PRODUCTION OF ANTI-CORROSION MATERIALS FROM UAE DATE PALM WASTE

Nour Shehadeh AbdelRahman

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PRODUCTION OF ANTI-CORROSION MATERIALS FROM UAE DATE PALM WASTE

Nour Shehadeh AbdelRahman

This thesis is submitted in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering

Under the Supervision of Professor. Ali H. Al-Marzouqi

April 2019
Declaration of Original Work

I, Nour Shehadeh AbdelRahman, the undersigned, a graduate student at the United Arab Emirates University (UAEU), and the author of this thesis entitled "Production of Anti-Corrosion Materials From UAE Date Palm Waste", hereby, solemnly declare that this thesis is my own original research work that has been done and prepared by me under the supervision of Professor Ali H. Al-Marzouqi, in the College of Engineering at UAEU. This work has not previously been presented or published, or formed the basis for the award of any academic degree, diploma or a similar title at this or any other university. Any materials borrowed from other sources (whether published or unpublished) and relied upon or included in my thesis have been properly cited and acknowledged in accordance with appropriate academic conventions. I further declare that there is no potential conflict of interest with respect to the research, data collection, authorship, presentation and/or publication of this thesis.

Student’s Signature: __________________________ Date: 12/6/2019
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Abstract

Palm tree serves as the main source of biomass in the Gulf countries. The United Arab Emirates (UAE) alone is blessed with more than 40 million date palm trees, which generate a huge amount of waste annually. The main objective of this thesis is to examine the ability of producing a corrosion inhibitor from date palm tree waste, starting by extracting lignin from different parts of the date palm tree and characterizing the extracted lignin, converting lignin to sodium lignosulfonate, while selecting the optimum condition for the conversion reaction and characterizing the prepared lignosulfonate. Finally, the corrosion efficiency for the prepared lignosulfonate is examined using potentiostat corrosion test.

The results show successful extraction of lignin from three different parts of palm tree (fibers, rachis and leaflet) with lignin percentage of 20, 10 and 19, respectively. Klason lignin extraction method and characterization of lignin was performed and the results were compared with literature indicating similar physical and chemical properties to previous works and studies. Furthermore, the optimum conditions for the reaction were determined to be: 4 hours reaction time, 100°C temperature, 0.9 (g/g) reactants to lignin ratio, 25 (g/L) lignin concentration, and 0.5 M NaOH concentration. Corrosion rate of the produced sodium lignosulfonate was determined by using the Potentiostat corrosion test, the corrosion rate of tested samples reached 1.05 (mm/yr) with the addition of sodium lignosulfonate, which indicates that the produced sodium lignosulfonate can act as a good inhibitor and can be used to protect carbon steel from corrosion. Moreover, the increased of sodium lignosulfonate concentration from 5 ppm to 30 ppm decreased the corrosion rate by 19.49%.

This study can be of high benefit to the country as the organic non-toxic
corrosion inhibitor can then be produced locally from a feedstock, which is currently used as a waste in UAE society. This goes in line with UAE government’s 2021-2030 vision of ensuring more sustainable development while preserving the environment.

**Keywords:** Sustainability, UAE Date Palm Waste, Anti-Corrosion, Lignocellulosic Biomass, Environment, Corrosion.
إعداد مادة مضادة للصدأ من مخلفات نخيل دولة الإمارات

المنخفض

تمتاز دولة الإمارات بوفرة أشجار النخيل التي يتجاوز عددها أربعين مليون نخلة متوزعة في مختلف مناطق الدولة. على سبيل المثال يوجد في مدينة العين ما يقارب ثمانية مليون نخلة. تنتج كل واحدة منها ما يقرب عن 25 كغ من المخلفات سنويا فقط من سعف النخيل وهو ما يعادل 200 مليون كغم من مخلفات سعف النخيل سنويا كما ذكرت تقارير بلدية العين. تحتوي المخلفات النباتية بشكل رئيسي على مركبات اللجنوسيلوز وهي مكونات غنية يمكن الاستفادة منها في إنتاج مواد ذات قيمة عالية كالمواد المضادة للصدأ. لكن على الرغم من الفائدة التي تجني من مخلفات شجر النخيل فإنه بأغلب الأحيان يقام بحرقها أو طمرها بدلا من إعادة تدويرها أو استغلالها. و من ناحية أخرى، يعد المايلد ستيل أو الصلب المعدن الأساسي الذي يستخدم كوحدة بناء في أغلب الصناعات في الوقت الحالي نظرا لخصائصه الميكانيكية المميزة للعديد من التطبيقات و رخص سعره مقارنة بالأنواع الأخرى من المعادن ولكن مع ذلك فإنه و مثل غيره من المعادن قد يتعرض للتآكل الناجم عن تعرضه لبعض العوامل البيئية مع الوقت مما يؤدي إلى ضعفه و هشاشةه وبالتالي يشكل تحديا كبيرا على الصعيد الصناعي.

لذا فإن الهدف من هذه الاطروحة هو حل مشكلتين قائمتين رئيسيتين الأولى هي تواجد مخلفات النخيل بكميات هائلة والثانية هي مشكلة تآكل المعادن المستخدمة في أغلب الصناعات كوحدة بناء رئيسية. وتقوم فكرة المشروع على استخلاص مركبات اللجنوسيلوز من مخلفات النخيل وتحويل جزء منها لمدة مضادة للصدأ بحيث تعتبر مداي قابليتها وكفاءتها لمنع الصدأ أو التقليل منه بإجراء العديد من التجارب و دراسة ما إذا كان بالإمكان الاستغناء عن المواد الكيميائية المستخدمة كمضادات للصدأ حتى الوقت الحالي و استبدالها بمضاف الصدا العضوي المنتج من مخلفات النخيل إضافة إلى إجراء تقييم الأثر البيئي للمنتج لدراسة مدى تأثيره على البيئة.

أهم نتائج هذه الدراسة هي التمكن من استخلاص اللجنين بنجاح من ثلاث أجزاء مختلفة من مخلفات النخيل وهي السعف و الليف و الغصن بابتخاذ طريقة كلاسون حيث تم دراسة وصف اللجنين المستخرج من الأجزاء الثلاثة لتأكد من صفاته الفيزيائية والكيميائية وقد أثبتت النتائج نشابة الصفات بين اللجنين المستخرج بهذه الأطروحة مع الدراسات المنشورة مسبقا. يتبع
استخراج اللجنين تحويله الى مادة اللجنوسلفونيت والتي بدورها تعتبر مادة مضادة للصدأ كما تم اثباته حديثاً. من خلال هذه الأطروحة تم ايجاد العوامل أساسية الأمثل للتفاعل الكيميائي وهي درجة الحرارة، مدة التفاعل، نسبة وزن المتفاعلات الرئيسية، تركيز هيدروكسيد الصوديوم ووزن اللجنين المستخدم، لانتاج لجنوسلفونيت ذو قدرة أكبر على منع صدأ المعادن. أخيراً أظهرت نتائج دراسة اختبار دراسة تحليل الوزن معدل كفاءة عالية نسبياً وهي %82.4812. تعني أن اللجنوسلفونيت المنتج قادر على حماية المادن من الصدأ بنسبة اثنان و ثمانون بالمئة.

نتيجة فكره هذه الأطروحة سيعود بالنفع على دولة الإمارات كما أنه يتفق مع رؤية حكومة الإمارات الاقتصادية 2030-2021 في خلق بيئة مستدامة من خلال استخدام الموارد والحد من التلوث والحفاظ على البيئة الفريدة لدولة الإمارات.

مفهوم البحث الرئيسية: الإستدامة، مخلفات النخيل، اللجنين، الصدأ.
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Dedication

To my beloved parents and family
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<tr>
<td>ρ</td>
<td>Density of the Corroding Material (g/cm³)</td>
</tr>
<tr>
<td>ΔE(t)</td>
<td>Potential Scan (V)</td>
</tr>
<tr>
<td>A</td>
<td>Absorbance at 280 nm</td>
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<tr>
<td>A</td>
<td>Pre-exponential Factor (s⁻¹)</td>
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<tr>
<td>B</td>
<td>Stern-Geary Coefficient (V)</td>
</tr>
<tr>
<td>bₐ</td>
<td>Anodic Tafel Slopes (V)</td>
</tr>
<tr>
<td>bₑ</td>
<td>Cathodic Tafel Slopes (V)</td>
</tr>
<tr>
<td>CR</td>
<td>Corrosion Rate (mm/year)</td>
</tr>
<tr>
<td>CS</td>
<td>Carbon Steel</td>
</tr>
<tr>
<td>DOE</td>
<td>Design of Experiment</td>
</tr>
<tr>
<td>dx/dt</td>
<td>Thermal Decomposition Rate of Conversion</td>
</tr>
<tr>
<td>Ea</td>
<td>Activation Energy (J/mol)</td>
</tr>
<tr>
<td>EW</td>
<td>Weight of the Corroding Species (g)</td>
</tr>
<tr>
<td>f(X)</td>
<td>The Function of Conversion</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>H</td>
<td>Calibration Factor for the Bomb Calorimeter (MJ°C)</td>
</tr>
<tr>
<td>HVC</td>
<td>High Value Chemical</td>
</tr>
<tr>
<td>i</td>
<td>Current Density (A)</td>
</tr>
<tr>
<td>i_corr</td>
<td>Current Density (μA/ cm²)</td>
</tr>
<tr>
<td>k</td>
<td>Reaction Rate Constant</td>
</tr>
<tr>
<td>m</td>
<td>Mass of Benzoic Acid (g)</td>
</tr>
<tr>
<td>mμA</td>
<td>Meter.microAmpere</td>
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<tr>
<td>Symbol</td>
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<tr>
<td>n</td>
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<td>R</td>
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<td>T_0</td>
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<td>Weight of the Pyrolyzed Sample (g)</td>
</tr>
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<td>w_\infty</td>
<td>Final Residual Weight (g)</td>
</tr>
<tr>
<td>w_o</td>
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<tr>
<td>X</td>
<td>Conversion</td>
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Chapter 1: Introduction

1.1 Overview

Corrosion is the caustic attack of a metal by reaction with its environment. The gradual rusting causes metals to wear out, leading to serious damages to piping systems and equipment. Corrosion engineers, with the support of corrosion scientists, aim to reduce material losses, economic losses and accidents arising from corrosion of pipes, tanks, and metal components of machines, ships, bridges and marine structures. Inhibitors are typically used to prevent or reduce corrosion. Currently most used corrosion inhibitors are made from the petrochemical industry, making it expensive, unsustainable and toxic in nature to humans and the environment. Therefore, it is important to develop new corrosion inhibitors that are environmentally acceptable, relatively inexpensive and produced from a sustainable natural resource. The United Arab Emirates and the surrounding Gulf nations are home to millions of date palm trees that generate millions of metric tons of waste annually. In UAE most of the waste from palm trees is currently turned into compost, traditional social applications or burned to generate heat despite their high lignocellulosic content that can be processed into more valuable products such as corrosion inhibitors, fuel generation and bio-based chemicals. Bio refineries as compared to petro-refinery can produce products from date palm waste in an efficient, cheap and environmentally friendly manner. Therefore, the goal of this study was to develop new techniques of extracting corrosion inhibitors from UAE date palm waste.
1.2 Statement of the problem

The United Arab Emirates and the surrounding Gulf nations are home to millions of date palm trees and in particular the *Phoenix dactylifera* species. Date palm residues represent a major quantity of biomass as lignocellulosic materials. This biomass is mostly made up of carbohydrates containing cellulose and hemicellulose, attached with lignin. Most of the waste from palm trees is currently turned into compost or burned to generate heat despite its high lignocellulosic content which could be processed into more valuable products such as fuel and bio-based chemicals. Use of lignocellulosic waste through controlled thermochemical techniques can cause much less damage to the environment compared to other methods.

Corrosion is the caustic damage of metals caused by the reaction of metals with their environment. The serious consequences of the corrosion process have become a significant issue universally. Inhibitors are typically used in order to prevent or reduce corrosion. It is essential to develop environmentally acceptable and inexpensive inhibitors since most of the chemical inhibitors currently in use have a toxic nature and/or very high cost such as the most common anticorrosion agent tributyltin (TBT). Therefore, natural products should be considered for the development of safer and more sustainable corrosion inhibitors.

