static indices of brittleness is based on the first important assumption of crack-filled porous media as predicted by the classical Griffith's crack theory. Suppose the porous media is crack-free, the energy partitioning rule of

Elsheby used to derive index of brittleness would still remain valid, however, in this case, the crack compressibility should be replaced with the compressibility of pores. This implies that the derivations are valid for both crack-filled and crack-free porous media respectively. For the specific case of a circular pore, the aspect ratio equal unity and both indices of brittleness can be equally adapted. The second important point is that the pre-existing cracks (pores) is assumed to be embedded in a solid isotropic matrix. To account for anisotropy, we considered the directionality of elastic parameters by measuring the acoustic velocity with respect to three different orientations. The derivation of brittleness with respect to anisotropy has not been considered in this study and could be a topic of future research.

4.3 Experimental Measurements

4.3.1 Shale Description

Qusaiba shale samples in their native state as received from the Rub' Al-Khali Basin, Saudi Arabia were selected in the present study. Qusaiba shale is a Silurian-age source rock of the Paleozoic Total Petroleum System (PTPS) of the northwest Saudi Arabia and considered to be the main producer of Saudi Arabia's Ghawar field (Lawal et al., 2020). It is deposited under marine environment of major time transgression (Hirnantian glaciation stage). The basal section, also referred to as the Lower Silurian Qusaiba shale of the Qalibah Formation serve as an important oil and gas source rock in the Arabian Peninsula. The Qusaiba shale samples, oriented vertically and horizontally (denoted as V and H respectively) to the bedding were precisely ground to a cylindrical shape.

4.3.2 Micro-CT Measurement

Prior to other lab measurements, micro-CT imaging is used to provide nondestructive visualization of the amount and distribution of the internal cracks of the shale samples. The Three-dimensional digital images of selected shale samples were scanned by the Versa XRM-500 micro-CT scanning machine. The images are generated from the attenuation of the X-ray beam measured at different angles. The extent to which the shale sample attenuate the X-ray beam corresponds to the attenuation coefficient of the sample, a function of bulk density, atomic number and the intensity of the X-ray. The energy of the probing X-ray is also a function of the scanning parameters including power (10W), source voltage (140–160 KV), exposure time (1– 4 seconds), flux count, and projection (1601 projections). The preview image is generated by translating the sample with respect to the plane of detection.

4.3.3 Density and Porosity Measurements

The dimensions (length and diameter) of the samples were measured with a Vernier caliper to compute the volume based on cylindrical geometry and their corresponding masses measured with a high precision weighing balance. Four different measurements were made in each case for the sake of precision and the average value of the measurements is used for computing the bulk density as the ratio of mass and volume. Based on the proposed formula of brittleness, porosity (expressible in terms of bulk and grain density) is an important input parameter. This is the need for bulk and grain density measurements. It is important to note that we found measurement of porosity by this method to be well-suited for very low porosity rocks like shale. By default, the grain

density can only be measured on rock chips or powder, for this reason, the measurements of grain density were delayed until after destructive measurement of uniaxial compressive strengths were carried out.

4.3.4 Geomechanical Measurements

Geomechanical measurements were conducted in two stages. In the first part, acoustic velocities (nondestructive) were measured nondestructively on the horizontal shale plugs at three different orientations, 0° , 45° , and 90° respectively while in the second part uniaxial compressive strengths (destructive) were measured on the same sample. The sequential measurements were carried out in accordance with the ASTM guideline using the computer-controlled AUTOLAB 1500 of New England Research. Following the ASTM recommendations, the characteristic dimension of the measured shale samples comply with the length-to-diameter ratio of 2:1. For representative and reliable data, the end effect is also well-taken care of by ensuring the ends of sample to be flattened and paralleled. This is done by repeated end-face grinding which is checked to be within the allowable limits of 0.025 mm. Afterwards, the shale sample were encased in a flexible non-porous rubber sleeve before it is placed in the core holder of AUTOLAB 1500. The essence of the rubber sleeve is to contained rock fragments upon crushing and prevent them from getting into the AUTOLAB system. The acoustic velocities of the Qusaiba shale samples were measured at different values of the confining pressure from 5×10^6 to 35×10^6 Pa, details of methodology can be found in Jin et al 2014 (Jin et al., 2014). For uniaxial compressive strength, stress (load) is applied according to a specified strain rate on the sample towards its failure. An LDTV (linear variable differential transformer (

sensor is spaced around the sample to measure the radial and axial displacements that are mic and static s modulus and Poisson ratio. The dyna'required to compute Young geomechanical parameters derived from these measurements were used to compute the corresponding dynamic and static indices of brittleness.

4.4 Results and Discussion

4.4.1 Cracks Contents, Porosity and Elastic Parameters

The concentration of cracks in solid, shale in our case is considered as the physical dominating factor responsible for the cracking condition of brittle materials. This fundamental assumption yields relation for brittleness from the ratio of the elastic energy of the crack and bulk solid. For convenience, the work done required to create elastic energy under compressive stress is redefined in term of pressure-volume product or volume-compressibility ratio. The direct observation of submicroscopic cracks under high resolution micro-CT imaging is shown in Figure 6.3. It is evident from this visual and qualitative information that the different orientations of the cracks strongly influenced the elastic and hydraulic properties of shale specimens and of course their brittleness (see later discussion on the dynamic index of brittleness). To ease experimental measurement, it is further assumed that the random distribution of cracks is the prime cause of the intrinsic anisotropy of shale. Therefore, shale is considered as isotropic and elastic but the crack distribution is anisotropic. The horizontal shale plugs denoted as 2H, 3H and 4H were used to capture the orientation of the cracks but it is not practical with vertical plugs.

The newly proposed formula of brittleness is also a function of porosity. Experimental values of porosity were derived from grain and bulk densities measurements. The grain density is measured from pycnometer while the bulk density is calculated from dimensions of the plugs measured from digital calliper. The density and porosity data are given in Table 6.2. In addition to crack distributions and porosity, dynamic elastic parameters vis-a-vis acoustic velocities are the required input for dynamic index of brittleness. The measured acoustic velocity is listed in Table 6.3. For static index of brittleness, the required static elastic parameters derived from uniaxial compressive strength is tabulated in Table 6.6.

Table 4.2: Density and Porosity Data of Qusaiba Shale

Rock ID	L (mm)	D (mm)	ρ_b (g/cc)	ρ_b (g/cc)	$\emptyset$ (%)
2V	52.33	25.18	2.64	2.77	4.69
2H	52.72	25.03	2.73	2.78	1.79
3H	52.15	25.32	2.67	2.79	4.30
4H	55.05	25.24	2.72	2.78	2.16

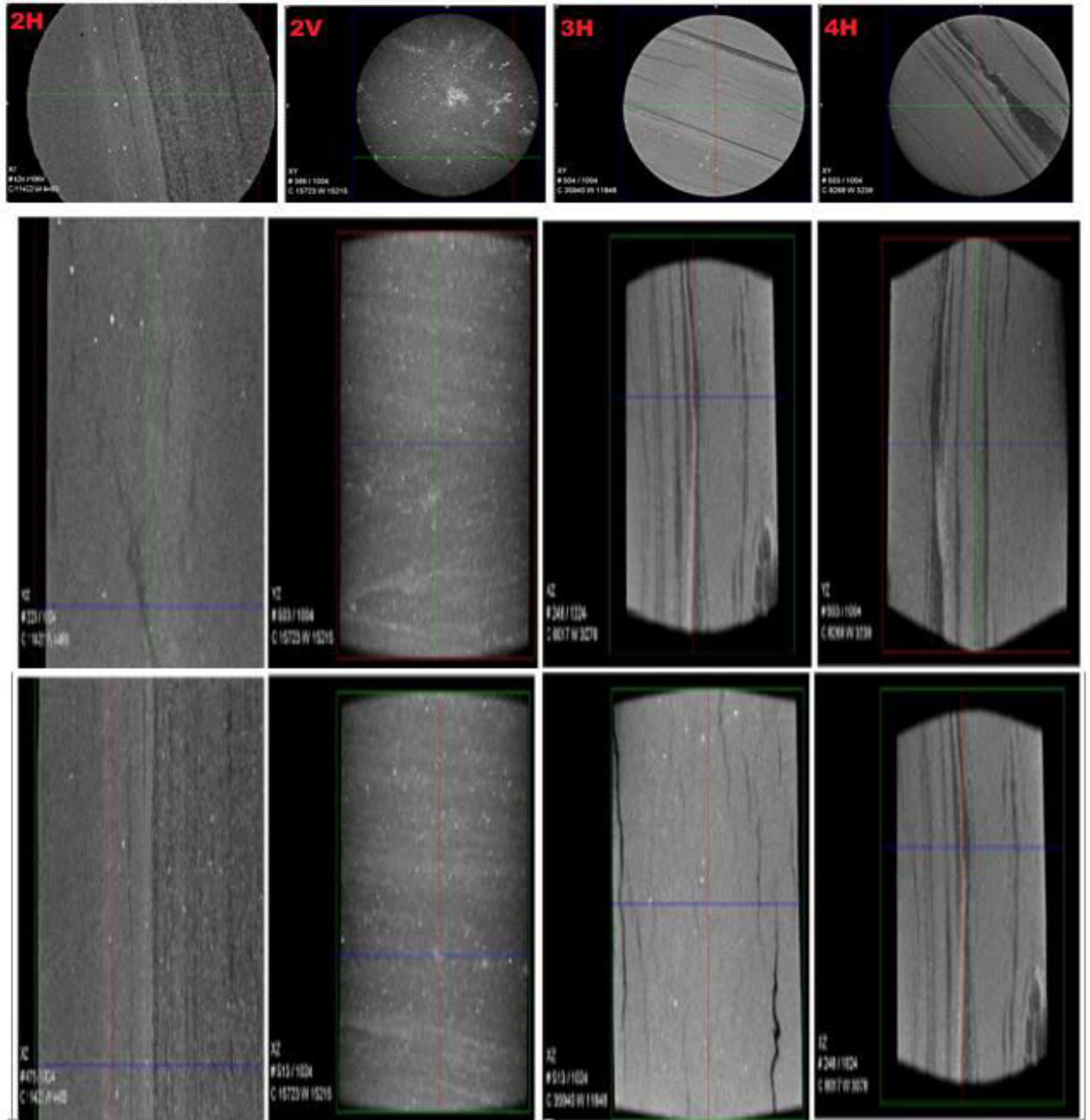


Figure 4.3:Micro-CT images of Qusaiba shale plugs (X: xy-axis, Y: yz-axis, Z: xz-axis)

Table 4. 3: Velocity measurement at three orientations

Rock ID	$P_c \times 10^6$ Pa	Orientation to bedding plane					
		0°		45°		90°	
		V_p m/s	V_s m/s	V_p m/s	V_s m/s	V_p m/s	V_s m/s
2H	5	5112	2561	3985	2497	3320	2119
	10	5212	2621	4033	2564	3495	2144
	15	5424	2687	4330	2625	3705	2212
	20	5439	2698	4426	2678	3971	2273
	25	5499	2716	4578	2703	4135	2312
	30	5537	2726	4610	2740	4148	2347
	35	5575	2737	4610	2752	4236	2378
3H	5	4999	2775	3608	2257	5255	3261
	10	5191	2818	3674	2305	5374	3286
	15	5328	2830	3759	2422	5426	3314
	20	5436	2854	3904	2504	5480	3309
	25	5563	2846	4041	2577	5535	3322
	30	5992	2853	4103	2615	5609	3329
	35	5586	2853	4218	2667	5572	3326
4H	5	5303	2867	4358	2518	3668	2190
	10	5410	2937	4555	2606	3761	2228
	15	5521	2960	4672	2674	3992	2279
	20	5521	2992	4783	2697	4066	2303
	25	5598	2983	4811	2742	4191	2337
	30	5598	2996	4929	2771	4258	2366
	35	5637	2996	4929	2795	4312	2398

4.4.2 Dynamic Index of Brittleness

To evaluate the dynamic index of brittleness denoted by γ_s , according to equation 14, estimate of porosity $\emptyset$, acoustic velocities V_p and V_s and crack aspect ratio α must be known. Laboratory data on porosity and Poisson's ratio can be readily available but crack aspect ratio is usually rare. Both P and S wave velocities were measured at three

directions 0° , 45° and 90° on the horizontal shale plugs under increasing confining pressures; step-wise increased from 5×10^6 to 35×10^6 Pa. On the basis of compression theory (see Zimmerman, 1991), the confining pressure readings were converted to crack aspect ratio for the respective shale sample by least squares regression fit shown in Figure 6.4 to Figure 6.6. The corresponding functional form of the linear regression used to derived the aspect ratio α at the 0° , 45° and 90° orientation respectively are listed in Table 6.4. To illustrate the orientating effect of cracks as shown in the micro-CT images, the dynamic index of shale brittleness is calculated in Table 6.5 with respect to orientation at the maximum confining pressure of 35×10^6 Pa. This result shows the directional behavior of brittleness due to the random size distribution of cracks for the horizontal samples. Quantitatively, the inequality $v_{45^\circ} < v_{90^\circ} < v_{0^\circ}$ holds in the case of Poisson's ratio with the same order of magnitude for the three cases of the horizontal shales plugs. Although, the numerical values of the crack aspect ratio and brittleness at 0° , 45° and 90° orientations are of the same order of magnitude, different inequalities expressed by equations 20 and 21 apply. Based on the physical interpretation that the smallest value of γ implies highest brittleness, it is clear from the inequalities of equation 21 that the perpendicular, parallel and inclined orientations are energetically favorable for 2H, 3H and 4H respectively. This information will be essential for reliable engineering design analysis of effective zones appropriate for fracking operations.

