# SYNTHESIS AND CHARACTERIZATION OF CATIONIC-DIUTAN GUM TO ENHANCE THERMAL STABILITY FOR OIL & GAS APPLICATION



اونيؤرسيتي مليسيا قهع السلطان عبدالله UNIVERSITI MALAYSIA PAHANG AL-SULTAN ABDULLAH

# MASTER OF SCIENCE

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### SYNTHESIS AND CHARACTERIZATION OF CATIONIC-DIUTAN GUM TO ENHANCE THERMAL STABILITY FOR OIL & GAS APPLICATION

## NORHANIS BINTI ARBAA'IN



Thesis submitted in fulfillment of the requirements و نیو for the award of the degree of UNIVERSIT Master of Science PAHANG AL-SULTAN ABDULLAH

Faculty of Industrial Sciences and Technology

UNIVERSITI MALAYSIA PAHANG AL-SULTAN ABDULLAH

APRIL 2024

#### ACKNOWLEDGEMENTS

In the name of ALLAH S.W.T, the Most Gracious and Most Merciful.

Alhamdulillah, all praise to ALLAH for providing me the strength and His blessing to complete this work. Special appreciation goes to my kind-hearted supervisor, Dr. Rasidi Roslan, for his supervision and constant support. His invaluable help of constructive comments and suggestions throughout the experimental and thesis work have contributed to the success of this research. I would like to thank my cosupervisor, Professor ChM. Dr. Mohd Hasbi Ab Rahim and Professor Dr. Jamil Ismail for their assistance and knowledge sharing throughout the research activity and thesis writing.

Appreciation to the entire laboratory assistant and the Faculty of Industrial Sciences and Technology office staff for their cooperation during my studies period. Not to forget all my friends for their kindness and moral support during my study. Thanks for the friendship and memories. This research would not have been possible without the financial support from the University Malaysia Pahang Al-Sultan Abdullah under grant no. of RDU170237 and RDU190330. Special thanks to the Centre of Excellence for Advanced Research in Fluid Flow (CARIFF) for their laboratory facilities.

Last but not least, my deepest gratitude goes to my beloved family and husband for their endless love, prayers, and encouragement. To those who indirectly contributed to this research, your kindness means a lot to me. Thank you very much.

> اونيۇرسىتى مليسىيا قهڭ السلطان عبدالله UNIVERSITI MALAYSIA PAHANG AL-SULTAN ABDULLAH

#### ABSTRAK

Bendalir berasaskan air telah digunakan selama berabad-abad dalam aplikasi minyak dan gas, terutamanya sebagai bendalir penggerudian. Kemajuan teknologi telah menunjukkan penambahan tanah liat, bahan polimer, dan banyak bahan lain yang dimasukkan ke dalam cecair berasaskan air untuk membuat sistem bendalir yang teguh untuk memenuhi permintaan pelbagai keadaan takungan dan untuk meningkatkan pengeluaran minyak dan gas. Cecair boleh disesuaikan untuk polimer larut air dengan sifat pelikatan atau pembentuk gel. Memandangkan minyak dan gas di telaga cetek semakin berkurangan, penerokaan minyak dan gas berlaku dalam keadaan takungan yang lebih dalam dan lebih ekstrem, yang mengehadkan prestasi cecair gel yang sedia ada. Pada suhu tinggi, cecair pembentuk gel akan mengalami degradasi dan kehilangan kelikatannya. Tanpa mengorbankan keselamatan alam sekitar, penambahbaikan cecair untuk pembentuk gel 'hijau' adalah lebih baik berbanding menukar fokus ke arah polimer sintetik yang mana meningkatkan hanya sedikit kestabilan terma berbanding bahan biopolimer. Di antara biopolimer, diutan gum (DG) dipilih kerana berat molekulnya yang tinggi dan sifat heliks berganda. Penggunaan DG masih boleh dianggap baru dalam industri minyak dan gas; oleh itu, pelbagai potensinya boleh diterokai. Untuk mempertingkatkan lagi sifat DG asli, kationisasi DG telah dijalankan dalam penyelidikan ini. Biopolimer kationik diutan gum (CDG) telah dihasilkan dengan menggabungkan kumpulan amina kuaterner pada struktur DG untuk meningkatkan sifat reologi dan terma. Modifikasi dijalankan melalui tindakbalas antara DG dengan N-(3kloro-2-hidroksipropil) trimetil ammonium klorida (CHPTAC) pada kepekatan berbeza untuk menghasilkan CDG dengan menggunakan natrium hidroksida sebagai mangkin. Kationisasi bagi polisakarida menggunakan CHPTAC mengakibatkan penurunan %H dari 5.54% kepada 3.81% dan peningkatan %N dari 0.72 kepada 0.83. Keputusan darjah penggantian (DP) ini menunjukkan pembentukan alkoksida pada kumpulan hidroksil polisakarida dan penyambungan CHPTAC ke dalam struktur polisakarida. Keputusan spektroskopi inframerah transformasi Fourier (FTIR) mengesahkan penggabungan unsur kationik ke dalam rantai CDG dengan peningkatan keamatan puncak pada 1411 cm<sup>-1</sup> yang dikaitkan dengan getaran regangan C-N. Morfologi permukaan yang diperhatikan melalui mikroskop pengimbasan elektron pancaran medan (FESEM) menunjukkan bahawa permukaan licin DG telah ditukar kepada struktur retikular sfera penghubung selepas pengubahsuaian CHPTAC. Kelikatan cecair pengegelan CDG meningkat selepas pengubahsuaian disebabkan oleh interaksi rantai elektrostatik. Walau bagaimanapun, untuk CDG dengan kepekatan CHPTAC yang lebih tinggi, kelikatan telah menurun. Selain itu, sifat kelikatan menunjukkan bahawa kawasan seperti dataran tinggi diperhatikan, menandakan tindak balas gel yang stabil terhadap kekerapan. Ini menunjukkan keupayaan penggantungan CDG yang sangat baik. Daripada analisis termogravimetrik (TGA) dan analisis kalorimetri pengimbasan pembezaan (DSC), ciri terma sedikit meningkat untuk CDG berbanding dengan DG. Analisis kestabilan terma menggunakan ujian penuaan terma statik menunjukkan bahawa CDG adalah stabil sehingga 170 °C. Secara kesimpulannya, pembangunan kationik diutan gum (CDG) menjanjikan peningkatan sifat termal dan reologi sistem bendalir berasaskan air, menjadikannya calon berpotensi untuk pelbagai keadaan rizab minyak dan gas yang mencabar.

#### ABSTRACT

Water-based fluids have been used for centuries in oil and gas applications. Technological advancements, particularly the addition of clay, polymer material, and many other substances into the water-based fluids, were made to create a robust fluid system to suit the demands of various reservoir conditions and to enhance oil and gas production. The fluids can be tailored for water-soluble polymers with viscosifying or gelling properties. As the oil and gas in the shallow wells become depleted, the oil and gas exploration has moved into deeper and more extreme reservoir conditions, which limited the performance of the currently available gelling fluids. At high temperatures, the gelling fluids will experience degradation and lose their viscosity. To preserve environmental safety, it is more favorable to improve 'green' gelling fluid produced from biopolymer material instead of changing focus towards synthetic polymers with only slightly better thermal stability. Amongst the biopolymers, diutan gum (DG) was chosen due to its high molecular weight and double helical structure. The application of DG can still be considered new in the oil and gas industry; therefore, many of its potentials need to be explored. The cationization of DG was conducted in this research to further enhance the properties of DG. Cationic diutan gum (CDG) biopolymer was developed to improve the thermal and rheological properties of water-based gelling systems for upstream petroleum applications. The modification process involved incorporating a quaternary amine group onto the diutan gum (DG) structure by mixing DG with varying concentrations of N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) in the presence of sodium hydroxide as a catalyst. The cationization resulted in a decrease in %H from 5.54% to 3.81% and an increase in %N from 0.72 to 0.83, indicating the successful formation and grafting of CHPTAC onto the polysaccharide structure. Fourier transform infrared spectroscopy (FTIR) confirmed the incorporation of cationic moieties into the CDG chains, observed through an increase in the intensity of the C-N stretching vibration peak at 1411 cm<sup>-1</sup>. Field emission scanning electron microscopy (FESEM) revealed that the smooth surface of DG transformed into a connective spherical reticular structure upon CHPTAC modification. The viscosity of the CDG gelling fluid increased due to electrostatic chain interaction, except for CDG with higher CHPTAC concentrations, which exhibited decreased viscosity. Additionally, the viscoelasticity properties displayed a plateau-like region, indicating a stable gel response towards frequency and excellent suspension capability of CDG. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) demonstrated a slight improvement in thermal characteristics for CDG compared to DG. Furthermore, the thermal stability analysis using a static thermal aging test confirmed that CDG remained stable up to 170 °C, highlighting its potential to meet the high-temperature requirements of the upstream petroleum industry. In conclusion, the development of cationic diutan gum (CDG) presents a promising approach for enhancing the thermal and rheological properties of water-based gelling systems, making it a potential candidate for various challenging oil and gas reservoir conditions.

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## LIST OF SYMBOLS

+	plus
~	tilde, almost equal to
%	percentage
σ	shear stress
$\eta$	viscosity
γ	shear rate
°C	degree celcius
°C/min	degree celcius per minute
cm	centi meter
cm <sup>-1</sup>	per centimeter
cP	centi poise
G′	elastic modulus
G″	viscosity modulus
g/L	gram per litre
g/mol	gram per mole
Hz	hertz
K min <sup>-1</sup>	Kelvin per minute
kV	kilo volt
L	liter
m	meter
mg	milli gram
ml	milli meter
mg/L	milligram per liter
ml/min	millileter per minute psa
pН	potential hydrogen
S	second
$s^{-1}$	per second
Tg	اونيورسيني مد glass transation temperature الله
Tm	melting transation temperature
wt.%	weight percentage
	<b>AL-SULTAN ABDULLAH</b>

## LIST OF ABBREVIATIONS

AFM	atomic force microscopy
AGU	anhydroglucose unit
API	American Petroleum Institute
BC	before century
С	carbon
CDG	cationic-diutan gum
CHPTAC	n-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride
CMC	carboxymethylcellulose
CWG	cationized welan gum
DG	diutan gum
DNA	deoxyribonucleic acid
DS	degree of Substitution
DSC	differential scanning calorimetry
EOR	enhancing oil recovery
FESEM	field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
GG	guar gum
Н	hydrogen
HEC	hydroxyethylcellulose
HPAM	hydrolyzed polyacrylamide
HTHP	high temperature high pressure
IR	infrared
KBr	potassium bromide
LVER	linear viscoelastic region
Ν	nitrogen
$NaBH_4$	sodium tetrahydridoborate
NaOH	sodium hydroxide
NMR	nuclear magnetic resonance in his nuclear magnetic resonance
RNA	ribonucleic acid
RP	recommended practice
SCB	A sugarcane bagasse ABDULLAF
SPE	Society of Petroleum Engineers
TGA	thermogravimetric analysis
VEA	viscosity-enhancing agents
WG	welan gum
XG	xanthan gum

#### **CHAPTER 1**

#### **INTRODUCTION**

#### 1.1 Background of Research

The widespread application of viscous fluids in oil reservoirs has become a standard approach for improving the production of oil and gas through various operations such as fracturing, drilling, completion, and workover (Barati and Liang, 2014; Fink, 2015). The primary purpose of the fracturing fluid is to transport sand or proppant into underground formations. By injecting the fluid at high pressure, it creates minute cracks in the rock, while the proppant acts as a support to keep the fractures open. As a result, this process facilitates the flow of natural gas from shale fissures into the oil well, leading to a significant boost in both oil and gas production (Zhao et al., 2016). In a drilling operation, the viscous drilling fluid, also called drilling mud, is used to suspend the cuttings and carry cuttings out from the drill hole. Apart from that, it also functions as a coolant and a cleaner for the drill bit (Yalman et al., 2022). Meanwhile, the completion fluid is used during the completion step or re-completion of the drilling process. There are several completion operations, such as perforating the casing, cementing, and setting the pump and tubing. The completion fluid plays a part in controlling the pressure of the well, and preventing the casing from blowing out or collapsing due to overpressure (Caenn et al., 2011). Similarly, the workover fluid employed during restoration work in the well is also used to control the well pressure. This remedial work includes removing the tube, logging, replacing the pump, deposit or sand cleaning and reperforating (Panamarathupalayam and Manzolelua, 2022).

Water or an aqueous solution can be transformed into a more viscous fluid by incorporating a thickening or gelling agent, typically polymers. Several polymers are employed to achieve this effect, including various polysaccharides like guar gum and its derivatives (Mao et al., 2023; Xiong et al., 2022), xanthan gum (Nsengiyumva and

Alexandridis, 2022), carboxymethyl cellulose (Soares et al., 2020), and hydroxyethyl cellulose (Ouaer and Gareche, 2019). Typically, water-based fluids are favored over oilbased fluids due to their environmentally friendly nature, biodegradability, and renewable resource origin. Nevertheless, as the focus of oil exploration shifts towards reservoirs with higher temperatures, traditional gelling agents' utility has diminished due to their inability to endure the elevated temperatures. When biopolymers are subjected to temperatures surpassing 148 °C, they experience thermal degradation, causing a reduction in their viscosity (Hassan et al., 2022). As a result, extensive research has been conducted to enhance the thermal characteristics of gelling fluids, which can be categorized into three approaches: (1) modification involving crosslinkers, fluid loss additives, and antioxidants (Fink, 2021; Liang et al., 2017), (2) alterations to the structure of the gelling agents (Dai et al., 2017; Shi et al., 2018; Yang et al., 2017), and (3) utilization of double helical biopolymers (such as xanthan, diutan, and welan gum) which are believed to be well-suited for reservoirs with high temperatures and salinity levels (Elella et al., 2021; Li et al., 2020b; Xu et al., 2015).

Among the three techniques applied to improve the thermal characteristics of gelling fluids, double-helical biopolymers utilization, particularly diutan gum (DG), emerges as an exceptionally promising and economically viable strategy. DG, sourced from *Sphingomonas sp.*, is a natural, high-molecular-weight microbial polysaccharide initially employed in the cement and concrete industry. DG has demonstrated its effectiveness in enhancing cement paste performance through increased viscosity (Zhang et al., 2010). One of the remarkable features of DG is its temperature insensitivity and almost complete independence from the effects of salinity. This characteristic results in consistent apparent viscosity and dynamic modulus, allowing DG to maintain its viscosity even at temperatures as high as 75 °C (Xu et al., 2015). Remarkably, DG retains 90% of its viscosity even at 90 °C, making it particularly well-suited for applications in high-temperature environments (Li et al., 2017).

In this study, diutan gum (DG) was selected as the primary gelling agent for comparison, given its intriguing rheological characteristics that align well with high-temperature and high-salinity conditions. To enhance the DG's thermal properties, its structure underwent modification through the substitution of quaternary amine groups on the hydroxyl groups, thus yielding cationic-distant gum (CDG). The selection and

utilization of CHPTAC for the modification of diutan gum (DG) were thoroughly justified based on several key factors. Firstly, CHPTAC is widely recognized for its ability to introduce quaternary ammonium groups onto polymer backbones, enhancing their cationic character and imparting desirable properties such as improved solubility, stability, and rheological behavior. Additionally, previous studies have demonstrated the successful modification of various polysaccharides using CHPTAC, indicating its efficacy as a modifying agent. Furthermore, considering the intended application of the modified DG in our study, which may involve interactions with charged species or surfaces, the cationic nature of CHPTAC-modified DG could offer unique advantages in terms of compatibility and performance. Thus, the selection of CHPTAC for DG modification was based on its proven effectiveness, compatibility with DG, and its potential to confer desirable properties for the intended application. The DG and CDG samples underwent comprehensive analysis and characterization via diverse methods, including field emission scanning electron microscopy (FESEM), elemental analysis, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FTIR). For the formulation of the gelling fluid, both DG and CDG were hydrated within a saline solution using a high-speed mixer. The thermal stability of the gelling fluids (DG and CDG) was probed using a hot rolling oven, following the standards set by the American Petroleum Institute (API RP 13I, 2016). API RP 13I, the "Recommended Practice for Laboratory Testing of Drilling Fluids," offers standardized procedures for evaluating the properties of drilling fluids essential for safe and efficient oil and gas drilling operations. The standard encompasses a wide array of tests, including density, viscosity, filtration, rheology, fluid loss, pH, electrical stability, chloride content, alkalinity, calcium content, solids content, and emulsion stability. Through detailed instructions on sample preparation, equipment setup, measurement techniques, and quality assurance, API RP 13I ensures accurate and reliable testing outcomes. Applicable to both water-based and oil-based drilling fluids across various drilling stages, this standard serves as an indispensable resource for drilling engineers, fluid specialists, and laboratory technicians, facilitating the assessment of drilling fluid performance to meet operational requirements while minimizing risks. Furthermore, their rheological behaviors and suspension capability were assessed using a rheometer operating in oscillation mode.