The aim of this study was to extract lignin from UAE date palm waste, convert it to a value-added product, lignosulfonate (corrosion inhibitor) under environmentally friendly multi chemical reactions. Then subsequently, to test this anti-corrosion material for corrosion prevention. The goal was to solve the problem of UAE date palm waste in a more environmentally friendly way by converting it into an anti-corrosion compound in order to also solve corrosion problems.
1.3 Research objectives

The main objectives of this work are:

1) Extract lignin from different parts of date palm tree.
2) Study the effects of different parameters (ie. particle size, date palm tree type and different parts of the date palm tree) on the lignin yield.
3) Convert lignin to sodium lignosulfonate.
4) Study and characterize the prepared lignosulfonate.
5) Perform anti-corrosion test using lignosulfonate as a corrosion inhibitor.
6) Compare the corrosion results with the existing corrosion inhibitor.

1.4 Limitation of the study

One of biggest challenges of this study was lack of information about lignosulfonate in general and lignosulfonate reaction as well as the methods of converting lignin to lignosulfonate. Characterization of lignin, and comparison to literature was also a challenge as there were variation in reported results in most of the previous studies. This is due to the complexity of lignin, which will be discussed in the next chapter. Despite the wide abundance of date palms in many regions worldwide, little or no information is available regarding different parts of date palm biomass lignin valorization using klason isolation technique.

1.5 Organization of this thesis

Chapter 1 covers a brief overview of the problem statement, research objectives and the limitations of this study. Chapter 2 introduces biomass and its main components, describes lignin in more details, discusses the conventional techniques in
extracting lignin, the alternative techniques of converting lignin to lignosulfonate and their characterization, and a literature review summarizing recent work done by researchers worldwide. The experimental work and methodology is discussed in Chapter 3. In Chapter 4, the experimental results are presented and explained. Finally, Chapter 5 summarizes the findings and suggests recommendations.
Chapter 2: Relevant Literature

2.1 Biomass importance and utilization

Use of biomass and other renewable energy sources is expected to increase in the future due to the negative effects of fossil fuels including: global warming, depletion of petroleum reserves and price fluctuations [1]. To solve environmental and long-term economic uncertainties, conversion of lignocellulosic biomass to biofuels and high value chemicals presents a sustainable and viable option for future energy security and reducing green-house gases [2]. Unlike fossil fuels that add CO₂ to the atmosphere when burned, lignocellulosic biomass is a cleaner-burning resource. For instance, ethanol obtained from biomass has been reported to have the potential to reduce greenhouse gas emissions by almost 80% [3].

2.2 Biomass composition

The huge potential of biomass has led to the current increase in research for the development of biomass utilization into high value chemical products and biofuels. Generally biomass consists of polysaccharides, lignin, extractive and ash as shown in Figure 1.
Lignocellulosic biomass is a naturally occurring sustainable resource, comprising of hemicellulose, cellulose and lignin [5]. These fractions have the potential to produce high value chemicals. For example, hemicellulose and cellulose have for a long time been used in the textile and paper industries. Due to their durability and structural uniformity, cellulose nanocrystals act as a base for new polymer composite materials [6, 7]. Figure 2 shows the main components in the plant.
Figure 2: Simple plant structure [8]

Despite the need to fully utilize the three components of lignocellulosic biomass, most recent research is focusing on hemicellulose and cellulose utilization, destroying lignin through various methods of delignification [9]. However, energy generation and future chemical reliance on lignocellulosic biomass needs maximum biomass utilization. Lignin fractions, despite having a complex polymeric structure, have a large potential for production of high value chemicals [10].

Lignocellulosic biomass is commonly found in many parts of the world including the sea and land. It can even be found in adverse climates like deserts; making it a viable sustainable resource to contribute to future energy security and chemical industries. Despite the huge availability of date palm lignocellulosic biomass in the Middle East, which is a precursor for high value chemicals (HVC) production, most of the waste from palm trees is currently turned into compost or burned to
generate heat. UAE alone has over 30 million date palm trees and each palm tree, on average produces around 12-15 new leaves every year and the same amount is usually cut from each tree [11], in total generating approximately 1.2 million tonnes of waste annually. Characterization and value addition to this waste instead of burning it, can be an opportunity to produce HVCs and successfully introduce the bio-refinery concept to UAE and the surrounding region, which has been known for petrol-refinery for decades.

Palm biomass is a type of lignocellulosic biomass which comprises of mainly cellulose, hemicellulose and lignin [12]. The three components all have unique chemical structures and properties. Cellulose, which is the main constituent of wood carbohydrates is a polysaccharide of glucose units linearly inter-linking each other by β-1,4-glycosidic bonds [13]. Structure of cellulose molecule is shown in Figure 3.

![Cellulose molecular structure](image)

**Figure 3:** Cellulose molecular structure [14]

Hemicellulose, is a hetero-polysaccharide with different structures in both soft and hard wood. Hemicellulose binds fibers to form inter-fiber bonding. Due to its low strength compared to cellulose, it can easily be hydrolyzed by dilute acids or bases [15]. Structure of hemicellulose molecule is shown in Figure 4 and lignin will be discussed in more details in the next section.
2.3 Lignin

Lignin is the second most abundant natural polymer on earth making up to 10–30% of lignocellulosic biomass [16]. Lignin is a class of complex organic polymers that form significant structural materials in plants; it fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components, especially in vascular and support tissues: xylem tracheids, vessel elements and sclereid cells. Figure 5 shows the connection between lignin and the other lignocellulosic biomass components in plants. Lignin is covalently linked to hemicellulose and therefore cross-links different plant polysaccharides, conferring mechanical strength to the cell wall, specifically in wood and bark. And by extension along the plant as a whole, it gives rigidity and protects the plant from rotting easily [17-19]. About $20 \times 10^9$ tonnes of lignin is produced each year by photosynthesis. This makes an almost indefinite reserve of lignin as a raw material without competing with food products [20]. An important source of lignin is the spent pulping liquors, known as black liquor, where lignocellulosic materials, like wood, corn stalks, straw, bagasse, and the like, are processed to isolate the cellulose fibers or pulp from the lignin [21].
2.3.1 Chemical structure of lignin

Chemically, lignin is a three-dimensional, highly cross-linked macromolecule made up of a number of structural units. These units are similar in configuration and can be regarded as a common skeleton which is a phenylpropane or C$_6$-C$_3$ or C$_9$ type. In the natural unrefined form, the molecular structure of lignin deviates according to the source and is so complex that molecular structure has never been completely described [23, 24]. Lignin molecule is composed of three types of substituted phenols: coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol by enzymatic polymerization as shown in Figure 6; yielding a massive number of functional groups and linkages [20].
2.3.2 Importance of lignin in plant

The cell wall consists of several layers which are depicted in the schematic representation in Figure 7. The layers of the cell wall from outer to inner are as follows: middle lamella, the primary wall, the secondary wall (divided into the L1, L2, and L3 layers), and the hollow inner region called the lumen. The primary (outer) wall is composed of a network of randomly arranged cellulose microfibrils connected to an amorphous phase of hemicellulose and lignin, which act as a matrix for the cellulose bundles [23]. On the inner secondary wall, three layers are usually present and in each
one the cellulose microfibrils are helically arranged in relation to the long axis of the elementary fiber. Lignin is found mainly in the middle lamella and the secondary wall. Lignin concentration in plant material is high mainly in the region of middle lamella [26, 27].

![Schematic representation of plant cell wall](image)

Figure 7: Schematic representation of plant cell wall [14]

### 2.3.3 Applications of lignin

Lignin has substantially enhanced properties in comparison to other natural polymers, and is marked by a relatively high strength, high resistance, and rigidity. Lignin is also a worthy substance for heat and sound insulation. Formulations comprising lignin can be used in carbon fiber composites, adhesive binders, food and beverage additives, resins and coatings, nutritional supplements, PU-based foams, films, paints, and plastics. Lignin polymers may be created at low cost, and can be used as replacement for feedstocks developed from fossil fuel or petrochemical resources in the making of various products [20]. Despite its complex structure, lignin has a great potential to act as a precursor for production of bio-fuels and high value
chemicals (HVC) after valorization. Production of HVC from lignin involves isolation of non-lignin fractions using different extraction methods [28, 29].

2.3.4 Lignin isolation methods

Isolation of lignin is a significant initial phase that decides the scale-up and optimization of many of the industrial processes regarding this natural polymer, as well as most of the final applications of any lignin derived from them [30]. Lignin can be isolated from various raw materials, i.e. wood and black liquor. Many procedures that have, been developed through the years have their roots in the wood chemistry and pulp industries. Broadly speaking, the methods described in the literature for the isolation of lignin can be divided into two main classes depending on whether lignin is the object or residue of the separation [31]. The first class involves the removal of cellulose and other components (by hydrolysis), leaving lignin as an insoluble residue. The main methods used under the first class are: Klason, Willstätter, Urban, Periodate, Cuproxam, Halse, Fredenhagen, Fengel, Runkel and Acid detergent lignin or acid hydrolysis) [29, 32-38]. The second class involves the removal of lignin from the cellulose and other components. Previous studies followed the second class applying different techniques such as Brauns Native lignin, Milled Wood lignin (Björkman), Cellulolytic Enzyme, Enzymatic Mild Acidolysis Lignin, Dioxane Acidolysis Lignins, Organosolv Lignin, Alcoholysis lignin, Phenol lignin, Alkali lignin, Steam exploded system and Brown rot lignin [30, 39-44]. The extraction methods are presented in Table 1.
Several methods for isolating lignin from wood or herbaceous plants have been used so far, but none of them leave lignin unchanged after isolation. Whatever method is employed, the resulting lignin preparation is no longer identical to native lignin [46]. To distinguish the different lignins obtained, these are usually named after the author of the procedure. Nevertheless, regardless of the method used to isolate lignin, the final ground biomass is usually set free from various “extractives”, such as fatty substances, resins, and volatile oils. This is generally accomplished by extracting the lignified material with an organic solvent or a mixture of these (preferably an alcohol/benzene solution) [30].
Although all kinds of biomass in principle can be converted into fuels and HVCs, the use of edible crops for these applications cannot be justified in a world of increasing population whose demand for food is a priority in contrast to energy and chemical demands. To prevent competition with the use of land and resources used to produce food, it is recommended to use second-generation biomass (that not in direct competition with human survival) to produce fuels and chemicals.

HVCs have applications in the food and fragrance industries, and as fuel additives [11]. Lignocellulosic palm biomass provides an opportunity for future production of HVCs in the Gulf region. The large abundance of palm trees in the region, and the increasing negative economic and environmental pressures facing the petroleum industry are powerful motivations for promoting research in this new field of biomass utilization for green growth. Lignin remains a potential source of HVCs despite its complex molecular structure varying in different plant species [47-50]. Therefore, lignin valorization is important to reduce its resistance to chemical and biodegradation.

2.4 Lignosulfonate

Lignin, while abundant, has very limited industrial applications. Since lignin is water insoluble and not reactive, it requires modification to develop its potential applications. In contrast to other wood based materials, such as cellulose, which can be easily modified [51], modification of lignin is challenging due to the structural complexity of lignin. In the absence of any modification, the α position of phenyl propene subunits in lignin Figure 8 presents the most reactive site [52]. However, the β-O-4 aryl ether linkages and other interconnecting bonds create significant steric
hindrance or occupy the available reactive α site (i.e. α-O-4 aryl ether bonds), which leads to unreactivity of lignin [53].

![Figure 8: Coniferyl phenyl propene subunit with numbered reaction positions [52]](image)

Various processes have been reported for modifying lignin structure. These methods include demethylation, reduction, oxidation, hydrolysis, phenolation, sulfonation and hydroxymethylation. Researchers have claimed that phenolation and hydroxymethylation are more effective than reduction, oxidation and hydrolysis in increasing the reactivity of lignin [54] as they increase the reaction sites, and are capable of increasing the reactivity of lignin [55]. Therefore, hydroxymethylation and phenolation were chosen to increase the reactivity of lignin in this study.

