

**FRACTURE CLEANUP USING THERMOCHEMICAL
FLUIDS (TCFs)**

BY

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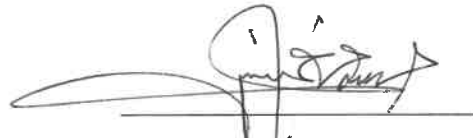
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|To my beloved parents, wife, sons, uncle, relatives and friends |

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TABLE OF CONTENTS

ACKNOWLEDGMENTS	V
TABLE OF CONTENTS.....	VI
LIST OF TABLES	XI
LIST OF FIGURES	XIII
LIST OF ABBREVIATIONS.....	XVIII
ABSTRACT.....	XIX
ملخص الرسالة.....	XXI
CHAPTER 1 INTRODUCTION	1
1.1 Problem Statement and Motivation	1
1.2 Objectives	2
1.3 Chapters Description	2
CHAPTER 2 LITERATURE REVIEW	4
2.1 Thermochemical Reaction Kinetics	4
2.2 Biopolymer Frac Fluids Gelling Agents	5
2.2.1 Guar-based Polymers.....	6
2.2.2 Cellulose-Based Polymers	8
2.2.3 Cross-linked Polymers.....	9
2.2.3.2 Metal-Crosslinked Gel Fluids.....	11
2.3 Frac Fluids Breakers.....	11

2.4	Frac Fluids Breaking by Thermochemical Fluids (TCFs): A Potential Mechanism	13
2.5	Methods of Assessing Frac Fluid Polymer Degradation	17
2.5.1	Viscosity Measurement	17
2.5.2	Molecular Weight Changes Assessment	18
2.6	Thermochemical Fluids: Reaction Control and Applications.....	20
2.7	Emulsion Breaking	21
2.8	Aqueous Phase Trapping Removal	23
2.7	Fracture Conductivity Modeling	24
CHAPTER 3		28
THERMALLY ACTIVATED NITROGEN/HEAT GENERATING REACTION: A KINETIC STUDY		28
3.1	Introduction	28
3.2.	Experimental Work	30
3.3	Experimental Setups	32
3.4	Experimental Design	34
3.5	Results & Discussion.....	35
3.5.1	Effect of Reactants Concentration and Temperature	35
3.5.2	Effect of pH.....	38
3.5.3	Effect of Salinity	39
3.4.	Kinetic Study.....	41
3.6	Conclusions	47
CHAPTER 4		50

ADVANCING SUSTAINABILITY THROUGH EMULSIFICATION OF THERMOCHEMICAL FLUIDS: EXPLORING EMULSION CHARACTERISTICS AND RHEOLOGICAL PROPERTIES	50
4.1 Introduction	51
4.2 EXPERIMENTAL Work.....	55
4.2.1 Materials	55
4.2.2 Equipment and Methodology.....	56
4.3 Results and Discussion	59
4.3.1 Characterization of Emulsifier Systems.....	59
4.3.1.4 Effect of Emulsifier Concentration.....	68
4.3.2 Models for Emulsion Viscosity	71
4.3.3 Effect of TCFs Volume Fraction	75
4.3.4 Emulsification of Mixed TCFs in Diesel	78
4.4 Discussion	85
4.5 Conclusions	87
CHAPTER 5	88
EMULSIFICATION AND PH CONTROL FOR SUSTAINABLE THERMOCHEMICAL FLUIDS REACTIVITY	88
Abstract.....	88
5.1 Introduction	89
5.2 Experimental Work	92
5.2.1 Materials	92
5.2.2 Equipment and Methodology	93
5.2.3 Preparation of Emulsions.....	94
5.2.4 pH Measurement.....	94

5.2.5 Autoclave Testing.....	95
5.3 Results and Discussion	95
5.3.1 Reactivity of Emulsified TCFs in Diesel.....	95
5.3.2 Reactivity of Emulsified TCFs Versus Neat TCFs.....	96
5.3.3 Effect of Emulsifier Type.....	98
5.3.4 Effect of Concentration, Temperature, Volume Fraction and Agitation	100
5.3.5 Effect of Emulsifier Concentration.....	100
5.3.6 Effect of Temperature	102
5.3.7 Effect of TCFs Volume Fraction.....	103
5.3.8 Effect of Emulsification Method and Agitation	104
5.3.9 Impact of pH an Initial Pressure on the Reactivity of Neat TCFs	105
5.4 Discussion.....	107
5.6 Conclusions.....	109
CHAPTER 6	111
INVESTIGATIONS OF THERMOCHEMICAL FLUIDS POTENTIAL FOR CLEANUP OF POLYMER-BASED FRACTURING FLUIDS.....	111
6.1 Introduction.....	112
6.1.1 Guar Gum Derivatives As Frac Fluids Thickening Polymers	112
6.1.2 Fracturing Fluid Breakers.....	114
6.1.3 Degradation of Fracturing fluid Polymers.....	115
6.2 Methodology and Equipment.....	116
6.2.1 Materials	116
6.2.2 Autoclave	117
6.2.3 HTHP Filter Press	117
6.2.4 Thermal Gravimetric Analysis	117

6.2.5 Viscosity Measurement	118
6.2.5 Thermal Shock Test.....	118
6.2.6 Thermal Degradation of Fracturing Fluids	118
6.2.6 Coreflooding Experiments.....	119
6.3 Results and Discussion	120
6.3.1 Characterization of Guar Gum-Based Polymers.....	120
6.3.2 Heating Properties of Thermochemical Fluids	124
6.3.3 Viscosity of Fracturing Fluids	126
6.3.4 Polymer Degradation Potential by Thermochemical Fluids	130
6.3.5 Coreflood Experiments: Assessing TCFs as Cleanup Fluid	132
6.4 Discussion.....	138
6.5 Conclusions	140
REFERENCES	141
VITAE.....	157

LIST OF TABLES

Table 2.1	Some guar gum derivatives [17]	7
Table 2.2	Breakers and the fracturing fluids they degrade [23] (Al-Muntasheri et al., 2018)	9
Table 2.3	Properties of common crosslinkers [30](Economides and Nolte, 2000)	11
Table 3.1	A summary of the experimental plan.....	35
Table 3.2	Composition of formation water (F.W)	40
Table 3.3	Initial reaction rates of NaNO_2 and NH_4Cl at different concentrations and at 90°C	41
Table 3.4	pH value of different NaNO_2 and NH_4Cl solutions at ambient temperature before testing.....	42
Table 3.5	pH Values of ammonium chloride solutions measured at ambient temperature and at 50°C	43
Table 4.1	Classification and characteristics of emulsions	53
Table 4.2	Composition of the emulsifiers used in this study	56
Table 4.3	pH values of 1 vol% of emulsifier in deionized water and 4M of each TCF . 60	
Table 4.4	Conductivity of diesel, emulsifiers and 4M NH_4Cl and 4M NaNO_2	60
Table 4.5	Zeta potential and pH values of emulsifiers at 1 vol% in bentonite suspension systems.....	61
Table 4.6	Conductivity of Individual 70% emulsified 4M TCFs in Diesel with 1% emulsifier	64
Table 4.7	Power-law parameters for 70% emulsified 4M NH_4Cl in diesel with 1% surfactant.....	73
Table 4.8	Power-law parameters for 70% emulsified 4M NaNO_2 in diesel with 1% surfactant.....	73
Table 4.9	Power-law parameters for 70% emulsified 4M NH_4Cl in diesel with 5% surfactant.....	75
Table 4.10	Power-law parameters for 70% emulsified 4M NaNO_2 in diesel with 5% surfactant.....	75

Table 5.1	Composition, ionic properties and pH values of the emulsifiers used in this study	93
Table 5.2	Effect of pH and initial pressure on the reaction triggering temperature, and generated pressure	109
Table 6.1	A summary of coreflood experiments conducted for different fracturing fluid systems	120
Table 6.2	HPG borate-crosslinked fracuring fluid.....	127
Table 6.3	CMHPG dual (borate/zirconate) crosslinked fracuring fluid	128
Table 6.4	Slick water fracturing fluid	128

LIST OF FIGURES

Figure 2.1	Guar chemical structure [16].	6
Figure 2.2	Structure of hydroxypropyl guar gum [20]	7
Figure 2.3	HEC and CMHEC's chemical structures [21].	8
Figure 2.4	Borate-crosslinked guar the bond of ether is potential to enzyme breakage (-R represents an additional guar compound), [27].	10
Figure 2.5	Decomposition of persulfate in aqueous solution [32].	12
Figure 2.6	Potential sites for sulfate free-radical attach in guar-based polymers [33]	13
Figure 2.7	Effect of temperature on breaker release [2]	16
Figure 2.8	Pressure effect on breaker release [2].	16
Figure 2.9	Impact of temperature on HPG's adsorption capacity at condition of pH: 8.5 and HPG concentration of 3500 ppm [20]	17
Figure 2.10	Illustration of GPC, molecule A size > molecule B size, and molecule B PDI > molecule A PDI [49].	20
Figure 3.1	Methodology used to determine (a) initial reaction rate (b) average reaction rate	32
Figure 3.2	Water displacement setup.	33
Figure 3.3	Closed system setup.	34
Figure 3.4	Effect of concentration on (a) evolved nitrogen gas, (b) generated pressure	36
Figure 3.5	Effect of temperature on (a) evolved nitrogen gas, (b) generated pressure...	36
Figure 3.6	Effect on initial reaction rate: (a) concentration; (b) temperature	37
Figure 3.7	Effect on average reaction rate: (a) concentration; (b) temperature	38
Figure 3.8	Pressure generated and reaction rate of 4M NaNO ₂ + 4M NH ₄ Cl at 90°C as a function of time	38
Figure 3.9	Effect of pH on (a) generated pressure, (b) initial reaction rates of 4M/4M solutions at 90°C in the closed system	39

Figure 3.10	Effect of salinity (D.I, 5, 10 and 20% F.W) on the reactivity of nitrogen/heat generating system.....	40
Figure 3.11	Effect of excess concentration of NaNO_2 versus excess concentration of NH_4Cl on the reaction rate	42
Figure 3.12	pH Values of ammonium chloride solutions measured at ambient temperature and at 50°C	43
Figure 3.13	Linear relation graph of $\ln t-1/T$	45
Figure 3.14	Linear relation graph of $\ln K-1/T$	46
Figure 3.15	Linear relation graph of $\lg t-\lg C_o$	47
Figure 4.1	A chart including the experimental design.....	57
Figure 4.2	Impact of emulsifier (1 vol%) on (a) surface tension of DI water and diesel, and (b) IFT between diesel and TCFs.....	62
Figure 4.3	Drop tests in water for TCFs/diesel emissions.	64
Figure 4.4	Viscosity of 70% emulsified NH_4Cl and NaNO_2 in diesel with 1% emulsifier	66
Figure 4.5	Optical microscopy of 70% emulsified NH_4Cl and NaNO_2 in diesel with 1% emulsifier	66
Figure 4.6	Droplet size distributions of 70% emulsified NH_4Cl and NaNO_2 in diesel with 1% emulsifier	67
Figure 4.7	Polydispersity index of 4M NH_4Cl and 4M NaNO_2 in diesel emulsion with 1% emulsifier	68
Figure 4.8	Viscosity of 70% emulsified NH_4Cl and NaNO_2 in diesel with 5% emulsifier	69
Figure 4.9	Optical microscopy of 70% emulsified 4M TCFs in diesel with 5% emulsifier	70
Figure 4.10	Droplet size distribution of 70% emulsified NH_4Cl and NaNO_2 in diesel with 5% emulsifier	70
Figure 4.11	Photos of individual emulsified 70% 4M TCFs in diesel with 5% emulsifier after viscosity measurement cycles at temperatures of 25 to 90°C	71
Figure 4.12	Polydispersity index of 70% 4M NH_4Cl and 4M NaNO_2 in diesel with 5% emulsifier.....	71

Figure 4.13	Shear stress versus shear rate for individual emulsion of 4M NH_4Cl and 4M NaNO_2 in diesel with 1% emulsifier	72
Figure 4.14	Shear stress versus shear rate for individual emulsion of 4M NH_4Cl and 4M NaNO_2 in diesel with 5% emulsifier	74
Figure 4.15	Viscosity of emulsified 50% and 70% NH_4Cl and NaNO_2 in diesel with Emulsifier-A at a concentration of 1%	76
Figure 4.16	Photos of individual emulsified 50% TCFs in diesel with 1% Emulsifier-A after viscosity measurement cycles of 25 to 90°C	77
Figure 4.17	Particle size distributions of 50% individual emulsified 4M NH_4Cl and 4M NaNO_2 in diesel with Emulsifier-A	77
Figure 4.18	Potential destabilization mechanism of 4M NaNO_2 in diesel with 1% Emulsifier-B	86
Figure 5.1	A schematic representation of the experimental work performed in this study	94
Figure 5.2	Effect of emulsification on the heat generated from the reaction of 70% individual emulsified 4M TCFs compared to neat 4M TCFs at 95°C.	96
Figure 5.3	Reactivity of (a) 4M neat TCFs versus (b) 70% individual emulsified 4M TCFs at 95°C with emulsifier-A	98
Figure 5.4	Reactivity of 4M neat TCFs and 70% individual emulsified 4M TCFs in diesel with different emulsifiers at (1%) and 95°C (a) pressure and (b) normalized reactivity	99
Figure 5.5	Reactivity of 70% individual emulsified 4M TCFs in diesel with different emulsifiers at (5%) and 75°C, (a) pressure and (b) normalized reactivity and reaction rate	99
Figure 5.6	Photos of different emulsion systems with 5% of emulsifiers following autoclave testing at 75°C	100
Figure 5.7	Generated pressure from emulsified 4M TCFs in diesel as a function of: (a) time and (b) Emulsifier-A concentration	101
Figure 5.8	Effect of Emulsifier-A concentration on the reactivity of 4M TCFs emulsified in diesel at 95°C	101

Figure 5.9	Effect of temperature on the reactivity of 70% Emulsified 4M TCFs in diesel with Emulsifier-A at (a) 1, (b) 3 and (c) 5 vol%, (d) reduction in reactivity	102
Figure 5.10	Effect of temperature on the reactivity of 70% 4M TCFs emulsified in diesel with Emulsifier-A at 1 vol%, (a) pressure and (b) normalized reactivity.....	103
Figure 5.11	Effect of volume fraction on the reactivity of emulsified 4M TCFs in diesel with 1% Emulsifier-A at 75°C	104
Figure 5.12	Effect of the emulsification method on the reactivity of 4M TCFs in diesel with 1 vol% Emulsifier-A at 95°C (a) individual versus mixed emulsification, (b) reduction in reactivity and (c) individual emulsified followed with mixing versus mixed emulsified system.....	105
Figure 5.13	(a)Effect of pH on generated pressure by 5M TCFs and (b) relationship between TCFs pH values and maximum pressure	106
Figure 5.14	(a) Effect of pH on generated heat by 5M TCFs and (b) relationship between TCFs pH values and maximum temperature.....	107
Figure 5.15	(a) Effect of initial pressure on delay time of 5M TCFs reaction and (b) relationship between initial pressure and time to trigger TCFs reaction ...	107
Figure 6.1	Chemical structures of guar gum (GG), hydroxypropyl guar gum (HPG), carboxymethyl guar gum (CMG) and carboxymethyl hydroxypropyl guar gum (CMHPG) polymers.....	113
Figure 6.2	Thermal degradation of guar-based and slick water fracturing fluids.....	119
Figure 6.3	FTIR spectrum of guar gum	121
Figure 6.4	FTIR spectrum of hydroxypropyl guar (HPG).....	122
Figure 6.5	FTIR spectrum of carboxymethyl hydroxypropyl guar (CMHPG).....	122
Figure 6.6	Thermal gravimetric analysis of guar gum and its derivatives.....	123
Figure 6.7	Effect of TCFs concentration on generated heat (a) generated temperature versus time and (b) relationship between TCFs concentration and generated maximum temperature	125
Figure 6.8	Effect of TCFs volume on generated heat at 90°C	125

Figure 6.9	Effect of pH on heat generated (a) generated temperature versus time and (b) relationship between TCFs pH values and maximum temperature	126
Figure 6.10	Viscosity of 40 lb HPG borate-crosslinked at 270°F.....	129
Figure 6.11	Viscosity of 40 lb CMHPG with combined borate and zirconate crosslinker at 320°F	129
Figure 6.12	Viscosity of 6lb slick water at 270°F.....	130
Figure 6.13	FTIR spectra of 40lb/1,000 gal linear gel polymers before and after thermal treatment at 500°F (a) GG, (b) HPG and (c) CMHPG.....	131
Figure 6.14	TGA before and after thermal treatment at 500°F for one hour of for linear gel polymers (a) GG, (b) HPG and (c) CMHPG.....	132
Figure 6.15	Thermal sock impact on viscosity of linear gels: (a) GG, (b) HPG, (c) CMHPG and(d) HVFR)	133
Figure 6.16	TGA of ammonium persulfate live and encapsulated breaker	134
Figure 6.17	Coreflood experiment for thermal treated (350°F) HPG-Borate crosslinked polymer	135
Figure 6.18	Coreflood experiment on CMHPG with dual crosslinker thermally treated at 450 and 500°F.	137
Figure 6.19	Coreflood experiments for slick water (a) with breaker and (b) thermally treated slick water	138
Figure 6.20	Pressure generated from the reaction of equimolar (5M) NH_4Cl and NaNO_2 as a function of pH values.....	139

LIST OF ABBREVIATIONS

C_o	: The Equimolar Concentration of NaNO_2 and NH_4Cl in M
C_H^+	: The Concentration of Acid in M
CMC	: carboxymethylcellulose
CGG	: Crude Guar Gum
CMHPG	: Carboxymethyl hydroxypropyl
CMHEC	: CarboxyMethylHydroxyEthylCellulose
K_d	: Dissociation Constant
DSC	: Differential Scanning Calorimetry
DLS	: Dynamic Light Scattering
DSA	: Drop Shape Analyzer
dc/dt	: The Reaction Rate
FTIR	: Fourier Transform Infrared Spectroscopy
HEC	: HydroxyEthylCellulose
HPG	: Hydroxypropyl Guar
GG	: Guar Gum
GPC	: Gel Permeation Chromatography
K	: The Reaction Kinetic
LBG	: Locust Bean Gum
PAM	: Polyacrylamide
PAM-PAANA	: Poly(Acrylamide-co-Acrylate)
TGA	: Thermal Gravimetric Analysis
TCFs	: Thermochemical Fluids
R	: The Ideal Gas Constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
RPPG	: Re-Cross-Linkable Preformed Particle Gel
ST	: Surface Tension (mN/m)
IFT	: Interfacial Tension (mN/m)
ISO	: International Organization for Standardization
NO_x	: Nitrogen Oxides

ABSTRACT

Full Name : Ali Abdullah Al-Taq

Thesis Title : Fracture Cleanup using Thermochemical Fluids (TCFs)

Major Field : Petroleum Engineering

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The Ph.D dissertation research investigates the potential application of thermochemical fluids (TCFs) in the forms sodium nitrite and ammonium chloride salts as fracture cleanup agents. The study is divided into four phases. The first phase studies, for the first time, the reaction kinetic of the TCFs activated thermally, while the second phase explores the emulsification of TCFs in diesel to form water-in-oil emulsions. In the third phase, we examine how emulsification and pH adjustments impact the control of TCFs reactivity, while the final phase explores the application of TCFs in cleaning up polymer-based fracturing fluids.

Sodium nitrite and ammonium chloride are key thermochemical salts in oil and gas. Research on their kinetics when activated with acids or heat is extensive. Heat activation is seen as a promising means of controlling this highly spontaneous reaction. A kinetic study was conducted on their reaction at 1–5 M and 50–90 °C, in closed and open systems, monitoring gas evolution and pressure. Ammonium chloride exhibited a higher order than sodium nitrite, with excess NH_4Cl enhancing the reaction due to its catalytic effects. The obtained kinetics ($dc/dt = -7.66 \times 10^{11} C_o^{2.45} e^{(-91.44 \text{ kJ/mol})/RT}$) differed from literature, impacting practical reactivity control and nitrogen generation optimization in the oil and gas industry.

Emulsification plays a crucial role in controlling reactivity in chemicals like NH_4Cl and NaNO_2 , with applications spanning diverse industries such as petroleum. TCFs' excessive reactivity limits applications, impacting success rates, but recent recommendations propose

their use for foamed fracturing fluids. This study examined three emulsifiers (A, B, C) for NH_4Cl and NaNO_2 solutions independently or as a composite in diesel. Results showed successful WO emulsions, with Emulsifier-A proving most effective, enhancing thermal stability. Emulsifiers B and C tended to activate TCF reactions due to low pH, but pH adjustment improved emulsion characteristics, showcasing potential for sustainability.

Managing chemical reactivity is vital for sustainable industry, reducing waste and energy consumption while protecting the environment. Emulsification is a key method for controlling reactivity, especially for highly reactive chemicals like NH_4Cl and NaNO_2 in industries like oil and gas. This study investigates emulsification techniques to mitigate TCFs' excessive reactivity, exploring different concentrations and emulsifier types in diesel. The research also examines pH adjustment as an alternative method to control TCFs' reactivity, considering factors like temperature and pressure. Results show potential for both emulsification and pH adjustment to enhance sustainability by optimizing TCFs' reactions in various applications, aiding in efficiency and success rates.

The study explores the use of TCFs as cleanup agents, aiming not only to degrade polymers and reduce viscosity but also to remove trapped water, a significant damage mechanism in low permeability shale formations post-fracturing. NH_4Cl and NaNO_2 were investigated for their reactions and substantial heat generation. Thermal degradation of guar gum polymer derivatives (HPG and CMHPG) was assessed using FTIR, TGA, viscosity measurements, and coreflood experiments. Results showed altered chemical and thermal properties in thermally treated polymers. Coreflood results indicated permeability regain of 87% for HPG borate-crosslinked, 96% for CMHPG dual crosslinked, and 90% for slickwater fracturing fluids. Thermally treated slickwater outperformed slickwater with a ammonium persulfate breaker in permeability regain.

ملخص الرسالة

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تاريخ الدرجة العلمية: ديسمبر 2003

هذا البحث الخاص برسالة الدكتوراه يستكشف التطبيق المحتمل للسوائل الحرارية الكيميائية (TCFs) في أشكال أملاح كلوريد الأمونيوم و نترات الصوديوم كوكلاء لتنظيف الكسور. الدراسة مقسمة إلى أربع مراحل. المرحلة الأولى تدرس، للمرة الأولى، حركية التفاعل لـ TCFs المنشطة حراريًا، بينما تستكشف المرحلة الثانية عملية تشكيل TCFs في الديزل لتكوين علاقات مائية في زيت. في المرحلة الثالثة، نقوم بدراسة كيفية تأثير عملية التشكيل وضبط درجة الحموضة على التحكم في نشاط TCFs، بينما تستكشف المرحلة النهائية تطبيق TCFs في تنظيف السوائل المكونة من البوليمر بعد عمليات الكسر.

نترات الصوديوم وكلوريد الأمونيوم هما أملاح حرارية كيميائية رئيسيتان تستخدم في صناعة النفط والغاز. البحث حول حركيتهم عند التنشيط بواسطة الأحماض أو الحرارة موسع. التنشيط بواسطة الحرارة يُعتبر وسيلة واعدة للتحكم في هذا التفاعل القوي والمتسارع. أجريت دراسة حركية على تفاعلهم عند تراكيز 1-5 M ودرجات حرارة تتراوح بين 50 و 90 درجة مئوية، في أنظمة مغلقة ومفتوحة، مع مراقبة تطور الغاز والضغط الناتج. أظهر كلوريد الأمونيوم ترتيبًا أعلى من نترات الصوديوم، حيث زادت تركيزات NH_4Cl الفائضة عن التفاعل بفعل تأثيرها التحفيزي. التفاعلات الناتجة والتي تمثلت في $(dc/dt = -7.66 \times 10^{11} C_o^{2.45} e^{(-91.44 \text{ kJ/mol})/RT})$ اختلفت عن المراجع، مما أثر على التحكم العملي في النشاط الكيميائي وتحسين إنتاج النيتروجين في صناعة النفط والغاز.

الاستحلاب أمر حيوي للتحكم في التفاعل الكيميائي في مواد مثل NH_4Cl و NaNO_2 ، مما يعتبر أمرًا حاسمًا في صناعات متنوعة مثل البترول. التفاعل الزائد لـ TCFs يحد من التطبيقات، مما يؤثر في نسب النجاح، ولكن التوصيات الحديثة تقترح استخدامها لسوائل الكسر الرغوية. استكشفت هذه الدراسة ثلاثة مثبتي الاستحلاب (A و B و C) للمحاليل المستقلة لـ NH_4Cl و NaNO_2 أو كخليط مركب في الديزل. أظهرت النتائج تكوين نجاح للمستحلابات المائية في الديزل، مع فاعلية Emulsifier

A الأكبر، وزيادة الاستقرار الحراري. أما Emulsifier-B و C، فكانتا تميلان إلى تفعيل التفاعلات TCF بسبب درجة الاس الهيدروجيني المنخفضة، ولكن ضبط درجة الحموضة قاد إلى تحسين خصائص الاستحلاب، مما يظهر إمكانية الاستدامة.

إدارة النشاط الكيميائي أمر حيوي لتحقيق صناعة مستدامة، مع تقليل الفاقد واستهلاك الطاقة وحماية البيئة. الاستحلاب هو وسيلة رئيسية للتحكم في التفاعل الكيميائي، خاصة بالنسبة للمواد عالية النشاط مثل NH_4Cl و NaNO_2 في صناعات مثل النفط والغاز. تستكشف هذه الدراسة تقنيات التشكيل للحد من النشاط الزائد لـ TCFs، مع استكشاف تراكيز وأنواع مثبتات مختلفة في الديزل. تفحص البحث أيضًا ضبط درجة الحموضة كوسيلة بديلة للتحكم في نشاط TCFs، مع النظر في عوامل مثل درجة الحرارة والضغط. تظهر النتائج إمكانية تحسين الاستدامة من خلال التشكيل وضبط درجة الحموضة عن طريق تحسين تفاعلات TCFs في تطبيقات متنوعة، مما يساعد في زيادة الكفاءة ونسب النجاح.

تستكشف الدراسة استخدام TCFs كمعامل لتنظيف الشرخ الصخري، بهدف ليس فقط تحليل البوليمرات وتقليل لزوجة السائل ولكن أيضًا إزالة المياه المحبوسة، وهي آلية تلحق أضرارًا كبيرة في تكوينات الصخور ذات النفاذية المنخفضة بعد عمليات الكسر. تمت دراسة NaNO_2 و NH_4Cl لتفاعلاتهم وتوليد حرارة كبيرة. تم تقييم تحليل البوليمرات المشتقة من بوليمر القوار (HPG و CMHPG) حيث تم استخدام التحليل الطيفي بالأشعة تحت الحمراء (FTIR)، وتحليل الوزن الحراري (TGA)، وقياسات اللزوجة، وتجارب التدفق الأساسي. أظهرت النتائج تغيرات في الخصائص الكيميائية والحرارية للبوليمرات بعد المعالجة الحرارية. أشارت نتائج التدفق الأساسي إلى استعادة النفاذية بنسبة 87% بالنسبة لبوليمر HPG المتصل بالبورات، و96% بالنسبة لبوليمر CMHPG المتصل بالبورات والزيروونات، و90% لسوائل الكسر بالماء الخفيف. أدت المعالجة الحرارية لسوائل الكسر بالماء الخفيف إلى تحسين أداء استعادة النفاذية مقارنة بسوائل الكسر بوجود مفتت البوليمر.

CHAPTER 1

INTRODUCTION

The primary function of hydraulic fracturing is to enhance the extraction of oil and natural gas from underground reservoirs. The key functions of hydraulic fracturing treatments include reservoir stimulation, enhanced oil and gas recovery, improved well productivity, unlocking tight formations, horizontal well development, and economic viability. To have effective hydraulic treatments and achieve all potential goals of these treatments, an effective cleanup stage should be carried out following the fracturing treatments,

1.1 Problem Statement and Motivation

The cleanup process is key in the success and outcome of fracturing treatments. Severe matrix-fracture damage can go as high as 99% for injection wells and 40–70% for production well [1]. The cleanup using oxidizers is considered the most common and successful method. The proper timing of gel breakdown is crucial when using oxidizing gel breakers; premature polymer oxidation can cause proppant settling, and a delay between fracturing and activating the gel breaker may lead to additional filter cake deposition on fracture faces, making breakdown challenging [1]. Breakers, such as acids, oxidizers, and enzymes, contribute to fracture cleanup solely through the degradation of frac fluid polymers.

The cleanup using thermochemical fluids (TCFs) is a promising technology due to several inherited advantages of this system. First, the generated heat is expected to degrade frac fluid polymers and reduce frac fluid viscosity. In addition, the generated heat will enhance and ensure the complete release of encapsulated breakers [2]. Moreover, the generated gas from the thermochemical fluids will reduce the hydrostatic pressure, allowing better well

cleanup. The reduction in hydrostatic pressure will enhance gas flux and thus provide better cleanup [3]. The reduction in hydrostatic pressure will enhance encapsulated breakers' release and thus provide better cleanup [2]. The TCFs were reported to be able to reduce the high capillary pressure, thus enhancing the trapped water removal [4]. Based on the above, thermochemical fluids are a promising technology to be evaluated for frac fluid cleanup.

1.2 Objectives

- Investigate the potential use of thermochemical fluids (TCFS) for fracture fluid cleanup.
- Investigate the use of thermochemical fluids with conventional breakers.
- Study the reaction kinetic of the thermochemical fluids activated by heat.
- Assess the emulsification and pH adjustment on the reactivity control of TCFs.

1.3 Chapters Description

The dissertation was written in a traditional paper-based format. The first chapter has an introduction to the conducted work, including research motivation and research objectives, after briefly highlighting the research gap that we are going to cover. The second chapter presents a detailed literature review to clarify fundamental concepts and show the current stage of research in this area. The chapters 3-5 consist of journal articles that have been published or submitted, with each article presented in a separate chapter. Chapter 3 addresses the thermally activated kinetic study of a nitrogen/heat generating thermochemical reaction. In the fourth chapter, sustainability advancements are explored through the emulsification of thermochemical fluids, delving into emulsion characteristics and rheological properties. Chapter 5 explores the influence of emulsification and pH control on the reactivity of sustainable thermochemical fluids. Chapter 6, entitled 'Investigations of Thermochemical Fluids Potential for Cleanup of Polymer-Based

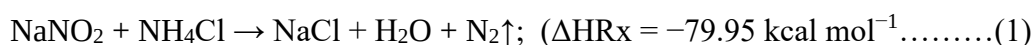
Fracturing Fluids,' explores the use of thermochemical fluids as a novel emerging cleanup technology.

CHAPTER 2

LITERATURE REVIEW

2.1 Thermochemical Reaction Kinetics

Exothermic reactions are defined as the chemical reactions associated with energy generation in terms of heat ($\Delta H < 0$). The most commonly used thermochemical in oil industry is the reaction of ammonium chloride (NH_4Cl) sodium nitrite (NaNO_2), as described below [5-7]:



This reaction is irreversible with $K_{\text{eq}} = 3.9 \times 10^7 \text{ Pa} \times \text{mole} \times \text{m}^{-3}$ at 25°C . To control this very vigorous reaction and utilize it in different applications, the reaction kinetics of NH_4Cl and NaNO_2 has been studied by several researchers as function of pH, reactants concentration, initial pressure, and temperature [5,8,9]. Contradictory findings regarding the reaction order kinetics have been reported, possibly due to variations in examined concentrations of reactants and catalysts. In agreement with Hughes et al. [10], Rubin et al. [11], and Harrison et al. [12], Nguyen et al. [5] examined reactant concentrations of 0.1 to 2.5 M and pH values of 3 to 7. They found that the reaction rate followed a first-order kinetics with respect to the concentration of ammonia and a second-order kinetics with respect to the concentration of nitrite species for all concentration ranges. Qian et al. [8] found that with the increasing reactant concentration, $\text{C}(\text{H}^+)$ and the temperature, the volume of nitrogen production increased. Based on their study, the optimal molar ratio of $\text{NaNO}_2/\text{NH}_4\text{Cl}$ was 1 : 1. The experimental kinetic equation determined of the N_2 generating process by NaNO_2 and NH_4Cl was:

$$dc/dt = -7.103 \times 10^7 C_{\text{H}}^{+1.3291} C_{\text{O}}^{2.0949} e^{(-51.28 \text{ kJ mol}^{-1})/RT}.$$

Where:

- dc/dt is the reaction rate
- C_{H}^+ is the equimolar concentration of acid in M,

- C_0 is the concentration of NaNO_2 and NH_4Cl in M,
- R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and
- T is the absolute temperature (K)

Dusenbury and Powell [14] observed the second order kinetics (first order with respect to total concentration of nitrite species) at very low concentration of total concentration of nitrite species (from 0.00243 to $0.094 \text{ mol dm}^{-3}$) and low pH (about 2.9).

Bispo et al. [9] investigated the reaction between ammonium chloride and sodium nitrite, aiming to optimize and ensure the maximum and fastest heat production with minimal side production of nitrous oxides. They determined that the optimal conditions included a concentration ratio of ammonium/nitrite equal to 1 and a catalyst concentration of $0.07 \text{ mol} \cdot \text{L}^{-1}$, with the temperature set at 5°C (seafloor level). Additionally, they observed that the gradual addition of the catalyst over time proved to be an effective strategy for reducing nitrogen oxides (NO_x).

In summary, the reaction kinetics of ammonium chloride and sodium nitrite can exhibit first-order kinetics for both reactants or first-order kinetics with respect to ammonium chloride and second order with respect to sodium nitrite, depending on the reaction conditions.

2.2 Biopolymer Frac Fluids Gelling Agents

The most common polymers used in viscosifying fracturing fluids are based on guar and cellulose polymers. Linear gel fluid is water containing a gelling agent such as guar, hydroxypropyl guar (HPG), hydroxyethyl cellulose (HEC), carboxymethyl hydroxypropyl guar (CMHPG) or carboxymethyl hydroxyethyl cellulose (CMHEC).

2.2.1 Guar-based Polymers

Guar gum and its associated products are considered the greatest material utilized as a frac gellant. The endosperm of guar beans is the source of guar, a natural polysaccharide. According to Rae and Lullo [14], guar beans are a widely grown crop in India, Pakistan, and some southern states of the United States. HPG, CMG, and CMHPG are derivatives of guar gum (Figure 2.1 and Table 2.1) are widely utilized in acid and hydraulic fracturing operations due to their adaptable chemistry, affordability, and availability [15]. Long mannose chains with pendant galactose residues make up the guar molecule, which has an average molecular weight in Daltons in the range of 200,000 to 2,000,000 [14].

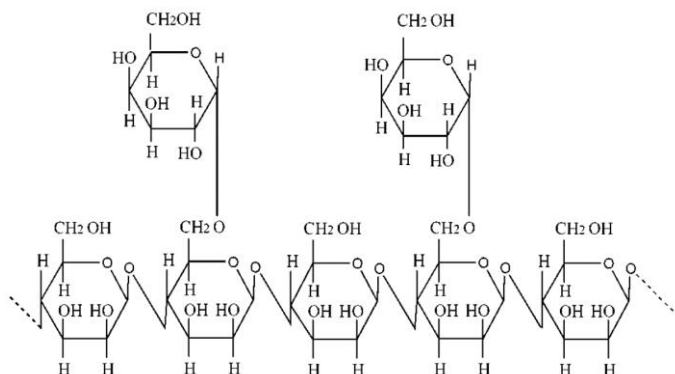


Figure 2. 1- Guar chemical structure [16].

As shown in Figure 2.1, the guar's structure consists of a linear backbone of β -1,4- linked mannose units with R-1,6-lined galactose units which are randomly attached as side chains. The mannose to galactose units ratio is 1.6:1 to 1.8:1. [16].

Table 2. 1-Some guar gum derivatives [17]

Derivative	Structure of substituent	Ionic charge
Hydroxy Propyl Guar (HPG)	$\text{CH}_2\text{-CH(OH)CH}_3$	Nonionic
Carboxy Methyl Guar (CMG)	$\text{CH}_2\text{-COO-Na}^+$	Anionic
Carboxy Methyl Hydroxy Propyl Guar (CMHPG)	$\text{CH}_2\text{-COO-Na}^+$ $\text{CH}_2\text{-CH(OH)CH}_3$	Anionic

Guar gums have an insoluble buildup of 10-14% relying upon gum virtue and technique for handling [18](Chatterji and Borchardt 1981). Guar gum tends to aggregate during the hydraulic fracturing process resulting in presence of unsuitable residue for fracturing [16](Cheng et al., 2002). Oil/gas productivity was negatively impacted by the resulting aggregates. To solve this issue, guar derivatives with low residue have been developed. In an alkaline medium, substitutes like chloroacetic acid, ethylene oxide, and propylene oxide were added to guar, resulting in the production of HEG, HPG, and CMG, respectively [16](Cheng et al., 2002). Guar derivatives are less insoluble and more soluble in water than native guar [19](Gulbis et al., 1987). The most widely used natural guar derivative, hydroxypropyl guar (HPG), has a molecular weight between 1 and 2 million, and its chemical structure is depicted in Figure 2.2 [16].

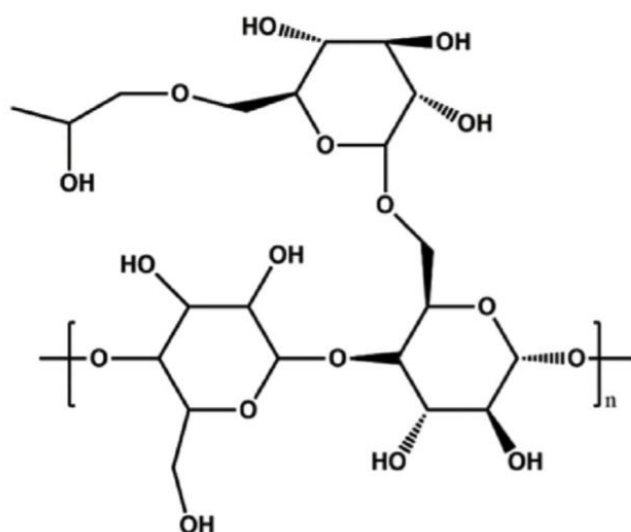


Figure 2. 2- Structure of hydroxypropyl guar gum [20]

2.2.2 Cellulose-Based Polymers

The most widely used organic compounds on Earth are polymers made of cellulose, such as HydroxyEthylCellulose (HEC) and CarboxyMethylHydroxyEthylCellulose (CMHEC), (Figure 2.3 [21]). A polysaccharide with the formula $(C_6H_{10}O_5)_n$ that makes up nearly 33% of all earth material is a cellulosan. It is a polysaccharide with a linear chain of glucose units present in several hundred to over ten thousand. When conductivity is the primary design consideration, HEC and CMHEC are utilized because they are completely solvable in water and leave a light residue. This is utilized in gravel packing and Frac/Packing applications.

Substitutes based on carboxymethylhydroxyethylcellulose (CMHEC) and carboxymethylcellulose (CMC) crosslinked with metal ions have been developed to replace guar products in harsh temperature and salinity conditions [22](Zhou et al., 2013).

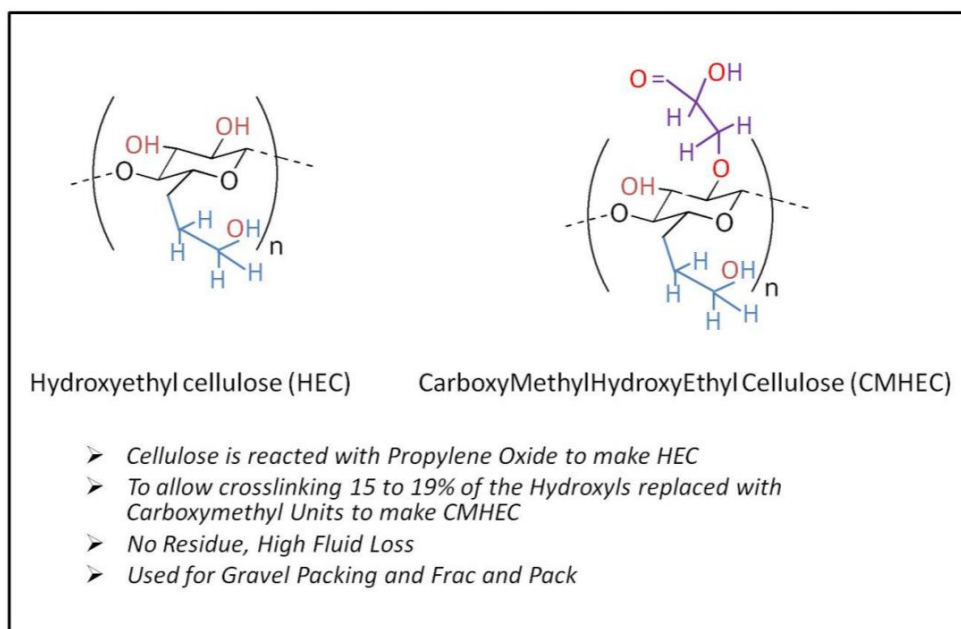


Figure 2. 3-HEC and CMHEC's chemical structures [21] (Montgomery 2013).

Table 2.2 depicts different brakers for different fracturing fluids. Acids including HCl and acetic acid, like oxidizing breakers, will attach to the spine of the polymer and ultimately

result in gel breakage, but they are much less selective and can generate a substantial quantity of residual material [23]. They are typically used to clean damaged fractures by a job in which the sufficient breaker was not used or the gel is thought not to have been broken. These fractures are thought to have been damaged. Additionally, they function by decrosslinking borate-crosslinked structures. They are typically utilized after a project is completed and placement becomes the primary concern.