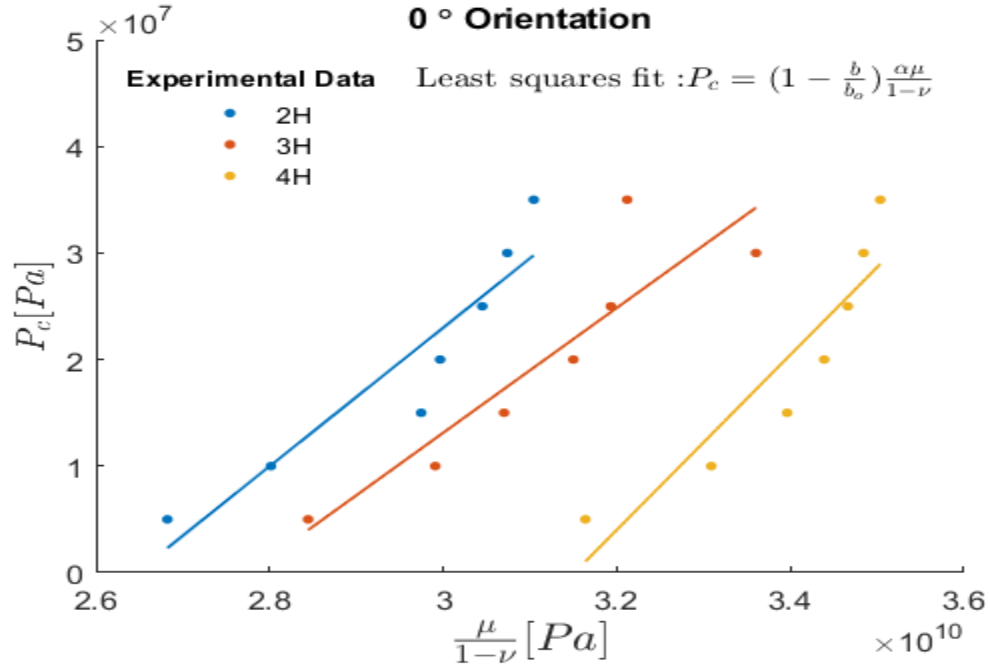


Figure 4.4: Confining pressure as function of $\frac{\mu}{1-\nu}$ at 0° orientation

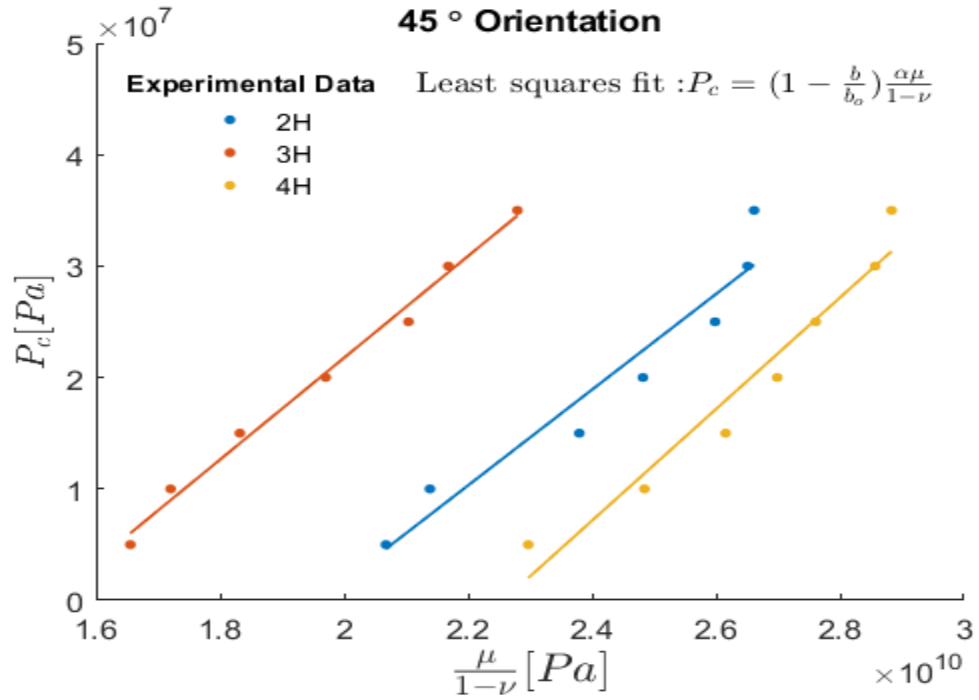


Figure 4.5: Confining pressure as function of $\frac{\mu}{1-\nu}$ at 45° orientation

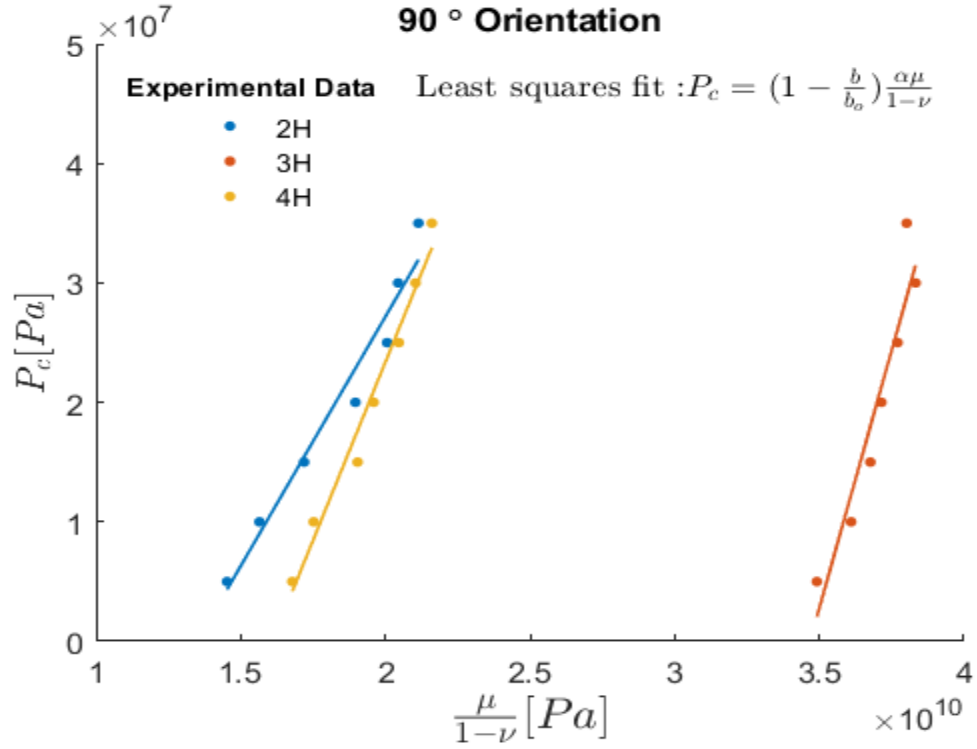


Figure 4.6: Confining pressure as function of $\frac{\mu}{1-\nu}$ at 90° orientation

Table 4. 4: Linear fit for calculating crack aspect ratio

Orientation	Rock Type	P_c
0°	2H	$0.0065 \left(\frac{\mu}{1-\nu} \right) - (2 \times 10^8) ; R^2 = 0.8743$
	3H	$0.0059 \left(\frac{\mu}{1-\nu} \right) - (2 \times 10^8) ; R^2 = 0.8229$
	4H	$0.0082 \left(\frac{\mu}{1-\nu} \right) - (3 \times 10^8) ; R^2 = 0.8453$
45°	2H	$0.0043 \left(\frac{\mu}{1-\nu} \right) - (8 \times 10^7) ; R^2 = 0.9282$
	3H	$0.0046 \left(\frac{\mu}{1-\nu} \right) - (7 \times 10^7) ; R^2 = 0.9916$
	4H	$0.0050 \left(\frac{\mu}{1-\nu} \right) - (1 \times 10^8) ; R^2 = 0.9465$
90°	2H	$0.0042 \left(\frac{\mu}{1-\nu} \right) - (6 \times 10^7) ; R^2 = 0.963$
	3H	$0.0086 \left(\frac{\mu}{1-\nu} \right) - (3 \times 10^8) ; R^2 = 0.9054$
	4H	$0.0060 \left(\frac{\mu}{1-\nu} \right) - (1 \times 10^8) ; R^2 = 0.9768$

Table 4.5: Calculation of dynamic index of brittleness γ_d with respect to orientation

Orientation							
		0°			90°		
ID	ϕ	v	α	γ_d	v	α	γ_d
2H	1.79	0.341	0.0065	99e-6	0.269	0.0042	88e-6
3H	4.30	0.324	0.0059	236e-6	0.223	0.0086	508e-6
4H	2.16	0.303	0.0082	181e-6	0.276	0.006	148e-6

$$\alpha(\text{angle}) = \begin{cases} \alpha_{90^\circ} < \alpha_{45^\circ} < \alpha_{0^\circ}, \text{ for } 2H \\ \alpha_{45^\circ} < \alpha_{0^\circ} < \alpha_{90^\circ}, \text{ for } 3H \\ \alpha_{45^\circ} < \alpha_{90^\circ} < \alpha_{0^\circ}, \text{ for } 4H \end{cases} \quad (20)$$

$$\gamma_d(\text{angle}) = \begin{cases} \gamma_{d45^\circ} < \gamma_{d0^\circ} < \gamma_{d90^\circ}, \text{ for } 2H \\ \gamma_{d90^\circ} < \gamma_{d45^\circ} < \gamma_{d0^\circ}, \text{ for } 3H \\ \gamma_{d0^\circ} < \gamma_{d45^\circ} < \gamma_{d90^\circ}, \text{ for } 4H \end{cases} \quad (21)$$

4.4.3 Static Index of Brittleness

The acoustic velocity measurements allowed us to probe the directional dependence of brittleness due to the random distribution of micro cracks. The limit of the range of confining pressure (5×10^6 to 35×10^6 Pa) may not be sufficient for the crack closure. On the other hand, the static compression experiments provide uniaxial compressive strengths that exceed the crack closure. The values of static index of brittleness computed from the uniaxial compressive strength and the static elastic constants are reported in Table 6.6. The decreasing value of the static index of brittleness γ_s from 752e-6 to 33.6e-6 in Table 6.6 shows that vertical shale plug (2V) is the least brittle and the horizontal shale plugs (2H, 3H and 4H) are more brittle with 4H being the most brittle shale. This is evident from the predominance of preexisting cracks (Figure 6.3) in the horizontal plugs compared to the vertical plug.

Table 4.6: Calculation of static index of brittleness γ_s

ID	L (mm)	D (mm)	ρ_b (g/cc)	ρ_g (g/cc)	ϕ (%)	UCS $\times 10^6$ Pa	ν	E $\times 10^9$ Pa	γ_s
2V	52.33	25.18	2.64	2.77	4.69	185.1	0.18	34.79	752E-6
2H	52.72	25.03	2.73	2.78	1.79	60.2	0.14	21.46	170E-6
3H	52.15	25.32	2.67	2.79	4.30	71.5	0.19	59.70	150E-6
4H	55.05	25.24	2.72	2.78	2.16	70.4	0.23	115.03	33.6E-6

4.4.4 Comparison with other methods

The underlying physics of brittleness as already pointed out by the Griffith's crack theory as the partition of energy due to crack surface is simple, however, quantitative prediction is difficult and not yet standardized. Due to the many applications of brittleness related problems in geology, engineering and materials science, there are several ways of predicting brittleness as tabulated in Table 6.1. Therefore, it is important to compare our current method of brittleness prediction from microcracks with the existing methods of prediction. For this purpose, we shall compare the merits and limitations of the newly proposed brittleness from microcracks with representative prediction of brittleness from rock mechanics, geophysics and mineralogy: stress-strain curve, ratio of elastic constant and ratio of rock minerals respectively. The basis of comparison as shown in Table 6.7 is with respect to the Griffith's crack theory, deformation and failure behavior, rock sample, laboratory techniques, potential field application and method of verification.

