



**ADDIS ABABA UNIVERSITY**  
**ADDIS ABABA INSTITUTE OF TECHNOLOGY**  
**SCHOOL OF CHEMICAL AND BIO- ENGINEERING**

**Study on the sorption capacity of biopolyol (derived from  
Khat straw) based polyurethane foam for removal of oil  
from wastewater.**

**By**

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Stream).**

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**Study on the sorption capacity of biopolyol (derived from khat straw) based polyurethane foam for removal of oil from wastewater.**

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**ADDIS ABABA UNIVERSITY**

**ADDIS ABABA INSTITUTE OF TECHNOLOGY**

**SCHOOL OF CHEMICAL AND BIO ENGINEERING**

**MASTER OF SCIENSE IN CHEMICAL ENGINEERING (ENVIRONMENTAL ENGINEERING STREAM)**

This is to certify that the thesis prepared by **Intisar Kadir**, entitled “**Study on the sorption capacity of biopolyol (derived from Khat straw) based polyurethane foam for removal of oil from wastewater.**” and submitted as a partial fulfillment for the award of the Degree of Master of Science in Chemical Engineering (Environmental engineering) complies with the regulations of the university and meets the accepted standards with respect to originality, content and quality.

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## **DECLARATION**

I declare that this thesis is presented for the degree of Master of Science in Chemical Engineering (Environmental Engineering). The thesis is my original work and has never been presented in part or in whole to any university, and that all the resource materials used for this thesis have been duly acknowledged.

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Signature: \_\_\_\_\_

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# **Study on the sorption capacity of biopolyol (derived from khat straw) based polyurethane foam for removal of oil from wastewater.**

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## **Abstract**

Polyurethane foam (PUFs) has emerged as a promising material for oil cleanup. However, its effectiveness is limited by its hydrophilic nature. In this study, petroleum-based polyol was replaced with different amounts of biopolyol (25–100 w/w) to prepare biopolyol-based PUFs with enhanced oil sorption capacity. The biopolyol was obtained by liquefying khat straw using glycerol as a solvent and sulfuric acid as a catalyst. The foams were produced using the "two shot" technique. The resulting foams were characterized using Fourier transform infrared spectroscopy (FTIR), Nuclear magnetic resonance (NMR), Scanning electron microscope (SEM), Differential scanning calorimetry (DSC), Thermogravimetric analysis (TGA), Density and Mechanical strength test measurements. The FTIR and NMR spectra indicated that urethane linkages in biopolyol-based PUFs were formed, indicating that the chemical structure of the polymer was preserved despite the incorporation of biopolyol. SEM results showed that the cell shape is significantly affected by the biopolyol content, which resulted in inhomogeneous, irregular, and large cell shapes. TGA revealed that the onset temperature ( $T_{\text{onset}}$ ) of the foams decreased with increasing liquefied biopolyol concentration, indicating alterations in thermal stability. The hydrophobicity of the foams increased with higher liquefied biopolyol content, as observed in the one-factor-at-a-time test. The density measurement reveals that as the liquefied biopolyol content increases, so does the density of PUFs, while the mechanical strength decreases. Notably, the modified foams exhibited improved oil sorption capacity in an oil and PUF/oil/water system. The optimum oil sorption capacity of 26.9 g/g was obtained at PUF-25, 20% of oil to water percentage and 60 minutes of contact time for laboratory-prepared waste water and 24.98 g/g for actual garage wastewater sorption tests. These results highlight the potential of Khat derived liquefied biopolyol-based PUFs as effective oil adsorbents for water cleanup applications.

**Keywords:** Biopolyol; Khat; Liquefaction; Oil sorption; Polyurethane foam; RSM.

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## **Acronyms and Abbreviation**

ASTM	American Society for Testing and Materials
BBD	Box Behnken design
DSC	Differential scanning calorimetric
DTG	Derivatives of thermogravimetric analysis
FTIR	Fourier transforms infrared spectroscopy
NMR	Nuclear Magnetic Resonance
RSM	Response Surface Methodology
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
LKS	liquefied khat straw
OFAT	One-factor-at-a-time
PEG (400)	Polyethylene glycol (400)
PU	polyurethane
PUF	polyurethane foam

# 1 INTRODUCTION

## 1.1 Background of the study

The deterioration of environmental conditions has emerged as a prominent and persistent issue in our daily lives. The rapid pace of industrialization and urban development has contributed significantly to the alarming degradation of our environment (Sanghamitra et al., 2021; Vasilachi et al., 2021). Water, an essential resource for life on our planet, is highly vulnerable to environmental degradation. As a result, water pollution has sparked wide spread attention and concern on a global scale (de Medeiros et al., 2022; Geissen et al., 2015). Many pollutants are emerging in our environment. Oil and grease in water systems can be a source of pollution and harm the environment. Oil and grease can be found in wastewater from various sources, including the food processing industry, restaurants, farms, slaughterhouses and garages. The increased use of oil in development and high-demand oil-processed food, as well as improper discharge of oil into water drains, both industrially and domestically, are contributing factors (Abdul Hamid et al., 2016). High concentrations of oil and grease can cause clogging in the sewer system. Clogged sewers can cause overflow and water pollution, including pathogen exposure (Abdul Hamid et al., 2016). Excess oil clogs in treatment units, necessitating cleaning and replacement of pipes. This led to an increase in maintenance and inspection costs (Abd El-Gawad, 2014; de Medeiros et al., 2022).

Several methods have been used to remove oil, including a variety of filters (Okiel et al., 2011), gravity separation, biological processes, air flotation (Tansel & Pascual, 2011), chemical coagulation, and adsorption. One commonly used technique and has gained wide attention for removing organics dissolved in water is the process of adsorption. According to a previous study, the benefits of using adsorption methods include high oil removal efficiency, low cost, reusability, and low processing cost (Abdul Hamid et al., 2016).