#### **1.2 Problem Statement**

In modern oil exploration, a notable shift has been towards investigating highertemperature reservoirs. Several modifications have been introduced to different biopolymers to adapt to these challenging conditions. One prominent example involves the application of borate as a crosslinker to enhance the thermal stability of guar gum, enabling it to withstand temperatures up to 148 °C (Nianyin et al., 2022). However, this crosslinking process results in a gelling fluid with exceedingly high viscosity, surpassing 1000 cPs. Such viscosity levels are well above the ideal range for creating fractures, typically requiring lower viscosities of 2-30 cPs for weaker formations and 100-500 cPs for stronger formations (Montgomery, 2013). Undoubtedly, higherviscosity fluids offer greater strength and resilience, especially in high-temperature environments. Nevertheless, the drawback lies in the necessity for elevated pumping pressures during operations due to the increased viscosity. To overcome this limitation associated with crosslinked-guar gum, xanthan gum emerges as a viable alternative and finds widespread usage as a water-soluble polymer. Nevertheless, xanthan gum's application is limited to moderate temperatures (90 °C), failing to address the existing challenges related to high-temperature wells. Nonetheless, a recent development involves modifying xanthan gum by incorporating quaternary amine groups into its structure, which has been shown to enhance its thermal stability (Shi et al., 2018). The discovery is intriguing because traditional xanthan gum is typically utilized at temperatures below 100 °C. However, the addition of quaternary amine groups through modification significantly improved its thermal stability. This enhancement resulted from the stronger electrostatic interaction among the chains, leading to a reinforced gellike structure. As a consequence, the modified xanthan gum could be effectively employed at higher temperatures, reaching approximately 120 °C. Building upon this remarkable finding, the study aimed to investigate the effects of introducing quaternary amine groups to modify diutan gum (DG). Given that unmodified DG already demonstrates resilience at temperatures around 120-150 °C, the anticipation was that the structural modification with quaternary amine groups would further augment its thermal stability. As a result, DG could become a promising candidate for highpressure, high-temperature (HPHT) oil and gas applications, owing to its exceptional thermal stability and ability to maintain viscosity and suspension properties even under elevated temperatures and pressures.

In the domain of oil and gas exploration, the evolution of materials for waterbased fluids is a critical aspect. Traditionally, synthetic polymers have dominated this field due to their advantageous properties, such as stability and viscosity control. However, growing environmental concerns and the need for sustainable solutions have prompted a shift towards biopolymers. This transition is motivated by the desire to mitigate the environmental impact of oil and gas operations and comply with increasingly stringent regulations. Consequently, biopolymers like diutan gum (DG) have emerged as viable alternatives to synthetic polymers. DG's emergence is driven by its exceptional thermal stability, viscosity, and suspension properties, particularly in high-temperature, high-pressure (HTHP) environments encountered during oil and gas exploration. By offering a sustainable and effective solution, DG addresses the limitations of synthetic polymers while meeting the industry's evolving needs for environmentally friendly and performance-driven materials in water-based fluids.

#### 1.3 Objectives

This research is dedicated to investigating the impact of incorporating a quaternary amine into diutan gum (DG) to improve its properties. To accomplish this goal, the study has formulated the following specific objectives:

- 1. To optimize the modification of DG to CDG with quaternary amine groups.
- To investigate the rheological properties and suspension capabilities of cationized DG.
- 3. To investigate the effect of cationization on the physicochemical properties of cationized DG.

#### **1.4** Scope of the Study

This research project was investigated in three distinct phases, outlined as follows:

#### Phase 1

To fulfill the first objective, the enhancement of CDG was pursued through the introduction of quaternary amine groups into the hydroxyl groups of DG, employing N-

(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC). This modification will be limited to the use of CHPTAC only. Different concentrations of CHPTAC (ranging from 0.5 to 4.0 ml) were incorporated into 30 g of DG to evaluate the influence of varying CHPTAC levels on DG's structure. This modification was verified by subjecting both DG and CDG to FTIR analysis, which revealed the presence of an amine functional group in CDG. Furthermore, FESEM imaging was employed to visually inspect and compare the morphologies of DG and CDG.

#### Phase 2

To achieve the second objective, the viscosity of both DG and CDG gelling fluids was evaluated using the Malvern Kinexus Lab+ rheometer. The assessment was carried out under room temperature conditions, employing cup and bob geometry while maintaining a shear rate of 170 s<sup>-1</sup>. By exposing the samples to a range of shear rates spanning from 0.01 to 1000 s<sup>-1</sup>, flow curves were generated. Moreover, to investigate the suspension capabilities of the DG and CDG gelling fluids, a rheometer with plate and plate geometry was employed. The linear viscoelastic region (LVER) was established through a strain sweep ranging from 0.1% to 1000% at a frequency of 1 Hz. Furthermore, a frequency sweep spanning from 0.01 to 100 Hz was conducted. The resultant elastic modulus (G') and viscosity modulus (G") derived from these evaluations were analyzed to quantify the fluids' suspension abilities.

Phase 3 AL-SULTAN ABDULLAH

To fulfill the third objective, Thermal Gravimetric Analysis (TGA) was employed to investigate the weight loss and decomposition temperature of both DG and CDG. Furthermore, Differential Scanning Calorimetry (DSC) analysis was conducted to explore the glass transition (Tg) and melting temperature (Tm) of these materials. To evaluate the thermal stability of the DG and CDG gelling fluids when subjected to high temperatures of up to 200 °C, an autoclave was employed. This enabled the observation of how the fluids responded under elevated temperature conditions, providing valuable insights into their stability and performance at extreme thermal situations.

#### **1.5** Significance of the study

This study is focused on the modification of DG with CHPTAC. DG is one of the double-helical biopolymers believed to be suitable for high temperature and high salinity conditions. Furthermore, DG is a biopolymer that is characteristically biocompatible, biodegradable, and environmentally friendly. This study will provide a significant outcome to overcome the limitations of oil exploration in higher-temperature reservoirs. In addition, this research also contributes to a better understanding of the cationization of DG since although there are many cationization studies that have been done on several types of polysaccharides, none were done on DG. Besides, the parameters and results obtained in this study are beneficial for the development of an effective fluid for high-temperature oil and gas exploration activities.

#### 1.6 Thesis Organization

The overall structure of this thesis consists of five chapters (Chapters 1 - 5). Chapter 1 is first presented, explaining the research background and defining the problem statement, objectives, scope of the study, and significance of the study. Chapter 2 contains further knowledge, strength, and limitations of the currently used gelling fluids, together with relevant investigation and ideas to improve it by using CDG. The following chapter is Chapter 3, which provides the experimental setup and research methodology, a list of materials, and methods utilized for DG and CDG synthesis and optimization. This chapter also includes the characterization and method to analyze the properties of the CDG gelling fluid. After that, all the results and findings from this study are presented in Chapter 4. Finally, Chapter 5 summarizes all the results obtained, concludes the research outcome, and provides several recommendations for further research.

#### **CHAPTER 2**

#### LITERATURE REVIEW

#### 2.1 Background

This chapter presents a comprehensive literature review on water-based fluids for use in high-temperature and high-pressure reservoirs in the oil and gas industry. A brief history of oil and gas exploration is given and includes the operational methodology. Several issues relating to this industry are addressed in this chapter. As the world's dependence on petroleum-based products increases, continuous effort and research for sustainable sources of water-based fluids are necessary. Therefore, several new solutions are discussed based on previous reports and literature to tackle the problem. Furthermore, this chapter also covers the utilization of polymers, especially polysaccharides, in the oil and gas industry. This also includes the theoretical background of polysaccharides cationization and its capability to enhance the oil and gas industry in extreme conditions.

#### 2.2 Fluid for the oil and gas industry

The history of the oil and gas industry started in 347 BC in China (Al-Sheikh Jadeer, 2022). A wellbore of approximately 240 m was drilled using bamboo poles with bits attached to it. It was a significant achievement in the history of drilling and allowed for the extraction of natural gas and brine from the earth. Since then, the technology has greatly developed. The classification of oil and gas wells into shallow, deep, and ultra-deep wells is based on their depth and the drilling techniques used to access them. Each well type presents unique challenges and requires specific drilling fluids and techniques. Understanding these differences is critical to the success of oil and gas operations (Pu et al., 2022).

Shallow wells are typically less than 500 feet deep and are drilled using conventional drilling techniques. These wells access oil and gas reserves in relatively shallow formations, such as sandstone or limestone. Shallow wells are generally less expensive to drill and operate than deeper wells but also tend to have lower production rates and shorter lifespans (Jackson et al., 2015). Deep wells are typically between 500 and 10,000 feet deep and are drilled using a combination of conventional and advanced drilling techniques, such as directional drilling and hydraulic fracturing. These wells are often used to access oil and gas reserves in deeper formations, such as shale or tight sandstone. Deep wells are generally more expensive to drill and operate than shallow wells, but they also tend to have higher production rates and longer lifespans (Ma et al., 2016). Ultra-deep wells are typically deeper than 10,000 feet and are drilled using advanced drilling techniques, such as extended-reach drilling and managed pressure drilling. These wells are frequently utilized to reach oil and gas deposits in incredibly deep formations, like salt domes or subsea reservoirs. Ultra-deep wells are the most expensive and technically challenging type of wells to drill and operate, but they can also have the highest production rates and the longest lifespans (van Oort et al., 2021). The drilling of shallow, deep, and ultra-deep wells requires different types of drilling fluids and techniques, depending on the characteristics of the formations being drilled and the desired properties of the fluids. For example, drilling fluids used in ultra-deep wells must be able to withstand high temperatures and pressures while also providing lubrication and preventing formation damage (Zhu et al., 2017). L-SULIAN

Nowadays, due to the global demand for energy, which increased by 81%, oil and gas explorations have moved toward deeper and extreme reservoirs (Liden et al., 2017). Drilling for hydrocarbons in extremely deep wells is challenging because of high temperatures and pressure in the wellbores. This type of reservoir is known as an unconventional reservoir. Figure 2.1 shows the illustration of the conventional reservoir and unconventional reservoir. The oil and gas could be obtained straightforwardly from conventional reservoirs without specialized tools or technology. In comparison, the oil and gas extraction from the formation is more difficult from the unconventional reservoir due to the harsh conditions in the wells. Other than temperature and pressure, other considerations must be taken into account for unconventional hydrocarbon formation, such as the mineralogy, pH, poor permeability and porosity, rock morphology, and shale condition (Everett et al., 2012).



Figure 2.1 Illustration of conventional and unconventional reservoir Source: (Haswell and Shearman, 2019)

For traditional reservoirs, the wellbore is often drilled vertically and directly into the petroliferous strata, which are layers of rock containing oil and gas. However, horizontal drilling is necessary for the unconventional reservoirs to acquire oil and gas. The traditional methods or fluids are unsuitable as they will degrade under the high temperatures and pressure found in the hostile environment of the unconventional reservoirs. For example, the utilization of hydroxyethyl cellulose for the completion process is commonly used in conventional wells because it can be easily removed (Liu et al., 2021) but it cannot be used in unconventional reservoirs due to it being unstable at high temperatures. Another example is the commonly used bentonite in fresh-water mud, which cannot be used when the salinity rises. This led to inept flocculation and clay swelling, leading to increased fluid loss and reduced viscosity (Sami, 2016). Therefore, an advanced fluid is needed to tackle the wide range of difficulties in horizontal drilling.

As the oil and gas industry is essential to the global economy for fuel in numerous sectors such as transportation, heating, and electricity generation, this industry relies on various fluids to facilitate the exploration, drilling, completion, and production of oil and gas reserves. One of the most crucial fluids used in the oil and gas industry is drilling fluids. Also known as drilling muds, these fluids play a vital role in the drilling process, helping to lubricate the drill bit, carry cuttings to the surface, and control the pressure in the wellbore (Mohamed et al., 2021). Drilling fluids are typically a mixture of water, clay, and various additives such as polymers, surfactants, and weighting agents (Kania et al., 2015). The selection of drilling fluids depends on several factors, including the type of formation being drilled, the drilling conditions, and the desired properties of the fluid. For example, drilling fluids may be formulated with high viscosity in shale formations to prevent the fluid from leaking into the formation and causing damage. Drilling fluids have revolutionized the oil and gas industry, enabling drilling operations to occur at greater depths and under more challenging conditions (Jain et al., 2015).

After the drilling process, completion fluids are used to clean out the wellbore and prepare the well for production. Completion fluids can also be used to control pressure in the well and prevent formation damage during the completion process. The selection of completion fluids depends on the type of reservoir being produced, the desired flow rate, and the desired characteristics of the fluid. Completion fluids can be water-based, oil-based, or synthetic-based, depending on the needs of the well (Khan et al., 2022).

One of the most challenging aspects of the oil and gas industry is extracting oil and gas from tight formations. This process is accomplished through hydraulic fracturing, which involves injecting fracturing fluids into the formation to create fissures that allow oil and gas to flow more easily. Fracturing fluids are typically a mixture of water, sand, and chemicals such as friction reducers, biocides, and scale inhibitors. The selection of fracturing fluids depends on several factors, including the type of formation being fractured, the desired flow rate, and the characteristics of the reservoir. For example, fracturing fluids may be formulated with high viscosity in formations with high clay content to prevent the fluid from leaking into the formation and causing damage. Fracturing fluids have been the subject of much controversy in recent years, with concerns about the environmental impact of the chemicals used in the process (Barati and Liang, 2014).

Another crucial element of the oil and gas sector is the production fluids. These fluids, normally made up of water, oil, gas, and numerous pollutants and impurities, are created simultaneously during the oil and gas extraction. The sale of natural gas liquids and other byproducts can help the oil and gas industry's bottom line, and the production fluids themselves can be a sizable source of income. Before the oil and gas can be sold, the production fluids must be separated and treated, and the water must be disposed of correctly to protect the environment. For instance, additional treatment and processing may be necessary for reservoirs with significant gas content to extract the gas and stop it from escaping into the atmosphere. Stringent environmental laws govern production fluid handling and disposal; noncompliance with these laws can result in hefty fines and penalties (Abdel-Aal et al., 2015).

In brief, the oil and gas industry relies on a variety of fluids to facilitate exploration, drilling, completion, and production. The selection of fluids depends on several factors, including the type of formation, the drilling conditions, and the desired properties of the fluid. Understanding the characteristics and properties of these fluids is critical to the success of oil and gas operations. The industry must also balance the economic benefits of oil and gas production with the environmental impact of fluid use and disposal. As the industry continues to evolve, there will be increasing pressure to develop new and innovative fluids that are more environmentally friendly and sustainable. Moreover, conventional fluids are unsuitable for High-Pressure High-Temperature (HPHT) operations in the oil and gas industry because they cannot withstand these extreme conditions and can break down or evaporate, leading to wellbore instability, lost circulation, and equipment failure. HPHT wells are becoming increasingly important as conventional oil and gas reserves are depleted and new reserves are found in deeper, hotter, and higher-pressure formations. However, these extreme conditions pose significant challenges to drilling, completion, and workover operations, and there is a need for advanced research to develop better HPHT fluids and techniques to overcome these challenges.