Table 2. 2- Breakers and the fracturing fluids they degrade [23] (Al-Muntasheri et al., 2018)

Breakers	Fracturing-Fluid Type			
	Metal-Crosslinked Biopolymers	Borate-Crosslinked Biopolymers	Metal-Crosslinked Synthetic Polymers	Phosphate Esters (Gelled Hydrocarbons)
Oxidizers	Yes	Yes	Yes	–
Weak acids	–	Yes	–	–
Enzymes	Yes	Yes	–	–
Decrosslinking agents	Yes	–	Yes	–
Calcium and magnesium oxides	–	–	–	Yes

2.2.3 Cross-linked Polymers

Crosslinked polymer gels were developed to enhance fracture fluids' viscosity without increasing polymer concentration. The viscosity of gelled fluids is significantly increased by tens of hundreds of magnitudes when polymers are crosslinked [24]. The crosslinked polymers can be divided into two main classes: borate and metal-crosslinked gel fluids.

2.2.3.1 Borate-crosslinked Gel Fluids

In fracturing operations, the most common gels are guar that has been borate-crosslinked and HPG [23,25,26]. Hydrated polymers are crosslinked with borate ions in borate-crosslinked gel fracturing fluids, resulting in increased viscosity. A reversible crosslink is produced by altering the fluid system's pH when using borate (Figure 2.4). The crosslink/decrosslinking nature of borate fluids, according to Gandossi and Von Estorff [26], makes them easier to clean and effectively restores their permeability and

conductivity. Temperature and pH have an impact on the number and strength of crosslink bonds, which determine viscosity and proppant-carrying capacity [25]. The fluid is transported into the formation via tubing during a hydraulic fracturing treatment. The pH, the number of crosslink bonds, and the fluid's viscosity will all be affected by the subsequent rise in temperature, which will disrupt the chemical equilibrium. At around the pH worth of 8.2, borate particles will frame a 3-layered network with the cis-hydroxyl locales in the polymer, in this way further expanding the thickness of breaking liquids and the ideal pH worth of 10.5 was found [24].

The most widely used crosslinker today is borate forms including organic borate compounds, boric acid, and Ca and Mg salts with slow solubilities.

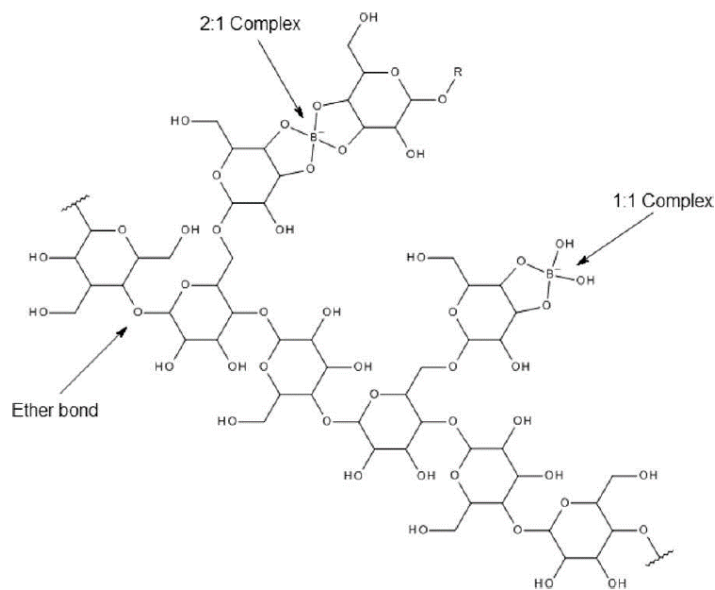


Figure 2.4- Borate-crosslinked guar the bond of ether is potential to enzyme breakage (-R represents an additional guar compound), [27]

2.2.3.2 Metal-Crosslinked Gel Fluids

Metal-based crosslinking specialists used to upgrade polymer gel thickness were executed in hot downhole in the mid-1970s [28]. Crosslinking with metal ions like Ti^{4+} , Zr^{4+} , and Al^{3+} occurs in water-soluble polymers. For the side chains of guar (galactose), crosslinking occurs through cis-OH pairs [29]. Table 2.3 compares the descriptions of these crosslinkers [30]. Zirconium acetate, titanium triethanolamine, or zirconium ammonium lactate are examples of organic ligands or chelators that make up the majority of metal crosslinkers [14]. Harris et al. [31] discovered that metal-crosslinked fracturing fluids outperformed borate-crosslinked fluids in terms of proppant transport. However, the proppant transport properties of both fluids were superior to those of non-crosslinked fluids.

Metal crosslinkers can be effective and stable at low fluid pH levels comparatively with borate crosslinkers, [28]. Low solution pH also minimizes scaling potential, making it suitable for the production of CO₂-energized water-based fracturing fluids. Low fluid pH has advantages as well. However, metal crosslinked fluids are shear sensitive and can be damaged when pumped at high injection rates. In metal crosslinked fluids, delay crosslinking additives could be used to reduce the risk of shear damage.

Table 2. 3- Properties of common crosslinkers [30](Economides and Nolte, 2000)

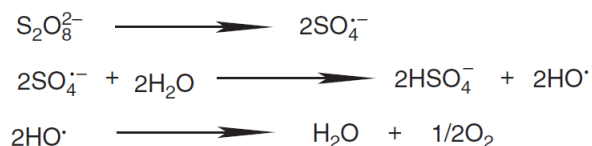
Crosslinker Crosslinkable polymers	Borate Guar, HPG, CMHPG	Titanate Guar, HPG, CMHPG, CMHEC	Zirconate Guar, HPG, CMHPG, CMHEC	Aluminum CMHPG, CMHEC
pH Range	8-12	3-11	3-11	3-5
Upper Temperature (°F)	325	325	400	150
Shear Degraded	No	Yes	Yes	Yes

2.3 Frac Fluids Breakers

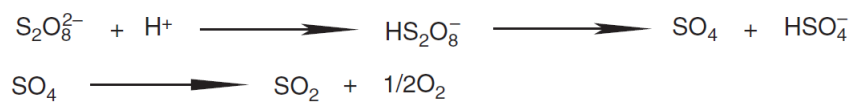
Fracture fluids cleanup is a critical stage that contributes to the success of the fracturing operations. The cleanup stage involves the breaking of the frac fluids and following back the well. Breakers include acids, oxidizers, and enzymes that are typically used to break

the backbone of polymers and thus reduce fluids' viscosity and make them easy to clean. Different oxidizers and enzymes have been studied in the lab and implemented successfully in the field as fracture fluids breakers. Oxidizers include persulfates, peroxides, bromate, and chlorites. Persulfates may present as sodium persulfate, ammonium persulfate, and potassium persulfate. Persulfate salts dissociate in water to form an anion ($\text{S}_2\text{O}_8^{2-}$) and this anion generates sulfate-free radicals that react with the polymers [23]. The mechanisms of persulfate dissociation in water as a function of pH were proposed by Kolthoff and Miller [32].

(a) Uncatalyzed reaction



(b) Hydrogen-ion catalyzed reaction



(c) In strong acid



Figure 2. 5-Decomposition of persulfate in aqueous solution [32]

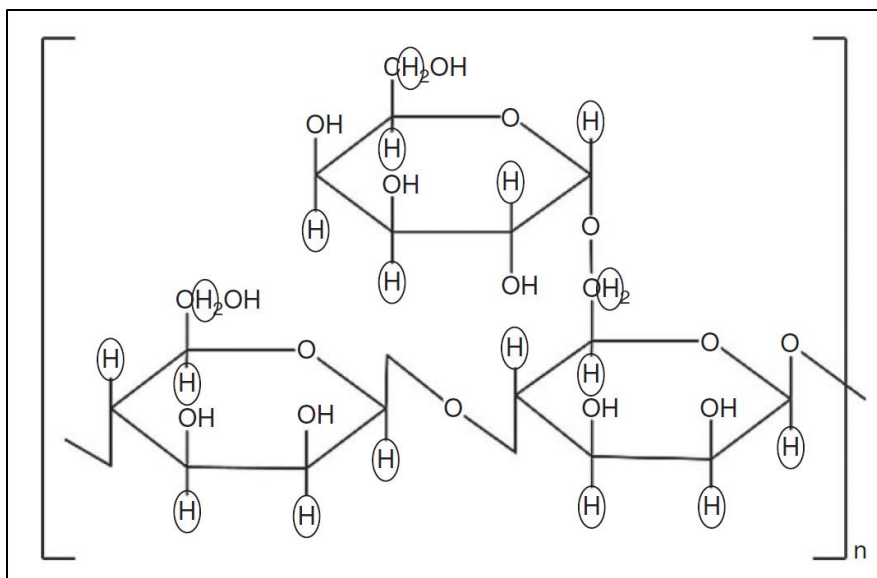


Figure 2. 6-Potential sites for sulfate free-radical attach in guar-based polymers [33]

The degradation of re-cross-linkable preformed particle gel (RPPG) was examined by Zhou [34](2019) to determine the effects of temperature, breaker type and concentration, gel size, concentration, aging time. The breakers utilized in the investigation of the gel's extent of degradation were high temperature-activated NaBrO_3 , $\text{Ca}(\text{ClO})_2$, and $\text{Na}_2\text{S}_2\text{O}_8$. According to their findings, the temperature and breaker type and concentration had the greatest impact on the degradation of re-cross-linkable preformed particle gels. The highest degradation on RPPG was achieved by $\text{Na}_2\text{S}_2\text{O}_8$ activated by NaOH in comparison to the other breakers examined [35]. The degradation of the borate crosslinked hydroxypropyl guar (HPG) fluid system was experimentally investigated in terms of temperature, breaker type, and polymer concentration. According to the findings of the test, while the rate of polymer degradation increased with an increase in temperature, and breaker concentration but decreased with the increase in polymer concentration.

2.4 Frac Fluids Breaking by Thermochemical Fluids (TCFs): A Potential Mechanism

The potential mechanism of the TCFs involves heat generated by those chemicals and its impact on the reduction in viscosity and degradation of frac fluid polymers. Gel permeation

chromatography and measurements of viscosity and molecular weight were used by Bradley et al. [36] to investigate the guar gum degradation by high temperatures of and discovered that both heat and flow significantly contributed to the material's degradation. They also discovered that heat degradation, in particular, produced a lot of small molecules, which led to a significant raise in polydispersity.

In order to investigate their breakage mechanisms, K  k [37,38] measured the rheological properties of guar gum (GG) and locust bean gum (LBG) at elevated treatments (100 and 121  C). He inferred that it was the activity of free extremists at higher temperatures that caused polymer corruption. Yagoub and Nur [39] demonstrated that, at the examined upper limit temperature of 100  C, guar gum's viscosity significantly decreased. Using thermal analysis methods such as, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), Leung et al. [40](1987) investigated the chemical changes and the thermal degradation behavior of polyacrylamide (PAM) and poly(acrylamide-co-acrylate (PAM-PAANA). Also, chromatography/mass spectrometry (GC/MS) and solid-state carbon-13 cross-polarization/magic angle spinning nuclear magnetic resonance (CPMASNMR) were used to investigate the chemistry changes due to the thermal degradation. They discovered that CO₂ gas evolution occurred after the NH₃ evolution of PAM and PAM-PAANA.

K  k et al. [41] investigated the rheological properties of guar gum (GG) and locust bean gum (LBG) in response to elevated-temperature treatments by employing a rheometer with a high-pressure cell. Because of this, it is now possible to test the viscosity at temperatures above 100 degrees Celsius as well as when the polymer suspension is heated from 20 to 121 degrees Celsius before being cooled back to the ambient temperature in a manner that resembles a cycle of sterilizing food. The estimated activation energies for depolymerization determined at a number of constant temperatures were 63 kJ/mol for GG and 98, 104, and 110 kJ/mol for three distinct LBG samples, respectively. The GG is more susceptible to thermal degradation than LBG as indicated by molecular weight shifts

estimated during heating. The observed behavior is observed because the LBG was better able to collaborate.

Hussain et al. [42] performed a TGA analysis on crude, hydrolyzed, and purified guar gum samples to assess the effect of temperature rise over time. In N₂ environment, temperatures of 30 to 1200 °C were examined with a constant heating rate of 10 C/min. The crude guar gum (CGG) TGA curves revealed the existence of three distinct weight reduction zones. At 345–760 °C, the weight loss in the third zone resulted in a mass reduction of 32.243%, which may have been caused by the degradation of the polymer's backbone (primary alcohol–CH₂OH). According to the thermal stability results, CGG loses mass as temperature rises in three distinct zones, which is consistent with our studies' findings regarding CGG. Thermochemical treatment was found to decrease capillary pressure by 57% [43] which will impact positively frac fluids cleanup.

Based on the above, thermochemical fluids are expected to be good frac fluid breakers since they tend to decrease viscosity and have a high potential to degrade frac fluid polymers by the anticipated free radical degradation mechanism. Also, generated nitrogen from thermochemical fluids will reduce the hydrostatic pressure and thus provide better cleanup. In addition, thermochemical fluids will enhance breaker release by increasing downhole temperature and reducing hydrostatic pressure by the generated heat and gas (Figs. 2.7 and 2.8). Moreover, increasing the temperature above 85°C tended to decrease the adsorption capacity of HPG (Figure 2.9) as observed by Wang et al. [20].

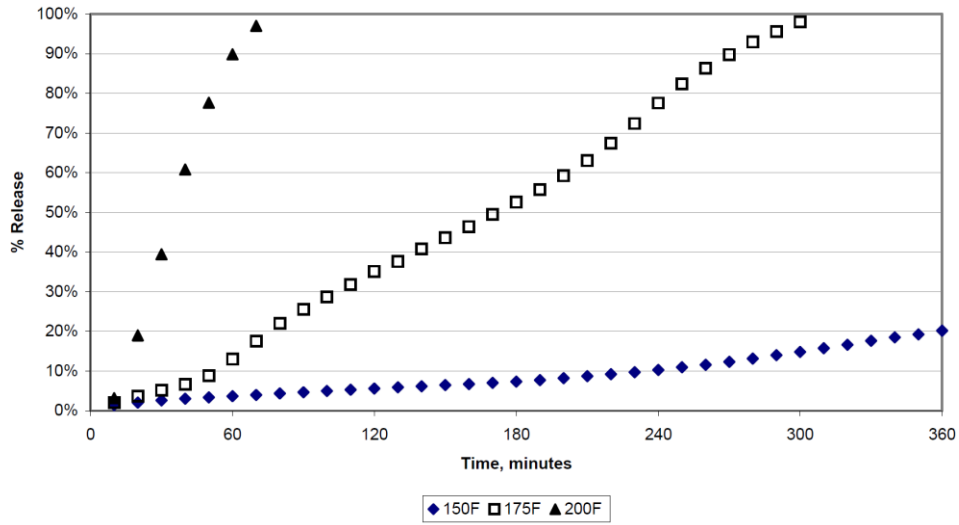


Figure 2. 7-Effect of temperature on breaker release [2]

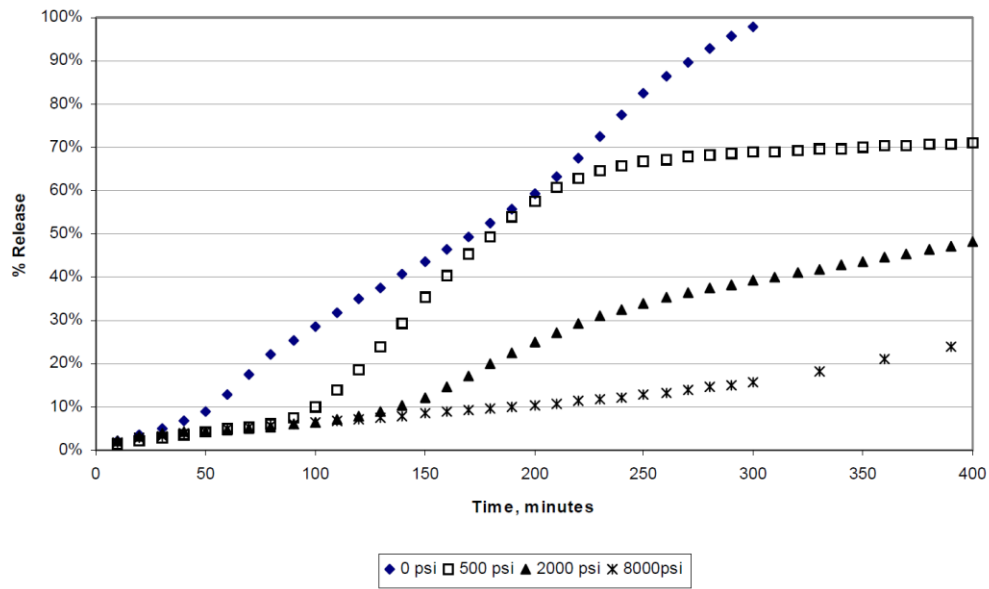


Figure 2. 8-Pressure effect on breaker release [2]

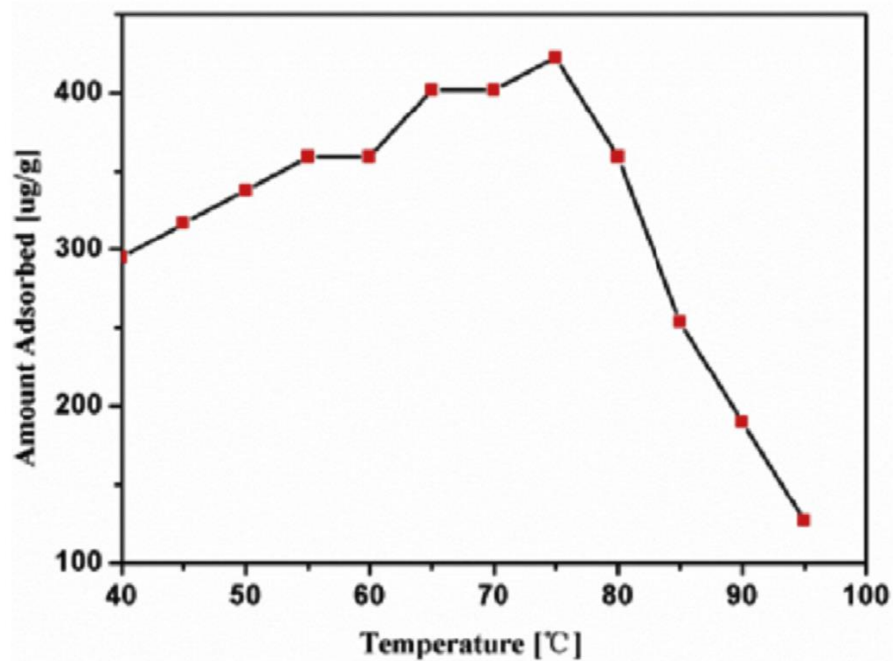


Figure 2. 9- Impact of temperature on HPG's adsorption capacity at condition of pH: 8.5 and HPG concentration of 3500 ppm [20]

2.5 Methods of Assessing Frac Fluid Polymer Degradation

Different techniques have been used to assess frac fluid polymer breakage including viscosity measurement, regained permeability, changes in polymer average molecular weight (MW) by gel permeation chromatography (GPC), size exclusion chromatography, and zero shear rate viscosity measurement.

2.5.1 Viscosity Measurement

Viscosity measurements of frac fluids before and after exposure to breaker treatments are commonly used to assess polymer degradation and thus the efficiency of different breaker systems. By breaking the guar polymer into smaller, lighter fragments, chemical breakers reduce its viscosity. Consequently, the flow-back of residual polymer will be facilitated by the viscosity reduction, allowing for rapid polymer recovery [44]. The viscosity

measurement technique is a simple method but insufficient to assess polymer frac fluids degradation since many fluids having reduced viscosity may contain high molecular weights polymer fragments. The decrease in fluid's viscosity is not always associated with molecular weights reduction [45]. "Adequately reduced viscosity" and gross concentrations of fragments with average molecular weights exceeding 1,200,000 demonstrate that reduced viscosity is not fully indicative of molecular weight reduction in broken crosslinked fluids [46].

2.5.2 Molecular Weight Changes Assessment

Molecular weight changes in frac fluid polymers following cleanup treatments might be the most practical method to assess polymer degradation by breakers. Different techniques are used to assess molecular weight changes of polymers including ultra-filtration molecular weight cut-off, zero-shear rate viscosity, gel permeation chromatography, and size exclusion chromatography.

2.5.2.1 Ultra-Filtration Molecular Weight Cut-Off technique

For zirconate-crosslinked CMHPG, guar crosslinked with borate, and guar crosslinked with zirconium, Brannon and Tjon-Joe-Pin [46] measured average molecular weight changes using this method. This examination provides a percentage of the solvent material's weight level across various size ranges. The broken gel solutions are filtered through semipermeable membranes using centrifugation to separate the variously sized polymer fragments for testing. Consequently, there are no fragments in the filtrate that are very big to go through the membrane. Ultrafree-CL filters are calibrated with dextrans standards. Using the specified molecular weight cutoff membranes, the fragments were divided into nominal molecular weights of 1,200K, 300K, 100K, 30K, 10K, and 5K. The MWCO investigations yield two results: the weight percent (wt%) of polymer parts measured at temperatures higher than 1,200 K and the average subatomic load of polymer parts at 1,200 K (AvMW1, CO) [46].

2.5.2.2 Zero-Shear-Rate Viscosity

Capillary viscometers of the type of Ubbelohde and Ostwald are used to determine viscosity-average molecular weight. The zero-shear-rate viscosity η_0 is a limiting value that cannot be measured directly; rather, it must be estimated by extrapolation (Shaw 2[47]). Estimation of polymer molecular weight can be performed based on the Mark-Houwink-Sakurada relationship which is given as follows [48]:

$$\eta = K(M_w)^a$$

Where:

η : the intrinsic viscosity, K and a are constants for a given polymer/solvent/temperature system, and M_w is viscosity average molecular weight.

$$\eta_{rel} = t/t_s \dots\dots\dots(3)$$

$$\eta_{sp} = (t/t_s) - 1 \dots\dots\dots (4)$$

$$\eta_{red} = \eta_{sp}/c \dots\dots\dots(5)$$

$$\eta_{inh} = \ln \eta_{red} / C \dots\dots\dots (6)$$

Where η_{rel} is the relative viscosity, η_{sp} is the specific viscosity, η_{red} is the reduced viscosity and η_{inh} is the inherent viscosity.

2.5.2.3 Gel Permeation Chromatography (GPC)

Gel Permeation Chromatography (GPC) has been utilized as an effective technique to determine the average molecular weights of polymers. Figure 2.10 shows a simple representation of a GPC column and its working principles where PDI refers to the polydispersity index [49]. Initially, GPC is run using standards of known molecular weight to determine the peak associated with each polymer fragment's average molecular weight (M_p) being measured. Almubarak et al. [49] used this technique to determine polymer

average molecular weight exposed to different breakers and thus assessed the performances of the breakers.

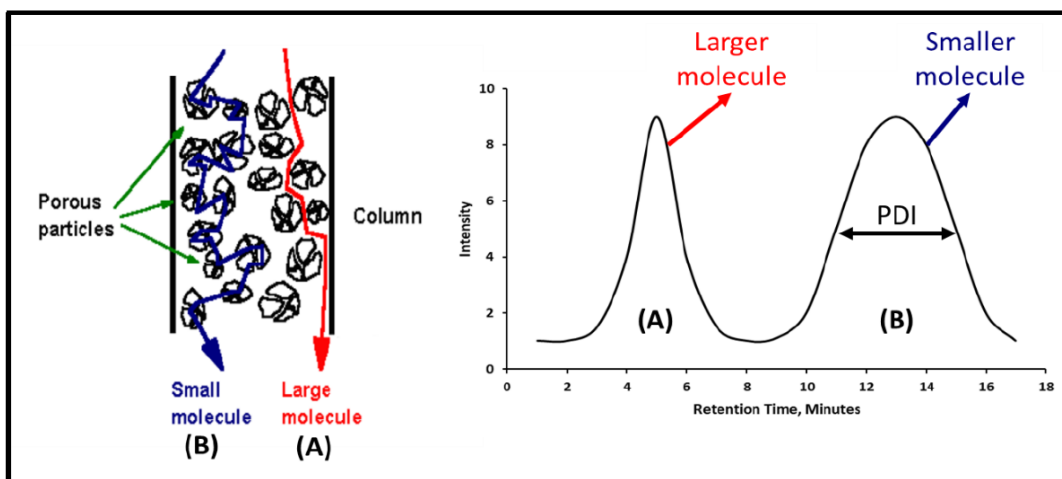


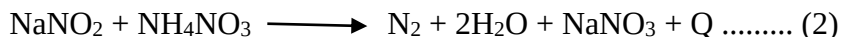
Figure 2. 10-Illustration of GPC, molecule A size > molecule B size, and molecule B PDI > molecule A PDI [49]

2.6 Thermochemical Fluids: Reaction Control and Applications

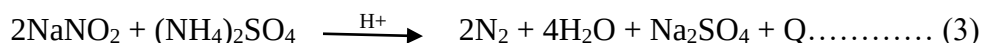
The ammonium chloride and sodium nitrite reaction can be controlled either using chemical or physical means. Nguyen et al. [6] reported two different fuses, chemical and physical. The chemical fuses included steps of series reactions, autocatalytic reactions, and retardants. The physical fuses are mainly physical separation of either reactants or the catalyst. This involved physical separation like the used of coiled tubing for one of the reactants during dewaxing, dispersion, emulsification, and encapsulation.

This thermal reaction of sodium nitrite and ammonium chloride has been utilized widely in oil industry in different applications including removal of paraffin/wax deposition, gas hydrates and filtercake removal [50-5]. Al-Taqi et al. [52] presented a case history where the thermochemical activated by a weak organic acid was successfully applied to remove oil-based mud filtercake damage for an oil producer well. Their reaction was controlled by injecting one of the salt through the production tubing while injecting the second through the coiled tubing. Several researches have been conducted on utilizing thermochemical

salts on various fields of oil industry oil industry applications including fracturing of tight gas reservoirs, removal of condensate, enhancing the gas productivity for shale gas reservoirs, removal of emulsion blockage after drilling, and removal of water blockage [53-55]. However, there are other exothermic reactions that generate in addition to heat nitrogen gas as given below [50]:



where Q is the heat generated. The reaction products are N₂ gas, H₂O, NaNO₃, and heat. A 3-M solution produces 400 scf [11 std m³] of N₂ gas and 132,500 Btu heat/bbl solution [879 MJ/m³]. The NaNO₃ produced by the reaction yields a brine that is equivalent to a 9.7 lbm/gal [1162 kg/m³] NaCl brine. While this brine is generally non-damaging to most producing formations, it's worth noting that the presence of nitrate in the reaction products could potentially serve as a source of nutrients for bacteria. Another thermal chemical reaction with some applications in oil industry is given by the following chemical reaction [56]:



The thermal chemical reaction described has been employed for removing crude oil sludges from storage tanks. However, this type of thermochemical reaction is not recommended for downhole applications, as it may lead to the formation of sulfate scale when mixed with high-calcium ion formation water. Taking the above into consideration, NH₄Cl and NaNO₂ are among the most promising thermochemical salts for downhole applications, including fracture cleanup

2.7 Emulsion Breaking

Emulsion is a common formation damage typically encountered in oil wells and may result in partial or total loss of well productivity. Emulsion breaking is a key to restore productivity of damaged wells. Different techniques and chemicals have been evaluated in laboratories and implemented in the field for emulsion breaking treatments.

All of the W/O emulsions formed from the distillation residues of crude oils could be partially broken by the application of moderate amounts of heat [57]. Fjelde [58] found that the emulsion can cause severe formation damage in core-floods at 90°C and these damages were partly removed during aging at higher temperature (120 and 150°C).

Martínez-Palou et al. [59] carried out a comparative study between microwave and oil bath heating with regard to water separation time from O/W emulsion. The effect of a chemical demulsifier and salt content on the O/W emulsion was also investigated. Microwave dielectric heating of O/W emulsions showed a greater degree of water separation in less time than conventional oil bath heating. Water separation of O/W emulsions increased with microwave power and salt content of the aqueous phase, and in the presence of a chemical demulsifier. They found that the use of a salty solution or seawater helped to increase the separation of water of the O/W emulsion because of the salting-out effect that diminished surfactant's solubility in water.

Alade et al. [60] utilized a thermochemical reaction involving reaction of ammonium chloride with sodium nitrite to generate in-situ heat and nitrogen gas to remove emulsion blockage using coreflood experiments. They observed that the temperature of the system could be raised to ≈ 170 °C (from 100 °C initial temperature) and pressure of 1,600 psia, under controlled conditions. A stable water-in-oil (W/O) emulsion was prepared and used as a damaging fluid. Ultimately, about 72% of the W/O emulsion was removed from the core sample by injecting 1 PV of thermochemical fluids. In addition, the pressure profile, observed during the flooding experiment, shows that no precipitation or damage was induced during the thermochemical flooding. The obtained results are encouraging and suggest that thermochemical fluids can be utilized to remove emulsion blockage.

2.8 Aqueous Phase Trapping Removal

Phase trapping and water-blocking, commonly occur during drilling and completion operations, are considered to be the primary causes of near-wellbore formation damage, especially in tight reservoirs, resulting in very low productivity. This type of formation damage can be bypassed using hydraulic fracturing. Another approach is to stimulate near wellbore using different acids (HCl, mud acid, etc.). Matrix acidizing is considered to be effective in removal of near wellbore damage in carbonate reservoirs.

Liu et al. [61] investigated experimentally the wettability alteration by quaternary ammonium fluoride salt and its potential to mitigate aqueous phase trapping damage in original water-wet, tight sandstone gas reservoirs. The result of the core flow test indicated that both the flow back rate and gas relative permeability were significantly improved by 40% and 20% respectively. Panga et al. [62] presented the development of a chemical system for water-block prevention in gas/condensate wells. The chemical system alters the formation wettability to intermediate gas wet conditions thereby decreasing the capillary forces and enhancing the cleanup of trapped water at low drawdown pressures. Adsorption/desorption characteristics of these chemicals and temperature stability are also investigated for long-term prevention of water blocks. The results revealed that some of the examined chemicals showed higher volumes of brine cleanup and lower flow initiation pressure gradient are observed after the treatment.

Li et al. [63] presented utilization of microwave (MW) heating as a new technique to remove water blocking. Based on their laboratory results, MW heating can heat layers rapidly when compared to other cleanup methods including formation heat treatment (FHT). Another advantage of MW is that it does not cause second damages or environmental pollution.

Jamaluddin et al. [64-67] presented several papers concerning utilization of formation heat treatment process in removal of water blocking. The primary mechanisms of the FHT process are to vaporize blocked water, dehydrate clay-bound water, destroy clay lattices and possibly create microfractures due to thermally induced stresses, with the objective of removing near-wellbore drilling induced skin damage.

Kang et al. [68] found that with the increase of treatment temperature, mass decreases, acoustic transit time increases, and permeability and porosity increase. Permeability begins to increase dramatically if treatment temperature exceeds the threshold value of thermal fracturing, which is 600~700°C, 500~600°C, 300~500°C, and 300~400°C for shale, mudstone, tight sandstone, and tight carbonate rock, respectively.

Al-Nakhli et al. [53] showed that using thermochemical was able to remove condensate banking where the cumulative condensate recoveries were 72.97%, 68.09% and 43.38% for sandstone, limestone and shale samples, respectively.

Based on the above literature, thermochemical fluids may have a good potential to be utilized for water blockage treatment.

2.9 Fracture Conductivity Modeling

The impact of fracture fluids on reservoir performance was recognized as early as the 1950's [69]. According to Seales et al. [69], though most agree that these fluids have the potential to damage the formation, the mechanisms that cause this damage, and the relative impact of each on reservoir performance is still being debated. Damage caused by fracture fluid may be classified as damage inside the fracture and damage inside the matrix [70]. Matrix damage is further subdivided into absolute and relative permeability damage [71]. Seales et al. [69] addressed several types of fracture damage including proppant crushing, proppant embedment, proppant plugging, and proppant diagenesis, absolute permeability damage in the matrix due to clay particle swelling or particle migration, polymer invasion, and scale or paraffin precipitation. Relative permeability damage usually accompanies

absolute permeability damage and is the direct result of fluid saturation and rock wettability changes.

Wang et al. [72] were the first to simulate the effect of flowing yield stress, polymer residue, and filtercake. They used a reservoir simulator to model how polymers in the fracture affect fracture fluid. They incorporated mathematical expressions for static yield stress. They also included the effects of proppant crushing, gel residue plugging and the formation of a filter cake on the cleanup behavior and the resulting gas flow rates.

Wang et al. [70] continued from their previous work [72] on the effect of gel damage on fracture cleanup and used reservoir simulation to analyze systematically the factors that affect fracture fluid cleanup and gas recovery from tight-gas wells . They used a systematic approach of modeling each factor contributing to fracture cleanup including simulation of single-phase flow, simulation of gas/water two-phase flow, simulation of proppant-crushing effect, simulation of polymer filter cake, simulation of gel damage.

Wang et al [72] in order to study the yield stress effect on the fracture fluid cleanup and gas production, they first look at the basic rheological models for the fracture fluids. Viscosity (μ) defined as the ratio of the shear stress (τ) to the shear rate (γ) is given as below.

$$\mu = \frac{\tau}{\gamma} \dots\dots\dots (1)$$

The polymer gel exhibits yield stress after leak-off and the rheology can be described by the Herschel-Bulkley model. To characterize the fracture fluid flow and polymer behavior, they choose a model by Yi [73]:

$$\tau = \tau_0 + K' \left(\frac{dv}{dr} \right)^{n'} \dots\dots\dots (2)$$

$$\mu_{nn} = \left\{ \begin{array}{l} \frac{KK_r \left(-\frac{\partial \phi}{\partial L} \right)}{\left[\frac{KK_r}{\mu_{eff,nn}} \left(\left(-\frac{\partial \phi}{\partial L} \right) \right) \right]^{\frac{1}{n'}}}} \\ +\infty \quad \left(-\frac{\partial \phi}{\partial L} \right) \ll \beta \tau_o \end{array} \right\} \dots\dots\dots (3)$$

$$\mu_{eff,nn} = \frac{K'}{12} \left(9 + \frac{3}{n'} \right)^{n'} (72C\phi(S_{nn} - S_{ir,nn})KK_{r,nn})^{\frac{1-n'}{2}} \dots (4)$$

$$\beta = N_n \sqrt{\frac{\phi(S_{nn} - S_{ir,nn})C}{2KK_{r,nn}}} \dots\dots\dots (5)$$

$$\text{The capillary pressure is } P_C = P_{ne} - P_{nn} \dots\dots\dots (6)$$

$$S_w + S_g + S_{gel} = 1.0 \dots\dots\dots (7)$$

Where, τ is shear stress, τ_o is static yield stress, K' is consistency index, and n' is power law index. If power law index $n' < 1$, the fluid is shear-thinning; if $n' = 1$, the fluid is Newtonian; and if $n' > 1$, the fluid is dilatant, shear thickening.

Wang et al. [72] summarized his review on fracture damage mechanisms and cleanup as follows:

- Fracture damage with 90% or higher reservoir formation permeability loss will decrease the gas production rate [74].
- High fracture conductivity will help the fracture fluids to clean up after the fracture treatment [75-77].
- Capillary pressure will affect fracture fluid cleanup. The higher the capillary pressure, the less fluids will be recovered [78].
- To recover more of the fracture fluids, we need to use surfactants and increase the pressure gradient in the fracture.
- A large pressure drawdown helps to clean up the fracture fluid more quickly and produce more gas as long as the fracture propping agent is not crushed. However, not all of the fracture fluid can be recovered during the cleanup process [75].

- It is necessary to take relative permeability hysteresis into account in the mathematical analysis of the cleanup process and well productivity performances [78].

Prior to simulation of cleanup and ultimate improvement of frac conductivity by thermochemical treatment, mass and heat transfer of thermochemical fluids in a fractured porous medium have to be understood. In this regard, Aljawad et al. [79] presented a model of heat transfer of thermochemical fluids in a fractured porous medium which consisted of an integrated wellbore, fracture, and reservoir mass and heat transfer models. The model showed that in most cases the thermochemical fluids were consumed within a short distance (15 ft) from the wellbore in most of scenarios. The main equations used in this model including wellbore and fracture and reservoirs are given below:

The one-dimensional (1-D) continuity equation in the wellbore can be written as:

$$\frac{\partial \rho_f}{\partial t} = \frac{2\gamma}{R_w} \rho_f u_{L,p} - \frac{\partial(\rho_f u_z)}{\partial z}$$

CHAPTER 3

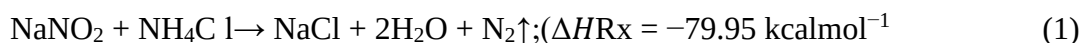
THERMALLY ACTIVATED NITROGEN/HEAT GENERATING REACTION: A KINETIC STUDY

Abstract

Sodium nitrite and ammonium chloride are the most widely used thermochemical salts in the oil and gas industry. The kinetics of this reaction when activated with acids or acid precursors were the subject of extensive research by several researchers. The activation of such a highly spontaneous/vigorous reaction by heat is considered a promising reaction control. In this work, a kinetic study was carried out for the reaction of sodium nitrite and ammonium chloride salt activated by heat at 1–5 M and temperatures of 50–90 °C. The study was carried out in both closed and open systems, with the monitoring of gas evolution and generated pressure. The study showed a relatively higher order for ammonium chloride than sodium nitrite. The excess amount of ammonium chloride, a weak acid, enhanced the reaction as it could be catalyzed by both heat and acid. The obtained kinetics of the nitrogen generating reaction is given as $dc/dt = -7.66 \times 10^{11} C_o^{2.45} e^{(-91.44 \text{ kJ/mol})/RT}$. The reaction kinetics in this study differs from what is reported in the literature regarding the order of NH_4Cl , which was reported to be higher than that of NaNO_2 under examined conditions. This study has practical significance for controlling the reactivity of the $\text{NH}_4\text{Cl}/\text{NaNO}_2$ nitrogen/heat generating system and calculating/optimizing nitrogen generation for a specific field application.

3.1 Introduction

The most commonly used thermochemicals in the oil industry are ammonium chloride and sodium nitrite where their reaction is given below [5-7]:



(irreversible $K_{eq} = 3.9 \times 10^{71} \text{ Pa} \cdot \text{mol} \cdot \text{m}^{-3}$ at 25 °C)

To control this very vigorous reaction and utilize it in different applications, the reaction kinetics of NH_4Cl and NaNO_2 has been studied by several researchers as a function of pH, reactant concentration, initial pressure, and temperature. [5,9,12]. Contradicting findings for the kinetics reaction order were reported, which might be attributed to different examined concentrations of reactants and catalysts. In agreement with Hughes et al. [10]. Rubin et al. [12] and Harrison et al. [13], Nguyen et al. [5] examined reactant concentrations of 0.1–2.5 M and pH values of 3–7 and found that the reaction rate followed first-order kinetics for the concentration of ammonia and second-order kinetics for the concentration of nitrite species for all examined concentration ranges. Dusenbury and Powell [14] observed the second-order kinetics (first order with respect to the total concentration of nitrite species) at a very low concentration of nitrite species (from 0.00243 to 0.094 mol dm⁻³) and low pH (about 2.9).

The effect of the acid concentration was found to influence the reaction rate and was considered in the kinetic equation in some studies [8, 80]. Qian et al.[8] found that with the increasing reactant concentration, $C(\text{H}^+)$, and temperature, the volume of produced nitrogen increased. Based on their study, the optimal molar ratio of $\text{NaNO}_2/\text{NH}_4\text{Cl}$ was 1. The experimental kinetic equation determined through the N_2 generating process by NaNO_2 and NH_4Cl was $dc/dt = -7.103 \times 10^7 C_{\text{H}^+} 1.3291 C_o^{2.0949} e^{(-51.28 \text{ kJ/mol})/RT}$.

Bispo et al. [9] studied ammonium chloride and sodium nitrite reaction to optimize and ensure the greatest and fastest heat production with minimum side production of nitrous oxides. They found that the optimum conditions included ammonium/nitrite equal to 1 and a catalyst concentration of 0.07 mol·L⁻¹, for a case in which the temperature was 5°C (seafloor level). Also, they found that adding the catalyst over time was a good strategy to decrease NO_x. To sum up, the reaction kinetics of ammonium chloride and sodium nitrite can be a first order of both reactants or first order for ammonium chloride and a second order for sodium nitrite, depending on the reaction conditions.

Different acids were investigated as thermochemical fluids (sodium nitrite and ammonium chloride) and reaction catalysts, including HCl acid, citric acid, and acid precursors (esters). In addition, oxidizers, such as ammonium persulfate, were investigated as the thermochemical reaction activator. The acid-activated thermochemical reaction is associated with the generation of side products and pollutant gases such as nitrogen oxides. Bispo et al. [9] reported that the percentage of nitrogen oxides could reach more than 25% of the produced gases for the acid-activated reaction under certain conditions.

As promising techniques, in situ nitrogen gas/heat generation reactions have been given more attention by several researchers nowadays. In situ generated N_2 and heat can be utilized to provide better foam quality for different field applications, including well cleanout, enhanced oil recovery (EOR), and fracturing operations [43,52,55,81,82]. Therefore, understanding the rate of nitrogen gas generation is crucial to design required foam quality under specific field conditions. In this study, the reaction kinetics of a thermally activated $NH_4Cl/NaNO_2$ reaction was studied. Salt concentrations of 2, 3, 4, and 5 M and a temperature range of 70, 80, and 90°C were investigated. Thermally activated $NaNO_2$ and NH_4Cl reactions are not anticipated to produce NO_x since nitrite solutions can produce NO_x at pH values below 6.0 [83].

3.2. Experimental Work

3.2.1. Materials

Sodium nitrite ($NaNO_2$) and ammonium chloride (NH_4Cl) used in this study were ACS reagent grade obtained from Honeywell and Thermo Fisher Scientific, respectively. Deionized water with a resistivity of 18.2 $M\Omega \cdot cm$ was used in preparation of the salt solutions. Sodium hydroxide used to adjust pH of $NaNO_2/NH_4Cl$ solutions was an ACS grade reagent obtained from Thermo Fisher Scientific.