Firstly, our current approach clearly considered the effect of pre-existing cracks, whereas other methods of brittleness do not directly take this into account or can only be implied. For example, in this case of stress-strain curve method, it is not explicitly stated if the effect of the pre-existing cracks is captured. The ratio of elastic constant or mineral

fraction do not take this into consideration as well. Secondly, the partition of energy between the crack surface is another important corollary of the Griffith's crack theory which is generally ignored when evaluating brittleness. For example, the ratio of elastic constant, mineralogy and the conventional stress-strain curve illustrated in Figure 6.1 do not account for this effect, however, our methodology and the refined form of stress-strain as pre-and post-peak strength attempt to capture this important condition. Thirdly, the resulting failure of rock is also important for brittleness evaluation and it is well represented by our method as well as the stress-strain curve. On the other hand, this effect is not explicit from the ratio of elastic constants and rocks minerals, and if it does, the next question is which elastic constant or rock minerals would reflect this behavior. Another point of concern is that, brittleness defined from mineralogy on the basis of powdered rock may be difficult or impossible to upscale to those defined on intact core plugs as demonstrated by our method and those from stress-strain curve and ratio of elastic constant. In addition, laboratory prediction of brittleness based on destructive and non-destructive measurement techniques can limit the application of existing methods for potential field application. Our method as well as the ratio of elastic constant can be easily explored for this purpose using conventional well-log data. However, the choice of elastic constant that is sensitive to brittleness prediction is still a concern. With mineralogy log, although, expensive and rarely available, the ratio of rock mineral can also be adopted, in this case, the defining minerals of brittleness need to be further addressed. Finally, how to verify the existing formulas of brittleness is still a research gap that need to be addressed. Our method on the basis of microcrack is an added advantage as the computed index of brittleness is verifiable.

Table 4.7: Merits and limitations of brittleness prediction

Criteria	microcracks	stress-strain curve	ratio of elastic constant
Pre-existing cracks	yes	maybe	no
Ratio of energy	yes	maybe	no
Failure behavior	yes	yes	maybe
Rock sample	core plugs	core plugs	core plugs
Destructive	yes	yes	yes
Non-destructive	yes	no	yes
Lab-based	yes	yes	yes
Field application	yes	no	yes
Verification	yes	no	no

4.5 Conclusions

The energy contribution of shale oil and shale gas to the petroleum industry and the global energy budgets at large is conditional to the efficiency and effectiveness of shale fracking. This makes the technical and economic significance of brittleness evaluation so crucial for any shale play development. A new methodology and a mathematical equation is proposed to calculate brittleness based on energy ratio. To design a reasonably accurate characterization procedure, a working definition of brittleness is defined from the point of view of pre-existing cracks. The pre-existing cracks is considered as the critical index for brittleness evaluation because it controls the partitioning of energy between the crack inclusion and the matrix. These new brittleness characterization methods showed that the 3 cylindrical shale samples plugged horizontally are more brittle compared to the one plugged vertically. This is presumably due to the presence of pre-existing cracks which are favorable to brittle behavior of the investigated rocks. These quantitative and qualitative analyses will help locate the horizontal shale section that is energetically

favorable to aid hydraulic fracturing treatment in the high potential regions that can produce more hydrocarbon.

The main findings are summarized below:

1. The crack distribution indicates the weakening effect and as a result low crack energy relative to the total energy will be required for high index of brittleness.
2. The proposed formula as a function of acoustic velocities, elastic constants, porosity and crack aspect ratio was developed for dynamic and static index of brittleness respectively. The dynamic index of brittleness can be calculated nondestructively from velocity measurements whereas the static index of brittleness can be calculated from geomechanical parameters derived from destructive measurements.
3. The effects of cracks orientation must be taken into account to gain insights into directional dependence of brittleness. For example, crack orientation changing from parallel 0° , to incline 45° and perpendicular 90° is used to capture the directional dependence of dynamic index of brittleness.
4. The calculated index of brittleness is well correlated with the sub-microscopic crack distributions observed with micro-CT scanner.

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CHAPTER 5

Surface Relaxivity of Conventional and Unconventional Reservoirs from Rock Cuttings

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Abstract

Surface relaxivity (ρ) is an intrinsic rock property that makes low-field NMR a valuable tool for determining pore size distribution of geological formations. Its value can vary considerably in different rocks depending on the type and distribution of the rock minerals, its surface wettability and petrophysical properties. Therefore, laboratory measurement of ρ is required on a case by case basis. However, existing NMR methods are expensive, complex, and most often require supplementary non-NMR and expensive measurements. Rock samples are also required to be well consolidated and cylindrical so that experiments can be run at high pressures – a barrier for measurements of unconsolidated and thinly laminated unconventional rocks. This study proposes a new NMR method termed ‘NMR grain sizing method’, that uses different grain sizes of a given rock to generate pores of corresponding sizes. Using a geometric constant, grain specific surfaces are transformed to pore surfaces, and the governing NMR equation is rearranged so that we have a method that measures ρ from rock cuttings. This approach is simple, inexpensive, and does not require supplementary measurements. It offers an added advantage for characterizing thinly laminated formations. A proof of concept is

demonstrated for three unconventional rocks (Qusaiba shale, Jafurah carbonate mudrock and Eagle Ford) and two conventional rocks (Berea sandstone and Indiana limestone). The ranges of surface relaxivity are $96.9 - 134.5 \mu\text{m/s}$ (Qusaiba shale); $62.07 - 106 \mu\text{m/s}$ (Jafurah carbonate mudrock); $55.9 - 68.72 \mu\text{m/s}$ (Eagle Ford); $35.51 - 43.2 \mu\text{m/s}$ (Berea sandstone); and $33.2 - 40.54 \mu\text{m/s}$ (Indiana limestone). All ρ measurements are reproducible with 95% confidence interval. The measured values for Indiana limestone and Berea sandstones were validated with micro CT based pore network models and also compare well with literature data. Measurement of Qusaiba shale and Jafurah carbonate source rocks are apparently reported for the first time here.

5.1 Introduction

Nuclear magnetic resonance (NMR) relaxation measurement, also called NMR relaxometry, is the domain of nuclear magnetic resonance (NMR) techniques that is popular in petroleum geosciences. The principle of NMR borehole logging is based on measurements of relaxation signals due to the nuclear spin of protons present in fluid saturated geological rocks. The total signal is proportional to the number of protons present in the bound and free reservoir fluids. Such data give vital petrophysical information about the reservoir rocks such as porosity, permeability, free fluid index, capillary bound fluids, and viscosity of the reservoir fluids. A recent review (Liu et al., 2020) elucidates the applications of NMR relaxometry in characterizing unconventional reservoirs such as shale and coal bed methane, which in recent decades have become an important source of energy in United States, Canada, Australia, and other countries.

Two kinds of relaxation times are measured (Kenyon, 1997; Kleinberg et al., 1993; Mitchell et al., 2013; Mitchell and Fordham, 2014): spin-lattice relaxation time (longitudinal relaxation time) symbolized as T_1 and spin-spin relaxation time (transverse relaxation time) denoted as T_2 . The magnetic source for these measurements can be separated into three classes as high, intermediate and low field respectively (Mitchell et al., 2013). In addition to measuring the absolute values of the relaxation times, it is of geological and petrophysical interest to extract the model parameters of relaxation time such as bulk fluid relaxation time T_{2b} , diffusion coefficient (D), and surface relaxivity (ρ_2). The corresponding surface relaxivity of the two relaxation times are denoted as ρ_1 (longitudinal relaxation) and ρ_2 (transverse relaxation). Since NMR relaxation time is inversely related to surface relaxivity, it is expected that ρ_2 will be greater than ρ_1 when T_1 is greater than T_2 . Each of these model parameters would provide specific petrophysical information. For example, T_{2b} is related to fluid viscosity, surface relaxivity is the controlling parameter to estimate pore size, while diffusion coefficients can be used to estimate tortuosity. However, these parameters are challenging to resolve from NMR relaxation time because they are coupled. The primary emphasis of several investigations has been on surface relaxivity partly because it is not only related to pore size but also mineralogy, permeability, T_2 cut-off and wettability. Recent laboratory measurement has demonstrated that surface relaxivity is of critical importance to determine the pore size of coal from NMR (Zheng et al., 2019). Surface relaxivity is also affected by mineralogy (Saidian and Prasad, 2015; Sulucarnain et al., 2012; Washburn et al., 2017). Wettability measurement of shale samples have been reported to be related to surface relaxivity (Sulucarnain et al., 2012). Numerical simulation also confirm that

NMR permeability and T_2 cut-off are both a function of surface relaxivity (Hidajat et al., 2002).

While surface relaxivity is an important rock parameter, it cannot be measured directly from only NMR relaxometry of the rock. NMR relaxation times in conjunction with pore size are needed before surface relaxivity can be determined. The pore size data are usually obtained from Diffusion NMR, BET gas adsorption, mercury injection capillary pressure (MICP), backscattered electron imaging (BSEI), optical image analysis (OIP), and micro-CT. Based on MICP supported measurements, the ratio of ρ_2 and ρ_1 ranges from 2.9 – 9.6 for sandstones (Mitchell and Fordham, 2014). With BET supported measurements, ρ_2/ρ_1 ratio is the range of 1.97 – 4.5 for carbonate (Mitchell and Fordham, 2014). Table 5.1 summarizes the values of surface relaxivity for some selected sedimentary rocks.

There seem not to be a unique method of determining surface relaxivity. Zheng et al., (Zheng et al., 2019) emphasized that there is no satisfactory agreement between surface relaxivity determined from BET (low-pressure Nitrogen adsorption) and MICP. Laboratory data reported on sandstones using BET, diffusion NMR (PFG), MICP, BSEI and OPI also indicate different values of surface relaxivity (Basan et al., 1997). The discrepancy between values of surface relaxivity reported by these techniques can be attributed to the differences in the scale of measurements. Generally, the least value of surface relaxivity is reported from the BET because BET ‘sees’ different surface. In some cases, limitations in sample handling and preparation using one method (with a large scale of measurement) can make another method (with a low scale of measurement) a viable alternative.

Table 5.1: Surface relaxivity of some selected sedimentary rocks

Geologic Formations	Pore Data	Size	$\rho_2(\mu\text{m/s})$	References
Limestone	MICP	1-3.2		(Marschall et al., 1995)
Sandstone	BSEI	-		(Basan et al., 1997)
Sandstone	OPI	-		(Basan et al., 1997)
Sandstone	Pulse Field Gradient (PFG) NMR	-		(Basan et al., 1997)
Sandstone	MICP	13.73-30.96		(Mitchell and Fordham, 2014)
Limestone	BET	2.17-7.32		(Mitchell and Fordham, 2014)
Shale	BET	0.39-2.54		(Saidian and Prasad, 2015)
Weber sandstone	Pulse Field Gradient (PFG) NMR	22.9-28.7		(Wang et al., 2018)
Madison Limestone	Pulse Field Gradient (PFG) NMR	30.1-38.7		(Wang et al., 2018)
Coal	MICP	3.36-8.4		(Zheng et al., 2019)
Coal	BET	0.77-1.91		(Zheng et al., 2019)
Indiana Limestone (small pore)	Analytical	204		(Afrough et al., 2019)
Indiana Limestone (large pore)	Analytical	195		(Afrough et al., 2019)
Berea Sandstone	Analytical	237		(Afrough et al., 2019)
Sandstone	Micro-CT	10-93		(Lucas-Oliveira et al., 2020)

Generally, the least value of surface relaxivity is reported from the BET because BET ‘sees’ different surface. In some cases, limitations in sample handling and preparation using one method (with a large scale of measurement) can make another method (with a low scale of measurement) a viable alternative. For example, some shale samples can be very tight, fissile, and fragile such that saturation and mercury injection into them can be very challenging. It was pointed out that the pore system of unconventional tight rocks are challenging to characterize (Adeyilola et al., 2020) and diffusion experiments are complicated because the presence of small pores would strongly restrict diffusion

(Kleinberg and Horsfield, 1990; Saidian and Prasad, 2015). Similarly, for fragile shale, capillary pressure as low as 315 psi (2.17 MPa) can be destructive (Yuan et al., 2018). Furthermore, previous techniques are generally expensive and time consuming. Consequently, a certain value of surface relaxivity is commonly assumed to be representative of a given lithology. For instance, surface relaxivity of sandstone is generally taken as $3\mu m/s$ (Washburn et al., 2017). A constant surface relaxivity value may be valid for monomineralic rocks but certainly not in multimineralic rocks.

This paper proposes a new approach that directly measures surface relaxivity from NMR relaxometry experiments alone using different granular packs of mono-sized grains ranging from 1 to 4 mm. This approach is motivated by the need to characterize the surface relaxivity of a thinly laminated carbonate-dominated source rock from Saudi Arabia Jafurah basin. Jafurah shale holds promising unconventional shale gas reserves in Saudi Arabia. It is brittle, fragile, and thinly laminated, making it impossible to drill cylindrical plugs needed for conventional NMR petrophysical studies. We present the theoretical background and methodology used to characterize rock cuttings from unconventional shales such as Jafurah, Qusaiba, Eagle ford and conventional rocks like Indiana limestone and Berea sandstone. Section 1.1 gives a theoretical background to the constitutive equation for our experiments. Section 1.3 gives an overview of the rock samples used in the experiments. The experimental apparatus and methods conducted to validate our model are elaborated in section 2, while section 3 presents and discusses the results. Finally, section 4 presents the conclusion. A supplementary information section is presented to give more data for the reader's reference.

