

**APPLICATION OF CYCLIC EXOTHERMIC AND ENDOTHERMIC
THERMOCHEMICAL FLUIDS FOR TIGHT RESERVOIRS**

BY

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A Thesis Presented to the

COLLEGE OF GRADUATE AND INTERDISCIPLINARY STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

PETROLEUM ENGINEERING

DECEMBER, 2024

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

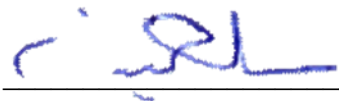
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This is dedicated to my mother, siblings, and my future family |

ACKNOWLEDGMENTS

May the blessings, protection, love, goodness and all mercy of the Almighty Sovereign God, the creator of all mankind continue to follow us for all the days of our lives. I extend my genuine thanks to him who predestined me to accomplish my Master's degree in Petroleum Engineering at King Fahd University of Petroleum and Minerals successfully. It was a journey of endurance, commitment and determination. My stay at KFUPM for this graduate program was richly rewarding, with always tasks to accomplish, thanks to the scholarship committee for guaranteeing me this full international scholarship. I also thank the departmental academic and non-academic staff who equipped me with a great deal of invaluable knowledge and unwavering support in the different study areas through my entire coursework period.

Regarding my research (thesis), I'm immensely grateful for the unconditional support from my advisor Dr. Talal Al Shafloot, who supported me along with my entire committee members; Dr. Arshad Raza, Prof. Mohamed Mahmoud, Dr. Sulaiman Alarifi, and Dr. Amjed Hassan to let me live my dream of accomplishing the program in the minimum number of semesters. They ensured the smooth running of my research without any interruptions. I also extend my appreciation to all the lab engineers whose labs I visited to conduct tests required for my research. Their strong willingness to add value to my research and skills was unimaginable. May God bless them and reward them according to his riches in glory. I continue to thank all good people I met and became friends with me in the new environment, they made me feel at home. Lastly, I appreciate the full communication, support, and continuous prayers from my family back home. These played a very big role throughout my entire academic journey of this program.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	V
TABLE OF CONTENTS	VI
LIST OF TABLES	IX
LIST OF FIGURES	X
LIST OF ABBREVIATIONS	XIII
ABSTRACT.....	XV
ملخص الرسالة	XVII
CHAPTER 1 INTRODUCTION.....	1
1.1 Background	1
1.2 Problem Statement and Objectives	5
CHAPTER 2 LITERATURE REVIEW.....	7
2.1 Shale Rock Characterization.....	7
2.1.1 Clay Mineralogy and Shale Instability	8
2.1.2 Total Organic Carbon Content	10
2.1.3 Permeability	11
2.2 Breakdown Pressure	12
2.2.1 Breakdown Pressure Models	14
2.2.2 Experimental Works and Findings	16
2.3 Reducing Breakdown Pressure Through Inducing Thermal Shock.....	18
2.3.1 Inducing Heat.....	18
2.3.2 Reducing Temperature	20

CHAPTER 3 METHODOLOGY	21
3.1 Sample Information.....	22
3.1.1 Sample Characterization	22
3.1.2 Sample Preparation	22
3.2 Sonic Experiments	23
3.3 Brittleness Index Measurement	25
3.4 Micro CT scans	26
3.5 Preparation of Thermochemical Solutions	27
3.5.1 Endothermic Mixture	28
3.5.2 Exothermic Mixture	28
3.6 Sequence of Thermochemical Treatment	29
3.6.1 Endo – Exo Sequence (Sequence #1).....	29
3.6.2 Exo – Endo Sequence (Sequence #2).....	31
3.7 Breakdown Experiments	32
3.8 Scratch Tests	35
3.9 TOC Measurement	36
CHAPTER 4 RESULTS AND DISCUSSION.....	38
4.1 Effect of Drilled Hole on Sample Elastic Properties	38
4.2 Effect of Drilled Holes in Samples on Brittleness Index	40
4.3 Impact of Thermochemical Treatment Sequences on Inducing Thermal Shock to The Samples ..	42
4.3.1 The Endo-Exo Thermochemical Treatment Sequence (Sequence #1).....	43
4.3.2 The Exo-Endo Thermochemical Treatment Sequence (Sequence #2).....	48
4.4 Impact of Thermochemicals on Dynamic Elastic Properties and Brittleness Index	53
4.5 Impact of Thermochemical Treatment Sequences on Breakdown Pressure of samples	55
4.6 Impact of Thermochemical Treatment Sequences on Hardness of The Samples	58

4.7	Effect of Thermochemical Treatment Sequences on TOC Maturation Potential	60
4.8	Micro CT scan Visualization of The Internal Structure of the samples.....	62
4.8.1	Before Thermochemical Treatment.....	62
4.8.2	After Endothermic – Exothermic Thermochemical Treatment	63
4.8.3	After Exothermic – Endothermic Thermochemical Treatment	64
4.8.4	After Breakdown Experiment.....	65
CHAPTER 5	CONCLUSIONS AND RECOMMENDATIONS	67
5.1	Conclusions.....	67
5.2	Recommendations	69
REFERENCES.....		72
VITAE.....		82

LIST OF TABLES

Table 1: Lab results on Elastic properties and propagation of waves within different samples (before and after drilling holes).....	39
Table 2: Results showing changes in B.I concerning Elastic sample properties before and after drilling holes	41
Table 3: Sequence #1 temperature changes across 3 cycles due to endothermic-exothermic reactions.....	48
Table 4: Sequence #2 temperature changes across 3 cycles due to exothermic-endothermic reactions	53
Table 5: Scratch test results recorded after scratching samples.....	58
Table 6: Observed TOC data reflecting the changes in mass of the respective samples before and after thermochemical treatment	61

LIST OF FIGURES

Figure 1: Effect of mineralogy on breakdown pressure (Al-Nakhli et al., 2019).....	4
Figure 2: Permeability ranges of unconventional reservoir rocks and measurement ranges of different experimental methods (Sander et al., 2017). The gradient across the measurement ranges of several methods emphasizes the specific range in which they exhibit optimal effectiveness.	12
Figure 3: A schematic of the experimental workflow	21
Figure 4: Preparation of (a) Shale samples and (b) Organic-rich Jordan Carbonate	23
Figure 5: Proceq Pundit pl-200 setup (Vp and Vs measuring device).....	25
Figure 6: Micro-CT scan device setup.....	27
Figure 7: Schematic of thermochemical treatment	29
Figure 8: (a) Core heater, (b) Temperature sensor, (c) Temperature logger, (d) Sodium Hydroxide solution, (e) Ammonium chloride powder, (f) Sodium Nitrite solution, (g) Ammonium Chloride solution, (h) Deionized water, (i) Empty beaker, (j) Formic acid, (k) Core holder	32
Figure 9: (a) Sealed gap between the metallic rod and sample with (b) epoxy	33
Figure 10: Constant temperature set-up for the samples during breakdown experiment	34
Figure 11: (a) Pressure flow pump and (b) pressure logging computer	34
Figure 12: (a) scratch test equipment and (b) Scratch analysis computer device.....	36
Figure 13: Variation of Elastic properties across different samples before and after drilling holes centrally.....	40
Figure 14: Trend of B.I on shale samples (before and after drilling holes).....	42

Figure 15: Temperature build-up profile on the EF1.2 sample	44
Figure 16: Endothermic mixture activity on sample EF1.2	45
Figure 17: Exothermic fluid activity on sample EF1.2.....	46
Figure 18: End of Exothermic activity on sample EF1.2	46
Figure 19: Graphical representation of the endothermic-exothermic treatment sequence	47
Figure 20: Temperature build-up on sample EF1.3 before exothermic reaction treatment	49
Figure 21: Initial thermal shock on sample EF1.3 and exothermic mixture reaction	50
Figure 22: Endothermic reaction activity and system temperature restoration to the surroundings.....	50
Figure 23: Exothermic-Endothermic sequence on sample EF1.3.....	51
Figure 24: Temperature profiles of Endo - Exo and Exo - Endo sequences on EF1.2 and EF1.3 respective samples	52
Figure 25: Elastic properties of the tested samples before and after thermal shock	54
Figure 26: Variation of B.I in samples before and after thermal shock.....	55
Figure 27: Breakdown pressure combined plot of EagleFord shale samples with time..	57
Figure 28: Breakdown pressure of Eagle Ford shale samples and Organic-rich Jordan carbonate samples.....	57
Figure 29: Hardness of the samples after the scratch test.....	59
Figure 30: Bar graph plots highlighting changes in TOC before and after thermochemical treatment.	62

Figure 31: Initial scans of (a) EF1.1 (base), (b) EF1.2 (en-ex) sample, (c) EF1.3 (ex-en), J3 (base), J2 (en-ex), and J1 (ex-en).....	63
Figure 32: EF1.2 sample (a) before treatment, and (b) after treatment	64
Figure 33: EF1.3 sample (a) before treatment, and (b) after treatment	65
Figure 34: Breakdown scans (a) EF1.1 (base), (b) EF1.2 (en-ex), (c) EF1.3 (ex-en), J3 (base), J2 (en-ex), and J1 (ex-en)	66

LIST OF ABBREVIATIONS

AR	:	As Received
B. I	:	Brittleness Index
BDP	:	Breakdown Pressure
CARBOLOG	:	Carbon Organic Log
CT	:	Computed Tomography
DOC	:	Depth of Cut
EF	:	Eagle Ford
EM	:	Electromagnetic
Endo	:	Endothermic
EOM	:	Extractable Organic Matter
EOR	:	Enhanced Oil Recovery
Exo	:	Exothermic
GRI	:	Gas Research Institute
IR	:	Infrared
ISE	:	Intrinsic Specific Energy
IUPAC	:	International Union of Pure and Applied Chemistry

JC	:	Jordan Carbonate
LLNL	:	Lawrence Livermore National Laboratory
LN₂	:	Liquid Nitrogen
MICP	:	Mercury Injection Capillary Pressure
NGS	:	Nitrogen Generating System
NMR	:	Nuclear Magnetic Resonance
RF	:	Radio Frequency
SEM	:	Scanning Electron Microscopy
SRV	:	Stimulated Reservoir Volume
TOC	:	Total Organic Carbon
XRD	:	X-Ray Diffraction

ABSTRACT

Full Name : [Stewart Peter Matovu]

Thesis Title : [Application of Cyclic Exothermic and Endothermic Thermochemical Fluids for Tight Reservoirs]

Major Field : [Petroleum Engineering]

Date of Degree : [December, 2024]

The oil and gas industry has consistently demonstrated advancements in technology since its inception in 1847, putting more focus on unconventional hydrocarbon reservoirs. Given the complexity inherent in extracting oil and gas from such reservoirs, researchers continue exploring innovative technologies that are more cost-effective, environmentally friendly, and improve the recovery rate of trapped oil within these reservoirs to optimize the process. In this context, a novel technology, centered on using cyclic thermochemical fluids to stimulate unconventional formations thereby reducing breakdown pressure which has an impact on reducing cost in hydraulic fracturing is proposed in this research. By sequentially applying these fluids, the objective is to induce thermal shock within the rock, thereby altering its mechanical characteristics and potentially generate hydrocarbons from the total organic carbon content (TOC). These fluids serve a dual role, both releasing and absorbing heat from the rock matrix. To evaluate the efficacy of this method, shale core samples with various organic content are used. The study aims to investigate how varying the sequence of cyclic thermochemical fluid treatments impacts the change in TOC, mechanical properties, and breakdown pressure. Results showed that breakdown pressure was reduced by 79.28% and 82.58% in shale and organic-rich carbonate samples respectively when cyclic endothermic – exothermic thermochemical treatment method was applied, reduction

in young's modulus in all thermochemically treated samples and changes in Poisson's ratio showcase the effectiveness of thermochemical application. Additionally, TOC reduction by 0.94% and 0.78% in the respective samples was noticed, which qualifies the method to have the potential of supporting TOC maturation. The findings of this research on the field scale can improve the efficiency of hydraulic fracturing operations by minimizing cost involved through reducing breakdown pressure, improve efficiency of hydrocarbon recovery through formation of microfractures, and environmental consideration through reducing impact of high pressures during hydraulic fracturing job. |

ملخص الرسالة

الاسم الكامل: ستيوارت بيتر ماتوفو

عنوان الرسالة: تطبيق السوائل الثرموكيميائية متناوبة الطور (طاردة للحرارة وماصة للحرارة) للخزانات غير التقليدية

التخصص: هندسة البترول

تاريخ الدرجة العلمية: ديسمبر، 2024

لقد أظهرت صناعة النفط والغاز تقدمًا تكنولوجيًا مستمرًا منذ نشأتها عام 1847، مع تركيز متزايد على مكان الهيدروكربونات غير التقليدية. ونظرًا للتعقيدات المتأصلة في استخراج النفط والغاز من هذه المكامن، يواصل الباحثون استكشاف تقنيات مبتكرة تكون أكثر فعالية من حيث التكلفة وصديقة للبيئة، فضلًا عن تحسين معدل استخلاص النفط المحتجز في هذه المكامن لتحقيق أفضل أداء ممكن. وفي هذا السياق، يقترح هذا البحث تقنية جديدة تعتمد على استخدام (Breakdown Pressure) سوائل ثرموكيميائية دورية لتحفيز التكوينات غير التقليدية، مما يقلل من ضغط الانهيار ويساهم في خفض تكاليف التكسير الهيدروليكي. ومن خلال تطبيق هذه السوائل بشكل متسلسل، يُهدف إلى إحداث صدمة حرارية في الصخر، وبالتالي تغيير خصائصه الميكانيكية مع إمكانية توليد الهيدروكربونات من المحتوى. وتقوم هذه السوائل بدور مزدوج، إذ تطلق وتمتص الحرارة من مصفوفة الصخر (TOC) العضوي الكلي لتقييم فعالية هذه الطريقة، تم استخدام عينات من الصخور الطفلية (الشيل) ذات محتوى عضوي مختلف. وتهدف الدراسة إلى استقصاء كيفية تأثير تغيير تسلسل المعالجات بالسوائل الثرموكيميائية الدورية على التغير في المحتوى والخصائص الميكانيكية وضغط الانهيار. وقد أظهرت النتائج انخفاض ضغط الانهيار بنسبة (TOC) العضوي الكلي 79.28% و 82.58% في عينات الشيل والكربونات الغنية بالمواد العضوية على التوالي عند استخدام المعالجة الثرموكيميائية الدورية (ماصة للحرارة – طاردة للحرارة). كما لوحظ انخفاض في معامل يونغ في جميع العينات التي خضعت للمعالجات الثرموكيميائية، إضافةً إلى تغيّرات في معامل بواسون، مما يؤكد فعالية التطبيق الثرموكيميائي. بنسبة 0.94% و 0.78% في العينات (TOC) علاوة على ذلك، تم رصد انخفاض في المحتوى العضوي الكلي المذكورة، الأمر الذي يشير إلى إمكانية مساهمة هذه الطريقة في تعزيز نضوج المحتوى العضوي.

ومن منظور تطبيقي ميداني، يمكن لهذه النتائج أن تحسّن كفاءة عمليات التكسير الهيدروليكي عبر خفض التكاليف المرتبطة بانخفاض ضغط الانهيار، وتعزيز فعالية استخراج الهيدروكربونات من خلال تكوين شقوق دقيقة ، إضافةً إلى الجانب البيئي عبر الحد من تأثير الضغوط العالية أثناء عمليات التكسير الهيدروليكي (microfractures).

|

CHAPTER 1

INTRODUCTION

1.1 Background

In the oil and gas industry, the search for new technologies to improve hydrocarbon recovery and optimize extraction procedures has become an increasingly important endeavor. However, producing hydrocarbons from tight reservoirs such as low permeability carbonates, tar sands, tight shale, and ultra-tight sands is not an easy task. Several techniques and experimental studies have been used and investigated respectively over the years to ease the extraction of hydrocarbons, such as fracking (Hattori et al., 2017), thermochemical acid fracturing (Tariq et al., 2020), explosive and propellant fracturing (Zazovsky, 2004), cryogenic fracturing (Cha et al., 2014), electrohydraulic fracturing (Wesley and Ayres, 1984), and foam fracturing (Wanniarachchi et al., 2017). According to Zhang et al., (2016), hydraulic fracturing is the most commonly applied stimulation method to yield hydrocarbons from tight reservoirs. In this technique, a water mixture, proppants and chemicals are injected at high pressure into the reservoir which creates and enlarges fractures in the rock formation. The proppants hold the fractures open once the hydraulic pressure is removed, allowing for the flow of oil and gas to the wellbore. In horizontal wells, fracking is often performed in multiple stages along the length of the horizontal section to maximize the area of influence and improve recovery rates. Understanding the

breakdown pressure is critical for selecting the proper pump rates, fluid properties, and operational sequence. Accurately predicting it ensures that the treatment pressure surpasses the rock's tensile or shear strength to create new fractures. Knowing the breakdown pressure helps engineers choose fracturing fluid densities, viscosities, and additives (e.g., friction reducers) that can generate the required pressure while minimizing friction losses. Secondly, pump horsepower and pressure ratings must safely exceed the anticipated breakdown pressure. Underestimating breakdown pressure can cause equipment failure or incomplete fracturing whereas overestimating it leads to excessive safety margins and unnecessary costs. Understanding the fracture initiation and propagation ensures the fracture grows in the desired direction and length. This can significantly affect reservoir hydraulic contact and, hence, the productivity of the well. Reducing the initial pressure needed to break the rock results in less horsepower and smaller equipment requirements, lowering both capital and operational costs. If the breakdown pressure is lower, it becomes easier to initiate multiple fractures such as in multi-stage fracturing. This can lead to better stimulation coverage and higher overall hydrocarbon recovery. Some of the methods implemented to reduce breakdown pressure include; injecting acid ahead of the fracturing fluid which can dissolve minerals near the wellbore, reducing near-wellbore stress and plugging, and thereby lowering the pressure required to break the formation. Alternating between injection and shut-in periods (cyclic injection) can help relieve stress concentrations near the wellbore. Over multiple cycles, this can lower the pressure needed to initiate a fracture. Introducing thermochemical fluids that either release or absorb heat can create localized thermal stresses in the rock. The induced temperature changes alter rock properties (expanding or contracting microcracks), ultimately lowering the threshold

for breakdown pressure. Optimizing perforation size, phasing, and entry-hole friction can reduce localized near-wellbore pressure requirements (Nakhwa et al., 2007). By improving fluid distribution into the formation, the necessary breakdown pressure can drop. An experimental study done by Al-Nakhli et al., (2013) unveiled that macro-fractures were created in the core samples due to an exothermic reaction. The concept was based on injecting chemical components before hydraulic fracturing job, where gas and heat were generated. The temperature and gas increase created more pressure that resulted in mechanical and thermal fracturing.