3.2 Methodology of Gas Producing and Pressure Generating Reaction Tests

This study used a standard method for determining the kinetics of compounds that give gaseous products. The amount of gas that evolved at atmospheric pressure was measured as a function of time using the water displacement method [8]. In a volumetric round flask, 5 mL of each salt solution at different equimolar and variable concentrations was added. Water in a volumetric cylinder was displaced by gas produced, and the amount of gas that evolved was measured as a function of time. The vapor pressure reported at the examined temperature was detected from the gas-produced volume.

Also, a VINCI pressure–volume–temperature (PVT) cell with a total volume of 40 cm³ was used for the pressure generation tests. A 10 mL two-salt mixture at an equivalent volume was introduced into the preheated PVT cell at the designated temperature. The pressure generated due to the thermochemical reaction was monitored at a time interval of 2 s.

The pH measurements for ammonium chloride and sodium nitrite solutions at different concentrations were performed before and after gas production tests. From the generated data, initial and average reaction rates were determined using the typical methodology used (Figure 3.1).

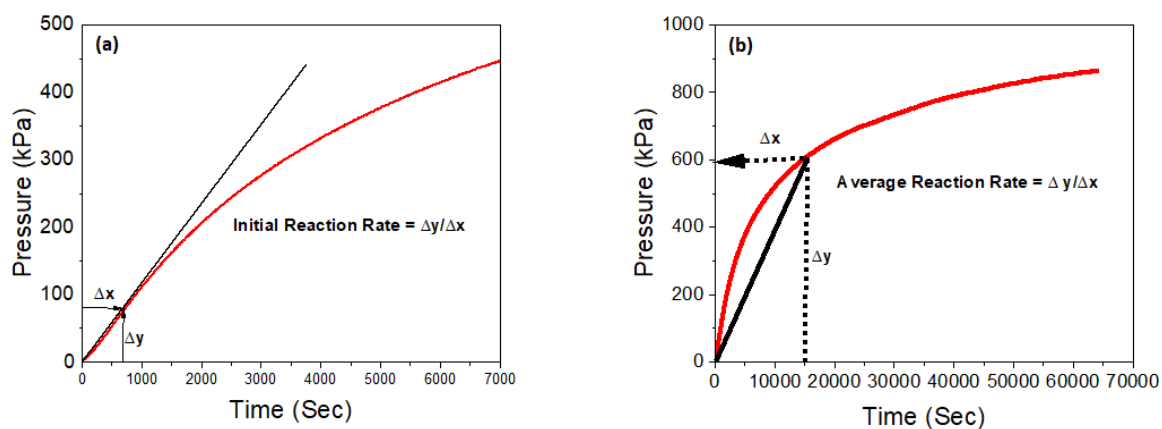


Figure 3.1-Methodology used to determine (a) initial reaction rate (b) average reaction rate

The initial reaction rates were determined from the slope of the tangent to the reaction curve and passing by the origin, while the average reaction rates were determined from the slope for the line going from origin to the time point of interest.

3.3 Experimental Setups

Figure 3.2 shows the water-displacement set-up used to measure evolved nitrogen gas due to reaction of ammonium chloride and sodium nitrite.



Figure 3.2-Water displacement setup

The closed system used to monitor generated pressure due to evolved nitrogen gas from the thermochemical reaction is shown in Figure 3.3. It consists of a VINCI Educational PVT cell for phase behavior analysis connected to analog and digital pressure gauges. An oil bath is used to maintain the transparent PVT chamber temperature as required. The pressure generated by the reaction was monitored as a function of time by a nearby PC. The pH measurements were conducted using an AccumetAR-15pH meter utilizing a microprobe, glass body single-junction Ag/AgCl reference with an auto temperature compensation

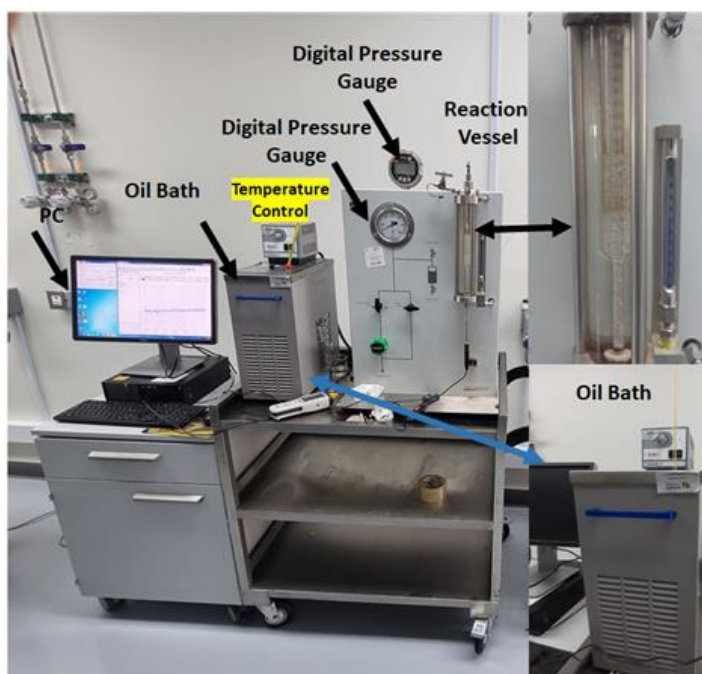


Figure 3 3-Closed system setup.

3.4 Experimental Design

The experimental work conducted in this study involved the use of open and closed system as given in Table 3.1. The effect of reactants concentration was investigated in order to study the reaction kinetics of $\text{NaNO}_2/\text{NH}_4\text{Cl}$ system that involved measuring reaction rate and determining reactants order. The effect of temperature was addressed in order to determine the activation energy of the thermally activated $\text{NaNO}_2/\text{NH}_4\text{Cl}$ reaction and frequency factor.

Table 3.1-A summary of the experimental plan

Nitrogen Production from Open System Set-up			
	Effect of Concentration		Purpose
1 st Batch	Equimolar	Variable Molarity	To study kinetics order of reaction and reaction rates
	2, 3, 4, and 5M	2M NaNO ₂ and 4M	
2 nd Batch	Effect	of 70, 80 and 90°C	To determine activation energy
Pressure Generation from Closed System Set-up			
	Effect of Concentration		Purpose
1 st Batch	Equimolar	Variable Molarity	To verify and support open system results
	2, 3, 4, and 5M	2M NaNO ₂ and 4M	
2 nd Batch	Effect	of 50, 60 70, 80 and	

3.5 Results & Discussion

3.5.1 Effect of Reactants Concentration and Temperature

The reaction of sodium nitrite and ammonium chloride was assessed through the measurement of gas produced and pressure generated as a function of time. In addition, the effect of temperature and concentration was investigated to study the kinetics of this reaction. Figure 3.4 shows that nitrogen gas evolved, and pressure generated increased as the two salts concentration was increased for the examined concentrations (1, 2, 3, 4 and 5M). Similarly, increasing the temperature in the examined range (50, 60, 70, 80, and 90°C) increased the gas generated pressure, as shown in Figure 3.4. The low concentration (1M) and low temperatures (50 and 60°C) were examined using the closed system since the system can be run overnight at an automated mode.

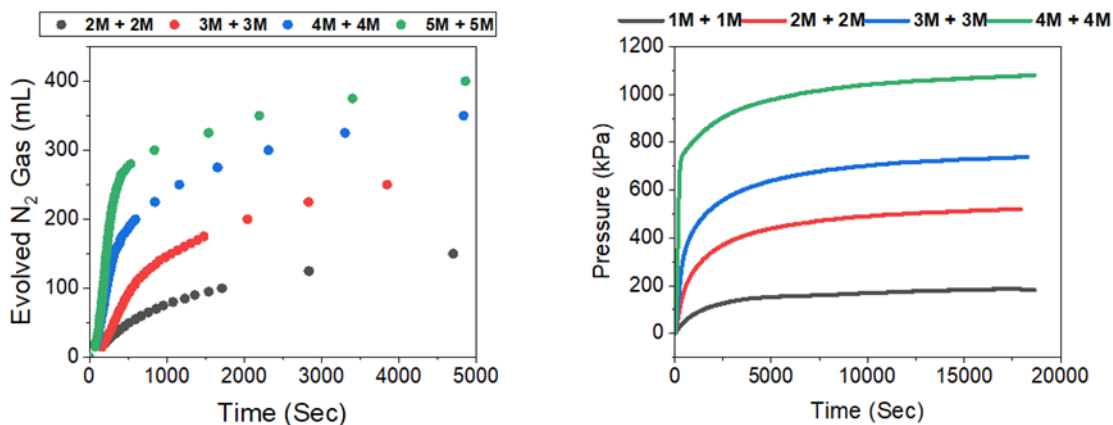


Figure 3.4-Effect of concentration on (a) evolved nitrogen gas, (b) generated pressure

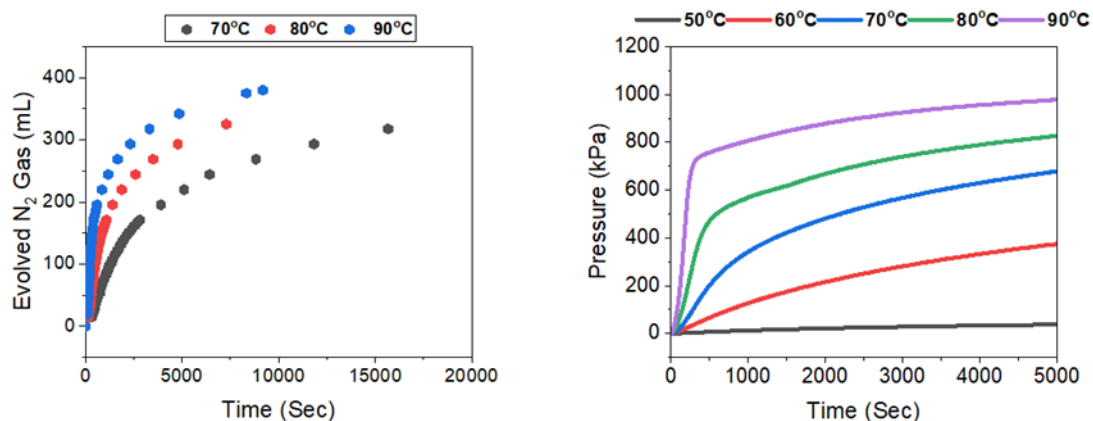


Figure 3.5-Effect of temperature on (a) evolved nitrogen gas, (b) generated pressure

From the pressure obtained data and utilizing ideal gas law, initial reaction rates can be determined as follows:

$$PV = nRT \dots\dots\dots (2)$$

Where P is the pressure in Pascal, Pascal = J/m³, V is the volume in L, n is the number of moles, R is the gas constant (J.mol⁻¹.K⁻¹), T is the temperature in Kelvin.

$$C = \frac{n}{V} = \frac{1}{RT} P \dots\dots\dots (3)$$

$$\frac{dC}{dt} = \frac{1}{RT} \frac{dP}{dt} \dots\dots\dots (4)$$

dP/dt can be obtained from generated pressure and based on that initial rates can be determined as given in Eqn. 4. Figure 3.6 shows both concentration and temperature had significant impact on initial rates of $\text{NaNO}_2/\text{NH}_4\text{Cl}$ reaction where exponential reaction is observed for both. The effect of thermochemical concentration and temperature on the average reaction obtained for the period of 15,000 seconds is illustrated in Figure 3.7. Unlike the initial reaction rate, there is a linear relation between the average reaction rate and the concentration; as the concentration was increased the reaction rate increased. The impact of temperature on the average reaction rate was more than that for concentration where polynomial of second order was obtained for curve fitting. However, the impact after 70°C was much less. Figure 3.8 shows the reaction rate of the thermochemicals tended to increase significantly at the early time of the reaction and then decreased to reach a plateau. Because this behavior of this reaction, more attention was given to the initial rates.

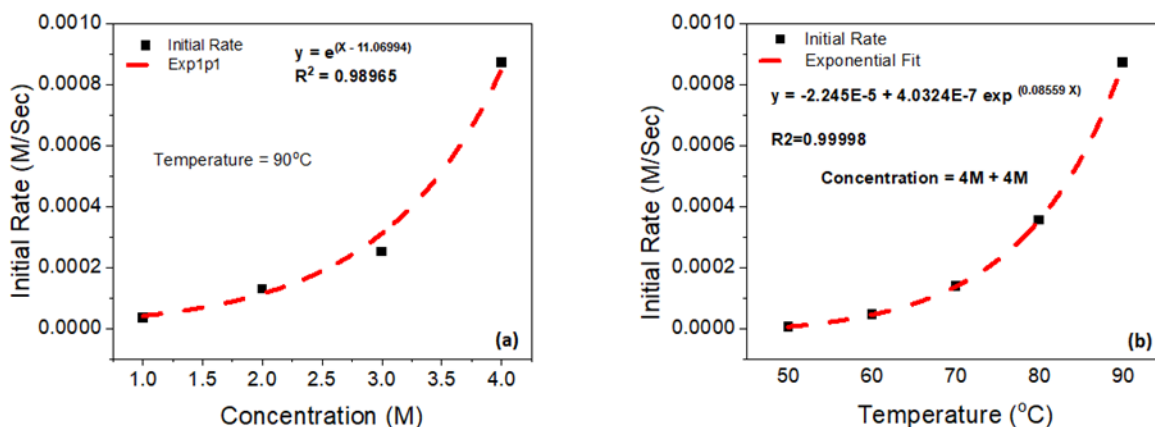


Figure 3.6-Effect on initial reaction rate: (a) concentration; (b) temperature

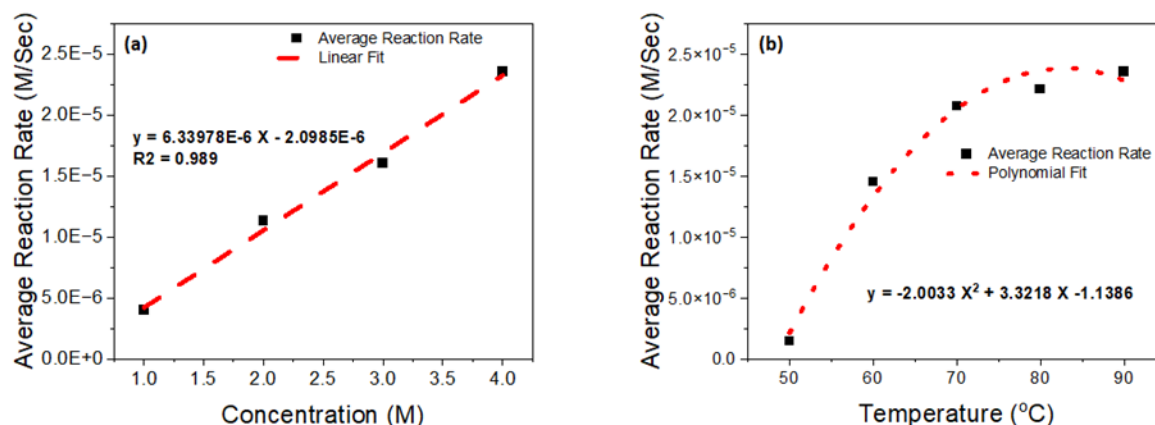


Figure 3.7-Effect on average reaction rate: (a) concentration; (b) temperature

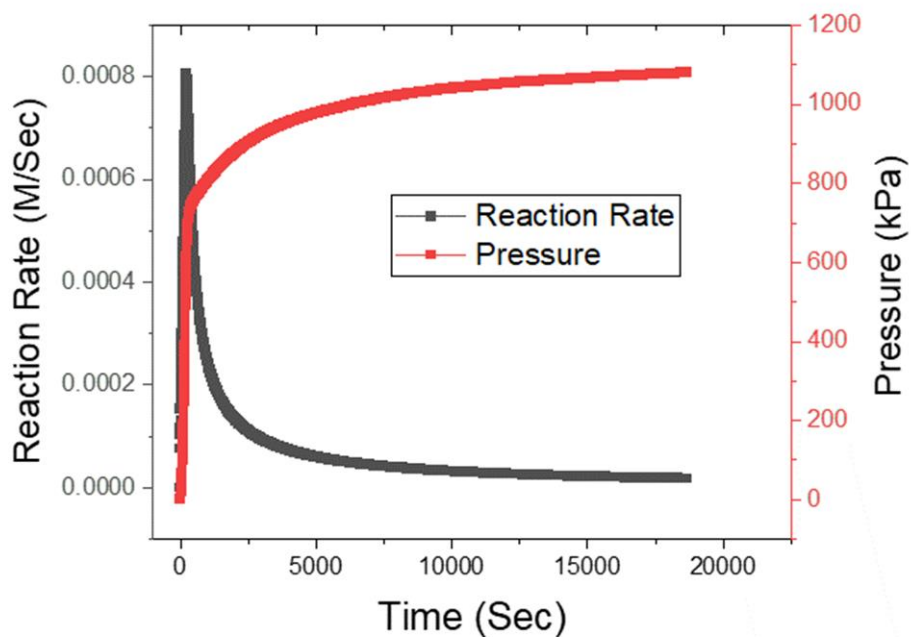


Figure 3.8-Pressure generated and reaction rate of 4M NaNO₂ + 4M NH₄Cl at 90°C as a function of time

3.5.2 Effect of pH

The effect of pH on reactivity of NaNO₂/NH₄Cl solutions at equimolar concentration of 4M and at 90°C was investigated using the closed system. The pH values examined ranged from 6.5 to 8.5. Figure 3.9-a shows the pressure generated while Figure 3.9-b shows the initial reaction rates for NaNO₂/NH₄Cl at 4M/4M solutions with different pH values. The

results showed that the reactivity of nitrogen/heat generating reaction was significantly influenced by solution pH. As the solution pH value was increased the reactivity decreased where the initial reaction rate for a solution with a pH value of 6.54 was higher by more than 20-time than that for a solution with pH valued of 8.54. The initial rate for equimolar (4M) $\text{NaNO}_2/\text{NH}_4\text{Cl}$ system at 90°C and for the examined pH range is governed by a second order polynomial equation as given below:

$$\text{Initial rate (Y)} = 0.1559(\text{pH})^2 - 0.00279.477 (\text{pH}) + 0.1248 \dots \dots \dots (5)$$

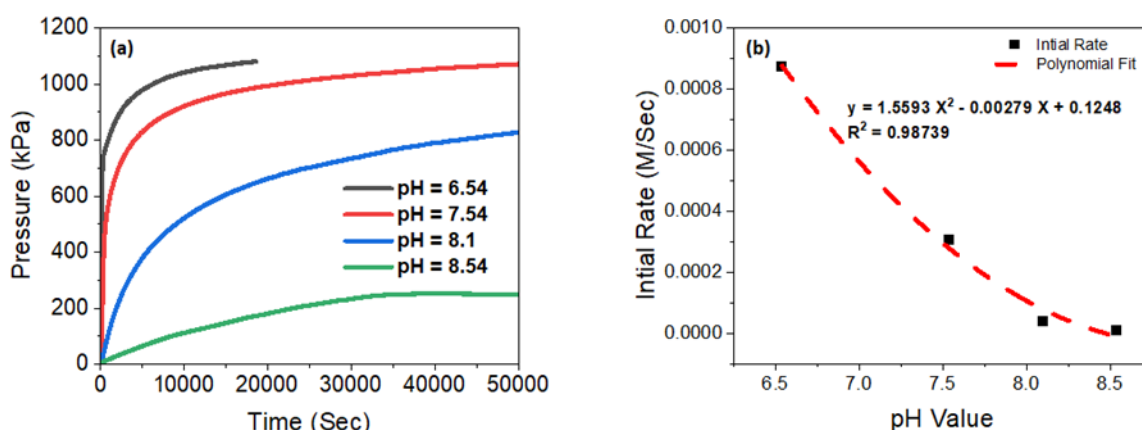


Figure 3.9-Effect of pH on (a) generated pressure, (b) initial reaction rates of 4M/4M solutions at 90°C in the closed system

3.5.3 Effect of Salinity

The effect of salinity on the reactivity of the thermochemicals of interest in this study was investigated. Application of thermochemicals in upstream operations will expose these chemicals to high salinity formation water (Table 3.2). In this study, formation water solutions at 5, 10 and 20% were used to prepare thermochemicals at equimolar of 4M/4M and their reactivity was examined in comparison with that prepared using deionized water (D.I.) at 90°C in the closed system. Figure 3.10 shows the buildup pressure in kPa due to generated nitrogen gas as a function of thermochemical systems base-water salinity. The results showed that water salinity enhanced thermochemicals reactivity at the early time and had minor impact at the end. It was observed that thermochemicals prepared in F.W showed foamability which might contributed to relatively higher reactivity.

Table 3.2-Composition of formation water (F.W)

Ion	Ion Concentration (mg/L)	Salt Used	Mass of Salt (g/L)
[Ca ²⁺]	13,045.04	CaCl ₂ .2H ₂ O	47.95
[Mg ²⁺]	3,133.08	MgCl ₂ .6H ₂ O	28.88
[Na ⁺]	65,658.12	NaCl	167.00
[K ⁺]	576.89	KCl	1.10
[HCO ₃ ⁻]	0	-	-
[SO ₄ ²⁻]	0	-	-
[Cl ⁻]	134,437.82	-	-

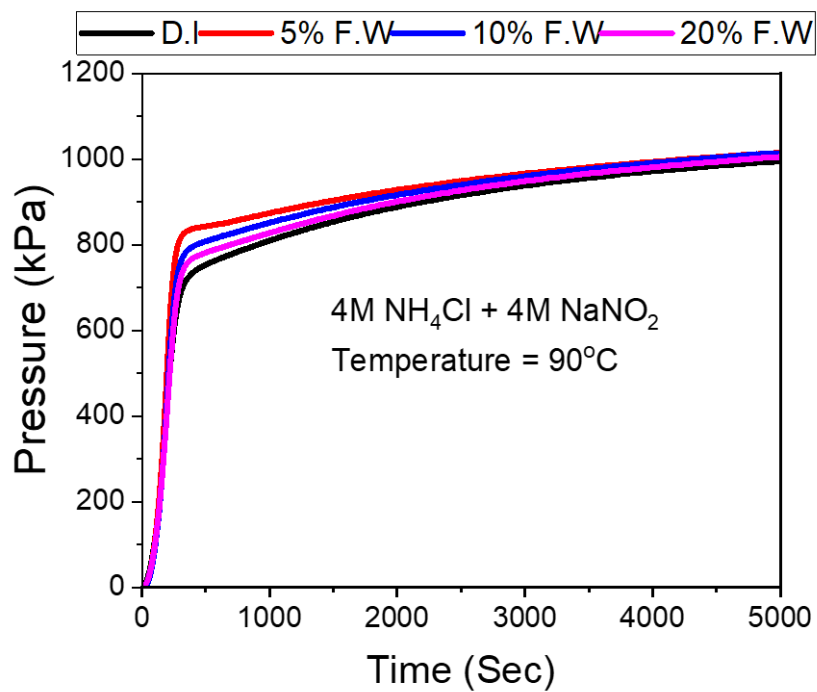


Figure 3.10-Effect of salinity (D.I, 5, 10 and 20% F.W) on the reactivity of nitrogen/heat generating system

3.6 Kinetic Study

The kinetic study conducted in this work for the thermally activated $\text{NaNO}_2/\text{NH}_4\text{Cl}$ reaction was mainly based on the results obtained from the open system (evolved N_2), while the closed system results (generated pressure) were used as supportive evidence. The kinetic equation of the reaction between NaNO_2 and NH_4Cl in the absence of acid can be expressed as given in equation (6).

$$\text{Rate} = K [\text{NaNO}_2]^x [\text{NH}_4\text{Cl}]^y \rightarrow -\frac{dc}{dt} = K [\text{NO}_2]^x [\text{NH}_4\text{Cl}]^y \dots\dots\dots (6)$$

In the practical field application, the gas generating rate of the in-situ N_2 generating systems can be predicted by the kinetic equation of the $\text{NaNO}_2/\text{NH}_4\text{Cl}$ mixture according to certain formation conditions [8]. In situ nitrogen gas generation from this thermochemical reaction is proposed to be utilized in foam generation for different oilfield applications, including fracturing, well cleanout, and EOR operations, where downhole geothermal heat is one of the suggested mechanisms to initiate this reaction [84-87]. From the gas evolved measurements, initial reaction rates of NaNO_2 and NH_4Cl at different concentrations and at 90°C were obtained as given in Table 3.3.

Table 3.3-Initial reaction rates of NaNO_2 and NH_4Cl at different concentrations and at 90°C

Trial	NaNO_2, (M)	NH_4Cl, (M)	Initial Rate (mL/sec)
1	4	4	0.4566
2	4	2	0.1638
3	2	4	0.2336

Incorporating of obtained data (Table 3.2) into Eqn. 6, gives the reactants order as given below:

$$\left(\frac{4}{2}\right)^x = \left(\frac{0.4566}{0.2336}\right) = 1.955 \rightarrow x = 0.967; \left(\frac{4}{2}\right)^y = \left(\frac{0.4566}{0.1638}\right) = 2.78 \rightarrow y = 1.479$$

Based on obtained x and y , Eqn. 6 becomes:

$$-\frac{dc}{dt} = K [NO_2]^{0.967} [NH_4Cl]^{1.479}$$

The results revealed that the thermally activated reaction kinetics at 90°C was nearly first order for NaNO₂ and nearly 1.5 for NH₄Cl. Figure 3.11 supported these findings and showed that the gas evolved, and the pressure generated was more at a higher concentration of NH₄Cl. This can be explained by the fact that the excess amount of NH₄Cl, a weak acid, tends to drop the pH value of the NaNO₂/NH₄Cl mixture (Table 3.4), which makes the reaction triggered by two mechanisms heat and acid, and the thus higher reaction rate is observed compared with the case of excess NaNO₂.

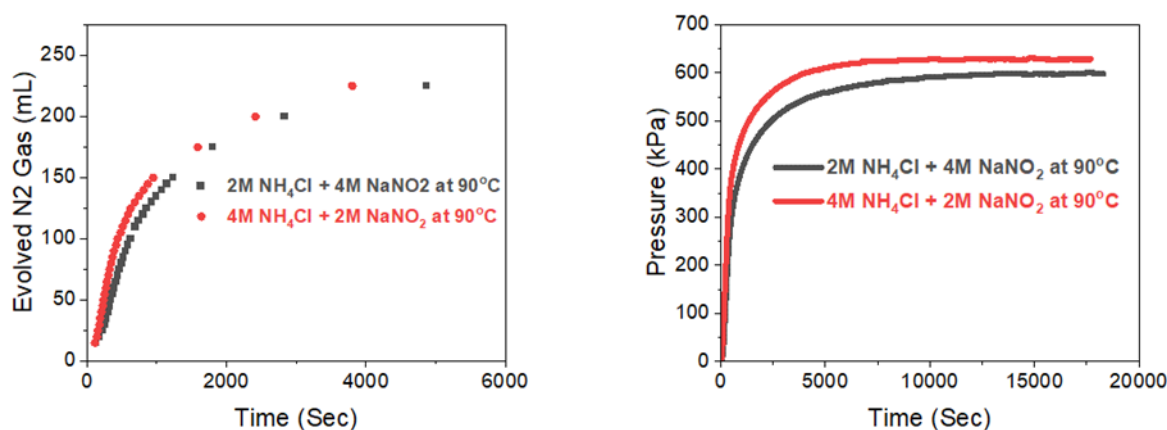


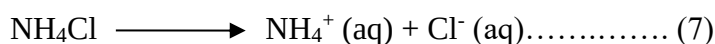
Figure 3.11-Effect of excess concentration of NaNO₂ versus excess concentration of NH₄Cl on the reaction rate

Table 3.4-pH value of different NaNO₂ and NH₄Cl solutions at ambient temperature before testing

Salt Type and Concentration	pH	Salt Type and Concentration	pH
2M NaNO ₂	7.84	2M NaNO ₂ + 2M NH ₄ Cl (11)	6.13
3M NaNO ₂	7.93	4M NaNO ₂ + 2M NH ₄ Cl (11)	6.41
4M NaNO ₂	8.10	2M NaNO ₂ + 4M NH ₄ Cl (11)	5.94

2M NH ₄ Cl	4.58	2M NaNO ₂ + 2M NH ₄ Cl (11)	6.13
3M NH ₄ Cl	4.61	3M NaNO ₂ + 3M NH ₄ Cl (11)	6.34
4M NH ₄ Cl	4.44	4M NaNO ₂ + 4M NH ₄ Cl (11)	6.32

Ammonium chloride is very soluble in water with a reported solubility at 25°C of 383.0 g/L [88] where ammonium ion and chloride ion are formed as given:



Ammonium ion dissociates in water to give acidic proton (H⁺) and ammonia (Eqn. 4), and the dissociation constant (K_d) at 25°C in dilute solution is 5.01×10^{-10} [88,89].



As a result of higher dissociation at a higher temperature, a drop in pH values of NH₄Cl solutions was observed at 50°C compared to that at ambient temperature (Table 3.5). These results indicate that thermochemical mixtures with excess NH₄Cl are expected to have lower pH values and higher associated reaction rates.

Table 3.5-pH Values of ammonium chloride solutions measured at ambient temperature and at 50°C

Concentration of NH ₄ Cl (M)	2	3	4
pH at ambient temperature	4.58	4.61	4.44
pH at 50°C	4.34	4.26	4.05

In another attempt to study the reaction kinetic, K in equation (6) was replaced by Arrhenius equation to give the following equation:

$$\frac{dc}{dt} = Ae^{-\frac{\Delta E}{RT}} [\text{NaNO}_2]^x [\text{NH}_4\text{Cl}]^y \dots\dots\dots (9)$$

where A and ΔE (kJ mol^{-1}) are the frequency factor and the apparent Arrhenius activation energy, x and y are reaction orders of NaNO_2 and NH_4Cl , and $[\text{NaNO}_2]$ and $[\text{NH}_4\text{Cl}]$ are the concentrations of NaNO_2 and NH_4Cl in molar, R is the ideal gas constant ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$), and T (K) is the absolute temperature. When an equimolar concentration is considered for the two salts, ($[\text{NaNO}_2] = [\text{NH}_4\text{Cl}] = C$), and $x + y = n$ then, equation (3) becomes

$$\frac{dc}{dt} = Ae^{\left(-\frac{\Delta E}{RT}\right)} C^n \dots\dots\dots (10)$$

We followed the same method of Qian et al. [8] where transposing and integrating of equation (10) as given in the Appendix yields equation (11):

$$t = \frac{k^{n-1}-1}{1-n} A^{-1} e^{\frac{\Delta E}{RT}} C_o^{n-1} \dots\dots\dots (11)$$

where k is the ratio of the initial concentration and the current concentration of each reactant (theoretical GPV/(theoretical - real-time), C_o (M) is the initial concentration of NaNO_2 and NH_4Cl , t (s) is the time consumed for collecting a certain gas volume. Note that GPV stands for the gas production volume which was measured at 1 atm. Taking the common and natural logarithms of both sides results the following equations

$$\log t = \log \left(\frac{k^{n-1}-1}{n-1} \right) - \log A + (1-n) \log C_o + \frac{\Delta E}{2.303RT} \dots (12)$$

$$\ln t = \ln \left(\frac{k^{n-1}-1}{n-1} \right) - \ln A + (1-n) \ln C_o + \frac{\Delta E}{RT} \dots\dots\dots (13)$$

The activation energy for the thermally activated reaction of 4M NaNO_2 with 4M NH_4Cl was determined using two methods. In the first method, the time that the reaction produced a certain gas volume (50, 100, 150, 200, 250, and 300 mL) was recorded at various temperatures (343, 348 353, 358 and 363 K) with the presence of 4M of each reactant. Then, plotting of $\ln t$ versus $1/T$ gives linear relation for the examined produced volumes

of nitrogen gas (Figure 3.12). From the average slope of the six lines, a calculated apparent Arrhenius activation energy of 90.55 kJ/mol was obtained.

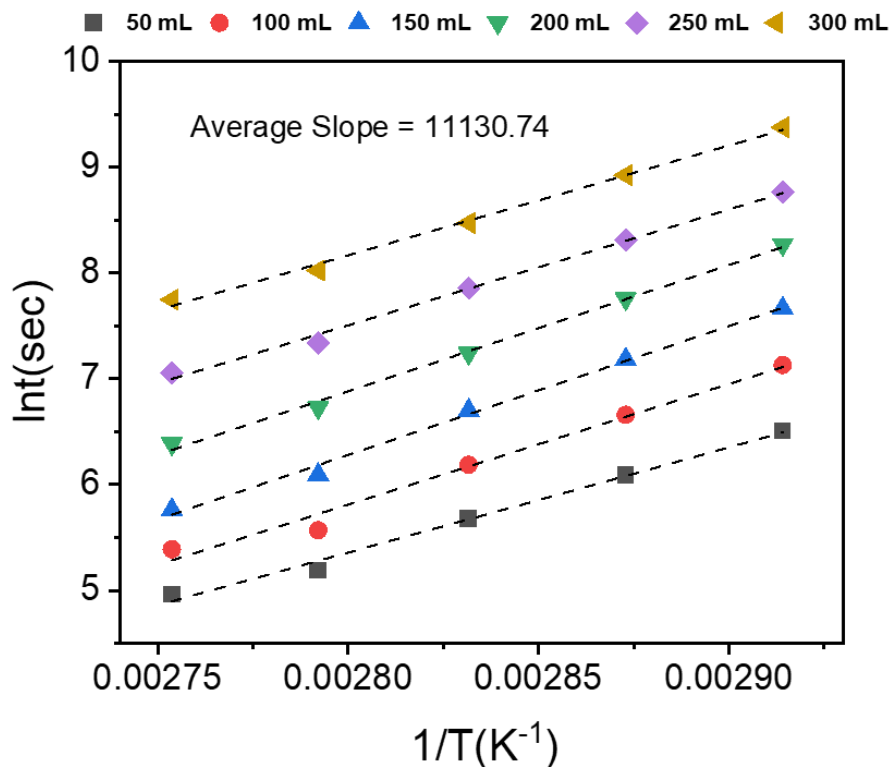


Figure 3.12-Linear relation graph of $\ln t$ - $1/T$

In the second method, the apparent Arrhenius activation energy was determined from the linear relation between the reaction constant, $\ln K$, to $1/T$ as given by the Arrhenius equation.

The reaction constants calculated from initial rates and kinetic reaction orders (Table 3.1) were used to determine the apparent Arrhenius activation energy. Figure 3.13 shows a linear relationship between the $\ln K$ and $1/T$. The calculated activation energy based on the slope obtained was found to be 90.353 kJ/mol, which is comparable to that obtained from plotting $\ln t$ versus $1/T$ (92.54 kJ/mol). The average activation energy based on the two

methods is 91.44 kJ/mol. The activation energy obtained by Qian et al. [8] is lower (51.28 kJ/mol) than the one obtained in this study due to the catalyst (authigenic acid) used in their study. It is well addressed that catalyst tends to lower the activation energy. Based on intercepts of linear relation in Figures. 3.11 and 3.12, the calculated average frequency factor (A) based on equations (12-a and 13-a) is 7.66×10^{11} .

$$A = \log\left(\frac{k^{n-1}-1}{n-1}\right) - \log A + (1-n) \log C_o \dots (12-a)$$

$$B = \ln A \dots \dots \dots (13-a)$$

Where A and B are the intercepts of Eqn. 12 and 13, respectively.

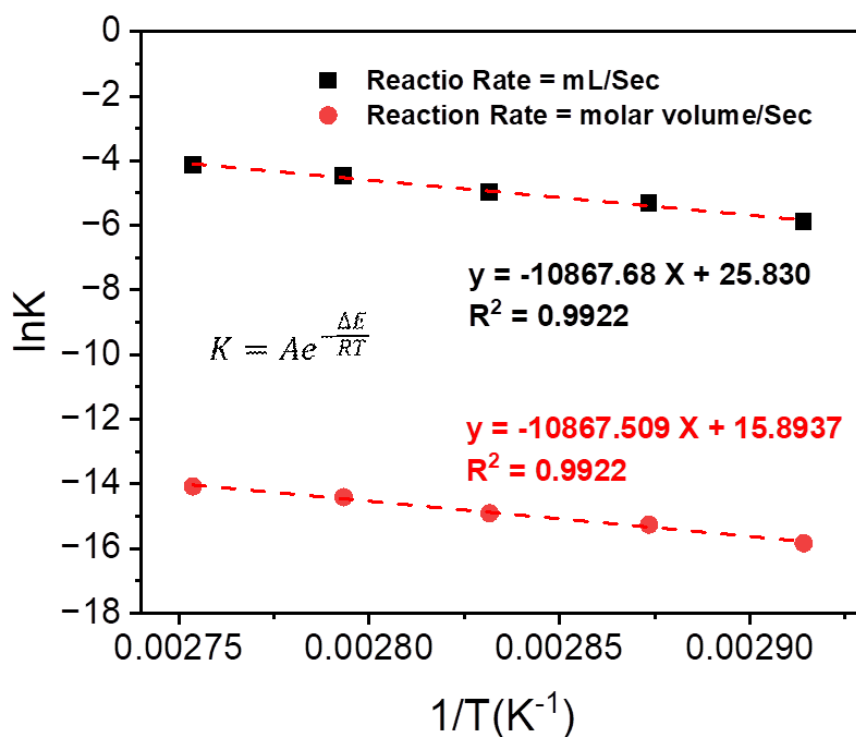


Figure 3. 13- Linear relation graph of $\ln K$ - $1/T$

The reaction rate order was obtained from plotting $\log t$ versus $\log C_o$ (Figure 3.14), which gives a linear relation for four lines generated at three different k (the ratio of the theoretical

produced gas volume to (theoretical volume – real-time volume)). The average slope of the four lines is equal to the (1-n) as given in Eqn. 12, where n is the order of reactants. The calculated reactants order is 2.346, comparable to that obtained from the initial reaction rates result (2.45).

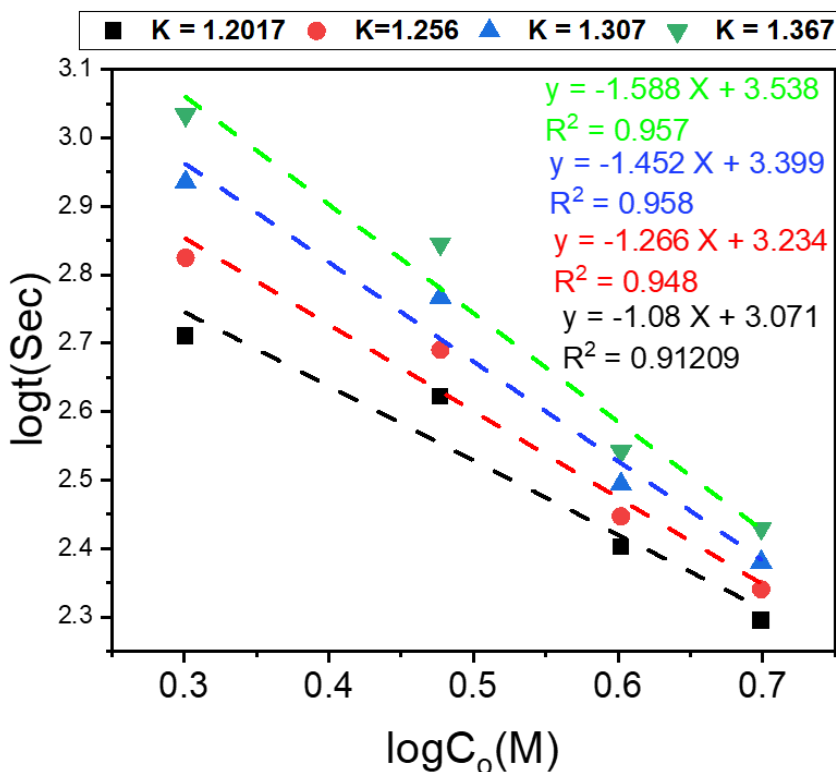


Figure 3. 14-Linear relation graph of logt-logC₀

3.7 Conclusions

The kinetics of the reaction between NH₄Cl and NaNO₂ activated thermally was studied, and the rate of the reaction was monitored by measuring the volume of nitrogen gas evolved as a function of time. The effect of reactants concentration and temperature was investigated.

- Nitrogen gas production and associated buildup pressure were found to increase as NaNO₂ and NH₄Cl concentration and temperature were increased.