Numerous efforts have been made to optimize the reservoir's potential to produce oil and gas. As an example, a study was conducted by Galindo and co-workers to create a high-performance water-based drilling fluid (Galindo et al., 2015). They have produced a novel synthetic polymer for the HPHT well that can withstand up to 200 °C. Likewise, Zha et al. described two types of novel polymers used in brine-based drilling fluids that demonstrated exceptional thermal stability for up to 72 hours (Zha et al., 2015). Furthermore, the realization of the best thermally stable fluid system can be achieved by utilizing blended polymers. However, it is not cost-effective since there are too many combinations to produce such polymers. Another problem with blended

polymers is their difficulty in controlling the system. There are various things to consider, such as crosslinkers (Nianyin et al., 2022), viscosifier (Xie et al., 2018), fluid loss additives (Amanullah et al., 2016), shale stabilizers (Jiang et al., 2020), de-flocculant (Ghazali et al., 2018), friction reducers (Ba Geri et al., 2019), emulsifiers (Islamov et al., 2019), lubricants (Lan et al., 2020), density control (Bageri et al., 2020), and corrosion inhibitor (Askari et al., 2021). These additives may be practical and reliant on reservoir conditions. Nevertheless, using less additives during the exploration is still beneficial. In this study, surface functionalization to improve the properties of the fluid is foreseen to minimize this problem.

The fluid used in oil and gas industries can be divided into two, which are oilbased and water-based fluids. Oil-based fluids are more thermally stable than waterbased fluids. However, water-based fluidsare more environmentally friendly, hence 85% of drilling fluids used in recent years was composed of a water-based system (Fink, 2021). As the industry intensifies, a high-temperature water-based fluid is required to fulfill the current demand. This is because their stability at high temperatures remains low compared to oil-based fluids (Tehrani et al., 2007). Besides that, fluid loss, hydration, additives degradation, and clay dispersion could also be affected by thermal conditions (Wenjun et al., 2014). Since the regulation toward environmental pollution has become tighter, many companies have switched to the water-based fluid to avoid the fines and high cost of litigation action (Amanullah, 2007). In addition, the usage of oil-based fluids will disturb the geochemical analysis since it is hard to differentiate the oil-based fluids from the oil that comes from the formation. Furthermore, gas is more soluble in oil, creating a dangerous situation when an unanticipated gas influx into the well could not be detected until it is too near the surface. In contrast, this influx is easily detected and safely controlled in water-based fluids. Moreover, water-based fluids are preferable for use in high-pressure wells because they are less compressible than oil-based fluids. A higher compressibility will lead to an increase in viscosity. Therefore, this situation has led to the search for a superior water-based system with excellent rheological control and to retard problems associated with shales when exposed to the high temperature wellbore.

#### 2.3 Synthetic and bio-based polymer in oil and gas application

In the oil and gas fluid system, a gelling or thickening agent is an important component to be considered and can be categorized into synthetic-based fluids (SBFs) and water-based fluids (WBFs). The main function of this material is to control the fluids flow while performing the exploration. For example, the fluids need to be viscous enough (40 to 60 cPs) to hold the drill cutting, especially during the drilling, to pause and suspend the cutting (Werner et al., 2017). The cutting here refers to the cut or crushed rock (Figure 2.2). The fluids must be adequately viscous for fracturing application to carry the proppant for cracking the shale or oil formation (Figure 2.3a). A proppant is a solid material, usually sand, which meets suitable physical and chemical standards with varying sizes from 8 and 140 mesh (F. Liang et al., 2016). Specially engineered proppants are also available, as shown in Figure 2.3b.



Figure 2.2 Sample of drill cuttings under a 10x microscope Source: (Adebayo and Babatuyi, 2020)



Figure 2.3 (a) Illustration of cracked shale in fracturing operation (b) Example of industrial proppants

Source: (Guo et al., 2022)



SBFs are formulated with synthetic base fluids that are derived from various chemical compounds, such as esters, olefins, or linear alpha-olefins. These synthetic base fluids offer several advantages over traditional petroleum-based fluids, such as improved thermal stability, reduced toxicity, lower environmental impact, and better lubricity. SBFs can also be customized to meet specific oil well conditions and drilling objectives, making them popular for challenging drilling operations. Some common types of SBFs used in the oil and gas industry include ester-based fluids, olefin-based fluids, and linear alpha-olefin-based fluids (Gagnon and Bakhtyar, 2013).

Ester-based fluids are derived from organic acids and alcohols and have excellent thermal stability, biodegradability, and low toxicity. They are often used in HPHT drilling and completion operations to reduce wellbore damage, improve lubricity, and enhance well productivity (Kania et al., 2015). Olefin-based fluids, on the other hand, are derived from alpha-olefins and have good thermal stability, low toxicity, and high flash points. They are frequently employed in deepwater drilling operations where the fluid must remain stable and effective at high pressures and temperatures. Linear alpha-olefin-based fluids are derived from linear alpha-olefins and have excellent thermal stability, low toxicity, and good lubricity. They are frequently utilized in difficult drilling operations where conventional fluids might not be effective, such as in deepwater, high-pressure, and high-temperature wells (Emami et al., 2014). SBFs can be further enhanced by adding high-performance additives, such as organophilic clays, polymers, and synthetic oils, to improve their rheological properties, such as yield point, gel strength, and shear rate (Murtaza et al., 2021). These additives can optimize the SBF's performance for specific well conditions, such as controlling formation pressure, preventing formation damage, or enhancing well productivity. Overall, SBFs offer several advantages over traditional petroleum-based fluids and are a popular choice for HPHT drilling and completion operations in the oil and gas industry. However, SBFs are more expensive than water-based fluids and may require special handling and disposal procedures, which should be taken into account when selecting the most suitable fluid for each well.

One of the most well-known water-soluble synthetic polymers is partially hydrolyzed polyacrylamide (HPAM). HPAM is a water-soluble polymer widely used in the oil and gas industry to enhance oil recovery. It is an anionic polyacrylamide with a negative charge on its molecule and is highly effective in increasing the viscosity of injected water and reducing its mobility, allowing for more efficient oil displacement (Abidin et al., 2012). It is also stable at high temperatures and pressures, which is critical for enhanced oil recovery (EOR) operations that involve steam injection or hot water flooding. The temperature limit of HPAM can vary depending on the specific grade of HPAM used and the conditions of the application. HPAM is generally stable at temperatures up to 80-90 °C and can maintain its viscosity-enhancing properties within this range (Tamsilian et al., 2020). However, HPAM can undergo thermal degradation at higher temperatures, reducing its molecular weight and viscosity-enhancing properties that can compromise HPAM's effectiveness in EOR applications and increase the risk of environmental harm. In addition, HPAM can also be vulnerable to high salinity levels. In some cases, the presence of high salt concentrations in the reservoir can cause HPAM to undergo hydrolysis, which can result in a reduction of its molecular weight and viscosity-enhancing properties. This can compromise its effectiveness in EOR applications and reduce the efficiency of the oil recovery process. This phenomenon occurs because of the increase in the rete of hydrolysis of amide functional groups, which generates an increased amount of acrylic acid on the HPAM backbone. This increment subsequently results in the loss thickening ability of the polymer (Pu et al., 2018). It has been reported that when exposed to a temperature of 50 °C in the presence of divalent ions, the hydrolysis rate of HPAM was extended. As the

temperature rises to the range of 60–70 °C, the hydrolysis rate assumes a moderate pace, transitioning into a rapid rate as the temperature climbs to 90 °C (Oliveira et al., 2019). Some modification has been done to improve the properties of HPAM for high-temperature application (Abdullahi et al., 2019; Haruna et al., 2019; Zheng et al., 2017). However, unlike polysaccharides, polyacrylamide is commonly known as not biodegradable by microorganisms (Caulfield et al., 2002). Responsible and regulated use of HPAM is crucial to minimize potential environmental impacts. Proper handling and disposal methods should be followed to prevent HPAM from persisting in the environment and causing harm to aquatic organisms.

As the global demand for oil and gas continues to rise, there is an increasing need for more efficient and sustainable technologies for oil and gas exploration and production. Biopolymers, which are naturally occurring polymers derived from renewable sources, have been gaining attention as potential alternatives to synthetic polymers in oil and gas fluids. Biopolymers offer several advantages over synthetic polymers, including biodegradability, low toxicity, and compatibility with various reservoir conditions. The use of biopolymers in oil and gas fluids can improve fluid viscosity, reduce interfacial tension, and enhance oil recovery, among other benefits (Pu et al., 2018). Biopolymers such as xanthan gum, guar gum, chitosan, and alginate have been studied extensively for their potential in EOR applications. For instance, xanthan gum and guar gum have been shown to increase the viscosity of fluids used in hydraulic fracturing operations, while chitosan has effectively reduced interfacial tension and increased oil recovery in laboratory experiments. While using biopolymers in oil and gas fluids is still in its early stages, it holds promise for more sustainable and environmentally friendly oil and gas exploration and production. In this context, the utilization of biopolymers in oil and gas fluids is an area of ongoing research and development, with the aim of improving the efficiency and sustainability of oil and gas operations (Patel et al., 2015).

Various biopolymers have been used in the oil and gas industry, including xanthan gum, guar gum, starch-based biopolymers, cellulose-based biopolymers, and chitosan. Xanthan gum is commonly used in drilling fluids due to its high viscosity and shear-thinning behavior (Villada et al., 2017), while guar gum is often used in hydraulic fracturing fluids due to its water-holding capacity and compatibility with various

chemicals (Thombare et al., 2016). Starch-based biopolymers are known for their low cost and biodegradability, while cellulose-based biopolymers such as CMC and HEC are used as viscosifiers and fluid loss control agents in drilling fluids (Ali et al., 2022). Chitosan has been studied for its potential to form gels and its biocompatibility in oil and gas fluids. Other biopolymers such as alginate, pectin, and carrageenan have also been researched for their potential use in oil and gas fluids (Martău et al., 2019). Biopolymers often possess distinct linear, double, or triple helical structures, along with rigidity and charge-neutral chains. These attributes enhance their thickening capabilities and stability, making them suitable for use in demanding reservoir conditions. Several biopolymers have been investigated for their applicability in the oil and gas sector, as demonstrated in Table 2.1. According to the table, Hydroxyethyl cellulose (HEC) and Carboxymethyl cellulose (CMC) are typically employed in low-temperature scenarios (<90 °C), as their apparent viscosity tends to drop below 10 cP (Bai et al., 2018). Conversely, xanthan gum (XG), welan gum, and scleroglucan can maintain fluid stability at temperatures ranging from 100 to 120 °C (Castillo et al., 2015; Gao, 2015; Li et al., 2017). Guar gum has traditionally served as a viscosifier in fracturing fluids. However, the practical utilization of biopolymers has faced constraints as the oil and gas industry transitions towards reservoir conditions characterized by high temperatures (exceeding 120 °C) (Al-Hajri et al., 2022). Companies that depend on biopolymerbased fluid are limited to only operating at formation temperatures lower than 150 °C to avoid biopolymer degradation (Galindo et al., 2015). At elevated temperatures, the biopolymer is prone to hydrolyze at the acetal linkage in their backbone, leading to the loss of suspension and viscosity (Weaver et al., 2003). Therefore, finding an advanced biopolymer that can endure this extreme condition is necessary.

Biopolymer	Advantages	Reference
Hydroxyethylcellulose (HEC)	<ul> <li>Excellent thickening properties</li> <li>Provides pseudoplastic behavior (shear-thinning)</li> <li>Stable over a wide range of place of the sector of the sector</li></ul>	Abbas et al., 2013
Carboxymethylcellulose (CMC)	<ul> <li>Versatile thickening and stabilizing agent</li> <li>Forms clear solutions</li> <li>High viscosity even at low concentrations</li> </ul>	Marques et al., 2018

Table 2.1Example of biopolymers used in the oil and gas industry

Biopolymer	Advantages	Reference
Guar gum (GG	<ul> <li>Highly effective thickener and stabilizer</li> <li>Forms viscous solutions even in cold water</li> <li>Compatible with a wide range of other ingredients</li> </ul>	Wang et al., 2015
Xanthan gum (XG)	<ul> <li>Exceptional thickening and stabilizing properties</li> <li>Provides pseudoplastic behavior</li> <li>Effective even in low concentrations</li> </ul>	Jang et al., 2015
Welan gum (WG)	<ul> <li>High thermal stability</li> <li>Excellent thickening and gelling properties</li> <li>Forms stable gels over a broad pH range</li> </ul>	C. Gao, 2016
Scleroglucan	<ul> <li>Strong thickening and stabilizing properties</li> <li>Forms clear and stable solutions</li> <li>Effective at low concentrations</li> </ul>	Fariña et al., 2001
سلطان عبدالله UNIVERSIN AL-SULT Diutan gum (DG)	<ul> <li>Good thickening, stabilizing, and gelling</li> <li>properties</li> <li>Exhibits high stability over a wide range of pH and temperature</li> <li>Suitable for various applications as an alternative to other gums</li> </ul>	Arbaa'in et al., 2020

Table 2.2Continued

## 2.4 Biopolymers and microbial polysaccharides

Generally, polymers consist of repeating monomer units that are bonded together to form larger structures with linear, branched, or network structures.Biopolymers have a more complex molecular organization with well-defined hierarchical levels that contribute to their 3D structure and function (Dassanayake et al., 2018). This complexity is similar to that of hemoglobin, where the precise structure and shape are essential to its function. Biopolymers are synthesized by living organisms,
including animals, yeast, bacteria, and plants. Additionally, materials produced through synthetic chemistry using biological sources such as proteins, vegetable oils, fats, sugars, and resins can also be considered biopolymers. Synthetic polymers, on the other hand, generally have simpler and more random structures (Hernández et al., 2014). As their name suggests, biopolymers are materials that can be broken down enzymatically or non-enzymatically in vivo, making them environmentally friendly and biodegradable (Prajapati et al., 2019). However, some biopolymers are non-biodegradable, such as polythioesters derived from microbial fermentation. These materials have several advantages in the production of bio-based plastics (Andreeßen and Steinbüchel, 2019). Therefore, biopolymer classification differs depending on several aspects, including the origin (bio-based or non-bio-based), degradability, and repeating unit, as shown in Figure 2.4 (Mohan et al., 2016).



Figure 2.4 Classification of biopolymers Source: (Mohan et al., 2016)

However, the main classification of biopolymers, as generally reported, is based on their repeating or monomeric units. One major group of biopolymers is the polynucleotides, such as deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). Polynucleotides are composed of a long chain of 13 or more nucleotide monomers. The second major biopolymer group is the polypeptides, such as proteins and myoglobin (muscle tissues). A polypeptide is a series of amino acids joined by peptide (also called amide) bonds. A peptide is a short chain of amino acids linked by peptide bonds, while a dipeptide is a two-amino acid accompanied by a loss of water molecules in its formation. The unit of amino acid in polypeptides is called the *residue*. All peptides except cyclic peptides have an N-terminal ( $\alpha$ -amino group) and C-terminal ( $\alpha$ -carboxyl group) at the end of the chain. This creates a polarity in polypeptides and the amino end is taken to be the starting position of the chain (aminoterminal residue). Finally, the third biopolymer group is the polysaccharides, such as starch from plants and glycogen from animals. A polysaccharide is comprised of monosaccharide chains linked via an O-glycosidic bond (Holdt and Kraan, 2011). The monosaccharide (simple sugar) is the basic unit of carbohydrate. The simplest forms of sugar are glucose, fructose and galactose because they cannot be further hydrolyzed to a simpler chemical compound.