Scholars have focused on developing new materials with a high sorption capacity. Some materials used for oil sorption include sugarcane bagasses (Brandão et al., 2010), vegetable fibers (Annunciado et al., 2005), clays (Ahmad et al., 2005), and polyurethane foams (PUFs) (Duong & Burford, 2006), among others.

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PUFs are excellent at absorbing oil due to their small pores and hydrophobic properties. Additionally, they are effective at removing solid pollutants by altering their dimensions and incorporating various chemicals (Santos et al., 2017). Recently, there has been significant research on developing PU composites for environmental remediation purposes.

Numerous studies have explored the potential benefits of adding fillers to PUFs in order to enhance their flexibility, strength, and chemical resistance (Nikkhah et al., 2015). Even small amounts of filler can lead to noticeable improvements in these properties. Recent research has focused on utilizing modified PUFs, such as PUF-nanoclay (Nikkhah et al., 2015), PUF-silica-DTMS (J. Wang & Geng, 2015), PUF-activated carbon (Zilouei & Asadinezhad, 2015), PUF-ZnO-PA (B. Li et al., n.d.), and PUF-carbon nanotubes (Keshavarz et al., 2015), for oil absorption purposes. Additionally, there is a growing interest in replacing petroleum-based materials with renewable resources, such as biopolyols derived from plant sources, in the production of chemical and polymer products. Some scientists believe that plant-based biopolyols could serve as a viable alternative to petroleum-based polyols for the creation of bio-based polyurethane (Laurichesse et al., 2014).

Hence, this study aimed to assess the potential of Khat-derived biopolyol as a partial substitute in PUFs synthesis for efficient removal of oil from wastewater. Biopolyol was synthesized by liquefaction process from khat straw using glycerol as the solvent and sulfuric acid as the catalyst. These biopolyols were subsequently incorporated with petroleum derived polyol to form hydrophobic and oilophilic PUFs. The study investigated the characteristics and effectiveness of the resulting PUFs sorbent for oil cleanup from wastewater.

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## **1.2 Statement of the problem**

The expansion of industrialization and urbanization in recent decades has led to a significant increase in the volume of oily wastewater from various sources like metal fabrication, textiles, restaurants, households, and garages (Kadier et al., 2022). As a result, surface and groundwater resources have become heavily polluted, causing adverse environmental and human health impacts (de Medeiros et al., 2022; Methods, M., & Opportunities, 2021). Oil has limited natural biodegradability, and its presence in ecosystems can disrupt their proper functioning for extended periods. Therefore, it is crucial to remove oil from wastewater before disposal to mitigate these issues (Abd El-Gawad, 2014; Williams et al., 2012). There are various methods available for removing oil from wastewater (Abdul Hamid et al., 2016).

Adsorption is considered one of the most effective and profitable methods for removing oil contaminants from wastewater, as it can efficiently remove or recover the oil (Vasilachi et al., 2021; Zhao et al., 2021). Many studies have focused on developing new sorbent materials with high oil adsorption capacity for remediating oil-polluted water (Nikkhah et al., 2015). Compared to conventional sorbent materials, 3D porous polyurethane foams (PUFs) are promising candidates for oil removal due to their advantages of low cost, good compressibility, and high adsorption ability (Oribayo et al., 2017). However, most PUFs lack selectivity for oil adsorption from oily water, resulting in low water-oil separation efficiency. As a result, there is an urgent need to develop new oil adsorption PUFs that have high selectivity for efficiently adsorbing oil from oily water (Oribayo et al., 2017; Wu et al., 2014).

Researchers have directed their attention towards enhancing the oil/water selectivity of PUFs through surface modification. Various substances such as nanoclay, graphene oxide, silicon, and lauryl methacrylate have been used to modify PUFs. However, many of these modification processes involve complex, multi-step procedures and require the use of numerous chemicals. Additionally, researchers have not given sufficient consideration to optimizing the process parameters that influence the adsorption process. Therefore, there is a need for the development of a simple fabrication method to modify PUFs and create a novel adsorbent material, while also focusing on optimizing the process parameters involved in the modification process.

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## **1.3 Objectives**

### **1.3.1 General objective**

The general objective of this study was to **Study on the sorption capacity of biopolyol (derived from Khat straw) based polyurethane foam for removal of oil from wastewater.**

### **1.3.2 Specific objectives**

The specific objective of this research is to;

- Prepare and characterize biopolyol from Khat straw using liquefaction method.
- Prepare and characterize PUFs using biopolyols with different proportions.
- Study the individual and interaction effect of variables (biopolyols/polyol wt%, oil to water percentage and contact time) on the oil adsorption capacity and find the optimal operating conditions.

## **1.4 Significance of the study**

The discharge of oil into the environment results in serious environmental problems. Therefore, the successful completion of this study was significant to various stakeholders. The development of bio-based polyurethane foam with a markedly improved capacity for oil adsorption may result from the use of biopolyol in part place of petroleum-based polyol. This foam could find applications in various areas where oil cleanup is needed. Furthermore, incorporating biopolyols synthesized from liquefied khat straw into the production of polyurethane foam has the potential to reduce the costs associated with importing petroleum-based polyol. By substituting these expensive raw materials with biopolyols derived from waste materials like khat straw, the research offers a way to minimize the reliance on imported resources and decrease production expenses. Furthermore, the research demonstrates the conversion of waste materials into valuable resources, promoting sustainability and minimizing environmental impact.