Al-Nakhli et al., (2019) investigated the effects of different compositions of cement blocks and cylindrical core plugs from various rocks, including Calcareous rock, Eagle Ford shale, and Scioto sandstone. The study incorporated both conventional and thermochemical fracturing experiments, as depicted in **Figure 1**. Their findings indicated that the innovative fracturing method significantly lowered the breakdown pressure across all rock types. Additionally, it facilitated the formation of artificial sweet spots by generating micro-fractures around the fracture zones and near the borehole. These micro-fractures played a crucial role in weakening the rock strength, thereby reducing the breakdown pressure. Complementing this, Tariq et al., (2019) experimentally examined a novel thermochemical fracturing technique to reduce the fracture pressure of high-strength rocks. Their results showed a decrease in breakdown pressure by 38% and 60%, along with a reduction in breakdown time by 19.3% and 17.3%, respectively. Notably, shorter breakdown times lead to lower volumes of fracturing fluids required, ultimately reducing the overall cost of hydraulic fracturing operations.

In a distinct study, Tariq et al., (2020) demonstrated the effectiveness of thermochemical fluids in stimulating unconventional formations. Utilizing both experimental and mathematical approaches to analyze thermochemical reactive behaviors and their outcomes, the study found that thermochemical fluids could create synthetic sweet spots by generating multiple micro-fractures around the wellbore area. This process significantly reduced the breakdown pressure from 2167 psi to 900 psi, outperforming conventional hydraulic fracturing methods.

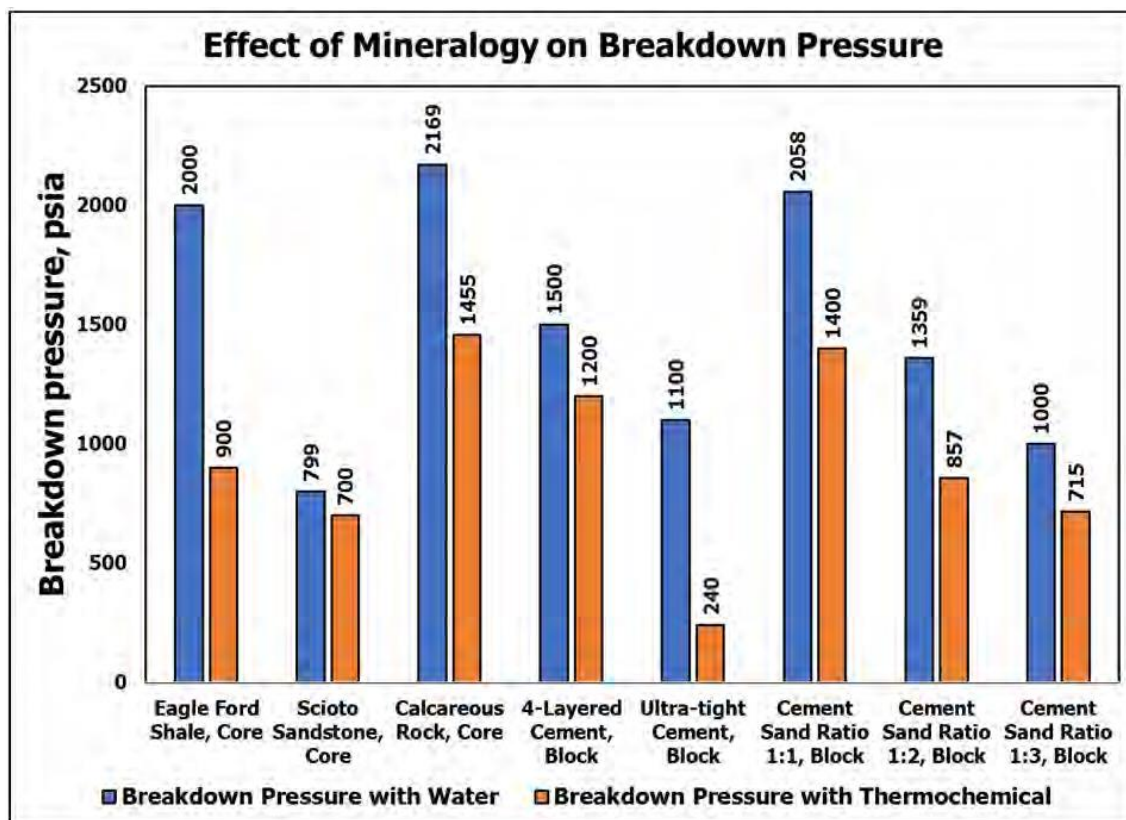


Figure 1 Effect of mineralogy on breakdown pressure (Al-Nakhli et al., 2019)

1.2 Problem Statement and Objectives

There is a clear need to reduce breakdown pressure for high breakdown pressure formations and thermochemical treatment could be a potential option due to their thermodynamic potential of raising and reducing material temperature. However, there is a limited understanding to the influence of cyclic treatment, the sequence of thermochemical treatment, and potential maturation of TOC.

This cyclic thermochemical approach repeatedly heats and cools shale formations, allowing precise manipulation of rock properties at the molecular level. Exothermic fluids expand the formation and create micro-fractures by releasing heat, while endothermic fluids remove heat and compress the rock. This dual process causes a controlled “thermal shock” that increases permeability, reduces breakdown pressure, and can even accelerate the maturation of organic matter.

Beyond enhancing yield and efficiency, the cyclic thermochemical treatment method offers adaptability to unique reservoir conditions, making oil and gas extraction both more economical and environmentally responsible. By lowering the energy needed to fracture the rock and unlocking previously unviable deposits, cyclic thermochemical techniques may set a new standard in resource development, extending existing well lifespans and transforming the overall viability of unconventional hydrocarbon production.

This research has the following objectives;

- Investigates the effect of sequence thermochemical treatment on the mechanical properties of the shale and organic-rich carbonate

- Examines the potential reduction in the breakdown pressure under ambient conditions, revealing the reduction in tensile stress of the rock.
- Investigates the possibility of Total Organic Carbon Content maturation in shale rock through cyclic thermochemical treatment.

CHAPTER 2

LITERATURE REVIEW

To fully understand the concept of cyclic endothermic and exothermic thermochemical treatment to reduce breakdown pressure and monitor the maturation of organic-rich shale, it is very important to first fully understand the background of the rock formation characterization, the nature of thermochemical reactions, fluid transport, and the need for hydraulic fracturing.

2.1 Shale Rock Characterization

Characterizing the heterogeneous structure of shale rocks plays a very important role in the understanding of their gas storage, fluid transport, and geomechanical properties. Shale is a fine-grained sedimentary rock that is composed mainly of clay minerals and tiny fragments of other minerals such as quartz and calcite (Potter et al., 2012). Sometimes these shale rocks are referred to as mudstones because of their extremely fine particles which can be less than 4 μ m, hence resulting in micro to nano-Darcy permeabilities (Suarez-Rivera et al., 2010). Even though many shales look similar to the naked eye, their mineralogy and total organic content exhibit a wide range of compositions (Sone and Zoback, 2013). Understanding deformational properties becomes a fundamental task to better optimize operational procedures in shale gas reservoirs (Britt and Schoeffler, 2009). Shales are a highly prevalent sedimentary rock that has been extensively studied and

characterized in previous studies. However, the development of unconventional shale gas reservoirs with poor permeability has necessitated the modification of conventional laboratory characterization methods to accommodate the intricate characteristics of these geological formations. The laboratory employs non-destructive and destructive petrophysical and geomechanical testing methodologies to conduct systematic shale characterization workflows (Josh et al., 2012).

2.1.1 Clay Mineralogy and Shale Instability

According to Sliwinski et al., (2010), analysis of rock mineralogy plays an important part in the evaluation of shale formations and has a significant impact on their brittleness, (Jarvie et al., 2007). The mechanical characteristics of rocks can vary significantly depending on the percentage of quartz-carbonate clays present. Shales containing a significant amount of quartz typically exhibit high brittleness and possess a greater Young's modulus, whereas shales with a higher proportion of clay are less prone to brittleness (Rickman et al., 2008). Hence, the consideration of rock mineralogy in shale plays holds significant importance in the context of drilling and hydraulic fracturing activities.

A higher proportion of clay minerals generally imparts ductility to the rock, making it less brittle under stress. Clay can also swell or react with fluids, which may alter pore structure and contribute to weakening the rock matrix. Consequently, shales with high clay content often exhibit lower Young's modulus and reduced fracture conductivity, which are critical considerations during hydraulic fracturing operations (Du et al., 2018). Total organic

carbon (TOC) content also plays a pivotal role in shaping shale's mechanical properties. Higher TOC typically suggests the presence of more kerogen or organic matter that can be softer or more compliant than the surrounding mineral matrix. This may result in locally reduced rock strength and altered brittleness, affecting the ease of fracture initiation and propagation. Understanding both clay content and TOC is therefore essential for designing effective completion strategies and forecasting shale reservoir performance.

Numerous studies from researchers; Horsrud, (2001); Rybacki et al., (2015, 2016); Sone & Zoback, (2013); and Steiger & Leung, (1992) have shown that the mechanical properties of shale are heavily influenced by its heterogeneous composition, particularly the relative proportions of clay minerals, total organic carbon (TOC), and other mineral constituents. Laboratory tests and field observations indicate that higher clay content generally lowers brittleness and Young's modulus, while greater organic content can reduce rock strength and increase ductility. Researchers employ a variety of experimental methods such as uniaxial and triaxial compression tests (García et al., 2008; Lee et al., 2016), acoustic velocity measurements (Dewhurst et al., 2002; Domnesteau et al., 2002; Omovie & Castagna, 2019), and nanoindentation (Liu et al., 2016; Ping et al., 2015) to unravel the complexities of shale deformation. These efforts underscore the need to factor in shale's mineralogy and organic content when designing drilling and completion strategies, as they play a critical role in fracture initiation, propagation, and ultimate reservoir productivity.

2.1.2 Total Organic Carbon Content

Total Organic Carbon (TOC) is a measure of a source rock's organic matter and typically needs to exceed 1.0–1.5 wt% for the rock to be considered a promising hydrocarbon source. Elevated TOC can lower mechanical properties such as Young's modulus by organic material's low density and limited strength. Nonetheless, TOC represents a key factor in hydrocarbon generation, with its extractable and convertible fractions determining how much oil or gas can form as the rock matures. To assess TOC beyond laboratory core analyses where continuous sampling may be impractical, well log-based methods such as $\Delta\log R$ from Passey et al., (1990), CARBOLOG from Bessereau et al., (1991), and AI models from Khoshnoodkia et al., (2011) and Tan et al., (2013, 2015) have been implemented successfully. Finally, thermochemical processes present additional opportunities to harness TOC by inducing controlled heating and cooling cycles that can help generate hydrocarbons or facilitate their release, thereby expanding the economic feasibility of unconventional reservoirs.

Alqahtani et al., (2013) examined the influence of total organic carbon (TOC) on the acoustic and mechanical characteristics of different source rock formations. Their findings indicated that the core samples from the low permeability Eagle Ford formation exhibit a high level of maturity and are predominantly composed of calcite minerals. The Mancos shale samples exhibit reduced maturity and include a high proportion of quartz. The Green River outcrop samples consist of juvenile shale that is predominantly composed of dolomite, with a significant presence of total organic carbon. Conclusively, they discovered that high total organic carbon (TOC), kerogen content, and maturity levels lead to a

decrease in sonic velocities and Young's Modulus. Out of all the samples, the Green River samples exhibited the lowest sonic velocities because of their age and the high total organic content they contained.

2.1.3 Permeability

Permeability is an essential property of reservoir rocks that is necessary for accurately modeling the production of hydrocarbons. Henry Darcy initiated the study and documentation of moving water via a sand filter in the 1850s. This was done to provide water supply to the city of Dijon, France (Freeze and Cherry, 1979). He discovered that his observations might be explained by an empirical principle called Darcy's law (Darcy, 1856). Nevertheless, the complete understanding of shale permeability remains challenging due to the complex process of simulating fluid movement through nanoscale throats.

Shales exhibit extremely low permeability often in the micro to nano-Darcy range due to compaction and diagenesis processes that reduce both porosity and fluid flow pathways. This ultra-low permeability limits the natural movement of hydrocarbons and necessitates the application of hydraulic fracturing. By creating artificial fractures, hydraulic fracturing overcomes these restrictions, providing pathways for hydrocarbons to flow and be economically produced from tight formations. **Figure 2** below provides a summary of the permeability variations found in unconventional gas reservoir rocks, as well as the experimental techniques used to determine permeabilities within that range. The ranges

offered are approximate estimations and are derived from the data collected by Sander et al., (2017).

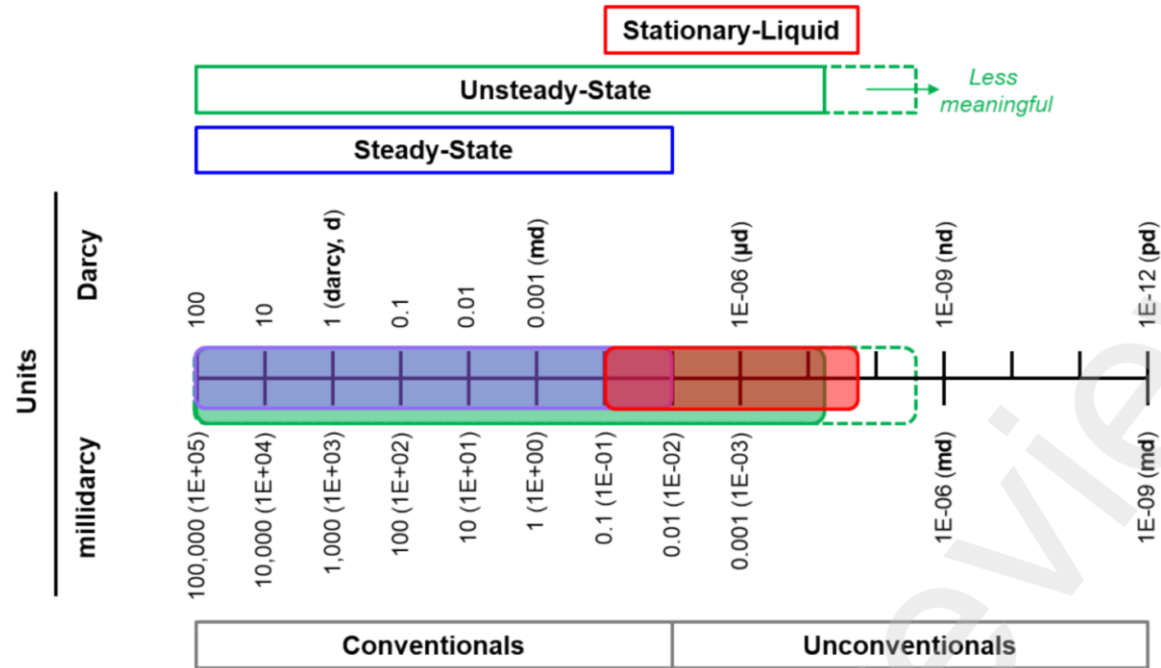


Figure 2 Permeability ranges of unconventional reservoir rocks and measurement ranges of different experimental methods (Sander et al., 2017). The gradient across the measurement ranges of several methods emphasizes the specific range in which they exhibit optimal effectiveness.

2.2 Breakdown Pressure

The breakdown pressure in shale rocks is an essential parameter in the context of hydraulic fracturing operations, (Guo et al., 1993). Fracture initiation pressure is the least amount of pressure needed to develop or spread cracks in the rock formation. On the other hand, breakdown pressure is the pressure needed to propagate fractures in an unstable manner. Comprehending and precisely identifying the breakdown pressure is essential for

optimizing the design and implementation of hydraulic fracturing treatments, as well as for ensuring the economic and environmental sustainability of oil and gas production from shale formations. Breakdown pressure unveils the understanding of the mechanical behavior of the rock under stress conditions imposed by fluid injections. In shale formations, which are typically characterized by low permeability, inducing fractures is necessary to enhance fluid flow and improve recovery rates of hydrocarbons. The mechanical properties of the rock, such as Young's modulus, Poisson's ratio, and tensile strength, primarily determine the rock's ability to resist fracturing, (Barree et al., 2009). Shale rocks, with their layered and anisotropic nature, often exhibit varied mechanical behavior that can significantly affect breakdown pressures. Additionally, the existing in-situ stresses within the earth, including the overburden stress (vertical stress due to the weight of overlying rocks) and horizontal stresses, play a vital role in determining the pressure needed to initiate fractures. The orientation and magnitude of these stresses influence the direction and complexity of the fracture network. More so, the fluid properties based on the type of fluid used in the fracturing process, such as viscosity, and the rate at which it is injected also impact the breakdown pressure. More viscous fluids or higher injection rates generally require higher pressures to initiate fractures, (Ishida et al., 2004). Furthermore, depth and temperature are important factors to consider as well. Deeper formations are subject to higher confining pressures, which can increase the breakdown pressure. Similarly, temperature variations with depth can affect the rheological properties of the shale and the fracturing fluid, thus influencing the required pressure.

2.2.1 Breakdown Pressure Models

2.2.1.1 Classic Breakdown Model

Hubbert and Willis, (1957) introduced the foundational (or “classic”) breakdown model, which explains fracture initiation in a well when the minimum tangential compressive stress at the wellbore wall equals the rock’s tensile strength. Under linear elastic assumptions and considering the rock to be impermeable (with no initial pore pressure), the breakdown pressure is given by

$$P_b = 3\sigma_{hmin} - \sigma_{hmax} + \sigma_t \quad (2.1)$$

But in the presence of pore pressure, the breakdown pressure can be estimated as;

$$P_b = 3\sigma_{hmin} - \sigma_{hmax} + \sigma_t - P_0 \quad (2.2)$$

where P_b is the breakdown pressure, σ_t is the tensile strength of the rock, P_0 is the initial pore pressure, and σ_{hmin} and σ_{hmax} are the minimum and maximum horizontal stresses, respectively. Intuitively, in the case of negligible tensile stress, the equation above becomes

$$P_b(\sigma_t = 0) = 3\sigma_{hmin} - \sigma_{hmax} - P_0 \quad (2.3)$$

2.2.1.2 Haimson Model

Haimson, (1968) proposed a second breakdown model that, like the original, assumes breakdown occurs when the minimum tangential effective stress at the wellbore equals the rock's tensile strength. The distinction is that Haimson's approach applies Biot's poroelastic theory, introducing parameters such as Poisson's ratio ν and Biot's coefficient α . Notably, this model uses the "apparent tensile strength," which differs from conventional tensile strength values obtained via Brazilian or direct tensile tests

$$P_b = \frac{3\sigma_{hmin} - \sigma_{hmax} + \sigma_t - \alpha \frac{1-2\nu}{1-\nu} P_0}{2 - \alpha \frac{1-2\nu}{1-\nu}} \quad (2.4)$$

Schmitt and Zoback, (1989) contended that the Terzaghi effective stress relation is unsuitable for rocks with low porosity. They believed that utilizing a modified effective stress rule, specifically $\sigma' = \sigma - \beta P$, where $0 \leq \beta \leq 1$ could be more suitable. After presenting this concept, they derived the subsequent breakdown

$$P_b = \frac{3\sigma_{hmin} - \sigma_{hmax} + \sigma_t - \alpha \frac{1-2\nu}{1-\nu} P_0}{1 + \beta - \alpha \frac{1-2\nu}{1-\nu}} \quad (2.5)$$

2.2.1.3 Fracture Mechanics Model

This type of model uses the basis of fracture mechanics as it was reported by Abou-Sayed et al., (1978) and Rummel, (1987). The fracture mechanics model assumes that breakdown happens when a fracture initiates unstable extension. Based on this assumption, the

breakdown equation is obtained from the expression, $K_1 = K_{1c}$. Below is the breakdown equation, where L is the length of the fracture, r_w represents the well radius, K_{1c} is the fracture toughness, and f , g , h_0 , and h_a are functions of the fracture length and well radius.

$$P_b = \frac{1}{h_0(L, r_w) + h_a(L, r_w)} \left[\frac{K_{1c}}{\sqrt{r_w}} + \sigma_{hmax} f(L, r_w) + \sigma_{hmin} g(L, r_w) \right] \quad (2.6)$$

2.2.1.4 Ito Point Stress Model

Ito and Hayashi, (1991), introduced a model where fracture initiation occurs within the rock at a specific distance from the wellbore, once the minimum effective stress equals the rock's tensile strength. This distance is determined by the material's properties and is analyzed under linear elastic conditions.