5.2 Theoretical Background

The mathematics describing the physics of NMR relaxometry is the well-known Bloch-Torrey equation. Originally introduced as a differential equation of vector fields by Bloch (Bloch, 1946) and further extended by Torrey (Torrey, 1956) to capture diffusion effects. The solution and simplification of the Bloch equations was developed for biological cell (Brownstein and Tarr, 1979) and sedimentary rocks (Cohen and Mendelson, 1982). Cohen and Mendelson derived equation 1 to establish that the relaxation rate is related to the surface to volume ratio of pore space of sedimentary rocks. This equation is generally valid for low-field NMR relaxation rates because the diffusion effect of T_2 becomes negligible at low resonance frequency and short pulse spacing or echo times (Kleinberg et al., 1994). As simple as these equations appear, there are three unknowns for each case of longitudinal and transverse relaxation times. Therefore, it is impossible to resolve the unknown model parameters (bulk fluid relaxation time, surface relaxivity and surface-to-volume ratio of pore) from NMR measurement alone.

$$\frac{1}{T_i} = \begin{cases} \frac{1}{T_{1b}} + \frac{1}{T_{1s}} = \frac{1}{T_{1b}} + \rho_1 \frac{S}{V}, & i = 1 \\ \frac{1}{T_{2b}} + \frac{1}{T_{2s}} = \frac{1}{T_{2b}} + \rho_2 \frac{S}{V}, & i = 2 \end{cases} \quad (1)$$

where T is the relaxation time, $\frac{1}{T}$ is the relaxation rate, ρ is the surface relaxivity, $\frac{S}{V}$ is the surface-to-volume ratio of the pore space, the superscripts b and s indicate the bulk and surface effect while the subscripts 1 and 2 denote the longitudinal and transverse mode of relaxation respectively.

Strictly speaking, the surface-to-volume ratio is the derivative of the pore shape for indicating pore size (Brownstein and Tarr, 1979; Cohen and Mendelson, 1982). In this context, we can recast equation 1 as equation 2 by expressing the surface area as derivative of the volume with respect to the characteristic length l_p and r_p .

$$\frac{1}{T_i} = \begin{cases} \frac{1}{T_{1b}} + \frac{1}{T_{1s}} = \frac{1}{T_{1b}} + \rho_1 \frac{dV}{V}, & i = 1 \\ \frac{1}{T_{2b}} + \frac{1}{T_{2s}} = \frac{1}{T_{2b}} + \rho_2 \frac{dV}{V}, & i = 2 \end{cases} \quad (2)$$

In equation 2, the symbol dV denote the derivative of an arbitrary pore volume. Because this volume is not known, the original solution of Brownstein and Tarr (Brownstein and Tarr, 1979) was implemented in rectangular, cylindrical and spherical coordinates corresponding to a planar, cylindrical and spherical geometry. If the pore is assumed to be cylindrical in shape, its surface-to-volume ratio is characterized by two length parameters (radius and length) as shown in equation 3. To represent the pore shape as a cylinder would further complicate the problem with the addition of one extra parameter. For simplification, the cylindrical pore can be assumed to be a needle-like pore or capillary model with $l_p \gg r_p$ such that $l_p \rightarrow \infty$ and thus the reciprocal of l_p becomes negligible. Because of the symmetry of a sphere, only the radius of the sphere is required to characterize the surface-to-volume ratio of spherical pore given by equation 4.

$$\frac{dV_{p,c}}{V_{p,c}} = \frac{\frac{\partial}{\partial r_p}(\pi r_p^2 l_p) + \frac{\partial}{\partial l_p}(\pi r_p^2 l_p)}{\pi r_p^2 l_p} = \frac{2(\pi r_p l_p + \pi r_p^2)}{\pi r_p^2 l_p} = 2 \left(\frac{1}{r_p} + \frac{1}{l_p} \right) \approx \frac{2}{r_p} \quad (3)$$

$$\frac{dV_{p,s}}{V_{p,c}} = \frac{\frac{d}{dr_p} \left(\frac{4}{3} \pi r_p^3 \right)}{\frac{4}{3} \pi r_p^3} = \frac{3}{r_p} \quad (4)$$

Assuming a spherical pore, the representation of the transverse relaxation time is given by equation 5.

$$\frac{1}{T_2} = \frac{1}{T_{2b}} + \frac{1}{T_{2s}} = \frac{1}{T_{2b}} + \frac{3\rho_2}{r_p} \quad (5)$$

With the simplification of equation 5, independent measurements of T_{2b} and r_p for the confined rock fluid and pore size respectively is needed before surface relaxivity can be estimated from relaxation time. To overcome this limitation, we consider the pore-grain volume relationship expressed by equation 6.

$$V_p = \frac{\phi}{(1 - \phi)} V_g \quad (6)$$

Where, V_p is the pore volume and V_g is the grain volume.

Assuming, a spherical pore and spherical grain, we have:

$$r_p = \left(\frac{\phi}{(1 - \phi)} \right)^{\frac{1}{3}} r_g \quad (7)$$

In conformity with the IUPAC nomenclature, we use the width $w = 2r$ instead of radius r to generalize the characteristic length of a planar and the diameter of a spherical geometries. Using this notation equation 7 becomes:

$$w_p = \left(\frac{\phi}{(1 - \phi)} \right)^{\frac{1}{3}} w_{g,s} \quad (8)$$

In the context of NMR relaxometry, equation 8 becomes:

$$w_p = \left[\frac{\phi_{\text{NMR}}}{(1 - \phi_{\text{NMR}})} \right]^{\frac{1}{3}} w_{g,s} \quad (9)$$

Where, w_p is the width of the pore, $w_{g,s}$ is the width of a sphere-like grain and ϕ_{NMR} is the NMR porosity.

By substituting equation 9 into equation 5, the transverse relaxation time for spherical grain becomes equation 10.

$$\frac{1}{T_2} = \frac{1}{T_{2b}} + \frac{1}{T_{2s}} = \frac{1}{T_{2b}} + 6\rho_2 \left[\frac{(1 - \phi_{\text{NMR}})}{\phi_{\text{NMR}}} \right]^{\frac{1}{3}} \frac{1}{w_{g,s}} \quad (10)$$

Simplifying further, we have:

$$\frac{1}{T_2} = \frac{1}{T_{2b}} + \frac{1}{T_{2s}} = \frac{1}{T_{2b}} + \left[\frac{216(1 - \phi_{\text{NMR}})}{\phi_{\text{NMR}}} \right]^{\frac{1}{3}} \frac{\rho_2}{w_{g,s}} \quad (11)$$

Rewriting 11 in the form of equation 1, we have:

$$\frac{1}{T_2} = \frac{1}{T_{2b}} + c_{g,s} \frac{\rho_2}{w_{g,s}} \quad (12)$$

where is $c_{g,s} = \left[\frac{216(1 - \phi_{\text{NMR}})}{\phi_{\text{NMR}}} \right]^{\frac{1}{3}}$ is the geometric constant for a spherical grain, $w_{g,s}$ is the diameter of the spherical grain and ϕ_{NMR} is the NMR porosity.

It is important to note that the assumption that T_{2b} is about four order of magnitude larger than T_{2s} led to the derivation of equation 1 (see reference (Cohen and Mendelson, 1982) for more detail). To directly measure surface relaxivity without information of the pore size, we modified equation 1 as equation 12. If the assumption of $T_{2b}/T_{2s} = 10^4$ is

further imposed, the bulk relaxation rate $\frac{1}{T_{2b}}$ can be put to zero, then equation 1 and 12 would reduce to equation 13. We shall refer to equation 13 for surface relaxivity determination as an approximate model.

$$\frac{1}{T_2} = \rho_2 \frac{S}{V} = \frac{\rho_2 C_{g,s}}{w_{g,s}} \quad (13)$$

5.3 Experimental apparatus and methods

In this section, we present the experimental apparatus and procedures conducted to validate the model presented in equation 12. Qusaiba shale, Jafurah Carbonate Murdock, Eagle Ford, Indiana limestone, and Berea sandstone were all studied. Low field NMR experiments were conducted on all the samples, while gas sorption isotherm (BET analysis) was conducted on only Jafurah, while X-ray micro CT based pore network model was conducted on Berea sandstones and Indiana limestones.

5.3.1 Preparation of rock cuttings

Each of the intact rock samples were crushed in a grinding machine into cuttings and further disintegrated by successive hammering. The experimental design aimed at sieving the rock samples into 4 different grain fractions of 1mm, 2mm, 3.35mm (hereafter denoted as 3 mm) and 4 mm as shown in Figure 5.1. This range is selected to ease the saturation and packing of the cuttings. For effective sieve analysis of the prescribed grain sizes, a stack of sieves of 0.5mm, 1mm, 1.7mm, 2mm, 2.8mm, 3 mm, 4mm and 4.75 mm were arranged vertically in this order on a mechanical shaker. The rock cuttings were placed in the topmost sieve of 4.75mm and cuttings of less than 0.5mm were collected in

a receiving pan at the bottom of sieves. The reason for the intermediate sieves such as 1.7mm and 2.8mm was to properly distinguish the grain sizes. For example, the 1.7mm sieve is used to separate the 1mm and 2mm grain sizes, while 2.8mm helps to discriminate 2mm from 3 mm grain size. This step is essential for the overall effectiveness of the low-field NMR grain sizing. The shaker was switched on allowing for sufficient time of 5-10 minutes to agitate the samples in accordance with the standard practice in section 7.3.2.1 of the API Recommendation Practice (API, 1998).

The crushing, hammering, sieving and sorting is not systematic and as a result the amount of each grain size collected after sieving is not always perfectly the same. As experience shows, more of 1mm and 2mm grain size is usually retrieved compared to the 3 mm and 4 m grain size. The procedure which is manually demanding need to be repeated until the required volume for each grain size is obtained. It may be said that the process of repeated hammering and sieving is lengthy and laborious, but the availability of rock cuttings obtained at the wellsite during drilling will minimize the labor. In addition, the human intervention required for successive sorting and collecting of the grain fractions is also not necessary with the use of the “automatic drill cuttings sampler” (Horeth, 1966). It is hoped that similar devices would be replicated for laboratory use in the nearest future to overcome these efforts.

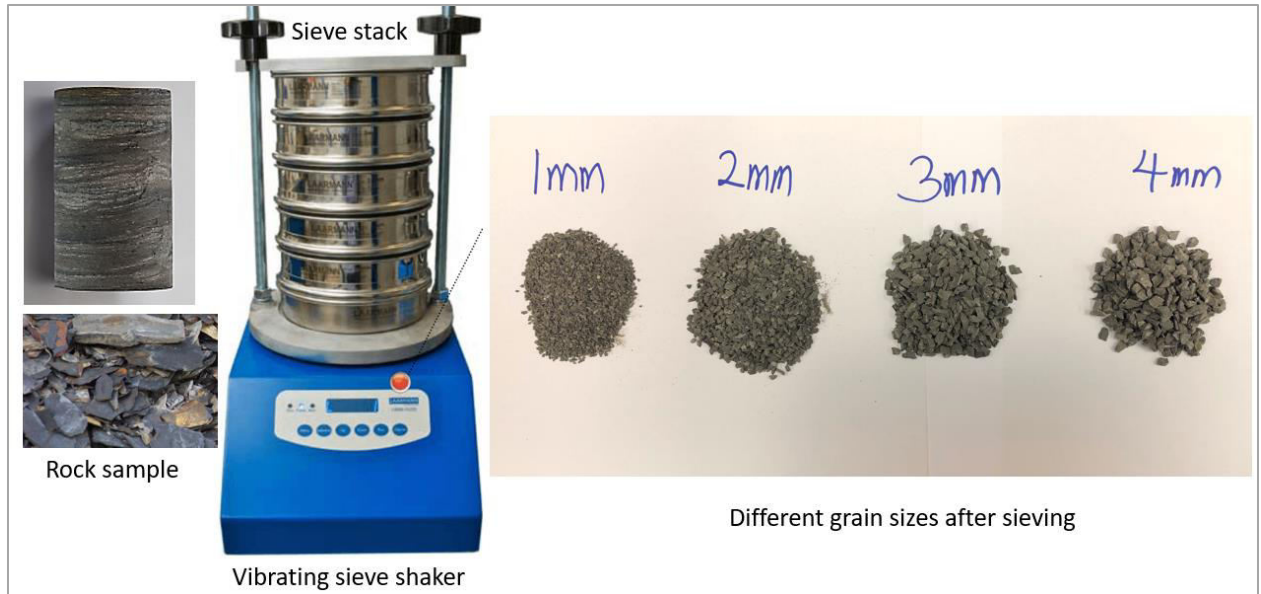


Figure 5.1: Preparation of rock cuttings

5.3.2 Saturation and Packing

A polytetrafluoroethylene (PTFE) rod is fabricated into a right circular cylinder tube to contain the rock cuttings for NMR measurement. The choice of PTFE material is to ensure that the detected NMR signal is only due to the rock and fluid interaction, without inference from the container. The recommended procedure (Meazza et al., 1996) of core re-saturation is followed to saturate the rock cuttings. The polytetrafluoroethylene (PTFE) tube was first filled with deionized water up to about 2 cm length. Small volume of rock cutting was then submerged in accordance with suggested practice of API (API, 1998) (section 5.2.1.1 of the API Recommended Practice) until 100% saturation is achieved. That is, the volume of the cuttings is wholly submerged. This procedure was then repeated until the whole length of the PTFE tube is filled with “soaked” cuttings. The excess surface/free water was completely dampened with paper towel as recommended by API protocol (API, 1998) (section 5.2.4.6.2 of the API Recommended

Practice). This is important to get rid of the free fluid effect on the NMR signal. As shown in Figure 5.2, the pseudo core (PTFE tube + saturated rock cuttings) was then carefully wrapped with a cling film to preserve the saturating fluid against evaporation during NMR measurement. It is important to mention that before adopting the API protocol, we observed partial or incomplete saturation when first filling the sample into PTFE tube followed by the addition of saturating fluid.