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### **1.5 Scope of the study**

To achieve the above-mentioned overall goals, the scope of the study should be addressed in the following manner. Biopolyols was synthesized from khat straw by using liquefaction process (by using pure glycerol (98%) and sulfuric acid (98%) as solvent and catalyst respectively). Then PUFs will be prepared by varying mixing proportions of biopolyol and polyol. The characterization covers hydroxyl number, molecular weight distribution and viscosity of biopolyols using standard test methods, functional group of both biopolyols and PUFs using FTIR, surface morphology of PUFs using SEM, thermal behaviour of PUFs using TGA and DSC and NMR analysis. The oil sorption capacity of PUFs was conducted in batch-wise process. A preliminary experiment was conducted to see the individual effect process parameters. The interaction effect parameters (biopolyol content, oil to water percentage and contact time) followed by statistical optimization of sorption capacity using the RSM (BBD) method was determined.

## **2 LITERATURE REVIEW**

### **2.1 Water Pollution**

The 3rd World Water Forum, held in Kyoto in 2002, highlighted a concerning global statistic - that approximately 2 million tons of pollutants, including sewage, industrial waste, and agricultural runoff, are discharged into water bodies around the world every day (Sanghamitra et al., 2021). This staggering amount is nearly equivalent to the weight of the entire global population and results in the production of nearly 1500 km<sup>3</sup> of wastewater globally (Geissen et al., 2015; Vasilachi et al., 2021). Access to safe and reliable potable water has become a major concern for the international community, particularly in developing and underdeveloped countries, due to this severe water pollution problem (Vasilachi et al., 2021). Water pollution is a critical worldwide issue that urgently requires comprehensive monitoring and implementation of solutions. Poor sanitation is a leading contributor to water pollution globally. As a result, over 50% of freshwater fish species and nearly one-third of amphibians worldwide are threatened with extinction (Geissen et al., 2015).

Rapid urbanization and population growth have led to the generation of significant amounts of oil-containing wastewater. This oily wastewater poses a potential risk of pollution, as oil can be present in various forms and concentrations, including single and multiple species (Sanghamitra et al., 2021). Oily wastewater is generated from diverse sources, such as kitchens, refineries, gas stations, vegetable oil industries, tanneries, slaughterhouses, commercial vessels, and offshore oil loading and unloading operations. Discharging these oily effluents into water bodies, land, and sewer lines without proper treatment can have various adverse ecological effects (Vasilachi et al., 2021; Zhao et al., 2021). The ecological impacts of oily wastewater include killing fish, obstructing photosynthesis, destroying natural landscapes, reducing crop production, polluting soil, water, and groundwater resources, and potentially endangering human health due to toxic and carcinogenic components (Kadier et al., 2022). Therefore, one of the most crucial issues is the remediation and treatment of oily wastewater (Sanghamitra et al., 2021).

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## **2.2 Methods of oil removal from wastewater**

Various remediation techniques have been employed in efforts to remove oils and other organic pollutants from water, including the use of adsorbents, air flotation (Tansel & Pascual, 2011), chemical dispersants, solidifiers, in-situ oil burning in water, mechanical clean-up, and bioremediation (Nikkhah et al., 2015). However, these traditional oil spill cleanup methods have limitations in their effectiveness. They suffer from low efficiency, potential for secondary environmental pollution, high costs, long cycle times, and complex operating conditions. As a result, the traditional approaches to oil spill cleanup and wastewater treatment have proved to be inadequate in fully addressing the challenges posed by oil and organic pollutants in water bodies. More effective and efficient solutions are needed to overcome the shortcomings of these conventional remediation techniques (Arunagiri et al., 2021).

Among the various oil removal strategies, the use of porous adsorbents is particularly appealing and promising. This is because the oil pollutants are adsorbed and retained within the adsorbent matrix, enabling the eventual recovery of the oil from the semi-solid sorbent phase. The adsorption-based approach is also less harmful to the environment compared to in-situ oil burning, which often produces severe secondary pollutants. The ability to adsorb and recover the oil, rather than burning it, makes the adsorbent-based method a more environmentally-friendly option (Oribayo et al., 2017).

## **2.3 Adsorption**

Adsorption is a process where substances are transferred from one phase and concentrated on the surface of another phase. In this context, the adsorbent is the phase that does the adsorbing, while the adsorbate is the material that gets concentrated or adsorbed onto the surface of the adsorbent (Rahmat et al., 2016).

Traditional porous adsorbents made from natural materials, such as corn stalks, vegetable fibers, cotton grass fibers, cotton grass mats, and kapok fiber (Dong et al., 2015), are cheap, biodegradable, and easily available. However, these natural adsorbents have low sorption capacity and high total cost of the removal process, making them less favorable choices for oil spill cleanup (Oribayo et al., 2017; Zilouei & Asadinezhad, 2015). Various other

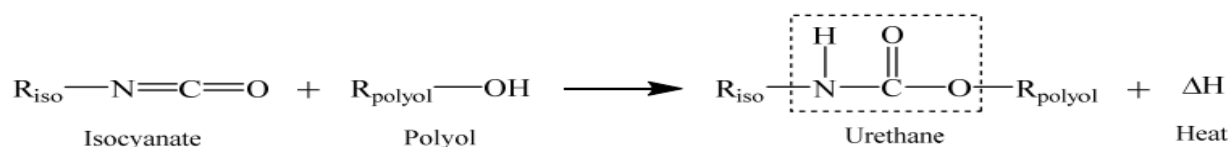
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materials, including aerogel (Hayase et al., 2013) and calcium carbonate, have also been used to separate oils from water. However, these oil-adsorbing materials have drawbacks, such as high cost, low sorption capacity, poor hydrophobicity, complex fabrication procedures, and limited durability and recyclability (J. Wang & Geng, 2015). Synthetic organic sorbents, such as those made from polymeric materials like PU, polypropylene, polyethylene, and cross-linked polymers, are commonly used in oil spill cleanup. This is primarily due to their preference for oil and ability to repel water (Ge et al., 2014). However, these synthetic organic sorbents typically have low oil/water selection capacities and are non-biodegradable (H. Li et al., 2012; Zilouei & Asadinezhad, 2015). Despite these limitations, oil sorbents based on PUFs with a special three-dimensional (3D) porous structure have shown promise due to their high uptake capacity, low cost, and excellent flexibility. Recently, there has been growing interest in the fabrication of superhydrophobic PUFs for oil cleanup using various methods (Arunagiri et al., 2021; H. Li et al., 2012; Nikkhah et al., 2015; Okiel et al., 2011; Wu et al., 2014; Y. Yang et al., 2015).