A comprehensive study by Guo et al., (1993) highlighted the limitations of the conventional breakdown model, noting that Brazilian-derived tensile strengths underestimate actual breakdown pressures and vary with specimen size. Their findings support a fracture mechanics perspective in which breakdown pressure signifies the transition from stable fracture growth to an unstable propagation phase.

2.2.2 Experimental Works and Findings

Breakdown pressure is influenced by a combination of in-situ stresses especially the minimum and maximum horizontal stresses as reported by Hubbert and Willis, (1957), the rock's tensile or "apparent" tensile strength (Ito and Hayashi, 1991; Guo et al., 1993), poroelastic parameters such as Biot's coefficient (Haimson, 1968), and the specific

mechanics of fracture initiation whether at or away from the wellbore (Ito and Hayashi, 1991). Laboratory tensile strength measurements, such as those from the Brazilian test, may underestimate true breakdown pressures, and fracture mechanics studies show that stable fracture growth can occur before an unstable fracture propagates at breakdown. Consequently, accurately predicting breakdown pressure requires accounting for these factors

Several studies have reported that altering the rock temperature prior to or during fracturing operations can significantly affect breakdown pressure. Injecting cold fluids (well below the reservoir's temperature) can induce thermal contraction in the near-wellbore region. This "thermal shock" lowers the local rock stresses or weakens the rock's tensile strength, thereby reducing the pressure required to initiate and propagate fractures (Okpobiri et al., 2020; Wang et al., 2016). Conversely, injecting high-temperature fluids such as steam or hot water can cause thermal expansion in the rock matrix, potentially raising local stresses or creating pre-existing microcracks that also alter the breakdown pressure (Xu and Wong, 2013). Additionally, some researchers have experimented with thermochemical fluids that generate or absorb heat on demand, effectively reshaping the stress field around the wellbore before the main fracturing stage (Zhang et al., 2018). By tuning the timing and magnitude of temperature changes, these thermally driven methods can help control breakdown pressure, enhance fracture complexity, and improve overall stimulation efficiency in various reservoir types.

2.3 Reducing Breakdown Pressure Through Inducing Thermal Shock

2.3.1 Inducing Heat

Inducing heat is one approach to lower the pressure required for fracture initiation in tight formations. Rather than relying solely on high-pressure fluid injection, this method deliberately introduces heat to the subsurface rock via steam injection, radiofrequency heating, or exothermic chemical reactions to create temperature gradients. These gradients weaken the rock matrix, reduce near-wellbore stresses, and thereby lower the breakdown pressure needed to initiate fractures (Okpobiri et al., 2020). By taking advantage of thermal contraction or expansion effects, operators can enhance permeability and fluid mobility, allowing hydrocarbons to be extracted from previously inaccessible or low-yield zones.

2.3.1.1 Steam Injection Method

High-pressure steam injection heats the rock matrix, causing expansion and reduced fracture resistance. Although Wong and Chau, (2004) found tensile fracturing in Cold Lake shale unlikely due to the stress conditions required, subsequent steaming cycles still proved beneficial in oil sand/shale operations. For instance, Smith et al., (2004) reported that following cyclic steam stimulation below a known hydraulically induced shale fracture, no additional casing failures occurred, allowing Imperial Oil to extract substantial reserves efficiently.

2.3.1.2 Radiofrequency Heating Method

Radiofrequency (RF) heating applies electromagnetic waves to selectively heat rock formations, causing thermal expansion that enhances hydrocarbon flow. Early work at the American Illinois Institute of Technology used a vertical electrode to heat shale slowly, while Lawrence Livermore National Laboratory (LLNL) harnessed RF's stronger penetration (Pan et al., 2012). Despite promising results, power consumption and generator placement remain major hurdles. Hu et al., (2020) experimentally and numerically showed that electromagnetic (microwave) heating can induce micro and macro-fractures in shale particularly those rich in pyrite and clay without water, offering an eco-friendly, renewable-energy-driven method for shale stimulation.

2.3.1.3 Exothermic Reactions

Exothermic reaction methods offer an innovative strategy to lower breakdown pressure (BDP) by injecting reactive chemicals into the reservoir to generate localized heat and weaken the formation. Early applications by McSpadden et al., (1986), used thermochemical reactions to dissolve paraffin wax in producing wells, yielding cost-effective results for both high- and low-productivity wells. Khalil et al., (1994) similarly employed thermochemical fluids to remove paraffin from subsea production lines. Al-Nakhli, (2015) later demonstrated that pressure and temperature pulses from thermochemical fluids significantly expanded the Stimulated Reservoir Volume (SRV) in shale and other rock samples, while Wang et al., (2018) combined thermochemical fluids with surfactants to form in-situ foams for enhanced oil recovery, achieving a 20%–34% increase in production. Additional work has explored thermochemical reactions for wax removal (Rocha et al., (2003), organic scale removal (Amin et al., 2007), sludge removal

(Rocha et al., 2007), heavy oil recovery (Alade et al., 2019), in-situ steam generation (Mahmoud et al., 2019), thermochemical fracturing (Tariq et al., 2019), and filter cake removal (Mahmoud, 2019). Collectively, these studies confirm that exothermic reactions can reduce the pressure needed to initiate fractures, improve reservoir permeability, and enhance overall hydrocarbon recovery from tight formations.

2.3.2 Reducing Temperature

After the rock has been heated whether through steam injection, exothermic fluids, or other thermal methods, injecting cooler fluid or allowing the rock to cool rapidly creates a sharp thermal gradient that induces tensile stresses (Lu and Cha, 2022). This thermal contraction weakens the rock matrix, promoting microcracks and lowering its overall mechanical integrity. As a result, the minimum wellbore pressure necessary to initiate a fracture (breakdown pressure) decreases, because less stress is required to propagate a crack through a rock already under thermal strain. This process harnesses the contrast between the previously elevated rock temperature and the subsequent cooling phase to alter in-situ stresses, effectively reducing the energy and fluid pressure needed to open fractures. Zhang et al., (2016) specifically examined the effect of lowering injection temperature on fracturing behavior. Their experiments showed that introducing cooler fluids into a sandstone reservoir caused thermal contraction near the wellbore, thereby reducing local stresses and lowering the breakdown pressure needed to initiate fractures.

CHAPTER 3

METHODOLOGY

To make the research successful, a detailed stepwise methodology was followed to meet the objectives of this research as shown in **Figure 3**. Sample preparation (size), the apparatus and measurement devices used, the preparation of thermochemical mixtures, and their respective concentrations and volumes were discussed in this chapter. The discussion also involves measurement techniques to achieve the necessary parameters under investigation.

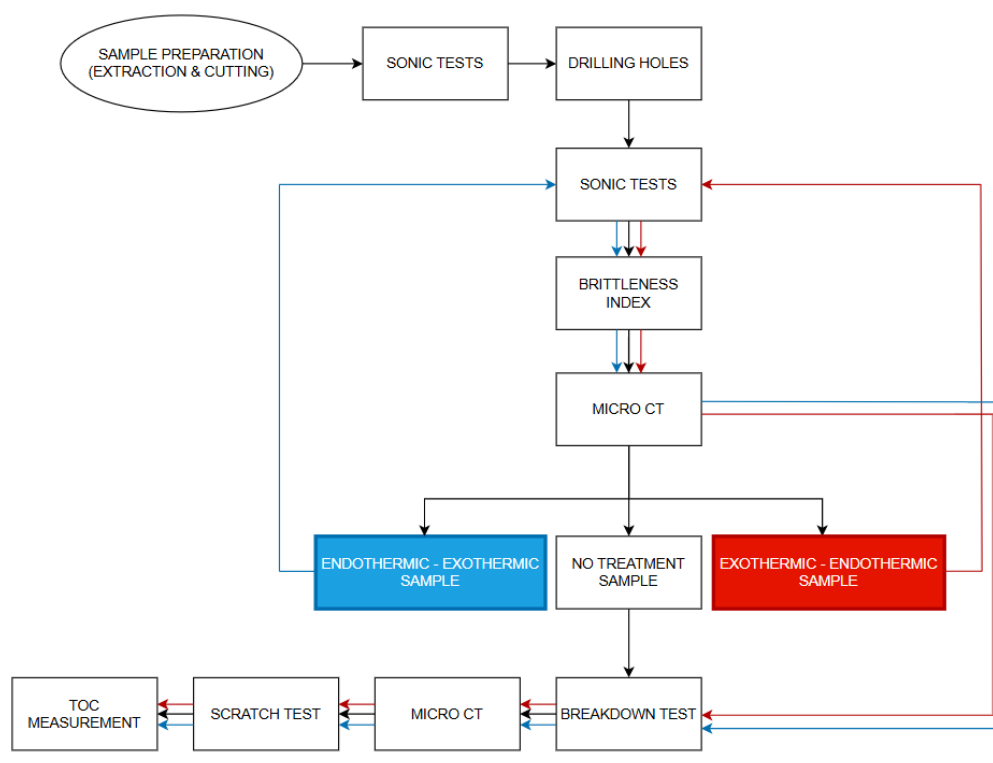


Figure 3 A schematic of the experimental workflow

3.1 Sample Information

3.1.1 Sample Characterization

Eagle Ford shale and Organic-rich Jordan Carbonate samples were characterized in the laboratory through X-ray diffraction to determine the mineralogical composition of these samples. Eagle Ford shale was predominantly composed of Calcite content of up to 82%, 5.1% Quartz, 4% Gypsum, 4% Dolomite, 2.4% Kaolinite, 1.4% Illite, and ~3% TOC. On the other hand, Organic-rich Jordan Carbonate with TOC of ~16% predominantly had Calcite and Calcium Magnesium Carbonate, with minor amounts of Apatite, Quartz and Clay. Gypsum and Pyrite were locally abundant presenting a minor fraction of <1% on average.

3.1.2 Sample Preparation

The preparation of samples was conducted in two phases. First, an 8-inch long and 1.5-inch diameter Eagle Ford shale core was cut into four sister samples, each 2-inch long using a Dewalts cutting machine for cutting rocks and core plug samples. Since shales are brittle, it was emphasized that the cores are carefully cut without introducing cracks to them. The wet-cutting option was more feasible for such a scenario. Three of these samples were actively used throughout the entire set of experiments, and the fourth sample served as a backup due to the scarcity of the core shale samples. Secondly, after carrying out the sonic tests to investigate the propagation of the plane and shear wave velocities to quantify the

dynamic elastic properties in three out of four samples, holes 10mm (3/8 inch) wide were vertically drilled to a depth of half the length (1 inch) of the sample using a manual drilling machine. 3 samples of Organic-rich Jordan Carbonate were also prepared in the same manner for comparison purposes in this research, except the varying sizes in lengths as shown in **Figure 4** below



Figure 4 Preparation of (a) Shale samples and (b) Organic-rich Jordan Carbonate

3.2 Sonic Experiments

The purpose of these experiments was to investigate the propagation of the sonic waves velocities through the samples using proceq pundit pl-200 device (**Figure 5**). These results were later used to compute the dynamic elastic properties of the samples including Young's modulus (E) and Poisson ratio (ν) as shown below.

$$E = \frac{\rho v_s^2 (3v_p^2 - 4v_s^2)}{v_p^2 - v_s^2} \quad (3.1)$$

$$\nu = \frac{(V_p^2 - 2V_s^2)}{2(V_p^2 - V_s^2)} \quad (3.2)$$

Where V_p and V_s are plane and shear wave velocities respectively, ρ is the sample bulk density.

These experiments were carried out in four phases; before introducing the hole in the samples, after introducing the holes in the samples, after the first 3 cycles of treatment with thermochemical mixtures (Endothermic–Exothermic) also known as the forward sequence and later after the second set of 3 cycles of treatment with thermochemical mixtures (Exothermic–Endothermic) also known as the reverse sequence. The mass (g) using a digital weighing machine for each sample was obtained, length (mm), and Diameter (mm) of the samples were measured using a Vernier caliper to calculate the bulk density (g/cc). High viscosity silicone grease was applied to the top and bottom surfaces of the samples before placing them on the device stage to ensure good acoustic coupling between the sample and the transducers during V_p (P-wave velocity) and V_s (S-wave velocity) measurements. This coupling minimizes the loss of acoustic signals and improves the accuracy of the measurements.

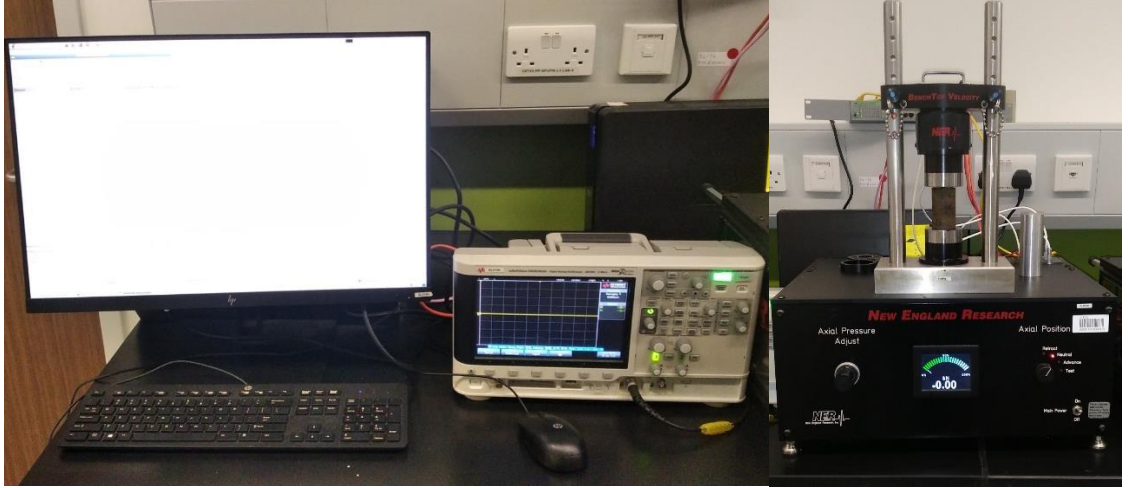


Figure 5 Proceq Pundit pl-200 setup (Vp and Vs measuring device)

3.3 Brittleness Index Measurement

Estimating brittleness index (B.I) is used to evaluate the potential "fracability" of unconventional reservoirs. B.I can be derived from various rock property data, including mineralogical composition, elastic properties, and rock strength characteristics. The B.I provides an indicative measure of the ease with which the reservoir rock can be fractured, facilitating the assessment of its suitability for hydraulic fracturing operations. For this research, the brittleness index was obtained from **Equation 3.3** shown below, where E is Young's modulus value observed in each sample; ν is Poisson's ratio observed in the same sample. The higher the result obtained, the more brittle the sample was compared to the other samples.

$$\text{B.I} = \frac{50}{7}(E - 28\nu + 10.2) \quad (3.3)$$

3.4 Micro CT scans

This technique provides high-resolution 3D images of the internal structure of the samples, including its pore network, mineral distribution, and fractures. The obtained data are used to make microstructural analyses such as microfractures and fracture propagation after the breakdown experiment. After analyzing the base cases without chemical treatment, 2 sets of data were obtained after exposing other samples to a different set of conditions such as sequence thermochemical treatment 1 and 2, as well as also after the breakdown experiment to analyze the fracture propagation and orientation.

Typical scanning parameters on a Zeiss Xradia Versa XRM-500 (**Figure 6**) for Eagle Ford shale samples include using an X-ray source voltage of approximately 100–140 kV at a current of about 50–100 μA , coupled with exposure times of 1–3 seconds per projection. The total number of projections might range from 1000 to 2000 over a full 360° rotation, and voxel sizes are commonly set between 1 and 5 μm to capture microfractures and fine pore structures. To minimize artifacts and enhance contrast, a moderate beam filter such as aluminium or copper is often employed alongside detector corrections such as flat-fielding and beam-hardening corrections, with the potential for pixel binning (1×1 or 2×2) to boost signal-to-noise. These settings typically yield scan durations of 2 to 5 hours, depending on the desired resolution and the number of projections.



Figure 6 Micro-CT scan device setup

3.5 Preparation of Thermochemical Solutions

As discussed earlier, the thermochemical treatment of samples followed two sequences with the objective of inducing thermal shock to the samples where endothermic-exothermic was sequence #1, and then exothermic-endothermic was sequence #2. The preparation of these thermochemical mixtures requires precise measurements. For this preparation, 4 beakers, were required and a measuring cylinder. The choice of the endothermic/exothermic mixture is based on the reaction kinetics performed before the experiment to determine the optimum concentration that would give the maximum endothermic/exothermic activity.