Polysaccharides can be further divided into either homopolysaccharides, which contain all equivalent monosaccharides, or heteropolysaccharides, which are comprised of different monosaccharides. Polysaccharides are also called glycan, where glyc- is sugar and *-an* for the polymer. They typically are 200 to 2500 monosaccharides long. Usually, each monosaccharide unit contains six-carbon  $(C_6H_{10}O_5)n$  and is linked by oxygen, as shown in Figure 2.5. The manner in which the monosaccharide is connected, either linear or branched and the assortment of this makes a distinctive type of polysaccharide. Figure 2.6 shows the schematic structure of polysaccharide molecules where (a) is an unbranched molecule; (b-e) is technically branched and behaves as linear polymers; (f) is a cluster type of branching found in amylopectin; (g) is branchon-branch (bushlike structure) found in Arabic gum. The (b-d) is the short branch of mono-, di-, or trisaccharide unit, which (b) is equally divided, (c) is haphazardly dispersed, and (d) is clustered along the backbone chain (Kabir et al., 2022). The main function of polysaccharides is to provide cellular structure and energy storage. They signify an important polymer class to the living system for their nutritional values and as an industrial utility.



Figure 2.5 Example of polysaccharide molecular structure – amylose



Figure 2.6 Schematic structure of polysaccharides Source: (BeMiller, 2001)

Aside from plants and animals, microorganisms are also a significant source of polysaccharides. There are sustainable sources of polysaccharides that are produced by different microbial species and as ubiquitous natural substances on Earth. As an example, those species belong to the genera *Leuconostoc*, *Aureobasidium*, *Alcaligenes*, *Pseudomonas*, *Bacillus*, *Arthrobacter*, *Xanthomonas*, and *Sphingomonas* (Couto et al., 2019; Elshafie et al., 2017; Li et al., 2017; Patel et al., 2015; Soudmand-asli et al., 2007;

Xu et al., 2015). Microbial polysaccharides are biodegradable polymers that have an impressive potential due to their significant useful properties, such as thickening, stabilizing, emulsifying and gelation. The characteristic of different microbial polysaccharides is tailored by the hereditary control of the microorganisms, making it reasonable for high-value oil exploration applications such as drilling, fracturing fluid and polymer flooding. Microbial polysaccharides have a hydroxyl center, ionic carboxylate center, and oxygen molecules (Xu et al., 2019a). This may prompt dipolar, ion-dipolar, and hydrogen bonding interactions with itself or with other substances in a solution. In general, they can be utilized in numerous settings, such as in beautifying agents (Baptista and Freitas, 2021), nourishments (Kanlayavattanakul and Lourith, 2015), pharmaceutics (Ng et al., 2020), paints (Paul et al., 1986), water treatment (Freitas et al., 2014), and oil recovery (Xu et al., 2019b).

Xanthan, scleroglucan, dextran, welan, gellan, and diutan are examples of microbial-based polysaccharides. Among these, dextran was the first commercialized microbial polysaccharide, followed by xanthan (Kang and Pettitt, 1993). However, the manufacture, content, and rheological properties of xanthan gum (XG) for fracturing, drilling, and pipeline cleaning fluid have received the greatest attention. Due to molecular aggregation via hydrogen bonding and biopolymer entanglement, XG fluid exhibits considerable shear-thinning behavior with a low power-law index. This has improved injectability for field operations (Pu et al., 2018). In addition, XG can increase the viscosity of the injected water at a low concentration, which improves the mobility ratio because of its high molecular weight properties. XG also is one of the widely used polymers in polymer flooding techniques for enhanced oil recovery (EOR) along with HPAM. However, both of them cannot excel in harsh reservoir conditions. The environmental issue regarding the usage of HPAM and the XG's susceptibility to microbial degradation has limited its applications (Rellegadla et al., 2017). Alternatively, a microbial polysaccharide named diutan gum was introduced to improve the limitations faced by the XG.

# 2.5 Diutan gum

Diutan gum (DG) is a bacterial polysaccharide synthesized through aerobic fermentation by *Sphingomonas* sp. ATCC53159 (Coleman et al., 2008). It constitutes an anionic biopolymer composed of a recurring six-sugar unit. The unit encompasses  $\beta$ -

1,3-D-glucopyranosyl,  $\beta$ -1,4-L-glucuronopyranosyl,  $\beta$ -1,4-D-glucopyranosyl, and  $\alpha$ -1,4-1-rhamnopyranosyl segments within the backbone structure. Additionally, a twosaccharide L-rhamnopyranosyl side-chain is linked to the glucopyranosyl residue via  $(1\rightarrow 4)$  linkage. Refer to Figure 2.7 for a visual representation (Banerjee et al., 2009). The resulting polymer is composed of glucose, mannose, and glucuronic acid units and has a unique structure providing distinctive physicochemical properties. Unlike other polysaccharides such as xanthan gum, DG has a highly branched and complex structure that allows it to form highly viscous solutions at low concentrations. Its unique structural characteristics make it an attractive ingredient in a wide range of products. In various applications, Diutan gum (DG) typically serves as an agent for thickening, binding, emulsifying, suspending, and stabilizing. It is also biodegradable, biocompatible, and environmentally friendly and is approved by the FDA as a food additive while being generally recognized as safe (GRAS) (Li et al., 2017). DG is a non-gelling polysaccharide with a three times higher molecular weight of about  $3-5 \times$ 10<sup>6</sup> g/mol compared with welan gum, which belongs to the same sphingans family as diutan (Khayat and Mikanovic, 2012). Besides welan, gellan and rhamsan gum also belong to the sphingans family, with the same tetrasaccharide backbone but different side chains (García González et al., 2019a).



Figure 2.7 Molecular structure of diutan gum Source: Banerjee et al., (2009)

According to the statistic on Scopus indexes publication, there are about 60 articles published on diutan gum utilization. The first application of diutan gum was published about two decades ago at the Society of Petroleum Engineers (SPE) conference. Navarrete et al. have reported the efficiency of DG to compare with XG

and welan gum at ambient temperature at the lowest salt concentration system (Navarrete et al., 2001). Despite two decades of research, studies on DG are still progressing and continue to garner interest. Moreover, the number of publications on the topic of DG has been accelerating since 2015. Other than the oil and gas industry, DG is also used in the cement and concrete industries. The high viscosity and gel-like properties of DG make it effective in controlling the flow properties and preventing segregation of the cement mix. Additionally, the hydrophilic nature and high molecular weight of DG contribute to its ability to retain water in the cement mix, which is vital for proper curing and prevention of cracking. However, the optimal dosage and application methods of DG in cement-based systems may depend on the specific application and desired performance properties. For instance, DG has been used as a viscosity-modifying agent in cement slurries because it effectively controls bleeding by forming a viscous gel (Sonebi, 2006; Zhang et al., 2010). Bleeding here means the liquid state on the surface of fresh concrete due to heavy particles' settlement. It is a normal condition, but excessive bleeding can be problematic. Moreover, DG has efficacy in oil-well grout because it can maintain its high viscosity in the alkaline solution containing concentrated calcium ions despite the elevated temperatures (Vazquez and Pique, 2016). Furthermore, the addition of DG in cement grouts has introduced a shear-thinning behavior compared with grout without viscosity-enhancing agents (VEA). VEAs are the material used to enhance self-consolidating and underwater concrete (Bessaies-Bey et al., 2022). LIAN

DG is a unique biopolymer polysaccharide because of its high molecular weight properties. Interestingly, an investigation of DG rheological properties by Xu et al., showed that DG gelling fluid could be produced at a very low concentration of 0.12 g/L because of its molecular properties (Xu et al., 2015). The effect of molecular weight and longer chain of DG has also increased the apparent viscosity of grout (at the low shear rate) because of the chain's intertwining and entanglement. However, at a high shear rate, the viscosity is dropped due to the change of polymer alignment and applied shear force, thus improving the fluidity (Song et al., 2006). For the polymer flooding technique, the utilization of water-soluble high molecular DG has increased the viscosity of injection water. Therefore, the solution mobility ratio is reduced, improving the injectivity profile reverse phenomenon and enhancing the volumetric sweep efficiency (Wu et al., 2012). In other words, the high viscosity prompts a viscous pressure gradient at different porosity layers where the injected DG could flow from the high permeability to the low permeability area and improve the oil recovery.

Another specialty held by DG is its molecular structure. DG possesses a perfect helical chain conformation known to have a better local stiffness than coiled conformation (Tinland and Rinaudo, 1989). Moreover, the longer side chains located on the helix's backbone will stabilize the double helix and encourage the backbone association. During the change in temperature and counter ionic concentration, common polysaccharides tend to have a coil-helix transition. This transition is also dependent on polysaccharide concentration, where polysaccharide molecules are irregular coils in a diluted solution and have the potential to become double helix in a concentrated solution. However, for DG, its long side chain and strong intermolecular and intramolecular interaction have contributed to the self-association molecular (helical aggregation) at low concentrations (Xu et al., 2019a). In addition, the higher stability of the double helix conformation is achieved by the folded side chain on the helix. This conformation can shield the carboxylate groups from the surrounding particles or crosslink with calcium ions, thus increasing the stability of the DG structure (Lee and Chandrasekaran, 1991). Furthermore, DG is nearly independent of the cationic environment (Na<sup>+</sup> and Ca<sup>2+</sup>) owing to its perfect double helix molecular configuration اونيۇرسىتى مليسيا قھة السلطان عيد (Huang et al., 2022)

# Numerous studies have shown that the DG biopolymer possesses excellent salt

Numerous studies have shown that the DG biopolymer possesses excellent salt tolerance (Y. Li et al., 2017; K. Liang et al., 2019; Xu et al., 2019). It is crucial to have high salinity resistance because of the practical conditions in the oil and gas industry. Water is necessary for the DG fluid formulation, though it is difficult to find freshwater for offshore operations. Normal operations need about 4 to 15 million L of freshwater, which incurs a high cost for transportation, time and space to store the freshwater (Y. Gao et al., 2015; Van Domelen & Haggstrom, 2011). Therefore, the usage of seawater is ideally more practical. However, the salinity or the chemical composition in seawater might affect the fluid formulation such as hydration rate, breaker, crosslinker or other additives. Na<sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, Mg2<sup>+</sup> and SO4<sup>2-</sup> are the compositions that contribute to the salinity of seawater while other elements like iron, boron, strontium and barium only minorly contribute to salinity. The salinity of seawater is also dissimilar at different locations, as displayed in Table 2.2 (Harris & van Batenburg, 1999). In order to prepare

the fluid, hydration of the polysaccharide (gelling agent) in water is crucial to increase the viscosity. This process requires water absorption by a polysaccharide (interaction by ester function group) to change its configuration from a compact state of coils into a more relaxed state. Viscosity is the parameter to measure hydration and a stable viscosity reflects the maximum hydration (Alohaly et al., 2016).

Component	Danish North Sea (mg/L)	Mediterranean Sea (mg/L)	Offshore Angola (mg/L)	South China Sea (mg/L)	Gulf of Mexico (mg/L)	Arabian Gulf (mg/L)
Sodium	8800	12300	14200	9900	11000	16180
Potassium	400	380	210	400	470	700
Calcium	420	500	300	420	650	650
Magnesium	1550	1790	630	1170	1220	1730
Strontium	6	_	5	7	10	_
Chloride	22000	22000	15000	18000	19700	31000
Bicarbonate	140	140	95	110	90	_
Carbonate	_	-	_	_	40	_
Sulfate	3300	2900	1400	2500	3310	4020
TDS	36600	40010	31850	32500	36500	54000

Table 2.3Typical seawater chemical ion composition

Source: Harris and van Batenburg (1999)

As discussed earlier, the need to find a high-performance gelling agent for extreme conditions in the oil and gas industry is necessary. Sonebi et al. reported that DG gelling fluid is stable in the temperature range of 25-75 °C (Sonebi, 2006). In another report, DG fluid is claimed to hold a thermal stability range from 5 to 150 °C, demonstrating a strong water retention capacity and great suspending ability (Diltz and Zeller, 2001). Besides, the viscosity of DG is stable after 90 days of aging at 85 °C, and 16% of oil recovery was obtained in the core flooding test (Liang et al., 2019). DG has been used as an alternative for XG because the former fluid system is inadequate for the complex conditions in the newer wells. Sarber and co-workers have conducted a study to substitute XG with DG in a solid-free mud system for side-track laterals drilling and for non-rig coiled tubing operations. The main problem is the limitation in pump pressure at the surface, which is only equipped with pressure up to 5000 psi. The higher the XG loading, the higher the pressure will be, despite the fact that it is vital to maintain a low pressure to minimize the coiled tubing fatigue. Changing the fluid system to DG has improved the hole-cleaning process and resulted in a 20% reduction in pumping pressure (Sarber et al., 2010). Since DG is a new polysaccharide for the oil and gas industry compared to xanthan, further studies are needed. Therefore, in the

present study, surface modification via cationization of DG was performed to investigate the reaction and changes in DG properties.

# 2.6 Cationization of polysaccharides and its characterizations

The most common method for cationic modification of polysaccharides is through etherification using a 2-hydroxy-3-(trimethylammonium) propyl group, which is obtained by reacting the biopolymer with 2,3-epoxypropyltrimethylammonium chloride (EPTAC). However, EPTAC is unstable and toxic, making it unsuitable for industrial applications. Therefore, 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) has replaced the previously used EPTAC as a safer and more environmentally friendly reagent for cationization (Santinon et al., 2022). CHPTAC is a quaternary ammonium compound commonly used for the cationization of natural polysaccharides such as cellulose, chitosan, and starch. It is a stable, water-soluble, and biodegradable reagent that can efficiently introduce cationic charges onto the polysaccharide backbone through etherification reactions (Prado and Matulewicz, 2014).

The reaction mechanism proposed for the conversion of CHPTAC to EPTAC and its subsequent reaction with polysaccharides involves three steps as illustrated in Figure 2.8. CHPTAC undergoes a base-catalyzed dehydrohalogenation reaction to form EPTAC, which is then allowed to react with the hydroxyl groups on the polysaccharide surface, leading to the ring-opening of the epoxide. This reaction occurs with various polysaccharides such as cellulose, chitin, starch, and chitosan. The reaction between EPTAC and the polysaccharide surface results in the formation of an intermediate EPTAC-polysaccharide complex. The intermediate then undergoes further reaction to form a crosslinked product. The crosslinking reaction involves the nucleophilic attack of the hydroxyl group on the polysaccharide by another hydroxyl group on the EPTAC molecule, forming a covalent bond between the two polysaccharide chains. The crosslinking reaction may also involve the formation of ether bonds between the polysaccharide and EPTAC or a combination of ether and covalent bonds (de Almeida and da Silva, 2021).



Figure 2.8 Formation of the epoxide and nucleophilic attack of the alkoxide to the epoxide.

Source: Prado & Matulewicz (2014)

Cationization has found broad application in enhancing the characteristics of polysaccharides (Prado and Matulewicz, 2014). Introducing modifications to the cationic portion through anionic polymers can yield inter-polyelectrolyte complexes featuring hydrogel-like structures. This expansion of structural possibilities extends their utility across diverse industries, including textiles, food, cosmetics, papermaking, wastewater treatment, pharmaceuticals, and the petroleum sector. The polysaccharide itself is biodegradable since it is derived from natural products, thus favorable for green products in terms of low cost and toxicity (Janarthanan et al., 2016). For instance, in flocculation, a cationic starch derivative has been used as an alternative to toxic cationic polyacrylamides or synthetic flocculants (Krentz et al., 2006). Several chemical modifications involving the cationic moiety on polysaccharides and their specific application purposes are listed in Table 2.3.