Figure 5.2: Saturation and Packing of rock cuttings

5.3.3 NMR Measurements

A benchtop low-field NMR equipment (Oxford Instrument Oxford Geospec2™) was used to perform T_2 relaxation measurements on the saturated rock cuttings. The laboratory low-field NMR spectrometer operating at 0.05 T is equipped with Green Imaging Technologies (GIT) system. We have found GIT system to be user-friendly software because of the possibility for the sequentially measure T_2 relaxation and saturation. The conventional procedure of CPMG is followed and the experimental

parameters include: Tau time of 0.1ms, and T_2 max of 1800 ms with signal-to-noise ratio generally greater than 100.

5.3.4 BET Measurement

A small chip from the Jafurah carbonate source rock was taken for surface area measurement based on isotherm gas adsorption with Nitrogen gas as the adsorbate. Assuming a monolayer surface based on Brunauer-Emmett-Teller (BET) theory, the amount of nitrogen adsorbed on the surface of the Jafurah sample was recorded as a function of the partial pressure of nitrogen. A linear fit of the BET equation was used to generate the slope and intercept which was then used to calculate the total surface area. The surface area normalized to the mass of Jafurah sample was calculated as $9.68 \pm 0.02 \text{ m}^2/\text{g}$. The surface area per unit mass can be converted to surface area per unit volume using:

$$S/V = (S_m \rho_g)(1 - \phi) / \phi \quad (14)$$

where $S/V \text{ (m}^2/\text{m}^3\text{)}$ is the surface area per unit volume, $S_m \text{ (m}^2/\text{g}\text{)}$ is the surface area per unit mass, $\rho_g \text{ (g/cm}^3\text{)}$ is density and ϕ is the porosity.

5.4 Results and Discussions

5.4.1 NMR T_2 and Grain Size

NMR T_2 measurements were performed on four cuttings of different grain sizes per rock type, making a total of 20 cuttings. The T_2 relaxation times for the different grain sizes of

these rock types (shale, sandstone, and carbonate) are listed in Table 5.2. For each grain size, three experiments were conducted after repacking and saturating the grains. The T_2 profiles displayed in Figure 5.3 showed that the NMR T_2 distribution generally varies with the grain size of each rock type. The different trend in the porosity measurements can be attributed to different packing arrangements. The NMR T_2 spectra (Figure 5.3) are dominated by macro pores. This is possibly due to the loose packing of the millimeter-sized grains. Hence, implying that the effect of the micro-pore and the connected phase between the micro and macro pore is negligible on the T_2 spectrum. The implication of this large pore effect is that some of these macro pores particularly due to the 3mm and 4mm grain sizes may not completely obey the fast diffusion limit, that is $\frac{\rho r_p}{D} \ll 1$, where ρ is the surface relaxivity, r_p is the pore size and D is the self-diffusion of the saturating fluid. The constraint imposed by the fast-diffusion limit suggest that the grain size should not exceed 4mm. Importantly, the Brownstein-Tarr parameter established that the practical resolution limit of the NMR grain sizing technique is 4mm.

Table 5.2: Results of T₂ measurements of bulk water and rock cuttings

Rock samples	Grain width (mm)	Experiment 1		Experiment 2		Experiment 3	
		T ₂ log mean (ms)	NMR $\emptyset$	T ₂ log mean (ms)	NMR $\emptyset$	T ₂ log mean (ms)	NMR $\emptyset$
Qusaiba	1	823.47	0.52	700.856	0.478	623.158	0.445
	2	1034.108	0.497	855.386	0.458	814.653	0.446
	3	1458.932	0.501	1078.278	0.428	1078.278	0.428
	4	1098.547	0.481	993.687	0.469	1004.944	0.486
Jafurah	1	787.043	0.392	906.755	0.393	964.436	0.411
	2	899.241	0.376	1101.67	0.406	1182.66	0.41
	3	1354.716	0.394	1388.87	0.426	1319.89	0.443
	4	1371.433	0.382	1674.2	0.407	1421.48	0.412
Eagle	1	1215.026	0.465	1101.124	0.408	1061.699	0.396
	2	1466.308	0.375	1302.732	0.368	1318.245	0.357
	3	1680.553	0.416	1695.385	0.404	1682.796	0.45
	4	1796.696	0.427	1537.76	0.423	1709.877	0.445
Sandstone	1	1007.842	0.603	939.083	0.515	989.646	0.543
	2	1085.696	0.532	903.557	0.532	950.115	0.511
	3	1152.431	0.526	1111.243	0.536	1134.972	0.519
	4	1234.942	0.518	1141.31	0.507	1172.381	0.539
Carbonate	1	1273.905	0.512	1208.406	0.487	1200.855	0.475
	2	1524.45	0.534	1460.302	0.492	1432.684	0.499
	3	1577.733	0.536	1550.413	0.531	1571.671	0.546
	4	1538.061	0.509	1513.963	0.543	1537.387	0.538

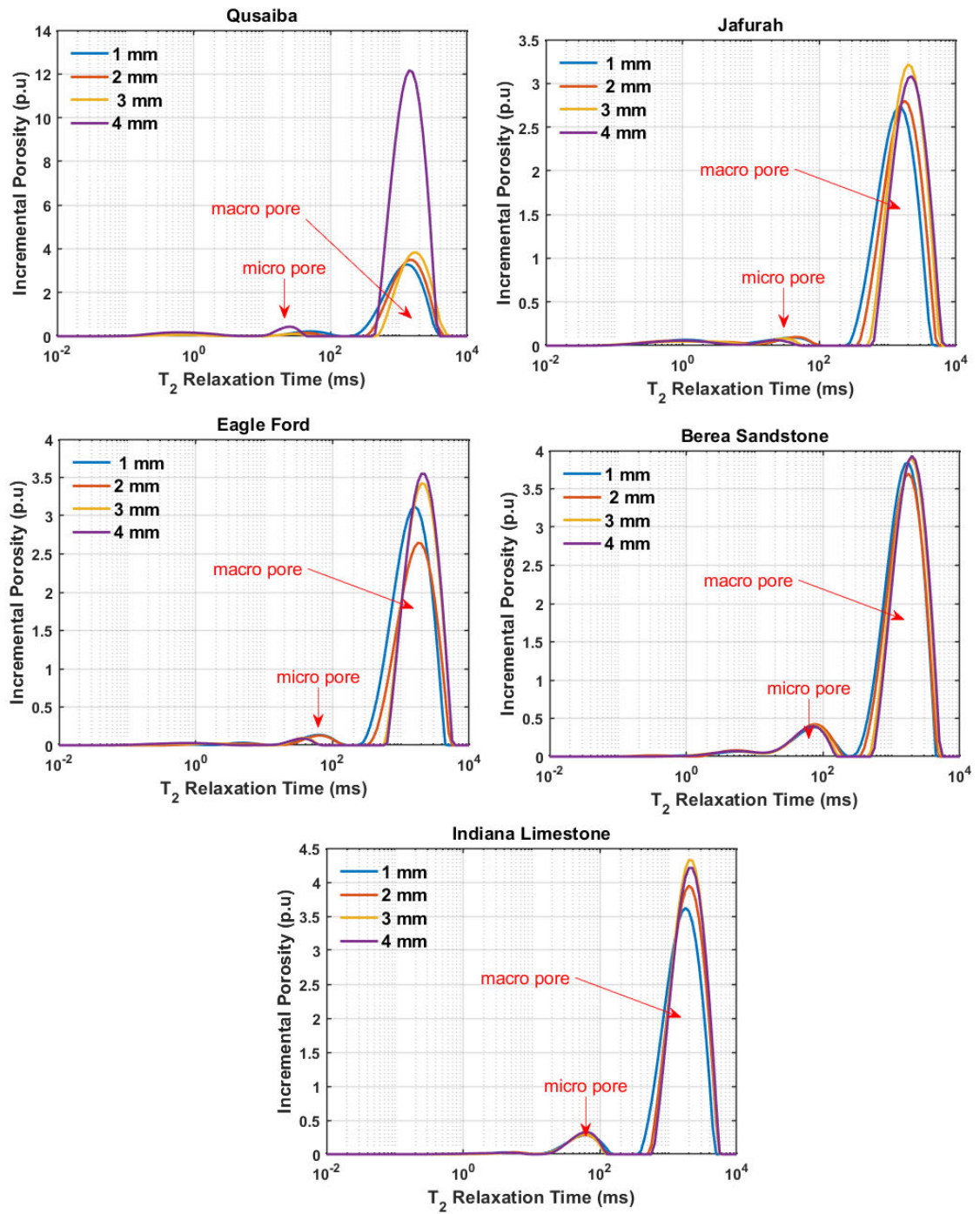


Figure 5.3: NMR T_2 distribution-grain size relationship

5.4.2 Calculation of Bulk Fluid Relaxation Time and Surface Relaxivity

Based on equation 13, linear regression models were generated with the data extracted from Table 5.2. The values of the T_{2b} and ρ_2 for each experiment correspond to the intercepts and slopes, respectively, of the linear equations displayed in Figure 5.4. The estimated values of T_{2b} for the deionized water saturating these rock samples are completely different from the T_{2b} of 2800 ms measured when it exists as a bulk fluid. This observation is in agreement with the study of Brownstein and Tarr (Brownstein and Tarr, 1979) that the T_{2b} value for bulk water is different for the water confined inside a biological cell. The established explanation of this effect is that T_{2b} of water is influenced by the presence of dissolved oxygen and paramagnetic elements (Bloembergen et al., 1948). In the case of fluid-saturated rocks, there is a likely tendency that the natural state of the fluid would be altered by the chemical composition of rocks. In other words, the amount and type of dissolved solids is likely to change the pH and salinity of the deionized water. This is evident with the deionized water exhibiting different color after saturation. This color difference is immediately obvious during the saturation of the samples, particularly for the source rocks. To validate this observation, T_{2b} and pH of the distilled water before and after NMR measurements is measured and reported in Table 5.3.