3.5.1 Endothermic Mixture

The molar mass of NaOH is 40g/mol and that of NH₄Cl (Ammonium Chloride) is 53.5g/mol. 8g (0.2 moles) of NaOH (Sodium hydroxide) were weighed on a digital scale and then dissolved in 50 ml (0.05 l) of deionized water in one beaker at ambient conditions. The resultant prepared solution was at 4M concentration (refer to **Equation 3.4**). The dissolution of NaOH beads in deionized water is exothermic, so care must be taken to avoid direct contact of the solution/beaker with bare hands. Separately, a 53.5g of NH₄Cl (Ammonium chloride) were weighed, poured in a dry beaker and covered to avoid any early interaction with water. The dissolution of NH₄Cl is endothermic. In a measuring cylinder, 50 ml of deionized water was also prepared ready to mix with the NH₄Cl powder and NaOH solution during the endothermic reaction.

$$\text{Molarity, } M(\text{mol/l}) = \frac{\text{moles}}{\text{Volume of Solution (l)}} \quad (3.4)$$

3.5.2 Exothermic Mixture

The molar mass of NaNO₂ is 69g/mol. 13.8g of NaNO₂ (Sodium Nitrite) were weighed on a digital scale and then dissolved in 50 ml of deionized water in another beaker at ambient conditions. The resultant prepared solution had a 4M concentration. When NaNO₂ crystals are dissolving in deionized water, the reaction to form this solution is endothermic. Separately, a 4M solution of NH₄Cl was prepared by dissolving 10.7g in 50 ml of deionized water at ambient conditions as well in a fourth beaker. As earlier mentioned in 3.5.1, the solubility process of the NH₄Cl powder is endothermic.

3.6 Sequence of Thermochemical Treatment

An open system of the thermochemical treatment process on the samples was considered to eliminate the effects of pressure generated from the gases as a result of the reactions (Nitrogen gas during exothermic reaction and Ammonium gas during the endothermic reaction). The figure below presents a schematic that highlights the thermochemical treatment process on the samples.

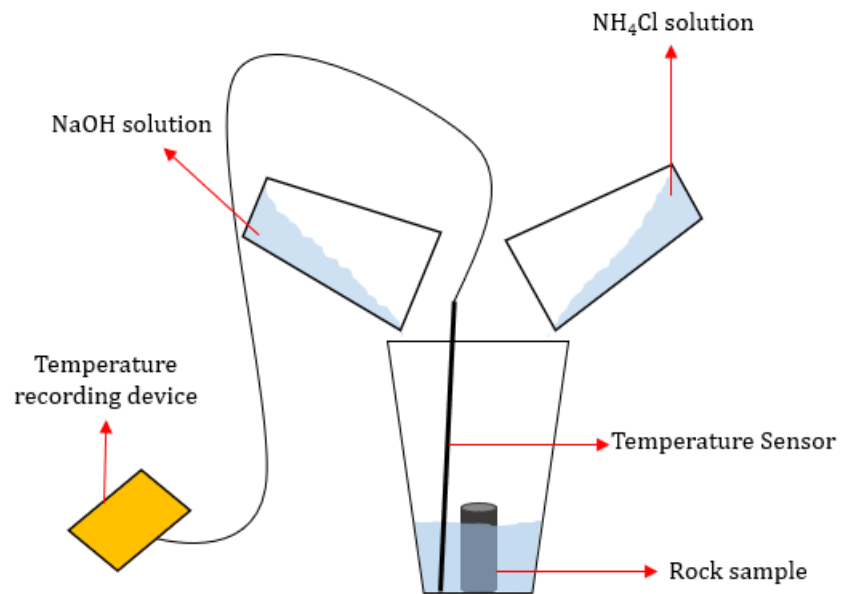
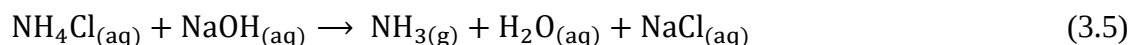


Figure 7 Schematic of thermochemical treatment

3.6.1 Endo – Exo Sequence (Sequence #1)

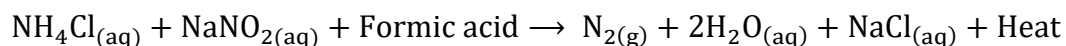
The samples that were to be exposed to thermal shock through sequence treatment of endothermic-exothermic thermochemical fluids were heated first to a temperature of approximately 150°C in a core holder connected to a heater. The temperature logging

device rod set to keep contact with the samples from the start to the end of the experiment, was inserted in the middle of the drilled borehole to monitor any temperature fluctuations or increments as the fluids react. The samples at 150°C were drawn from heating core and lowered in a beaker containing NH₄Cl powder. Immediately, the prepared 4M solution of NaOH was immediately added to the same beaker followed by 50 ml of deionized water from the measuring cylinder. The temperature logging device continued to monitor temperature reduction caused by the endothermic reaction (see chemical **Equation 3.5**) of the mixture components until no further temperature reduction was observed.



The samples were immediately transferred to a dry beaker and prepared solutions of NaNO₂ and NH₄Cl were simultaneously added to the beaker that contained the samples followed by 1 ml of formic acid to initiate and catalyze the exothermic reaction (see chemical **Equation 3.6**). With the temperature logging device rod still in contact with the samples, the temperature build-up in the samples was monitored until no further temperature increase was noticed. This marks the end of the (endo-exo) experiment. Two more cycles of the same treatment sequence were repeated for each sample. The end products of the reacted solutions in the beakers were discarded and the samples were washed with deionized water and dried in an oven at 50°C, and later taken for micro-CT scanning to visualize effect of thermal shock on the internal structure of the samples.

(3.6)



3.6.2 Exo – Endo Sequence (Sequence #2)

This is a reversed sequence of the treatment experiment discussed in sub-section 3.6.1. The samples prepared specifically for this sequence were heated to approximately 150°C to simulate reservoir temperature. The hot samples were transferred from the heating core holder to a dry beaker, and while keeping the temperature sensor rod intact with the samples and continuously logging, the prepared solutions that formed an exothermic reaction were poured in the same beaker followed by 1 ml of formic acid to immediately activate the chemical reaction. The temperature rise was continuously monitored until there was no further increase noticed.

The samples were immediately transferred to the beaker containing NH_4Cl powder, with the addition of prepared NaOH solution followed by 50 ml of deionized water from a measuring cylinder. The temperature fluctuation was monitored until there was no further reduction in temperature. Two more cycles were repeated on each sample for this particular sequence. Fluids were discarded, the samples were washed with deionized water and dried under an oven temperature of 50°C. The micro-CT scan was later used to visualize any microfractures caused by this reverse thermal shock sequence. **Figure 8** below shows the set up used for the thermochemical treatment processes under the fume hood.

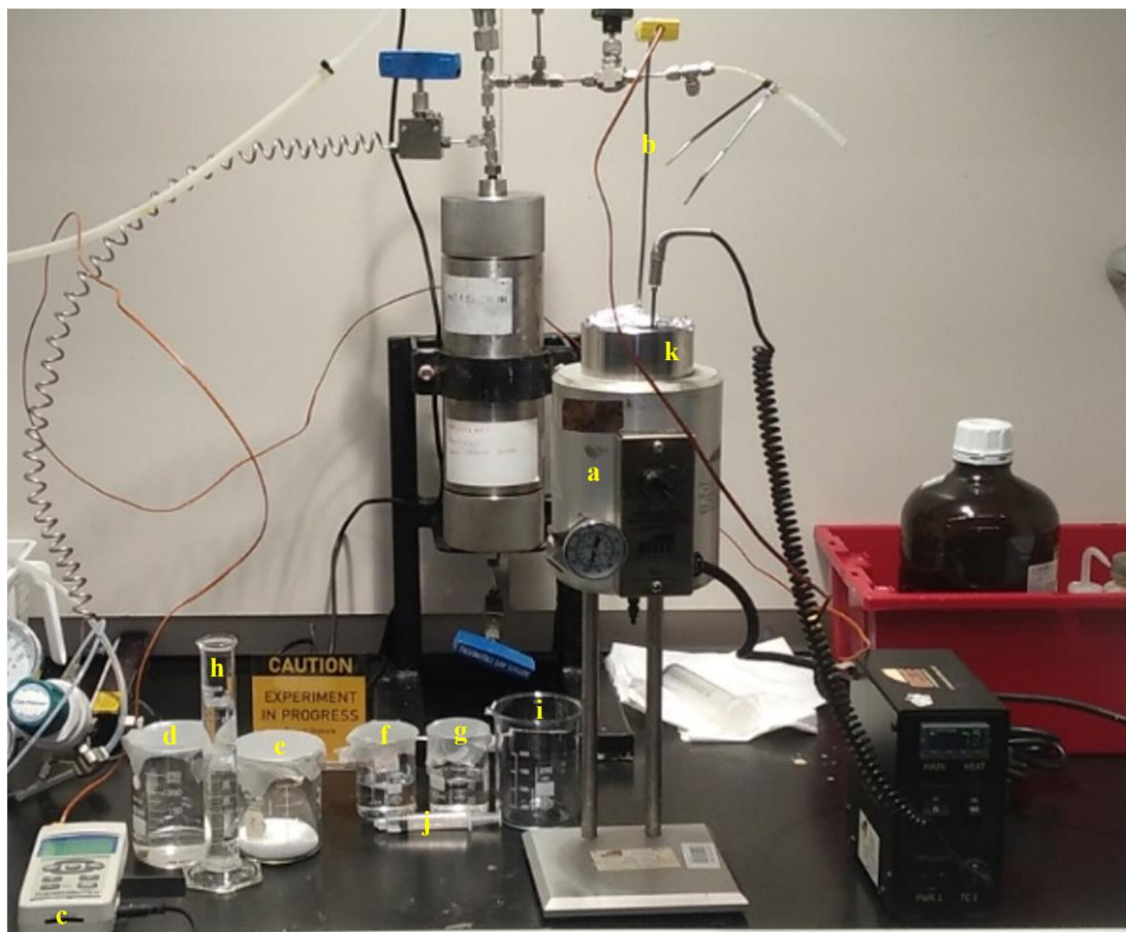


Figure 8 (a) Core heater, (b) Temperature sensor, (c) Temperature logger, (d) Sodium Hydroxide solution, (e) Ammonium chloride powder, (f) Sodium Nitrite solution, (g) Ammonium Chloride solution, (h) Deionized water, (i) Empty beaker, (j) Formic acid, (k) Core holder

3.7 Breakdown Experiments

To perform the breakdown experiments, hollow high-pressure metallic tubings were inserted, positioned, and fixed vertically at half the depth of the drilled hole with the application of epoxy to tighten the rod within the samples (see **Figure 9**). The prepared samples were left to stand for at least 24 hours to guarantee complete sealing and solidification of epoxy between the tubing and the samples. The samples were then subjected to a constant surrounding temperature of approximately 50°C in a core holder

covered in a jacket (see **Figure 10**). A pressure test was conducted before the actual breakdown experiment to guarantee no leakages were observed through the joint connections. The pressure was then released through the pump (see **Figure 11a**) and water flowed at a rate of 0.1ml/min while logging the pressure data in the computer (see **Figure 11b**) to accommodate a smooth pressure build-up until the samples broke down. When the samples broke down, the pump was immediately stopped, and sections were closed to stop the water flow.

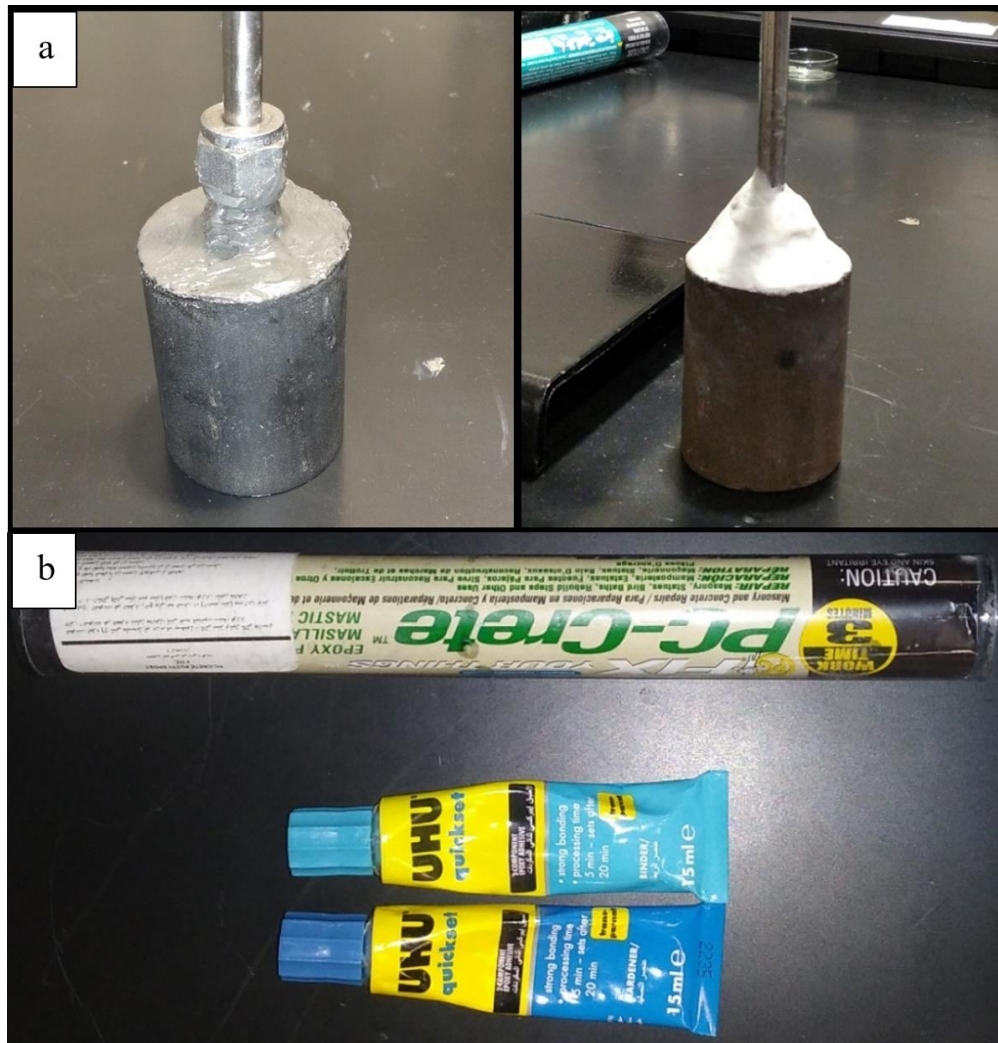


Figure 9 (a) Sealed gap between the metallic rod and sample with (b) epoxy



Figure 10 Constant temperature set-up for the samples during breakdown experiment

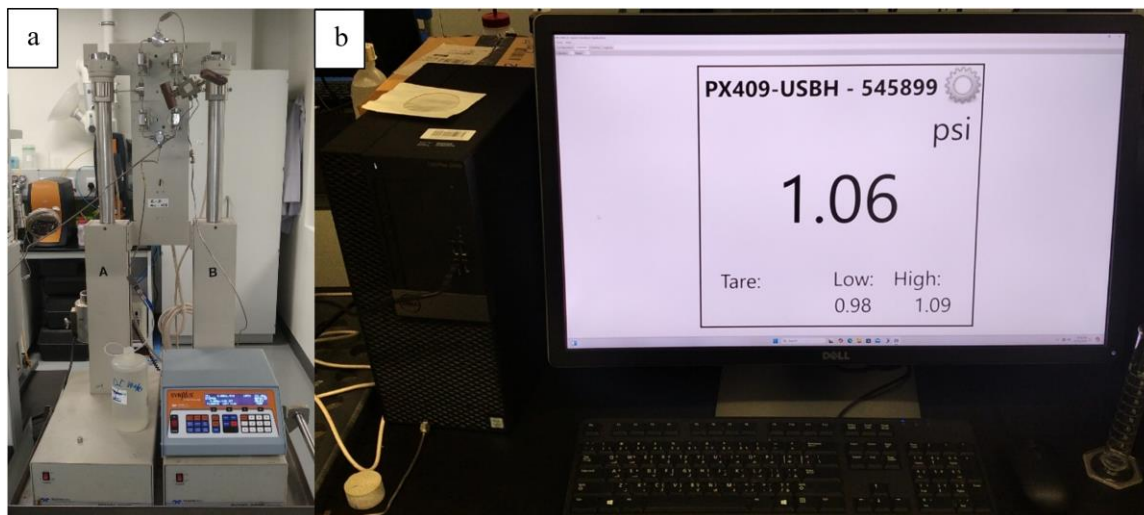


Figure 11 (a) Pressure flow pump and (b) pressure logging computer

3.8 Scratch Tests

Scratch tests were carried out using a scratch machine called Epslog Wombat (see **Figure 12a**) with the aim of determining the change of hardness in the samples through measuring the intrinsic specific energy (ISE) defined by **Equation 3.7**. ISE is the amount of energy needed to achieve unit volume removal of material while accounting for factors such as the tool geometry, applied forces, and mechanical properties of the material. During the levelling process, a minimum groove depth of 0.4 mm was considered, depth of cut (DOC) of 0.1 mm, and a cleaning DOC of 0.05 mm. in order to have an accurate estimate of ISE of the samples under test, 7 scratches (number of DOC) were required with a minimum DOC of 0.05mm, considering an increment DOC of 0.05 mm. A total minimum of 4 to 5 scratches were selected by manually selecting those points that show the highest linearity trend (highest R^2). These are the data points obtained when the scratch was performed in the ductile regime. The points obtained in the brittle mode were excluded/deselected.

$$ISE, \varepsilon = \frac{F-VI}{wd} \quad (3.7)$$

Where, F defines the required force to cut the rock by one-unit volume, VI represents the vertical intersect, w and d are the cutter width and depth of cut respectively.



Figure 12 (a) scratch test equipment and (b) Scratch analysis computer device

3.9 TOC Measurement

Total Organic Carbon (TOC) refers to the amount of organic carbon present in the rock samples and can be used to estimate the potential for hydrocarbon generation. This parameter was determined using Rock-Eval analysis. First, the scratched powder obtained from the scratch tests for each sample was used in this experiment after pounding it in a

mortar to make it finer. In the initial heating phase, the sample underwent pyrolysis in an inert atmosphere, heating from ambient temperature to around 600°C. During this phase, hydrocarbons were released and detected, with the S1 peak representing free hydrocarbons and the S2 peak indicating hydrocarbons generated from kerogen cracking. In other words, the S1 (hydrocarbons generated) represented amounts of hydrocarbons (oil and gas) generated from the organic matter in the rock sample whereas S2 (hydrocarbons still present) represented amounts of hydrocarbons that were still present in the rock sample and have not been generated yet. Following pyrolysis, the oxidation phase heated the remaining sample to about 850°C in the presence of oxygen to measure residual carbon. Detection of released hydrocarbons and CO_2 was conducted using a flame ionization detector (FID) and an infrared detector (IR), respectively. Finally, TOC was calculated by summing the carbon content from both phases, using correction factors to account for detection efficiency and sample weight (Bisutti et al., 2004)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of Drilled Hole on Sample Elastic Properties

The shale samples were initially weighed and their initial mass was recorded. Drilling holes (0.375 inches in diameter and 1 inch deep) into the samples reduced the mass on the second weighing, reducing the bulk density. Since bulk density strongly influences the travel of Plane (V_p) and Shear (V_s) waves in a material, the elastic properties of the samples were generally reduced. The effective cross-sectional area through which the waves propagate was diminished when a hole was drilled. This reduction led to lower wave speeds because the rock's ability to transmit stress waves was reduced. The drilled hole also acted as a stress concentrator, which scattered the waves and reduced speed. **Table 1** shows the sample data of the elastic properties before and after drilling holes. The table also lists the results on propagation speed of sonic waves through the samples before and after drilling holes centrally. As evidenced by **Figure 13** below, the data indicates that Young's moduli and Poisson's ratios of the respective samples under test showed a small decrease due to reduction in the travel speeds of Plane (V_p) and Shear (V_s) waves through the rock samples.