- The reactivity of nitrogen/heat generating system is strongly influenced by pH values and reaction temperature.
- The water salinity had negligible impact on the reactivity of the nitrogen/heat generating system.
- Excess concentration of NH_4Cl with respect to NaNO_2 concentration tended to have a higher reaction rate compared with the same excess concentration of NaNO_2 with respect to NH_4Cl concentration.
- The kinetics order of NH_4Cl was higher than that of NaNO_2 , as revealed from evolved gas results and supported by generated pressure data.
- The kinetic of thermally activated nitrogen generating reaction of $\text{NH}_4\text{Cl}/\text{NaNO}_2$ is given as $dc/dt = K[\text{NaNO}_2]^{0.97}[\text{NH}_4\text{Cl}]^{1.48} = -7.66.2 \times 10^{11} C_o^{2.45} e^{(-91.44 \text{ kJ mol}^{-1})/RT}$

APPENDIX

$$Rate = K [NaNO_2]^x [NH_4Cl]^y \rightarrow -\frac{dc}{dt} = K [NO_2]^x [NH_4Cl]^y$$

At equal concentration $[NO_2] = [NH_4Cl] = C$

$$n = x + y; \frac{dc}{dt} = kC^n$$

$$K = Ae^{\frac{-\Delta E}{RT}}; \frac{dc}{dt} = C^n Ae^{\frac{-\Delta E}{RT}}$$

$$\frac{dc}{C^n} A^{-1} e^{\frac{\Delta E}{RT}} = dt \rightarrow A^{-1} e^{\frac{\Delta E}{RT}} \int_0^t \frac{dc}{C^n} = \int_0^t dt$$

$$A^{-1} e^{\frac{\Delta E}{RT}} \int_0^t \frac{dc}{C^n} = \int_0^t dt \rightarrow t = \frac{1}{1-n} (c_t^{1-n} - c_0^{1-n}) A^{-1} e^{\frac{\Delta E}{RT}}$$

$$t = \frac{1}{1-n} (c_t^{1-n} - c_0^{1-n}) A^{-1} e^{\frac{\Delta E}{RT}} \rightarrow t = \frac{1}{1-n} \left(\frac{c_t^{1-n}}{c_0^{1-n}} - 1 \right) A^{-1} e^{\frac{\Delta E}{RT}} c_0^{1-n}$$

$$t = \frac{1}{1-n} \left(\frac{c_t^{1-n}}{c_0^{1-n}} - 1 \right) A^{-1} e^{\frac{\Delta E}{RT}} c_0^{n-1} \rightarrow t = \frac{1}{1-n} \left[\left(\frac{c_t}{c_0} \right)^{1-n} - 1 \right] A^{-1} e^{\frac{\Delta E}{RT}} c_0^{1-n}$$

C_o is the theoretical gas produced volume (T_v), C_t is the theoretical gas produced volume – real time produced volume R_v .

$$\left(\frac{c_t}{c_0} \right)^{1-n} = \left(\frac{T_v - R_v}{T_v} \right)^{1-n}; \text{ and } k = \frac{T}{T - R_v} \implies \left(\frac{c_t}{c_0} \right)^{1-n} = (k^{-1})^{1-n}$$

$$t = \frac{k^{n-1} - 1}{1-n} A^{-1} e^{\frac{\Delta E}{RT}} c_0^{n-1}$$

$$\log t = \log \left(\frac{k^{n-1} - 1}{n-1} \right) - \log A + (1-n) \log C_0 + \frac{\Delta E}{2.303RT}$$

$$\ln t = \ln \left(\frac{k^{n-1} - 1}{n-1} \right) - \ln A + (1-n) \ln C_0 + \frac{\Delta E}{2.303RT}$$

CHAPTER 4

ADVANCING SUSTAINABILITY THROUGH EMULSIFICATION OF THERMOCHEMICAL FLUIDS: EXPLORING EMULSION CHARACTERISTICS AND RHEOLOGICAL PROPERTIES

Abstract

Emulsification serves various purposes, including controlling the reactivity of highly reactive chemicals. Thermochemical fluids (TCFs), such as ammonium chloride (NH_4Cl) and sodium nitrite (NaNO_2) salts, have been utilized in diverse applications, including the petroleum industry. The excessive reactivity of TCFs limits their applications and consequently negatively impacts the potential success rates. One of the recent recommendations concerning TCFs is their use for the in-situ generation of foamed fracturing fluids. Controlling the reactivity of TCFs ensures that chemical reactions are optimized, minimizing chemical waste and maximizing efficiency, while the utilization of foamed fracturing fluids conserves water resources and reduces the overall environmental footprint of industrial processes. Both aspects are crucial for achieving sustainability goals by reducing resource consumption and environmental impact.

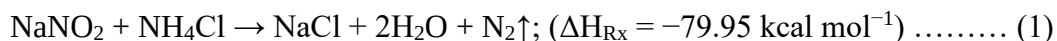
This study examined three distinct emulsifiers, , each containing a surfactant and cosurfactant each designated as A, B and C for NH_4Cl and NaNO_2 solutions independently or as a composite mixture in diesel. This study examined three distinct emulsifiers designated as A, B, and C, for NH_4Cl and NaNO_2 solutions independently or as a composite mixture in diesel. Laboratory results demonstrated that water-in-oil (WO) emulsions of TCFs in diesel were achieved using the three emulsifiers under examination. The 70% TCFs/diesel emulsions exhibited pseudoplastic fluid characteristics and followed the Power-law model. The increase in TCFs volume fraction and emulsifier concentration positively influenced the emulsion properties, including its thermal stability. Emulsifier-A

demonstrated the most effective emulsification capability, as evidenced by relatively higher viscosity and smaller droplet size distributions. Emulsifier-B and Emulsifier-C, with low pH values, due to the presence of acetic acid in their compositions, tended to activate the reaction of the TCFs. Raising the pH levels of the mixed TCFs solutions before the emulsification process enhanced the emulsion characteristics of those prepared with Emulsifier-B and Emulsifier-C. The paper presents a detailed characterization of WO emulsions of TCS-in-diesel using three distinct emulsifiers and explores their potential contribution towards sustainability.

Keywords; Thermochemical Fluids; Emulsification; Characterization, Rheology, Sustainability.

4.1 INTRODUCTION

Thermochemical fluids (TCFs) have wide applications in different sectors of industries, including the oil industry. Ammonium chloride (NH_4Cl) and sodium nitrite (NaNO_2) salts are considered the most common TCFs used in the oil industry due to their relatively low cost, excessive generation of heat, and environmentally friendly products (N_2 , NaCl , and H_2O). They are highly reactive chemicals, and their exothermic chemical reaction is given as per the following equation [5-8]:



It is an irreversible reaction with $K_{eq} = 3.9 \times 10^{71} \text{ Pa} \times \text{mol} \times \text{m}^{-3}$ at 25°C .¹ This TCFs system's high reactivity limits its applications, suggesting the need to investigate different methods to control its reactivity. Al-Taq et al. [90] showed that the reaction rate of $\text{NH}_4\text{Cl}/\text{NaNO}_2$ is highly influenced by the pH values of the system and the triggering temperatures. Generally, the reaction rate of a chemical reaction is governed by reactant concentration, temperature, catalysts, and inhibitors. For a reaction to occur, the activation energy must be overcome by catalysts or by providing the required energy. Physical and chemical methods can be used to control a chemical reaction. Thermochemical reactions are classified as fused reactions when they are delayed [91]. Nguyen et al. [8,91] discussed

several techniques to delay heat release from the TCFs ($\text{NH}_4\text{Cl}/\text{NaNO}_2$), including chemical fuses and physical methods. The chemical fuses include series reactions, autocatalytic reactions, and retardants. The physical techniques include physical separation, encapsulation, and emulsification. Unlike in oil production operations where emulsion presents a problem, emulsion may present as a solution in several fields, including food, medicine, and detergent industries. Emulsification also provides an effective method to control the reactivity of highly reactive chemicals in the oil industry. Emulsification of individual $\text{NH}_4\text{Cl}/\text{NaNO}_2$ system components has been successfully applied in several dewaxing operations for short pipelines in the Campos Basin, Brazil [51]. The fact that the heat release must be postponed for much longer makes adopting this method for lengthy pipes difficult. Acetic acid, as the reaction activator, was emulsified together with NH_4Cl . Almubarak et al. [92] proposed emulsifying these two salts to treat deep water blockage.

Emulsion, defined as a mixture of two immiscible liquids, can be classified based on the dispersion of one phase into another and droplet size distributions. Emulsions can exist in four forms, but the most common ones are oil-in-water (OW) and water-in-oil (WO). The other emulsions are water-in-oil-in-water (w/o/w) and oil-in-water-in-oil (o/w/o). In the OW emulsion, the oil is the dispersed phase, while the water is the continuous phase, whereas water is the dispersed phase and oil is the continuous phase in the WO emulsion. Emulsions can also be classified based on their droplet sizes into macroemulsions (conventional), microemulsions, and nanoemulsions [93-96]. Table 4.1 shows these emulsions' most common droplet size distributions and some of their physical properties. The droplet size order of these emulsions increases as follows: microemulsion < nanoemulsion < macroemulsion. There might be an overlap in droplet size distributions among these emulsions, as revealed in the literature, and in this case, other parameters should be considered to distinguish between them. Macroemulsions are weakly to moderately stable and, with time, will break into oil and water, while microemulsions are thermodynamically stable. Nanoemulsion is thermodynamically unstable but kinetically stable.

Table 4.1-Classification and characteristics of emulsions

Type of Emulsion	Macroemulsion	Nanoemulsion	Microemulsion	References
Droplet Size	>500 nm	< 500 nm	<1000 nm	Smoleński et al. [93]
	>400 nm	100-400 nm	10- 100 nm	Ma et al. [94]
	1-100µm	20-500	10-100 nm	Gupta et al. [95]
		20-200 nm	1-100 nm	Mariyate et al. [96]
Droplet Shape	Spherical	Spherical	Spherical and lamellar	
Appearance	Milky/turbid/ Opaque	Translucent or transparent	Transparent/clear	
Stability	Thermodynamically unstable /weakly kinetically stable	Kinetically stable	Thermodynamically Stable	
Surfactant Concentration	Low	Low	High	

Several factors, including emulsifier concentration, aqueous phase salinity, the proportion of each phase, emulsion droplet size, and temperature, influence emulsion stability. Generally, the emulsion stability tends to decrease as a function of temperature. Bera et al. [97] found that the coalescence of a flowing oil-in-water emulsion increased notably after 50°C within a temperature range of 20 to 70°C. Similarly, Wang et al. [98] observed that formation water/heavy oil emulsion tended to destabilize above a temperature of 60°C.

The destabilization caused by temperature is attributed to higher temperatures making the oil less viscous, increasing droplet collisions, and widening the density disparity between

distinct emulsion phases. Consequently, the interfacial layer surrounding the droplets loses some mechanical strength, enhancing the effectiveness of demulsification [99]. Wang et al. [99] also noted that a more stable emulsion was achieved with a lower water cut. Emulsions become difficult to stabilize when the salinity exceeds 10,000 mg/L.

The droplet size of emulsions influences their stability, with smaller droplet sizes contributing to higher stability. Stok's law, provided below, is employed to evaluate emulsion stability. According to this law, the sedimentation rate decreases as the average droplet size of the emulsion decreases and its viscosity increases [99]. This principle holds true unless bimodal emulsions are considered [100].

$$v = \frac{2r^2(\rho - \rho_o)g}{9\eta} \dots\dots\dots (2)$$

where, v is the creaming or settling rate, which depends on several factors: the droplet radius (r), the density of the droplet (ρ), the density of the continuous phase (ρ_o), the viscosity of the continuous phase (η), and the local acceleration due to gravity (g). These variables collectively influence the destabilization rate of emulsion systems by accounting for the densities of both the dispersed and continuous phases, the size of the dispersed phase droplets, and the viscosity of the continuous phase.

All emulsifiers have both hydrophilic and hydrophobic groups, making them soluble in water and oil. Because of this property, emulsifiers tend to reduce the interfacial tension (IFT) between oil and water, ultimately forming emulsions. The preferential solubility of emulsifiers in oil or water depends on their affinity (partitioning) toward oil and water phases. The formation of water-in-oil emulsions usually requires that an emulsifier has good oil solubility and preferentially partitions into the oil phase rather than the water phase [101]. In contrast, emulsifiers used to prepare oil-in-water emulsions have good solubility in water and preferentially partition into the water phase. The hydrophilic-lipophilic balance (HLB) of emulsifiers is typically employed to select proper emulsifiers for each

emulsion type. Emulsifiers with low HLB are typically used to prepare WO emulsions, while those with high HLB are used to prepare OW emulsions.

Emulsification of TCFs has been proposed to control the reactivity of this highly reactive chemical system, and the emulsified TCFs system has been applied successfully in several applications to remove organic deposits, hydrate blockages and filtercake removal [51,52]. The TCFs are currently considered for various field application including in-situ generation of foamed fracturing fluids. Controlling the reactivity of TCFs ensures that chemical reactions are optimized, minimizing waste and maximizing efficiency, while the utilization of foamed fracturing fluids conserves water resources and reduces the overall environmental footprint of industrial processes. Both of these aspects play a crucial role in achieving sustainability goals by reducing resource consumption and environmental impact. To the best of the author's knowledge, no study has been conducted to investigate the emulsification of TCFs. In this study, we carried out a detailed investigation of the emulsification of TCFs using three emulsifiers.

4.2 Experimental Work

4.2.1 Materials

Sodium nitrite and ammonium chloride used in this study were ACS reagent grades obtained from Honeywell and Fisher Scientific, respectively. Deionized water (DI) with a resistivity of 18.2 M Ω ·cm was used to prepare the salt solutions and bentonite suspension systems. An ACS-grade reagent sodium hydroxide obtained from Fisher Scientific was prepared at 6M and used to adjust the pH of NaNO₂/NH₄Cl solutions. Concentrated HCl acid, an ACS reagent grade obtained from Fisher Scientific, was used to adjust the pH of bentonite colloidal systems. Three emulsifier systems, referred to as Emulsifier-A, Emulsifier-B, and Emulsifier-C, with compositions given in Table 4.2, were obtained from local providers and used in this study to prepare TCFs in diesel emulsions. A commercial diesel with 0.78 g/cm³ density was used in the preparation of emulsions of interest. A

commercial bentonite sample, used in drilling fluids, was used in the zeta potential measurements of bentonite suspensions with/without emulsifiers.

Table 4.2-Composition of the emulsifiers used in this study

Emulsifier-A		Emulsifier-B		Emulsifier-C	
Component	Function	Component	Function	Component	Function
Tall oil fatty acid amine	Surfactant	Amines, tallow alkyl, acetates	Surfactant	Fatty Acid amine	Surfactant
Amine Coco-alkyl Acetate		Heavy aromatic naphtha		Ethylene glycol	Cosurfactant
Ethylene Glycol	Cosurfactant	Ethane-1,2-diol	Cosurfactant	Heavy aromatic petroleum naphtha	To reduce an emulsion viscosity
Acetic acid		Acetic acid 1,2,4 trimethylbenzene		Acetic acid Naphthalene	

4.2.2 Equipment and Methodology

A summary of the experimental design performed in this study including different tests and analyses is given in in Figure 4.1.

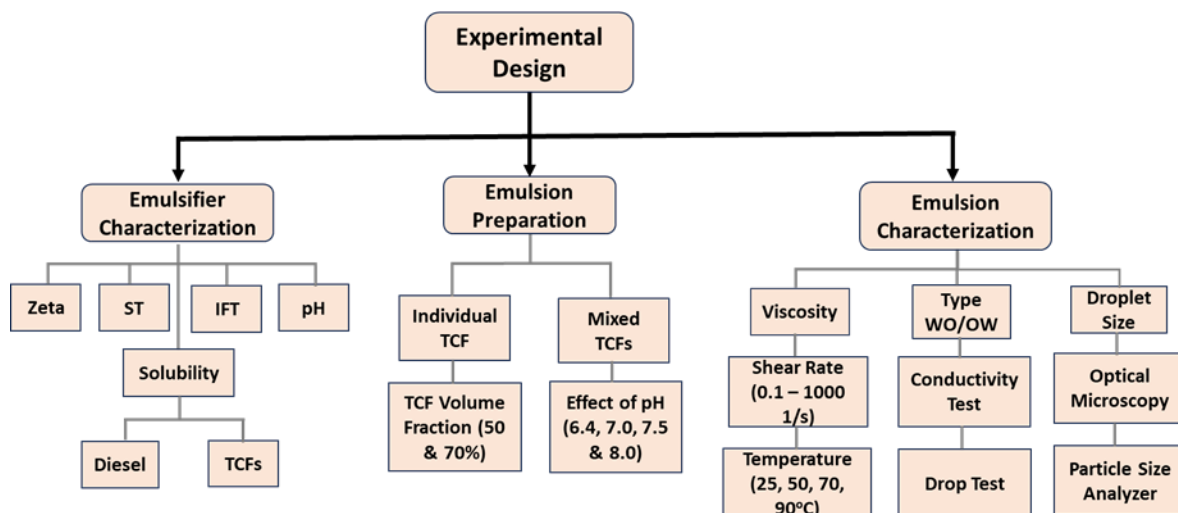


Figure 4. 1- A chart including the experimental design

4.2.2 Preparation of Emulsions.

A high shear rate Silverson- L5M-A model mixer was used to prepare TCFs in diesel emulsions. TCFs-in-oil emulsions at a ratio 70/30 vol% were prepared by first dissolving the emulsifier at a concentration of 1 vol% in diesel and allowing it enough time to mix thoroughly by agitating the mixture at around 3,000 rpm for 2 min. Subsequently, the aqueous thermochemical phase was gradually introduced to the hydrocarbon phase of diesel, and the solutions were mixed at a high speed of 10,000 rpm for 10 minutes to ensure the formation of emulsions.

4.2.3 Conductivity Measurement

The conductivity of TCFs in diesel emulsions was measured following the preparation using an EUTECH CyberScan PCD650, which can provide concurrent measurement of conductivity, pH, dissolved oxygen, and temperature, all at the same time. It has a conductivity measuring range from 0 to up to 500 mS/cm. The conductivity tests were conducted to ensure formation of water-in-oil emulsions.

4.2.4 Viscosity Measurement

Anton Paar RheoCompass viscometer was used to measure viscosities of prepared TCFs/diesel emulsions as a function of shear rate (0.1 to $1,000\text{ s}^{-1}$) and at four different temperatures (25 , 50 , 70 , and 90°C) over consecutive cycles. The sample volume used in the viscosity measurement was 15 mL .

4.2.4 Droplet size Distributions and Optical Microscopy

The prepared emulsions were observed using an optical microscope (BH-2; Olympus, Tokyo, Japan), and image captures were obtained for each emulsion. Also, Anton Paar Analyzer 500, with a measurement range of 0.3 to $10\text{ }\mu\text{m}$, was used to measure the droplet size distributions of emulsions prepared in this study. The measurement principle relies on the dynamic light scattering (DLS) technique.

4.2.5 Surface and Interfacial Tension Measurement

To measure the surface tension of diesel and TCFs incorporating emulsifiers, as well as the IFT of the oil-water interface we used a drop shape analysis on instrument Drop Shape Analyzer (DSA-100) and software DSA1 (Krüss GmbH, Germany). The technique involves developing a pendant water drop on the tip of a needle that is submerged in the oily phase. The programme automatically recognises the drop profile and fits it using the Laplace capillarity equation to determine the IFT. The surface tension can be determined also from the image of the drop in air using drop shape analysis.

4.2.6 pH Measurement

A Thermo Scientific™ Orion Star™ A111 Benchtop pH Meter was used to measure pH values of TCFs and bentonite suspension systems with and without emulsifiers.

4.2.7 Zeta-Potential Measurement

Zeta potential was measured for emulsifier samples in bentonite suspensions using Anton-Paar-Particle Size Analyzer (Litesizer 500). The bentonite concentration used was 0.2 wt%, and the emulsifier concentration was 1 vol%. Two methods were deployed to assess this study's ionic charge of emulsifiers. The first method involved aging the bentonite sample at 0.2 wt% in DI water for 24 hours, and emulsifiers were added individually to a sample of bentonite suspension. The second method involved the addition of the emulsifiers initially into the DI water, and then bentonite samples at 0.2 wt% were added to those solutions and aged at room temperature for 24 hours. The samples were mixed using an ultrasonic bath before and after aging, centrifuged at 3,000 rpm for 5 minutes, and portions of the samples were then taken for zeta potential measurement.

4.3 Results and Discussion

4.3.1 Characterization of Emulsifier Systems

The emulsifiers used in this study were characterized by their acidity/basicity, ionic charge, and partitioning in aqueous and hydrocarbon phases. As depicted in Table 4.2, all emulsifiers contain both a surfactant and cosurfactant. The effect of adding 1 vol% emulsifier into deionized water, 4M NH_4Cl , and 4M NaNO_2 on the pH value of obtained solutions is given in Table 4.3. The results for DI water showed that Emulsifier-C exhibited the highest acidity with a pH value of 1.62, followed by Emulsifier-B with a pH value of 4.74, while Emulsifier-A was basic with a pH value of 9.51. The relatively high pH value of 1 vol% of Emulsifier-A is likely attributable to the presence of amine coco-alkyl acetate. On the contrary, the low pH of Emulsifier-C is associated with the presence of acetic acid. Emulsifier-B exhibits a pH value of 4.74, attributed to the inclusion of a buffer system (acetic acid/acetates). The impact of emulsifiers on pH values of 4M NH_4Cl and 4M NaNO_2 was less significant, but the same trend of acidity for Emulsifier-B and C and basicity for Emulsifier-A were maintained.

Table 4. 3- pH values of 1 vol% of emulsifier in deionized water and 4M of each TCF

Fluid Type	Without Emulsifier	Emulsifier-A	Emulsifier-B	Emulsifier-C
Diesel	6	-	-	-
DI water	6.5	9.51	4.74	1.62
4M NH ₄ Cl	4.44	6.8	5.19	3.2
4M NaNO ₂	8.10	9.1	5.7	5.3

The conductivity of diesel, emulsifiers and the TCFs at 4M is depicted in Table 4.4. Despite the higher salinity of 4M NaNO₂ (275.98 g/L) compared to 4M NH₄Cl (213.96 g/L), the conductivity of the latter (370.50 mS/cm) surpasses that of the former salt (197.10 mS/cm). The higher conductivity of NH₄Cl might be attributed to the greater polarity compared to that of NaNO₂. Emulsifier-A is not conductive, while Emulsifier-B has the highest conductivity of 660.90 mS/cm followed by the Emulsifier-B which has a conductivity of 9.35 mS/cm. As expected, diesel has a conductivity of zero.

Table 4. 4-Conductivity of diesel, emulsifiers and 4M NH₄Cl and 4M NaNO₂

Fluid	Diesel	4M NH ₄ Cl	4M NaNO ₂	Emulsifier- A	Emulsifier- B	Emulsifier- C
Conductivity, mS/cm	0	370.50	197.10	0	660.90	9.35

The results of zeta potential measurements conducted for the bentonite suspension with and without the emulsifiers are depicted in Table 4.5. The pH value of the colloidal system has its impact on the generated zeta-potential of bentonite suspension as reported by Mekhamer, 2010.¹⁰¹ The low pH value of the bentonite colloidal system tends to shift the zeta potential toward more positive while the high pH tends to shift the zeta potential

toward more negative. Even though the pH value of Emulsifier-C is low (1.48 and 2.18), it shifted the zeta potential of the bentonite toward more negative, indicating that Emulsifier-C is negatively charged. Emulsifier-B, with a pH value on the slightly acidic side (pH = 4.13 and 4.17), shifted the bentonite zeta potential from the negative to the strongly positive indicating that Emulsifier-B is positively charged. Emulsifier-A, which has a basic pH, is expected to shift the zeta potential towards a more negative; nevertheless, this modest shift suggests that Emulsifier-A is likely to be of a non-ionic nature.

Table 4.5--Zeta potential and pH values of emulsifiers at 1 vol% in bentonite suspension systems

	pH	Zeta Potential (mV)	Conductivity (mS/cm)	Distribution peak (mV)
The emulsifiers were added to the suspension bentonite systems. Aging time = 24 hours				
DI water	9.77	-39.79	0.329	-34.81
Emulsifier-A	10.83	-40.73	0.087	-40.73
Emulsifier-B	4.17	76.43	0.356	68.15
Emulsifier-C	1.48	-67.06	10.72	-60.56
The bentonite samples were added to deionized water including the emulsifiers. Aging time = 24 hours				
DI water	9.54	-36.56	0.079	-33.98
Emulsifier-A	9.64	-43.23	0.087	-40.73
Emulsifier-B	4.13	96.12	0.265	87.68
Emulsifier-C	2.18	-80.14	1.106	-82.96

The solubility of emulsifiers investigated in this study in an aqueous phase (4M TCFs) and a hydrocarbon phase (diesel) was assessed by mixing these emulsifiers at 1 vol% in these phases separately. The partitioning of these emulsifiers in the diesel was significantly greater than that in the 4M TCFs. The preferential solubility of these emulsifiers in the oil

phase makes them suitable candidate emulsifiers for the formation of water-in-oil emulsions [101].

The effect of examined emulsifiers on the surface tension of water and diesel, and IFT was investigated as shown in Figure 4.2. The addition of emulsifiers to diesel at 1 vol% had almost no effect on the surface tension of diesel. In contrast, the addition of these emulsifiers to the DI water was able to reduce its surface tension from 72.27 to as low as 8 mN/m for Emulsifier-C. The ST of 4M NH₄Cl and 4M NaNO₂ were 74.39 and 71.19 mN/m, respectively.

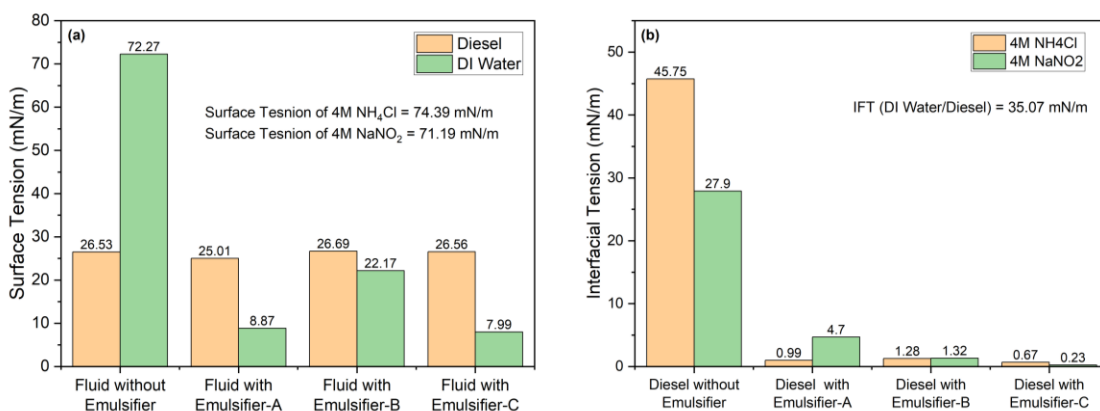


Figure 4.2- Impact of emulsifier (1 vol%) on (a) surface tension of DI water and diesel, and (b) IFT between diesel and TCFs

The interfacial tension between the two liquids given by Equation 3 [102] can give insight about the role of the IFT on the emulsion stability.

$$\gamma = \frac{(\rho_2 - \rho_1)\omega^2 D^3}{32} \dots \dots \dots (3)$$

In this context, ρ_1 and ρ_2 stand for the density of the dispersed and continuous phases, respectively. ω represents the angular velocity of rotation, and D indicates the maximum diameter of the stable droplet at equilibrium. As indicated by the equation, there is a clear correlation between the interfacial tension (IFT) and droplet size; as the IFT decreases, the

size of the emulsion droplets also diminishes. It is widely recognized that emulsions characterized by smaller droplet sizes tend to be more stable compared to those with larger droplets.

The IFT of the diesel containing the examined emulsifiers and the TCFs at 4M were measured at an ambient temperature of 24°C. The IFT results obtained for diesel with DI water, 4M NH₄Cl, and 4M NaNO₂ are shown in Figure 4.2. The IFT between diesel and DI water was 35.07 mN/m and was found to increase when diesel was mixed with 4M NH₄Cl (45.75 mN/m). Conversely, when diesel was combined with 4M NaNO₂, the IFT decreased to 27.9 mN/m. Even though the density difference is more for diesel and 4M NaNO₂ than for diesel and 4M NH₄Cl, the first system has lower IFT. Hence, the IFT is proportional to the difference in liquid-liquid densities ($\gamma \propto \Delta\rho$). In addition, nitrite ions are polar, while ammonium ions are non-polar. Based on these factors, it is expected that there is some interaction between nitrite ions and diesel components, which results in a lower IFT.

Overall, the presence of emulsifiers in diesel tended to reduce the IFT significantly, indicating that these emulsifiers can be used as emulsifiers for TCFs and diesel. Hence, one of the main properties of the emulsifiers is to reduce the IFT between the two immiscible phases. The IFT between Emulsifier-A and NH₄Cl solution was much less than that with NaNO₂ solution, while the opposite is observed for Emulsifier-C. The IFTs for NH₄Cl and NaNO₂ solutions, including Emulsifier-B with diesel, were comparable.

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4.3.1.1 Emulsion Type

A conductivity test was utilized to identify the emulsion's continuous (external) phase for TCF/diesel emulsions. This test relies on the observation that the aqueous phase conducts electricity, whereas the oily phase does not, and the emulsion's continuous phase predominantly influences the emulsion's electrical conductivity. As given in Table 4.6, the

conductivity for all individual emulsified 4M TCFs with emulsifiers at 1 vol% were zeroes to nearly zeroes, indicating that all emulsions were water-in-oil type. The conductivity was zero for the same emulsion prepared with emulsifiers at 5 vol%.

Table 4. 6- Conductivity of Individual 70% emulsified 4M TCFs in Diesel with 1% emulsifier

Emulsifier Name/TCFs Type	Conductivity, $\mu\text{S}/\text{cm}$			
	Without Emulsifier	Emulsifier-A	Emulsifier-B	Emulsifier-C
DI Water				
Diesel				
4M NH_4Cl		0.72	0.19	0.15
4M NaNO_2		0.43	7.55	0.00

An emulsion drop test was used to identify the emulsion's continuous (external) phase to support the conductivity test. In this test, a droplet of the formed emulsion was placed in the TCFs sample. If the placed droplet was found to disperse, then the external phase is the same as the fluid used for the test and vice versa. Figure 4.3 shows some images of TCFs/diesel emulsions droplets in TCFs, which confirmed that they were WO emulsions.¹⁰³ The conductivity of 4M TCFs in diesel with 5% emulsifier was zero for all examined emulsifiers. This indicates that increasing emulsifiers concentration will improve WO emulsion characteristics.

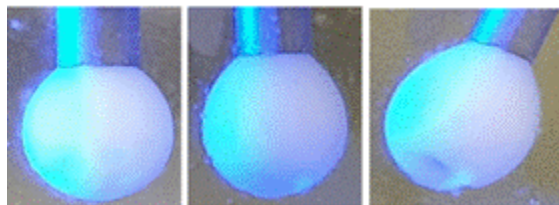


Figure 4.3- Drop tests in water for TCFs/diesel emissions.

4.3.1.2 Individual Emulsification of TCFs.

The first batch of experimental work included emulsification of NH_4Cl and NaNO_2 in diesel as individual solutions using the three emulsifiers of interest in this study.

4.3.1.3 Viscosity of TCFs/Diesel Emulsions with 1% Emulsifier.

The viscosity is primarily influenced by the viscosity of either the dispersed phase or the continuous phase, the distribution of particle sizes, and the characteristics of the emulsifying agents.¹⁰⁴ Sodium nitrite (NaNO_2) and ammonium chloride (NH_4Cl) at an equimolar concentration of 4M were individually emulsified in diesel to form W/O emulsions using three emulsifiers (Emulsifier-A, Emulsifier-B, and Emulsifier-C) at a concentration of 1 vol%. Figures 4.4 and 4.5 show viscosity and optical microscopy of individual emulsified 4M NH_4Cl and NaNO_2 in diesel with 1% Emulsifier-A, Emulsifier-B, and Emulsifier-C. All emulsions exhibited the characteristics of pseudoplastic fluids (shear thinning behavior), and their viscosity decreased as temperatures increased. The apparent viscosity of NH_4Cl /diesel emulsions prepared using Emulsifier-A and Emulsifier-B was higher than the corresponding NaNO_2 /diesel emulsions. The IFT measurements (Figure 4.2) support these findings for Emulsifier-A (lower IFT with NH_4Cl than NaNO_2). In contrast, the apparent viscosity of NH_4Cl /diesel emulsion prepared using Emulsifier-C was less than the corresponding NaNO_2 /diesel emulsion, which agrees with IFT measurements; hence, lower IFT with NaNO_2 (Figure 4.2). These results agree with the optical microscopy images, which showed bigger droplet sizes for NaNO_2 /diesel emulsions prepared using Emulsifier-A and Emulsifier-B compared to the corresponding NH_4Cl /diesel emulsions. In contrast, the opposite was observed for Emulsifier-C (Figure 4.5) solution compared to that with NaNO_2 solution.

The emulsion with the highest viscosity among NaNO_2 /diesel emulsions was the one prepared using Emulsifier-A, whereas, for NH_4Cl /diesel emulsions, the highest viscosity was achieved with Emulsifier-B. A significant reduction in viscosity at 70 and 90°C was

observed for all emulsion systems, and some experienced emulsion phase separation, as with the case for 4M NaNO_2 in diesel emulsion prepared using Emulsifier-B.

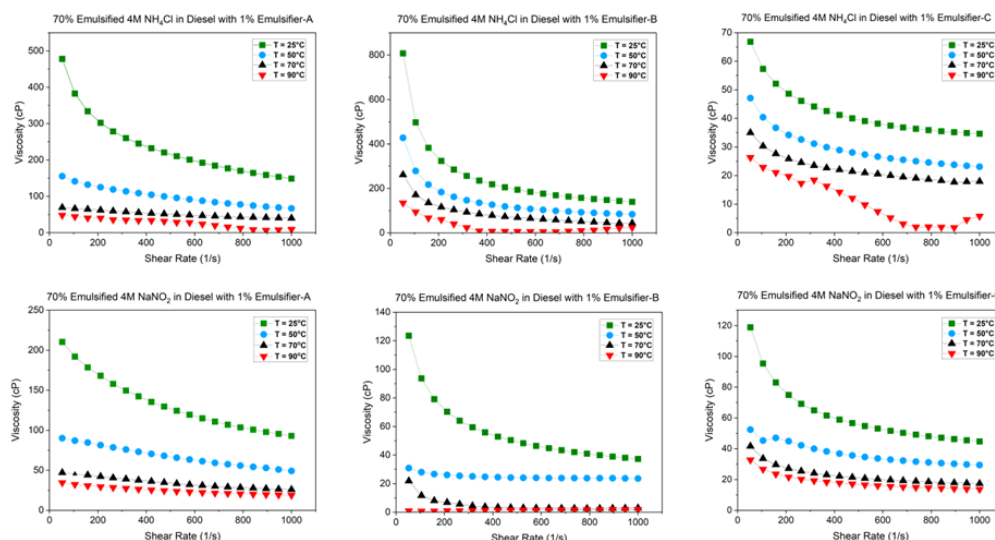


Figure 4.4-Viscosity of 70% emulsified NH_4Cl and NaNO_2 in diesel with 1% emulsifier

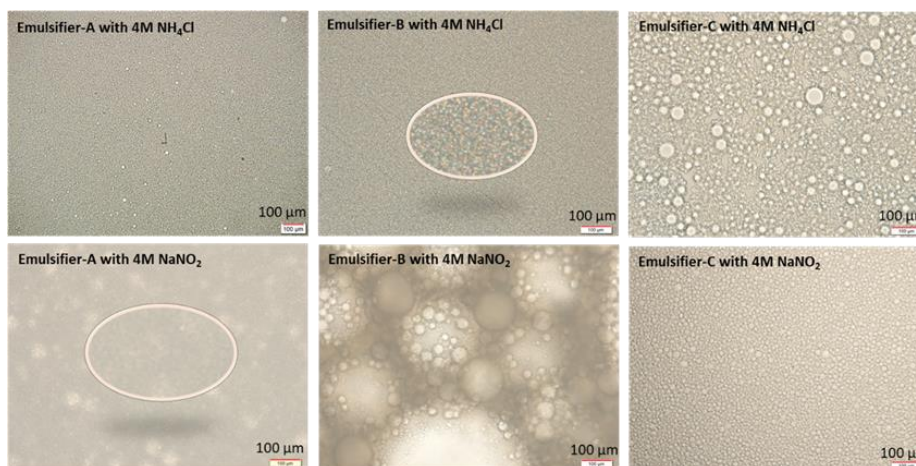


Figure 4.5- Optical microscopy of 70% emulsified NH_4Cl and NaNO_2 in diesel with 1% emulsifier

Droplet size distributions of 70% emulsified NH_4Cl and NaNO_2 in diesel with 1% of Emulsifier-A, Emulsifier-B, and Emulsifier-C, are shown in Figure 4.6. Multiple peaks of droplet sizes with varying intensities can be seen in all emulsion plots presented in Figure 4.6. The droplet size distributions and polydispersity index, PI, (Figure 4.7) indicate that

all emulsion systems are heterogeneous. To have a monodisperse system, PI value should be less than 5%, while the system with $PI > 70\%$ is extremely heterogeneous (ISO standards ISO 22,412:2017 and ISO 22,412:2017). The PIs obtained for these emulsion as shown in Figure 7 indicate that they are in the middle range of heterogeneity.

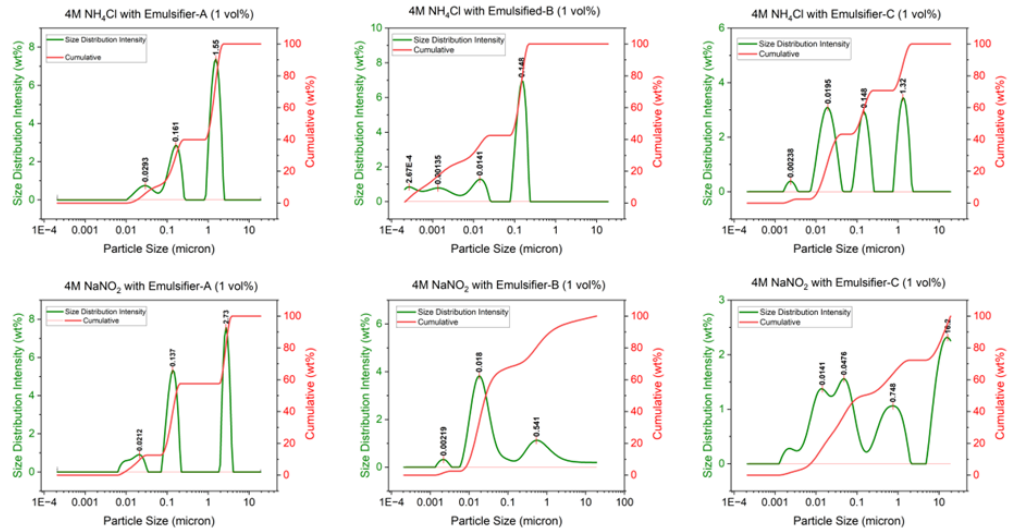


Figure 4.6-Droplet size distributions of 70% emulsified NH_4Cl and NaNO_2 in diesel with 1% emulsifier

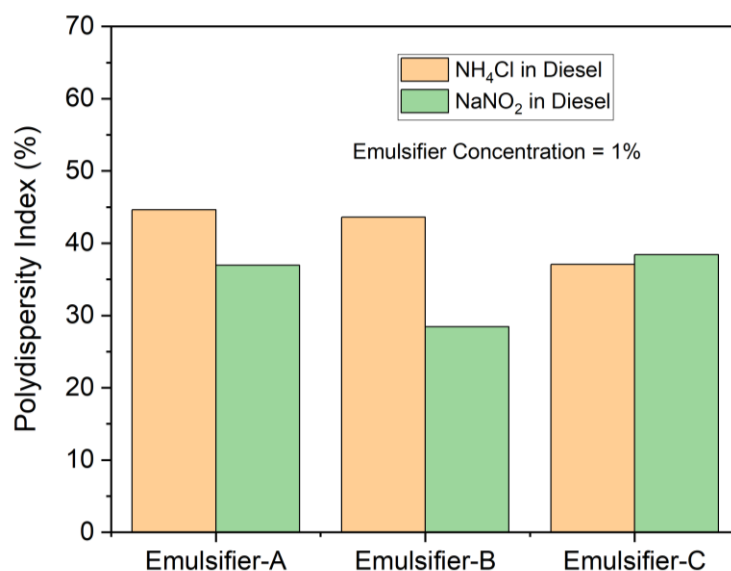


Figure 4.7-Polydispersity index of 4M NH₄Cl and 4M NaNO₂ in diesel emulsion with 1% emulsifier

4.3.1.4 Effect of Emulsifier Concentration

The emulsifier concentration was increased from 1 to 5 vol% to assess the impact of emulsifier concentration on the properties of TCFs in diesel emulsions. The viscosity, optical microscopy, and droplet size distributions of individual emulsified TCFs with 5% emulsifier are shown in Figures 4.8-4.10. The viscosity obtained with 5% for all emulsifiers was higher than those obtained with 1% emulsifiers (Figure 4.4 and Figure 4.8). However, NaNO₂ emulsion formed using Emulsifier-B experienced a significant reduction in viscosity, and phase separation following viscosity measurements at 90°C was observed (see Figure 4.11). The same emulsion at an ambient temperature was stable, unlike that prepared using an emulsifier concentration of 1%. Overall, the results reveal that increasing the emulsifier concentration enhances emulsion stability, which agrees with the increase in emulsion viscosity.

Optical microscopy images obtained for emulsions prepared with Emulsifier-A and Emulsifier-C were too small to observe, while that prepared with Emulsifier-B was clear with bigger droplet sizes for the NaNO_2 emulsion compared with the NH_4Cl emulsion (Figure 9). The findings are consistent with the viscosity outcomes. Optical microscopy images reveal that the NaNO_2 emulsion, when prepared with Emulsifier-A, exhibited smaller droplets than the NH_4Cl emulsion, aligning with the higher viscosity observed in the NaNO_2 emulsion. Conversely, Emulsifier-B and Emulsifier-C resulted in higher viscosities for NH_4Cl emulsions, corroborating the optical microscopy images displaying smaller droplets in NH_4Cl emulsions, as depicted in Figure 4.8.

Droplet size distributions of 70% emulsified NH_4Cl and NaNO_2 in diesel with 5% Emulsifier-A, B, and C separately are shown in Figure 4.9. The NH_4Cl emulsions with 5% emulsifiers are monomodal (having only one peak), as shown in particle size distribution curves (Figure 4.10). In contrast, NaNO_2 emulsions with 5% emulsifiers are identified with bimodal peaks. The polydispersity indexes for these emulsions are shown in Figure 4.12, indicating they are in the middle range of heterogeneity.