Table 5.3: Values of T_{2b} and pH of distilled water

	Pre-NMR Measurements		Post-NMR Measurements			
	DI	DIQ	DIJ	DIE	DIB	DII
T_{2b} (ms)	2800	1983.2	1993.9	2047.3	2031.3	2423.6
pH	7.09	8.35	7.71	9.07	9.19	9.60

DI=deionized water; DIQ=deionized water extracted from Qusaiba; DIJ=deionized water extracted from Jafurah; DIE= deionized water extracted from Eagle Ford; DIB=

deionized water extracted from Berea sandstone; DII=deionized water extracted from Indiana limestone

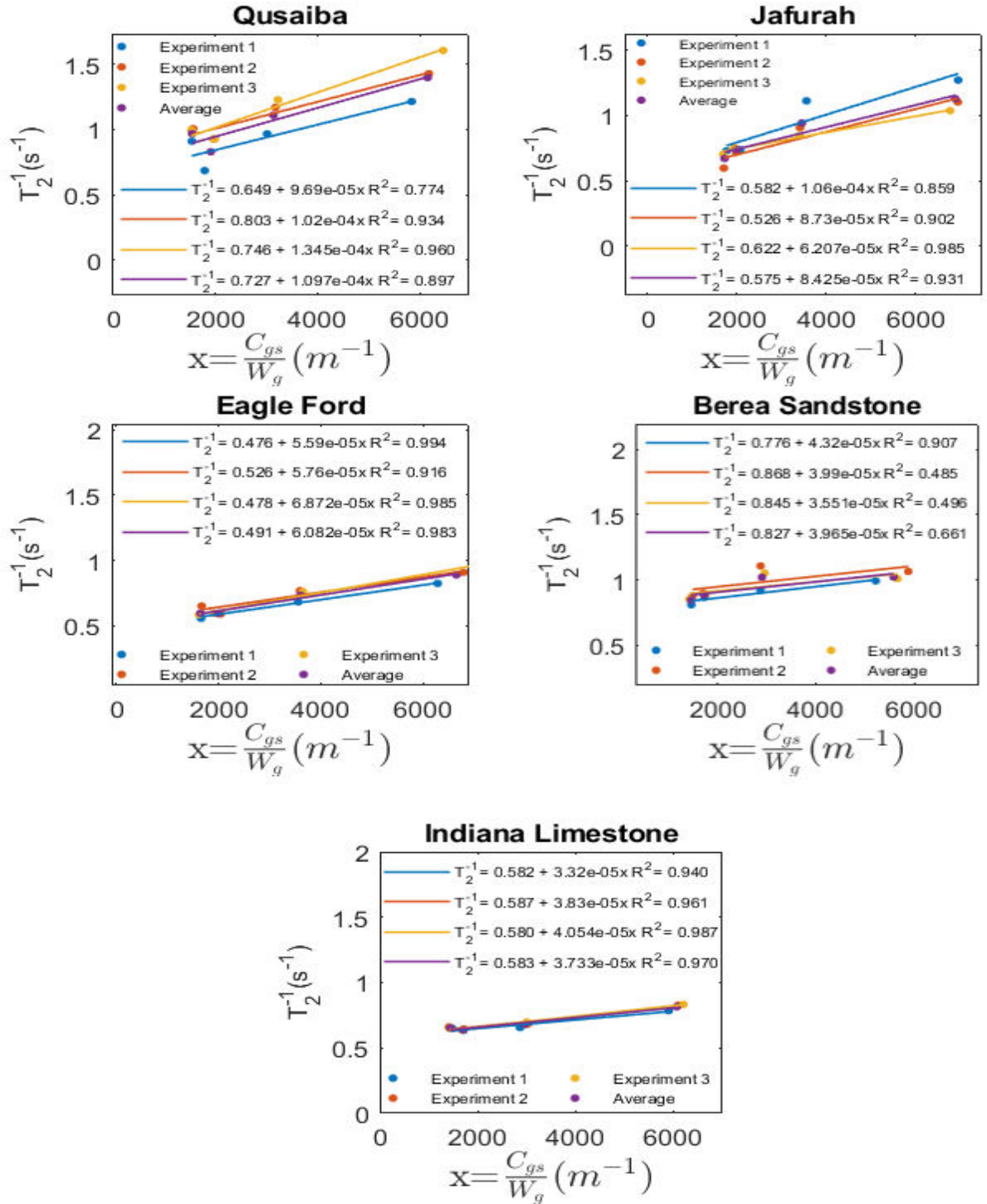


Figure 5.4: T_2^{-1} versus $\frac{C_{gs}}{W_g}$ for Spherical Grain Model

5.4.3 Spatial Variation of T_{2b} and ρ_2

Theoretical and simulation study suggests surface relaxivity is not uniform but vary in space (Arns et al., 2006; Ryu, 2008). This theoretical conclusion was investigated in this study for the T_{2b} and ρ_2 of each rock type with three repeated measurements. As shown in Table 5.2, different values of porosity were recorded for each of the three packing arrangements. The variation of $\frac{C_{gs}}{W_g}$ is reflected by the change in porosity. Because $\frac{C_{gs}}{W_g}$ is related to $\frac{1}{w_p}$ or surface-to-volume ratio of the pore space, different packing or grain arrangement can result in the spatial arrangement of the grains and then a variation of pore distribution. Consequently, the values of T_{2b} and ρ_2 varied with the pore geometry. These variations are illustrated in Table 5.4. Therefore, the average of these three measurements can be considered as the effective T_{2b} and ρ_2 for each grain size.

Table 5.4: Values of T_{2b} and ρ_2 based on spherical grain model

Formation	Exp. 1	Exp. 2	Exp. 3	Avg	Exp.1	Exp. 2	Exp. 3	Avg
	$T_{2b}(\text{ms})$				$\rho_2(\mu\text{m/s})$			
Qusaiba	1540.4	1244.9	1341.4	1376.1	96.9	102	134.5	109.7
Jafurah	1717.2	1901.3	1607.3	1740.4	106	87.3	62.07	84.25
Eagle Ford	2102.7	1900.2	2095.5	2035.1	55.9	57.6	68.72	60.82
Berea Sandstone	1289.2	1152.3	1184.0	1209.4	43.2	39.9	35.51	39.65
Indiana Limestone	1718.7	1703.6	1725.6	1716.1	33.2	38.3	40.54	37.33

5.4.4 Effect of T_{2b} on ρ_2

The surface relaxivity, ρ_2 appears to correlate with the position of macro pore peak. Consequently, for the fast diffusion limit to guarantee the linearity between T_2 and pore size, the large pore effect need to be compensated by the bulk T_{2b} . However, in a

confined state, T_{2b} and T_{2s} as the two components of T_2 cannot be measured directly and as a results the approximate model (equation 14) is commonly used for surface relaxivity prediction. With the given uncertainties associated with pore size measurements, the correct determination of surface relaxivity is further bound with errors in the presence or absence of large pore effect. For example, in any natural rock with long T_2 due to large pores, surface relaxivity will be under-estimated with the use of $\rho_2 = \frac{r_p}{T_2}$ instead of $\rho_2 = \left(\frac{1}{T_2} - \frac{1}{T_{2b}}\right)r_p$. To account for the large pore effect on representative and realistic surface relaxivity determination, two recent studies (Duschl et al., 2015; Lucas-Oliveira et al., 2020) considered T_{2s}^{-1} as the difference between the T_2^{-1} of the saturated rock and T_{2b}^{-1} of the bulk fluid. It is important to note that T_{2b} here is measured as the free/bulk fluid. In our case, we check the validity of this approximation by ignoring the bulk T_{2b} so that the linear regression models for different rock types can be fitted with equation 14. We observe that the plots in Figure 5.5 become nonlinear when the compensating effect of the T_{2b} is neglected. In addition to this observation, the comparison of the spherical grain and approximate models for the different rock types is listed in Table 5.5. Note that the surface relaxivity based on the approximate model is substantially larger than the spherical grain model. Interestingly, for the linearity between the T_2 of the micro-pore and its corresponding pore size to hold, the large pore effect will be excluded and the approximate model would be satisfied. This further implies that decreasing pore size would be equivalent to increasing surface relaxivity ρ because T_2 is directly proportional to pore size but inversely proportional to surface relaxivity ρ . In other words, the faster relaxation of the micro pore with short T_2 of about 100ms would translate to higher surface relaxivity.

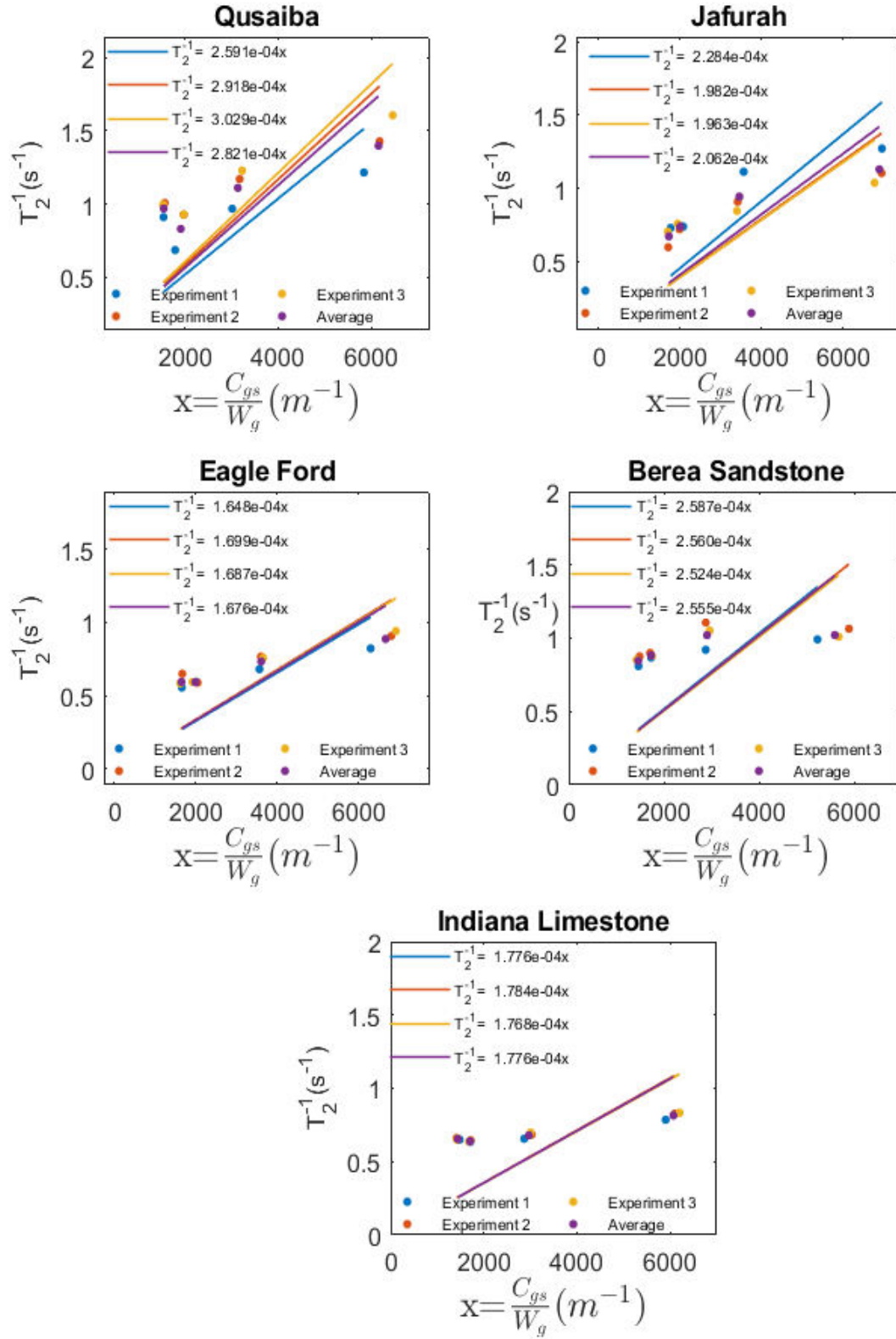


Figure 5.5: T_2^{-1} versus $\frac{C_{gs}}{W_g}$ for Approximate Model

Table 5.5: Comparison of spherical grain and approximate models

	Spherical Grain Model				Approximate Model			
	Exp. 1	Exp. 2	Exp. 3	Avg	Exp.1	Exp. 2	Exp. 3	Avg
Formation	$\rho_2 (\mu\text{m/s})$				$\rho_2 (\mu\text{m/s})$			
Qusaiba	96.9	102	134.5	109.7	259.1	291.8	302.9	282.1
Jafurah	106	87.3	62.07	84.25	228.4	198.2	196.3	206.2
Eagle Ford	55.9	57.6	68.72	60.82	164.8	169.9	168.7	167.6
Berea Sandstone	43.2	39.9	35.51	39.65	258.7	256.0	252.4	255.5
Indiana Limestone	33.2	38.3	40.54	37.33	177.6	178.4	176.8	177.6

5.4.5 Effect of grain shape

The rock cuttings are irregular in shape and size. The variations in size can be controlled by systematic sieve analysis and the irregularity in shape can be idealized by simplified geometry. In our previous analysis, we assumed spherical geometry for the grains and pores which was parameterized by a dimensionless constant denoted as C_{gs} . To study the geometric effect of the grain shape on T_{2b} and ρ_2 for the same measurement, we considered a cubic grain and spherical pore. For this case, the equivalent of equations 9 and 12 are given as equations 15 and 16 respectively. The linear regression of the data for this case are illustrated in Figure 5.6. The intercept of the fitted linear equations (see Figure 5.6) is the same as that of the spherical grain model (see Figure 5.4). This is due to the fact that the same condition of saturation and fluid volume is applied in both cases. However, there are distinctive differences between the values of the ρ_2 for the same rock type. The ρ_2 value estimated based on the cubic grain model is consistently higher than that of the spherical grain model (see Table 5.6). This suggest that the specific shape of the rock cutting can significantly influence the values of C_{gs} and C_{gc} for the spherical

grain and cubic grain model, respectively. Thus, like the pore geometry, the assumed grain shape also influences the derived value of surface relaxivity ρ_2 .

$$w_p = \left(\frac{6}{\pi}\right)^{\frac{1}{3}} \left[\frac{\phi_{\text{NMR}}}{(1 - \phi_{\text{NMR}})} \right]^{\frac{1}{3}} w_{g,c} \quad (15)$$

$$\frac{1}{T_2} = \frac{1}{T_{2b}} + c_{g,c} \frac{\rho_2}{w_{g,c}} \quad (16)$$

where w_p is the width of the pore, $w_{g,c}$ is the width of a cubic grain, ϕ_{NMR} is the NMR porosity and $c_{g,c} = \left[\frac{36\pi(1-\phi_{\text{NMR}})}{\phi_{\text{NMR}}} \right]^{\frac{1}{3}}$ is the geometric constant connecting pore surface-to-volume ratio and grain surface-to-volume ratio.