### 2.4 Polyurethane Foam

The concept of urethanes was first developed by Wurtz in 1849. However, the significant milestone in the development of polyurethanes (PUs) came in 1937 when Otto Bayer created PUs by reacted a polyester diol with a diisocyanate. This was a notable advancement, as it involved a novel class of polymerization reaction known as step polymerization (Gama et al., 2018). PUs are polymers that result from the reaction between the isocyanate functional groups (-NCO) and the hydroxyl groups (OH) of a polyol. The term "urethane" refers to the linkage that is created during this exothermic reaction, which produces urethane groups (Akindoyo et al., 2016).



**Figure 2-1: Reaction scheme of urethane production**

Where  $\text{R}_{\text{iso}}$  is derived from the isocyanate monomer,

$\text{R}_{\text{polyol}}$  is derived from the polyol component.

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PU is block copolymers composed of low molecular weight polyester or polyether blocks covalently bonded by a urethane group (-NHCO-O-). Polyisocyanate, a polymer containing polyhydroxyl groups (such as polyester or polyether polyols), and a chain extender, typically a low molecular weight diol (such as 1,4-butanediol) or diamine (such as 1,4-dibutylamine), are used in the production of PU. PU has distinct advantages such as low density, low thermal conductivity and moisture permeability, a high strength-to-weight ratio, and high dimensional stability (Y. Yang et al., 2015). PU foams are commonly classified as flexible, semi-rigid, or rigid foams based on mechanical properties and core densities (Mahmood et al., 2016).

### **2.5 Raw materials and preparation of PUFs**

#### **2.5.1 Raw Materials**

An isocyanate, a polyol, a co-cross linking agent, physical and/or chemical blowing agents, catalysts, and a surfactant are all included in the PU foam formulation, with each playing a specific role in the chemical reactions that occur during the formation of PU foam (Peyrton & Avérous, 2021).

- I. **Isocyanate** - Isocyanate are crucial components for the synthesis of PU. They are di- or polyfunctional compounds that contain two or more -NCO groups per molecule. Isocyanate can be classified as aliphatic, cycloaliphatic, polycyclic, or aromatic, such as toluene diisocyanate (TDI), methylene diphenyldiisocyanate (MDI), and xylene diisocyanate (XDI) (Gama et al., 2018; Peyrton & Avérous, 2021). Isocyanate have a cumulated double bond sequence,  $R-N=C=O$ , where the reactivity is primarily determined by the positive character of the carbon atom. This carbon atom is susceptible to nucleophilic attacks from species with available electrons, and oxygen and nitrogen can act as electrophiles (Gama et al., 2018).

In the case of aromatic isocyanate where R is an aromatic group, the negative charge from the  $N=C=O$  sequence gets delocalized into the aromatic ring. As a result, aromatic isocyanate exhibit higher reactivity compared to aliphatic or cycloaliphatic isocyanate (Cui et al., 2017). Isocyanate should be handled with caution because they are toxic and can pose health risks if not handled, stored, and applied properly.

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II. **Polyol** - Polyol are compounds with two or more hydroxyl groups in a single molecule. Polyol are classified into monomer and polymeric polyol based on their molecular weights (Mw) (Gama et al., 2018). Polyol with functionalities ranging from 2 to 8 and Mw ranging from 200 to 8000  $\text{gmol}^{-1}$  are commonly used in the production of PU (Y. Wang et al., 2019).

Because polyether polyol has a higher polydispersity index and a lower viscosity, it is preferred over polyester polyol because it produces PUFs with superior mechanical properties (Aniceto et al., 2012). PU is made from polyester polyol that has both aromatic and aliphatic structures. Because the aromatic structure gives the rigidity of the finished product, aliphatic polyester polyol is primarily used in the production of flexible PU, while aromatic polyester polyol is primarily used in the production of rigid PUFs (Mahmood et al., 2016).

III) **Blowing agents** - The process by which PUFs form their cellular structure involves the blowing agents. There are two types of blowing agents:

- a) Physical blowing agents are solvents with low boiling points, like pentane, acetone, or hexane that expand the polymer by vaporization.
- b) Chemical blowing agents (such as water) that expand the polymer by the  $\text{CO}_2$  produced.  $\text{CO}_2$  and pentane are now commonly used as a blowing agent. About 4.6 to 4.8 parts of water for every 100 parts of polyol is the maximum amount that can be used. Over this level of water, there could be fire or scorching foam.

IV) **Surfactant** - surfactants are copolymers made of ethylene oxide-co-propylene oxide (poly) grafts and a silicone backbone. In addition to stabilizing cells and influencing cell size and foam air permeability, surfactants also emulsify incompatible formulation ingredients, lower surface tension, encourage bubble nucleation, and prevent rupture by localized thinning until the cell-opening event happens (Mahmood et al., 2016).

V) **Catalysts** - Both the isocyanate and blowing agent reactions as well as the isocyanate and polyol reactions are accelerated by catalysts. The most widely used catalysts are amines or tin catalysts. Proper expansion is accomplished by striking a balance between gas generation (blowing) and polymerization (gelling).

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Thus, altering the kind and amount of catalyst has an enormous impact on development (Gama et al., 2018).

### **2.5.2 Preparation of PUFs**

The production process of PUFs involves several steps, including preparation of mixing, foaming, curing, and post-processing. This process involves urethane formation, cross linking reactions, and foaming reactions (Akindoyo et al., 2016; Gama et al., 2018).