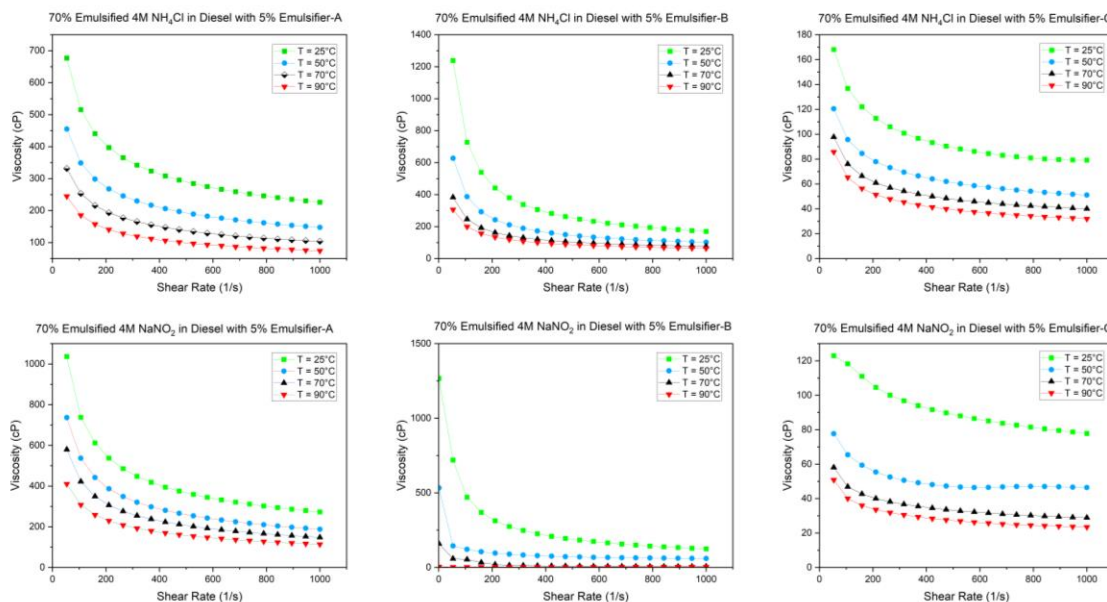


Figure 4.8-Viscosity of 70% emulsified NH_4Cl and NaNO_2 in diesel with 5% emulsifier

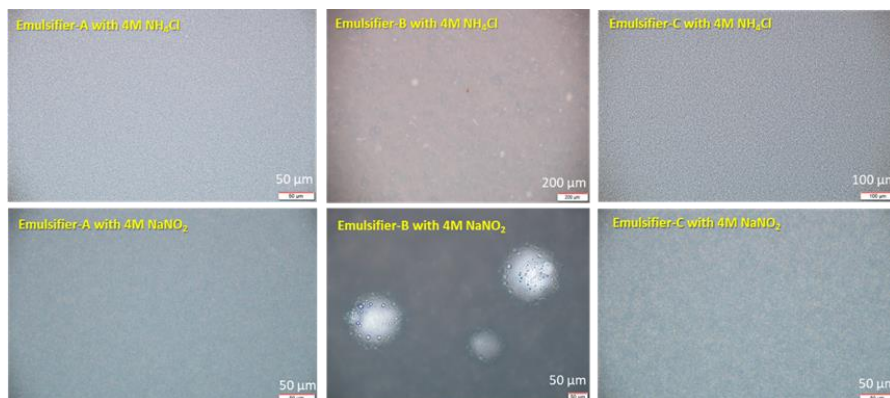


Figure 4.9-Optical microscopy of 70% emulsified 4M TCFs in diesel with 5% emulsifier

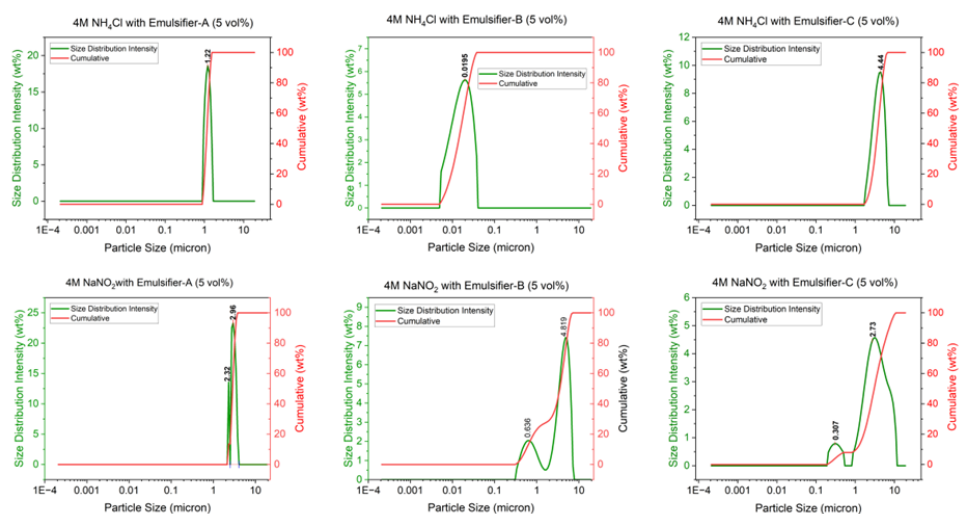


Figure 4.10-Droplet size distribution of 70% emulsified NH_4Cl and NaNO_2 in diesel with 5% emulsifier



Figure 4.11-Photos of individual emulsified 70% 4M TCFs in diesel with 5% emulsifier after viscosity measurement cycles at temperatures of 25 to 90°C

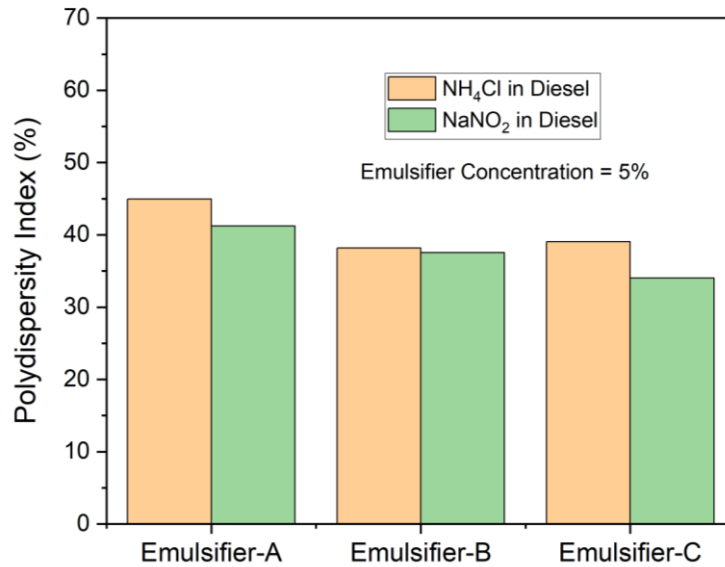


Figure 4.12-Polydispersity index of 70% 4M NH₄Cl and 4M NaNO₂ in diesel with 5% emulsifier

4.3.2 Models for Emulsion Viscosity

Emulsified 70% TCFs in diesel were found to have the characteristics of pseudoplastic fluids for all examined emulsifiers. Log plots of the shear stress versus shear rate for 70% emulsions with 1% emulsifier follow the power-law model, as shown in Figure 4.13. The viscosity, especially at the shear rate range of 50 to 1,000 s⁻¹, fits the power-law model very well. The power-law model in the below equation is commonly used to characterize the general viscosity behavior of non-Newtonian fluids, such as polymers, concerning temperature and shear rate change.

$$\mu_a = K\dot{\gamma}^{n-1} \dots \dots \dots (4)$$

Where μ_a is the apparent viscosity, $\dot{\gamma}$ is the shear rate, K is the consistency index and n are the power-law index. Emulsions with Emulsifier-B could not maintain power-law behavior at high temperatures of 70 and 90°C for NaNO₂ emulsion and at 90°C for NH₄Cl emulsion due to emulsion stability problems. Also, NH₄Cl emulsions prepared using Emulsifier-A

and Emulsifier-C failed to maintain power-law behavior at 90 °C due to emulsion stability problems. Power-law parameters, including power-law index, n , and consistency index, K , are calculated for each emulsion system of NH_4Cl and NaNO_2 . The power-law index remained relatively constant across the temperature range investigated for the Emulsifier-A and Emulsifier-C emulsion systems. This suggests that their shear-thinning behavior was consistent, indicating that temperature did not influence any alteration in their shear-thinning behavior. However, the power-law index for Emulsifier-B emulsion systems decreased as temperature increased. The consistency index was found to decrease as the temperature increased for all examined emulsion systems which is consistent with the behaviour of non-Newtonian fluids. It is observed that at 90 °C and at high shear rates of > 600 and 200 s^{-1} emulsions with Emulsifier-A and Emulsifier-C, respectively deviated from linearity which might be due to the shear induced emulsion destabilization [103].

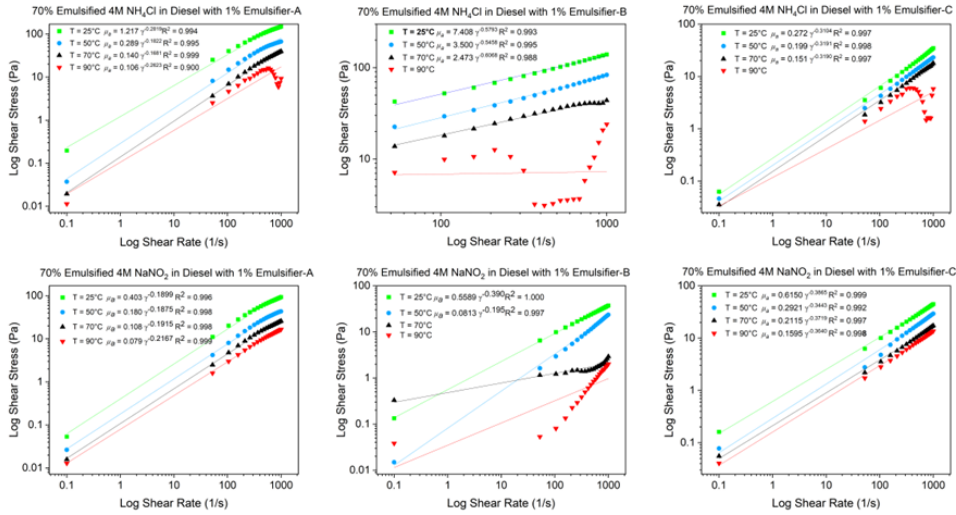


Figure 4.13-Shear stress versus shear rate for individual emulsion of 4M NH_4Cl and 4M NaNO_2 in diesel with 1% emulsifier

Table 4.7-Power-law parameters for 70% emulsified 4M NH₄Cl in diesel with 1% surfactant

Temperature (°C)	Power-Law Index (<i>n</i>)			Consistency Index (<i>K</i>) g/(cm·s ²⁻ⁿ)		
	Surfactant- A	Surfactant- B	Surfactant- C	Surfactant- A	Surfactant- B	Surfactant- C
25	0.7181	0.86973	0.68957	1.2166	0.6253	0.2720
50	0.81774	0.54407	0.68086	0.2885	0.0414	0.1987
70	0.83188	-	0.68097	0.1400	-	0.1509
90	0.73769	-	-	0.1061	-	-

Table 4.8-Power-law parameters for 70% emulsified 4M NaNO₂ in diesel with 1% surfactant

Temperature (°C)	Power-Law Index (<i>n</i>)			Consistency Index (<i>K</i>) g/(cm·s ²⁻ⁿ)		
	Surfactant- A	Surfactant- B	Surfactant- C	Surfactant- A	Surfactant- B	Surfactant- C
25	0.81012	0.59145	0.61348	0.4033	0.6253	0.6150
50	0.81249	0.91564	0.65567	0.1801	0.0414	0.2921
70	0.80848	-	0.68097	0.1076	-	0.2115
90	0.78327	-	0.63598	0.0789	-	0.1595

Figure 4.14 shows the shear stress versus shear rate log plots for 70% 4M NH₄Cl and 4M NaNO₂ emulsion with emulsifier concentrations of 5%. The plots show that all emulsion systems follow the power law behavior except some of the Emulsifier-B emulsion systems at 90°C for NH₄Cl emulsion and at 70 and 90 °C for the NaNO₂ emulsion system. Table 4.8 and 4.9 give the power-law parameters for the 70% emulsions prepared using an emulsifier concentration of 5% for NH₄Cl and NaNO₂ emulsion systems, respectively.

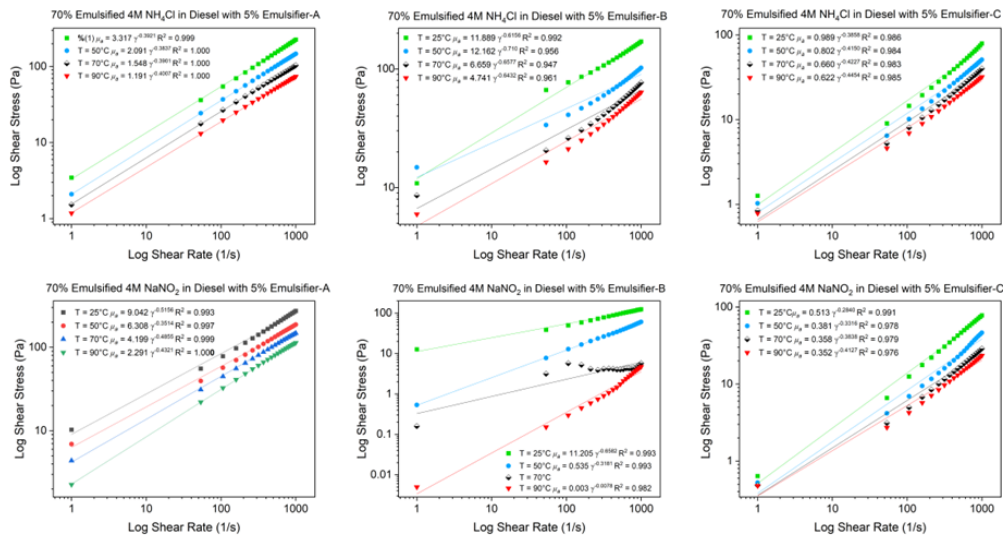


Figure 4.14-Shear stress versus shear rate for individual emulsion of 4M NH_4Cl and 4M NaNO_2 in diesel with 5% emulsifier

Tables 4.10 and 4.11 give the power-law parameters for the 70% emulsions prepared using a surfactant concentration of 5% for NH_4Cl and NaNO_2 emulsion system, respectively. The consistency index was found to decrease as a function of temperature for all emulsion systems. The power-law indices of emulsions with Emulsifier-A and Emulsifier-C were found to be nearly constant as a function of temperature indicating that these emulsions maintained the same shear thinning behaviour throughout the examined temperatures. For Emulsifier-B NaNO_2 emulsion system, the power-law index was found to increase as function of temperature indicating that temperature influenced shear thinning behaviour of this emulsion system and thus its ultimate stability. For 4M NH_4Cl emulsion system with Emulsifier-B, the variation in power-law index was very small indicating that increasing surfactant concentration to 5% help to enhance emulsion stability. Emulsions prepared using Emulsifier-C experienced small reduction in in the power-law index as a function of temperature indicating of little impact of temperature on emulsion stability.

Table 4.9-Power-law parameters for 70% emulsified 4M NH₄Cl in diesel with 5% surfactant

Temperature (°C)	Power-Law Index (<i>n</i>)			Consistency Index (<i>K</i>) g/(cm·s ²⁻ⁿ)		
	Surfactant-A	Surfactant-B	Surfactant-C	Surfactant-A	Surfactant-B	Surfactant-C
25	0.60789	0.38454	0.61423	3.3170	11.8886	0.9888
50	0.61625	0.2896	0.58498	2.0909	12.1624	0.8018
70	0.60991	0.33231	0.57726	1.5484	6.6592	0.6599
90	0.59927	0.35682	0.55464	1.1915	4.7408	0.6221

Table 4.10-Power-law parameters for 70% emulsified 4M NaNO₂ in diesel with 5% surfactant

Temperature (°C)	Power-Law Index (<i>n</i>)			Consistency Index (<i>K</i>) g/(cm·s ²⁻ⁿ)		
	Surfactant-A	Surfactant-B	Surfactant-C	Surfactant-A	Surfactant-B	Surfactant-C
25	0.48437	0.34179	0.71598	9.0423	11.2050	0.5134
50	0.48592	0.68189	0.66842	6.3075	0.5250	0.3814
70	0.51454	-	0.61622	4.1988	-	0.3581
90	0.56785	1.00779	0.58734	2.2914	0.0034	0.3516

4.3.3 Effect of TCFs Volume Fraction

The most promising emulsifier (Emulsifier-A) was examined for the effect of TCFs volume fraction on the property of formed emulsions. In addition to the 70%, a volume fraction of 50% TCFs was considered. The comparative viscosities of 50% to 70% of NH₄Cl and NaNO₂ in diesel emulsions as a function of shear rates and temperatures are shown in

Figure 4.15. The viscosity of 50% emulsions is much less than that for 70% ones. In addition, different viscosity profiles are observed. While the 70% emulsions exhibited pseudoplastic fluids property of shear thinning, the 50% emulsions exhibited a slight shear thickening behavior from 50 to 1,000 s^{-1} . The emulsions were stable after the viscosity measurement cycles at temperatures up to 90°C, as shown in Figure 4.16. Figures 4.17 and 4.18 show the optical microscopy images and particle-sized distributions of 50% emulsions. Three distinct peaks characterize particle size distributions of 50% 4M NH_4Cl emulsion, while only two peaks are observed for 50% 4M NaNO_2 . This may indicate that NaNO_2 emulsion is less heterogeneous than NH_4Cl and may explain the slight increase in viscosity obtained for NaNO_2 emulsion.

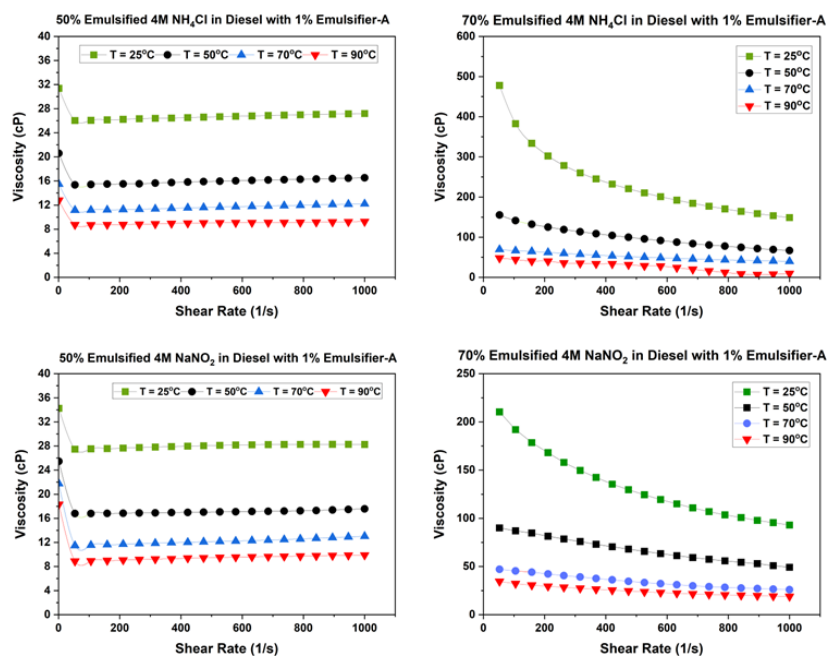


Figure 4.15-Viscosity of emulsified 50% and 70% NH_4Cl and NaNO_2 in diesel with Emulsifier-A at a concentration of 1%



Figure 4.16-Photos of individual emulsified 50% TCFs in diesel with 1% Emulsifier-A after viscosity measurement cycles of 25 to 90°C

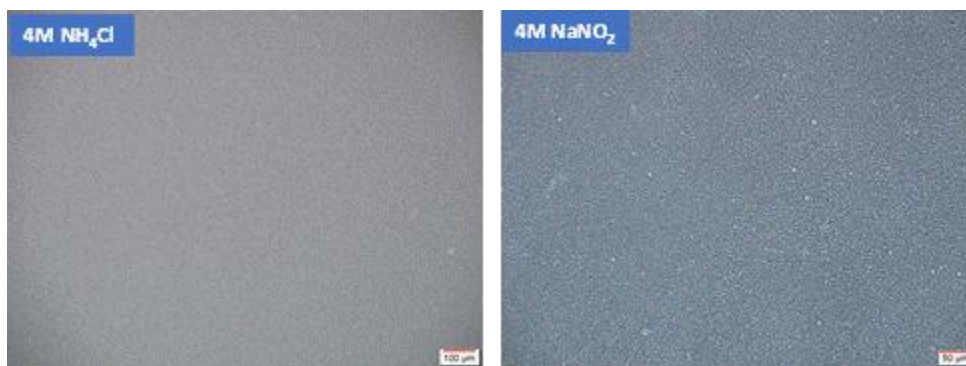


Figure 4.17-Optical microscopy of 50% individual emulsified 4M NH_4Cl and 4M NaNO_2 in diesel with Emulsifier-A

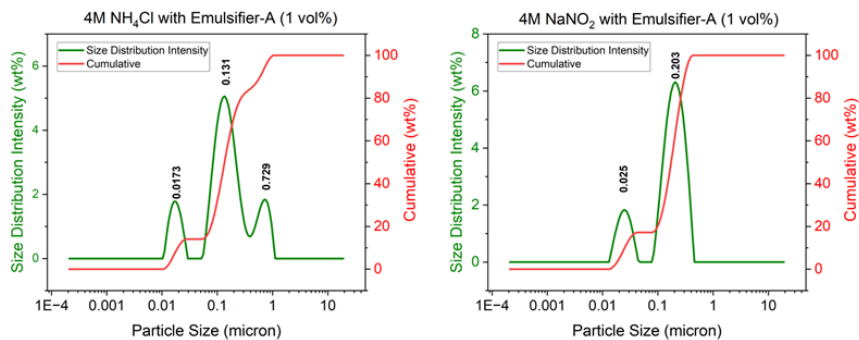


Figure 4.18-Particle size distributions of 50% individual emulsified 4M NH_4Cl and 4M NaNO_2 in diesel with Emulsifier-A

4.3.4 Emulsification of Mixed TCFs in Diesel

The potential of emulsification of the two thermochemical fluids (NH_4Cl and NaNO_2) as a mixture was examined using the three surfactants as emulsifiers. The performance of emulsions obtained was assessed at low and high temperatures. It is really challenging to emulsify chemicals that are a source of heat generation since emulsions are highly destabilized by temperature elevation. Emulsifications of mixed 4M TCFs were prepared in which a mixture of 1:1 volume ratio of equimolar NH_4Cl and NaNO_2 was added to the premixed diesel with surfactant and mixed at 10,000 rpm for 10 minutes. The effect of pH values, in the range of 6.4 to 8, on the retardation of TCFs reactivity was examined. It is generally well addressed that the impact of pH is pronounced on the formation and stability of emulsion, but it is a function of temperature, surfactant type and hydrocarbon and brine composition too [103-106].

In this study, the pH value of mixed $\text{NH}_4\text{Cl}/\text{NaNO}_2$ solution was adjusted to the required pH using concentrated HCl acid before it was mixed with diesel containing a proper emulsifier. Figure 4.18 shows the apparent viscosity obtained for a 70% 4M TCFs emulsified in diesel with Emulsifier-A at a concentration of 1% as a function of pH values. The viscosity at 25°C was found to increase as pH value increased from 6.42 to 7.54 but with more shear thinning behaviour. However, the apparent viscosity at 50°C experienced a reduction and exhibited less shear thinning upon increasing the TCFs pH values. Increasing the pH to 7.5 and above was able to improve emulsion resistance to shear at 70°C as indicated from viscosity measurements. At 90°C, all emulsions were found to experience shear-induced instability as indicated from viscosity profiles. Optical microscopy images and particle size distributions these emulsion with different pH values of TCFs are shown in Figures 4.19 and 4.20, respectively. The droplet size was to increase with increasing pH values.

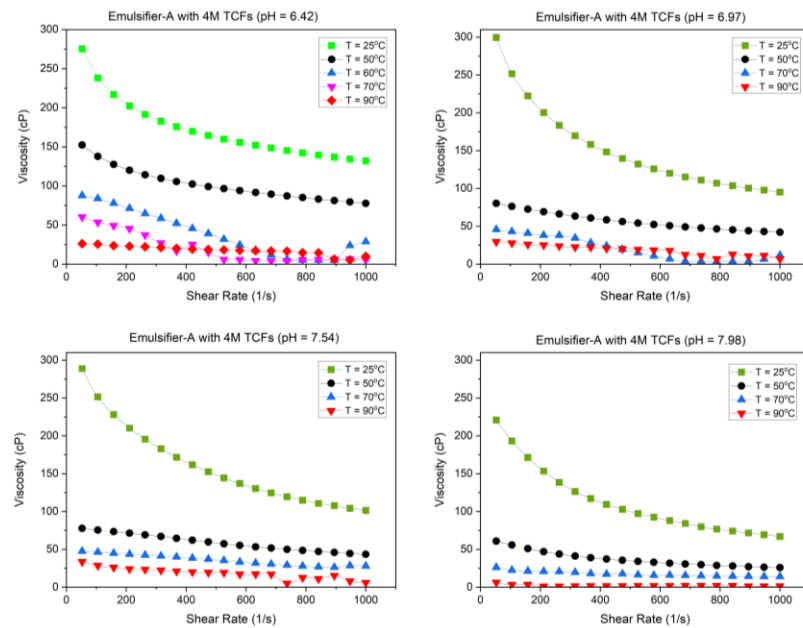


Figure 4.19-Viscosity of emulsified 4M TCFs with different pH values in diesel with1% Emulsifier-A at different temperatures and shear rates

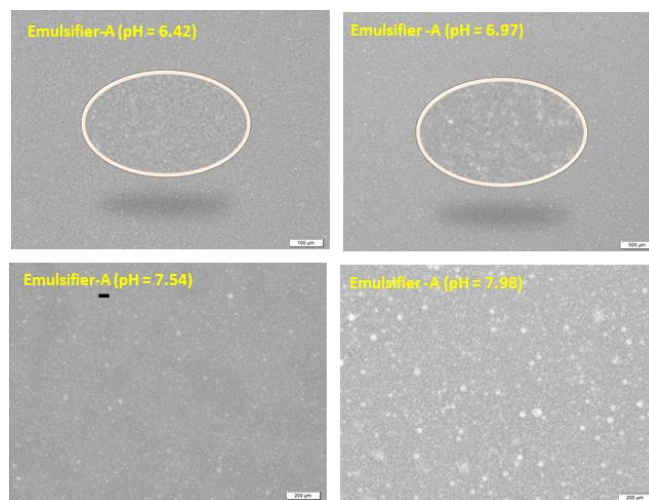


Figure 4.20-Optical microscopy of 70% emulsified 4M TCFs in diesel with Emulsifier-A (a) pH = 6.42 and (b) pH = 6.97

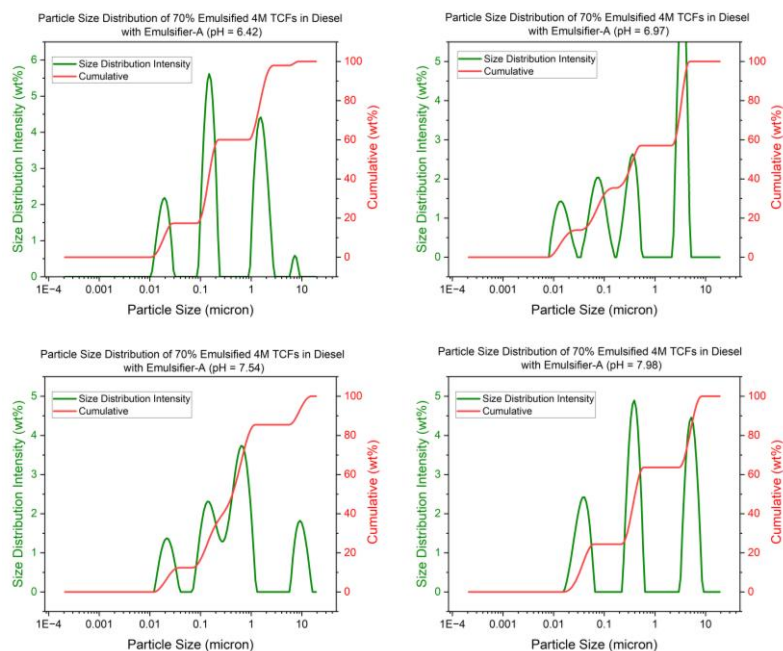


Figure 4.21-Particle size distribution of 70% 4M TCFs at different pH values in diesel with Emulsifier-A at 1 vol%

For emulsions prepared using Emulsifier -B, increasing the TCFs pH values to 7.08 and 7.54 resulted in increasing emulsion's apparent viscosity which is an indication of more stable emulsions (Figure 4.21). However, increasing the TCFs pH value to 8 resulted in decreasing the emulsion apparent viscosity compared with emulsion system without adjusting the pH value. The conductivity measurements of prepared emulsions support the viscosity results as shown in Figure 4.22. Figures 4.23 and 4.24 show the optical microscopy images and particle size distributions of these emulsions with different pH values of TCFs, respectively. Optical microscopy images show that increasing the pH resulted in decreasing of emulsion droplet sizes which is in agreement with viscosity results.

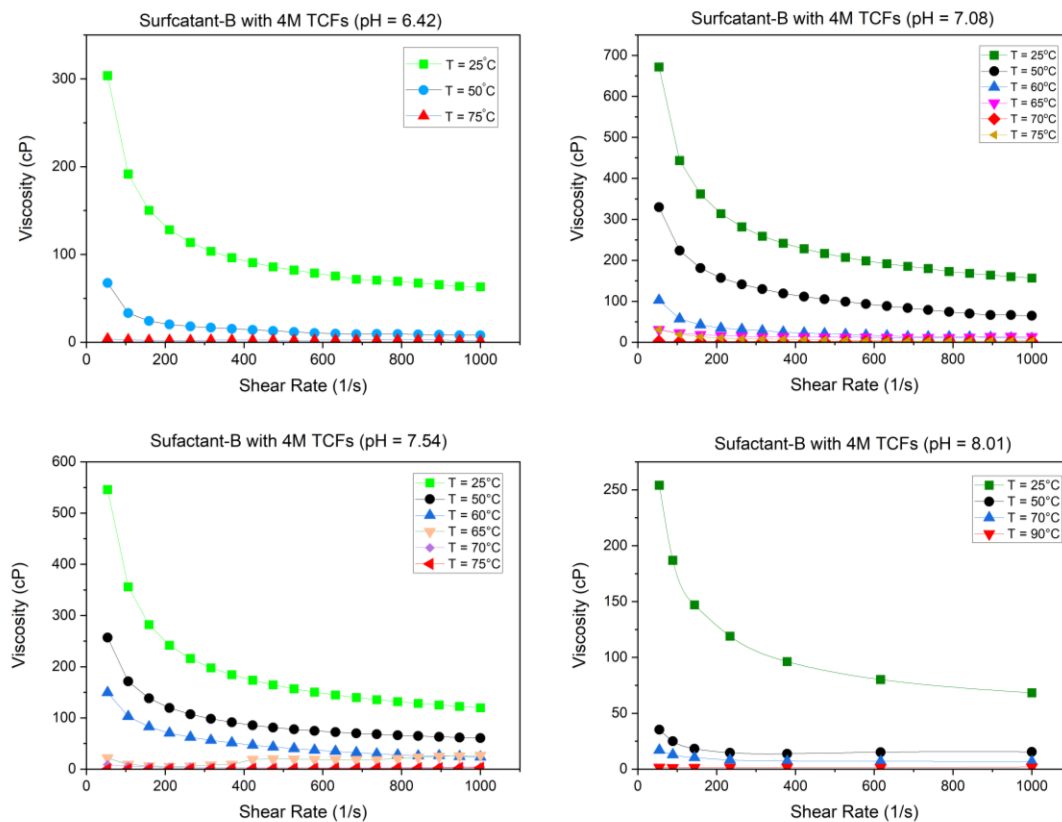


Figure 4.22-Viscosity of emulsified 4M TCFs with different pH values in diesel with 1% Emulsifier-B at different temperatures and shear rates

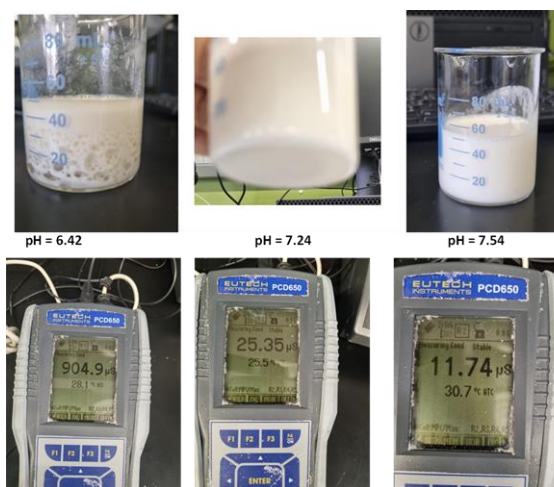


Figure 4.23-Conductivity of mixture of 4M NH_4Cl and 4M NaNO_2 with 1% Emulsifier-B

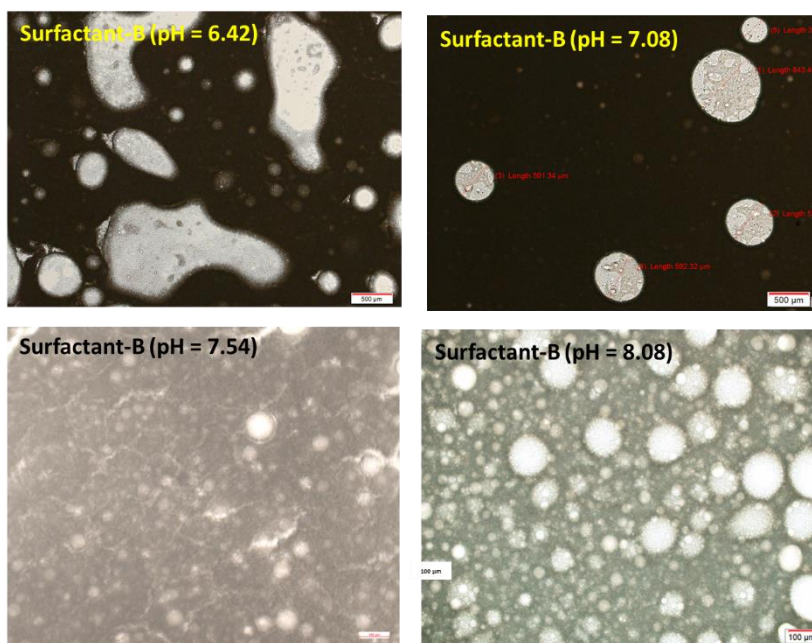


Figure 4.24-Optical microscopy of 70% emulsified 4M TCFs in diesel with Emulsifier-B at pH = 6.42, pH = 7.08, pH = 7.54 and pH = 8.01

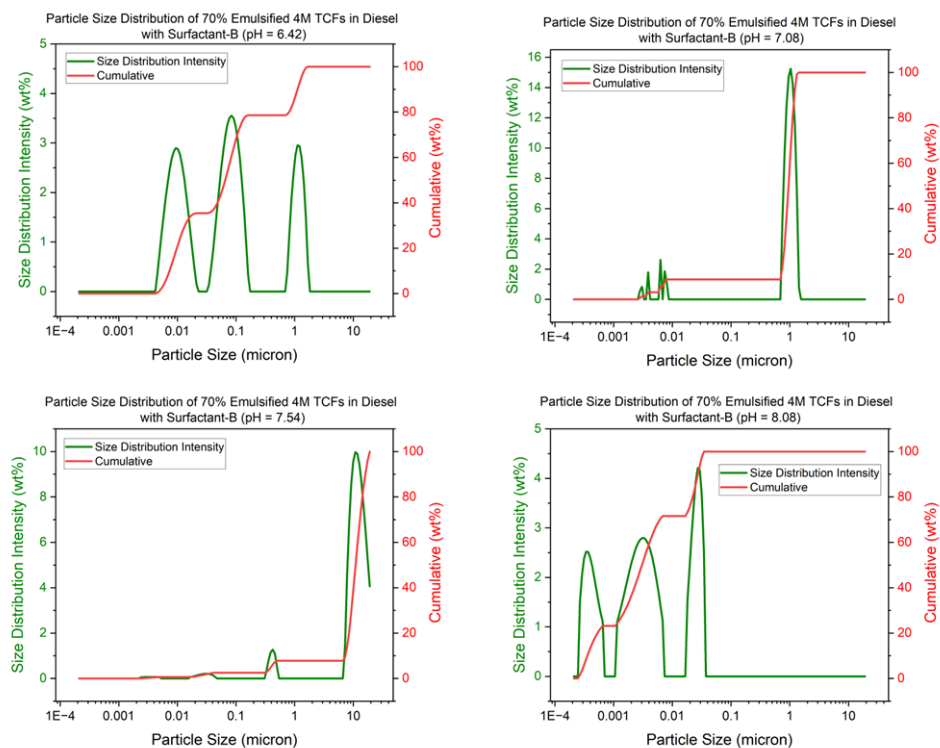


Figure 4.25-Particle size distribution of 70% 4M TCFs at different pH values in diesel with S Emulsifier-B at 1 vol%

The mixed TCFs emulsion prepared using Emulsifier -C without adjusting the pH value was found to result in generation of a reactive solution due to the acidic nature of this surfactant. Figure 4.25 shows the apparent viscosity 70% emulsified TCFs in diesel as function of TCFs pH values. The highest apparent viscosity was obtained for emulsion with a pH value of 7.66. The optical microscopy images and particle size distributions of these emulsions as function of pH values are shown in Figures 4.26 and 4.27, respectively. Unlike the optical microscopic images of emulsions with TCFs of pH values of 7.07, 7.66 and 8.08 which were taken immediately following the preparation, the microscopic image taken for emulsion with TCFs having a pH value of 6.42 was after 24 hours. Figure 4.28 shows the particle size distributions obtained.

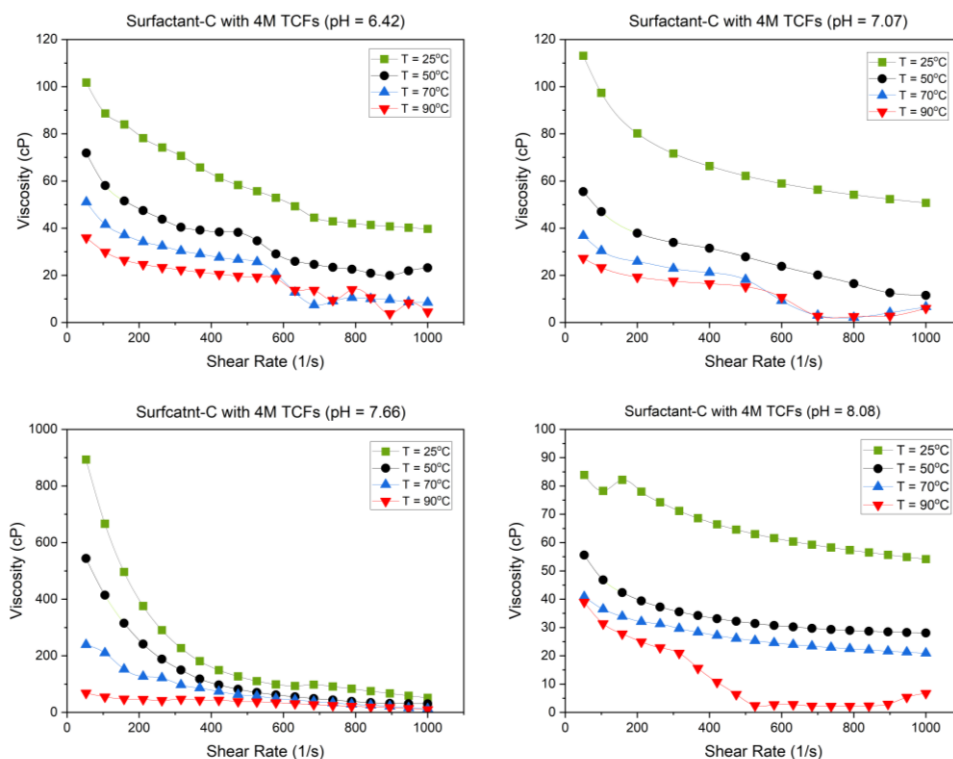


Figure 4.26-Viscosity of emulsified 4M TCFs with different pH values in diesel with 1% Emulsifier-C at different temperatures and shear rates

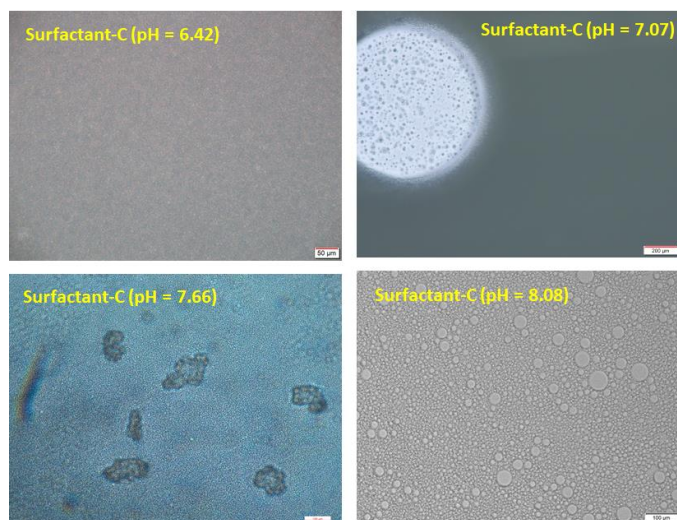


Figure 4.27-Optical microscopy of 70% emulsified 4M TCFs in diesel with Emulsifier-C at pH = 6.42, 7.07, 7.5 and 8.08

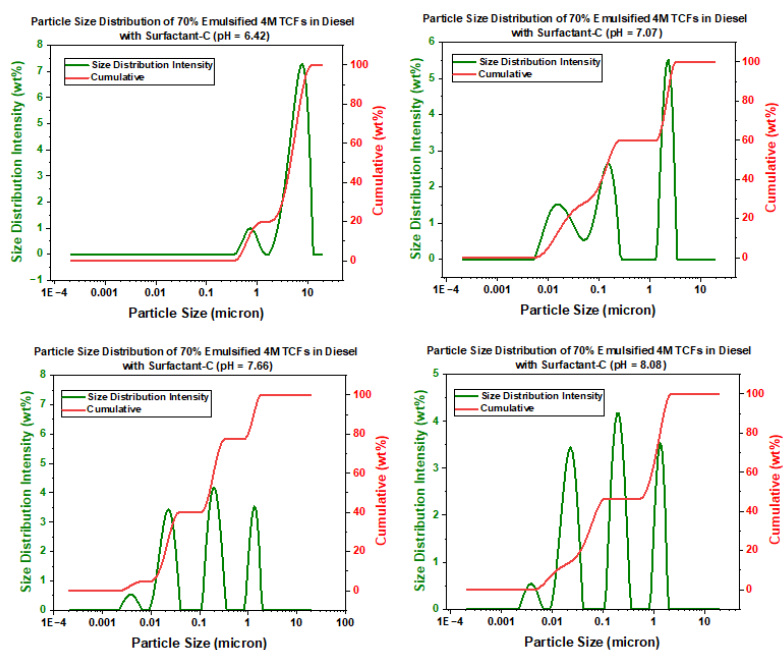


Figure 4.28-Particle size distribution of 70% emulsified 4M TCFs with Emulsifier -C: pH = 6.42, 7.07, 7.66 and 8.08.