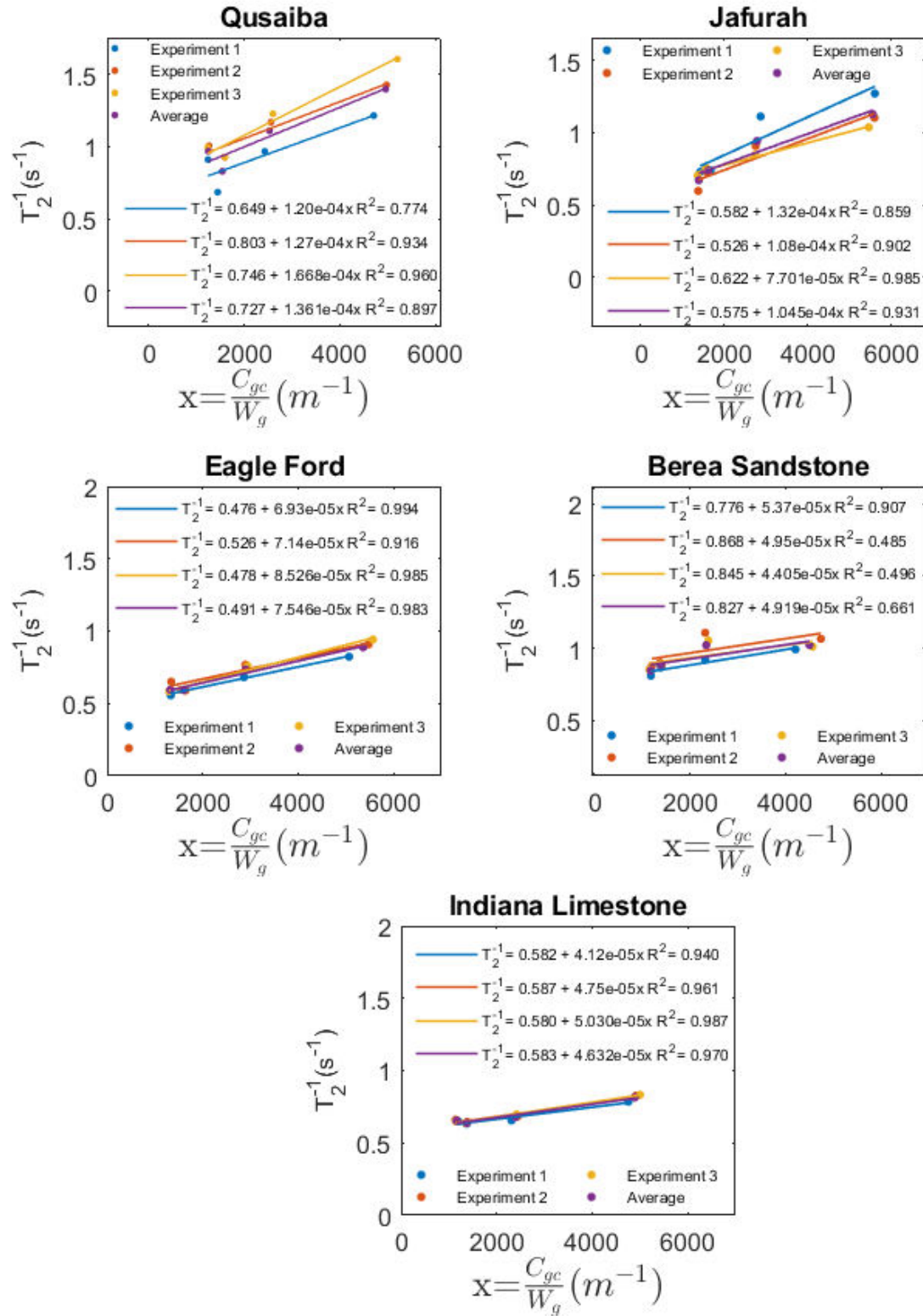


Figure 5.6: T_2^{-1} versus $\frac{C_{gc}}{W_g}$ for Cubic Grain Model

Table 5. 6: Comparison of spherical and cubic grain models for estimate of ρ_2

Formation	Spherical Grain Model				Cubic Grain Model			
	Exp. 1	Exp. 2	Exp. 3	Avg	Exp.1	Exp. 2	Exp. 3	Avg
	$\rho_2(\mu\text{m/s})$				$\rho_2(\mu\text{m/s})$			
Qusaiba	96.9	102	134.5	109.7	120	127	166.8	136.1
Jafurah	106	87.3	62.07	84.25	132	108	77.01	104.5
Eagle Ford	55.9	57.6	68.72	60.82	69.3	71.4	85.26	75.46
Berea Sandstone	43.2	39.9	35.51	39.65	53.7	49.5	44.05	49.19
Indiana Limestone	33.2	38.3	40.54	37.33	41.2	47.5	50.3	46.32

5.4.6 Surface relaxivity of Source Rocks and Reservoirs Rocks

The NMR surface relaxivity is a function of mineralogy, pore size and saturating fluid. Since the pore size generated from the loose packing of the different rocks grains and the saturating fluid is relatively constant, it is expected that the surface relaxivity of the investigated rocks would be within the same order of magnitude. In view of this fact, the distinctive differences in surface relaxivity of these rock types is primarily due to their mineral constituents. As shown in Table 5.5, the surface relaxivity values of the source rocks (Qusaiba, Jafurah and Eagle Fold) are generally greater than those of the reservoir rocks (Berea sandstone and Indiana Limestone). For these source rocks, Qusaiba shale has the highest surface relaxivity, followed by Jafurah and Eagle Fold. The chemical composition of these source rocks listed in Table 5.7 revealed that the paramagnetic and ferromagnetic contents of Qusaiba shale is significant compared with the other source rocks. This also explain why the surface relaxivity of the source rocks are greater than the reservoir rocks. For the reservoir rocks, the surface relaxivity of sandstone (Berea sandstone) is higher but comparable with that of the carbonate (Indiana limestone). These values are in line with the surface relaxivity of sandstone and Indiana limestone recently

reported surface relaxivity of sandstone and carbonate, e.g. see, Wang et al (Wang et al., 2018), Afrough et al (Afrough et al., 2019) and Lucas-Oliveira et al (Lucas-Oliveira et al., 2020). However, surface relaxivity of carbonate such as limestone derived from MICP is smaller e.g. see, Marschall et al (Marschall et al., 1995). Carbonate is a multi-porosity rock system and NMR is primarily sensitive to pore size, whereas MICP “sees” pore throat diameter. With the mismatch between pore size and pore throat diameter, MICP supported measurement is not recommended for carbonate (Mitchell and Fordham, 2014). This resolution problem suggests that constant value of NMR surface relaxivity do not strictly apply.

Table 5.7:Chemical Composition of Rock Samples

Elements	Magnetic Property	Qusaiba (wt.%)	Jafurah(wt.%)	Eagle Ford (wt.%)	Berea Sand
O	Paramagnetic	46.3	48.5	47.4	-
Na	Paramagnetic	0.6	-	-	0.23
Mg	Paramagnetic	2.0	-	-	0.36
Al	Paramagnetic	14.9	3.6	1.3	5.38
Si	Diamagnetic	23.6	7.6	5.8	84.8
S	Diamagnetic	-	3.2	-	-
K	Paramagnetic	5.3	0.8	-	3.5
Ca	Paramagnetic	-	34.7	45.4	2.11
Ti	Paramagnetic	0.8	-	-	-
Fe	Ferromagnetic	6.5	1.6	-	2.49

5.4.7 Effect of Potential Determining Minerals

To investigate the effects of mineral type on surface relaxivity, we plot the 95% confidence interval on the prediction coefficients for the average of the three measurements in Figure 5.7. The upper bound and the lower bound of the confidence interval are denoted by the dash purple and yellow dash lines respectively. The interval

width for Indiana limestone, Eagle and Jafurah are relatively low compared to those of Qusaiba shale and Berea sandstone. This can be explained in terms of variable chemical composition. The mineralogy of the carbonate rocks such as Indiana limestone, Eagle ford and Jafurah is mainly dominated by calcite. It is very likely that only calcium resulting from calcite would be the determining paramagnetic element influence the NMR measurements for Indiana limestone. Elemental analysis indicates that three major paramagnetic elements including oxygen, aluminum, calcium would influence NMR measurements for Eagle ford. In case of Jafurah, three major paramagnetic elements (oxygen, aluminum, calcium, and potassium) and one ferromagnetic elements (iron) are contributing to NMR measurement. For Qusaiba, six paramagnetic elements and one ferromagnetic element are the potential determining minerals on the NMR measurements. The iron content of Qusaiba shale is 6.5 wt.% compare with the 1.6 wt.% for Jafurah. The competing magnetic interactions among the different ferromagnetic and paramagnetic elements is mostly dominant in Qusaiba shale compare with Jafurah and Eagle Ford. It is very likely that the heterogeneous mineral constituents of Berea Sandstone would be responsible for its larger interval width compare with that of Indiana limestone. From the 95% confidence interval and elemental composition, it can be deduced that relative confidence interval width increases with the iron content.