On the other hand, sulfonation of lignin provides lignin with unique properties. Therefore, the sulfonation of lignin may render lignin with such properties that are required for specific applications. Sulfomethylation of lignin has been conducted through various pathways; it is usually conducted in two steps: hydroxymethylation followed by sulfonation [56]. Or alternatively, the sulfomethylation can be completed in one-step; methylation through the addition of formaldehyde, and sulfonation using sodium sulfite simultaneously. Both paths are shown in Figure 9.
2.4.1 Properties of lignosulfonate

Lignosulfonates, or sulfonated lignin, are water-soluble anionic polyelectrolyte polymers, which are usually byproducts from the production of wood pulp using sulfite pulping. Lignosulfonate molecules have very broad ranges of molecular mass (they are very polydisperse). A range of from 5,000–400,000 g/mol has been reported for softwood lignosulfonates with lower values reported for hardwoods [58]. The amorphous nature of lignin and its inherent complexity presents a great difficulty for characterizing lignin. The sulfonation of lignin creates even more difficulties [59].

Lignosulfonates is mainly classified into sodium lignosulfonate, calcium lignosulfonate and magnesium lignosulfonate. Sodium lignosulfonate is the major
product of this complex polymer that has a large market. In addition, there are other types of lignosulfonate, which are not commercialized yet such as ammonium, aluminum and chromium. A major driver for the future will be finding new applications for various types of Lignosulfonate [60].

2.4.2 Application of lignosulfonate

Currently, the major applications of lignosulfonates include their use as: concrete additives, animal feed, dyestuff, cosmetics, absorbents, gypsum board, brick manufacturing, dust control, adhesives, vanillin, organic solvent, deflocculating clays, suppressing non-toxic dust, plasticizers in concretes, plasterboard, oil drilling mud, carbon black, coal gasification, dispersants, binders, tanning leather, emulsions, pelletizing/granulation, micronutrients, and many more. The use of lignosulfonates as a precursor for the production of chemicals has limited scope. The conversion of lignosulfonates to vanillin is the most successful process of this kind. Recently, significant research has focused on studying the ability of sodium lignosulfonate as corrosion inhibitor [61-72]. Lignosulfonates can also be used to reduce the water needed for cement production.

2.5 Corrosion

Corrosion can be described as noxious attack reaction on metal stimulated by the surrounding environment. It is the most devastating problem of modern technology, which poses a serious threat to many industries [73]. In practice, most of the acidic industrial applications such as refining crude oil, acid pickling, industrial cleaning, acid descaling, oil–well acid in oil recovery and petrochemical processes use mild steel. However, corrosion makes the use of mild steel as a construction material
in industrial sectors quite challenging. Therefore, there is a strong need to develop reliable corrosion inhibitors [73].

Recently research have focused on studying the ability of sodium lignosulfonate as corrosion inhibitor [70]. Lignosulfonate contains both hydrophilic groups (sulfonic, phenyl hydroxyl, and alcoholic hydroxyl) and hydrophobic groups (carbon chain), as shown in Figure 10. Lignosulfonate is an anionic surfactant, possessing a certain degree of surface activity [74], which may promote surface adsorption and further particle dispersion to form a thin film on the metal; that helps prevent corrosion and scale inhibition.

Corrosion inhibition for sodium lignosulfonate could be improved by increasing the sulfonic group and increasing the negative charged density. As the number of sulfonic groups increase the solubility of sodium Lignosulfonate increases [75].

It is widely accepted that the water solubility of lignin depends on the content of hydrophilic groups. The introduction of a sulfonic group can improve the solubility of lignin [75].
2.5.1 Measurement of corrosion

Corrosion is an electrochemical process of oxidation and reduction reactions. As corrosion occurs, metals release electrons (oxidation reaction), which are gained by elements in the corroding solution (reduction reaction) [76]. Since there is a current or flow of electrons in the corrosion reaction, corrosion can be measured and controlled electronically. Therefore, controlled electrochemical experiments can be used to measure the corrosion properties of metals and metal components in combination with various electrolyte solutions [76].

In order to test the corrosion properties of a metal in an electrolyte solution, a polarization cell consisting of an electrolyte solution, a reference electrode, a counter electrode(s), and the metal sample of interest (working electrode) is used. This device is schematically shown in Figure 11. The electrodes are connected to an electronic instrument called a potentiostat [77]. The reference and counter electrodes are placed in the electrolyte solution. It is desirable for the electrolyte solution to closely resemble the actual application environment of the material being tested. In the solution, an electrochemical potential (voltage) is generated between the various electrodes. The corrosion potential (E_{CORR}) is measured by the potentiostat as an energy difference between the working electrode and the reference electrode [77].

Electrochemical corrosion experiments measure and/or control the potential and current of the oxidation/reduction reactions [78]. Several types of experiments are possible by manipulating and measuring these two variables. In potentiostatic and potentiodynamic experiments, a potential is imposed on the working electrode and the resulting current is measured.
A potentiostatic experiment imposes a constant potential on the working electrode for a specific time period. The measured current is plotted versus time [78].

In potentiodynamic experiments, the applied potential is increased with time while the current is constantly monitored. The current (or current density) is plotted versus the potential. After the potential is scanned to a predetermined current density or potential, the potential scan may be reversed while the current continues to be measured. A potentiodynamic scan like this is referred to as reverse polarization [78].

On the other hand, in galvanodynamic or galvanostatic experiments, the current is imposed and the potential is measured as a response. Galvanodynamic methods plot the variation in potential verses the controlled current, while galvanostatic tests maintain a constant current and plot the change in potential verses time [78].

![Schematic representation of the Polarization Unit](image)

Figure 11: Schematic representation of the Polarization Unit

Therefore, the objective of this project is to solve two current problems; recycling of waste biomass and corrosion prevention. The solutions presented here
help solve an environmental issue and an industrial challenges. In the present work, lignin will be extracted from the lignocellulosic waste of date palm tree and converted to sodium lignosulfonate, which it will be tested as a corrosion inhibitor.
Chapter 3: Research Methodology

3.1 Materials

All chemicals used unless stated otherwise, were supplied by Sigma Aldrich and were of appropriate purity for application in this study. The biomass samples were collected from adult local size (10-15 years old) date palm trees in Al-Ain, UAE (24122 N, 554441 E).

3.2 Biomass pretreatment

Given the arid climate in the region, this lignocellulosic biomass was collected as naturally dried samples with less than 9 wt% moisture content, however, they were washed to remove any field contaminants and then dried under shade. Dried biomass was chopped, grinded and sieved (mesh 60) 250 micron particle size. American Standard test procedures were adopted for various physical-chemical analyses.

3.3 Biomass characterization

3.3.1 Biomass proximate and ultimate analysis

Proximate analysis of the biomass samples was determined according to ASTM D3173 (inherent moisture content); where triplicate samples were dried for 24 hours and 2 g in triplicates was weighed and kept in desiccator for 12 hours. The difference in weight before and after signified inherent moisture content, Volatile matter was determined according to ASTM D3175 where 1 g sample was weighed in an empty crucible and then placed in a furnace, set and operated at 950°C for exactly 7 minutes. Loss in weight after cooling was calculated and the deduction of inherent moisture off the weight loss, gave the volatile matter. Two g sample in triplicates was accurately weighed in a clean dry crucible and the samples were placed in a furnace at
575°C for 3 hours, cooled under desiccator conditions for 1 hour and the difference in weight before and after expressed as a percentage signified ash content according to ASTM D3174 (ash) and ASTM D3172-07a (Fixed carbon) methods was calculated from [100- (moisture content + Ash + volatile matter)] [79]. The ultimate analysis of the sample to determine C, H, O, S and N contents was performed by the automatic elemental analyzer (Flash EA1112, CE Instruments).

3.3.2 Biomass heating values determination

The heating values of the samples were determined according to DIN 51900 method using bomb calorimeter model IKA C 2000; where 0.5 g crushed biomass sample was pelletized and placed in a quartz crucible connected with a fuse wire (15 cm). The crucible was placed inside the bomb calorimeter and charged with oxygen to approximately 200 Psi for about 10 seconds. The heat of combustion was computed from the temperature observations before ($T_o$), during and after combustion ($T_{max}$), taking into care for thermochemical and heat transfer corrections. The calorimeter was calibrated by combusting a standard known mass (m) of benzoic acid with a known heat of combustion (26.453 MJ/kg). Calibration and analysis of samples were done in triplicates and the calibration factor (H) for the bomb calorimeter, was calculated from benzoic acid calibration as follows:

$$H = \frac{m \times 26.453}{T_{max} - T_o}$$

The bulk density of biomass was determined as mass per unit volume using 500 ml graduated measuring cylinder according to the reference method [80].
3.3.3 Biomass thermogravimetric analysis

Thermogravimetric analysis of palm biomass was carried out using TGA (Q500 series, TA Instrument). For each experiment, a sample weight of 6.0 mg (±1.0) was used for thermo-gravimetric analysis. The heating rate was controlled at 10, 15, 20 and 25 °C/min from 25 to 900°C, using nitrogen as a carrier gas at 20 ml/min. During the thermo-decomposition process, the initial weight was recorded continuously as a function of temperature and time. The derivative (DTG) curve showed the weight loss of sample per unit time against temperature.

3.4 Lignin extraction

The adopted method for lignin determination is commonly known as klason lignin extraction [81]. Prior to isolation, the biomass was treated to remove extractive (proteins, waxes and resins) in accordance to TAPPI methods-T 204 cm-97 [82]. Biomass sample (5±0.01 g) was transferred to a weighed thimble tube and extracted with 150 mL of ethanol–benzene solvent (1/2 v/v) for 5 hours. The residue extract was oven dried at 103±2°C for 1 hour, cooled in a desiccator and later weighed to determine the extractive free biomass to be used for klason lignin extraction.

The extractive free biomass (1±0.1g) was treated with 20 ml of 72% H₂SO₄ for 2 hours while stirring at 37°C. The solution was then diluted to 3% H₂SO₄ and then refluxed at 80°C for 4 hours. After filtration, the insoluble lignin was oven dried at 105 ±1°C for 1 hour and cooled in a desiccator to obtain constant weight. The difference in weight before and after oven drying represents the insoluble lignin. The soluble lignin fraction was determined at absorbance 280 nm in UV spectrometer and calculated using the following equation.
\[ \text{Insoluble Lignin} = \frac{A}{110} \times \frac{\text{dilution}}{\text{Original sample weight}} \times 100 \% \] (2).

Where; A is the absorbance at 280 nm, 110 is the extinction coefficient measured in Lg⁻¹cm⁻¹.

3.5 Lignin characterization

3.5.1 Scanning electron microscopy

A JEOL /EO Scanning Electron Microscope (SEM) operated at 2 kV, spot size of 40 was used to image the samples before and after klason lignin extraction. To improve conductivity and quality of image, samples were coated with Au/C using a vacuum sputter coater.

3.5.2 Attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR)

ATR-FTIR analysis was performed to investigate the possible structural alteration between the samples before and after klason lignin extraction. Palm biomass samples before and after klason extraction were pressed uniformly against a diamond surface by a fixed sample holder anvil. Spectra were observed using a Bruker optics vertex system with inbuilt diamond-germanium ATR single reflection crystal. Spectra were obtained over a range of 400 and 4000 cm⁻¹ with 34 average numbers of scans and spectral resolution of 4 cm⁻¹.
3.6 Lignosulfonate production

Sulfomethylation modification technique was used to obtain sodium lignosulfonate from lignin.

The main reaction of sulfomethylation of lignin will involve three steps namely; ionization of the phenol component of lignin at an alkaline pH, methylation by the addition of formaldehyde (HCHO) and sulfonation by the addition of sodium sulfite (Na$_2$SO$_3$).