4.4 Discussion

Emulsification is an effective technique to control the reactivity of highly reactive chemicals physically. The current work investigates the emulsification of highly reactive chemical TCFs in diesel using three different emulsifiers as emulsifiers. A comprehensive characterization of TCFs-in-diesel emulsions has been performed, including various tests, analyses, and techniques. Individual emulsification is proven to be the more appropriate scenario since the emulsification of combined TCFs components (NH_4Cl and NaNO_2) is not suitable, especially at elevated temperatures ($> 50^\circ\text{C}$). The reaction of the TCFs of interest is triggered either by acid ($\text{pH} < 6$) or by heat (temperature $> 50^\circ\text{C}$). Therefore, encapsulating the TCFs in the diesel phase will not prevent their reaction at elevated temperatures or when the medium is acidic. These properties of TCFs suggest the need to increase the pH to prevent a premature reaction of the TCFs. Moreover, emulsification of combined TCFs is not recommended at downhole conditions, where high temperatures are typically encountered.

The instability observed in the emulsion containing 4M NaNO_2 with Emulsifier-B may be due to the disruption caused by the electrostatic attraction between the positively charged Emulsifier-B and the negatively charged nitrite anions, as depicted in Figure 4.29. Also, the resonance of nitrite ions (delocalization of π -electrons) and availability of unshared paired electrons in the nitrogen atom are all expected to interfere with the positively charged Emulsifier-B and potentially destabilize the NaNO_2 /diesel emulsion. There is a potential attraction between the positive charge in the emulsifier (deficient in electrons) and the nitrogen ion having a shared pair of electrons.

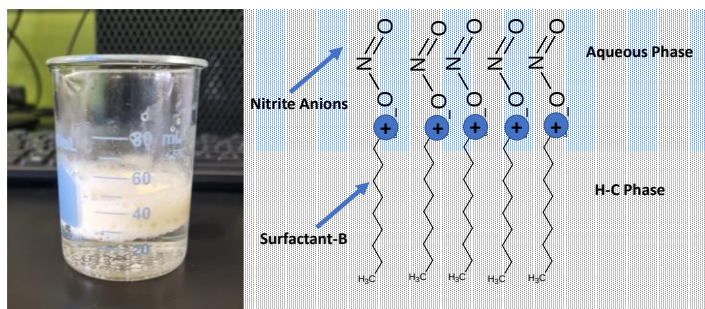


Figure 4.29-Potential destabilization mechanism of 4M NaNO₂ in diesel with 1% Emulsifier-B

The results showed that the emulsion characteristics of TCFs emulsified with Emulsifier-A were very promising for both individual and mixed TCFs. This is attributed to the relatively better emulsification properties of Emulsifier-A and a high basicity nature, which hinder the reactivity of the TCFs.

Recently, TCFs have been proposed for various upstream applications, including EOR, foamed acids and foamed fracturing fluids [84-86]. Applications of TCFs in upstream operations (downhole) require using a technique that isolates the TCFs components of being in touch to avoid activating these chemical reactions by temperature. In this regard, Al-Taq et al. [52] presented a field application of TCFs to remove filtercake damage. One chemical component was injected through the coiled tubing, and the other through the production tubing. However, the coiled tubing has its own limitations including complex well geometry which dictates the need to inject both TCFs components through the production tubing. With effective individual emulsification of TCFs, as with the case of Emulsifier-A, the two emulsified components can be injected simultaneously or one after the other using bullheading technique. It might be advisable to start with the heavier emulsion, which is typically NaNO₂, followed by the lighter one (NH₄Cl). For applications in high temperatures, it might be beneficial to have a spacer between the two emulsified components, which should have a comparable density.

As a consequence of this work, the effect of emulsification on the reactivity of TCFs will be investigated. In this regard, future work will include studying the effect of triggering temperatures, volume fraction of TCFs, and individual/in combination TCFs emulsified on the reactivity of TCFs using an autoclave reactor.

4.5 Conclusions

An extensive detailed experimental work on emulsification of TCFs in diesel was carried out in this study. A summary of main findings is given below:

- The TCFs, as individual and in combination, were emulsified in diesel using three distinct emulsifiers.
- Water-in-oil emulsions containing individuals TCFs in diesel were successfully generated using the three emulsifiers investigated in this study.
- The emulsifiers used in this study can be categorized based on lab analysis into positive, negative, and non-ionic types.
- All emulsifiers exhibited higher partitioning in diesel than in TCFs.
- As revealed from viscosity, optical microscopy, and particle size distributions, Emulsifier-A was the most promising emulsifier for the emulsification of 4M TCFs.
- The 70% TCFs in diesel emulsions formed were found to have the characteristics of pseudoplastic fluids and follow the power-law model.
- The increase in the volume fraction of TCFs from 50 to 70% and emulsifier concentration from 1 to 5% enhanced emulsion characteristics.
- The method of individual emulsification provided better emulsion properties than the mixed TCFs emulsification method and showed a potential contribution to sustainability.

CHAPTER 5

EMULSIFICATION AND PH CONTROL FOR SUSTAINABLE THERMOCHEMICAL FLUIDS REACTIVITY

Abstract

Managing chemical reactivity is crucial for sustainable chemistry and industry, fostering efficiency, reducing chemical waste, saving energy, and protecting the environment. Emulsification is used for different purposes, among them controlling the reactivity of highly reactive chemicals. Thermochemical fluids (TCFs), such as NH_4Cl and NaNO_2 salts, have been utilized in various applications, including the oil and gas industry. However, the excessive reactivity of TCFs limits their applications and consequently negatively impacts the potential success rates.

In this study, an emulsification technique was employed to control the high reactivity of TCFs explored at 50% and 70% in diesel, using three distinct emulsifier systems at concentrations of 1%, 3%, and 5% to form water-in-oil emulsions. The reactivity of 4M neat TCFs and emulsified solutions were examined in an autoclave reactor as a function of triggering temperatures of 65-95°C, volume fraction, and emulsifier type and concentration.

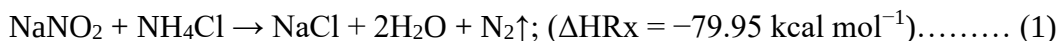
Additionally, the study explores an alternative method for controlling TCFs reactivity through pH adjustment. It investigates the impact of TCFs at pH values ranging from 6 to 10 and the initial pressure on the resulting pressure, temperature, and time needed to initiate the TCFs' reaction.

The results revealed that both emulsification and pH adjustment have the potential to promote sustainability by controlling the reactivity of TCFs' reactions. The findings from the study can be utilized to optimize various downhole applications of TCFs, enhancing the efficiency of TCFs reactions and success rates. The paper presents in detail the results obtained and discusses the potential contributions of the examined TCFs reactivity control techniques to sustainability.

Keywords; Thermochemical Fluids; Emulsification; Controlled Reactivity; Sustainability

5.1 Introduction

Thermochemical fluids (TCFs) have wide applications in different sectors of industries, including the petroleum industry. Ammonium chloride (NH_4Cl) and sodium nitrite (NaNO_2) salts are considered the most common TCFs used in the oil industry due to their relatively low cost, excessive generation of heat, and environmentally friendly products (N_2 , NaCl , and H_2O). They are highly reactive chemicals, and their exothermic chemical reaction is given as per the following equation [5-8]:



It is an irreversible reaction with $K_{eq} = 3.9 \times 10^{71} \text{ Pa} \times \text{mol} \times \text{m}^{-3}$ at 25°C .¹ The high reactivity of this TCFs system limits its applications, which suggests the need to investigate different methods to control its reactivity. Al-Taq et al. [90]) showed that the reaction rate of $\text{NH}_4\text{Cl}/\text{NaNO}_2$ is highly influenced by the pH values of the system and the triggering temperatures. These findings indicate that the reactivity of the TCFs can be controlled based on different applications requirements. Generally, the reaction rate of a chemical reaction is governed by reactants concentration, temperature, catalysts, and inhibitors. Essentially, for a reaction to take place, the activation energy must be overcome either by catalysts or by providing the required energy.

Physical and chemical methods can be used to control a chemical reaction. Thermochemical reactions are classified as fused reactions when they are delayed.² Nguyen et al. [8,9] discussed several techniques to delay heat release from typical TCFs ($\text{NH}_4\text{Cl}/\text{NaNO}_2$), including chemical fuses and physical methods. The chemical fuses include series reactions, autocatalytic reactions, and retardants. The physical techniques include physical separation, encapsulation, and emulsification. Unlike in oil production operations, where emulsion is usually presented as a problem, emulsion may be presented as a solution in several fields, including food, medicine, and detergent industries. Accordingly, emulsification also provides an effective method to control the reactivity of highly reactive chemicals in the oil industry. Emulsification of individual components of the $\text{NH}_4\text{Cl}/\text{NaNO}_2$ system has been applied successfully in several dewaxing operations for short pipelines in the Campos Basin, Brazil [51]. The need to delay heat release for an extended period makes the adoption of this method challenging for lengthy pipes. Acetic acid, as the reaction activator, was emulsified together with NH_4Cl . Almubarak et al. [92] proposed the emulsification of these two salts to treat deep water blockage.

Emulsification is employed to minimize environmental impacts and enhance energy efficiency as well [107,108]. In this context, the emulsification of heavy oil as an alternative fuel holds great promise in addressing environmental pollution and the energy crisis [107]. The critical factor lies in the micro-explosion phenomenon within the emulsion, which plays a vital role in improving fuel efficiency while simultaneously reducing harmful gas emissions. Gowrishankar and Krishnasamy [108] conducted a study indicating that a biodiesel-water emulsion exhibits greater potential for simultaneously reducing NO_x and smoke emissions while enhancing engine performance.

Emulsification has been proven to be an effective method for controlling the reactivity of HCl as a strong acid [109,110]. Zhang et al. [109] reported that micro-emulsified HCl acid significantly reduced the reactivity of HCl ; the emulsified acid dissolved only 1.23 grams of the core after one hour, while the regular HCl dissolved 1.68 grams in just 9 minutes.

Emulsified acid has been introduced to retard the strong HCl acid and applied successfully to provide deeper penetration and overcome the drawbacks of regular HCl acid.

Recent research has been dedicated to developing microemulsions of acid in diesel, offering improved stability and better control over the acid's reactivity [111-113]. These microemulsions are typically created using surfactants and cosurfactants in addition to the two immiscible fluids [113].

Wang et al. [111] successfully prepared an acid-in-aromatic solvent microemulsion by optimizing the surfactant-to-cosurfactant ratio. This microemulsion system exhibited smaller particle sizes and a slower mass transfer coefficient when compared to conventional emulsified acid at 60°C. The mass transfer coefficient of the microemulsion acid was more than one order of magnitude smaller than that of the conventional emulsified acid.

Dantas et al. [112] developed a low-reactive microemulsion system consisting of Alkonat L90 (a non-ionic surfactant), n-butanol (a co-surfactant), kerosene (as the oil phase), and an HCl acid solution (as the aqueous phase) at different concentrations (1.5%, 5%, 10%, and 15% wt%). This microemulsion acid was investigated for enhanced oil recovery (EOR) and was found to significantly increase oil recovery, contributing to sustainability.

Microemulsions offer new possibilities for controlled acid treatments. Saiyu et al. [113] developed a 70% acid-in-diesel microemulsion that included cetyltrimethylammonium chloride as a cationic surfactant, aliphatic ethoxylate alcohol AEO9 as a non-ionic surfactant, and butanol and n-octanol as cosurfactants. This microemulsified acid system exhibits small droplet sizes and excellent stability. Furthermore, when compared to a hydrochloric acid solution at the same concentration, it demonstrates remarkable corrosion

inhibition properties. Additionally, this microemulsified acid system can tolerate high salinity levels, up to $80 \text{ g}\cdot\text{L}^{-1}$, making it a promising candidate for use as an acidizing fluid in various applications.

Recently, TCFs have been proposed for various upstream applications, including EOR, foamed acids, and foamed fracturing fluids [85-87]. The upstream operations are often characterized by high downhole temperatures, one of the triggering reaction mechanisms of TCFs. The current study aims to assess the effectiveness of emulsification and pH adjustment as techniques to control TCFs reactivity and their potential to contribute to TCFs reaction sustainability. The study considered temperatures as a triggering mechanism for TCFs reactions to assess the effectiveness of these techniques in controlling the reactivity of TCFs.

5.2 Experimental Work

5.2.1 Materials

Sodium nitrite and ammonium chloride used in this study were ACS reagent grades obtained from Honeywell and Fisher Scientific, respectively. Deionized water (DI) with a resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$ was used in the preparation of the salt solutions and bentonite suspension systems. An ACS-grade reagent sodium hydroxide obtained from Fisher Scientific was prepared at 6M and used to adjust the pH of $\text{NaNO}_2/\text{NH}_4\text{Cl}$ solutions. Concentrated HCl acid and NaOH used in adjusting the pH of TCFs were ACS reagent grades obtained from Fisher Scientific. Three emulsifier systems, referred to as Emulsifier-A, Emulsifier-B, and Emulsifier-C, with compositions given in Table 5.1, were obtained from local providers and used in this study to prepare TCFs in diesel emulsions. The three emulsifiers all include both a surfactant and a cosurfactant. The relatively high pH value of 1 vol% of Emulsifier-A in DI water (9.51) is likely attributable to the presence of amine coco-alkyl acetate. Conversely, the low pH of Emulsifier-C is associated with the presence of acetic acid. Emulsifier-B exhibits a pH value of 4.74, attributed to the inclusion of a

buffer system (acetic acid/acetates). A commercial diesel with a density of 0.78 g/cm³ was used in the preparation of emulsions of interest.

Table 5.1-Composition, ionic properties and pH values of the emulsifiers used in this study

Emulsifier-A		Emulsifier-B		Emulsifier-C	
Component	Function	Component	Function	Component	Function
Tall oil fatty acid amine	Surfactant	Amines, tallow alkyl, acetates	Surfactant	Fatty acid amine	Surfactant
Acetic acid		Heavy aromatic naphtha		Ethylene glycol	Cosurfactant
Ethylene Glycol		Ethane-1,2-diol		Cosurfactant	Heavy aromatic petroleum naphtha
Amine	Cosurfactant	Acetic acid		Acetic acid	
Coco-alkyl					
Acetate		1,2,4 trimethylbenzene		Naphthalene	
Ionic Properties of Emulsifiers					
Non-ionic		Positively charged		Negatively charged	
pH values of 1 vol% Emulsifier in D.I Water					
9.51		4.74		1.62	

5.2.2 Equipment and Methodology

The experimental work, as illustrated in Figure 1, involved emulsion preparation and autoclave testing. The autoclave testing was divided into the reactivity study of emulsified TCFs and the investigation of the impact of pH and initial pressure on the reactivity of non-emulsified TCFs.

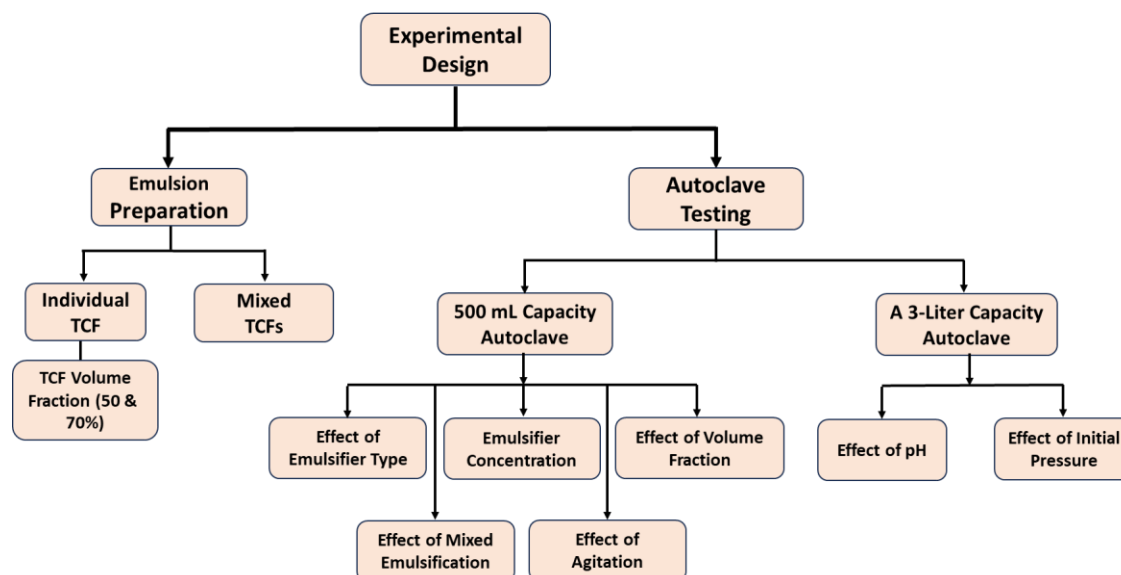


Figure 5. 1- A schematic representation of the experimental work performed in this study

5.2.3 Preparation of Emulsions

A high shear rate Silverson- L5M-A model mixer was used in the preparation of TCFs in diesel emulsions. TCFs in oil emulsions at 70/30 vol% were prepared by first dissolving the emulsifier at concentrations of 1, 3, and 5 vol% in diesel and allowing it enough time to mix thoroughly by agitating the mixture at around 3,000 rpm for 2 min. The aqueous thermochemical phase was gradually added to the hydrocarbon phase of diesel, and the solutions were allowed to mix at a high speed of 10,000 rpm for 10 minutes to ensure the formation of emulsion.

5.2.4 pH Measurement

Thermo Scientific™ Orion Star™ A111 Benchtop pH Meter was used to measure pH values of TCFs.

5.2.5 Autoclave Testing

In this study, two different autoclaves were employed to study the reactivity of TCFs: one for investigating the impacts of emulsification and the other for examining the influence of pH. OLT-HP-500 micro-mechanical mixing autoclave was used to examine the effect of emulsification on the reactivity of thermochemical fluids of interest in terms of generated temperature and pressure. The kettle body of the autoclave is Hastelloy, and it has a capacity of 500 mL and can tolerate 345 bar (34,500 kPa) pressure and 500°C temperature. It has an LCD where you can set and monitor the temperature. A pressure tracking device is connected to the system to monitor pressure generated as a function of time. All tests conducted in the autoclave were based on mixtures of a 1:1 ratio of NH_4Cl to NaNO_2 .

The other autoclave reactor used in this study has a capacity of 3 liters and can withstand a temperature of up to 500°C and a pressure of 10,00 psi. The reactor is equipped with software controls for monitoring and tracking both pressure and temperature. This particular autoclave system was utilized to explore how the pH levels affect the reactivity of TCFs. A total volume of 1.4 liters, consisting of equimolar (5M) NH_4Cl and NaNO_2 , was used, and the pH values under examination for the TCFs were 6, 7, 8, 9, and 10. The study also delved into the impact of the initial pressure provided by nitrogen gas at various levels, including atmospheric pressure (14.7 psi), 500, 750, 1,000, and 1,500 psi, on the reactivity of the $\text{NH}_4\text{Cl}/\text{NaNO}_2$ system when activated by heat.

5.3 Results and Discussion

5.3.1 Reactivity of Emulsified TCFs in Diesel

To assess the reactivity of emulsified TCFs, an autoclave testing was carried out where the pressure and heat (temperature increase) generated from the TCFs reaction were monitored for emulsified TCFs in diesel systems compared to the neat TCFs. The effect of emulsifier type and concentration, reaction triggering temperature, and TCFs fraction volume on the reactivity of TCFs were investigated.

5.3.2 Reactivity of Emulsified TCFs Versus Neat TCFs

The reactivity of TCFs is assessed by the heat and gas generated, which is reflected in changes in temperature and pressure, respectively. Figure 5.2 illustrates the comparison of reactivity between individual emulsified 4M TCFs in diesel and the neat 4M system at 95°C. For the sake of simplicity and comparative purposes, we assumed ideal gas conditions and neglected the contribution of excess heat from the emulsification to the generated pressure. Figure 2 demonstrates that the heat generated by the emulsified system, as reflected in the temperature change, was higher than that generated by the neat TCFs. The higher temperature increase in the emulsified TCFs is attributed to the lower specific heat capacity for diesel (2,050 J/kgC) compared to that for water (4,184 J/kgC). As known from the heat transfer equation, the change in temperature is inversely proportional to the specific heat capacity ($\Delta T \propto 1/C_v$). Moreover, the results showed that emulsification resulted in higher heat generation and retention compared to the neat system, clearly indicating that emulsification contributes to improved heat sustainability.

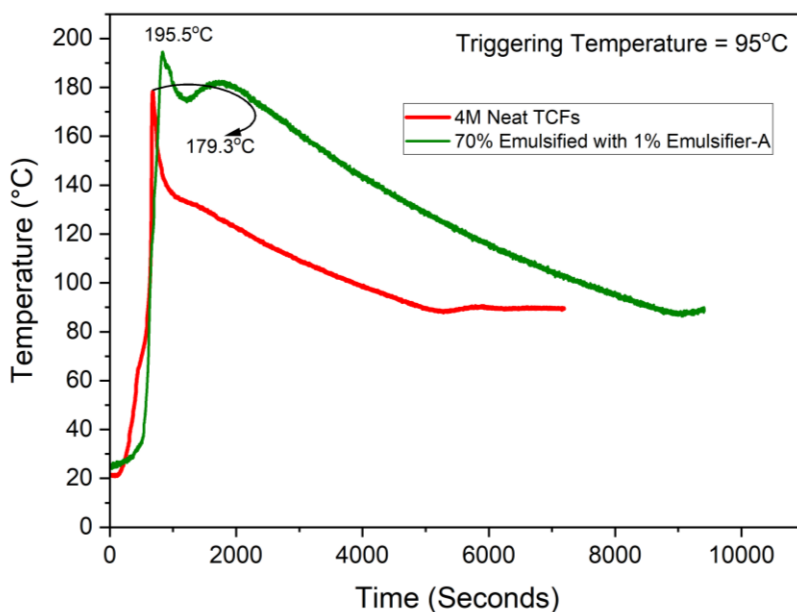


Figure 5.2-Effect of emulsification on the heat generated from the reaction of 70% individual emulsified 4M TCFs compared to neat 4M TCFs at 95°C.

The reactivity of emulsified and non-emulsified TCFs systems was assessed based on the pressure resulting from the generated nitrogen. Reactivity for a gas-producing reaction can be determined using the ideal gas law:

$$PV = nRT \text{ and } C = \frac{n}{V} = \frac{1}{RT}P \Rightarrow \frac{dC}{dt} = \frac{1}{RT} \frac{dP}{dt} \dots\dots\dots (2)$$

P represents the pressure in Pascals (Pa), V is the volume in liters (L), n is the number of moles, R is the gas constant ($J \cdot mol^{-1} \cdot K^{-1}$), and T is the temperature in Kelvin (K). So, the value of dP/dt can be determined from the generated pressure data and with this information, initial reaction rates.

In this study, we considered the maximum generated peaks as the ultimate reactivity of any system examined due to the gradual increase in temperature to the designated level. Figure 3 shows the pressure curves generated from neat 4M TCFs and 4M TCFs emulsified in diesel with 1 % Emulsifier A at 95°C. For the neat system, the pressure generated was corrected based on the $P_1V_1 = P_2V_2$ relation to match the volume of the emulsified system of 285.7 mL. The neat TCFs system exhibits a lower peak-plateau difference, primarily due to the generated heat, compared to the emulsified TCFs systems. However, it resulted in higher pressure due to nitrogen generation when compared to the emulsified 4M TCFs with Emulsifier-A. The higher peak-plateau difference in the emulsified systems can be attributed to the previously mentioned higher specific heat capacity of diesel. The results demonstrate that achieving a complete reaction in the emulsified 4M TCFs, as is the case with Emulsifier-B addressed in the next section, is associated with higher pressure and heat generation compared to the neat TCFs system. This, in turn, enhances the efficiency of TCFs reaction and overall sustainability.

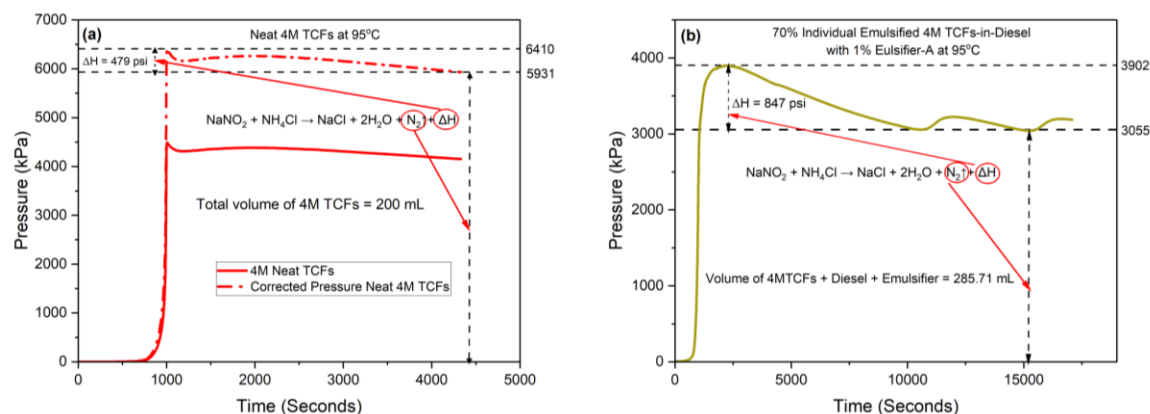


Figure 5.3-Reactivity of (a) 4M neat TCFs versus (b) 70% individual emulsified 4M TCFs at 95°C with emulsifier-A

5.3.3 Effect of Emulsifier Type

The impact of emulsification on controlling the reactivity of individual emulsified 4M TCFs at a concentration of 70% in diesel, using the emulsifiers of interest in this study at both 1% and 5% volume fractions, compared with neat 4M TCFs, was examined at temperatures of 95 and 75°C, as shown in Figures 4 and 5, respectively. The results revealed that the emulsion prepared using Emulsifier-B exhibited the highest reactivity (indicating the worst emulsification), while the emulsion prepared using Emulsifier-A exhibited the lowest reactivity (indicating the best emulsification). The same trend of performance was observed for emulsions prepared with 1 vol% and 5 vol% emulsifiers. These results are supported by the photos taken after the testing of emulsions with a 5 vol% emulsifier, which clearly showed a full separation of the emulsion prepared using Emulsifier-B (Figure 6). The lowest reactivity control observed for TCFs emulsion with Emulsifier-B might be attributed to the positive charge nature of this emulsifier, while the best reactivity control obtained for emulsion with Emulsifier-A might be attributed to the high pH value of this emulsifier (1% Emulsifier-A in DI water, pH = 10). Based on viscosity measurements, which indicated the highest viscosity for the NaNO₂ emulsion with Emulsifier-B and the highest viscosity for the NH₄Cl emulsion with Emulsifier-A, we examined the NH₄Cl/NaNO₂ emulsions with emulsifiers (A and B), as shown in Figure 4. This system exhibited the second-highest control of reactivity. Based on the results

obtained, Emulsifier-A was chosen for further investigation into various parameters that affect the reactivity of TCFs emulsion, including temperature, emulsifier concentration, and TCFs volume fraction.

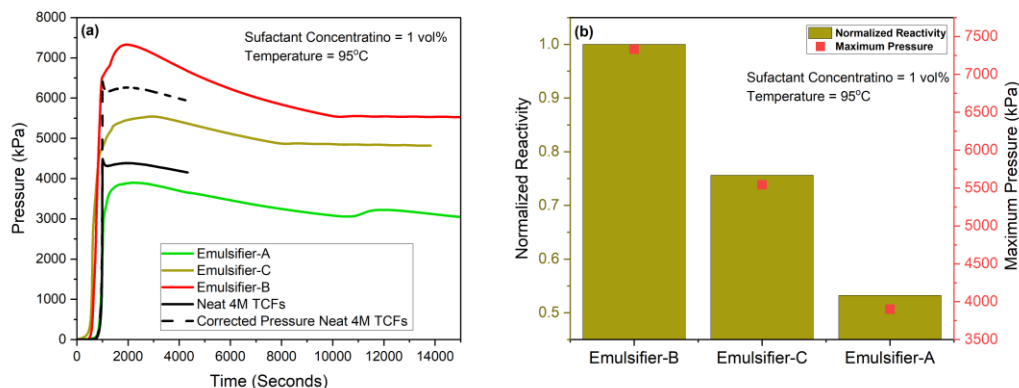


Figure 5.4-Reactivity of 4M neat TCFs and 70% individual emulsified 4M TCFs in diesel with different emulsifiers at (1%) and 95°C (a) pressure and (b) normalized reactivity

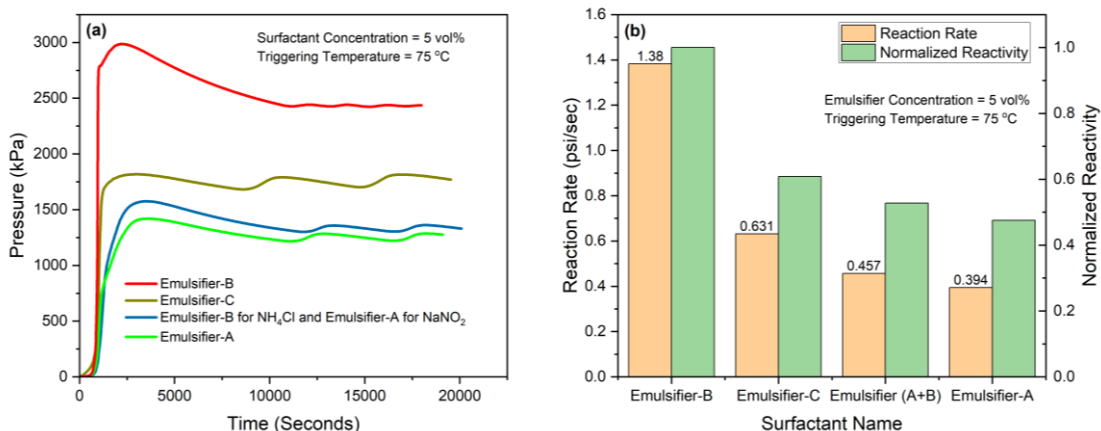


Figure 5.5-Reactivity of 70% individual emulsified 4M TCFs in diesel with different emulsifiers at (5%) and 75°C, (a) pressure and (b) normalized reactivity and reaction rate

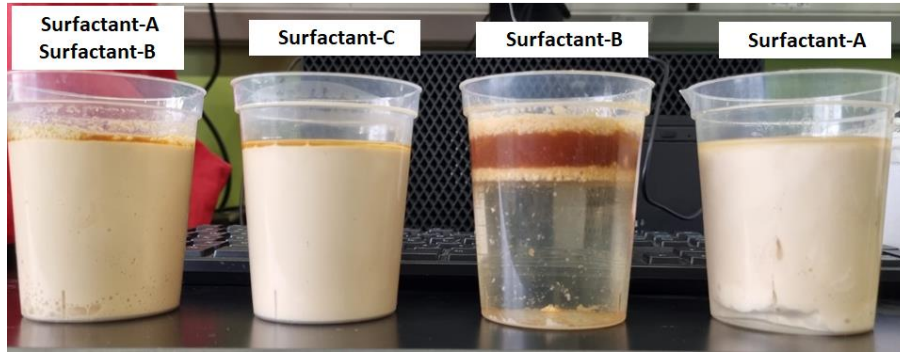


Figure 5.6-Photos of different emulsion systems with 5% of emulsifiers following autoclave testing at 75°C

5.3.4 Effect of Concentration, Temperature, Volume Fraction and Agitation

The effect of concentration, temperature, volume fraction, and agitation on controlling the reactivity of the TCFs in diesel emulsions with Emulsifier-A will be discussed in the following sections.

5.3.5 Effect of Emulsifier Concentration

The effect of emulsifier concentration on the reactivity of 70% of individual emulsified 4M TCFs with Emulsifier-A was investigated at a temperature of 95°C, as shown in Figure 7. The results showed that as the emulsifier concentration was increased, the reactivity of TCFs decreased for the examined concentration of 1, 3, and 5 vol%. The reduction in the reactivity, defined as the maximum pressure obtained, is governed by a polynomial of second order equation:

$$P_{\max} = 143 [C_A]^2 - 1441 [C_A] + 5200 \dots\dots\dots(3)$$

Where $P_{\max}$ is the pressure in kPa and C_A is the concentration of Emulsifier-A in vol%. The control in the reactivity of TCFs, defined as the reduction in the reactivity compared to the reactivity of 4M TCFs emulsion prepared with Emulsifier-B at 95°C (maximum $P = 7,330$ kPa), is governed by the following relation:

$$\text{Reactivity Control (\%)} = 1 - \frac{P_{\max} \text{ (kPa)}}{7330 \text{ kPa}} \times 100 \dots\dots(4)$$

Where P_{max} is the maximum pressure obtained at a certain concentration of Emulsifier-A. Figure 8 shows the reactivity control obtained at Emulsifier-A concentrations of 1, 3 and 5 vol%. When the emulsifier concentration was increased from 1 to 3 vol%, the reactivity control increased from nearly 47% to more than 70%. The highest reactivity control, exceeding 78%, was achieved at an emulsifier concentration of 5 vol%. The results indicate that the higher the emulsifier concentration, the greater the contribution to sustainability, as reactivity (reaction energy) is conserved for various downhole applications.

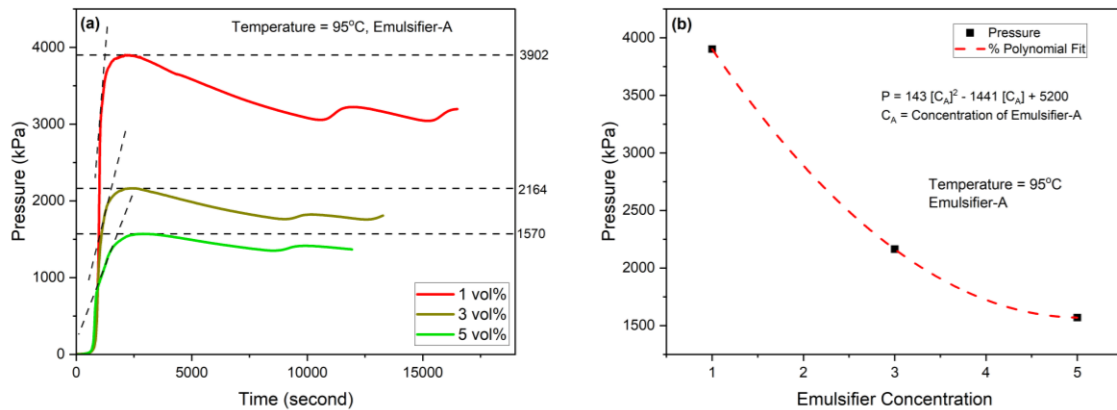


Figure 5.7-Generated pressure from emulsified 4M TCFs in diesel as a function of: (a) time and (b) Emulsifier-A concentration

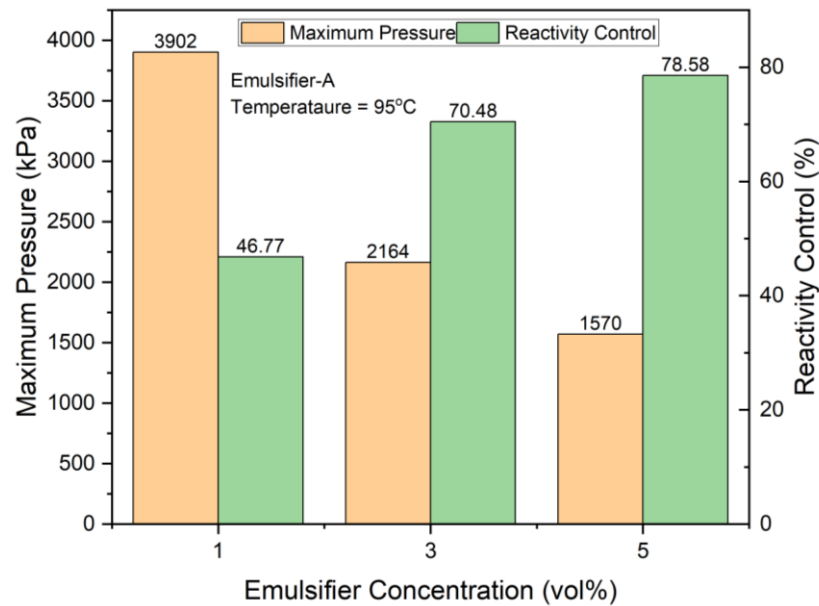


Figure 5.8-Effect of Emulsifier-A concentration on the reactivity of 4M TCFs emulsified in diesel at 95°C

5.3.6 Effect of Temperature

The influence of triggering temperature on the reactivity of 70% of individually emulsified 4M TCFs in diesel with Emulsifier-A at 1, 3, and 5 vol% was investigated, as shown in Figure 9. The reduction in TCFs' reactivity when decreasing the temperature from 95 to 75°C was evident, especially for emulsifier concentrations of 1 and 3 vol% (19% and 21%, respectively). The reduction in TCFs' reactivity at an emulsifier concentration of 5 wt% was less than that obtained for emulsifier concentrations of 1 and 3 vol% by a factor of two.

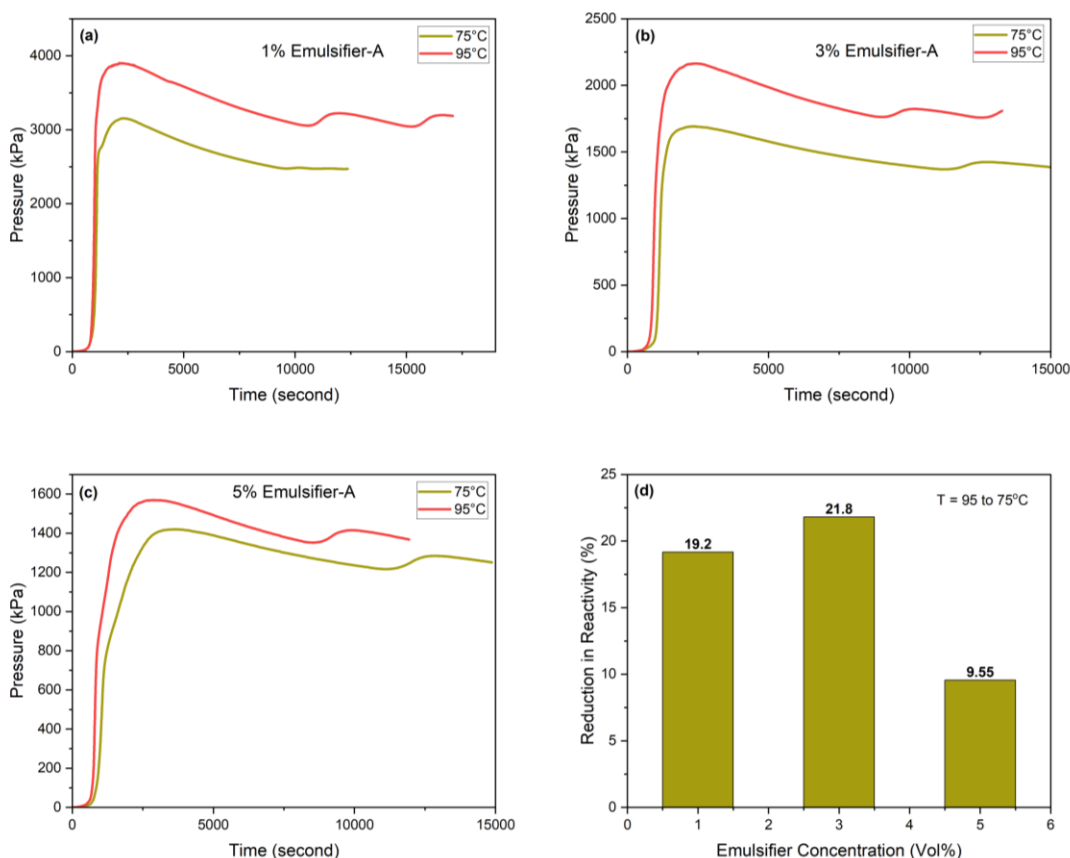


Figure 5.9-Effect of temperature on the reactivity of 70% Emulsified 4M TCFs in diesel with Emulsifier-A at (a) 1, (b) 3 and (c) 5 vol%, (d) reduction in reactivity

Figure 10 shows the effect of temperature on the reactivity of 70% 4M TCFs emulsified in diesel with 1 vol% Emulsifier-A at 65 and 75°C. It was found that temperature had a significant impact on TCFs' reactivity, where decreasing the temperature by 10 degrees (from 75 to 65°C) resulted in a reduction of TCFs' reactivity by more than 43%.