Cationic polysaccharide	Application	Reference
Agarose	general	(Prado et al., 2011)
Alpha-cellulose	paper making	(Moral et al., 2015)
Chitin	general	(Chen et al., 2010)
Dextran	clay suspension separation	(Ghimici et al., 2009)
Glucuronogalactoarabinoxylans (corn fiber)	General	(Šimkovic et al., 2009)
Guar	flocculating agent	(Pal et al., 2007)
Hemicellulose (sugarcane bagasse)	Biomass	(Ren et al., 2007)
Kappa (κ)-carrageenans	general	(Covis et al., 2016)
Konjac glucomannan	wastewater treatment	(Tian et al., 2010; Wang et al., 2018; Yu et al., 2007)
Pullulan	gene transfection carrier	(Jo et al., 2010)
Starch	general	(Kavaliauskaite et al., 2008)
Xanthan	general	(Shi et al., 2018)

Table 2.4	List of cationiza	tion of polysa	accharides from	previous	studies

Agarose is a polysaccharide obtained from seaweed. Prado and fellow researchers have reported the cationization of agarose, where different reaction parameters (temperature, time, reagent concentration, and addition of NaBH<sub>4</sub>) were tested to study their influence on the molecular weight of the substitution degree (Prado et al., 2011). The authors successfully synthesized cationized agarose with varying degrees of substitution ranging from 0.04 to 0.77. The concentration of CHPTAC used in the reaction was found to have a significant impact on the degree of substitution obtained. It was also observed that the optimum concentration of NaOH was crucial to achieving the desired degree of substitution, and insufficient amounts of NaOH led to reduced epoxide formation and reaction with the polysaccharide. Conversely, excess NaOH favored the degradation of the epoxide and a decrease in molecular weight. The authors also found that a reaction time of 2 hours was sufficient to achieve the importance of optimizing reaction conditions to obtain the desired properties of cationized agarose for specific applications.

Besides that, Kappa ( $\kappa$ )-carrageenan is also one of the polysaccharides extracted from red seaweed species. Attention toward the cationization of these anionic sulfated polysaccharides has risen due to their abundant source and favorable ecotoxicological properties. Another abundant polysaccharide is starch. It has been used in many applications such as pharmaceutical, cosmetics, textile, therapeutic, water treatment, and papermaking (Pal et al., 2008). Starch cationization can be classified into three: wet, semi-dry, and extrusion. In the wet process, the reaction is either in a homogeneous state in dimethyl sulfoxide or a heterogeneous state in an aqueous or alcoholic suspension in alkaline conditions (Prado and Matulewicz, 2014). Meanwhile, pullulan is favored in the biomedical industry due to its excellent biodegradability, non-immunogenic, and non-toxic properties. Furthermore, pullulan's thermal stability, film-forming ability, and high gas barrier properties have made it a suitable material for environmentally friendly food packaging, replacing non-biodegradable products (Li et al., 2020a). In cellulose, the strong intramolecular and intermolecular hydrogen bonds have made it difficult to process in a normal aqueous solution. Therefore, cationization of water-soluble hydroxyethylcellulose can be done to obtain the cationic cellulose by directly linking the quaternary ammonium group to the hydroxyls of the cellulose backbone. Several studies have also reported the utilization of urea in the cationization of cellulose to improve cellulose solubilization (Song et al., 2008; Yan et al., 2009).

The cationization of polysaccharides is commonly performed with amino or ammonium functional groups. Cationization has proven to be advantageous for enhancing the attributes of polysaccharides, thanks to their stable and non-toxic nature (Moral et al., 2015; Prado et al., 2011). As shown in Table 2.4, various ammonium salts can be utilized for the cationization process. Notably, N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) features in the list. This liquid cationic etherification agent is widely employed for cationization processes. Polysaccharides cationized with CHPTAC are non-toxic and readily biodegradable. Starch is one of the polysaccharides that has mainly been cationized by this reagent. In 2001, about 95% of CHPTAC (23,695 tons) was consumed in the European Union for starch cationization. Additionally, quaternary ammonium salts display an advanced gelling characteristic and are used as gelants in fluids for fracturing, completion, and drilling operations (Subramanian et al., 2010).

Salts
3-Chloro-2-hydroxypropyl dimethyloctadecyl ammonium chloride
3-Chloro-2-hydroxypropyl-dimethyloctyl ammonium chloride
3-Chloro-2-hydroxypropyl trimethyl ammonium chloride
3-Chloroethyl trimethyl ammonium chloride
2,3-Epoxypropyl trimethyl ammonium chloride
3-Chloro-2-hydroxypropyl dimethyidodecyl ammonium chloride
3-Chloro-2-hydroxypropyl dimethyltetradecyl ammonium chloride
3-Chloro-2-hydroxypropyl dimethylhexadecyl ammonium chloride
Diallyl dimethyl ammonium chloride

Table 2.5Quaternary ammonium compounds used for cationization of<br/>polysaccharides

Source: (Warren et al., 2001)

In a recent development, Shi and his team have successfully synthesized cationic xanthan gum (XG). This advancement involves the introduction of quaternary amine groups onto the XG backbone, with the primary aim of bolstering its rheological properties (Shi et al., 2018). The modification was confirmed by the appearance of a new signal at 18.266 ppm in <sup>13</sup>C Nuclear Magnetic Resonance (NMR) spectra and a new band at 1328 cm<sup>-1</sup> in FTIR spectra for cationic XG. The additional findings indicated notable enhancements in comparison to unmodified XG, particularly in terms of viscosity, elastic and viscous modulus, and thermal stability. Similarly, both DG and XG molecules exist as double helical polymers. A single helix (secondary structure) of polysaccharide is the intramolecular, regular, spatial arrangement of the random coil (primary structure). The chain conformation is the set of dihedral angles of the glycosidic linkage, repeated from residue to residue (Diener et al., 2019). Thus, a double helical or tertiary structure is a non-covalently chained intramolecular assembly from the same polymer chain in their secondary state or single helix. Polysaccharide characteristics like flexibility depend on the single helix, either loosely overlapped, twisted structure, or tightly intertwined supercoils. This conformational nomenclature is presented in Figure 2.9. The term primary, secondary, tertiary, and quaternary was established for protein and are also used to explain the polysaccharide structure hierarchy (Diener et al., 2019; Eggleston and Doyle, 2006). The use of a double-helical biopolymer in this study is believed to be suitable for high temperature and high salinity reservoirs and could deliver a high viscosity at low concentrations.



Figure 2.9 The schematic elucidation of the different ion-induced structures in a linear charged polysaccharide with an AFM height image representative. Source: Diener et al. (2019)

Considering the current advanced knowledge that Diutan gum (DG) boasts outstanding rheological properties, a pertinent question arises: would the introduction of surface functionalization to DG enhance its properties further, or could it potentially lead to their deterioration? In comparing the two gums, XG and DG, DG was found to have a better capacity under given viscosity, alkaline degradation resistance and temperature resistance (Hodder et al., 2004). Under certain thermodynamic conditions, helix-coil transitions usually happen upon temperature and counter ion concentration increase. The helical chain provides greater local rigidity, which often causes chains to be compressed into a physical gel formation (Tinland and Rinaudo, 1989). In the case of XG, the structure is converted to a random coil at high temperatures and high salinity, while DG remains in a double helix structure, as shown in Figure 2.10 (Xu et al., 2015). Therefore, applying the same modification of XG on DG structure is expected to increase its characteristics further.



Figure 2.10 The schematic representation for the molecular conformation transition of diutan gum and xanthan gum in aqueous solutions

Source: Xu et al., (2015)

# 2.6.1 Degree of substitution (DS) calculation

Various analytical characterizations can be performed to analyze the cationization of polysaccharides. DS calculation is one of the common methods to characterize the cationized polysaccharides. The DS and where the substitution happened on the monosaccharide unit along the chain of polysaccharides will greatly influence the properties of cationized polysaccharides. There are two types of procedures to evaluate the DS: elemental analysis of nitrogen and the Kjeldahl method (Figure 2.11). For data resulting from elemental analysis (Table 2.5), a calculation using equation 2.1 can be used to obtain the DS value. Table 2.6 presents the DS values of different cationic polysaccharides from previous studies. All polysaccharides in the table use the same cationic reagent (CHPTAC).

$$DS = \frac{(AGU \times \%N)}{(14 \times 100) - (x \times \%N)}$$
2.1

AGU stands for anhydroglucose unit within a polysaccharide structure. %N represents the nitrogen content based on dry weight, with 14 as the atomic weight of nitrogen, and *x* indicating the molecular weight of the cationic substituting group.



Figure 2.11 Illustration of apparatus set up in the Kjeldahl method

Table 2.6	Example of data	collection from	elemental	analysis
	-			•

Polymer	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Starch	39.31	6.36	0.12
CHPTAC	.37.71	7.82	7.34
Cationic starch1	39.66	6.64	2.85
Cationic starch2	= 39.24 MAL	AY 6.42 PAHANG	3.22
Cationic starch3	39.54	<b>6.53</b>	3.82
Cationic starch4	39.36	6.57	3.68

Source: Pal (2005)

Table 2.7The reported degree of substitution of various cationizedpolysaccharides.

Polysaccharide	Degree of substitution	References
Xanthan	0.017 - 0.043	Shi et al. 2017
Agarose	0.04 - 0.55	Prado et al
(κ)-carrageenans	0.13 - 0.75	Covis 2016
Starch	0.007 - 0.1215	Pal 2005
Guar	0.35	Huang 2007
SCB Hemicellulose	0.072 - 0.19	Ren 2007
Konjac glucomannan	0.15 - 0.46	Wang et al. 2018
Glucuronogalactoarabinoxylans	0.16 - 0.31	Simkovic et al. 2009
Xyloglucan	0.26 - 0.52	Pal et al. 2009

### 2.6.2 FTIR analysis

The FTIR analysis is an important characterization method to differentiate the functional group of the cationic polysaccharide and to confirm the occurrence of cationization. Figures 2.13 and 2.14 show two examples of the typical FTIR plot for polysaccharides and their cationized product using CHPTAC as the cationic reagent. Table 2.7 presents the FTIR result of CHPTAC produced by Pal and his fellow researchers. Usually, at a band around 3500 cm<sup>-1,</sup> there will be a stretching mode of the hydroxyl group. After that, around band 2900 cm<sup>-1,</sup> C–H stretching vibration is present. At the fingerprint region, which is wavenumber 1750 cm<sup>-1</sup> and below, the peak might vary depending on the different polysaccharides. For example, in the agarose sample, bands 776 cm<sup>-1</sup>, 892 cm<sup>-1,</sup> and 930 cm<sup>-1</sup> indicate  $\beta$ -galactose skeleton bending, the anomeric C–H from the  $\beta$ -galactopyranosyl residue and 3,6-anhydro-galactose respectively (Matsuhiro, 1996; Prado et al., 2011). In konjac glucomannan, 1050 cm<sup>-1</sup> and 1028 cm<sup>-1</sup> are attributed to stretching the vibration absorption peak of C–O–C, while the peak at 1735 cm<sup>-1</sup> indicates the carbonyl group (Wang et al., 2018).

Table 2.8The FTIR analysis of N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride (CHPTAC) based on literature.

Material	Wavenumber	Assignment	References
ou lui	(cm <sup>-1</sup> )		1
	3445	O–H stretching	5
CUDTAC	ER2910 MALA	C–H stretching	<b>C</b> S. Pal et al.,
CHPTAC		C–N stretching	2005
	675	C-Cl stretching	







Figure 2.13 FTIR plot of konjac glucomannan Source: Wang et al. (2018)

Table 2.8 displays the FTIR results of multiple polysaccharides that have been cationized using CHPTAC. The table reveals that all the present wavenumbers show either an increase or decrease in peak intensity or the appearance of new peaks. A significant finding among the studies shown in the table is the emergence of a new band at 1328-1479 cm<sup>-1</sup>, which indicates the formation of a C-N bond resulting from CHPTAC substitution on the polysaccharide backbone. Another effect of the cationic modification is the narrowing of the broad band of O-H stretching. In experiments on agarose and konjac glucomannan, they observed that the bands at 1482 cm<sup>-1</sup> and 1479 cm<sup>-1</sup> correspond to the C-H bending of the methyl groups in the quaternary ammonium. Moreover, an increase in the ether bond at 1043 cm<sup>-1</sup> confirms the quaternization reaction for sugarcane bagasse (SCB) hemicelluloses.

Polysaccharide	Assignment	Wavenumber (cm <sup>-1</sup> )	References
Xanthan	C-N stretching	1328	Shi et al., 2017
	C–H vibration	1416	
	C–O stretching	1731, 1634	
	C-H stretching	2800, 3000	
(κ)-carrageenans	C–N stretching	1479	Covis et al., 2016
Guar	C-N stretching	1397	Sagar Pal et al., 2007
Starch	C-N stretching	1404	S. Pal et al., 2005
Agarose	C-N stretching	1414	Héctor J. Prado et al.,
	C–H bending	1482	2011
	Ether bond	1080	
SCB	C-N stretching	1411	Ren et al., 2007
Hemicellulose	Ether bond	1043	
	C-H stretching	2920	
Konjac	C–H bending	1479	K. Wang et al., 2018
glucomannan			-

Table 2.9List of denoted changes in IR spectra of cationized polysaccharide

#### 2.6.3 Surface morphology



Surface morphology plays a critical role in the behavior of cationized polysaccharides. It can significantly impact their physical and chemical properties, including solubility, viscosity, and biocompatibility. As shown in Figure 2.15, the surface morphology of welan gum can change significantly upon cationization. In its native form (a), welan gum has a generally smooth surface with some granular shapes in localized areas. However, after cationization (b), the granular shape becomes more prominent across the entire surface of welan gum (Arbaa'in et al., 2020). This change in surface morphology may affect the interaction of cationized welan gum with other molecules and could have implications for its use in various applications. Figure 2.16 shows that XG in its native form (a) has a smooth surface, whereas cationized XG (b) has a rough surface with a visible crack, which is due to the grafting process that occurred on XG (Shi et al., 2018). Similarly, in Figure 2.17, cationized agarose (b) at low magnification appears similar to native agarose (a), but at higher magnification (c), a branched reticular structure is observed. The authors also note that at higher degrees of substitution, irregular and smooth particle shapes can be seen (Prado et al., 2011). Overall, there is no consistent pattern observed in these three cases, but the variety of transformations that occur during cationization is noteworthy and may have implications for the properties and applications of these polysaccharides.



Figure 2.14 Surface morphology of welan gum (a); cationized welan gum (b) Source: Arbaa'in et al. (2020)



Figure 2.15 Surface morphology of XG (a); cationized XG (b) Source: Shi et al. (2018) ERSITI MALAYSIA PAHANG AL-SULTAN ABDULLAH



Figure 2.16 Surface morphology of agarose (a); cationized agarose 200x (b); cationized agarose 50,000x (c)

Source: Prado et al. (2018)

# اونيۇرسىيتي مليسيا فهغ السلطان عبدالله 2.6.4 Thermal analysis VERSITI MALAYSIA PAHANG

Thermal analysis techniques such as TGA and DSC are commonly used to examine the effect of temperature on samples in a temperature range of 20 to 600°C. The TGA plot often exhibits two distinct regions corresponding to weight loss in polysaccharides. As depicted in Figure 2.18, the TGA profile of guar gum displays an initial weight loss attributed to the loss of water, followed by a second weight loss attributed to polysaccharide degradation. Cationized guar gum exhibits increased thermal stability due to the improved charge attraction, overcoming the mutual repulsion of positive charges of the loaded cationic moiety (Pal et al., 2007). In contrast, welan gum shows no significant improvement in thermal properties but a slight change in glass transition (Tg), as shown in Figure 2.19. The Tg temperature of cationized welan gum (146°C) is higher than that of the native gum (141°C) due to the increase in polarity after the reaction and provided a strong intermolecular interaction which hindered the molecular motion in the cationized welan gum (Arbaa'in et al., 2020).