The reaction was controlled to allow the pH during sulfonation at elevated temperature to drift from slightly acidic to slightly alkaline, during which time sequential sulfomethylation of the phenolic nucleus and sulfonation of the lignin side chain of the lignin molecule occurs (Figure 12). The following conventional experimental procedure [83] was adopted during the conversion of sodium lignosulfonate from lignin with our modification to the method used in the literature. 5 g of Klason lignin and 100 mL of deionized water were added into a 250 mL three-neck flask equipped with a stirrer, a thermometer, and a reflux condenser. The pH was adjusted to 10 by 0.5 M NaOH. Subsequently, 1.0 mL of formaldehyde was added to the solution. After that, 4 g of sodium sulfite was added to the solution then the reaction mixture was heated to 100°C and stirred for 3 h at 150 rpm. After the reaction, 25 M sulfuric acid was added to aid solidification (precipitation) of sodium lignosulfonate out of the solution. The product was centrifuged, washed and dried.
3.7 Screening experiment

There are possible competing side reactions such as sodium production, which mainly comes from sodium sulfite or the addition of acid used for precipitating the product. In order to eliminate the effect of the acid added and eliminate the side reactions, a screening runs have been done to finalize the best acid type and concentration to be used for solidifying the final product. Sodium lignosulfonate yield was determined, by using two main acids, sulfuric acid and hydrochloric acid, separately for precipitating sodium lignosulfonate. Acid concentration was varied keeping all the other reaction conditions constant.

3.8 Design of experiment (DOE)

DOE was used to select the optimum reaction condition in order to achieve optimum solubility, yield and purity. For sulfomethylation reaction, since there are different parameters that affect the final product, farther efforts are needed in order to select the best design parameters. The main parameters are time, temperature, sodium hydroxide concentration, reactant ratio and lignin concentration.

Previous studies have demonstrated that the more sulfonated groups of lignosulfonate and the greater the negative charged density, the greater the resulting
corrosion efficiency of sodium lignosulfonate [84, 85]. Another important parameter to consider is solubility, which is directly related to sulfonic group and the charge density [86]. In this study solubility is used as the main response; the higher solubility refers to presence of amount of sulfonated groups, resulting in higher corrosion efficiency.

Orthogonal experiment was selected as the main design, which revealed the complex cause-effect relationship between design parameters and performance. A key objective of this method was to uncover how the various design parameters and environmental factors affect the ultimate performance of the product or process being designed. Orthogonal arrays are special experimental designs that require only a small number of experimental trials to help discover main factor effects [87].

Taguchi’s orthogonal array was used to obtain the maximum solubility of SLS under optimized conditions [88]. In this study, L16 orthogonal design with five factors (each at four levels) was used to investigate the effect of parameters on the sulfomethylation reaction. The conditions listed in Table 2 were selected for conducting optimization analysis using a L16 orthogonal design. In each experiment, three samples were prepared to minimize the errors [89]. Taguchi’s orthogonal array was used to identify which process parameter significantly affected the sulfomethylation reaction and which combination levels of process parameters produced a maximum response [90].
Table 2: Taguchi’s orthogonal array

<table>
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<tr>
<th>Run No.</th>
<th>Time (hour)</th>
<th>Temperature (°C)</th>
<th>Sodium hydroxide Concentration (M)</th>
<th>Reactant/lignin ratio (g/g)</th>
<th>Lignin Concentration (g/L)</th>
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<td>1</td>
<td>80</td>
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To measure the solubility of lignosulfonate samples, 0.2 g of sodium Lignosulfonate (SLS), was suspended in 20 ml of deionized water by stirring at 100 rpm for 2 h at 30°C in a water bath shaker [91]. The solution was centrifuged at 1000 rpm for 10 min after which the supernatant was dried overnight in an oven at 60°C. Solubility was determined from equation (3) [92].

\[
SLS \text{ solubility (wt\%)} = \frac{\text{mass of dissolved SLS}}{\text{Initial mass of SLS}} \times 100\% \tag{3}
\]
3.9 Lignosulfonate characterization

3.9.1 Attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR)

The obtained sodium lignosulfonate was analysed with ATR-FTIR and compared with commercial sodium Lignosulfonate. SLS samples were pressed uniformly against a diamond surface by a fixed sample holder anvil. Spectra were observed using a Bruker optics vertex system with built-in diamond-germanium ATR single reflection crystal. Spectra were obtained over a range of 500 and 4000 cm\(^{-1}\) with 4 cm\(^{-1}\) of spectral resolution and 32 average numbers of scans per sample.

3.9.2 Thermogravimetric analysis

Thermogravimetric analysis of sodium lignosulfonate was conducted using thermogravimetric analyzer (Q500 series, TA Instrument). For each experiment, a sample weight of 6.0 mg (±1.0) was used. The heating rate was controlled at 20 and 25 °C/min from room temperature to 800°C. The analysis was carried out under nitrogen as a carrier gas at 35 ml/min. During the thermo-decomposition process, the initial weight was recorded continuously as a function of temperature and time. The derivative (DTG) curve showed the weight loss of sample per unit time against temperature.
3.10 Corrosion test using potentiostat

Potentiostat experiment was carried out using an AutoLab PGSTAT302N potentiostat following the Standard Reference Test Method for Making Potentiodynamic Anodic Polarization Measurements (ASTM G5 standard procedure) using the polarization unit (Figure 13)[93].

Figure 13: The Polarization Unit

A test solution of 1 L of 0.1 N HCl with distilled water (0.1 M) was prepared, the platinized auxiliary electrodes, salt-bridge probe, and other components were placed in the test cell and close to the center opening with a glass stopper. The salt bridge was then filled with the test solution. Then the temperature of the solution was brought to 25°C by immersing the test cell in a controlled-temperature water bath. Next, the oxygen levels in solution was reduced prior to immersion of the test
specimen, which was accomplished by bubbling an oxygen-free gas which is nitrogen at a rate of 150 cm$^3$/min for a minimum of 1/2 h.

The working electrode surface was prepared within 1 h of the experiment. The electrode surface was wet grinded with 240-grit SiC paper, wet polished with 600-grit SiC paper until previous coarse scratches were removed, rinsed, and dried. The surface area was determined by measuring all dimensions to the nearest 0.01 mm, subtracting the area under the gasket (usually 0.20 to 0.25 cm$^2$). After that the specimen was transferred to the test cell and the salt-bridge probe tip was adjusted so it was about 2 mm or 2 times the tip diameter, whichever was larger from the specimen electrode.

After that, the potentiostat was turned on and the corrosion rate was recorded as a function of time, until stable corrosion rate was reached for more than 30 minutes. At that time a 5 ppm sample of sodium lignosulfonate was added to the cell and the corrosion rate was recorded continuously as a function of time. Then the same procedure was repeated once the corrosion rate reached stable value, where 10 ppm sodium lignosulfonate was added to the cell, and again 30 ppm sodium lignosulfonate was added after reaching a constant corrosion rate. Corrosion rate was recorded as a function of time. Corrosion rate measurement was done every 5 min intervals using carbon steel (CS1018 material).

As explained in the Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements (ASTM G 59-97) [94], the polarization resistance can be related to the rate of general corrosion for metals at or near their corrosion potential ($E_{corr}$). Polarization resistance measurements are accurate and rapid way to measure the general corrosion rate. Real time corrosion monitoring is a common application. The technique can also be used as a way to rank alloys and inhibitors in order of their resistance to general corrosion [94].
In this method, a small potential scan, $\Delta E(t)$, defined with respect to the corrosion potential ($\Delta E = E - E_{corr}$), is applied to a metal sample. The resultant currents are recorded. The polarization resistance, $R_p$, of a corroding electrode is defined by equation (4) as the slope of a potential versus current density plot:

$$R_p = \left( \frac{\partial \Delta E}{\partial i} \right)_{i=0, dE/dt \rightarrow 0}$$  \hspace{1cm} (4)

The current density is given by $i$. The corrosion current density, $i_{corr}$, is related to the polarization resistance by the Stern-Geary coefficient, $B$.

$$i_{corr} = 10^6 \frac{B}{R_p}$$  \hspace{1cm} (5)

The dimension of $R_p$ is ohm-cm$^2$, $i_{corr}$ is m$\mu$A/cm$^2$, and $B$ is in V. The Stern-Geary coefficient is related to the anodic, $b_a$, and cathodic, $b_c$, Tafel slopes as per equation (6). The units of the Tafel slope is V.

$$B = \frac{b_a b_c}{2.303(b_a + b_c)}$$  \hspace{1cm} (6)

The corrosion rate, $CR$, in mm per year can be determined from equation (7) in which $EW$ is the equivalent weight of the corroding species (carbon steel specimen) in grams and $\rho$ is the density of the corroding material in g/cm$^3$.

$$CR = 3.27 * 10^{-3} \frac{i_{corr} * EW}{\rho}$$  \hspace{1cm} (7)
Chapter 4: Results

4.1 Biomass material characterizations and elemental analysis

The bulk density and High Heating Values (HHV) of the samples are presented in Table 3. The proximate analysis of original palm biomass parts, were conducted using corresponding standard ASTM methods and results were expressed in terms of ash content, volatile matter, fixed carbon and moisture content as shown in Table 4. For the different parts of the palm tree, the moisture content of the leaflet, rachis and the fibers was 4.3, 5.7 and 5.4 wt%, respectively (see Table 4). The ash content of the leaflet was 12.7 wt% and that of rachis and fibers was 6.1 wt% and 8.2 wt%, respectively. This ash content can be detrimental to the process as it has a tendency of reducing heat transfer during reactor operations such as heat transfer loss during pyrolysis, on the other hand once this ash is incinerated to obtain Oil Palm Ash (OPA), it can be used as a source of fertilizer due to its high potassium content [95]. Some research groups have utilized OPA to synthesize absorbents targeting toxic gas removal (i.e. sulfur dioxide, SO\textsubscript{x}). It is believed that the active compound (calcium, silica, potassium, alumina, and hydrated water) in the absorbent prepared from OPA is responsible for the high absorption capacity of SO\textsubscript{x} [95, 96].
Table 3: Bulk Density and Calorific Values of different parts of date palm biomass

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Bulk Density (kg/m³)</th>
<th>Calorific value, HHV (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This study</td>
<td>Literature</td>
</tr>
<tr>
<td>Leaflet</td>
<td>426±4</td>
<td>411a</td>
</tr>
<tr>
<td>Rachis</td>
<td>425±4</td>
<td>635a</td>
</tr>
<tr>
<td>Fibers</td>
<td>387±9</td>
<td>209a</td>
</tr>
<tr>
<td>Mixture</td>
<td>420±3</td>
<td>NA</td>
</tr>
</tbody>
</table>

a[97]; b[98]; c[99]

Table 4: Proximate analysis of different parts of date palm biomass

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Moisture (wt%)</th>
<th>Volatile matter (wt%)</th>
<th>Ash content (wt%)</th>
<th>Fixed carbon (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture</td>
<td>3.5±0.1</td>
<td>80.8±1.6</td>
<td>8.7±0.4</td>
<td>9.6±0.4</td>
</tr>
<tr>
<td>Leaflet</td>
<td>4.3±0.3</td>
<td>75.8±1.2</td>
<td>12.7±1.2</td>
<td>7.2±0.2</td>
</tr>
<tr>
<td>Rachis</td>
<td>5.7±0.2</td>
<td>84.6±1.8</td>
<td>6.1±1.0</td>
<td>3.6±1.0</td>
</tr>
<tr>
<td>Fibers</td>
<td>5.4±0.1</td>
<td>77.4±0.6</td>
<td>8.2±0.3</td>
<td>9.0±0.8</td>
</tr>
</tbody>
</table>

Elemental analysis on original biomass for palm biomass was carried out and the concentrations of phosphorous (P), calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K) are shown in Table 5. The results showed that Calcium, magnesium and sodium were highest in fibers. On the other hand, leaflet and rachis were most rich in potassium and phosphorous, respectively.
Table 5: Chemical composition (wt.%) of the different lignocellulosic parts of date palm

<table>
<thead>
<tr>
<th>Component</th>
<th>Leaflet</th>
<th>Rachis</th>
<th>Fibers</th>
<th>Mixture*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hemicellulose (wt %)</td>
<td>11.0±1.6</td>
<td>19.0±1.0</td>
<td>17.0±0.3</td>
<td>14.8±1.2</td>
</tr>
<tr>
<td>Cellulose (wt %)</td>
<td>21.0±2.6</td>
<td>32.0±1.0</td>
<td>33.0±1.2</td>
<td>30.2±1.2</td>
</tr>
<tr>
<td>Insoluble Lignin (wt %)</td>
<td>19.0±1.0</td>
<td>10.0±2.0</td>
<td>20.0±1.2</td>
<td>25.4±1.0</td>
</tr>
<tr>
<td>Soluble lignin (wt %)</td>
<td>1.0±0.0</td>
<td>1.0±0.0</td>
<td>1.0±0.0</td>
<td>1.0±0.0</td>
</tr>
<tr>
<td>Ethanol-Benzene Extractives (wt %)</td>
<td>29.0±3.8</td>
<td>14.8±1.0</td>
<td>9.0±3.0</td>
<td>16.0±2.0</td>
</tr>
<tr>
<td>Element Analysis (ppm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>33.0±0.6</td>
<td>28.9±0.6</td>
<td>30.8</td>
<td>26.3±0.4</td>
</tr>
<tr>
<td>P</td>
<td>10.9±0.2</td>
<td>16.7±1.8</td>
<td>6.7±1.6</td>
<td>12.0±0.4</td>
</tr>
<tr>
<td>Ca</td>
<td>196.5±8.0</td>
<td>158.2±20</td>
<td>305.9±28</td>
<td>166.6±12</td>
</tr>
<tr>
<td>Mg</td>
<td>24.0±2.2</td>
<td>21.4±3.0</td>
<td>46.6±8.0</td>
<td>21.2±2.0</td>
</tr>
<tr>
<td>Na</td>
<td>8.7±2.3</td>
<td>11.5±1.4</td>
<td>26.5±3.6</td>
<td>9.3±1.6</td>
</tr>
</tbody>
</table>

*Mixture refers to composition of; leaflet, rachis and fibers in 0.5:2:0.06 ratios, respectively according to their individual contribution in biomass bulk per unit length.