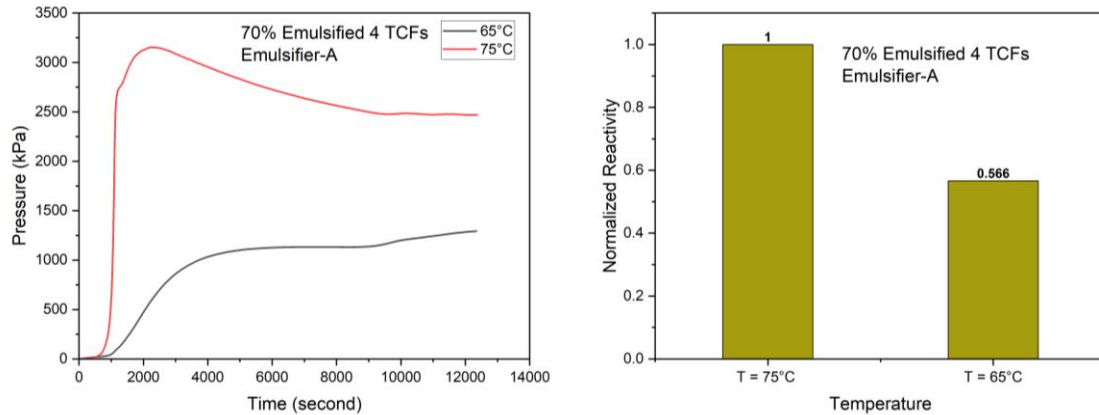


Figure 5.10-Effect of temperature on the reactivity of 70% 4M TCFs emulsified in diesel with Emulsifier-A at 1 vol%, (a) pressure and (b) normalized reactivity

5.3.7 Effect of TCFs Volume Fraction

Figure 11 shows the effect of TCFs volume fraction on the reactivity of emulsified 4M TCFs in diesel using 1% Emulsifier-A at 75°C. The results demonstrated that increasing the volume fraction of 4M TCFs from 50% to 70% resulted in a reduction of emulsified TCFs' reactivity by more than 18%. The results reveal that the higher the proportion of TCFs in the emulsion system, the better the reactivity control of TCFs, which is in favor of incorporating more TCFs and, thus contributing more to sustainability.

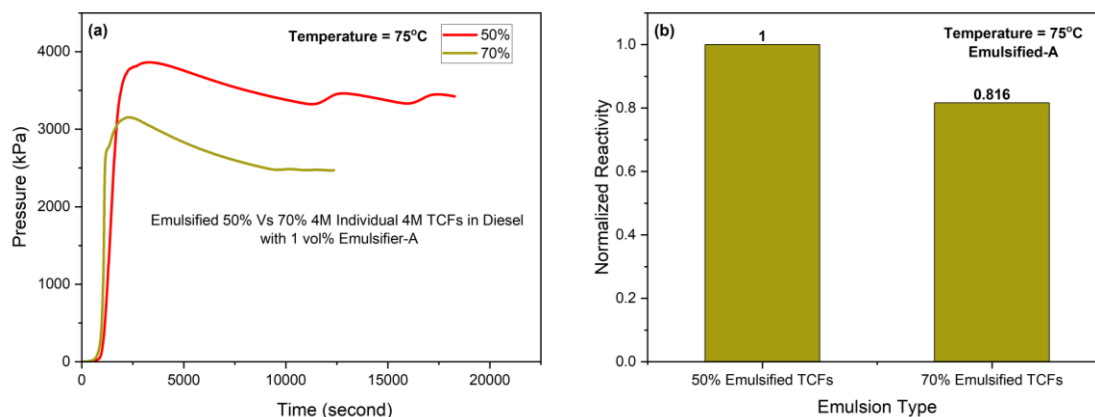


Figure 5.11-Effect of volume fraction on the reactivity of emulsified 4M TCFs in diesel with 1% Emulsifier-A at 75°C

5.3.8 Effect of Emulsification Method and Agitation

The effect of the emulsification method on the reactivity of TCFs at 95°C was examined for 70% of individual and mixed 4M TCFs using Emulsifier-A, as shown in Figure 12. Individual emulsification was found to provide better control over the reactivity of TCFs, resulting in a reduction of nearly 35% compared to the mixed emulsion.

To investigate the impact of agitation on the reactivity of TCFs, the 70% individually emulsified 4M TCFs in diesel were subjected to stirring at 100 rpm for 1 minute before conducting the autoclave testing. The results obtained for this system are compared with the mixed emulsified 4M TCFs as shown in in Figure 5.12. The results revealed that agitation allowed the individual TCF-encapsulated droplets to come into contact with each other, ultimately leading to the occurrence of the reaction. This is reflected in the high generation of pressure, as shown in Figure 5.12. The results suggest the importance of avoiding agitation of emulsified TCFs, especially during injection at high shear. To prevent interaction among the TCFs components during the injection stage, it would be more beneficial to use a spacer between them.

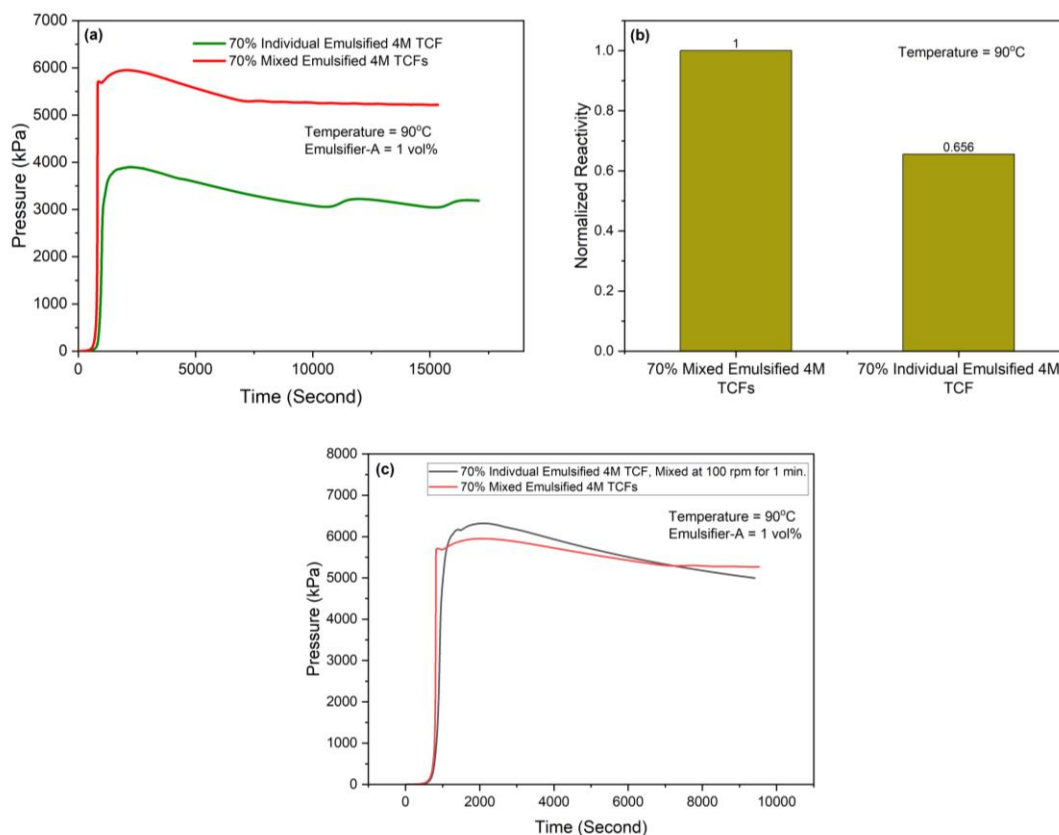


Figure 5.12-Effect of the emulsification method on the reactivity of 4M TCFs in diesel with 1 vol% Emulsifier-A at 95°C (a) individual versus mixed emulsification, (b) reduction in reactivity and (c) individual emulsified followed with mixing versus mixed emulsified system

5.3.9 Impact of pH and Initial Pressure on the Reactivity of Neat TCFs

Ammonium chloride is an acidic salt because it is derived from a weak base (ammonia, NH_3) and a strong acid (hydrochloric acid, HCl) [114]. Sodium nitrite is a salt derived from a strong base (sodium hydroxide, NaOH) and a weak acid (nitrous acid, HNO_2). The equimolar solution of NH_4Cl and NaNO_2 (2-4M) has pH values of 6.13-6.34 [90]. The reaction of thermochemical fluids (TCFs) of interest in this study is triggered either by acids or heat. Due to this inherent property of TCFs, their reactivity is highly influenced by pH. In this study, we investigated the effect of pH and initial pressure on the reactivity of TCFs using a 3-liter autoclave reactor. A total volume of 1,400 mL of an equimolar (5M) solution of NH_4Cl and NaNO_2 at a 1:1 volume ratio was used. The impact of pH

values (6, 7, 8, 9, and 10) on the generated pressure and heat is shown in Figures 13 and 14, respectively. The results showed that the pH values had linearly influenced the generated pressure until pH = 9, as given by the following relation:

$$P_{\text{peak}} \text{ (kPa)} = 2731.6 \text{ pH} - 2533 \dots\dots\dots (5)$$

Where P_{peak} represents the maximum generated pressure at a certain pH value. The results also showed that increasing pH values tended to extend the delay time to start the TCFs reaction, as given by the polynomial equation:

$$\text{Dely Time (min)} = 4.05 \text{ pH}^2 - 54.3 \text{ pH} + 207 \dots\dots\dots (6)$$

Figure 5.15 shows the impact of initial pressure on the time required to trigger the reaction. The delay time is given by the following relation:

$$\text{Dely time (min)} = 235.9 P_i^{-0.352} \dots\dots\dots (7)$$

Where P_i represents the initial pressure in kPa.

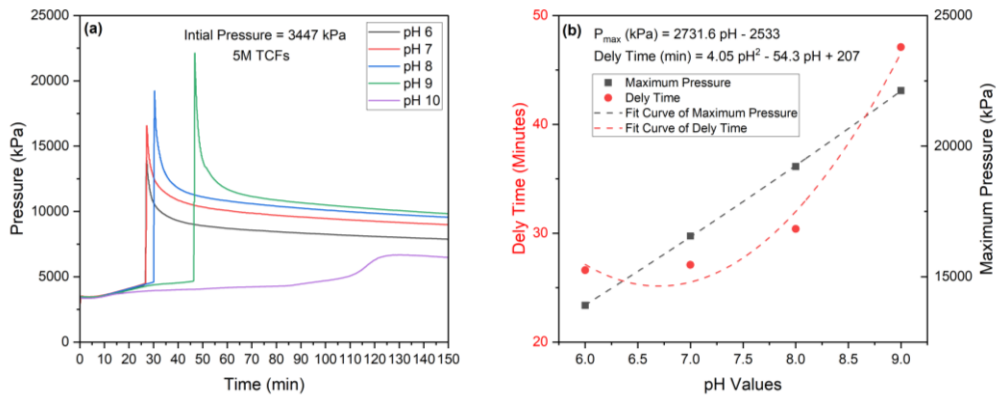


Figure 5.13-(a) Effect of pH on generated pressure by 5M TCFs and (b) relationship between TCFs pH values and maximum pressure

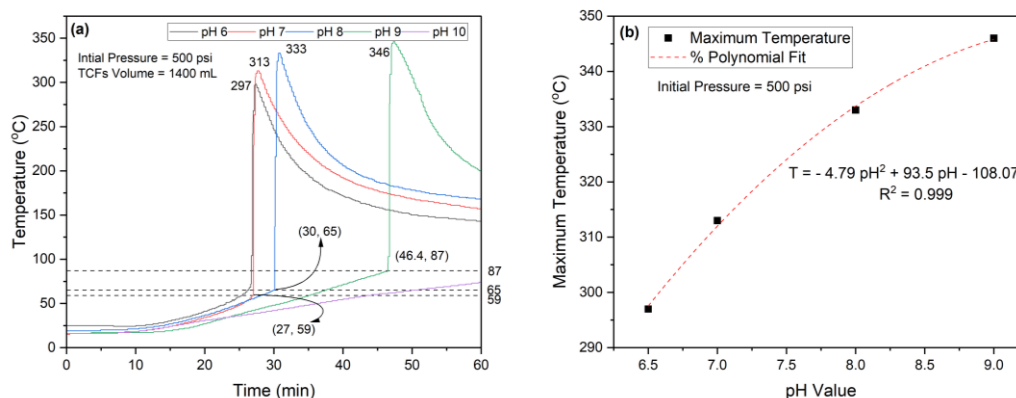


Figure 5.14-(a) Effect of pH on generated heat by 5M TCFs and (b) relationship between TCFs pH values and maximum temperature

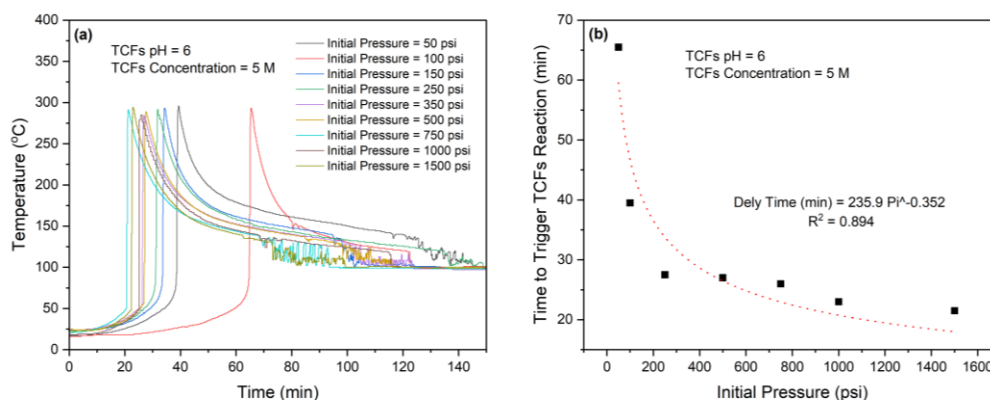


Figure 5.15-(a) Effect of initial pressure on delay time of 5M TCFs reaction and (b) relationship between initial pressure and time to trigger TCFs reaction

5.4 Discussion

The study revealed that the reactivity of TCFs can be effectively controlled using emulsification, where Emulsifier-A exhibited the best performance. The higher the emulsifier concentration, the better the reactivity control of TCFs. Upon the complete reaction of emulsified TCFs in diesel, as with the case of Emulsifier-B, a higher generation of pressure and temperature was reported when compared to neat TCFs. Emulsification of TCFs also prevents the premature reaction of TCFs, which results in chemical and energy waste. These findings indicate that the emulsion of TCFs will contribute to sustainability.

The data generated from the reactivity of emulsified TCFs systems, such as reactivity control, should be utilized to optimize applications of TCFs in various downhole conditions. The type of emulsified TCFs in terms of emulsifier concentration should be considered based on different well temperatures. Upon placement of the emulsified TCFs system, a demulsifier, including acids, might be injected to break the emulsion and activate the reactivity of TCFs for a specific downhole application.

Another method to control the reactivity of TCFs and ultimately enhance the outcomes of TCFs in industry is by adjusting the pH of TCFs. Increasing the pH of TCFs was associated with a delayed reaction time and an increase in pressure and temperature in a sequence of TCFs reactions. Also, initial pressure was found to influence the triggering temperature and time required to start the TCFs reaction. Table 5.2 gives the effect of pH and initial pressure on the triggering temperature, generated pressure, and time required to trigger the TCFs reaction. The study findings presented in Table 5.2 can be utilized for different downhole applications based on well temperature and pressure to accurately predict the time required to start the TCFs reaction at different downhole temperatures and pressures, enhancing the success of TCFs applications.

Based on these findings, the strategy of managing the reactivity of TCFs through the elevation of pH proves to be effective at low depths. Nevertheless, at greater depths characterized by elevated initial pressures, the emulsification method appears, as a more effective approach.

Table 5. 2-Effect of pH and initial pressure on the reaction triggering temperature, and generated pressure

Exp # 1	Molarity	Initial pH	Initial Pressure (psi)	Triggering Temperature (°C)	Max Pressure, psi	Time to triggering temperature (min)
1	5	9	0	115	1,730	73
2	5	9	500	86	3,209	46
3	5	8	0	105	2,032	30
4	5	8	500	65	2,788	30
5	5	6	500	72	2,017	26
6	5	7	500	59	2,402	27
7	5	8	500	65	2,788	30
8	5	10	500	170	966	>120 min (Partial reaction)

5.6 Conclusions

Extensive and detailed experimental work was carried out to assess the impacts of emulsification and pH adjustment on the reactivity of TCFs. A summary of the main findings is given below.

- Both emulsification and pH adjustment have the potential to promote sustainability by controlling the reactivity of TCFs' reactions.
- The reactivity of emulsified TCFs was found to be influenced by the emulsification method, emulsifier concentration, TCFs volume fraction, and triggering temperature.
- The method of individual emulsification provided better reactivity control than the mixed emulsification method.

- Among the studied emulsifiers used as emulsifiers, Emulsifier-A demonstrated the most effective control of the reactivity of emulsified TCFs in diesel.
- The high pH values of TCFs (up to pH = 9) were found to positively influence the generated pressure, temperature, and time to trigger TCFs reaction.
- Increasing initial pressure tended to decrease the time to trigger the reaction.
- The findings from the emulsification and pH adjustment study can be utilized to optimize various downhole applications of TCFs, enhancing the efficiency of TCFs reactions and success rates.
- The strategy of managing the reactivity of TCFs through the elevation of TCFs pH proves effective at low depths. Nevertheless, at greater depths characterized by elevated initial pressure, the emulsification method emerges as a more effective approach.

CHAPTER 6

INVESTIGATIONS OF THERMOCHEMICAL FLUIDS POTENTIAL FOR CLEANUP OF POLYMER-BASED FRACTURING FLUIDS

Abstract

Hydraulic fracturing operations are typically performed to stimulate the productivity of tight formations, especially unconventional reservoirs. Cleanup of fracturing fluids is an imperative stage in these operations, contributing significantly to the overall success of the process. Breakers, including acids, oxidizers, and enzymes, are commonly used to degrade polymers, reduce viscosity, enhance the flowback process, and ultimately facilitate the cleanup of the well.

The current proposed thermochemical fluids (TCFs) as cleanup fluids are not expected only to degrade polymers, reduce the viscosity, but will help to remove trapped water as one of the main damage mechanisms of low permeability shale formation following fracturing treatments. The TCFs investigated in this study were NH_4Cl and NaNO_2 where their reactions is associated with generation of substantial amounts of heat as determined from heating properties study using an autoclave reactor.

In this study, the thermal degradation of guar gum polymer derivatives, hydroxypropyl guar gum (HPG), and carboxymethyl hydroxypropyl guar gum (CMHPG), was assessed using Fourier Transform Infrared Spectroscopy (FTIR), Thermal Gravimetric Analysis (TGA), viscosity measurements, and coreflood experiments. Both FTIR and TGA analyses of liner gels of GG and its derivatives confirmed alterations in the chemical and thermal properties of these polymers following thermal treatments. The coreflood results showed a regained permeability of 87% for thermally treated HPG borate-crosslinked, 96% for CMHPG dual crosslinked (borate and zirconate), and 90% for slickwater fracturing fluids,

respectively. The regained permeability of thermally treated slickwater was even better than that for slickwater with a breaker. This paper will presents in detail these findings.

6.1 Introduction

6.1.1 Guar Gum Derivatives As Frac Fluids Thickening Polymers

Fracturing gelling polymers are classified into biopolymers, synthetic polymers, and composite systems (including synergistic blends and nanocomposites) [115]. The most common material in use today as a fracturing gallant is the guar gum and its derivatives. Guar gum and its derivatives hydroxypropyl guar (HPG), carboxymethyl guar (CMG), and carboxymethylhydroxypropyl guar (CMHPG) have been extensively used in hydraulic fracturing operations owing to their reliable and economical supply as well as flexible chemistry [116]. Figure 6.1 displays the chemical structures of the GG and its derivatives.

Guar gum (GG) is a non-ionic natural polysaccharide sourced from the seeds of *Cyamopsis tetragonolobus* (Leguminosae family). It comprises a (1,4)- β -D-mannopyranosyl linked d-mannopyranose backbone with random branch points of galactose via an α -1,6-linkage as shown in Figure 6.1 [117]. Guar gum has a molecular weight of 1-2 million grams per mole (g/mol). The GG derivatives have fewer residues (2-4% for HPG and 2-3% for CMHPG) compared to 6 -10 wt% for native GG. Upon breaking, guar produces an insoluble residue ranging from 6 to 10% [25]. The development of guar gum derivatives aimed to minimize the insoluble residue, bolster high-temperature stability, and enhance crosslinking performance in low pH conditions.

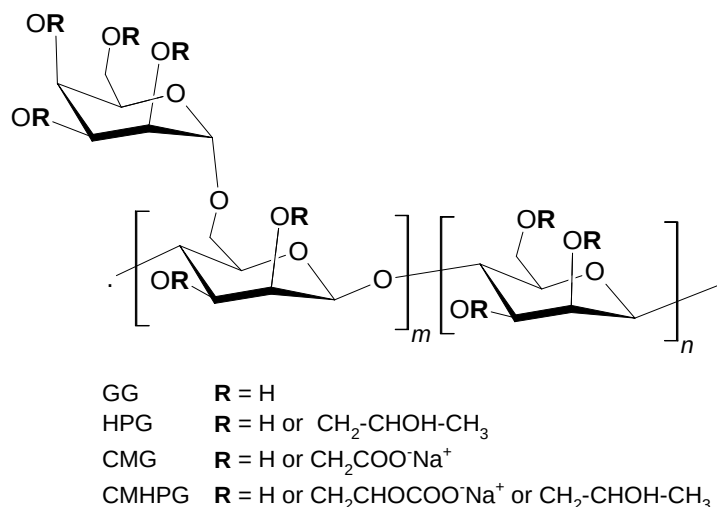


Figure 6.1- Chemical structures of guar gum (GG), hydroxypropyl guar gum (HPG), carboxymethyl guar gum (CMG) and carboxymethyl hydroxypropyl guar gum (CMHPG) polymers

When introduced to water, the GG polymer's hydroxyl groups have the ability to form numerous hydrogen bonds with water molecules, resulting in an increase in viscosity [21]. (Maroufi et al. [118]. Furthermore, GG can be a preferred choice for use in food packaging owing to its viscosity, emulsifying, binding, and gelling properties. It exhibits rapid solubility in cold water, maintains stability across a broad pH range, possesses film-forming capabilities, and is biodegradable [119].

The viscosity of hydraulic fracturing fluids is a crucial parameter that can significantly impact the success of the fracturing process, playing a role in fracture initiation, propagation, proppant transport, and overall well performance. Upon completion of the fracturing process, the viscosity of fracturing fluids needs to be low enough to facilitate the efficient cleanup of the fracturing fluid from the wellbore and the fracture network. The low viscosity of frac fluids will allow efficient removal of any remaining fluid residues in the fractures which can impede the flow of hydrocarbons. To reduce the frac fluids viscosity and remove/minimize formation damage, breakers are used as one of the main frac fluid additives.

In unconventional shale gas reservoirs, two primary types of formation damage, physical and chemical, are often observed after fracturing treatments, resulting in reduced reservoir permeability and fracture conductivity. These mechanisms include clay swelling, fines migration, particle invasion from the well into the reservoir, phase trapping damage, and stress damage [120]. Physical damage mechanisms are associated with the direct, nonchemical interaction between the formation and the working fluids used for drilling, completion, killing, or stimulating a well. The physical damage mechanisms in shale gas reservoirs include fines migration, particle invasion from well into reservoir, phase trapping damage and stress-related damage. Chemical damage mechanisms include incompatibility between formation rocks and working fluids (drill-in fluid, completion fluid, kill fluid, fracturing fluid, etc.), and incompatibility between reservoir fluid and working fluids.

6.1.2 Fracturing Fluid Breakers

Fracturing fluid cleanup is a critical stage that significantly contributes to the success of fracturing operations. This stage involves breaking down the frac fluid polymers and subsequently backflowing the well. Breakers, which include acids, oxidizers, and enzymes, are typically used to break the backbone of polymers, thereby reducing frac fluid viscosity and facilitating the cleaning process.

Various oxidizers and enzymes have been studied in the laboratory and successfully implemented in the field as breakers for frac fluids. Oxidizers include persulfates, peroxides, bromate, and chlorites. Persulfates can take the form of sodium persulfate, ammonium persulfate, and potassium persulfate. Persulfate salts dissociate in water to form the anion ($\text{S}_2\text{O}_8^{2-}$), generating sulfate-free radicals. These radicals attack the polymer chains, causing chain scission and resulting in the formation of smaller fragments [121].

Breakers, as one of the main additives in fracturing fluids, are designed to act after the fracturing operation is completed. Consequently, breakers are commonly encapsulated to prevent the premature breaking of frac fluid polymers. The encapsulation of these breakers helps control the timing of their activation, ensuring they are released at the desired stage of the fracturing process. Nevertheless, partially or intact polymeric fluids may leave behind residues upon fracturing, leading to a notable decline in effective permeability due to pore clogging in both the formation and proppant pack [122].

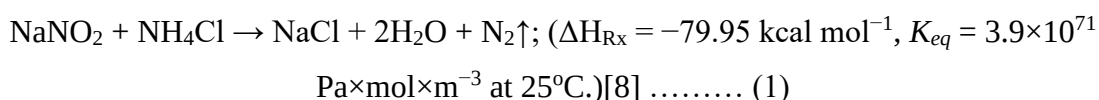
6.1.3 Degradation of Fracturing fluid Polymers

The current study investigates the potential use of TCFs, associated with generation of substantial amounts of heat, as cleanup fluids for fracturing fluids. Heat plays a critical role in the thermal degradation of polymers, influencing various reactions. Three primary reactions occur during nonoxidative thermal degradation: depolymerization, random chain scission, and side-group elimination [123]. Irrespective of the specific thermal degradation mechanism, this process invariably leads to the deterioration of macromolecular material properties. Exposure to high temperatures induces both irreversible physical and chemical changes in polymers. As macromolecules undergo degradation, there is a decrease in the molar mass of the polymer, accompanied by alterations in its chemical structure [123].

Elevated temperatures, primarily resulting from the geothermal gradient, have been documented to influence polymer stability. Consequently, extensive research has been conducted to enhance the resistance of fracturing fluid polymers to high temperatures. Du et al. [115] provided a review of water-soluble polymers crosslinked to enhance their temperature resistance, reporting upper temperature limits of 125 to 175°C for biopolymers, including guar gum and some of its derivatives. In the case of synthetic polymers, the maximum temperature resistance reached 230°C. Temperature resistance was determined through viscosity measurements [115,123].

Additionally, it was found that pressure positively influences polymer degradation [124,125]. It was observed that stepwise pressure increases from 500 to 10,000 psi caused the viscosity of the standard borate-crosslinked fluid to sequentially decrease at room temperature [125]. Murata et al. [125] investigated the thermal degradation of polyethylene in a stirred tank reactor through continuous flow operations under elevated pressures ranging from 0.1 to 0.8 MPa (14.50 to 116.03 psi). They concluded that reaction pressure directly contributes to the scission of C–C links during the thermal degradation of polymers.

The thermochemical fluids of interest in this study were NH_4Cl and NaNO_2 salts, the reaction of which is associated with substantial amounts of heat and of nitrogen gas, as follows:



Given the profound impact of heat and pressure on the degradation of polymers, the utilization of TCFs emerges as a promising approach for cleaning up fracturing fluids. Additionally, the generated nitrogen is expected to reduce the well hydrostatic pressure and ultimately enhance the cleanup process. Furthermore, the TCFs can remove phase trapping damage typically encountered in low permeability reservoirs. The current study investigates into the potential of TCFs, known for generating substantial heat and nitrogen gas, as effective cleanup agents in the context of fracturing fluids.

6.2 Methodology and Equipment

6.2.1 Materials

Sodium nitrite (NaNO_2) and ammonium chloride (NH_4Cl) used in this study were ACS reagent grades obtained from Honeywell and Thermo Fisher Scientific, respectively. Deionized water with a resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}$ was used in the preparation of the salt solutions. Sodium hydroxide used to adjust the pH of $\text{NaNO}_2/\text{NH}_4\text{Cl}$ solutions was an

ACS-grade reagent obtained from Thermo Fisher Scientific. Guar gum, HPG, CMHPG and high viscosity friction reducer (HVFR) polymer are commercial products obtained from service companies.

6.2.2 Autoclave

The autoclave reactor utilized in this study has a 3-liter capacity and can withstand temperatures of up to 500°C and pressures of 10,000 psi. Equipped with software controls for monitoring both pressure and temperature, the reactor was employed with a total volume of 1.4-liter, comprising equimolar NH_4Cl and NaNO_2 . The study investigated the impact of TCFs concentration, volume, and pH. The thermochemical fluid, initially pressurized at 500 psi, was heated at a rate of 4°C/min until the reaction occurred, after which the heater was turned off.

6.2.3 HTHP Filter Press

A standard HTHP filter press was used to perform cleanup tests under static conditions. The cell has a volume of 500 mL and can tolerate a pressure of 5,000 psi and a temperature of 500°F. The fracturing fluid was mixed with the TCFs and aged at a designated temperature and pressure for a designated period of time.

6.2.4 Thermal Gravimetric Analysis

Thermal Gravimetric Analysis (TGA) was performed using TGA Q 500 (TA) which was programmed at a heating rate of 20°C/min between 25 to 1,000°C under air atmosphere to determine weight loss and residual masses of examined samples.

6.2.5 Viscosity Measurement

The Chandler Engineering Viscometer Model 5550 was used to measure the apparent viscosity of the gelling samples under different shear rates and temperature values. This viscometer utilized standard R1/B5 bob and rotor combinations which require a sample volume of 52 cm³. Chandler viscometer uses a sliding carbon block for dry heating and the temperature sensor is mounted on the stator/bob to control sample temperature. A pressure of 500 psi was applied to minimize the sample evaporation, and to keep all generated gases in the liquid state. Viscosity measurements were performed under different shear rates according to the API RP 39 standard (the shear rate ranging between 25 and 100 s⁻¹). Some fluids were tested at a constant shear of 100 s⁻¹. Nearly, 25 cm³ of fracturing fluid was placed in the rheometer cup followed by adding breakers (if required) in the middle and the remaining amount of the 52 cm³ fracturing fluid was then added.

6.2.5 Thermal Shock Test

A thermal shock test was conducted using a Chandler viscometry Model 5550. The heating chamber was preheated to the designated temperature, simulating the heat generated from the TCFs reaction. The sample, incorporated into the cup, was then placed in the heating chamber while viscosity, shear rate, and sample temperature were monitored.

6.2.6 Thermal Degradation of Fracturing Fluids

Degradation of guar derivatives-based fracturing fluids (HPG and CMHPG) and slick water fracturing fluid was conducted by aging the fluids in an aging cell at temperatures of 350, 450, or 500°F, along with a pressure of 300 psi, for one hour. The one-hour aging time was selected based on Distributed Temperature Survey (DTS) data for the application of TCFs for filtercake, which showed a temperature stability of one hour [52]. After the cooling process, the thermally treated fracturing fluid was filtered through a 10-micron ceramic disc. Subsequently, the filtered thermally treated fracturing fluid was used in the coreflood experiments. Figure 6.2 shows the aging cell, filtration kit and fracturing fluids

before and after aging along. Another batch of thermal degradation tests involved the liner gels of GG, HPG and HVFR. These liner gels underwent TGA examination both before and after the degradation tests.

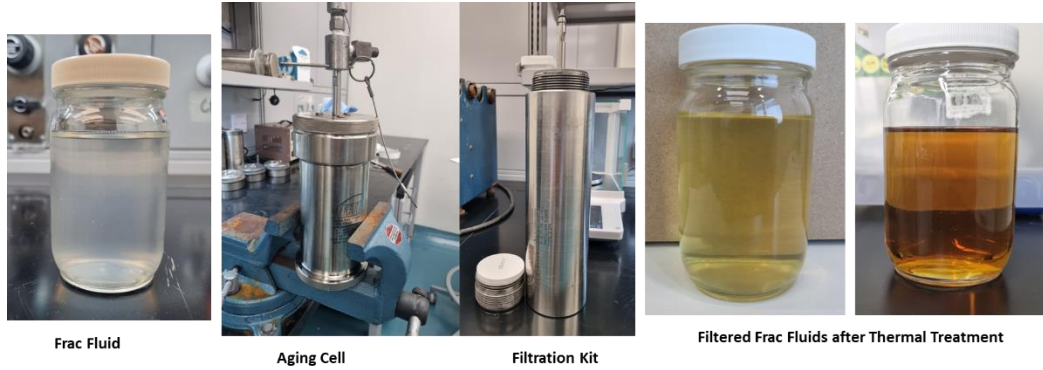


Figure 6. 2-Thermal degradation of guar-based and slick water fracturing fluids

6.2.6 Coreflooding Experiments

Coreflood experiments were conducted using Indian limestone and Berea sandstone core plugs, each with dimensions of 1.5 inches in diameter and 3 inches in length. A back pressure of 1,000 psi and an overburden pressure of 3,000 psi were applied. Sodium chloride solution at 7 wt% was used with Indiana limestone core plugs and potassium chloride solution at 3 wt% was used with Berea sandstone core plugs. The use of potassium chloride with Berea sandstone core plugs aims to prevent the potential issue of clay swelling, which is common in sandstone formations. The brine solutions were injected before and after injection of 5 pore volumes (PV) of the thermally treated fracturing fluids. Table 1 gives a summary of coreflood experiments conducted in this study.

Table 6.1-A summary of coreflood experiments conducted for different fracturing fluid systems

Experiment #	Core Plug Type	Brine	Fracturing Fluid System	Thermal Treatment Temperature (°F)
1	Indiana Limestone	7 wt% NaCl	HPG-borate Crosslinked	350
2	Indiana Limestone	7 wt% NaCl	CMHPG-dual crosslinked (borate and zirconate)	450
3	Indiana Limestone	7 wt% NaCl	CMHPG-dual crosslinked (borate and zirconate)	500
4	Berea Sandstone	3 wt% KCl	Slickwater with ammonium persulfate breaker	-
6	Berea Sandstone	3 wt% KCl	Slickwater	500

6.3 Results and Discussion

6.3.1 Characterization of Guar Gum-Based Polymers

Fourier-transform infrared spectroscopy (FTIR) and thermal gravimetric analysis (TGA) were utilized to characterize GG, HPG, and CMHPG samples in this study. The FTIR technique was employed to identify the types of functional groups present in GG and its derivatives by analyzing the positions and intensities of specific infrared absorption bands. Figures 6.2-6.4 display the FTIR spectra of GG, HPG, and CMHPG, respectively. These polymer samples exhibit comparable FTIR spectra for the main functional groups of OH, CH, CH₂, C=O, CO, and COC stretchings, as shown in Figures 6.3-6.5, confirming their common origin (guar gum).

Both the GG and HPG are nonionic polymers, while CMHPG has an anionic moiety. The spectrum obtained for GG polymer is comparable to that reported by Sowunmi et al. [116], Balan et al., [126] and Dutta et al. [127], while the obtained spectrum for HPG polymer is comparable to that reported by Zhu et al. [128].

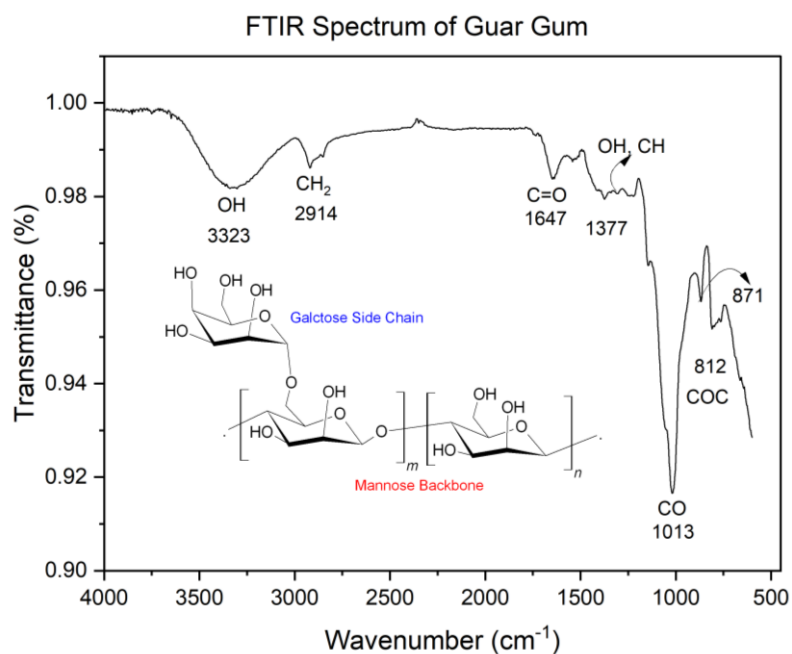


Figure 6.3-FTIR spectrum of guar gum

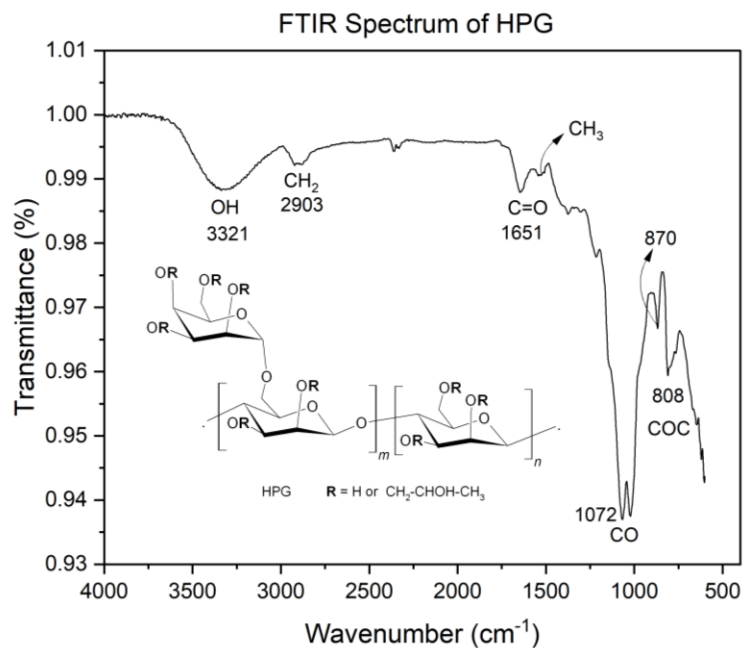


Figure 6.4-FTIR spectrum of hydroxypropyl guar (HPG)

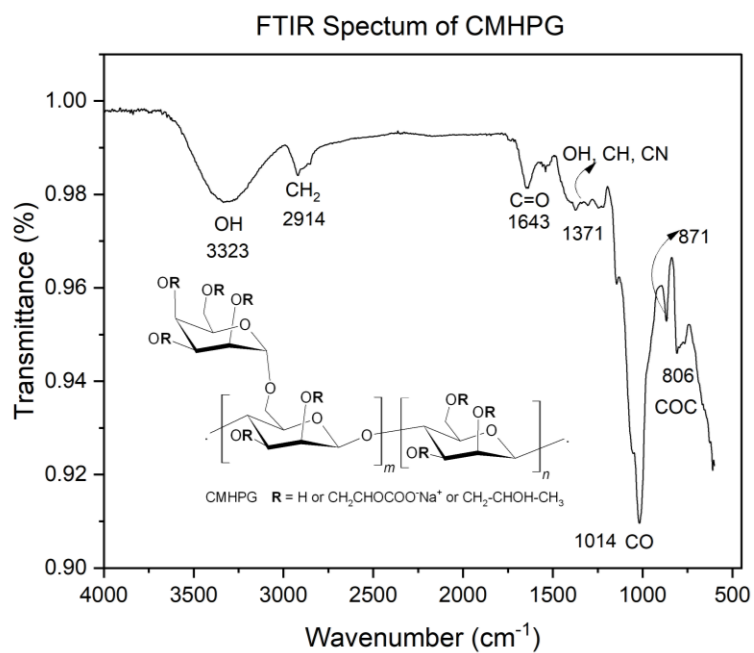


Figure 6.5-FTIR spectrum of carboxymethyl hydroxypropyl guar (CMHPG)

Thermal gravimetric analysis (TGA) is a crucial analytical technique for studying the thermal properties of polymers. This method involves measuring the weight change of a material as a function of temperature, providing valuable information about its thermal stability, composition, and various other properties. TGA thermograms affirms the initial and final decomposition temperature in various zones. Figure 6.6 shows the major decomposition stages for GG, HPG and CMHPG in the same plot. The TGA profile for GG is in agreement with that reported by Mahto and Mishra [129] while the TGA of HPG polymer is comparable with that obtained by Shen et al [130]. According to Mahto and Mishra [130], the maximum weight loss of 59.98 wt% occurred between 256 and 356°C was due to degradation of galactomannan backbone of GG. The weight loss in the range of 0 to 100°C is low (approximately 8 wt%) and might be attributed to the evaporation of small molecules, such as water. The three polymers experienced the highest decomposition of more than 50% at the zone from 243 to 360°C. The residual material of GG was more than 15 wt% which is attributed to the impurities commonly available in commercial guar gum. The GG derivatives showed lower residual material of 3.42 and 2.35 wt% for HPG and CMHPG, respectively. The results might align with the insoluble residues previously discussed for guar gum and its derivatives.