Table 1 Lab results on Elastic properties and propagation of waves within different samples (before and after drilling holes)

	Sonic velocities before hole drilling		Sonic velocities after hole drilling	
Sample Name	V_p (m/s)	V_s (m/s)	V_p (m/s)	V_s (m/s)
EF1.1	5570	3012	5606	2983
EF1.2	5577	2972	5616	2806
EF1.3	5540	3075	5564	2941
	Elastic properties before hole drilling		Elastic properties after hole drilling	
Sample Name	E_B (GPa)	ν_B	E_A (GPa)	ν_A
EF1.1	60.5	0.293	58.4	0.296
EF1.2	58.6	0.302	51.4	0.334
EF1.3	61.6	0.278	55.5	0.306

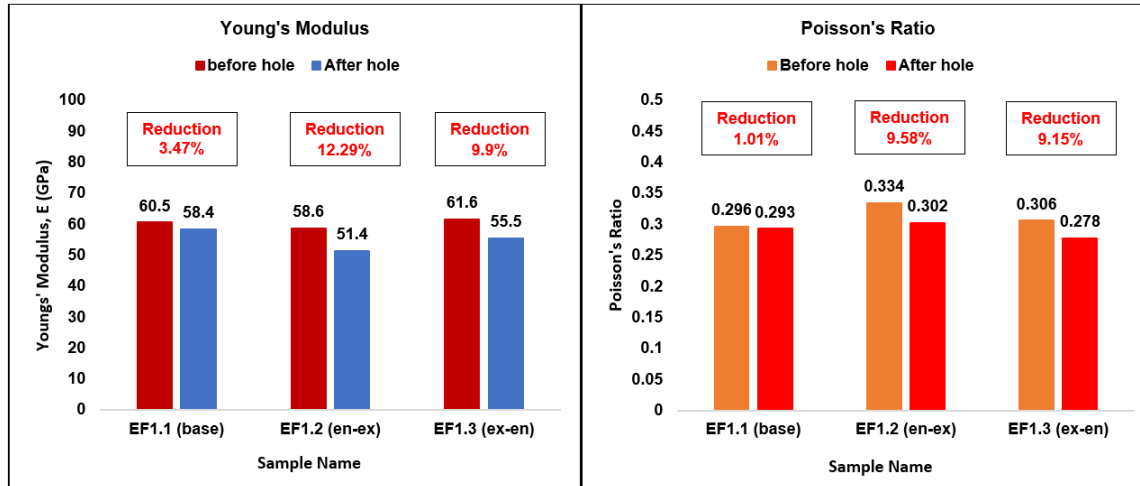


Figure 13 Variation of Elastic properties across different samples before and after drilling holes centrally.

4.2 Effect of Drilled Holes in Samples on Brittleness Index

The brittleness index results indicated that the respective brittleness indices of the different samples before the holes were drilled were higher than the ones after samples had been drilled with holes. The explanation for this is due to the variation of the elastic mechanical properties explained in the previous section. Drilling a hole reduced Young's modulus because the structural integrity of the rock was compromised, making it less stiff. Additionally, the potential changes in Poisson's ratio reflected alterations in the rock's ability to resist deformation and fracturing. The results observed in **Table 2** below clearly indicate a reduction in the brittleness index (B.I) of the respective samples due to drilling holes in them. Using **Equation 3.3**, the B.I was calculated based on the mechanical properties (Young's modulus, E , and Poisson's ratio, ν) of the shale samples before and after drilled holes. This equation is commonly used in evaluating rock formations for hydraulic fracturing. It effectively correlates with how rocks fracture under stress and

provides a direct assessment of material stiffness and ductility, important for understanding fracture mechanics. **Figure 14** is a graph that analyses the changes in the B.I of the respective samples before and after the holes were centrally drilled. The trend of the data verifies the heterogeneities in shale rocks from top to bottom of the core sample.

Table 2 Results showing changes in B.I concerning Elastic sample properties before and after drilling holes

Sample Name	Elastic properties before hole drilling		B.I before hole drilling	Elastic properties after hole drilling		B.I after hole drilling
	E_B (GPa)	ν_B		E_A (GPa)	ν_A	
EF1.1	5570	3012	446.4	5606	2983	430.80
EF1.2	5577	2972	431.03	5616	2806	373.20
EF1.3	5540	3075	457.26	5564	2941	408.09

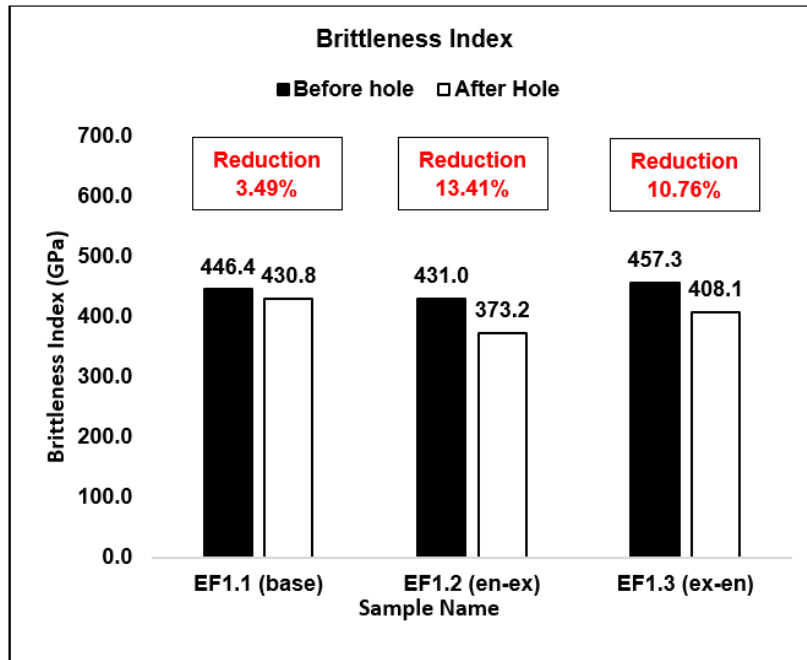


Figure 14 Trend of B.I on shale samples (before and after drilling holes)

4.3 Impact of Thermochemical Treatment Sequences on Inducing Thermal Shock to The Samples

As discussed earlier in the methodology chapter, the induced thermo-shock on the heated samples at $\sim 150^{\circ}\text{C}$ was due to the instantaneous mixture of solutions that reacted chemically to;

- (i) Absorb heat by suddenly reducing the sample temperature in a very short time interval (endothermic reaction).
- (ii) Release heat suddenly through acid activation to increase the sample temperature (exothermic reaction).

4.3.1 The Endo-Exo Thermochemical Treatment Sequence (Sequence #1)

The treatment of the heated sample at $\sim 150^{\circ}\text{C}$ with an endothermic mixture of prepared solutions triggered a significant reduction in the temperature of the sample as monitored by a temperature logging device from 151.8°C down to 6.3°C in just **11.5** minutes causing a huge difference in temperature of 145.5°C (**Figure 16**) . This time marked the overall endothermic reaction activity of the mixed solutions on the sample. It was also observed that within **30** seconds, the sample temperature had gone down to 31°C and further down to 25.8°C in the next approximately **30** seconds causing reduction temperature differences of 120.8°C and 126°C , respectively. **Figure 15** and **Figure 16** highlight the typical temperature logged data over time plotted on graphs to indicate the smooth temperature build-up of the sample to $\sim 150^{\circ}\text{C}$ and the reaction activity of the endothermic mixture to reduce the sample temperature respectively.

It can be observed that the sample achieved the desired temperature within **115.8** minutes with the temperature logging device rod directly inserted in the middle of the drilled hole of the sample. The minimum recorded temperature of the sample was 20.2°C , at the start of the logging and heating activity.

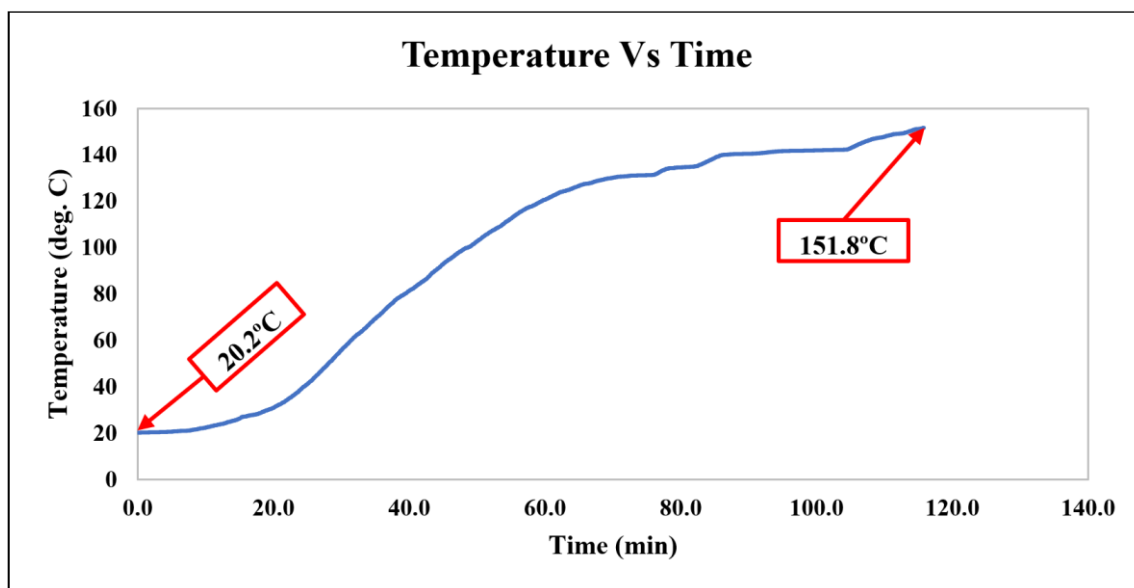


Figure 15 Temperature build-up profile on the EF1.2 sample

With clear observation from the graph above, the minimum temperature recorded was **6.3°C** and this marked the end of the endothermic reaction, as there appeared no further decrease in temperature. It was from this point onwards that the sample was then treated with an exothermic mixture. The sharp decrease in temperature (from **151.8 °C** to **~33.9 °C**) evidenced by the steep section of the graph signifies a very strong induced thermal shock in the smallest time interval (**18 seconds**).

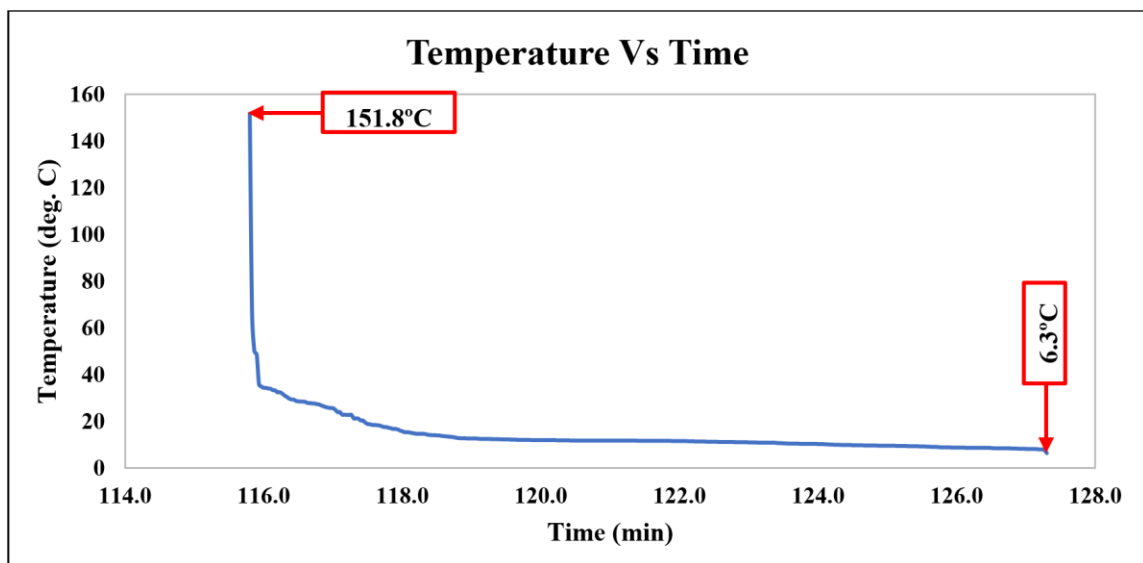


Figure 16 Endothermic mixture activity on sample EF1.2

The exothermic mixture generated heat upon activation with drops of formic acid, causing the fully immersed sample temperature to rise again from **6.3°C** to **44.3°C**. This temperature was recorded as a climax to the exothermic reaction. This reaction registered a temperature difference of **38°C** within **7.1** minutes. **Figure 17** is a temperature profile plot that displays the activity of the exothermic mixture to cause a rise in the temperature of the fully immersed sample. To ensure that all the components of the mixed fluids had fully reacted, the temperature-logging device remained active and the sample temperature was recorded further. This was seen going down to adjust to the room temperature, as evidenced by a profile plot in **Figure 18**.

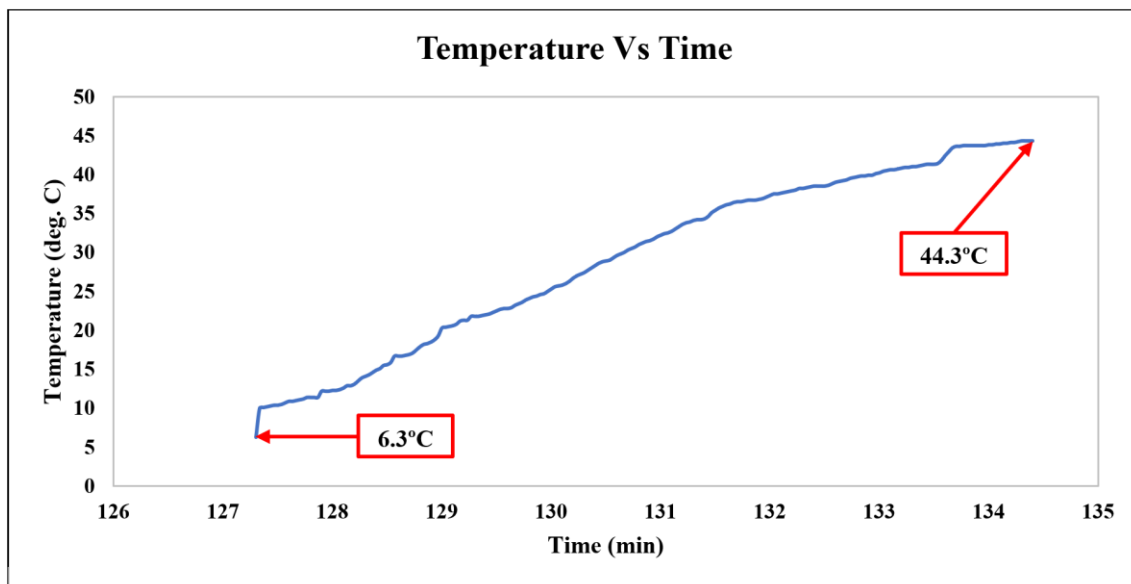


Figure 17 Exothermic fluid activity on sample EF1.2

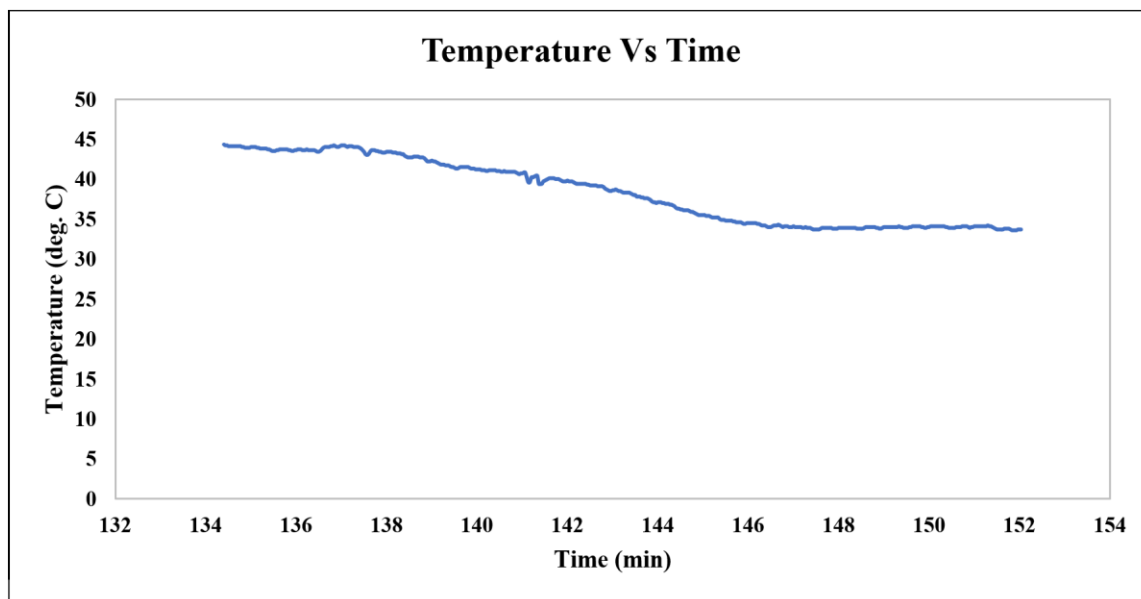


Figure 18 End of Exothermic activity on sample EF1.2

A series of events to graphically describe the thermo-shock process caused by the endothermic-exothermic thermochemical treatment sequence on the heated sample were

plotted as shown in **Figure 19**, typically presenting an example of one cycle of sample EF1.2. It was noted that the duration that led to the success of this experiment was approximately 2.5 hours.