When the three palm parts were mixed in a ratio (leaflet, rachis and fibers) to form a mixture sample, the elements composition in their decreasing order followed the trend; Ca>K>Mg>P>Na. The low elemental composition in the sample confirm the claim from local farmers supplying the raw biomass that “no artificial nutrient additives were added to the soil during palm tree cultivation period”.

As shown in Table 5, date palm tree biomass mainly consists of cellulose, hemicellulose, and lignin. There is more lignin (21 wt%) and cellulose (33 wt%) content in fibers than in leaflet (20 wt%, 21 wt%, respectively) and rachis (11 wt%, 32 wt%, respectively). Rachis has the highest hemicellulose content (19.0 wt%).

The mixture sample, which consist of the three palm parts had more cellulose (30.2 ±1.2 wt%), lignin (26.4 ±1.0 wt%) and least hemicellulose content (14.8 ±1.2
wt%). The results were similar to that reported in the literature (cellulose 32.49-50.33 wt%, lignin 21.70-35.89 wt%, hemicellulose 22.97-23.94 wt%) [100-102]. Removal of extractive (resins, carbohydrates and waxes) prior to klason lignin extraction is important [103, 104].

The ultimate analysis of the biomass showed that carbon (C) content of palm leaflet (44.1±0.2 %) was slightly higher than that of rachis and fibers (43.6 % and 43.2 ±0.1% respectively) (Table 6). Results of this study were in the same range as other reported lignocellulosic biomass [105], making UAE phoenix dicteylifera palm specie equally competitive for fuel and as a chemical source precursor.

Table 6: Ultimate analysis of different parts of date palm biomass (% on dry basis)

<table>
<thead>
<tr>
<th>Biomass</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O</th>
<th>O/C</th>
<th>H/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaflet</td>
<td>44.1±0.2</td>
<td>5.9±0.0</td>
<td>1.5±0.2</td>
<td>0.0</td>
<td>48.5±0.4</td>
<td>1.1±0.2</td>
<td>0.1±0.0</td>
</tr>
<tr>
<td>Rachis</td>
<td>43.6±0.0</td>
<td>6.1±0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>50.3±0.2</td>
<td>1.2±0.2</td>
<td>0.1±0.01</td>
</tr>
<tr>
<td>Fibers</td>
<td>43.2±0.1</td>
<td>5.7±0.1</td>
<td>0.8±0.0</td>
<td>0.0</td>
<td>50.3±0.2</td>
<td>1.2±0.2</td>
<td>0.1±0.02</td>
</tr>
</tbody>
</table>

4.2 Biomass thermogravimetric analysis

Results of the thermogravimetric analysis were expressed as a function of conversion, X and was defined as:

\[ X = \frac{(w_o - w)}{(w_o - w_{\infty})} \]  

(8)

Where; \( w_o \) is the initial weight of the sample; \( w \) is the weight of the pyrolyzed sample; \( w_{\infty} \) is the final residual weight.

The degree of conversion as a function of temperature for palm leaflet, rachis and fibers at selected heating rates of 10 °C/min, 15 °C/min and 20 °C/min is shown in
Figures 14-16 respectively, which was calculated from the TG data. The thermal decomposition for all investigated palm biomass parts, followed a similar trend showing an increase in conversion with increasing temperature. At lower temperatures for all the three parts of palm biomass, the small change in conversion was attributed to the vaporization of the inherent moisture attached on the surface of the sample. A similar phenomenon was reported for other biomass including soft and hard wood, as well as microalgae [106-109]. After moisture vaporization, the rate of decomposition increased with increasing heat rate, which is probably because there is more thermal energy to facilitate better heat transfer between the sample and the surroundings [110]. This increased thermal energy resulted in increased conversion. The maximum differential rate of conversion for palm leaflets occurred at 716, 718 and 725 °C at heating rates 10, 15 and 20 °C/min, respectively. On the other hand, the maximum differential rate of conversion for palm rachis occurred at 669, 683 and 698 °C at heating rates 10, 15 and 20 °C/min, respectively, and the maximum differential rate of conversion for palm fibers occurred at 715, 720 and 729 °C at heating rates of 10, 15 and 20 °C/min, respectively.
Figure 14: Conversion of palm leaflet as a function of temperature at different heating rates

Figure 15: Conversion of palm rachis as a function of temperature at different heating
4.3 Biomass differential thermogravimetric analysis

The differential rate of conversion, dX/dt, was obtained from differential thermogravimetric analysis (DTG) at heating rates of 10, 15 and 20 °C/min. The DTG curves of palm rachis for various heating rates of 10, 15 and 20 °C/min is shown in Figure 17. A large fraction of rachis biomass decomposed between 290°C and 700°C, and this was attributed to decomposition of hemicellulose, cellulose and lignin fractions that make up the biggest percentage of lignocellulosic biomass. The thermal decomposition peak between 290°C and 390°C was assigned to the decomposition of hemicellulose, and between 390°C and 520°C and the last peak between 520°C and 700°C, was assigned to the decomposition of cellulose and lignin, respectively. The DTG for palm leaflet and fibers had a similar decomposition temperature profile between 290°C and 700°C as that of rachis (see Figures 18 and 19). However, the decomposition peaks of hemicellulose and cellulose seemed to overlap giving two major decomposition regimes as opposed to rachis where all the three components were revealed for all the three investigated heating rates. The result of hemicellulose
and cellulose decomposition temperature profile for this work was in agreement with that reported in the literature by other researchers [111, 112], based on which the peaks in the DTG profiles of the present work were assigned. In another study, the thermal decomposition of wood revealed two decomposition peak regimes at lower temperatures, which were assigned to hemicellulose and cellulose [113]. The noticeable decomposition peak at lower temperatures below 290°C for all the three parts of palm biomass investigated at various heating rates was assigned to vaporization of the inherent adsorbed moisture on the surface of biomass. Furthermore increasing the heating rate from 10 °C/min to 20 °C/min, increased the rate of biomass decomposition but this never altered the decomposition trend, this is because increasing heating rate only provided more thermal energy in the system and the surrounding thus aiding more sample decomposition. The assignment of the three peaks to hemicellulose, cellulose and lignin is in accord with the fact that the chemical characteristics of hemicellulose are thermally labile and decompose first at relatively low temperature; cellulose is more thermally stable due to its crystalline structure and decomposes at higher temperatures compared to hemicellulose and due to its complex and relatively heterogeneous structure, lignin decomposes over a wide range of temperature, and in some cases it decomposes without showing a visible peak in the DTG curve [114].
Figure 17: Differential thermogravimetric curves of palm rachis at 10, 15 and 20 °C/min heating rates

Figure 18: Differential thermogravimetric curves of palm leaflet at 10, 15 and 20 °C/min heating rates
The thermal gravimetric analysis and differential thermogravimetric (DTG) curves are often used to assess the stability of polymeric materials. For processes like pyrolysis, the shapes of TG curves are determined by kinetic parameters such as activation energy, Arrhenius frequency factor and order of reaction. From the gravimetric data; the pyrolysis kinetic parameters were obtained using differential technique [115], and the thermal decomposition rate of conversion, $\frac{dX}{dt}$ was expressed as;

$$\frac{dX}{dt} = kf(X)$$  \hspace{1cm} (9)

Where $f(X)$ is the function of conversion and $k$ is the reaction rate constant and can be expressed by the equations below;

$$f(X) = (1 - X)^n$$  \hspace{1cm} (10)

Where $n$ is the reaction order.
The reaction rate constant was expressed by Arrhenius equation as:

\[ k = A \exp \left( -\frac{E_a}{RT} \right) \] (11)

Substituting equations (10) and (11) in equation (9), and then introducing natural logarithms on both sides, results the following:

\[ \ln(dX/dt) = \ln A + n \ln(1 - X) - \left( \frac{E_a}{RT} \right) \] (12)

\( E_a \) is the apparent activation energy and can be obtained from a linear relationship plot of equation (12) considering \( \ln(dX/dt) \) against \( 1/T \). Hence, for the different conversions different parallel straight lines with negative slope \( E_a/R \) were obtained from which apparent energies of activation were calculated. Taking an example of palm rachis, for conversion of 30\%, the corresponding temperature at different heating rate was 502\(^\circ\)C, 516\(^\circ\)C and 520\(^\circ\)C, for heating rates of 10 \(^\circ\)C/min, 15 \(^\circ\)C/min and 20 \(^\circ\)C/min, respectively. The values of \( \ln (dX/dt) \) were -7.8750, -7.4984 and -7.1995 with corresponding \( 1/T \) values of 1.2902x10\(^{-3}\), 1.2665x10\(^{-3}\) and 1.2613x10\(^{-3}\), respectively were obtained for the mentioned temperatures. These data and those of leaflet and fibers are shown in Figure 20, Figures 21-22 for different iso-conversion. The intercept \( \ln[A(1-X)^n] \) was calculated from Figures 20-22 for all conversions. Assuming the lower fixed apparent orders of 0 or 1, exponential constant can be obtained by curve fitting of equation (12).
Figure 20: Relationship between ln(dX/dt) and 1/T for palm leaflet for different conversions

Figure 21: Relationship between ln(dX/dt) and 1/T for palm rachis for different conversions
The apparent activation energy as a function of iso-conversion is shown in Figure 23 for palm leaflet, palm rachis and palm fiber biomass. From the same figure, activation energy generally has two regimes; first one for conversion from 10% to 60%, which depicts the energy barrier needed to decompose hemicellulose and cellulose and the second regime from conversion of 60% to 80%, which represents the energy barrier needed to overcome the decomposition of lignin. This apparent activation energy trend in principle is in agreement with the obtained results from DTG analysis. The average activation energy was; 252 kJ/mol, 200 kJ/mol and 164 kJ/mol, for leaflet, rachis and fibers, respectively. In comparison to other works, similar activation energy range was reported; 182.3 kJ/mol for cellulose derivatives [111]. And the variation in activation energies was reported for a scheme consisting of independent first order parallel reactions of a biopolymer component of hemicellulose, cellulose and lignin [116].
Figure 23: Calculated activation energies at different iso-conversions for thermal decomposition of palm leaflet, rachis and fibers

The pre-exponential factor obtained from equation (11), had a direct relationship with apparent activation energy. When the activation energy increased, the pre-exponential factor increased and the reverse was true, this result was in agreement with Friedman’s approach [115]. During the first decomposition regime, the pre-exponential factors were highest for leaflet (1.60x10^{17} s^{-1}), followed by rachis with 1.33x10^{10} s^{-1} and lastly fibers with 3.30x10^4 s^{-1}, at which point the weight loss corresponded to the thermal decomposition of hemicellulose and cellulose in the palm biomass parts investigated. The pre-exponential factors for leaflet, rachis and fibers, were higher when conversion was 80%, perhaps because of devolatilization of residual char.