The foaming process can be done by one shot or two shot methods. In one shot method all materials are loaded into a mixing container and mixed homogeneously before being poured into a mould. In the two-shot method, all other ingredients (polyols, blowing agents, catalysts, etc.) were premixed in the first stage before isocyanate was added in the second stage (Y. Yang et al., 2015).

The two-shot method offers some advantages over the one-shot method. It allows for greater control over the foam's properties, such as density, hardness, and other mechanical characteristics, by adjusting the composition of the A-side and B-side. It also provides the flexibility to produce foams with different properties without changing the entire formulation. Additionally, the two-shot method can be used for producing foams with different colors or layered structures by injecting different A-side or B-side formulations sequentially (Oribayo et al., 2017).

In the production of PUFs, there are two primary reactions: the blow reaction and the gelation reaction (Cinelli et al., 2013). The blow reaction (gas-producing reaction), involves the reaction between isocyanate and water. Water reacts with the isocyanate groups in the presence of a catalyst, leading to the formation of carbamic acid. Carbamic acid is unstable and decomposes into primary amine and carbon dioxide (CO<sub>2</sub>) (Oribayo et al., 2017). The CO<sub>2</sub> gas generated during this reaction acts as a blowing agent, expanding the foam and creating the characteristic cellular structure. The blow reaction occurs rapidly and is responsible for the initial expansion of the foam. Whereas, the gelation reaction (cross-linking reaction), involves the reaction between isocyanate and polyol. Isocyanate groups react with hydroxyl groups present in the polyol component, forming urethane linkages (Y. Wang et al., 2019). This cross-linking process gradually polymerizes the polyols and

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isocyanates, leading to the development of a three-dimensional network structure within the foam. The gelation reaction occurs more slowly compared to the blow reaction and is responsible for the foam's final mechanical strength, dimensional stability, and resistance to deformation.

Both the blow reaction and the gelation reaction are critical for the formation of PUFs. The blow reaction generates the gas necessary for foam expansion, while the gelation reaction provides the structural integrity and physical properties of the foam. If the blow reaction happens too rapidly, the cells may rupture before the polymer has sufficient strength to maintain the foam's structure, leading to foam collapse (Hu et al., 2014). If the gelation reaction occurs too quickly, it can result in closed-cell foam. The balance between these two reactions needs to be carefully controlled to achieve the desired foam characteristics, such as cell structure, density, and mechanical properties.

In order to adjust the balance between the blow reaction and the gelation reaction controlling the amount of water added into the reaction mixture, the composition of the polyol component added, the reaction temperature during foam production times and the isocyanate index, which is the ratio of the isocyanate content to the total reactive hydroxyl groups in the formulation is another important factor in balancing the blow and gelation reactions (Oribayo et al., 2017).

There are three measurements that helps to evaluate the reaction kinetics and ensure the foam's quality and properties meet the desired specifications of PUFs. These are cream time, gel time, and rise time (Ahvazi et al., 2011). The cream time is the time it takes for the polyol and isocyanate mixture to change from a clear to creamy colour. During the cream time, the initial reaction between the polyol and isocyanate occurs, resulting in the formation of a thicker, more viscous mixture. The gel time is the time needed for an infinite network to be formed; and the rise time is the time it takes for the foam to fully expand and reach the desired volume (Cinelli et al., 2013). During this phase, the foam grows significantly in size as the blowing agent (usually CO<sub>2</sub>) produced by the blow reaction expands the mixture into a cellular structure.

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Foam density is determined by the mass of the expanded polymer, which is proportional to the amount of blowing agents used (Santos et al., 2017). The addition of additives may also have an impact on these properties because a higher amount of denser solid material in the process increases the viscosity of the system and interferes with cell nucleation (Santos et al., 2017). The amount of blowing agents used has a direct impact on the mass of the expanded polymer, so foam density is usually affected. In other words, more blowing agents produce a lighter foam with lower density (Hernández-Ramos et al., 2023). Additionally, the addition of fillers can affect foam properties. the presence of unliquefied impurities during the foam production process increases the system's viscosity, which can interfere with the formation of foam cells. This interference disrupts the nucleation process, resulting in foam density changes (Bontaş et al., 2023) .

### **2.5.3 Modification of PUFs**

Ultralight PU sorbents with open-cell structures, low density, and high porosity are thought to be effective at oil absorption. However, it is important to note that PU is produced through a chemical reaction involving polyol and isocyanate. PU contains a variety of functional groups, including ethers, carbamates, and amides, which help it absorb oil and water (H. Li et al., 2012). An ideal commercial sorbent should possess several desirable characteristics, including selectivity, high adsorption capacity, ease of regeneration and reusability, good mechanical strength, affordability, and biodegradability (Zilouei & Asadinezhad, 2015).

Numerous research studies have been undertaken to enhance the oleophilic/hydrophobic properties of PU, focusing on surface modification of PU foams and investigating the impact of cell structure and foam density on the oil sorption capabilities of PU (Nikkhah et al., 2015). However, the large amounts of expensive modifying agents, organic solvents, high energy consumption, and the dependence on complicated and unusual fabrication techniques prevent these approaches from being widely used (Oribayo et al., 2017; Y. Yang et al., 2015). Therefore, the development of a simple, economical, and ecologically friendly process for producing hydrophobic and oleophilic porous materials with excellent selective absorption of oil from water is urgently needed.

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According to Nguyen et al (2012), the surface of the porous material skeleton was coated with a hydrophobic coating using the dip coating method to create a graphene-based sponge that is both superhydrophobic and superoleophilic. The optimum surface wettability required meticulous control over the dip coating times. This groundbreaking work has led to the successful development of several other hydrophobic porous materials. But in the process of making graphene oxide, this method produces a lot of acidic waste, requires a lot of steps, and calls for high concentrations of organic solvents (Y. Yang et al., 2015). Therefore, there is still a great deal of work to be done in order to create hydrophobic 3D porous oil adsorbents, as a more straightforward and eco-friendly method is required.