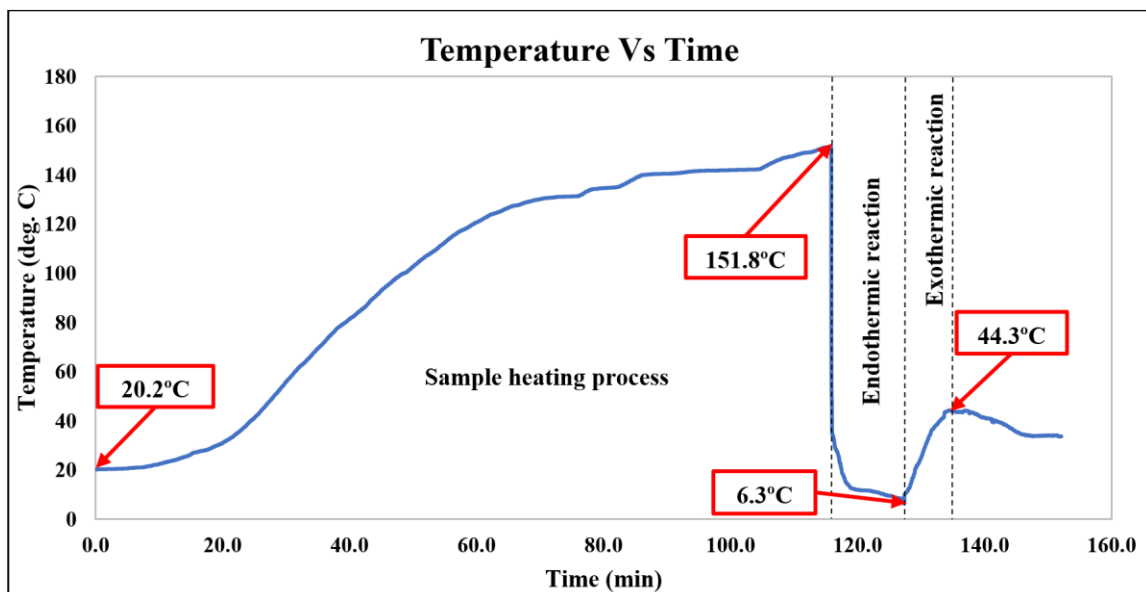


Figure 19 Graphical representation of the endothermic-exothermic treatment sequence

Table 3 below presents a summary of the overall temperature changes in the 3 cycles due to sequence #1 treatment involving application of endothermic thermochemical treatment first and later, exothermic thermochemical treatment. It can be seen that the change in temperature due to the exothermic reaction did not reach 150°C due to heat losses caused by an open system used.

Table 3 Sequence #1 temperature changes across 3 cycles due to endothermic-exothermic reactions

Sample Name	Cycle	Endo (ΔT in $^{\circ}\text{C}$)	Exo (ΔT in $^{\circ}\text{C}$)
EF1.2	1 st	145.5	38
	2 nd	143.1	37.3
	3 rd	144.7	37.8
J2	1 st	142.2	41.4
	2 nd	146.3	44
	3 rd	145.1	43.7

4.3.2 The Exo-Endo Thermochemical Treatment Sequence (Sequence #2)

The treatment of the initially heated sample at $\sim 150^{\circ}\text{C}$ with an exothermic mixture of prepared solutions triggered a rapid reduction in the temperature of the sample as monitored by a temperature logging device from **152.3°C** down to **28.2°C** in just **9 seconds** causing a huge temperature drop of **124.1°C** . The initial cooling effect caused by the endothermic solution mixture was due to the fact that the independent solutions had been prepared at ambient conditions. Therefore, their respective temperatures were largely lower than the sample temperature. After **9 seconds**, the exothermic reaction was activated and the temperature increased again, reaching **83.6°C** in just **32 seconds**. The reaction proceeded for **4 seconds** to ensure that all the solution mixture components had fully reacted, even though no further higher temperatures were recorded. **Figure 20** and **Figure 21** graphically represent the logged temperature data with time, specifically showcasing the

smooth temperature buildup of the sample, the initial thermal shock, and the exothermic mixture activity on the sample before sample immersion in an endothermic mixture.

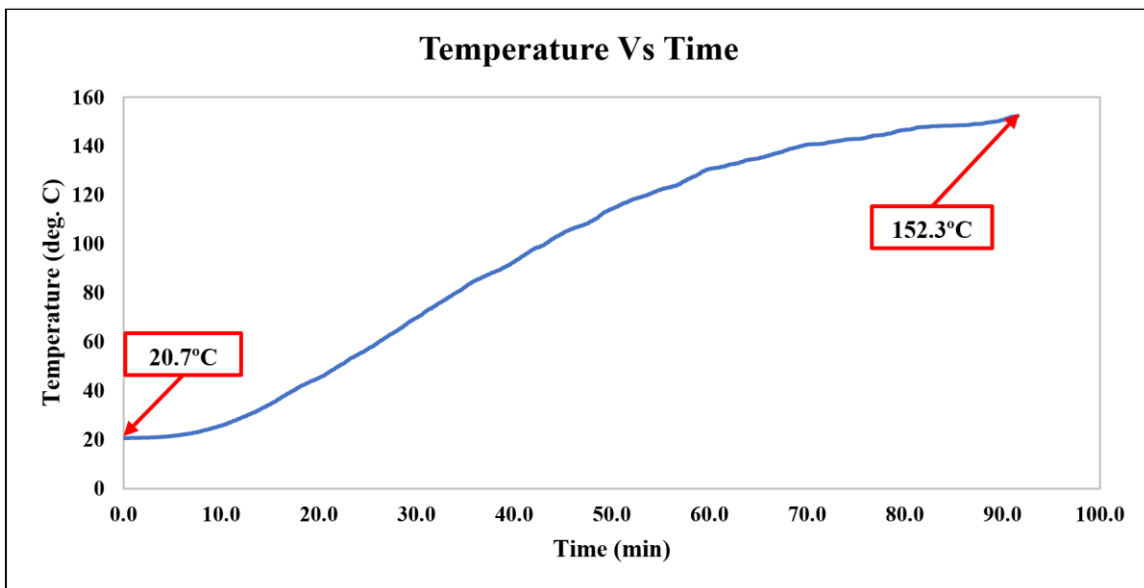


Figure 20 Temperature build-up on sample EF1.3 before exothermic reaction treatment

The sample was then immersed in an endothermic mixture which substantially decreased the temperature drastically from **83.6°C** to **2.3°C** within **6.4 minutes**, causing a huge temperature fall of **81.3°C**. This time was recorded as the period through which the endothermic reaction occurred. Beyond this time, the system started adjusting the temperature to match that of the surroundings. It was also observed that the initial immersion of the sample reduced the temperature suddenly to **28°C** from **83.6°C** within just **8 seconds** hence causing a temperature difference of **55.6°C**. **Figure 22** graphically plots temperature reduction on the sample due to the endothermic reaction of the solution mixture.

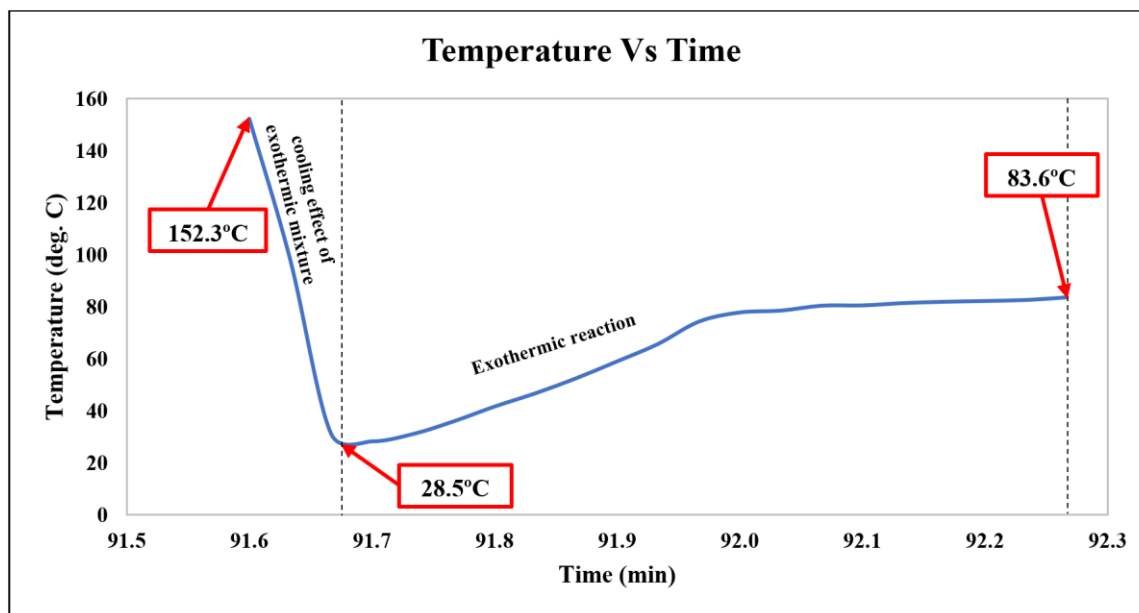


Figure 21 Initial thermal shock on sample EF1.3 and exothermic mixture reaction

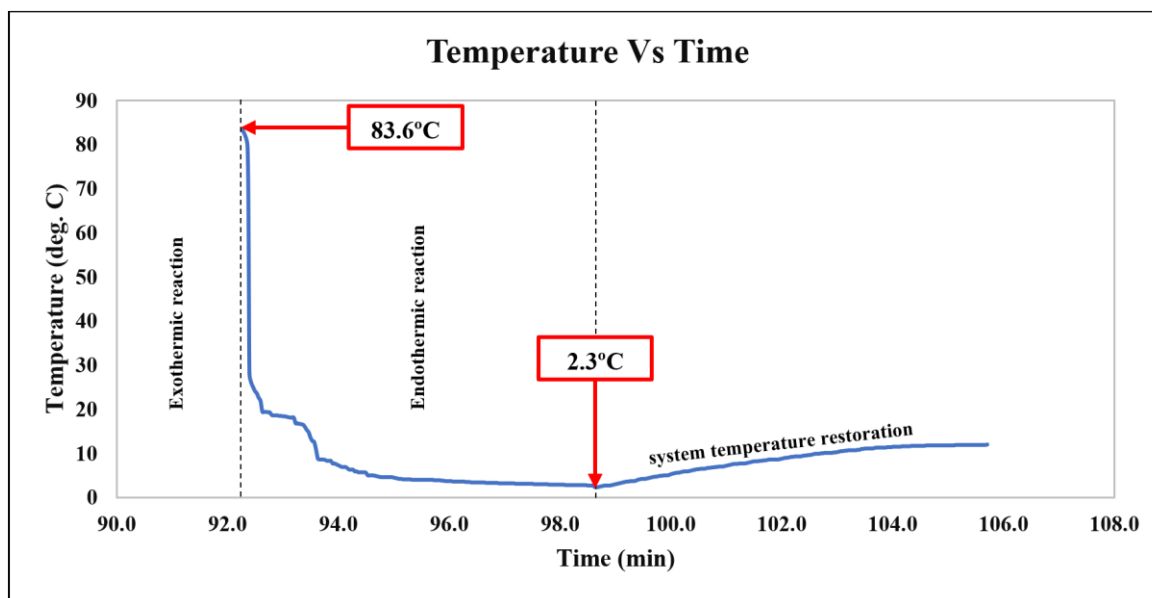


Figure 22 Endothermic reaction activity and system temperature restoration to the surroundings

A combined experimental process involving the whole exothermic – endothermic sequence is displayed in **Figure 23** below. This interprets the different temperature build-ups and fluctuations that induced thermal shock on sample EF1.3. The whole sequence was successfully conducted within a total time of **98.7 minutes**. Beyond this time, there were no lower temperatures registered and this marked the end of the experiment because the whole system began to adjust to the room temperature gradually as evidenced by the increase in temperatures.

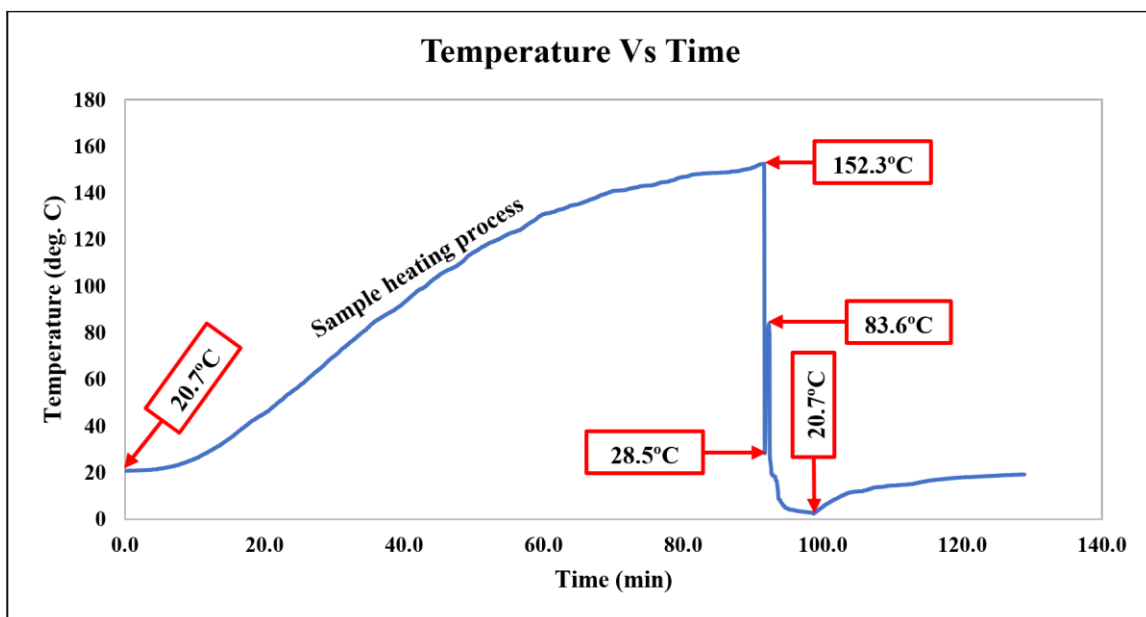


Figure 23 Exothermic-Endothermic sequence on sample EF1.3

Figure 24 below displays a combined graphical plot of one cycle for the two sequences on two samples (EF1.2 and EF1.3). With equal concentrations of the reaction mixtures, it can

be observed that the magnitude of temperature increases and decreases greatly through exothermic and endothermic reactions, respectively, based on the sample temperature.

Table 4 presents a summary of the overall temperature changes in the 3 cycles due to sequence #2 treatment involving application of exothermic thermochemical treatment first and later, endothermic thermochemical treatment.

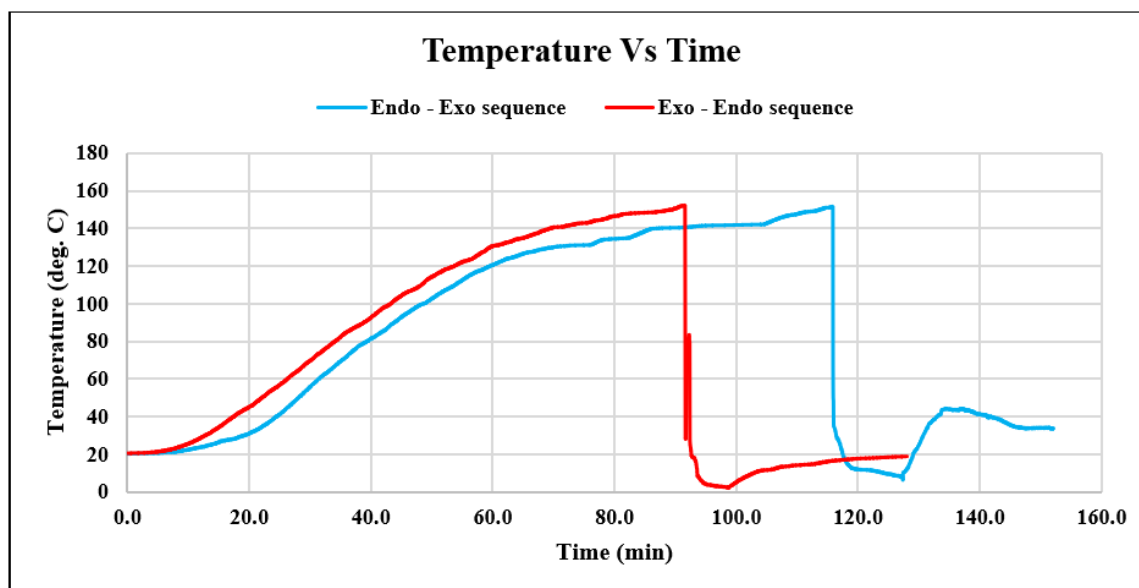


Figure 24 Temperature profiles of Endo - Exo and Exo - Endo sequences on EF1.2 and EF1.3 respective samples

Table 4 Sequence #2 temperature changes across 3 cycles due to exothermic-endothermic reactions

Sample Name	Cycle	Cooling effect of Exo (ΔT in $^{\circ}\text{C}$)	Exo (ΔT in $^{\circ}\text{C}$)	Endo (ΔT in $^{\circ}\text{C}$)
EF1.3	1 st	114.4	39.1	70.6
	2 nd	123.8	55.1	81.3
	3 rd	118.2	44.3	72.1
J1	1 st	118.4	41.3	70.4
	2 nd	118	44.0	66.3
	3 rd	116.1	38.2	74.8

4.4 Impact of Thermochemicals on Dynamic Elastic Properties and Brittleness Index

As discussed earlier in subsection **4.1**, the elastic properties obtained after thermochemical treatment of the samples based on the sonic tests conducted through measuring the velocities of the primary and secondary waves travelling through the thermally shocked samples. The results displayed in **Figure 25** show that the young's modulus of sample EF1.2 highly decreased after a thermochemical treatment with endothermic – exothermic sequence and that of sample EF1.3 decreased though not as much as with the reverse sequence thermochemical treatment. The decrease in young's modulus of (endo-exo) samples suggests that the endo – exo immersion sequence significantly weakened the sample due to the creation of a lot of microcracks during the thermal shock. These results align with the decreased brittleness index presented in **Figure 26** after utilizing **Equation 3.3**. In addition, the decrease in Young's modulus of (exo-endo) samples indicates that the

reverse immersion (exo–endo) also caused microfracture formation but not as much as in EF1.2 as confirmed by micro CT scan.

The rise in Poisson’s ratio suggests that the endo – exo treatment increased the sample’s ability to deform laterally because of the induced microcracks allowing lateral expansion under stress. The slight increase in Poisson’s ratio suggests the same results though not to a much effect as compared to sample EF1.2 due to few microcracks formed.