Furthermore, Sharma et al. (2020) reported an enhancement in the thermal stability of cationized Cassia tora gum, which showed approximately 45% weight loss compared to the 53% weight loss of native Cassia tora gum (Sharma et al., 2020). This demonstrated that cationization modification had indeed improved the thermal properties of polysaccharides.



Figure 2.17 TGA curve of native guar gum (GG), cationized guar gum (Cat GG4) and cationic reagent (CHPTAC)

Source: Pal et al. (2007)



Figure 2.18 DSC spectrum of native welan gum (WG) and cationized welan gum (CWG)

Source: Arbaa'in et al. (2020)

In contrast, the thermal stability of some cationized polysaccharides was found to be reduced after modification. In Figure 2.20, the TGA plot of cationized konjac glucomannan shows two degradation stages, with the first resulting from moisture loss and the second from polysaccharide degradation. However, the cationized konjac glucomannan degraded at a lower temperature (220 °C) compared to the raw sample (230 °C), with 63% weight loss for the former and 10% less for the latter (Wang et al., 2018). A similar trend was observed for cationized sugarcane bagasse (SCB) hemicellulose, with a lower decomposition temperature at 279 °C compared to native SCB hemicellulose at 292 °C. Moreover, the DSC analysis showed a larger exothermic peak for native SCB hemicellulose at 224 and 317 °C, whereas only a small peak was observed for the cationized sample at the corresponding temperature (Ren et al., 2007). The reduction in thermal stability can be attributed to the breaking of hydrogen bonds on the polysaccharide chains caused by the etherification process during cationization. This has led to the disintegration of intra and intermolecular interactions and subsequent polysaccharide decomposition (Biliaderis et al., 1980; Prado et al., 2011).



Figure 2.19 Thermal analysis of native konjac glucomannan (a) and cationized konjac glucomannan (b)

Source: Ren et al. (2007)

#### 2.6.5 Rheological analysis

Rheological properties refer to how a material responds to deformation under applied stress. Polysaccharides, including cationized ones, exhibit a wide range of rheological behaviors depending on factors such as concentration, temperature, and the presence of other compounds. Previous studies have also discussed the effect of the rheological properties of cationized polysaccharides. The rheological properties of the polymer product are important, especially in the fields requiring a controlled viscosity of a given texture. This is why the influence of cationization on polysaccharides should be monitored. For instance, the apparent viscosity of the XG has significantly increased after the introduction of CHPTAC (Figure 2.21a) (Shi et al., 2018). This is due to the electrostatic interaction between the chains. A similar increase in viscosity was also presented for DG (Arbaa'in et al., 2018). In the starch's case, the viscosity increases until the optimal CHPTAC concentration is reached. Further addition of CHPTAC then results in a decrease in the viscosity (Pal et al., 2005). Another interesting study showed that the degree of substitution also increased the viscosity, though the substitution would decrease the polysaccharide's molecular weight (Covis et al., 2016).

Other than the viscosity measurement, the modulus analysis has also been conducted on the individual linear visco-elastic region (LVER) of polysaccharides. Figure 2.21b shows the typical modulus plotted of xanthan polysaccharides, which consist of the elastic modulus (G') and viscous modulus (G''). The modulus shows an increasing pattern as the cationic moiety is incorporated in the XG. For each sample, the

elastic modulus was higher than the viscous modulus, indicating the fluid is in a gel-like structure (Li et al., 2012).



Figure 2.20 Rheological analysis of XG and cationized XG Source: Shi et al. (2017)

Figure 2.22 shows another example of a modulus diagram of native and cationized carrageenan polysaccharides. Most of the samples show the G' as dominant, indicating the fluid is in a gel-like structure. However, at certain frequencies, it is possible to observe the G' and G'' crossing to each other, showing that the characteristics of the sample have changed. If the G'' is dominant, it indicates that the fluid has a viscous liquid property. As shown in the figure, the cationized carrageenan with DS = 0.75 shows a loss in gel rigidity as the frequency increases. Conversely, the moduli increased after 0.07 Hz, which reflects the network's viscoelastic properties formed by carrageenan's cationization (Covis et al., 2016).



Figure 2.21 Rheological analysis of cationization of carrageenan polysaccharide Source: Covis et al. (2016)

# 2.7 Summary



In the comprehensive landscape of fluid technology within the oil and gas industry, Chapter 2 embarks on a meticulous exploration of the diverse array of materials and methodologies employed to optimize operational efficiency and address industry-specific challenges. Through an in-depth examination of synthetic and biobased polymers, the chapter elucidates their multifaceted applications, from improving drilling fluid performance to enhancing reservoir stimulation techniques. Additionally, the discussion extends to the promising realm of biopolymers and microbial polysaccharides, unveiling their potential as eco-friendly alternatives with tailored functionalities for various operational demands. With a dedicated focus on diutan gum, its unique rheological properties and compatibility with harsh reservoir conditions are dissected, underscoring its significance as a valuable additive in fluid formulations. Moreover, the exploration delves deeper into the realm of polysaccharide cationization, shedding light on the intricacies of characterizing these modified polymers through a spectrum of analytical techniques. From the fundamental calculation of degree of substitution to the nuanced insights gleaned from FTIR analysis and thermal profiling, each facet contributes to a holistic understanding of cationized polysaccharides' structure-function relationship. The chapter's meticulous delineation of these topics not only serves to consolidate existing knowledge but also lays a robust foundation for future research endeavors aimed at harnessing the full potential of fluid technology in

the oil and gas sector, propelling advancements towards sustainability, efficiency, and innovation.



# **CHAPTER 3**

#### METHODOLOGY

# 3.1 Introduction

This chapter presents the experimental procedure of the research study. The methodology is divided into two parts, which covers the synthesis of the cationic-diutan gum (CDG) using diutan gum (DG) powder and the preparation of the CDG gelling fluid. The characterization of CDG powder was studied using several methods, namely Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Field Emission Scanning Electron Microscopy (FESEM) and Elemental analysis for Degree of Substitution (DS) calculation. The DG and CDG powder were then used to produce a CDG gelling fluid. The DG and CDG gelling fluid were tested with a rheometer to study the viscous and viscoelastic behavior of the fluids. Finally, the CDG fluid was tested in an autoclave to determine its thermal stability at elevated temperatures to complete this study. The entire experimental work in this research is presented in a flow chart, as shown in Figure 3.1.

# 3.2 Materials

The Diutan gum (DG) used in this study was obtained from Permula Chemicals Sdn. Bhd. The quaternary amine group, which constitutes 60% wt.%, was sourced as N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) from Sigma Aldrich. Furthermore, essential reagents such as 95% ethanol, absolute ethanol, sodium chloride, and sodium hydroxide, crucial to the experiment, were also procured from Sigma Aldrich.

# **3.3** Synthesis of Cationic-Diutan Gum (CDG)

The synthesis of CDG was performed by dispersing 30 wt.% of DG in an ethanol-water solution (the mass fraction of ethanol is 85%), according to the method proposed by Shi L. et al. (2018). After that, the DG ethanol-water solution was mixed with sodium hydroxide (NaOH) aqueous solution (40 wt.%) up to pH 11.5 – 12. Figure 3.2a shows the pH meter used for the measurement. The mixture was stirred at ambient temperature for 40 minutes. The cationic modification was conducted by adding 60 wt.% of CHPTAC at different concentrations of 0.5, 1.0, 1.5, 2.0, 3.0, and 4.00 mL into the mixture and stirred at 70 °C for 2 hours. Figure 3.2b shows the setup for the CDG synthesis. The mixture was washed thoroughly with absolute ethanol via centrifugation. The washing was repeated three times to remove the water from the mixture completely. The samples were collected and dried in the oven at 80 °C.



Figure 3.1 (a) Insmark pH meter; (b)Experimental set up of CDG synthesis

### **3.4** Preparation of CDG Gelling Fluid

The CDG gelling fluid was prepared by dispersing 4.8 g of CDG powder in 1 L of 2 wt.% sodium chloride (NaCl) brine solution using a Silverson mixer (Figure 3.3) at 6000 rpm for 45 minutes at ambient temperature. The 2 wt.% of NaCl was used to mimic the salinity of seawater. The CDG concentration used here was chosen based on the standard for lab testing for drilling fluid (API RP 13I, 2006). The CDG gelling fluid was kept stationary overnight to remove any bubbles before being further tested for its rheological behavior and thermal stability.



Figure 3.2 Silverson mixer

# 3.5 Characterizations of CDG Powder 3.5.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR stands for Fourier transform infrared. It has two parts: the Fourier transform, a mathematical function used to convert data from a time domain to a frequency domain, and the infrared, the type of spectroscopy that involves the molecule's vibration. The FTIR covers a wide range of chemical applications, especially to identify functional groups in polymer and organic compounds. Figure 3.3 shows the schematic diagram of a FTIR spectrometer. The FTIR functions by using interferometry to record the information of the sample and a spectrum was resulted by Fourier Transform. During the process, the IR radiation will pass through the sample placed on the IR beam, which the sample will absorb and transmit. The resultant spectrum represents a molecular identification of the sample. This method is reliable because every molecule has its own unique spectral identification.



Figure 3.3 Schematic diagram of a FTIR spectrometer

For this research, the IR spectra of the DG powder and CDG powder were collected using a Spectrum One FTIR Spectrometer (Perkin Elmer, United States of America) (Figure 3.5a), using the potassium bromide (KBr) pellet method. The powder was mixed with KBr (1:100) and ground using a pestle and mortar. The mixture was placed in the pellet die and pressed using a Specac manual hydraulic press at 5 tons for 10 s to produce a thin pellet (Figure 3.5b). Each sample was then put into a sample holder and placed on the IR beam to record the spectrum. The pellet was scanned in the region of 700 to 4000 cm<sup>-1</sup> at a resolution of 2 cm, and the signal was detected in transmittance mode (%T).



Figure 3.4 (a) Perkin Elmer Spectrum One FTIR Spectrometer; (b) DG and CDG pellets ready to be placed on the sample holder

#### **3.5.2** Thermogravimetric Analysis (TGA)

TGA is a method of thermal analysis to measure the amount of mass changed in a material depending on temperature (25 °C to 1000 °C) or time at controlled atmospheres of nitrogen, air, helium, other gas, or in a vacuum. The temperature increases linearly with a gradient of 0 to 200 K min<sup>-1</sup>. This measurement provides information on thermal conditions since the material is temperature labile. The composition of the material is altered during the decomposition or volatilization in the presence of gases, so it is possible to examine the loss or mass gain. Apart from decomposition, oxidation and reduction, TGA is also used to evaluate the adsorptiondesorption of gases on porous solid and determine the material phase transition.

TGA instruments consist of a very sensitive analytical balance with a range of 5 to 20 mg, a furnace, a temperature programmer, an atmosphere control system and a microprocessor, which control, capture, and analyze data. For this research, the TGA was performed using a Perkin Elmer STA 6000 (Figure 3.6). The DG and CDG powder of approximately 2 mg each was placed in a sample pan and loaded onto the TGA balance. The pan resides in a furnace that was heated from 25 to 600 °C at a heating rate of 10 °C/min. Nitrogen gas with a flow rate of 20 ml/min was used as a purge gas and flowed through the sample during the testing. The temperature of the sample was read by thermocouples that were placed nearest to the sample. The change in sample mass was monitored during the experiment. A thermogram was derived to obtain more precise information on the various changes taking place in the sample under the analysis.



Figure 3.5 Perkin Elmer Thermal Analyzer

### **3.5.3 Differential Scanning Calorimetry (DSC)**

Differential scanning calorimetry (DSC) is a thermal analysis instrument used to measure the heat flow created within a sample while it is heated, cooled, or held at a constant temperature. Due to energy exchange with its environment, the sample may experience one or more phase transitions during these thermal changes. DSC has a wide range of applications, the most important of which is the characterization of materialspecific properties in a given sample, which includes parameters such as melting, crystallisation, glass transition, and specific heat capacity. Furthermore, DSC is useful for determining oxidation induction time, curing processes, kinetic reactions, polymorphism, and purity.



Figure 3.6 Netzsch differential scanning calorimetry

Heat flow from the furnace to the sample was measured relative to the heat flow from the reference material in the DSC experiment. The sample was placed in a crucible or pan with an identical sample and reference crucible, except that the reference crucible was normally empty. The temperature of the sample and reference was monitored using a thermocouple. DCS produced a differential thermogram, which displayed the needed heat flow against temperature. This study determined the glass transition (Tg) and melting temperature (Tm) of the DG and CDG sample using Netzsch DSC. Approximately 5 mg of DG and CDG were put in an aluminum sample pan and scanned at 25 °C to 250 °C. The analysis was conducted at a heating rate of 10 °C/min under a constant nitrogen gas flow of 20 ml/min.

#### 3.5.4 Field Emission Scanning Electron Microscopy (FESEM)

Field emission scanning electron microscopy (FESEM) offers detailed morphological information of samples at a heightened magnification level. Within the electron gun of a scanning electron microscope, the utilization of a field emission cathode leads to the generation of narrower probing beams, both at low and high electron energies. This advancement contributes to an enhanced spatial resolution while concurrently reducing issues related to sample charging and damage. When operated in a vacuum, electrons originating from a Field Emission Source undergo acceleration within a field gradient. The resultant electron beam subsequently traverses Electromagnetic Lenses, which serve to concentrate the beam onto the specimen. This interaction prompts the emission of various electron types from the specimen's surface. Subsequently, a detector captures these secondary electrons, and through a comparative analysis of their intensity with the scanning primary electron beam, an image of the sample surface is meticulously synthesized. This image is subsequently projected onto a monitor for visualization.

For this work, the morphological and structural details of the DG and CDG were obtained using a JSM-7800F (JEOL, Japan) FESEM with 5 kV accelerating voltage (Figure 3.8). The samples were coated with platinum to enhance the sample conductivity to create a clearer image. Before coating, the samples were freeze-dried to avoid structural damage.



Figure 3.7 JSM-7800F Field emission scanning electron microscopy

## 3.5.5 Elemental analysis

Elemental analysis is used to determine the quantity of the element in the given sample in weight percent. The sample was injected into a high-temperature furnace and the resulting combustion was passed through a specialized reagent to produce water, nitrogen and carbon dioxide. After that, the gases passed over copper to reduce nitrogen oxides to elemental nitrogen and remove excess oxygen. The gases then flowed into a mixing volume chamber with constant pressure and temperature to ensure the mixture's homogeneity. Lastly, the mixture went through a series of high-precision thermal conductivity cells to distinguish different elements in the mixture. The elemental analyses (carbon, hydrogen, and nitrogen) of the DG and CDG were performed using an EQPCL 200 Elementar, Germany, Vario Macro Cube elemental analyzer. The degree of substitution (DS) was investigated through elemental analysis of nitrogen. The subsequent equation, adapted from previous works (Haack et al., 2002; Prado et al., 2011), was employed for DS calculation:

$$DS = \frac{(403 \times \% N)}{1400 - (152 \times \% N)}$$
3.1

In this equation, 403 denotes the average molecular weight of a DG unit. %N signifies the nitrogen percentage on a dry basis. 1400 represents 100 times the mass of nitrogen, and 152 corresponds to the molecular weight of the cationic substituting group.