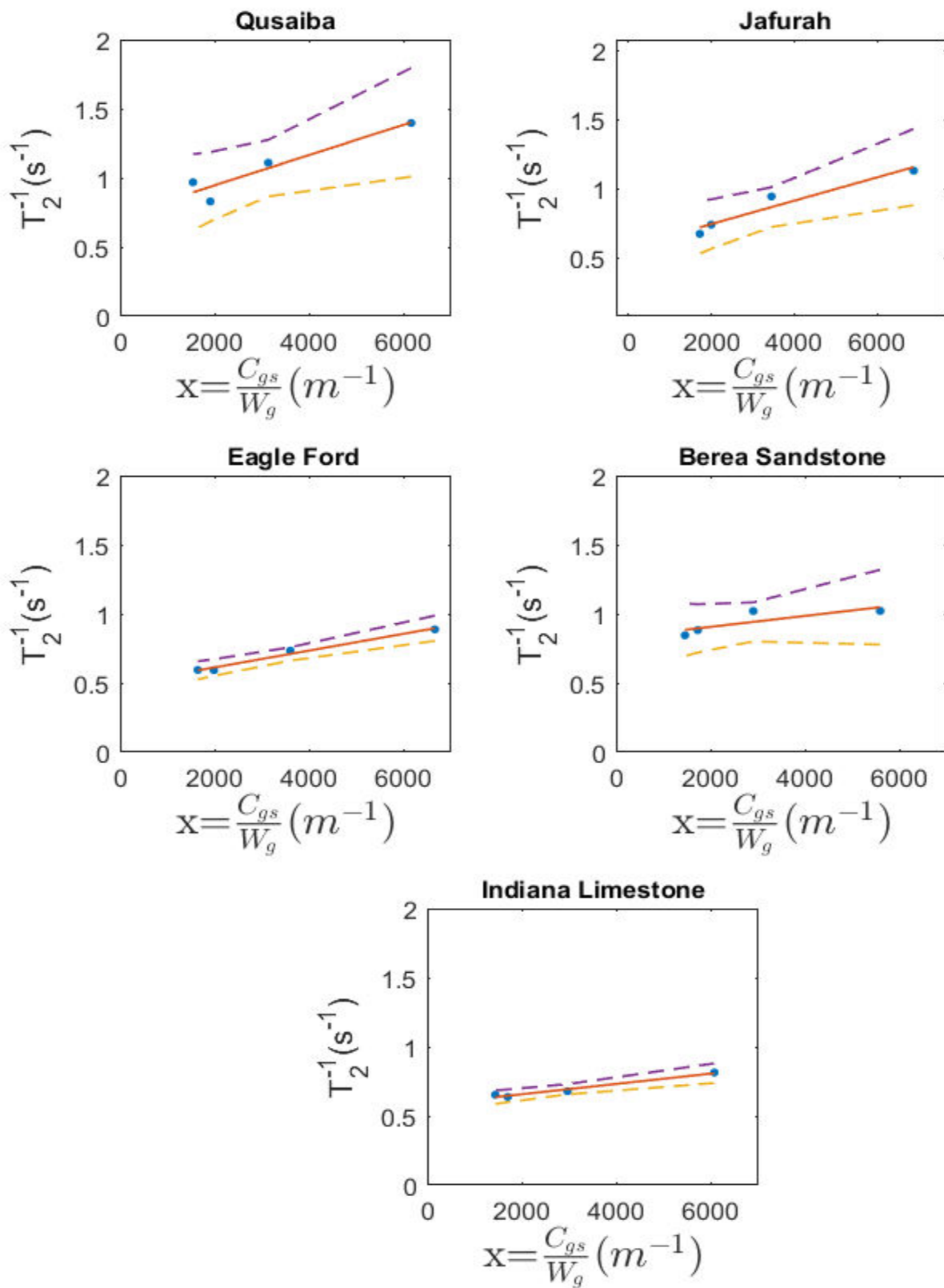


Figure 5.7: Effect of Mineralogy on 95% Confidence Interval

5.4.8 Comparison with other methods

A detailed study of the different techniques of estimating surface relaxivity is beyond the scope of this work. We concentrate on the measurement of BET Nitrogen adsorption for only the Jafurah sample and pore network modelling study on the carbonates and Berea sandstones. The average surface area per unit mass S_m for Jafurah sample as measured by BET Nitrogen adsorption is $9.67 \text{ m}^2/\text{g}$ and the average grain density ρ_g is measured as $2.467 \text{ g}/\text{cm}^3$. If $S/V = S_m \rho_g$, by adopting equation 14, the range of surface relaxivity ρ_2 as conducted on the 1mm, 2mm, 3mm and 4mm grain sizes fall in the range 0.0252-0.0536 $\mu\text{m}/\text{s}$. There is a several order of magnitude difference between the low-field NMR grain sizing and the BET approach. It is expected that the surface relaxivity calculated by integrating NMR and BET gas adsorption measurement would be significantly underestimated. This is because the pore size measured by the BET gas adsorption is on the nanometer scale. Combining the NMR measurements with the pore network models constructed from the digital 3D image obtained by X-ray micro CT scans, the surface relaxivity of Berea Sandstone and Indiana limestone were estimated as 94 $\mu\text{m}/\text{s}$ and 65 $\mu\text{m}/\text{s}$ respectively. With the NMR grain sizing, the corresponding surface relaxivity for these samples are in the range of 35.51 – 43.2 $\mu\text{m}/\text{s}$ and 33.2 – 40.54 $\mu\text{m}/\text{s}$ respectively. Although, the values of surface relaxivity obtained by combining NMR and micro-CT measurements are consistently higher than that of the NMR grain sizing, they are of the same order of magnitude (see Table 5.8). One would also argue that when combining NMR and X-ray micro CT pore network modelling, the two complementing measurements were done at significantly different scales. The NMR measurements were conducted on cylindrical rock sample (with volume of 50,000 – 60,000 mm^3) while the

3D pore network model represents only a tiny fragment of the rock (with volume $0.5 - 1\text{mm}^3$). Hence, scale effect could be responsible for the differences in surface relaxivity values obtained by grain sizing and those obtained by X-ray micro CT pore network modelling and BET as reported in Table 5.8.

Table 5.8: Comparison of ρ_2 ($\frac{\mu\text{m}}{\text{s}}$) measurements

Formation	NMR Grain Sizing	NMR/BET	NMR/PNM
Jafurah Mudrock	84.25	0.0536	-
Berea Sandstone	39.65	-	94
Indiana Limestone	37.33	-	65

For the comparison to be conclusive, we also rely on the comprehensive literature data discussing all existing methods for longitudinal surface relaxivity ρ_1 measured on sandstone. Based on spherical grain model, estimate of the transverse surface relaxivity ρ_2 of Berea sandstone by our NMR grain sizing method is in the range of $35.5 - 43.2 \mu\text{m/s}$. The recent measurement of transverse surface relaxivity ρ_2 on sandstone by (Lucas-Oliveira et al., 2020) using micro-CT data is the range of $10 - 93 \mu\text{m/s}$, which matches our NMR/micro CT pore network model on Berea sandstone. The transverse surface relaxivity ρ_2 values were converted to longitudinal surface relaxivity ρ_1 by assuming that the average ratio for ρ_2 and ρ_1 is 3.5 for sandstone. Based on this conversion factor, the values of ρ_1 for sandstone based on our NMR grain sizing and our NMR/micro CT pore network model measurement vary from 10.4 to $12.7\mu\text{m/s}$ and 2.9 to $27.4\mu\text{m/s}$ respectively. As shown in Figure 5.8, this range falls within the ρ_1 of sandstone estimated by BSEI, PFG NMR and MICP. The agreement of the NMR grain sizing method with four of the conventional techniques complementing NMR relaxation

measurement gives confidence on its applicability. For carbonate, the average surface relaxivity of Indiana limestone measured by NMR grain sizing is 37.33 $\mu\text{m/s}$ and 65 $\mu\text{m/s}$ for our NMR/pore network model. In Table 5.1, the longitudinal surface relaxivity ρ_1 for limestone measured by PFG NMR is in the range of 2.6-11 $\mu\text{m/s}$. Using BET, the values of ρ_2 for limestone range from 2.17 – 7.32 $\mu\text{m/s}$ and with MICP it varies from 1 – 3.2 $\mu\text{m/s}$. The surface ρ_2 of Indiana limestone from the NMR grain sizing is considerably larger than the values obtained using from BET and MICP. Again, this discrepancy can be attributed to the difference in scale of examination. Because carbonate usually have heterogeneous pore system, the assumption of inter-granular pores may not always apply for carbonate. To model the heterogeneity of surface relaxivity for carbonate rocks, the concept of apparent surface relaxivity ρ_{app} of inter-granular pores and intrinsic surface relaxivity ρ_{int} of micro-pores was introduced (Ramakrishnan et al., 1999). It was stated that the apparent surface relaxivity is one order of magnitude greater than the intrinsic surface relaxivity (Ramakrishnan et al., 1999). The expression (equation 17) to transform the apparent surface relaxivity ρ_{app} to intrinsic surface relaxivity ρ_{int} will be investigated in future work.

$$\rho_{app} \approx \rho_{int}(1 - \phi_{\mu}) + \sqrt{\frac{\phi_{\mu}D}{F_{\mu}T_{2\mu}}} \tanh\left(\sqrt{\frac{\phi_{\mu}F_{\mu}r_g^2}{DT_{2\mu}}}\right) \quad (17)$$

Where, ρ_{app} , ρ_{int} , ϕ_{μ} , F_{μ} , r_g , $T_{2\mu}$, and D are the apparent surface relaxivity, intrinsic surface relaxivity, micro-porosity, electrical formation factor of the microporous grain, grain radius, relaxation time of the microporous grain and diffusion coefficient for bulk water respectively.

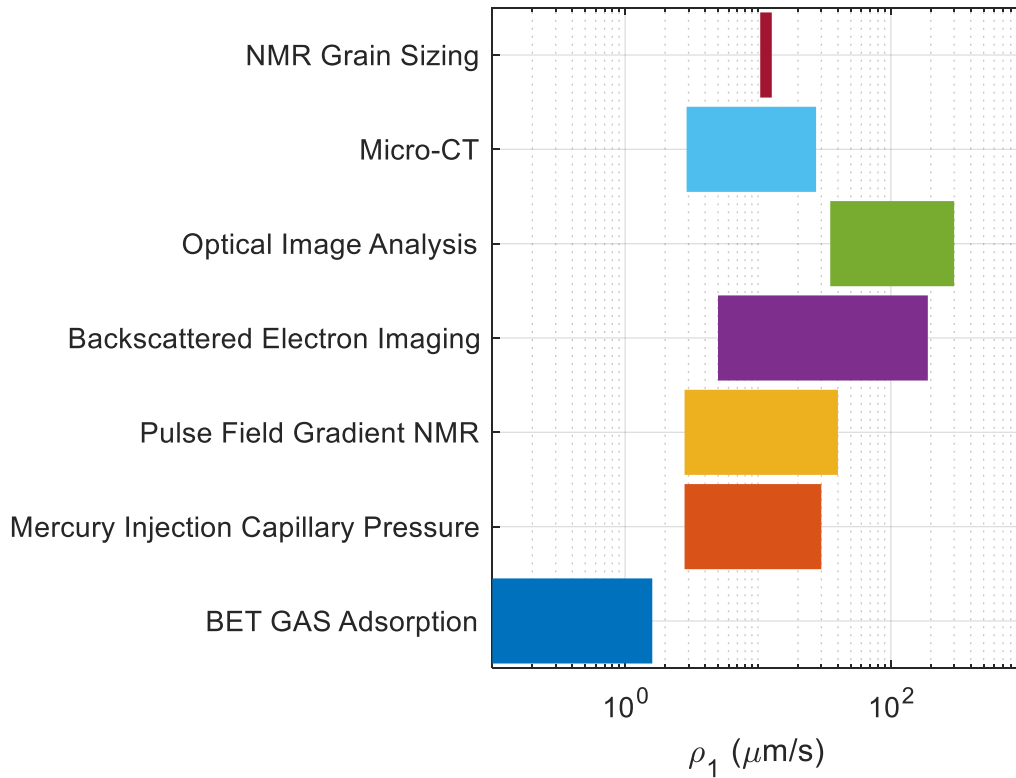


Figure 5.8: Comparison of ρ_1 values for sandstone updated after (Basan et al., 1997)

5.5 Conclusion

A novel technique for measuring NMR surface relaxivity termed as ‘grain sizing method’ has been proposed to study geological rocks. We gave the theoretical background, experimental procedures, method, and model validation. With the new ‘grain sizing method’, we easily measured the surface relaxivity of a variety of geological rocks and attempted to understand how their mineral constituents affect their surface relaxivity measurements. Following extensive experiments on a variety of unconventional shale rocks (Qusaiba, Jafurah, Eagle ford) and conventional rocks (Indiana limestone and Berea sandstones), the following important conclusions are drawn.

- 1) A 'grain sizing method' is a viable, simple, and cost-effective method of measuring NMR surface relaxivity. Unlike other methods, grain sizing method is a standalone method, requiring no complementary measurements. Hence, surface relaxivity measurements can be made without concerns about effect of using different probing fluids and different scales of measurement normally associated with other methods.
- 2) Relaxivity measurements can be conducted on drilled cuttings obtained at wellsite, and on highly laminated rock formations that are too fissile to be prepared for conventional measurements.
- 3) The effect of surface relaxivity on T_2 relaxation can be studied without neglecting the pore scale effect of bulk fluid. This study argued that localized presence of paramagnetic minerals, fluid compositional change in pores, and the resultant pH change at pore scale can make the effect of bulk fluid T_2 significant at pore scale as observed.
- 4) Iron minerals affected NMR relaxation time measurements and in turn rock surface relaxivity of Qusaiba, Berea sandstone and Jafurah. Indiana limestone rocks consist of 100% calcite, therefore the surface relaxivity measurements were repeatable with very high degree of confidence compared to other rocks with iron content.
- 5) Values of surface relaxivity range from 96.9 to 134.5 $\mu\text{m/s}$ for Qusaiba shale; 62.07 to 106 $\mu\text{m/s}$ for Jafurah carbonate mudrock; 55.9 to 68.72 $\mu\text{m/s}$ for Eagle Ford; 35.51 to 43.2 $\mu\text{m/s}$ for Berea sandstone; and 33.2 to 40.54 $\mu\text{m/s}$ for Indiana limestone respectively.

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CHAPTER 6

Conclusion and Outlook

The workflow for source rocks should include, the assessment of key rock properties including maturation, sorption and brittleness. Maturation (thermal maturity) provides crucial information on how different source rocks generate hydrocarbon. As carbonate source rocks have emerged as a viable source of shale gas, their characterization is of scientific and economic interest. Because these source rocks are unique due to their little or no vitrinite, an integrated methodology is proposed to study the kinetics and measure gas evolution potential of the Jafurah carbonate source rock. The important finding of this study indicate that the generative potential of methane is very high relative to carbon dioxide. Unlike the conventional reservoir rocks, source rocks do not exhibit predominant inter-particle pore storage. As a result, the fluid trapping mechanism is primarily accomplished through sorption in which hydrocarbon can be stored as liquids or gases in condensed phase. For this reason, the classical equation of hydrocarbon volume estimation based on the effective porosity of the connected pore space is no longer valid for source rocks. Instead, sorption analysis is required to quantify essentially the gas storage potential of source rocks. While previous studies were mainly devoted to isothermal condition, this work investigated the case of non-isothermal condition. The interesting finding is that the sorption capacity of methane generally increases with

temperature. However, high at very high temperature the sorption capacity reduces. This may be due to the decomposition of the kerogen at this temperature. Brittleness is another important parameter to assess the geomechanical behavior of source rocks towards hydraulic fracturing. The new approach of brittleness quantification in the terms of microcracks contents show that brittleness is directional dependence. This is important to guide the process of fracturing source rocks. It is important to emphasize that rock-fluid interaction is an essential step in the characterization workflow of source rock. This study shows how surface relaxivity can be measured from NMR relaxation measurements of different grain sizes for the purpose of characterizing the rock-fluid behavior of rocks.

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