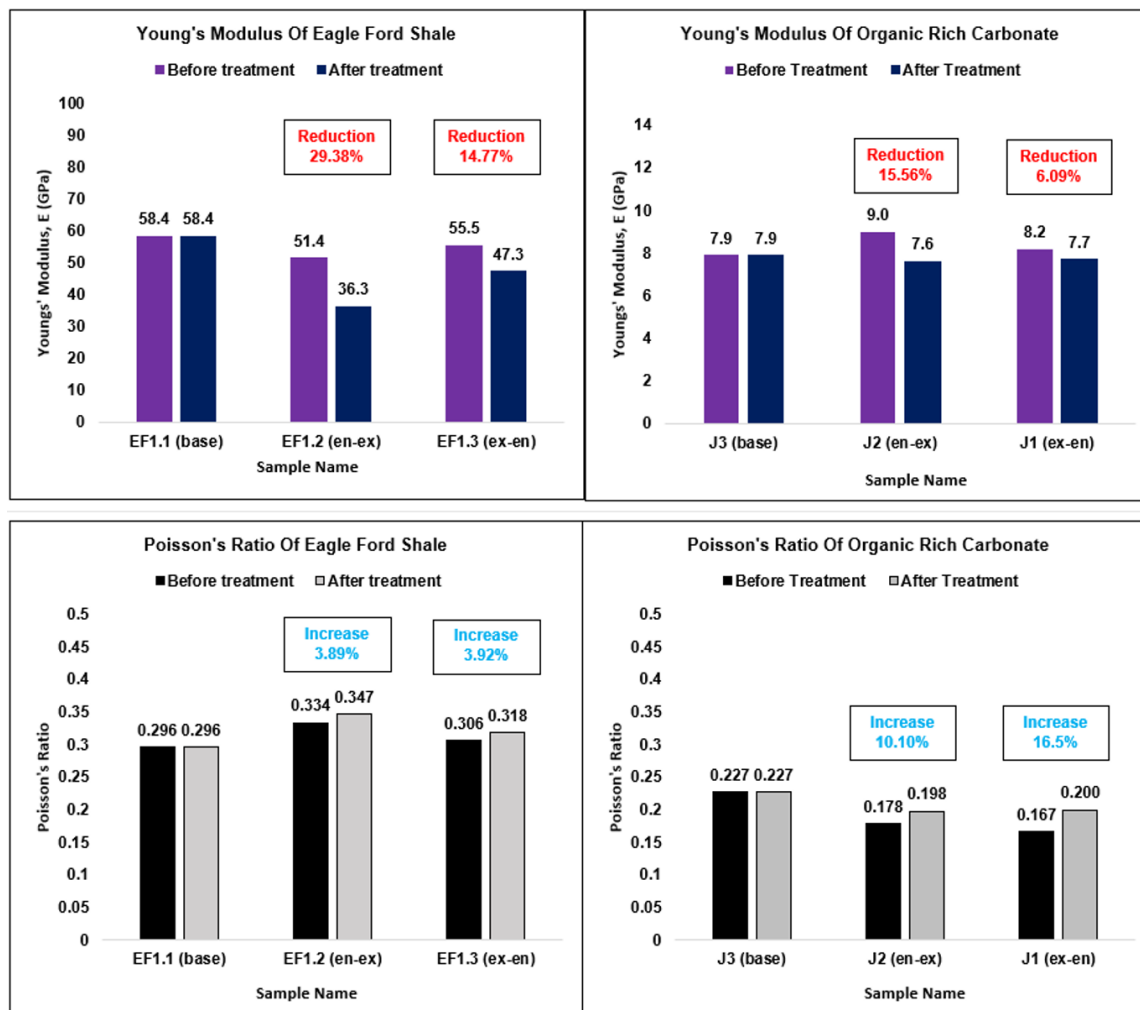


Figure 25 Elastic properties of the tested samples before and after thermal shock

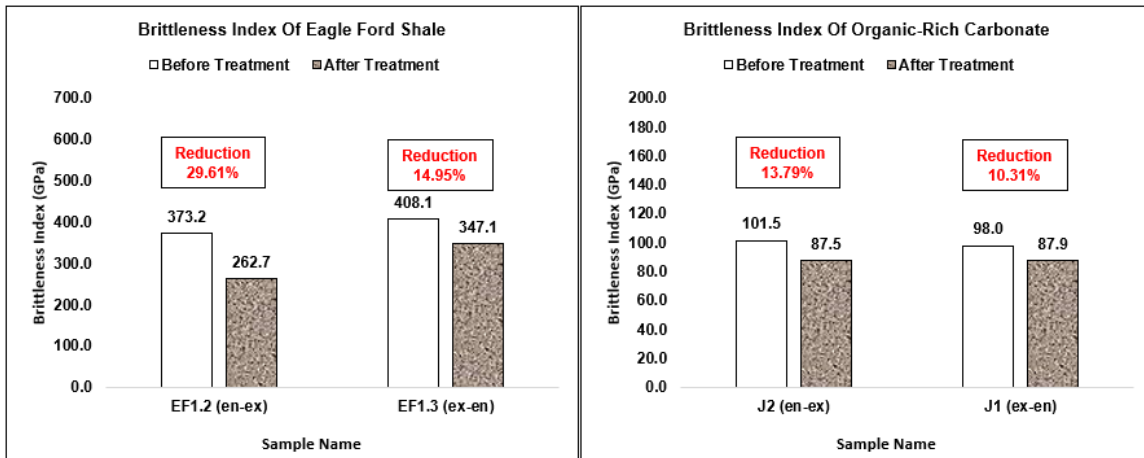


Figure 26 Variation of B.I in samples before and after thermal shock

4.5 Impact of Thermochemical Treatment Sequences on Breakdown Pressure of samples

A flow rate of 0.1ml/min was set on the pump to allow the fracturing fluid to flow into the drilled hole that had been tightly connected to a high-pressure tubing and sealed with epoxy. The fracturing fluid used throughout all the breakdown experiments was de-ionized water. The small flowrate set was aimed to create a smooth pressure build-up within the drilled hole., evidenced by the plotted data captured during logging in Error! Reference source not found.. The breakdown pressure of the untreated EF1.1 sample constantly subjected to a temperature of 50°C was **3048.35 psi**. It can be observed that from about 50 minutes, the pressure started to increase over a small change in time, generating a steep pressure plot until the sample was fractured hydraulically after **87.4 minutes**. Considering the same flowrate as in the first case, the same breakdown setup as on the EF1.1 sample

under the same conditions of temperature was repeated on the EF1.2 and EF1.3 samples after their respective sequence thermochemical treatment as explained in the earlier sections. Results showed that the EF1.2 sample registered its breakdown pressure of **631.57 psi** in **78.3 minutes** where as sample EF1.3 registered a breakdown pressure of **1274.05 psi** in **82.1 minutes**. The set of breakdown test results obtained clearly highlight a significant reduction in breakdown by sequentially treating the two samples with thermochemicals thereby inducing thermal shock in the rock samples. A huge difference of **2416.78 psi** in breakdown pressures of EF1.1 and EF1.2 registered a **79.28%** breakdown pressure reduction after endothermic – exothermic thermochemical treatment on EF1.2 sample. However, with the reverse sequence applied on EF1.3 sample (exothermic – endothermic thermochemical treatment), the breakdown pressure difference when compared with that of EF1.1 sample was **1774.3 psi** which is an approximate **58.21%** breakdown pressure reduction. **Figure 28** presents plots that highlight percentage breakdown pressure reduction in both sets of samples used in this experiment. This gives a proper comparison of the two sets of samples and the effect of thermochemical treatment to reduce breakdown pressure.

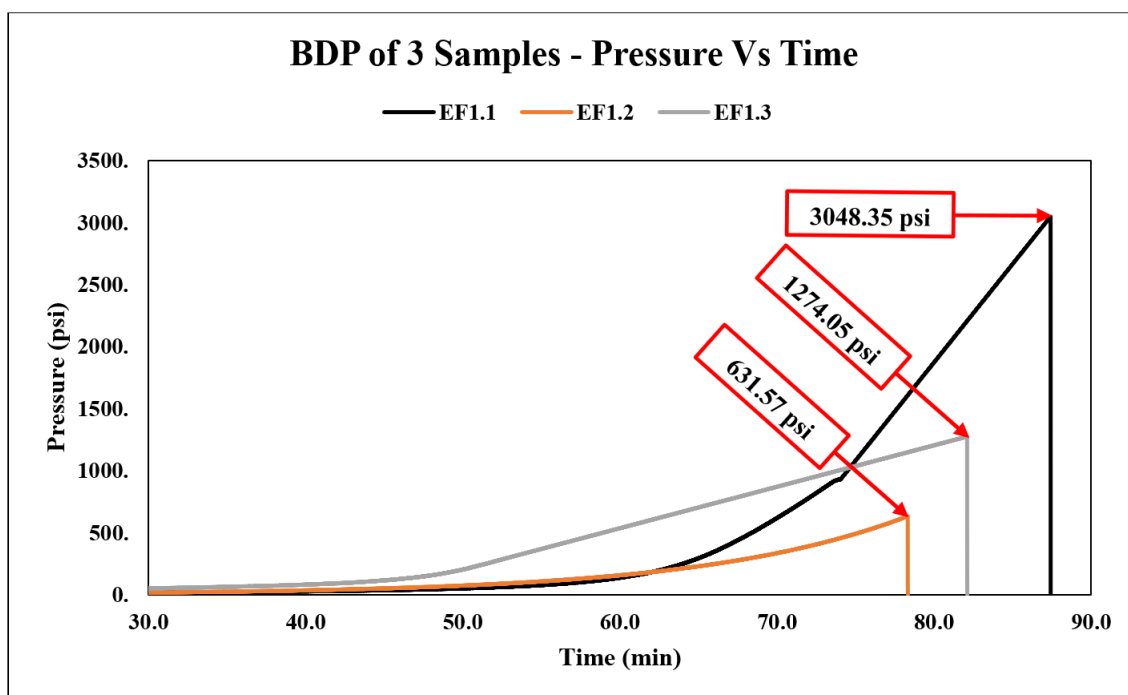


Figure 27 Breakdown pressure combined plot of EagleFord shale samples with time

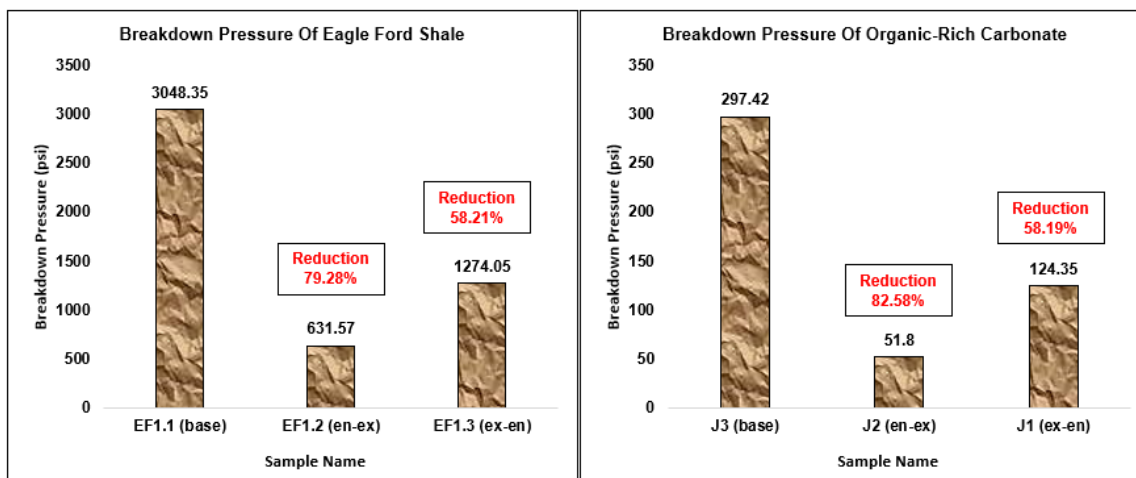


Figure 28 Breakdown pressure of Eagle Ford shale samples and Organic-rich Jordan carbonate samples

4.6 Impact of Thermochemical Treatment Sequences on Hardness of The Samples

Due to the high heterogeneity of rock bodies, the scratch test was conducted two times. The two initially marked surfaces of each sample produced the same trend of results based on the nature of the thermochemical sequence applied to the samples in comparison with the base case/untreated sample. As discussed in the methodology chapter, the scratch test was used to obtain the Intrinsic specific energy (ISE) of the rock samples because it is a robust indicator of the UCS as supported by several studies that demonstrated a strong correlation between the two. The mean, maximum and minimum values of ISE were recorded for each of the surface scratched and the results were summarized in **Table 5**.

Table 5 Scratch test results recorded after scratching samples

Sample Name	First Scratched Surface	Second Scratched Surface	Average Hardness
EF1.1 (base)	128.4	87.7	108.05
EF1.2 (en-ex)	103.5	67.3	85.4
EF1.3 (ex-en)	114.7	70.4	92.55
J3 (base)	44.9	40.2	42.55
J2 (en-ex)	35.5	31.7	33.6
J1 (ex-en)	40.2	32.3	36.25

Results indicated that the EF1.1 sample unexposed to thermal shock exhibited the highest strength in both scratched surface events. Its average hardness was seen to be **108.05 MPa** which is higher by **22.65 MPa** and **15.5 MPa** when compared with samples EF1.2 and EF1.3 respectively. It is clear that the thermal shock induced as a result of sequential thermochemical treatment reduced the samples' intrinsic specific energy, which correlated with the same reduction in hardness.

Based on the presented results, the endothermic–exothermic thermochemical treatment sequence on sample EF1.2 compromises the integrity of the rock matrix. The sample's average hardness was reported to be **85.4 MPa**, which is the minimum compared to **108.05 MPa** and **92.55 MPa** average hardness values registered by EF1.1 and EF1.3 respectively.

Figure 29 below depicts a comparison of the hardness of the surfaces of the two sets of samples under test.

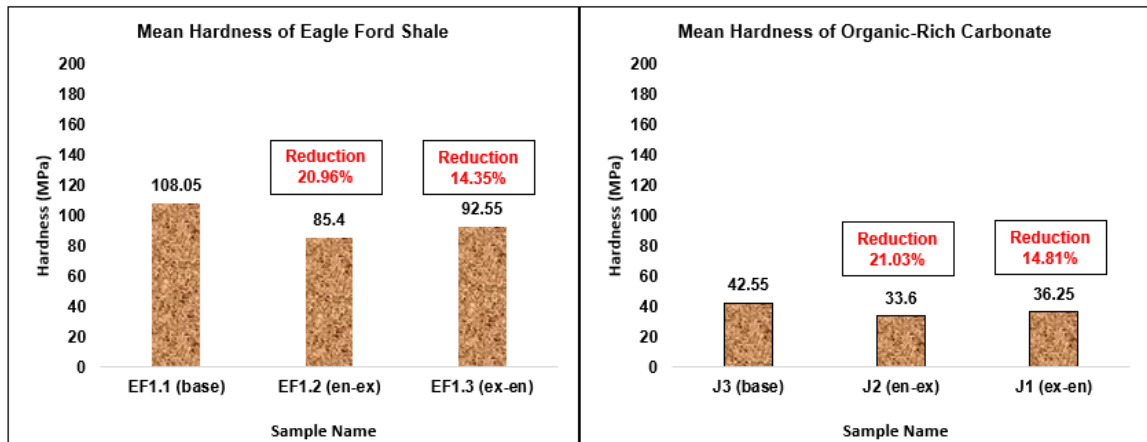


Figure 29 Hardness of the samples after the scratch test.

4.7 Effect of Thermochemical Treatment Sequences on TOC Maturation Potential

The scratched sample particles from the two surfaces were each collected and further pounded into very fine powder which were then tested through rock eval analysis. Results showed that the average total organic carbon within EF1.1 was originally **2.95%**. Since sample EF1.1 was the base sample, the rest of the samples EF1.2 and EF1.3 were assumed to originally have the same average amount of total organic carbon before thermochemically shocked by endothermic and exothermic reaction mixtures.

Upon applying an endothermic – exothermic thermal shock sequence on sample EF1.2, the sample powder was found to have reduced in total organic carbon by **0.78%**. this might imply that the reported average value of remaining TOC as a result of this sequence was **2.17%**. Furthermore, as another evidence of this reduction, the mass of EF1.2 after this thermochemical treatment was found to have reduced by **2.77 g** from its original (**131.29 g**).

With the reverse sequence of thermochemical treatment to induce thermal shock on sample EF1.2, the remaining TOC of this sample was found to be **2.72%**, slightly deviating from the TOC of the untreated sample (EF1.1) by **0.23%**. This slight deviation was supported by the slight reduction of mass of sample EF1.2 by **0.69 g** from its original (137.95 g). The changes in mass in the organic-rich carbonate samples is displayed in **Table 6**.

Table 6 Observed TOC data reflecting the changes in mass of the respective samples before and after thermochemical treatment

Sample name	Mass Before Treatment (g)	Mass After Treatment (g)	Change in Mass (g)	Change in Mass (%)
EF1.2 (en-ex)	131.29	128.52	2.77	2.11
EF1.3 (ex-en)	137.95	137.26	0.69	0.50
J2 (en-ex)	98.96	97.71	1.25	1.26
J1 (ex-en)	74.14	73.32	0.82	1.11

From the observation of results in **Table 6** above, and **Figure 30** below that shows the trend of TOC data across the 3 samples, it might indicate that the endothermic-exothermic thermochemical treatment sequence is a potential method that supports the maturation of TOC, having caused a huger reduction in TOC of EF1.2 sample compared to TOC of EF1.3 sample that was exposed to exothermic-endothermic thermochemical treatment. **Figure 30** below shows variations in TOC after thermo-shock of the two sets of samples. However, despite the changes in TOC observed after treatment with thermochemicals, uncertainties such as not testing from the same spot, anisotropic nature of rocks as well as the error margins from the testing equipment could have caused this discrepancy in the presented TOC changes. The reduction in mass could also suggest the dissolution of minerals into the solution thermochemical mixtures.

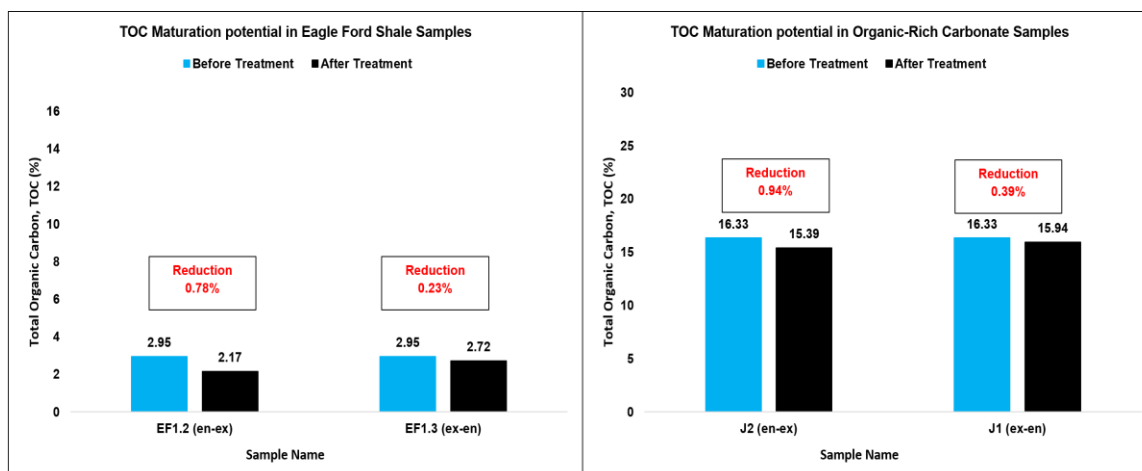


Figure 30 Bar graph plots highlighting changes in TOC before and after thermochemical treatment.