#### 3.6 Analysis of CDG fluid

## 3.6.1 Rheological testing

Rheology involves the examination of fluid behavior encompassing aspects of both flow (viscosity) and deformation (oscillation). Viscosity is characterized as the resistance a substance presents to flow. During rheological assessments, stress is applied to induce movement of the material at a specific velocity known as shear rate. In a standard viscosity test, a consistent shear rate is maintained, and the measurement captures the stress necessary for the material to achieve flow. There are three general flow behaviors for the viscosity as a function of shear rate: Newtonian, pseudoplastic (shear-thinning), and dilatant (shear-thickening). Viscosity testing is the most powerful
when it is used to simulate or mimic processes. The viscosity is calculated using the equation below:

$$\eta = \frac{\sigma}{\dot{\gamma}}$$
 3.2

Where

 $\eta$  = viscosity

 $\sigma$  = shear stress (force per area)

 $\dot{\gamma}$  = shear rate (change in strain with time)

Next, oscillation testing was performed to quantify the viscoelasticity properties of the sample. Viscoelasticity is one of the material's characters, where it consists of both viscous and elastic properties. The measuring geometry oscillated back and forth instead of continuously rotating the measuring geometry on the sample to obtain the viscoelasticity. From this testing, the complex modulus (G\*) of the sample was determined. The phase angle was also determined since different material has a different lag or phase angle between the applied and measured sinusoidal signal. The phase angle is zero for pure elastic material, while for pure viscous material, the phase angle is 90°. The rheology study for this testing combines the complex modulus and phase angle to create a storage and loss modulus. The storage modulus (G') represents the elastic properties, while the loss modulus (G") describes the viscous properties.

In this study, the viscosity of both DG and CDG gelling fluids was assessed using the Malvern Kinexus Lab+ rheometer, as shown in Figure 3.9. A cup and bob geometry setup, illustrated in Figure 3.10a, was employed. A consistent shear rate of  $170 \text{ s}^{-1}$  was applied to measure the viscosity of DG and CDG at varying concentrations. Viscosity measurements were conducted under two conditions: (i) at ambient temperature, and (ii) in a non-isothermal manner from ambient to 140 °C. Subsequently, the samples underwent shearing ranging from 0.01 to 1000 s<sup>-1</sup> to generate flow curves. For investigating suspension characteristics of DG and CDG fracturing fluids, oscillation testing was performed utilizing the Malvern Kinexus Lab+ rheometer with plate and plate geometry, as depicted in Figure 3.10b. This analysis required the identification of the linear viscoelastic region (LVER) through stress sweep testing spanning from 0.01 Pa to 300 Pa at a frequency of 1 Hz. Following this, a frequency sweep was executed, ranging from 0.01 to 100 Hz. All measurements were confined within the determined LVER region.



Figure 3.8Malvern Kinexus Lab+rheometer



Figure 3.9 Malvern Kinexus Lab+ measurement tools

## 3.6.2 Static Aging Test

The static aging test was conducted using a stainless-steel autoclave set and an oven, illustrated in Figure 3.10, to assess the thermal stability of both DG and CDG gelling fluids. The procedure involved recording the initial viscosity, transferring 180

ml of the sample into a 200 ml Teflon liner, and placing the autoclave in the oven at ambient temperature. The sample was then heated to a targeted temperature (100–180  $^{\circ}$ C) for 1 hour, followed by cooling at ambient temperature. The final viscosity was measured at a shear rate of 170 s<sup>-1</sup> to evaluate the viscosity loss after exposure to high-temperature conditions, thus providing insights into the fluid's thermal stability.



Figure 3.10 Stainless steel autoclave set with Teflon liner



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# 3.7 Flow Chart of Research Activities

Figure 3.11 Overall view of experimental work in this research

# **CHAPTER 4**

#### **RESULTS AND DISCUSSION**

#### 4.1 Introduction

This chapter provides a comprehensive investigation of the cationization process applied to diutan gum (DG) using CHPTAC. The impact of varying degrees of substitutions (DS) is also carefully examined. The chapter explores into an extensive analysis of the structural and physical attributes of cationic diutan gum (CDG), employing a range of techniques such as elemental analysis, FTIR, FESEM, TGA, and DSC, all aligned with the research objective. Furthermore, the rheological behavior and performance of both DG and CDG fluids are analyzed using a rheometer, while their thermal stability is assessed through the static aging test. This collective investigation contributes to a comprehensive understanding of the modifications and properties of CDG, furthering the goals of this research.

# AL-SULTAN ABDULLAH

# 4.2 Physical appearance of the sample

DG powder as used in this research has a white color and a smooth powdery property (Figure 4.1a). The substitution of CHPTAC on the surface of DG resulted in no significant difference in the physical appearance of the CDG sample, as shown in Figure 4.1b. Figure 4.2 shows a series of CDG fluids prepared by mixing the CDG powder with different degrees of substitutions of CHPTAC together with NaCl brine solution. The different degrees of substitutions of CHPTAC have affected the appearance of the CDG solution. The color of the solutions varies from translucent to clear and appears as a watery liquid up to gel-like consistency. These liquid properties will be further discussed in the rheology section.



Figure 4.1 (a) DG powder sample, (b) CDG powder sample



Figure 4.2 CDG gelling agent at difference CHPTAC concentration

# 4.3 Synthesis of cationized diutan gum (CDG)

The cationization reaction of DG was conducted in an aqueous solution under alkaline conditions with 2, 3-epoxypropyltrimethylammonium chloride (EPTAC). This etherification reagent (EPTAC) is formed in situ from the CHPTAC by applying a stoichiometric amount of base (NaOH) under heterogeneous conditions. In order to perform this cationic modification, a heterogeneous reaction was chosen instead of a homogenous reaction. This is to restrain the accumulation of charged groups in the external surface of the DG that can hinder the diffusion of reagent molecules into the DG structure. This method is similar to that used in the cationization reactions of XG and starch in several previous studies (Covis et al., 2016; Haack et al., 2002; Shi et al., 2018). However, the other parameters, such as reaction time, temperature, and NaOH concentration, was varied to obtain the optimum or different degree of substitutions. The utilization of NaOH was necessary to generate the epoxide, and the pH of the aqueous solution was maintained in the range of 11.5 - 12.0. The selected pH was normally used in the process of cationization, where the epoxide will remain at least 90% at 25 °C for 2 days at that pH (Prado and Matulewicz, 2014). The molecular structures of DG, CHPTAC, CDG, and the cationization mechanism of DG are depicted in Figure 4.3. The reaction initiates with the formation of alkoxide on the hydroxyl group of polysaccharides (DG), as demonstrated in Figure 4.3a. Subsequently, the alkoxide engages the epoxide on the CHPTAC, which is generated in situ by the previously mentioned alkaline medium. This interaction leads to the opening of the epoxide ring, resulting in the formation of hydroxy ether and its integration into the DG structure (Figure 4.3b). Subsequently, the cationized diutan is thoroughly washed with absolute ethanol to eliminate residual water before undergoing drying.



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Figure 4.3 Schematic representation for the CDG synthesis; (a) activation with NaOH, (b) reaction of DG with CHPTAC.

# 4.4 Degree of substitution (DS) from elemental analysis

This study uses the degree of substitution (DS) to describe the extent of cationization in a polymer, specifically in DG. The degree of substitution (DS) is the number of substituent groups attached per monosaccharide unit. It represents the average number of cationic groups attached to each repeating unit of the DG. In other words, it indicates how many hydroxyl groups on the DG have been replaced by the EPTAC molecule (Prado and Matulewicz, 2014). One common method to determine the degree of substitution involves measuring the amount of nitrogen present in the cationized polymer using elemental analysis. Since the EPTAC molecule contains a quaternary ammonium group, which contains nitrogen, the amount of nitrogen detected can be used to calculate the number of cationic groups attached to the DG. Table 4.1 displays the results of elemental analysis along with the DS values for DG and CDG. The elemental analysis outcomes highlight that there are negligible alterations in the carbon content (%C). Considering the cationization process's initiation with alkoxide formation on the hydroxyl group of the polysaccharide, a decrease in the hydrogen content (%H) was anticipated. This observation aligned with the %H reduction from

5.54% to 3.81% as the concentration of CHPTAC increased. In the DG sample, nitrogen was absent, but after undergoing cationization, the nitrogen content (%N) saw an increase from 0.72 to 0.83. This emphasizes the grafting of CHPTAC onto the CDG structure, as higher concentrations of the cationic reagent result in an increased availability of reagent molecules around DG, leading to a rise in %N.

The DS calculation utilizing %N yielded a similar trend, with values increasing from 0.23 to 0.26. However, this increase was not as pronounced as that reported by Prado et al. (2011). This difference could potentially be ascribed to the impact of NaOH, given that an equal quantity of NaOH is vital in the conversion of CHPTAC into epoxide. Additionally, the role of NaOH in ionizing the hydroxyl groups on the DG structure is essential, as these groups function as nucleophiles in the reaction. (Arbaa'in et al., 2020). In contrast, introducing an excessive quantity of NaOH can trigger epoxide degradation, ultimately resulting in a reduction in the molecular weight of the polysaccharide (Wang et al., 2018). This can be observed from the declining trend in the CDG gelling fluid viscosity as shown in Table 4.1. The viscosity decreased significantly, especially for the samples CDG4, CDG5 and CDG6. This is because the lower the molecular weight, the lower the viscosity of polysaccharides. In addition, epoxide could suffer from a secondary reaction that leads to the formation of a diol, which makes it unreactive to polysaccharides and decreases reaction efficiency (Heinze et al., 2004). Even more problematic, this diol displays reactivity with CHPTAC, resulting in the production of dimers and trimers of the cationizing reagent (Kavaliauskaite et al., 2008). Overall, the DS result showed a pronounced interchange between the DG and CHPTAC molecules since the DS was in the acceptable range. Several researchers have agreed that a DS of  $\geq 0.2$  is considered a high value, while < 0.2 is regarded as a low value for substitution (Covis et al., 2016; Prado and Matulewicz, 2014).

	CHPTAC (ml)	C (wt%)	H (wt%)	N (wt%)	DS	Viscosity cP
DG	0	38.45	4.27	0	0	104
CDG1	0.5	38.32	5.54	0.72	0.23	115
CDG2	1.0	38.05	5.55	0.73	0.23	112
CDG3	1.5	38.61	4.03	0.75	0.24	102
CDG4	2.0	38.35	4.08	0.77	0.24	80
CDG5	3.0	37.56	3.93	0.80	0.25	60

Table 4.1 CHN data, DS and viscosity of DG and CDG gelling fluid.

CDG6 4.0 38.22 3.81 0.83 0.26	5.81 0.83 0.26 48	G6 4.0	CDG6
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# 4.5 Functional group analysis of DG and CDG via FTIR

The FTIR analysis was initially conducted on CHPTAC, and the resulting spectrum is presented in Figure 4.4. The observed features in the spectrum can be attributed as follows: the broad and intense band at 3394 cm<sup>-1</sup> corresponds to O–H stretching vibrations, while the weak bands at 2966 cm<sup>-1</sup> are attributed to C–H stretching. The prominent peak at 1488 cm<sup>-1</sup> signifies C–H bending in the methyl group. The appearance of a peak at 1089 cm<sup>-1</sup> indicates the C-N stretching vibration of aliphatic ammonium. Notably, the region spanning 600 cm<sup>-1</sup> to 700 cm<sup>-1</sup> is linked to C–C I absorption bands. A comprehensive summary of these observations is provided in Table 4.2.

Table 4.2The FTIR of N-(3-chloro-2-hydroxypropyl) trimethyl ammoniumchloride (CHPTAC).

Material	Wavenumbe	er Assignment				
СНРТАС	3394 2966 1478 SA 1089 692 602	O–H stretching C–H stretching C–H bending C–N stretching				
اونيۇرسىيتى مليسىيا قەڭ السلطان عبدالله UNIVERSITI MALAYSIA PAHANG AL-SULTAN ABDULLAH						



Figure 4.4 FTIR spectrum of CHPTAC

Figure 4.5 visually illustrates the FTIR spectra of DG and CDG, achieved through varying CHPTAC concentrations. These spectra exhibit discernible characteristics: the peak centered at 3420 cm<sup>-1</sup> corresponds to the stretching vibration of O-H groups present within the DG and CDG structures. Additionally, the peaks situated at 2977 cm<sup>-1</sup> and 2935 cm<sup>-1</sup> correspond to the asymmetric and symmetric stretching vibrations of the C-H bond. A noteworthy feature is the prominent peak at approximately  $\sim 1730$  cm<sup>-1</sup>, which can be attributed to the adsorption of C=O bonds, particularly associated with acetyl groups (Diltz and Zeller, 2001). The FTIR spectrum exhibits C-C and C-O stretching vibrations at around 1600 cm<sup>-1</sup> and 1000 cm<sup>-1</sup>, respectively, signifying the existence of ether or ester groups within the polymer backbone (Xu et al., 2019a). The cationic modification of DG through the utilization of CHPTAC has induced notable alterations in the initial DG spectrum. Notably, the intensity of the O-H peak has slightly diminished post-cationic modification. This outcome can be attributed to the reaction between the hydroxyl groups on the DG backbone and the EPTAC molecule, resulting in the creation of ether linkages. This phenomenon reduces the amount of available free hydroxyl groups capable of vibration, subsequently leading to a reduction in the intensity of the O-H stretching vibration peak

(Shak and Wu, 2017). In addition, the formation of cationic groups on the DG backbone can also affect the hydrogen bonding interactions between the hydroxyl groups, leading to changes in the O-H stretching vibration peak intensity (Tarbuk et al., 2014). The C-H peak at 2935 cm<sup>-1</sup> has increased after the modification and was the result of the C–H stretching of the methyl group of quaternary ammoniums of the substituted reagent. This is because cationization usually involves the addition of a positively charged functional group (such as the EPTAC cationic group) to the polymer backbone, which can lead to changes in the conformation and hydrogen bonding of the polymer. These changes can affect the vibrational modes of the C-H bonds, leading to changes in their intensities in the FTIR spectrum. Furthermore, the increase in the intensity of a peak positioned at 1411 cm<sup>-1</sup>, assigned to the C–N stretching vibration, provided compelling evidence of the integration of cationic moieties onto the DG chains. The presence of the C-N bond is an important indicator of successful cationization, as this bond is formed when the EPTAC molecule reacts with the OH groups on the DG polymer backbone. Other studies also supported this result (Pal et al., 2005; Prado et al., 2011; Ren et al., 2007). Another band that shows an increment is at 1044 cm<sup>-1</sup>, corresponding to the ether linkage C–O–C.

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Figure 4.5 FTIR spectra for DG and CDG at different CHPTAC concentrations

# 4.6 Surface morphology of DG and CDG via FESEM

FESEM serves as a valuable tool for investigating into the morphology of polysaccharides, offering insights into their structural attributes. In this context, the gelling fluids comprised of DG and CDG underwent freeze-drying prior to FESEM scanning. As depicted in Figure 4.6(a)-(g), which portrays observations at 5000x magnification, the surface morphology of DG and CDG at various CHPTAC concentrations is evident. Figure 4.6(a) illustrates the smooth and well-organized multi-layered granular structure exhibited by the DG surface. Remarkable transformations emerge on the DG surface following CHPTAC modification. Specifically, the initially smooth DG surface evolves into a network of interconnected spherical reticular formations, as shown in Figure 4.6(b). With increasing CHPTAC concentrations, the spherical architecture transitions into a nearly cubic shape, as depicted in Figure 4.6(c). A further raise in CHPTAC concentration results in the dominance of more substantial, unconnected cubic structures, coupled with instances of agglomeration, as depicted in Figure 4.6(d)-(g). The cationization process can affect the surface morphology of cationized DG, as the introduction of cationic groups can alter the molecular

interactions between the polymer chains and affect the organization and packing of the chains at the surface. The introduction of cationic groups through cationization can lead to the formation of aggregates or clusters of these groups at the surface of the DG polymer (Huang et al., 2022). This happens because positively charged cationic groups repel each other, resulting in an electrostatic force separating them and creating surface structures composed of cationic groups, such as clusters or aggregates. Furthermore, these surface features can disturb the intermolecular interactions that are crucial in maintaining the polymer's structure, hence affecting the molecular organization and packing of the polymer chains. For example, suppose the cationic groups are located on the side chains of the diutan gum polymer. In that case, the formation of surface clusters or aggregates can create steric hindrance that prevents the polymer chains from adopting their normal conformation, simultaneously affecting the rheological properties of the modified DG polymer, such as its ability to form gels or its viscosity in a liquid formulation (Lai et al., 2020). When contrasting these findings with earlier research, it becomes evident that the cationic modification of polysaccharides yielded similar outcomes. This resemblance is apparent in investigations involving agarose (Prado et al., 2011) and XG (Shi et al., 2018), where the initial observation revealed a smooth surface morphology in the native polysaccharides. However, subsequent cationization led to the emergence of a complex branched reticular configuration, a transformation that exhibited heightened significance with increased concentrations of CHPTAC.