The addition of additives to PUFs formulations has a direct impact on the size and shape of the cells, as well as the density of the composites and the appearance of pores in their 3D structure. All of these properties can affect the composite foam's sorption capacity in comparison to the blank foam (Shimizu et al., 1997).

These days, the production of 3D porous materials based on lignocellulosic biomass resources is popular due to its affordability, ease of use, environmental friendliness, and renewable qualities, among other reasons (K. Li et al., 2014; Oribayo et al., 2017).

### **2.6 Biopolyol**

Biopolyols are a type of polyol derived from renewable biomass sources such as vegetable oils (soybean oil, castor oil, or palm oil), starches, sugar-based feedstock, lignocellulosic biomass, and other bio-based materials. They are considered more environmentally friendly than polyols derived from petroleum (Cui et al., 2017; Olszewski et al., 2022). Biopolyols help reduce reliance on fossil fuels and have a lower carbon footprint. They can be used as partial or complete substitutes for petroleum-based polyols in various applications (Hu et al., 2014; Ma et al., 2021) The resulting biopolyols can have similar or adjusted properties compared to petroleum-based polyols, depending on the specific feedstock and production methods used.

Biopolyol can be made from vegetable oils by tweaking certain spots in the fatty acid chain (Cinelli et al., 2013). This special biopolyol is good for making PU products like foams. But, using a lot of vegetable oil for this can clash with food supplies and the biodiesel business

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(Cinelli et al., 2013). Some researchers are looking into making biopolyols from lignocellulosic biomass instead, and they seem to work well for PU applications (Cui et al., 2017). The PU industry has been eyeing this idea for a while now (Hu et al., 2012; Olszewski et al., 2022).

Lignocellulosic biomass materials, such as wood and agricultural crop residues, are considered the most abundant renewable feedstock for the production of biopolyols (Nadányi et al., 2022). These biomass materials are primarily composed of three main structural components - cellulose (30-35%), hemicellulose (15-35%), and lignin (20-35%). The high hydroxyl group content within these lignocellulosic components makes them promising raw materials for the synthesis of biopolyols. These biopolyols can then be utilized in the production of bio-based PUF (Burnard, 2019; Kataoka et al., 2021).

Using lignocellulosic biomass in PU synthesis not only reduces the use of petroleum resources, but it also improves the mechanical properties of the PU and imparts other functional properties such as flame retardancy (Y. Pan et al., 2016), UV protection, and hydrophobicity (A. Lee & Deng, 2015; Oribayo et al., 2017).

### ➤ **Khat (*Catha edulis*)**

Khat or chat (*Catha edulis*) is an evergreen shrub that is native to the Middle East and the Horn of Africa. Millions of people chew its fresh leaves every day as a form of recreation because of its euphoric and psycho stimulant effects. Due to its economic appeal, khat cultivation by local farmers is expanding, resulting in a rapid reduction in annual crop production. Over two million farmers produce khat on more than 250,000 ha of land (Gabriel et al., 2021).

When the fresh leaves of the khat plant are harvested for local and international consumption, the older leaves and twigs are typically discarded as solid waste. This leads to significant amounts of khat waste in cities and towns, which not only detracts from their aesthetic appeal but also creates breeding grounds for rodents and disease-carrying organisms. Additionally, the presence of waste often encourages improper disposal practices, exacerbating the already poor sanitation conditions in these areas. Given the massive amount of waste generated, it is crucial to implement effective waste management systems. One potential solution is to

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convert this waste into valuable products such as biopolyols. This approach would address a range of socioeconomic issues by simultaneously mitigating ecological problems and offering economic benefits.

The composition of khat straw was referred from previous research papers (Gabriel et al., 2021). Table 2-1 shows values for cellulose, hemicelluloses, and lignin content of khat straw and other plant species.

**Table 2-1: Composition of khat straw and other plant species on dry basis (Burnard, 2019; Gabriel et al., 2021; Kataoka et al., 2021).**

Plant materials	Composition (%w/w) on dry basis		
	Cellulose	Hemicellulose	Klason lignin
Khat straw	39.4 ± 0.38	12.75 ± 0.52	28.67 ± 2.46
Hardwoods	40 – 55	24 – 40	18 – 25
Softwoods	45 – 50	25 – 35	25 – 35
Wheat straw	30	50	15
Corn cobs	45	35	15
Grasses	25 – 40	35 – 50	10 – 30
Switch grass	45	31.4	12

Recently, renewable natural resources for the development of recyclable and/or biodegradable Products have received much attention to protect the environment from pollution.

### **2.7 Methods of converting biomass to biopolyol**

Lignocellulosic materials are considered one of the most important natural sources for the production of value-added biopolyols. They are preferred due to their biodegradability, abundance, cost-effectiveness, high tensile strength, and stiffness (Jin et al., 2011; Mahmood et al., 2016). However, lignocellulosic biomass materials are solid in their natural state and must be converted into liquid polyols before they can be used to produce PUs. There are two

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major technologies used for this conversion: oxypropylation and liquefaction (Aniceto et al., 2012; Hu et al., 2014; Thakur et al., 2014).

### **2.7.1 Oxypropylation**

Oxypropylation of biomass is a process in which propylene oxide is added to biomass structures to create polymers. This is carried out at high pressure (1-10 atm) and temperature (100–200°C) using KOH as a catalyst (Grancharov et al., 2023). The resulting polyols are a mixture of various compounds, including oxypropylated biomass, poly (propylene oxide), and some unreacted or partially oxypropylated biomass that can be utilized in foam production (Hu et al., 2014). This process does not introduce additional OH-groups, but it does enhance the functionality of the biomass. However, a drawback is the use of hazardous chemicals such as propylene oxide (de Rezende et al., 2018; J. Zhu et al., 2024).