The range of pre-exponential factors assuming the overall reaction, 0th and 1st orders for conversion ranging from 10% to 80% were between; 1.57x10^0 s^{-1} to 1.38x10^{25} s^{-1} (0th order) and 1.74x10^0 s^{-1} to 6.91x10^{25} s^{-1} (1st order) for leaflet, 5.49x10^0 s^{-1} to 6.61x10^{26} s^{-1} (0th order) and 6.10x10^0 s^{-1} to 3.30x10^{27} s^{-1} (1st order) for rachis and
2.39x10^2 \text{ s}^{-1} \text{ to } 4.64x10^{15} \text{ s}^{-1} (0^{th} \text{ order}) \text{ and } 2.66x10^2 \text{ s}^{-1} \text{ to } 2.32x10^{16} \text{ s}^{-1} (1^{st} \text{ order}) \text{ for fibers.}

4.5 Characterizations after klason method

Since the klason method involved sulphuric acid that alters the material structural composition, ultimate analysis was performed before and after klason lignin extracted samples (Table 7).

After acid hydrolysis, the carbon and hydrogen content increased and oxygen content decreased; presumably sulphuric acid cleavage of cellulosic glycosidic bond releasing some oxygen from the biomass structure. The structural rearrangement with lignocellulosic material could have resulted in the increase of carbon and hydrogen content. The decrease in nitrogen content was as a result of benzene-ethanol extraction that removes resins and other protein-like materials. Palm biomass was free of any sulphur content; sulphur poison catalysts making it difficult during upgrading processes, thus its absence makes future catalytic upgrading easy.
Table 7: Ultimate analysis after klason (% on dry basis)

<table>
<thead>
<tr>
<th>Biomass</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O</th>
<th>O/C</th>
<th>H/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture- original</td>
<td>50.7±1.0</td>
<td>5.5±0.1</td>
<td>1.7±0.2</td>
<td>0.0</td>
<td>48.5±0.2</td>
<td>0.9±0.1</td>
<td>0.1±0.2</td>
</tr>
<tr>
<td>Mixture- klason</td>
<td>53.7±0.4</td>
<td>5.7±0.2</td>
<td>1.6±0.1</td>
<td>0.0</td>
<td>43.7±0.3</td>
<td>0.8±0.1</td>
<td>0.1±0.0</td>
</tr>
<tr>
<td>Leaflet- original</td>
<td>44.1±0.2</td>
<td>5.9±0.0</td>
<td>1.9±0.2</td>
<td>0.0</td>
<td>48.5±0.4</td>
<td>1.1±0.2</td>
<td>0.1±0.2</td>
</tr>
<tr>
<td>Leaflet- klason</td>
<td>51.3±0.3</td>
<td>5.1±0.0</td>
<td>1.5±0.2</td>
<td>0.0</td>
<td>41.7±0.8</td>
<td>0.8±0.1</td>
<td>0.1±0.0</td>
</tr>
<tr>
<td>Rachis- original</td>
<td>43.6±0.0</td>
<td>6.1±0.1</td>
<td>1.2±0.0</td>
<td>0.0</td>
<td>50.3±0.2</td>
<td>1.2±0.2</td>
<td>0.1±0.1</td>
</tr>
<tr>
<td>Rachis- klason</td>
<td>49.7±0.2</td>
<td>5.5±0.1</td>
<td>0.2±0.0</td>
<td>0.0</td>
<td>43.5±0.3</td>
<td>0.9±0.1</td>
<td>0.1±0.0</td>
</tr>
<tr>
<td>Fibers- original</td>
<td>43.2±0.1</td>
<td>5.7±0.1</td>
<td>0.8±0.0</td>
<td>0.0</td>
<td>50.3±0.2</td>
<td>1.2±0.2</td>
<td>0.1±0.2</td>
</tr>
<tr>
<td>Fibers- klason</td>
<td>46.0±1.0</td>
<td>4.1±0.3</td>
<td>0±0.0</td>
<td>0.0</td>
<td>49.9±1.0</td>
<td>1.1±0.1</td>
<td>0.1±0.0</td>
</tr>
</tbody>
</table>
4.5.1 Thermogravimetric analysis after klason

The results of gravimetric analysis before klason lignin extraction for the mixture biomass at different heating rates are shown in Figure 24.

![TGA and DTG curves for mixture of palm biomass](https://via.placeholder.com/150)

Figure 24: TGA (thermogravimetric analysis) and DTG (differential gravimetric) curves for mixture of palm biomass at heating rates of 10, 15, 20 and 25 °C/min

Increase in heating rate from 10 to 25 °C/min led to shift in temperature-conversion curves towards the right hand side. This was due to an increase in thermal energy and increased heat transfer between the sample and the surroundings thus causing slight increase in conversion. When considered for DTG, the mixture showed four decomposition regimes for all the four heating rates considered; the first regime is below 200°C and is presumably the inherent moisture adsorbed on the samples and has less impact on physicochemical nature of the sample as it can easily be removed by oven drying prior to reactor operations; between 280-380°C is the second regime and was assigned to decomposition of hemicellulose. In comparison to lignin and cellulose, hemicellulose is a random amorphous and thermally labile structure and
hence easy to decompose at lower temperatures. The results of hemicellulose decomposition were similar to those reported in the literature [117], hence providing more proof about hemicellulose decomposition temperature profile; The third regime between 380-550°C, was assigned to decomposition of cellulose. In contrast, cellulose is a long polymer of glucose units connecting one another by glycosidic bond and this increases its thermal stability thus higher decomposition temperature compared to hemicellulose [118]. The last regime between 550-650°C was assigned to lignin that is a crystalline polymer made up of propane alcohol units making it more stable and thus requires more thermal energy for decomposition. After klason lignin extraction, the decomposition trend changed as shown in Figure 25.

![Figure 25: TGA (thermogravimetric analysis) and DTG (differential gravimetric) curves of klason lignin method for mixture of palm biomass at heating rates of 10, 15, 20 and 25 °C/min](image)

The conversion graphs maintained a similar trend with increasing heating rate but more skewed to the right compared to conversion graphs in Figure 22 before klason extraction. For klason lignin extraction, DTG analysis showed two decomposition regimes in contrast to the four regimes seen before extraction for the same mixture.
sample. The first regime below 200°C was assigned to dehydration of inherent water adsorbed in the samples and the second peak had a wide decomposition temperature profile between 400-750°C and was assigned to lignin decomposition. Lignin is believed to have a wide decomposition temperature profile depending on different kinds of biomass with some literature reporting between 160-900°C [119].

At this stage of research it can only be postulated that; the wide decomposition trend from 400°C for this palm biomass is presumably due to residual cellulose that remains after acid hydrolysis or due to lignin wide range temperature decomposition profile. The biomass was then analyzed for morphological differences before and after klason lignin extraction for different palm biomass parts.

**4.5.2 Scanning electron microscopy**

Figure 26 (a)-(c) and (d)-(g) shows palm leaflet SEM images before and after klason lignin extraction, respectively. Leaflet before extraction has irregular morphologies of different shapes at investigated magnifications. However when focused in detail at elevated magnification X500 and X1500 in (b) and (c), respectively; concentrating on structure with yellow arrow, it can be seen that some particles are tubular-like, stacked together forming one definite cylindrical structure (Figure 26a-b) and when viewed much closer at X1500 these tubular-like stacks are hollow, separated from each other by walls and bound with fine strands on the outer surface.

By contrast after klason extraction, leaflet cylindrical morphologies were completely distorted to small regular spherical structures of measurable external diameter (140 µm) and the broken samples were viewed in details at X1500; spheres
here had different internal diameters, ranging from 4.50 µm and 8.67 µm for smallest and biggest particles, respectively. In analogy to lignocellulosic biomass, the cylindrical structure in Figures (a)-(c) was presumably a stack of lignin walls and hemicellulose strands binding the cellulose together to form lignocellulose structure with all the three components and this presumption was supported by DTG results in Figure 24 that showed existence of three components making up lignocellulosic material. However after klason lignin extraction, the sulphuric acid dissolved the hemicellulose and cleavage the cellulose glycosidic bonds, thus weakening strong cellulose bonds while exposing lignin. A similar argument was supported by DTG results in Figure 25 whereby after acid hydrolysis the hemicellulose and cellulose peaks disappeared.

Figure 26: Leaflet SEM images: (a) to (c) for original sample and (d) to (g) after klason lignin extraction
Figure 27 (a)-(c) and (d)-(g) show palm rachis SEM images before and after klason lignin extraction, respectively. The lignocellulose morphology in rachis showed unique irregular fibrils (hemicellulose and lignin) and helical chiral nematic ordering (cellulose). These helical structures were similar to what was reported in the literature [120], and can also be seen on right hand side of Figure 27(b), (c). However after klason lignin extraction, the helical chiral nematic ordering disappeared, a clear indication; that either cellulose was completely hydrolyzed by H$_2$SO$_4$ or it was broken down from hard crystalline structure to soft amorphous fibril cellulose.

Figure 27: Rachis SEM images: (a) to (c) for original sample and (d) to (g) after klason lignin extraction
The palm fibers SEM images before and after klason lignin extraction, respectively are shown in Figure 28 (a)-(d) and (e)-(h). When viewed under different magnifications, fibers showed cylindrical closed tubes having regular shapes with measurable external diameters and when the broken parts were viewed at X500 concentrating on part shown by the yellow arrow, the inner surface was closely packed with fibers of irregular patterns. On the other hand, after klason lignin extraction, the cylindrical shapes are deformed and spiral; hemicellulose binding cellulose and lignin disappeared, presumably dissolved by the sulphuric acid. The hollow-structures for fibers and leaflet klason lignin extraction seem to suggest that the morphologies of fibers and leaflets are close to each other than that of rachis.

Figure 28: Fibers SEM images: (a) to (d) for original sample and (g) to (h) after klason lignin extraction
When a mixture was taken from the three palm parts in a given ratio, the mixture SEM images were analyzed as shown in Figure 29 (a)-(c) and (d)-(g) for before and after klason lignin extraction, respectively. The morphologies of palm mixture before lignin extraction, showed structures of different sizes and shapes but similar to what was seen in Figures 26-28 for leaflet, rachis and fibers, respectively. This was a confirmation of existence of the three palm biomass parts with their lignocellulose morphologies. In contrast after klason lignin extraction, at all considered magnifications, palm mixture sample showed independent cross-linked semi-fused structures. SEM results indeed showed morphological differences before and after klason lignin extraction. However further characterization was done to understand the chemical and structural changes using FTIR measurements.

Figure 29: Mixture SEM images: (a) to (c) for original sample and (d) to (g) after klason lignin extraction
4.5.3 Fourier transform infrared spectroscopy for lignin

The results of FTIR absorbance bands were used to monitor the chemical bond rearrangement and structural changes of palm lignocellulose biomass before and after klason lignin extraction. The spectroscopy results in Figure 30 showed similar band trend for all samples before klason lignin extraction.

![FTIR spectra](image)

Figure 30: FTIR measurements for original leaflet, rachis, fibers and mixture palm biomass parts

On the other hand, after klason treatment as shown in Figure 31, all samples had a similar absorption trend, however; there was a noticeable shift in peaks position for date palm samples (leaflet, rachis, fibers and mixture) after klason lignin extraction in the region around 1000 and 1250 cm\(^{-1}\). This is clear evidence that klason lignin extraction altered the chemical and structural make up of palm biomass. The small band around 900 cm\(^{-1}\) representing glycosidic bond [β-(1→4)] in amorphous cellulose...
was observed in original sample, however was hardly seen in klason lignin extracted sample and similar phenomena was reported in the literature [44, 121].