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Figure 4.6 FESEM morphology of DG (a) and CDG at various concentrations (b)-(g).

#### 4.7 Thermal properties of DG and CDG via TGA and DSC

Figure 4.7 depicts the thermal degradation of DG and CDG using a thermogravimetry analyzer (TGA) throughout a temperature range of 20 to 600 °C. TGA thermograms of DG and CDG show two separate decomposition areas. The initial decomposition emerges below 100 °C, followed by a subsequent decomposition spanning 229 to 274 °C. The initial decomposition is ascribed to the expulsion of physically associated water or moisture from the surface of both DG and CDG. Following this phase, both DG and CDG remain stable until they approach 220 °C; this plateau could suggest a stage where the sample undergoes a transition from one physical or chemical state to another or where the decomposition process is temporarily hindered due to factors such as crosslinking. After which the second decomposition stage commences. This subsequent decomposition is characterized by fast degradation across all samples, culminating in an average weight loss of approximately 45%. This weight loss is attributed to the decomposition of the DG and CDG backbone. (Zohuriaan and Shokrolahi, 2004). The introduction of CHPTAC has induced a minor enhancement in the thermal stability of CDG (256 °C), contrasting with DG (250 °C). This improvement can be attributed to the increase in electrostatic attraction among the chains, which effectively counteracts the inherent repulsion stemming from the positive charges of the incorporated cationic moieties. As a result, the increase in the electrostatic attraction led to an increased force necessary to disrupt the chains, a phenomenon that has also been observed and reported in the case of guar gum (Pal et al., 2007).

Examination of the thermal characteristics involved the application of DSC to both DG and CDG, unraveling the thermal transitions caused by the cationic modification in DG. Illustrated in Figure 4.8, the glass transition temperature (Tg) observed at 86 °C for DG and within the range of 88 to 92 °C for CDG. The relatively weak and widened glass transitions can be attributed to the semi-crystalline composition inherent in both DG and CDG samples. Notably, the endothermic peak possessed by CDG is broader compared to DG samples, signify the disintegration of the intramolecular interactions within the amorphous region due to the etherification process (Ren et al., 2007). Furthermore, a subtle shift towards higher temperatures in the Tg peak for CDG was observed. This observation suggests an enhancement in the thermal characteristics of CDGs as a result of the cationization modification. This shift can be attributed to the intensified electrostatic attraction between the chains, a direct consequence of the cationization process, thus contributing to the improved thermal properties of CDGs.



Figure 4.7 TGA weight loss curves for DG and different concentrations of CDG

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Figure 4.8 DSC curves for the DG and different concentrations of CDG

# 4.8 Rheology analysis

The cationization process applied to both DG and CDG has demonstrated promising outcomes in terms of viscosity. This can be observed in Figure 4.9, which shows the viscosity of the gelling fluids for DG and CDG at 25 °C. As illustrated, the gelling fluid of DG exhibited a viscosity reading of 104 cP. Upon cationization, the viscosity of CDG1 and CDG2 experienced a rise of approximately 10%, reaching values of 115 and 112 cP, respectively. This modification fostered a robust expansion of electrostatic interactions within the cationic groups associated with DG, thereby enhancing the interconnection network of the chains (Prado et al., 2011; Shi et al., 2018). However, in the case of CDG3, CDG4, CDG5, and CDG6, a consistent decline in viscosity was noted. This is because the cationic groups introduced by CHPTAC can act as electrostatic repulsion sites, causing the polysaccharide chains to repel each other and become more dispersed. As a result, the solution becomes less viscous and more fluid. An alternative interpretation could stem from the fixed amount of NaOH in this investigation. Consequently, the utilization of higher concentrations of CHPTAC might impede the substitution of CHPTAC onto the hydroxyl groups of DG while concurrently fostering an agglomeration process. This supposition finds support in the observed morphology through FESEM, where an increase in CHPTAC concentration led to the development of substantial cubical structures that were disconnected and agglomerated. A parallel diminishing trend in viscosity was also reported in the context of starch cationization, where viscosity decreased once the optimal monomer concentration was attained (Pal et al., 2008). The interdependence of CHPTAC and NaOH concentrations plays a pivotal role in attaining optimal efficiency and the highest level of substitution. The successful formation of epoxide and the corresponding alkoxides from hydroxyl compounds within a polysaccharide relies on the adequate utilization of NaOH. Inadequate NaOH can result in reduced epoxide formation and diminished reactivity of hydroxyl groups. As discussed in subsection 4.4, an excessive amount of NaOH can lead to the degradation of epoxides and a subsequent reduction in the molecular weight of the cationized polysaccharide.

Other than that, viscosity testing could also determine the types of fluid flow. This testing is very advantageous to mimic the real condition or field application of the tested gelling fluid. As for DG and CDG samples, their flow behavior was determined to be shear thinning. This was proven by Figure 4.10, where a decreasing viscosity was resulted from the increasing shear rate. In this testing, four different shear rates were selected, which were 170, 340, 511, and 1022 s<sup>-1</sup>. These designated shear rates were selected based on standard practices in the petroleum industry following the American Petroleum Institute (API) standard. The standard was designed to simulate several situations, like mixing and pumping the gelling fluid into the reservoir where the liquid's strength and workability are essential to be determined. Shear-thinning fluid flow properties are favorable because it could lead to a relatively smaller resistance in a low permeable core and contribute more remarkable oil recovery in a heterogeneous reservoir (Luo et al., 2022). On the other hand, AlSofi and Blunt constructed a streamline-based simulation to prove that shear thinning could reduce sweep efficiency and recovery (AlSofi and Blunt, 2010). The question of whether shear thinning or shear thickening is more favorable for modifying the viscosity of polysaccharide solutions is still a topic of debate. This is because each reservoir has its unique properties, which may require specific treatment methods. Therefore, the argument for shear thinning or shear thickening depends on different circumstances. Ultimately, the choice between these methods may depend on factors such as the specific properties of the

polysaccharide, the intended application, and the conditions of the modification process.



Figure 4.10 Shear-thinning of DG

To gain a deeper comprehension of the viscoelastic properties of the gelling fluids of both DG and CDG, a dynamic viscoelasticity measurement test was conducted. This examination was carried out within the defined Linear Viscoelastic Region (LVER) to ensure that the structural integrity of the gelling fluid remained undisturbed during the application of force throughout testing. The rheological properties of the gelling fluid significantly shape the state of the polymer gel. As highlighted by Deshpande (2009), a gelling fluid with a high concentration will exhibit characteristics similar to a gel, where the dynamic elastic modulus (G') surpasses the viscous modulus (G''). Furthermore, these values remain relatively constant in relation to frequency variations (Deshpande, 2009). A fluid with higher viscosity or a less concentrated gelling fluid typically displays a point of intersection between G' and G''. This intersection frequency corresponds to a relaxation time that characterizes the initiation of the terminal or flow region for the fluid. The relationship between G' and G" with respect to oscillation frequency for both DG and CDG gelling fluids is depicted in Figure 4.11. As demonstrated in the rheogram, for DG, CDG1, CDG2, CDG3, and CDG4, the value of G' surpassed that of G'', with no indication of a crossover or intersection point. This pattern aligns with the rheological behavior observed in DG and is consistent with findings from several earlier investigations (Arbaa'in et al., 2018; García González et al., 2019b). An observable plateau-like region emerged, indicative of a consistent gel-like reaction across frequencies. This plateau reflects the harmonious interaction between neighboring DG or CDG biopolymers (Li et al., 2012). Following the introduction of CHPTAC, there was a subtle increase in the viscoelasticity of CDG, particularly for the CDG samples possessing the optimal NaOH concentration. Similar findings were also observed in the case of XG after undergoing cationization (Shi et al., 2018). Certainly, for both CDG5 and CDG6, an interesting trend emerged where the value of G'' surpassed that of G', suggesting the domination of the viscous modulus concerning oscillation frequency. Notably, at frequencies around 0.5 Hz and 1.0 Hz, a crossover point became evident. As a result, the behavior of CDG5 and CDG6 deviated, signifying their resemblance to viscous liquids, in contrast to the gel-like characteristics exhibited by the remaining fluids (Xu et al., 2019a). The behavior of G' and G'' also demonstrates an upward trend with the increase of frequency, implying the presence of a structure resembling that of a weak gel (Covis et al., 2016). The concept of a weak gel refers to a substance characterized by possessing infinite viscosity while concurrently exhibiting a diminishing equilibrium shear modulus. On the other hand, the attributes of a strong gel entail having G' greater than G'' and displaying near-independence across a wide range of frequencies (Douglas, 2018).



Figure 4.11 The dependence of elastic modulus (G') and viscous modulus (G") of DG and CDG

# 4.9 Effect of temperature on viscosity of DG and CDG gelling fluid tested using static aging test

Temperature analysis on DG and CDG gelling fluid is important to determine its high-temperature environment capabilities, especially for oil and gas deep wells. Usually, the standard practice is to measure the rheological characteristic under the ambient surface environment and extrapolate those measurements to reservoir conditions. In this study, samples were put in the autoclave set to determine the gelling fluid thermal stability, heated in the oven, and tested for their viscosity. Figure 4.12 shows some variations in the appearance of the liquid samples after being taken out from the oven. The appearance of the fluids can be attributed to their stability when exposed to temperature changes. Samples A and B exhibited a complete loss in viscosity, while sample C showed more than a 50% reduction in viscosity. In contrast, sample D maintained its gelling characteristic despite the temperature exposure. The investigation explored the impact of temperature on viscosity for DG and CDG, as depicted in Figure 4.13. CDG2's gelling fluid was chosen due to its consistent viscosity among various CDG types, and this was then compared against DG's gelling fluid. Both gelling fluids were enclosed within a closed-system autoclave to prevent evaporation and underwent a static aging test in an oven within the temperature range of 100 - 180°C. Upon assessing the viscosity measurements post-static aging, it became apparent that both samples remained stable up to 160 °C, with CDG2 displaying higher viscosity compared to DG. This stability can be attributed to the outstanding water retention capabilities stemming from the double-helical molecular structures inherent in DG and CDG2. These structures confer robust internal cohesion, thereby maintaining fluid viscosity even when exposed to elevated temperatures (Tako, 1994). Upon reaching a temperature of 170 °C, both DG and CDG2 viscosities exhibited a decline of 11% and 8%, respectively. At this elevated temperature, molecular movements accelerated, leading to a reduction in van der Waals forces and hydrogen bonds. Consequently, the entanglement of macromolecules decreased, resulting in the weakening of the network within the gelling fluids (Liang et al., 2019). Examinations conducted on both samples revealed that CDG experienced slightly less degradation, managing to retain its doublehelical structure better than DG. This resilience of CDG can be attributed to the enhanced elasticity and increased electrostatic interactions among CDG chains following cationization, rendering it more tolerant to temperature fluctuations compared

to DG. However, at a temperature of 180  $^{\circ}$ C, a substantial decrease in viscosity was observed in both samples, attributed to the degradation of the gelling fluid's network.



Figure 4.12 Different liquid conditions after the static aging



Figure 4.13 Effect of temperature on the viscosity of DG and CDG2



# **CHAPTER 5**

#### CONCLUSION

#### 5.1 Background

This chapter presents the conclusions achieved from the objectives mentioned in the first chapter and several recommendations for future works that can be considered to understand better diutan gum (DG) cationization for use in the oil and gas industry, particularly for the high-pressure, high-temperature reservoirs. In this research, DG was selected for cationization due to its favorable characteristics such as high molecular weight, being renewable, and non-toxic. DG gelling fluid is a translucent, no-phase separation fluid with a high efficiency and is a promising technology.

# 5.2 Conclusion

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Objective number 1 has been successfully achieved. The cationization of the DG was achieved by etherification with N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) at different concentrations in the range of 0.5 - 4.0 mL. As the CHPTAC concentration increases, the degree of substitution (DS) also increases. The Fourier transform infrared spectroscopy (FTIR) results confirmed the incorporation of cationic moieties into the cationic diutan gum (CDG) chains by the increase in the intensity of a peak at 1411 cm<sup>-1</sup> that is attributed to the C–N stretching vibration. The cationic moiety was chained to the DG by a covalent link, specifically the ether bond. The surface morphology of the DG portrayed in the FESEM result has also shown significant changes, proving the cationic modification had occurred.

For objective number 2, the thermal stability and Tg of the CDG showed a slight improvement, as shown by the TGA and DSC analyses. The thermal stability of the DG itself is already high enough to be applied in extreme reservoir conditions compared to other commercialized polysaccharide gelling agents. Therefore, even a slight increase in the thermal stability of CDG would be a great added value to the system. There was a 6 °C increment of the decomposition temperature and a 2 - 6 °C increment in the glass transition temperature of the CDG. The gelling fluid also exhibited a good tolerance toward temperature, as shown by its viscosity stability in Figure 4.9, where its structure remained thermally stable.

The rheological behaviors of the CDG fluids were studied and compared. The apparent viscosity increased for samples CDG1 and CDG2 but experienced a loss in viscosity as the DS of CHPTAC increased. This was due to the NaOH concentration during the cationization process. Excess NaOH will cause the epoxide's degradation, decreasing the DS. This excess NaOH would also reduce the molecular weight of the DG. There are two conditions that need to be taken into account to determine the discrepancy about the molecular weight. In one condition, the substitution of cationic groups into the CDG structure increases its molecular weight. In another condition, the degradation processes in the alkaline medium leads to a decrease in molecular weight. The flow curve exhibits a non-Newtonian property since the viscosity decreases as the shearing increases. From the modulus analysis, most of the samples showed a stable gel-like response, where no crossover was observed between the elastic modulus (G') and viscosity modulus (G"), indicating an excellent suspension capability of the gelling fluid. Fluids with good suspension capability would hold and carry the proppant well during oil exploration operations. Consequently, CDG would be a great candidate for the harsh conditions in deep oil reservoirs to meet the industry's urgent need for highperformance fluids.

## 5.3 Recommendation

The conclusion for this research was deliberated in the previous subsection and demonstrates that the cationization of DG is still deficient in several areas. Hence, listed below are several suggestions for future experiment that can be considered to improve the CDG for it to be used in high-performance fluid in the high-temperature high pressure (HTHP) reservoirs in the oil gas industry.

To better understand the cationization, the molecular weight of CDG needs to be determined before and after the cationization. This could provide an explanation for the decreasing pattern in the viscosity. Since many parameters (temperature, time, pH value, molecular weight, and NaOH concentration) will affect the cationization, optimization of the system need to be carried out first. However, this might take quite some time. Hence, it is recommended to identify the optimized temperature between 50 - 80 °C. Meanwhile, NaBH<sub>4</sub> can also be added to overcome molecular weight degradation in the alkaline medium. However, this would make the CDG more expensive on an industrial scale.

In addition, a detailed, comprehensive study on the CDG can be provided by NMR analysis. This would determine the position and degree of substitution of diutan with the cationic group. In the viscosity analysis, it is difficult to define the viscosity response toward temperature because the sample might dry upon heating due to evaporation while taking the rheological measurement. Therefore, it is suggested to conduct the rheological measurement using a high-pressure, high-temperature rheometer. This technique could also closely mimic the actual oil reservoir conditions.



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## APPENDIX A

## LIST OF PUBLICATIONS

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اونيۇرسىيتي مليسىيا قهڅ السلطان عبدالله UNIVERSITI MALAYSIA PAHANG AL-SULTAN ABDULLAH