### **2.7.2 Liquefaction**

Liquefaction is a thermochemical process used to convert solid lignocellulosic biomass into liquid polyols (Hu et al., 2014). This process typically involves elevated temperatures (150-250°C) and atmospheric pressure, along with the use of polyhydric alcohol liquefaction solvents (Hu et al., 2012, 2014). The liquefaction process can be catalyzed by either acids or bases, with acid catalysis being more common. During liquefaction, the polyhydric alcohol solvents degrade and decompose the biomass components into smaller, more soluble molecules through solvolytic reactions (Bontaş et al., 2023; Hu & Li, 2014). The different structural components of lignocellulosic biomass - hemicellulose, lignin, and amorphous cellulose - liquefy at different stages of the process. This is due to their varying structures and morphologies, with the amorphous components being more easily accessible to the liquefaction solvents. The liquefaction of crystalline cellulose, which has a well-packed structure, typically proceeds more slowly and continues until the later stages of the process. As a result, the liquefaction of cellulose is often considered the rate-limiting step in the overall biomass liquefaction process (Hu et al., 2012, 2014).

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The synthesis biopolyols are largely a mixture of different compounds rich in hydroxyl groups and can be used directly to produce various PU products such as foams, adhesives, and films (Basar et al., 2021). Solvents used as liquefying agents can be quite versatile, extensive, and costly. Ethylene glycol, ethylene carbonate, propanol, butanol, poly-ethylene glycol is examples of liquefying agents. However, the conventional liquefaction process relies heavily on petroleum-based solvents, which compromises its sustainability (Bontaş et al., 2023). This extensive use of petroleum-based solvents raises polyol production costs significantly, impeding future commercialization efforts (C. Yang et al., 2020). Therefore, there is a need to explore renewable sources of solvents and alternative techniques to produce bio-polyols (Cui et al., 2017, Ma, Q et al., 2023 ).

Crude glycerol, a byproduct of the biodiesel production process, has been demonstrated in earlier studies to be an efficient liquefaction solvent for lignocellulosic biomass. The utilization of crude glycerol in atmospheric biomass liquefaction processes is advantageous due to its renewable nature and lower cost compared to traditional polyhydric alcohols (Hu & Li, 2014). The study suggests that in the polyol and PU foam industries, using crude glycerol instead of petrochemical solvents could lower production costs and increase sustainability (Hu et al., 2012).

According to (Y. Wang et al., 2009), research was done on using partially purified crude glycerol as a liquefaction solvent to turn corn stover into biopolyols. The findings showed that varying a number of parameters led to higher liquefaction yields. It is yet unknown, though, whether these biopolyols are suitable for use in the manufacturing of polyurethane foam.

The hydroxyl numbers (the amount of free OH groups in the synthesized biopolyol), average molecular weight (GPC), GC-MS, and viscosity are the independent characteristics that are measured. Therefore, the functionality (number of OH groups), molecular weight, and viscosity are important factors that affect the characteristics of the PUFs, or products made using polyols (Bontaş et al., 2023).

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### **2.7.2.1 Factors Affecting the Efficiency of the Liquefaction of Lignocellulosic Biomass**

#### **I. Effects of biomass nature and loading**

The composition, structures, and morphologies of lignocellulosic biomass materials affect the efficiency of biomass liquefaction (Hernández-Ramos et al., 2023). A study of seven wood species discovered that softwood liquefied faster but recondensed earlier due to the presence of more reactive guaiacyl propane units. The liquefaction rates were discovered to be in the following order: wood, newspaper, business paper, and box paper. Different agricultural crop residues exhibited varying liquefaction behaviours (Hu et al., 2014).

According to the research (Hu et al., 2012), the biomass conversion ratios were about the same at 10% and 15% soybean straw content, at around 65%. But when they increased the biomass loading to 20% and 25%, the conversion ratio dropped to 54% and 51%. The hydroxyl number of biopolyols went down from 480 to 460 mg KOH/g when they increased the biomass loading from 10% to 15%. Biopolyols made from 20% biomass loading had a hydroxyl number of 463 mg KOH/g, which was pretty close to the 15% biomass loading.

#### **II. Liquefaction solvent**

One important factor that affects both the final product's structure and degree of depolymerization is the solvent used in the liquefaction process. Accordingly, liquefaction efficiency increases with increasing solvent polarity (Bontaş et al., 2023). They need to have the right polyol properties and be able to liquefy fast. The ability of the solvent to liquefy and the characteristics of the polyol determine which solvent is best. Typically, rigid or semi-rigid PU foam applications use glycerol and PEG-400 as liquefaction solvents; highly resilient PU foam applications use PEG-400 (Hu et al., 2014; Jin et al., 2011).

Polyhydric alcohols with the right molecular weights and hydroxyl numbers must be used as liquefaction solvents in order to produce high-quality biopolyols from the liquefaction of lignocellulosic biomass (Yao et al., 1996). In order to synthesize biopolyols and create PU foams, the majority of earlier studies liquefied lignocellulosic biomass using a solvent mixture of PEG-400/glycerol or crude glycerol. Since pure glycerol has been demonstrated to

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aid in the suppression of lignin re-condensation reactions, it is most frequently used as a co-solvent in liquefaction processes, such as a PEG-400/glycerol mixture (S. H. Lee et al., 2000). According to research, glycerol can be utilized straightaway as a solvent for biomass liquefaction in order to produce polyol without the need for expensive upgrading or refining procedures. This could enhance the sustainability and economics of lignocellulosic biomass liquefaction (Hernández-Ramos et al., 2023).

### **III. Catalyst**

During liquefaction, a sequence of hydrolysis and solvolysis reactions is the primary mechanism through which lignocellulosic biomass is broken down (Xu et al., 2014), which can be catalyzed by either acids or bases (Hernández-Ramos et al., 2023).