This shows a difference in crystallinity before and after klason lignin extracted samples and the effectiveness of klason method towards cellulose and hemicellulose removal. Moreover, strong peaks were observed around 1125 cm\(^{-1}\) for original sample and this was even stronger after klason lignin treatment, observed around 1070 cm\(^{-1}\).

![FTIR measurements for leaflet, rachis, fibers and mixture palm biomass parts after klason lignin extraction](image)

Figure 31: FTIR measurements for leaflet, rachis, fibers and mixture palm biomass parts after klason lignin extraction

This change suggests an increase in lignin proportion in klason lignin sample due to glycosidic bond cleavage in cellulose thus removing amorphous cellulose and dissolution of hemicellulose by sulphuric acid used during the klason lignin extraction. For original sample, the wide band around 1200 and 1250 cm\(^{-1}\) converged into small peak around 1250 after klason lignin extraction. This stronger exhibited peak after klason treatment was responsible for lignin [44], and this was after the removal of hemicellulose and cellulose that absorb within this region due to C-O bond stretching.
Similar results emphasizing the existence of hemicellulose and cellulose in the region around 1035-1200 cm$^{-1}$ and disappearance of these components after various treatment methods, was reported in the literature [122].

The region of wave length between 1300 to 1450 cm$^{-1}$ exhibits high molecular coupling of complex compounds possibly of lignin and carbohydrate in nature [123]. Ethanol-benzene extraction was carried out to extract our samples free of carbohydrates and other resins, therefore the vibrations in the preceding region were assigned to lignin. The band around 1458 cm$^{-1}$ is where CH$_2$ and CH$_3$-lignin structures deform and presumably this in turn reduces lignin recalcitrant to chemical treatment processes. Literature has reported that around 1515 to 1605 cm$^{-1}$ is due to stretching of C=C and C=O present in the lignin aromatic ring [124, 125]. The band for the range between 1595 to 2937 cm$^{-1}$ is because of C=O, C-H, CH$_2$ stretching of unconjugated hemicellulose, symmetrical and unsymmetrical CH$_2$ bond stretching in cellulose and stretching of aromatic ring vibration in lignin [23, 123-125]. It was therefore presumed that the decrease in peak intensity in the preceding mentioned region was due to bond cleavage that reduced cellulose content and the sulphuric acid hydrolysis that dissolved the hemicellulose during klason extraction process, leaving mainly lignin proportions. Moreover, the band trend never changed for samples before and after klason lignin treatment because lignin bond vibration and stretching is greater than that of hemicellulose and cellulose in this region. The chemical changes in band position between 3250 to 3885 cm$^{-1}$ is due to O-H stretching in methyl group of lignin [23, 100, 126]. Lignin is believed to have high absorption strength [127].

In general there was a clear distinction in chemical and structural orientation in the original samples after application of klason lignin method.
4.6 Screening experiments for precipitation of sodium Lignosulfonate

Screening experiments were conducted in order to select the best acid to be used to precipitate sodium lignosulfonate. Table 8 shows the screening runs and the yield of sodium Lignosulfonate. All runs were performed under the following reaction condition; 100°C, 3 hours, 0.9 CH₄NaO₄S/lignin ratio (g/g), 20 lignin concentration (g/L) and 0.5 NaOH M concentration. Percentage yield as a function of acid concentration is shown in Figure 32.

Table 8: Screening experiments results

<table>
<thead>
<tr>
<th>Acid used for precipitate</th>
<th>Acid conc.(M)</th>
<th>SLS mass (g)</th>
<th>SLS Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
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<td>0.000</td>
</tr>
<tr>
<td>HCl</td>
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<td>3.6314</td>
<td>35.990</td>
</tr>
<tr>
<td>HCl</td>
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<td>3.8336</td>
<td>37.994</td>
</tr>
<tr>
<td>HCl</td>
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</tr>
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<td>28.549</td>
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<td>H₂SO₄</td>
<td>40</td>
<td>2.4352</td>
<td>30.101</td>
</tr>
</tbody>
</table>
Result show that sulfuric acid gives higher lignosulfonate yield when compare with hydrochloric acid (the maximum yield was 57.9% using sulfuric acid while the maximum yield using hydrochloric acid was 37.9%). Also, as Figure 33 shows,
increasing the concentration of hydrochloric acid resulted in an increase in the byproduct formation and lower yield of sodium lignosulfonate; more white product obtained at 40 M HCl compared to 10 M HCl. Same trend was observed for different concentrations of sulfuric acid; darker product was obtained for 10 M H₂SO₄ as compared to 40 M H₂SO₄.

As Figure 33 shows hydrochloric acid increased the possibility of the side reaction resulting in more sodium thiosulfate (white precipitate) formation as compared to sulfuric acid. Therefore, sulfuric acid was a better option and in the subsequent experiments only sulfuric acid was used to precipitate SLS product.

4.7 Sodium Lignosulfonate characterization

4.7.1 Fourier transform infrared spectroscopy for SLS

FTIR spectra of lignin, commercial SLS and produced SLS are shown in Figure 34. Results show similar stretching and vibration bands for the two SLS samples. The strong and broad band around 3420 cm⁻¹ is due to the OH stretching in phenolic and aliphatic structures [85, 128, 129].
SLS showed bands at 2950 and 2850 cm\(^{-1}\), predominantly attributed to C–H vibration in methyl and methylene groups of side chains and aromatic methoxyl groups in SLS [130, 131]. The peaks at 2365 and 2335 cm\(^{-1}\) are associated with C–H stretching of methyl or methylene groups [86].

SLS had a shoulder around 1635 cm\(^{-1}\), originated from C=O vibration in aryl ketones [129]. The absorption peaks at 1585 and 1510 cm\(^{-1}\) is attributed to the aromatic functionality in lignin and benzene ring skeletal vibration [132]. The absorption peaks at 1463 and 1420 cm\(^{-1}\) confirms the presence of COO-group [133], which corresponds to C–H bending and C–H stretching of methylene groups [134]. The peak at 1200 cm\(^{-1}\) corresponds to C–O and C=O stretching vibration of the aromatic ring [135, 136].

The absorption peak at 1036 cm\(^{-1}\) in SLS samples corresponds to S=O stretching vibration, which attributed to sulfonate groups, that was not present in
unmodified lignin [137]. This confirmed the grafting of sulfonic groups to the lignin in the sulfomethylation reaction [134, 136].

In previous studies, the sulfonate group attached to lignin was confirmed by the major increase in the absorption peak at 1040 cm\(^{-1}\) in the FTIR spectrum of sulfomethylated sodium Lignosulfonate [134]. The spectral region below 1000 cm\(^{-1}\) is very difficult to analyze, because most bands are complex with various vibration contributions.

4.7.2 Thermogravimetric analysis of SLS

The degree of conversion for the decomposition for the prepared SLS as a function of temperature at selected heating rates of 20 °C/min and 25 °C/min is shown in Figure 35, which was calculated from the TG data. At lower temperatures, the small change in conversion was attributed to the vaporization of the inherent moisture attached on the surface of the sample.

After moisture vaporization, the rate of decomposition increased with increasing heat rate, for the reason that there is more thermal energy to enable better heat transfer between the sample and the surroundings [110]. This increased thermal energy resulted in increased conversion [107, 109].

SLS decomposed continuously above 250°C and reached almost 95% conversion at 800°C. On the other hand degradation of lignin (Figure 25) began at 250°C and reached almost 50% conversion at 800°C, which indicated faster decomposition of SLS in comparison to lignin. A similar phenomenon was reported in other studies for SLS samples [86, 127]. This increase in the thermal stability of SLS is caused by the inclusion of sulfomethylated groups in the modified lignin throughout sulfomethylation reaction [127], which add an advantage for its end-use applications as a dispersant and flocculants and other application [75]. TGA analysis clearly
confirmed that the introduction of sulfonate and methyl groups into lignin increased its thermal stability when compared to unmodified lignin. The maximum differential rate of conversion for SLS occurred at 800 and 810°C at heating rates 20 °C/min and 25 °C/min, respectively.

Figure 35: Conversion of SLS sample as a function of temperature at 20 °C/min and 25 °C/min heating rates

The differential rate of conversion, \( \frac{dX}{dt} \), was obtained from differential thermogravimetric analysis (DTG) at heating rates of 20 and 25 °C/min. DTG curves of SLS for heating rates of 20 and 25 °C/min are shown in Figure 36. DTG analysis showed three decomposition regimes for SLS between 50°C and 800°C. SLS degradation process takes place in a large temperature range which is due to the decomposition of lignin fractions that make up the biggest percentage of SLS.

The first regime below 200°C was assigned to dehydration of inherent water adsorbed in the samples and the next two regimes had a wide decomposition temperature profile between 400-750°C and was attributed to lignin decomposition.
Result of the SLS thermal degradation patterns was in agreement with that reported by other researchers in the literature [139-141].

Figure 36: Differential Thermogravimetric curves of SLS sample at 20 °C/min and 25 °C/min heating rates

4.8 Taguchi orthogonal array

In this study aqueous solubility is used as the main response; which means that a higher solubility of the produced SLS refers to the amount of sulfonic group present, which in turn corresponds to a higher corrosion efficiency. Previous studies have verified that the aqueous solubility of sodium lignosulfonate is directly related to the number of sulfonic groups [86]. Moreover, it has been proven that, the higher the number of sulfonated groups of lignosulfonate, the better the resulting corrosion efficiency of sodium lignosulfonate produced [84, 85]. Hence, it can be stated that solubility is an important parameter to consider with respect to the presence of sulfonic group [86].
Effect of different parameters (reaction time, Temperature, lignin concentration, reactant/lignin ratio, and NaOH concentration) on aqueous solubility of SLS product was studied using Taguchi orthogonal array. Sixteen runs were conducted and results of three replicates per run are shown in Table 9.
Table 9: Taguchi’s orthogonal array results

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Time (hour)</th>
<th>Temperature (°C)</th>
<th>NaOH (M)</th>
<th>Reactants/lignin ratio (g/g)</th>
<th>Lignin Concentration (g/L)</th>
<th>Solubility (wt%)</th>
<th>Average solubility (wt%)</th>
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<tr>
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<td>20</td>
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<td>Average solubility</td>
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<td>45</td>
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<td>0.9</td>
<td>15</td>
<td>82.95</td>
<td>83.95</td>
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</table>
Table 10 represent the response table for means of solubility data and demonstrates the factor ranks based on the most significant effect on aqueous solubility of the SLS produced. Results show that the most significant factor that affects the solubility is reaction time with more than 50% difference in solubility from lower to higher level (1 hr-4 hr). Reactant/lignin ratio has the lowest effect on solubility with rank number 5.

Table 10: Most significant factor from Taguchi’s orthogonal array results

<table>
<thead>
<tr>
<th>Factor Level</th>
<th>Time</th>
<th>Temp</th>
<th>NaOH concentration</th>
<th>Reactants/lignin ratio</th>
<th>Linin concentration</th>
</tr>
</thead>
<tbody>
<tr>
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</table>

*Delta=different in solubility value of level 1 and 4 for each factor

A contour plot is generated to see the interaction between reaction time and other factors (Figure 37). As shown from the figure, effect of reaction time is always dominant. This result, agreed with previous study, which showed that time has a major effect on the solubility of sodium Lignosulfonate produced [86].
4.9 Selecting the optimum condition for sulfomethylation reaction

Further experiments were conducted to study the effect of each parameter on aqueous solubility, of the SLS product and to select the optimum condition for the sulfomethylation reaction, by changing only one parameter at a time keeping all the other parameters constant.

4.9.1 Effect of NaOH concentration

The sulfonation of lignin is influenced by pH [75], and Figure 38 presents the effect of NaOH on the aqueous solubility of SLS product. The maximum solubility of 85.5 wt% was obtained at 0.5 M NaOH concentration (Table 11). The increase in solubility was due to the effect of NaOH on the progress of sulfomethylation reaction.
The improvement in the sulfomethylation of lignin is closely related to the extent of nucleophilic substitution of the hydroxyl group with a sulfonate group under alkaline conditions. Concentration of NaOH in solution should be sufficient enough to promote the sulfomethylation process. Below 0.5 M NaOH, alkaline concentration was not adequate for the reaction, and NaOH concentrations higher than 0.5 M provided an appropriate alkali atmosphere for the undesired side reaction to take place.