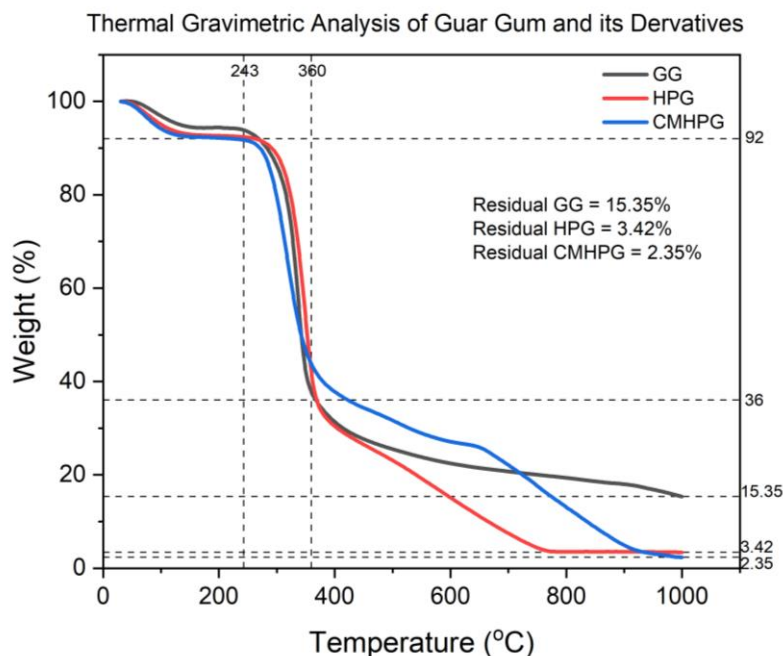


Figure 6.6-Thermal gravimetric analysis of guar gum and its derivatives

6.3.2 Heating Properties of Thermochemical Fluids

In this study, NH_4Cl and NaNO_2 salts were employed as thermochemical fluids, participating in a highly exothermic reaction outlined in the chemical equation addressed in Section 1.3. The study investigated the thermal energy generated by the TCFs exothermic reaction, analyzing how temperature varies with TCFs concentration, volume, and pH values. The thermal energy of TCFs reaction was assessed from the heat transfer which is reflected in the change in temperature as given in the below equation:

$$q = m C_v \Delta T \dots \dots \dots (2)$$

Where q is the quantity of heat in joules, m is the mass of the material in grams, C_v is the heating capacity of the material in $\text{J}/^\circ\text{C}$ and the ΔT is the change in temperature in $^\circ\text{C}$. It was found that generated heat was a function of TCFs concentration, volume and pH values, as shown in Figures 6.7-6.9, respectively. Figure 6.7a shows that as the TCFs concentration increased, the generated temperature increased. The highest temperature, 305°C , was obtained at a TCFs concentration of 7M, while the lowest temperature, 196°C , occurred at a TCFs concentration of 2M. The relation between the maximum temperature generated and the TCFs is given by the following quadratic equation (see Figure 6.7b):

$$T_{\text{max}} = - 6.41 C_{\text{TCFs}}^2 + 79.04 C_{\text{TCFs}} + 65.32 \dots \dots \dots (3)$$

Where T_{max} represents the temperature in $^\circ\text{C}$, and C_{TCFs} is the equimolar concentration of the thermochemical fluids in mol/L . As shown in Figure 6.8, the TCFs at 5M and with volume of 200 mL was associated with a temperature increase of up to 193°C , while the TCFs volume of 250 mL resulted in a temperature exceeding 201°C . The results align with the previously mentioned heat equation, which is dependent on the mass quantity. The results indicate that, in comparison to concentration, the volume of TCFs has a moderate impact.

The effect of pH values from 6 to 9 at an initial pressure of 500 psi was investigated for the heat generated at TCFs concentration of equimolar TCFs of 5M as shown in Figure 6.8.

The following relation (Figure 6.9b) gives the maximum obtained temperatures as a function of the pH values of TCFs:

$$T_{\max} = -4.79 \text{ pH}^2 + 93.5 \text{ pH} - 108.05 \dots \dots \dots (4)$$

The results indicate that as the pH value of TCFs increased, the maximum temperature also increased, reaching a peak of 346°C at a TCFs pH value of 9. These findings provide guidelines to optimize the use of TCFs for different field applications and for controlled reaction.

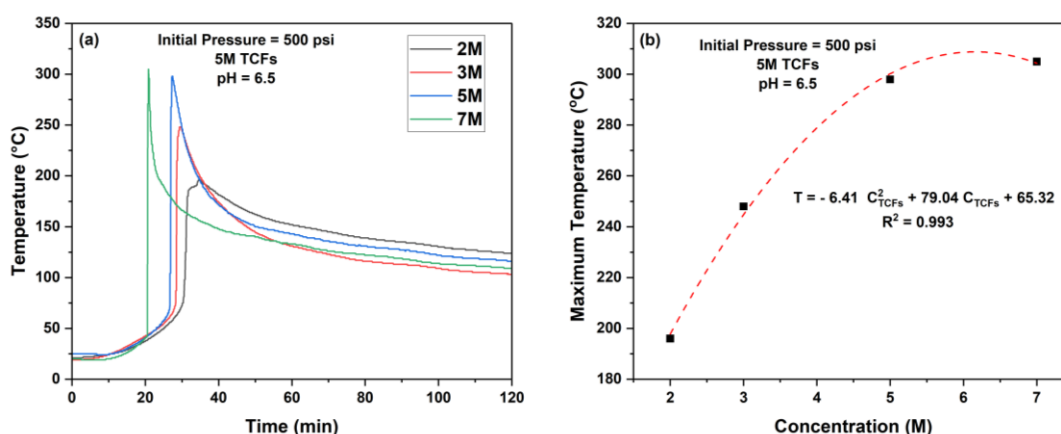


Figure 6.7-Effect of TCFs concentration on generated heat (a) generated temperature versus time and (b) relationship between TCFs concentration and generated maximum temperature

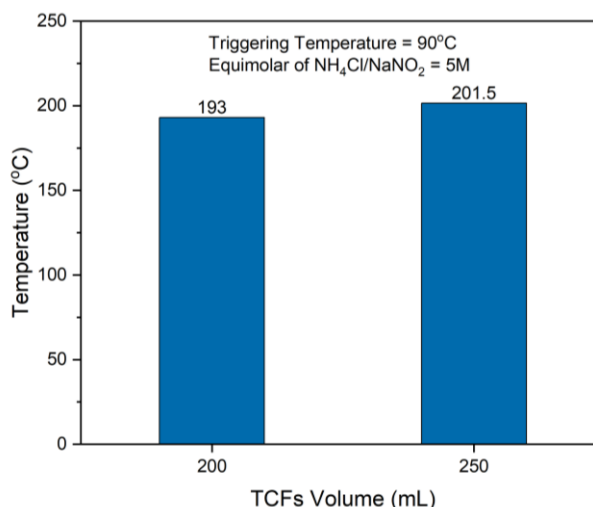


Figure 6.8-Effect of TCFs volume on generated heat at 90°C

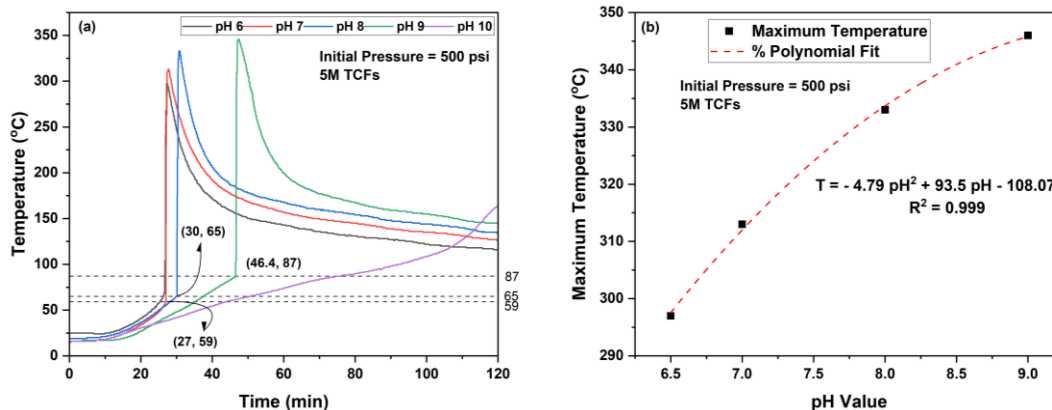


Figure 6.9-Effect of pH on heat generated (a) generated temperature versus time and (b) relationship between TCFs pH values and maximum temperature

6.3.3 Viscosity of Fracturing Fluids

The viscosity measurements were conducted on three different fracturing fluid formulations (Tables 6.2-6.4). The rheological properties of these fracturing fluids was measured as per API RP 39. The first formulation presented in Table 6.1 is for a borate-crosslinked HPG polymer, which includes other conventional frac fluid additives such as biocide, pH buffer, surfactant, and gel stabilizer. Figure 6.10 illustrates the viscosity of the HPG borate-crosslinked fracturing fluid at 270°F for a duration of two hours. The viscosity of this fracturing fluid system was maintained at more than 800 cP throughout the entire examination period.

The second fracturing fluid comprises CMHPG polymer with a combination of borate and zirconate-based crosslinkers. This system is more suitable for high-temperature reservoirs where the bottom hole static temperature (BHST) ranges between 300 and 330°F compared to a fluid solely crosslinked with borate. This system offers relatively long-term thermal stability and eliminates the traditional shear sensitivity associated with metal-crosslinked fracture fluids. Figure 6.11 shows the viscosity of the CMHPG dual-crosslinked system at 320°F as a function of shear rate for 2 hours. The viscosity of this system tended to decrease over time, but it maintained a high viscosity (> 300 cP) even at the end of the test. This

fracturing fluid system has significant potential for application in conventional reservoir fracturing, especially in cases where the fracture width is favourable.

The third fracturing fluid was slickwater containing a high-viscosity friction reducer (HVFR) polyacrylamide polymer, along with other typical additives as given in Table 6.3. The development of ultra-tight and tight unconventional reservoirs, such as tight gas and shale, has led to an increased use of slickwater. The viscosity of the slickwater system, at a shear rate of 100 s^{-1} , decreased from 15 cP at ambient temperatures to nearly 5 cP at 270°F, maintaining this viscosity level until the end of the 2-hour test duration.

Table 6.2-HPG borate-crosslinked fracuring fluid

Fluid	Additive	Concentration	Unit
Liner Gel	Water	1000	gpt
	Biocide	0.5	gpt
	HP, Gelling Agent (guar gum)	40	ppt
	HT Stabilizer	3	gpt
	Surfactant	1.0	gpt
	Clay Stabilizer	1.0	gpt
Cross-linker	Activator	20	ppt
	Borate Crosslinker	12	ppt
	Delaying Agent	60	ppt
	Stabilizer	1	ppt

Table 6.3-CMHPG dual (borate/zirconate) crosslinked fracuring fluid

Fluid	Description	Concentration	Unit
Linear Gel	Water	1000	gal
	Biocide	0.5	lb
	CMHPG Polymer	45	lb
	Clay Stabilizer	1.5	gal
	HT Gel Stabilizer	5	gal
	Stabilizer	5	gal
	Multifunctional	2	gal
	Surfactant	2	gal
	Stabilizer/Buffer	2	gal
Cross-linker	Caustic Soda	2	gal
	Dual Cross linker	2.4	gal

Table 6.4-Slick water fracturing fluid

Additive		Concentration	Unit
Biocide		0.25	gpt
HVFR	Polyacrylamide polymer	6	ppt
Clay Stabilizer	Polymer	0.5	gpt
Surfactant	Nonionic	0.5	gpt
Live Breaker	Ammonium persulfate	0.5	gpt

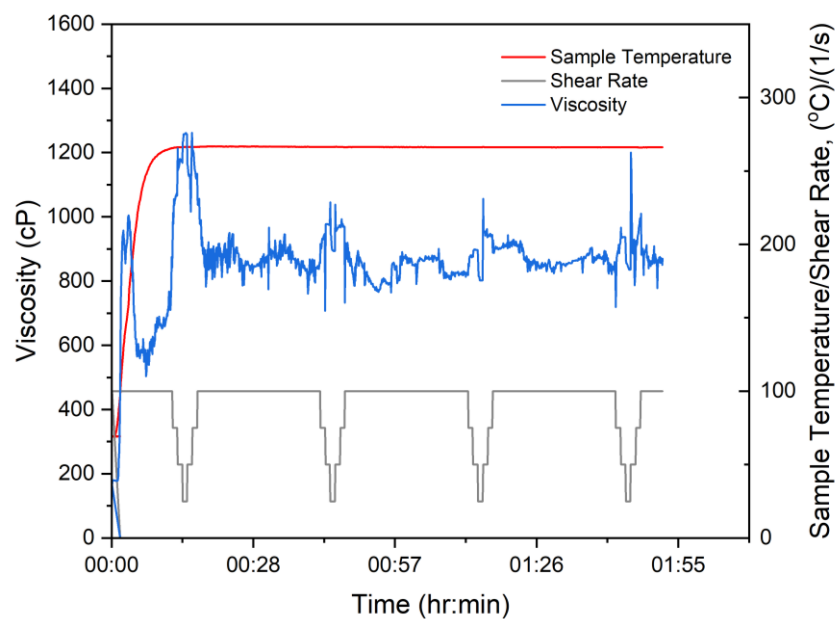


Figure 6.10-Viscosity of 40 lb HPG borate-crosslinked at 270°F

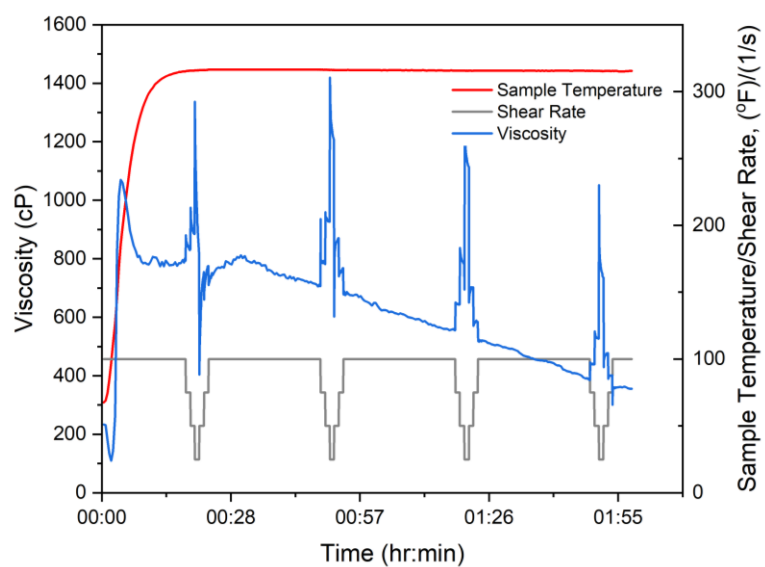


Figure 6.11-Viscosity of 40 lb CMHPG with combined borate and zirconate crosslinker at 320°F

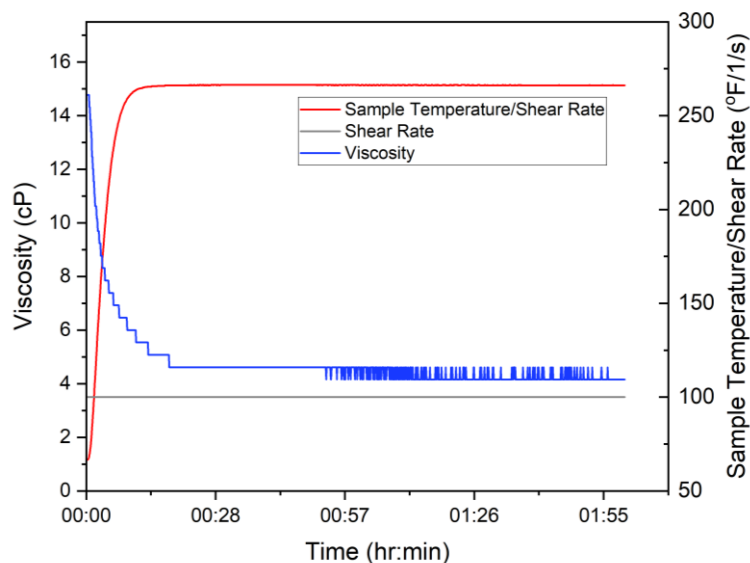


Figure 6.12-Viscosity of 6lb slick water at 270°F

6.3.4 Polymer Degradation Potential by Thermochemical Fluids

The nonoxidative thermal degradation of polymers involves three primary reactions: depolymerization, random chain scission, and side-group elimination.¹⁰ To assess the potential of TCFs to degrade the polymers examined in this study, Thermal Gravimetric Analysis (TGA) and Fourier Transform Infrared (FTIR) analyses were conducted on these polymers before and after thermal treatments. The FTIR spectra and TGA for GG, HPG and CMHPG polymers before and after the thermal treatment at 500°F for one hour are shown in Figures 6.13 and 6.14, respectively.

The thermal treatment of polymers involved aging the sample in an aging cell at 500°F and an initial pressure of 300 psi for one hour. Following, the aged samples were filtered through 0.45 µm filter paper, and the residues were subjected to FTIR and TGA analyses. The results, as shown in Figure 6.13, showed that there is some variation in FTIR spectra

before and after the thermal treatment, especially for the GG polymer spectrum. This might be attributed to the degradation of some polymer components.

The TGA results for GG, HPG, and CMHPG before and after thermal treatment exhibit clear variations, as shown in Figure 6.14. Beyond 100°C, the weight loss in the polymers after thermal treatment is significantly less than that observed before treatment, indicating a reduction in polymer mass caused by the thermal treatment. These findings suggest that the thermal treatment utilizing TCFs can be employed to degrade GG and its derivatives.

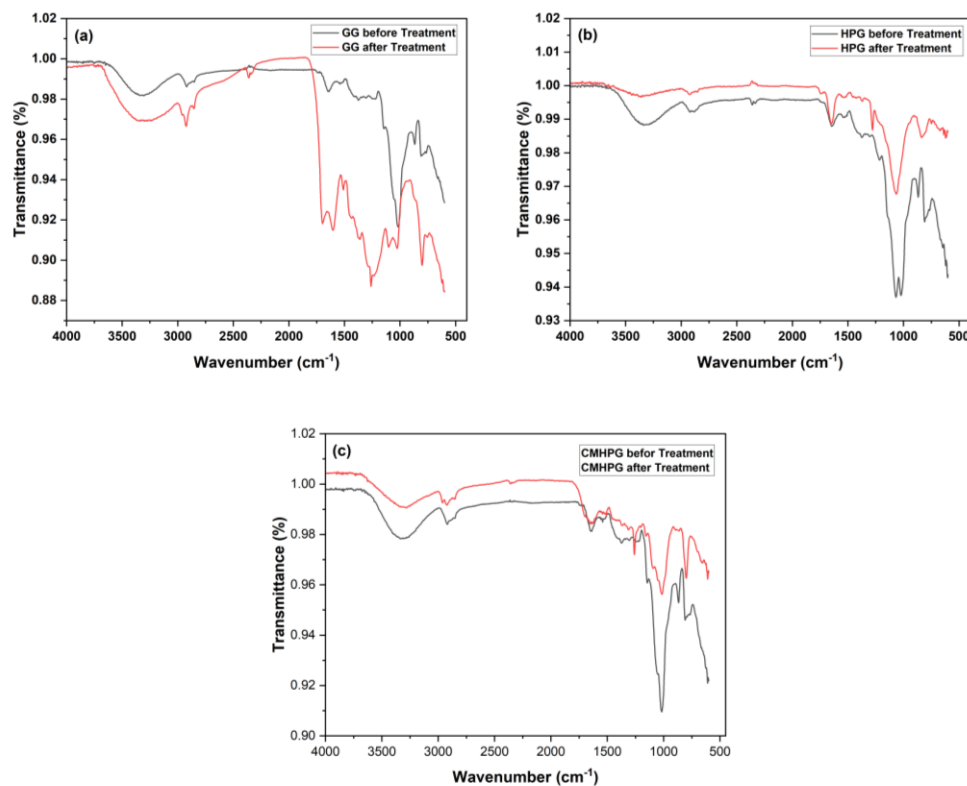


Figure 6.13 FTIR spectra of 40lb/1,000 gal linear gel polymers before and after thermal treatment at 500°F (a) GG, (b) HPG and (c) CMHPG

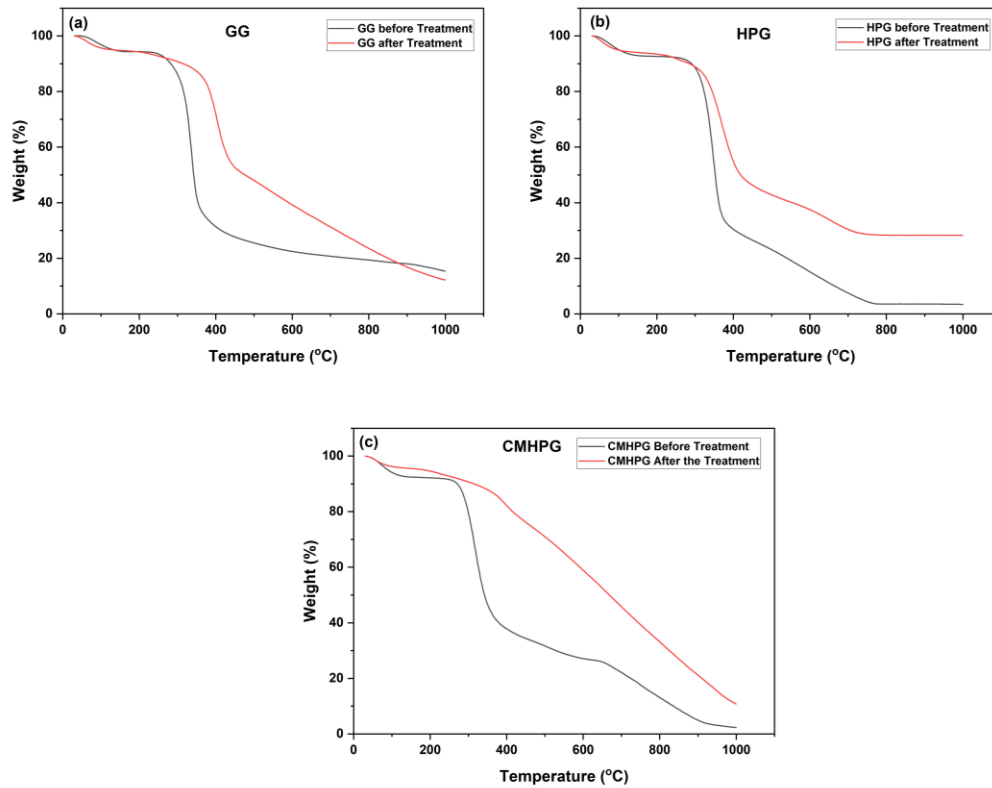


Figure 6.14 TGA before and after thermal treatment at 500°F for one hour of for linear gel polymers (a) GG, (b) HPG and (c) CMHPG

6.3.5 Coreflood Experiments: Assessing TCFs as Cleanup Fluid

Fracturing fluids cleanup process involves the use of breakers to degrade fracturing polymers and ultimately reduce their viscosity, making it easier to flow back. To assess the suitability of TCFs as cleanup fluids, we examined the viscosity of linear gel polymers, including GG, HPG, CMHPG, and HVFR, exposed to thermal shock testing simulating the heat generated from the TCFs, as illustrated in Figure 6.15. The ultimate impact of using TCFs as cleanup fluids was assessed through the analysis of regained permeabilities obtained from coreflood experiments (Figures 6.17-6.19).

During the thermal shock test, the viscosity of the linear gels was monitored as a function of temperature and time. The results revealed that the viscosity of the linear gels approached nearly zero even before the sample temperature reached 500°F. The GG and its derivatives experienced a reduction in viscosity to almost zero at temperatures between 275 and nearly 400°F. In contrast, the HVFR linear gel required a higher temperature, approximately 475°F. These findings reveal that TCFs can be utilized as cleanup fluids for fracturing fluids.

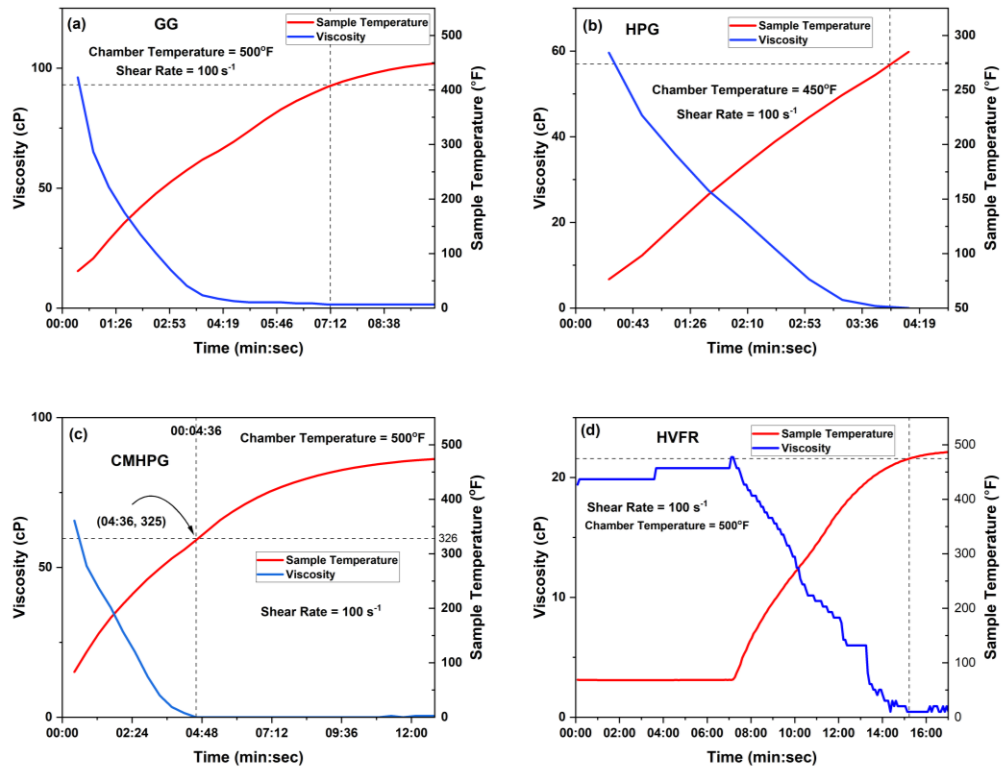


Figure 6.15-Thermal shock impact on viscosity of linear gels: (a) GG, (b) HPG, (c) CMHPG and(d) HVFR)

The use of encapsulated breakers in fracturing treatments is a common practice to achieve controlled release of active material, extend their activity, and reduce premature breakdown of polymers. The performance of encapsulated breakers is a function of breaker concentrations and downhole temperatures. Al-Taq et al. [131] observed that the performance of encapsulated breaker in reducing fracturing fluids viscosity enhanced with

increasing temperature. Figure 6.16 shows the TGA analysis for both live and encapsulated ammonium persulfate breaker. The results showed that both breakers experienced a weight loss more than 45 wt% in the region from 200 to 446°C, with the encapsulated breaker demonstrating greater temperature sensitivity. The live breaker showed no residual material, while the encapsulated breaker had nearly 9 wt% of residual material, which might be a source of formation damage.

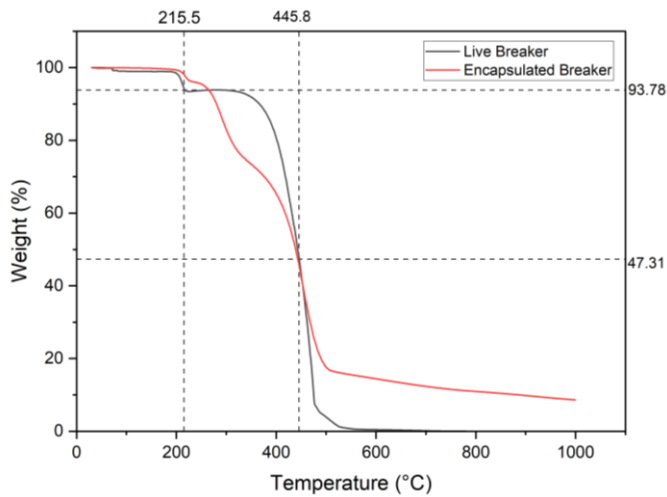


Figure 6.16-TGA of ammonium persulfate live and encapsulated breaker

A previous study reported that an increase in downhole pressure tended to decrease the release of active material from encapsulated breakers [132], which might be a concern for the application of TCFs, typically associated with generating a high increase in pressure. It is well-documented that the TCF reaction is linked to the generation of a high pulse pressure type, which has been reported to result in the formation of micro-fractures in cement blocks and core plugs [133-134]. Based on these findings, the pulse pressure generated by TCFs is expected to rupture the polymer films coating the breaker and thus result in more release of active material.

The coreflood experiments were conducted as an effective technique to assess the impact of TCFs as cleanup fluids. In this regard, the permeability of the core plug before and after

thermally treated fracturing was determined based on pressure drop-generated data. The calculated regained permeability is given as follows:

$$\text{Regained Permeability (\%)} = \frac{P_i}{P_f} \times 100$$

Where P_i and P_f represent the pressure drop due to the injection of brine solutions before and after injection of the thermally treated fracturing fluid, respectively. Three coreflood experiments were conducted on Indiana core plugs using the thermally treated HPG and CMHPG dual crosslinked formulations (Tables 6.1 and 6.2). The coreflood experiments were conducted at 220°F, with an overburden pressure of 3,000 psi and a back pressure of 1,000 psi (Figures 17 and 18). Figure 17 shows pressure drop due to the injection of 7 wt% NaCl brine and thermally treated ($T = 350^\circ\text{F}$) HPG-based fracturing fluid (Table 1). A regained permeability of 87.57% was obtained for the thermally treated HPG-borate crosslinked fracturing fluid. Since HPG gels are sensitive to temperatures more than 320°F [1], it was found that the thermal treatment of this fracturing fluid at 350°F was sufficient to break it.

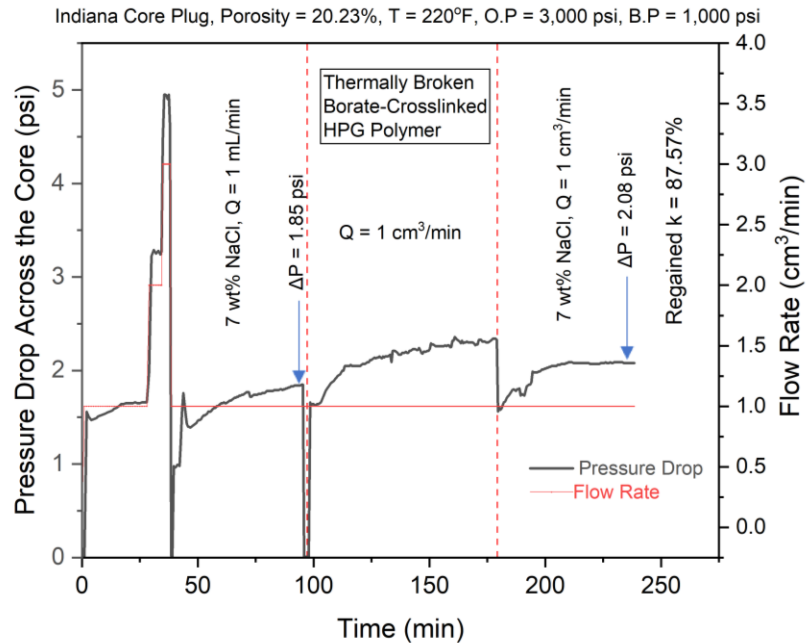


Figure 6.17-Coreflood experiment for thermal treated (350°F) HPG-Borate crosslinked polymer

A previous study reported that an increase in downhole pressure tended to decrease the release of active material from encapsulated breakers [133](Leo et al., 2002), which might be a concern for the application of TCFs, typically associated with generating a high increase in pressure. It is well-documented that the TCFs reaction is linked to the generation of a high pulse pressure type, which has been reported to result in the formation of micro-fractures in cement blocks and core plugs [134-135].^{24, 25} Based on these findings, the pulse pressure generated by TCFs is expected to rupture the polymer films coating the breaker and thus result in more release of active material.

The coreflood experiments were conducted as an effective technique to assess the impact of TCFs as cleanup fluids. In this regard, the permeability of the core plug before and after thermally treated fracturing was determined based on pressure drop-generated data. The calculated regained permeability is given as follows:

$$\text{Regained Permeability (\%)} = P_i/P_f \times 100$$

Where P_i and P_f represent the pressure drop due to the injection of brine solutions before and after injection of the thermally treated fracturing fluid, respectively. Three coreflood experiments were conducted on Indiana core plugs using the thermally treated HPG and CMHPG dual crosslinked formulations (Tables 6.1 and 6.2). The coreflood experiments were conducted at 220°F, with an overburden pressure of 3,000 psi and a back pressure of 1,000 psi (Figures 17 and 18). Figure 17 shows pressure drop due to the injection of 7 wt% NaCl brine and thermally treated ($T = 350^\circ\text{F}$) HPG-based fracturing fluid (Table 6.2). A regained permeability of 87.57% was obtained for the thermally treated HPG-borate crosslinked fracturing fluid. Since HPG gels are sensitive to temperatures more than 320°F²⁵, it was found that the thermal treatment of this fracturing fluid at 350°F was sufficient to break it.

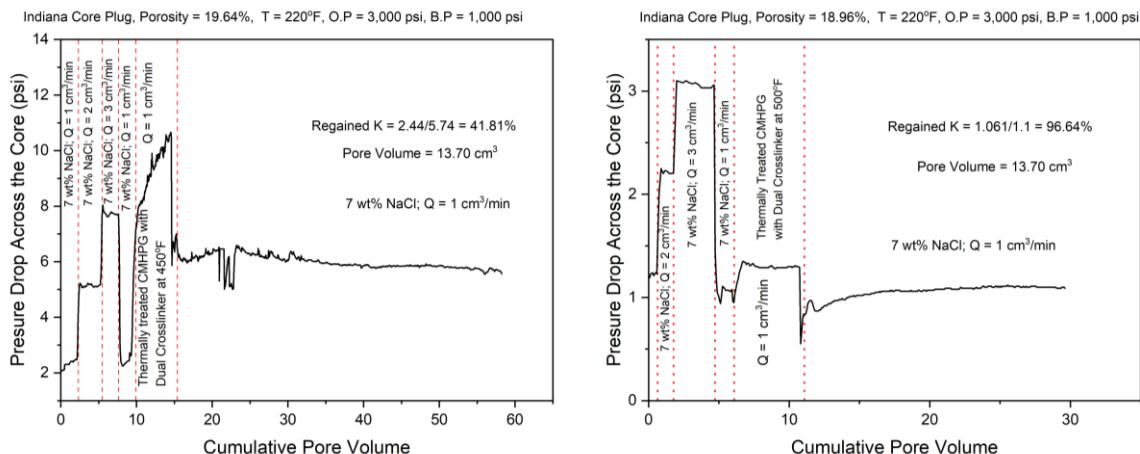


Figure 6.18-Coreflood experiment on CMHPG with dual crosslinker thermally treated at 450 and 500°F.

Another two coreflood experiments were conducted on slickwater (Table 6.3) using Berea sandstone core plugs. The coreflood experiments were conducted at 270°F, with an overburden pressure of 3,000 psi and a back pressure of 1,000 psi, as shown in Figure 19. The first experiment was conducted on slick water containing ammonium persulfate breaker at 0.5 gpt (Table 3). The fracturing fluid was aged at 270°F for 24 hours and then filtered through 10-micron ceramic disc before the use in the coreflood experiment. The results revealed that slick water including a breaker was not effective where only 41.81% was obtained. The same slickwater formulation without a breaker was thermally treated at 500°F for one hour, filtered through 10-micron ceramic disc and used in the coreflood experiment. The results showed that the regained permeability obtained was more than 90%. The results indicate that thermal treatment utilizing TCFs can be more effective than the use of breaker systems.

For the slickwater system (Table 6.3), two coreflood experiments were conducted on using Berea sandstone core plugs. The coreflood experiments were carried out at 270°F, with an overburden pressure of 3,000 psi and a back pressure of 1,000 psi, as shown in Figure 6.19. The first experiment was conducted on slickwater containing an ammonium persulfate breaker at 0.5 gpt (Table 6.3). The fracturing fluid was aged at 270°F for 24 hours and then filtered through a 10-micron ceramic disc before use in the coreflood experiment. The

results revealed that slickwater, including a breaker, was not effective, with only 41.81% regained permeability obtained. The same slickwater formulation without a breaker was thermally treated at 500°F for one hour, filtered through a 10-micron ceramic disc, and used in the coreflood experiment. The results showed that the regained permeability obtained was more than 90%. These results indicate that thermal treatment utilizing TCFs can be more effective than the use of breaker systems.

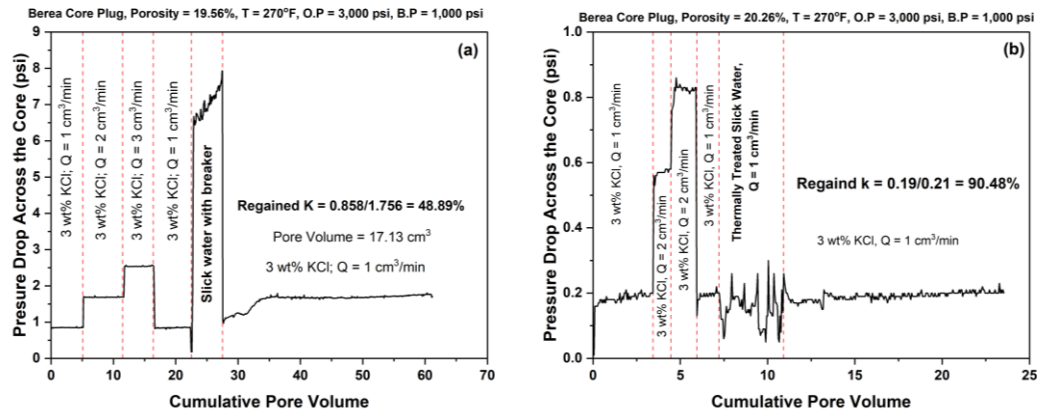


Figure 6.19-Coreflood experiments for slick water (a) with breaker and (b) thermally treated slick water

6.4 Discussion

Conventional fracturing fluid breakers, including acids, oxidizers, and enzymes, solely contribute to the cleanup of fractures by breaking the backbones of polymers incorporated in the fracturing fluids, which act as gelling agents. The cession of polymers polymer chains into small fragments by the breakers results in the reduction of fracturing fluids viscosity, ultimately facilitating fracturing fluid flowback and cleanup. The accepted reduction in fracturing fluids viscosity by breakers is ≤ 10 cP at 300rpm (511 1/s shear rate) [35].

The thermochemical salts of interest, $\text{NH}_4\text{Cl}/\text{NaNO}_2$, can contribute to fracturing fluid cleanup through various mechanisms, as inferred from experimental results obtained in this

study. These include viscosity reduction to nearly zero by heat, polymer degradation, and the reduction of well hydrostatic pressure through the generated nitrogen gas. In addition, the generated heat by the TCFs reaction can enhance the release of encapsulated breakers and thus provides better cleanup. Moreover, TCFs can mitigate phase trapping and formation damage typically induced by fracturing fluids in tight formations, such as unconventional shale reservoirs. Hassan et al [4](2019) reported that the thermochemical fluid treatment was able to reduce the high capillary pressure thus enhancing the trapped water removal. Moreover, the TCFs reaction is associated with a high pressure build up due to the generation of N_2 gas as shown in Figure 6.20. Hence, it was found that pressure positively influences polymer degradation [125,126].

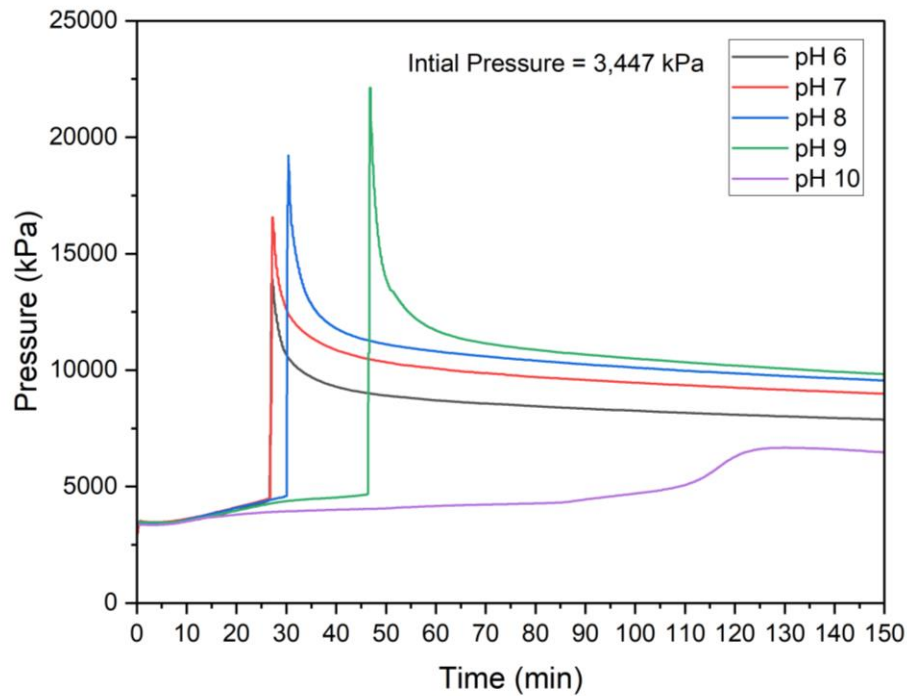


Figure 6.20. Pressure generated from the reaction of equimolar (5M) NH_4Cl and $NaNO_2$ as a function of pH values

6.5 Conclusions

- The reaction of TCFs in the forms of NH_4Cl and NaNO_2 was associated with the generation of substantial amounts of heat and nitrogen gas, which is a function of TCFs concentration, volume, and pH.
- The TGA analysis of guar gum and its derivatives (HPG and CMHPG) showed that major weight loss (56%) occurred in the region of 243 to 360°C; hence, TCFs at equimolar of 5M can generate a temperature of 343°C.
- The thermal shock tests demonstrated the effectiveness of thermal treatment on guar gum-based and HVFR linear gels, reducing their viscosity to nearly zero within short periods of time.
- Thermal treatment of liner gels containing GG, HPG, and CMHPG revealed substantial changes in their chemical and thermal properties, as inferred from FTIR and TGA analyses conducted on these samples before and after the thermal treatment.
- The regained permeabilities of 87.57%, 96.54%, and 90.48% were obtained for the thermally treated fracturing fluids of HPG borate crosslinked, CMHPG dual crosslinked, and slickwater fracturing fluid, respectively.
- These coreflooding results indicate that thermal treatment utilizing TCFs can be more effective than the use of breaker system, as observed in the case of the slickwater system.
- The study findings reveal that TCFs can be used as effective cleanup fluids for different fracturing fluid systems

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