4.8 Micro CT scan Visualization of The Internal Structure of the samples

This was done in different orientations to capture the formation of micro-fractures and the fractures after breakdown test. For the EF samples, the slices from top to bottom of the sample were preferred because they clearly displayed fracture propagation from the drilled hole more than any other orientation. For the organic-rich carbonate samples, the slices from left to right of the sample were considered since the samples were highly laminated. The micro-fractures and breakdown fractures were highly expected to occur along the laminations of the sample, which couldn't be visualized clearly through the top and bottom scans

4.8.1 Before Thermochemical Treatment

The purpose of this scan was to visualize the original internal appearance of the samples before any alteration in their internal structure, and later highlight the changes after thermal shock and after breakdown. **Figure 31** below highlights the initial results from the initial scan of each sample.

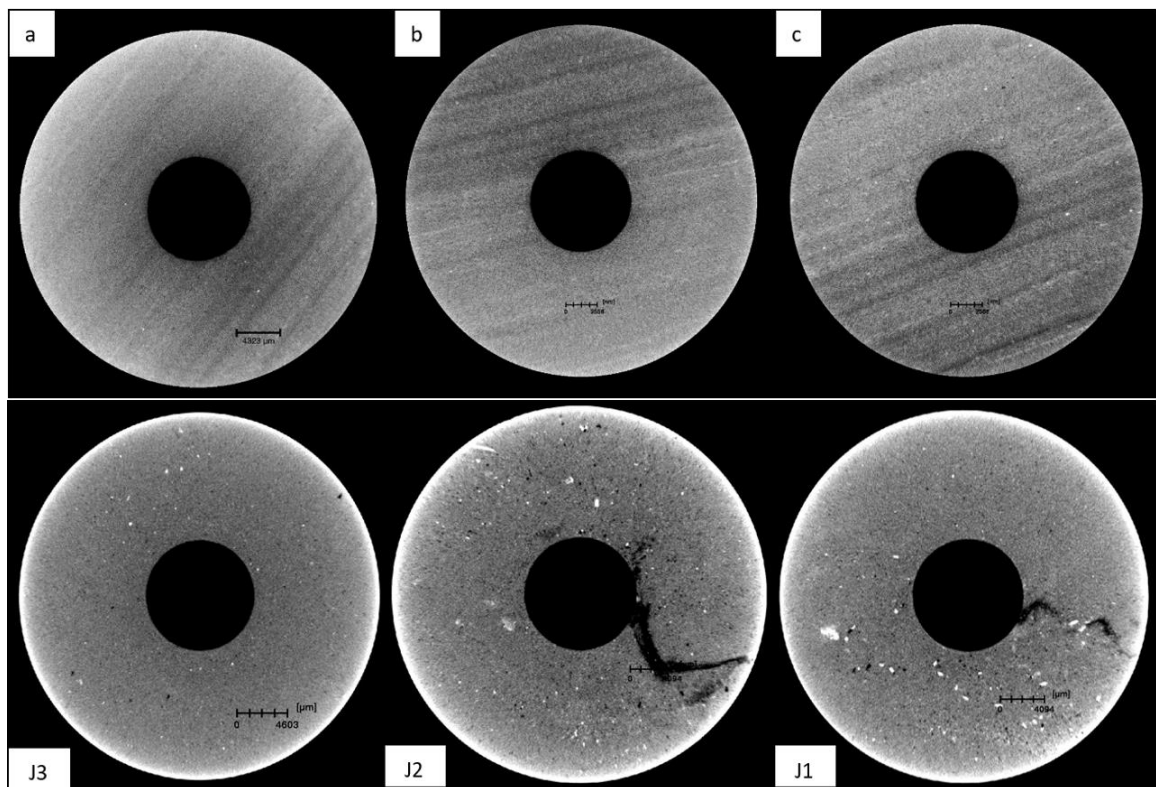


Figure 31 initial scans of (a) EF1.1 (base), (b) EF1.2 (en-ex) sample, (c) EF1.3 (ex-en), J3 (base), J2 (en-ex), and J1 (ex-en)

4.8.2 After Endothermic – Exothermic Thermochemical Treatment

A CT scan was run on the EF1.2 sample that was exposed to endothermic – exothermic thermochemical treatment to induce thermal shock. The purpose of this scan was to visualize whether microfractures had been generated due to this induced thermal shock by chemicals. **Figure 32** below compares a scan before and after thermochemical treatment of EF1.2 sample. However, microfractures were not visible due to the limitation in resolution.

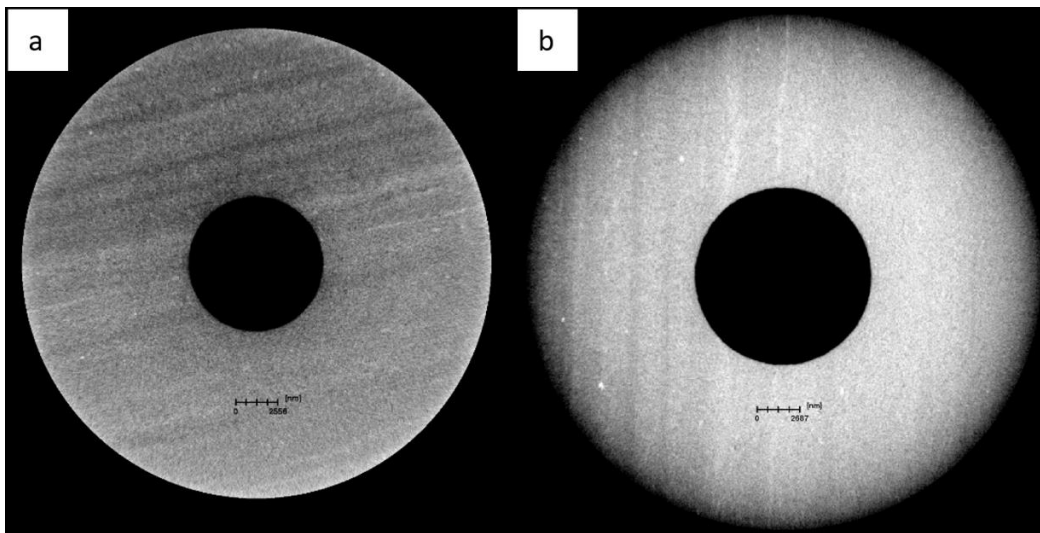


Figure 32 EF1.2 sample (a) before treatment, and (b) after treatment

4.8.3 After Exothermic – Endothermic Thermochemical Treatment

The same CT scan was run on sample EF1.3 after thermochemical treatment to analyze formation of any microfractures in the internal structure of the sample. The results were compared with the initial scan before treatment (see **Figure 33** below). However, due to the limitation in resolution of the CT scan, microfractures were not visible.

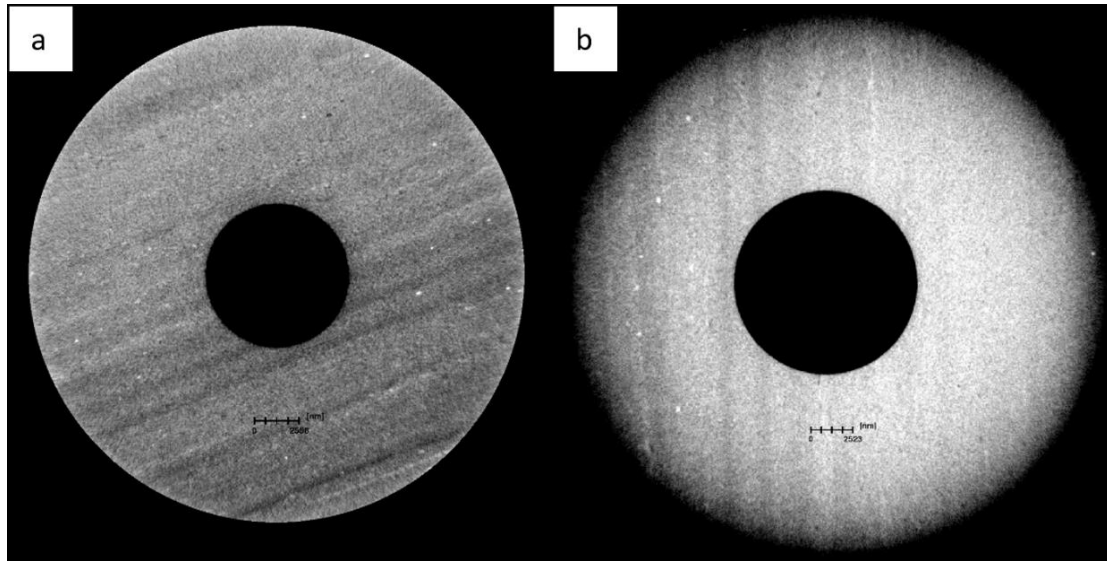


Figure 33 EF1.3 sample (a) before treatment, and (b) after treatment

4.8.4 After Breakdown Experiment

The purpose of this scan was to visualize the orientation and propagation of fractures generated when the samples were hydraulically fracked during the breakdown experiment. The EF1.1 sample was very tight because it didn't undergo thermal shock hence had no microfractures within. EF1.2 and EF1.3 samples had their breakdown pressures less than that of the EF1.1 sample because of formation of micro-fractures. The orientation from the scans shows that fractures were generated parallel to the axis of the EF samples. Organic-rich carbonate samples however, had fractures perpendicular to the axis because the samples were highly laminated. The scans targeted the borehole drilled in order to clearly visualize the microfractures as a result of thermochemical treatment. The propagation of these fractures from the drilled hole where maximum pressure was experienced to the other

parts of the samples away from it was also observed in both sets of samples. **Figure 34** below highlights a clear orientation and propagation of these fractures across the tested samples.

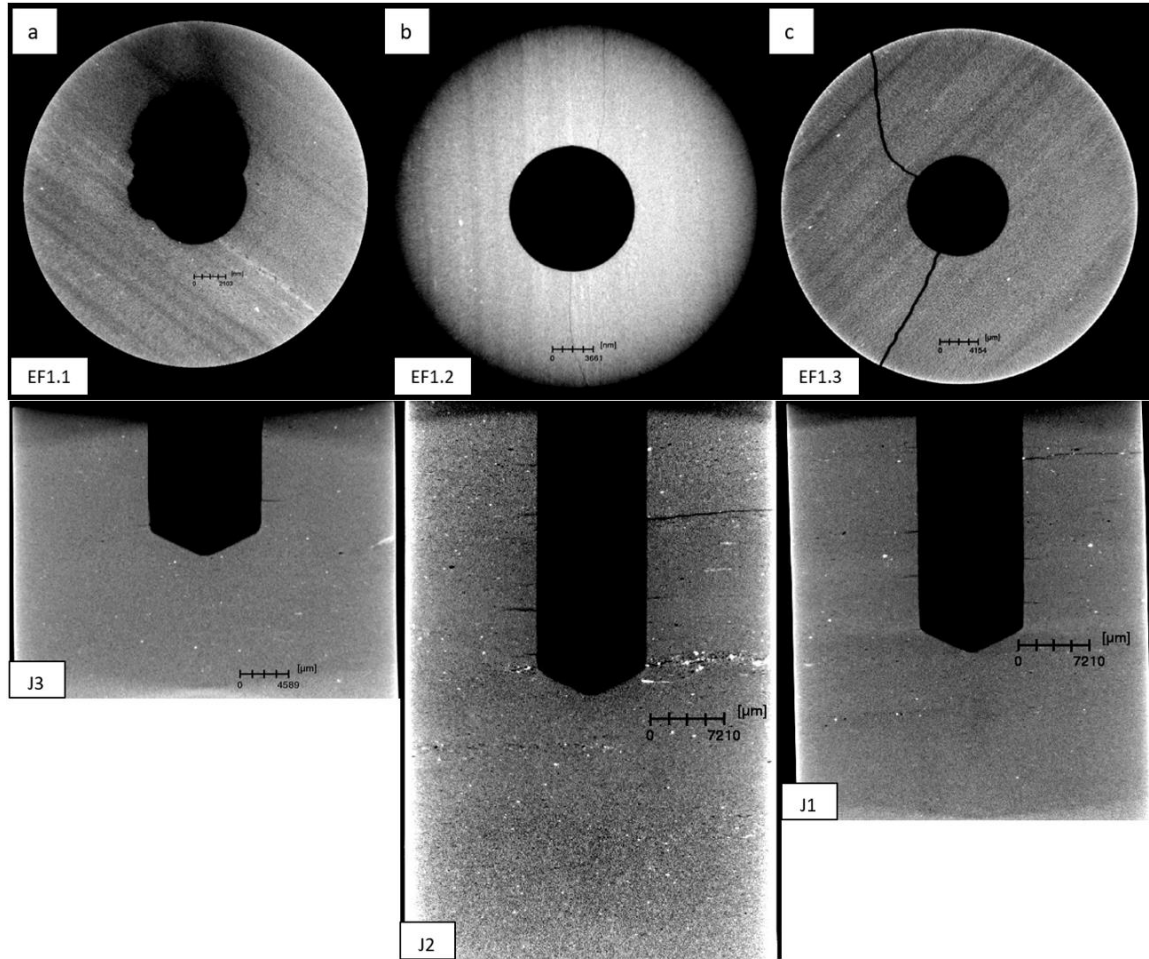


Figure 34 Breakdown scans (a) EF1.1 (base), (b) EF1.2 (en-ex), (c) EF1.3 (ex-en), J3 (base), J2 (en-ex), and J1 (ex-en)

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

- ✓ Endothermic–Exothermic cyclic treatment outperforms Exothermic–Endothermic cyclic treatment in reducing brittleness index (29.61% in Eagle Ford shale samples and 13.79% in organic-rich carbonate samples). A lower brittleness index implies that the material transitions more smoothly from elastic to plastic behavior. This provides insights into how fracture propagation might evolve under stress, which is crucial for designing fracturing strategies in unconventional reservoirs. This improved effectiveness appears linked to the initial cooling phase, which induces tensile stress and microcracking before subsequent heating. By softening the rock matrix and creating fracture pathways early in the cycle, the endothermic–exothermic sequence more efficiently reduces the stress threshold for fracture initiation, thus lowering the breakdown pressure.

- ✓ Cyclic heating and cooling with thermochemical fluids reduces Young’s modulus (29.38% in Eagle ford samples and 15.56% in organic-rich carbonate samples). Repeated thermal expansion and contraction weakens intergranular bonds, leading to microcrack formation that manifests as a lower Young’s modulus. This reduction in rock stiffness diminishes its ability to withstand external loads, making fracture

propagation less energy-intensive and thereby further decreasing the breakdown pressure.

- ✓ In formations with moderate to low organic content, thermochemical treatments appear especially beneficial. For example, in Eagle ford shale samples where TOC is low, the original breakdown pressure is high (3048.35 psi) and the amount of reduction is also high (79.28%). The controlled induction of thermal stress creates microfractures that compensate for limited natural porosity or existing fracture networks, enabling improved fluid flow pathways where conventional methods may have yielded suboptimal results.
- ✓ Breakdown pressure is strongly tied to Young's Modulus. Because Young's modulus indicates the rock's stiffness, higher moduli generally correspond to higher breakdown pressures. A stiffer rock resists fracturing until greater stress is applied. Conversely, formations with lower stiffness fail under comparatively lower pressures, emphasizing the importance of accurate mechanical property measurements.
- ✓ High organic-rich formations feature lower Young's modulus. Elevated organic content can weaken the matrix structure or introduce compliant kerogen phases. As a result, such formations often exhibit lower stiffness and reduced breakdown pressures. This insight has significant operational implications, as it points to potentially lower fracturing costs and simpler stimulation in highly organic shales.

- ✓ Rock hardness reduction through cyclic thermal stress. The heating–cooling cycles soften the rock mass by initiating microfractures at grain boundaries. Over time, these microfractures can coalesce into larger fracture networks, enhancing permeability and creating more favorable conditions for hydrocarbon release. This mechanical degradation is particularly valuable in tight formations, where natural permeability is minimal. Nevertheless, it might have negative impact from wellbore integrity perspective.
- ✓ TOC maturation assessment remains complex. While these treatments show clear mechanical benefits, determining the effect on kerogen maturation is less straightforward. More extensive geochemical and petrophysical analyses are required to quantify any changes in organic maturation levels, such as potential in-situ upgrading, before practical conclusions can be drawn about broader reservoir evolution. Additionally, the designed experiment was not intended for maturation, but testing its potential for TOC maturation was an objective for this research.

5.2 Recommendations

- ✓ Isolating the Treatment System to Minimize Pressure and Heat Losses:
Implementing an effective thermal insulation strategy during thermochemical treatments will help retain the heat generated by exothermic reactions and reduce unwanted absorption by endothermic fluids. This approach ensures that the energy

remains concentrated within the targeted zone, improving both the efficiency of the treatment and the consistency of temperature cycling.

✓ Increasing the Temperature Differential to Facilitate TOC Maturation:

A larger temperature change amplifies the stress contrasts that weaken the rock and can potentially accelerate the thermal maturation of organic matter. Adjusting reaction kinetics and volumes to achieve a broader temperature swing may enhance kerogen-to-hydrocarbon conversion, which is particularly valuable in organic-rich shales.

✓ Maintaining Elevated Temperatures for Extended Durations:

Allowing the formation to remain at higher temperatures for longer periods can promote continued thermal cracking of kerogen and sustain the maturation process of total organic carbon (TOC). This requires scheduling heat injection and soak times based on reservoir-specific geochemical data to optimize hydrocarbon generation potential.

✓ Exploring Additional Cycles of Endothermic–Exothermic Treatment:

Conducting more than three thermal cycles may further decrease the breakdown pressure and improve overall fracturing efficiency especially in very high strength formations. However, this should be balanced against potential risks to well integrity (collapse of the wellbore environment) and the cost-effectiveness of prolonged cyclic treatments. Pilot tests or numerical simulations are advised to determine an optimal number of cycles to control the thermochemical treatment and optimize it in a way without that won't cause rock failure under reservoir conditions. Additionally, tensile

strength tests for fracture pressure and COMSOL modelling for deformation study may be included.

✓ Recognizing Practical Limits to Breakdown Pressure Reduction

Although each thermochemical cycle can progressively lower the breakdown pressure, operators must maintain sufficient structural integrity within the wellbore. Exceeding safe thresholds could compromise casing or cement, leading to operational hazards. Ongoing monitoring of well integrity and stress distribution is essential to identify the point at which further reduction becomes impractical or unsafe.

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