Table 11: Effect of NaOH concentration on aqueous solubility of SLS product

<table>
<thead>
<tr>
<th>Run</th>
<th>NaOH concentration (M)</th>
<th>Solubility (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.25</td>
<td>65.75</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>85.25</td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
<td>77.75</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>73.1</td>
</tr>
<tr>
<td>5</td>
<td>1.25</td>
<td>72.4</td>
</tr>
</tbody>
</table>

Figure 38: Effect of NaOH concentration on aqueous solubility of SLS product

4.9.2 Effect of sodium hydroxymethyl sulfonate/lignin mole ratio

Figure 39 shows the effect of sodium hydroxymethyl sulfonate/lignin (CH₄NaO₄S/lignin) mol ratio on aqueous solubility of SLS product. The maximum solubility was 87.15%, which was obtained at a 0.9 mol/mol sodium hydroxymethyl
sulfonate/lignin ratio (Table 12). In the hydroxymethyl sulfonate/lignin range of 0.2 and 0.9 mol/mol ratio, the increase in solubility is attributed to the increase in the quantity of sodium hydroxymethyl sulfonate in the solution, which improved the amount of sulfonate groups in SLS molecule. The decrease in solubility at more than 0.9 mol/mol ratio is probably due to undesirable side reactions as explained in previous sections [56, 75].

Table 12: Effect of sodium hydroxymethyl sulfonate/lignin mole ratio on aqueous solubility of SLS product

<table>
<thead>
<tr>
<th>Run</th>
<th>CH$_4$NaO$_4$S/Lignin ratio (g/g)</th>
<th>Solubility (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3</td>
<td>62.3</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
<td>80.75</td>
</tr>
<tr>
<td>3</td>
<td>0.9</td>
<td>87.15</td>
</tr>
<tr>
<td>4</td>
<td>1.2</td>
<td>77.45</td>
</tr>
<tr>
<td>5</td>
<td>1.5</td>
<td>68.5</td>
</tr>
</tbody>
</table>

Figure 39: Effect of sodium hydroxymethyl sulfonate/lignin mole ratio on aqueous solubility of SLS product

4.9.3 Effect of reaction time

Figure 40 shows the effect of reaction time on aqueous solubility of SLS product. The maximum solubility of 86.6 wt% was obtained at 4 h (Table 13). When
reaction time was extended from 0 to 4 h, there was an increase in solubility. Further increase in the time of reaction had an opposite effect on aqueous solubility of SLS product, which could be due to the development of side reactions. In previous studies when the reaction time was extended from 2 to 5 h during the sulfomethylation of lignin from corn stalk, the solubility increased, and further increase in reaction time had no effect on solubility [75]. Sulfonation of esparto grass lignin studies showed similar results, were the maximum solubility of sodium lignosulfonate were obtained after 4 hours of reaction [57, 142].

Table 13: Effect of reaction time on aqueous solubility of SLS product

<table>
<thead>
<tr>
<th>Run</th>
<th>Time (h)</th>
<th>Solubility (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>30.8</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>48.25</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>69.7</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>86.6</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>62.45</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>58.05</td>
</tr>
</tbody>
</table>

Figure 40: Effect of time on aqueous solubility of SLS product
4.9.4 Effect of temperature

Figure 41 demonstrate the effect of temperature on aqueous solubility of the SLS product. When the reaction temperature was increased from 80 to 100°C, the solubility increased from 73.85 wt% to 88.8 wt% (Table 14), respectively. Pang and co-workers [143] have reported the sulfomethylation of calcium lignosulfonate, in which the maximum solubility was obtained at 90°C. The primary increase in solubility is due to more frequent collisions between the reactants at a higher temperature [57]. Li and co-workers reported similar results on the sulfonation of wheat straw hydroxymethyl ethanol lignin with sodium sulfite, in which increased temperature from 60 to 80°C resulted in an increase of the sulfonate group content from 0 to 1.22 mmol/g which as well resulted in increase of solubility [144]. Additional increase in temperature reduced the solubility, possibly due to formation of sodium thiosulfate at high temperatures [57]. Formation of sodium thiosulfate was reported in the treatment of softwood lignin with formaldehyde and sodium sulfite. A decrease in sulfonation degree from 1.45 to 1.05 mmol/g was accompanied by an increase in the production of sodium thiosulfate when the temperature was increased from 100 to 150°C [143].

Table 14: Effect of reaction temperature on aqueous solubility of SLS product

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature (°C)</th>
<th>Solubility (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>61.65</td>
</tr>
<tr>
<td>2</td>
<td>70</td>
<td>65.3</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>73.85</td>
</tr>
<tr>
<td>4</td>
<td>90</td>
<td>78.075</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>88.8</td>
</tr>
<tr>
<td>6</td>
<td>110</td>
<td>78.65</td>
</tr>
<tr>
<td>7</td>
<td>120</td>
<td>75.3</td>
</tr>
</tbody>
</table>
4.9.5 Effect of lignin concentration

Figure 42 shows the effect of lignin concentration on aqueous solubility of SLS product. The maximum solubility of 88.1 wt% was obtained at 25 g/L lignin concentration (Table 15). Solubility increased for lignin concentration up to 25 g/L. This might be due to more frequent and effective collisions between the reaction sites and the reactants as lignin concentration increased, resulting in enhanced sulfomethylation reaction [145].

The production of surface-active agents from lignin, which was obtained from pulping process was reported to have a similar trend, in which the first increase in lignin concentration increased the solubility to 90%, and additional increase caused a reduction in solubility [146]. The decrease in solubility with further increase in lignin concentration could be due to the limitation of stirring method of a magnetic bar (mechanical constrains) in the reaction setup [147].
Table 15: Effect of lignin concentration on aqueous solubility of SLS product

<table>
<thead>
<tr>
<th>Run</th>
<th>Lignin Concentration (g/L)</th>
<th>Solubility (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>75.45</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>79.35</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>84.2</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>88.1</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>80.8</td>
</tr>
<tr>
<td>6</td>
<td>35</td>
<td>78.7</td>
</tr>
</tbody>
</table>

Figure 42: Effect of lignin concentration on aqueous solubility of SLS product

The optimum condition for sulfomethylation reaction was at a reaction time of 4 hours, Temperature of 100°C, lignin concentration of 25 g/L, reactant/lignin ratio of 0.9 (g/g) and NaOH concentration of 0.5 M. An experiment was also conducted under the optimum condition for which the average solubility of 90.23 wt% was achieved, giving the highest solubility value among all runs. Therefore, the selected optimum conditions gave the maximum solubility, which should lead to better corrosion efficiency.
4.10 Corrosion Test

Corrosion test was performed using the potentiostat corrosion test method on the best two SLS product shown in Table 9 (runs 13 and 14) named SLS 13 and SLS 14, respectively. These products selected due to their high solubility. Results are presented in Figure 43–46.

![Corrosion rate for SLS 13 and SLS 14 at 5 ppm concentration](image)

Figure 43: Corrosion rate for SLS 13 and SLS 14 at 5 ppm concentration

Figure 43 shows the difference between SLS 13 and SLS 14 corrosion rate of carbon steel using 5 ppm SLS product as a main concentration. For SLS 14, a minimum corrosion rate of 1.21 mm/year was obtained at 300 h while it was 1.63 mm/year for SLS 13 for the same time. In general SLS 14 had higher corrosion protection efficiency with an average corrosion rate of 1.26 mm/year, compared to 1.62 mm/year which was obtained for SLS 13.
The difference between SLS 13 and SLS 14 corrosion rate of carbon steel using 10 ppm SLS is demonstrated in Figure 44. A 1.13 mm/year corrosion rate for SLS 14 was obtained at 360 h while for SLS 13 it was 1.49 mm/year at the same time. As in the case of 5 ppm concentration, SLS 14 showed a higher corrosion efficiency at 10 ppm with the average corrosion rate of 1.14 mm/year compared to SLS 13, which resulted in a rate of 1.51 mm/year.
To analyze the corrosion rates further, another SLS carbon steel concentration i.e. 20 ppm SLS concentration was chosen. Figure 45 illustrates the variation between SLS 13 and SLS 14 corrosion rates of carbon steel. It was observed that after 500 h, a corrosion rate of 1.42 mm/year was obtained for SLS 13, whereas for SLS 14 it was obtained to be 1.02 mm/year. In terms of corrosion efficiency, SLS 14 showed a higher corrosion efficiency compared to SLS 13, with an average corrosion rate of 1.05 mm/year compared to SLS 13 which resulted in a rate of 1.39 mm/year.

Figures 43-45, show that the higher the solubility of SLS product the more effective the sample is for protecting carbon steel against corrosion. Figure 46 shows average corrosion rate as a function of SLS concentration for two product (SLS 13 and SLS 14).

In general higher concentration of SLS product improved the corrosion protective efficiency, resulting in lower corrosion rate of carbon steel.
For example increasing SLS concentration from 5 to 30 ppm reduced the corrosion rate from 1.26 mm/year to 1.05 mm/year for SLS 14, and from 1.62 to 1.49 for SLS 13.

Similar observations were reported by other researchers for the corrosion efficiency of SLS samples on zinc sheet instead of carbon steel, in which increasing the concentration of SLS led to decrease in corrosion rate [84]. This clearly indicates that introducing more sulfonated group will result in improved protection of steel against corrosion, while is attributed to the higher solubility of the product [84].

![Graph showing corrosion rate vs SLS concentration](image.png)

**Figure 46:** Average corrosion rate for SLS 13 and SLS 14 at 5, 10 and 20 SLS product concentration

The desirable corrosion rate in industrial applications for carbon steel is $\leq 0.5$ mm/year [148]. The SLS corrosion inhibitors developed in this research show promising potential, especially sample 14 which resulted in a corrosion rate of 1.06 mm/year. Results obtained from the potentiostat corrosion test showed three main outcomes; 1) sodium lignosulfonate produced from klason lignin showed improved ability to prevent carbon steel against corrosion, 2) increasing the solubility of SLS
produced resulted in an increased corrosion efficiency, 3) increasing the concentration of SLS produced decreased the corrosion rate in agreement with previous studies. These results are promising, however more development is needed to improve the products in order to reach acceptable corrosion rate ($\leq 0.5$ mm/year) for commercial use.
Chapter 5: Conclusion

Undoubtedly, the extracted corrosion inhibitor from palm tree biomass showed promising results and was able to prevent carbon steel against corrosion. Lignin was successfully extracted from the three date palm parts, fiber, rachis and leaflet, and showed positive characterization results.

Different reaction conditions of the sulfomethylation reaction for lignin modification were studied and their significant effect on aqueous solubility of sodium lignosulfonate product was determined. The optimum conditions of sulfomethylation reaction were: reaction time of 4 hours, temperature of 100°C, lignin concentration of 25 g/L, reactant/lignin ratio of 0.9 (g/g) and 0.5 M NaOH. Characterization of the produced sodium lignosulfonate matches with the published and the commercial results. Maximum average solubility of 90.23 wt% was achieved by conducting experiment under the optimum condition of sulfomethylation reaction.

Potentiostat corrosion test results demonstrates the ability of sodium lignosulfonate to prevent carbon steel against corrosion with a minimum corrosion rate of 1.06 mm/year. Increasing the solubility of the produced sodium lignosulfonate is directly related to corrosion efficiency, in which the higher the solubility of SLS product, the more effective the sample is for protecting carbon steel against corrosion.

The main objective of this thesis, which was to examine the ability of producing a corrosion inhibitor from date palm tree biomass, was successfully conducted. It is recommended to modify the sulfomethylation reaction methodology in order to get SLS product with higher aqueous solubility as it will result in higher corrosion efficiency. Another suggestion is to perform detailed corrosion tests for
exposed metals used in industrial applications and to study the effect of SLS product on different types of steel, such as mild steel, and compare corrosion rate results with the desirable corrosion rate in industrial applications.
References


A. V. Marques, H. Pereira, J. Rodrigues, D. Meier, and O. Faix, "Isolation and comparative characterization of a Björkman lignin from the saponified


List of Publications