In the study Conducted by (H. Pan et al., 2012), the catalytic effects of sulfuric, phosphoric, and hydrochloric acids on the liquefaction of wheat straw were compared. It was discovered that sulfuric acid had the greatest catalytic effects and produced the least amount of residual biomass.

Based on other researches, increasing sulfuric acid loadings from 1% to 3% (% wt., based on liquefaction solvent) generally resulted in notable improvements in biomass liquefaction efficiency. For instance, the percent biomass residue for the liquefaction of soybean straw (Hu et al., 2012), wheat straw (H. Pan et al., 2012), and acid-hydrolyzed corncob (S. H. Lee et al., 2000) residues dropped from roughly 45% to less than 20% when sulfuric acid loadings were increased from 1% to 3%. The efficiency of biomass liquefaction was not significantly improved by raising sulfuric acid loadings to more than 3%, but there was a higher chance of harmful recondensation reactions occurring sooner (Silva et al., 2023). For most lignocellulosic biomass materials, sulfuric acid loadings of around 2–4 % provide a good balance between high liquefaction efficiency and effective retardation of detrimental recondensation reactions (Basar et al., 2021).

### **IV. Liquefaction temperature and time**

The temperature at which liquefaction occurs can vary significantly, ranging from 130 to 250 °C, primarily based on the kind of catalysts employed. While base-catalyzed liquefaction

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typically requires higher temperatures of about 250 °C to achieve comparable liquefaction efficiencies, acid-catalyzed liquefaction is typically carried out at temperatures ranging from 150–170 °C (Hernández-Ramos et al., 2023).

(Hu et al., 2012) reported that the biomass conversion ratio increased from 46% to 75% with an increase in reaction time from 45 to 360 minutes. Research from the past has shown that lignocellulosic materials like cotton stalk (Hassan and Shukry, 2008), wheat straw (Chen and Lu, 2009; Wang and Chen, 2007), corn bran (Lee et al., 2000), and bagasse can be liquefied using a PEG 400/glycerol binary solvent with biomass conversion ratios of roughly or higher than 90% in 180 minutes or less. The study's relatively lower conversion ratio could be explained by the use of different lignocellulosic biomass and a different liquefaction solvent (crude glycerol vs. PEG400/glycerol).

### **2.8 Summary of Previous Studies on the Removal of oil from water**

Various modified PUFs have been used in numerous studies to look into the adsorption of oil from wastewater. The surfaces of commercial polymer sponges, like PU and melamine sponges, can be altered with hydrophobic substances to boost their super-hydrophobicity and change their hydrophilicity to super-hydrophobicity, which significantly improves sorption selectivity (Pham & Dickerson, 2014).

Based on research conducted by (Q. Zhu et al., 2011), PUFs were first modified by electrolessly depositing a copper film onto the skeletons of the sponges, and then using a solution-immersion method to coat the skeletons with coatings that are both super hydrophobic and superoleophilic. After nine cycles, the resulting super-hydrophobic foams showed about 50–90% retention of their sorption capacity and selective sorption of different oils up to 13 times their weight.

Another study conducted by (Zhou et al., 2013), found that by treating PUFs with ferric chloride and PTES, and then adding pyrrole through vapor phase polymerization, they were able to create superhydrophobic coatings of PTES-polypyrrole. These coated foams retained about 85% of their sorption capacity after five cycles and were able to absorb oil from water at a rate of up to 20 times their own weight. Wang and Lin (2013) also developed a method to modify the surface properties of PUFs by coating them multiple times with a CNT/PDMS

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solution, drying them, and curing them at 120°C for 6 hours. The resulting superhydrophobic CNT-PDMS-coated foams had a high oil sorption capacity, up to 25 times their own weight.

This study presents a novel approach in which petroleum-based polyol is replaced with biopolyol derived from lignocellulosic biomass. This substitution enables the preparation of light, hydrophobic, and superoleophilic PUFs. These PUFs serve as ideal oil adsorbents, exhibiting exceptional performance in oil-water separation, high oil adsorption capacity, and effective oil recyclability.

### **3 MATERIALS AND METHODS**

#### **3.1 Chemicals and Equipment**

**Chemical:-** All chemicals utilized in the liquefaction of khat straw were glycerol (98%) used as a solvent, sulfuric acid (98%) as a catalyst, and sodium hydroxide (0.1N NaOH ) were used to neutralize the biopolyol were obtained from Rhankem Chemical trading. Chemicals used in the preparation of PUFs were Polyether Polyol as a source of hydroxyl groups (–OH), Toluene diphenyldiisocyanate (TDI) as a source of isocyanate groups (–NCO), and tin and amine catalysts to accelerate the reaction kinetics and surfactants to reduce surface tension, which are sponsored by the Royal Foam Factory. All chemicals were used as received without further purification.

**Equipment: -** During the experiment, various laboratory equipments were used to liquefy khat straw and prepare PUFs. The key laboratory apparatus employed in this study included a digital balance for measuring material weights, a lab mill used for crushing down khat straw, Sieve used to sieve the crushed sample of a different- sized sample, an oven drier for sample drying and moisture content measurement, Furnace to determine ash content, a beaker, a magnetic stirrer for solution mixing, an oil bath for heating the glycerol/khat straw composition, a water bath, a condenser for condensation purposes, an overhead mixer for continuous stirring of the glycerol/khat straw composition, filter paper, a pH meter for measuring the pH of the liquefied khat straw before and after neutralization, a three-necked bottom flask for placing the glycerol/khat straw composition, a cylindrical measurement used for measuring the volume of liquid samples, an Erlenmeyer flask for handling water/oil/sorbent for use on a shaker, a shaker for mixing the water/oil/sorbent, a Petri dish, a squeezer for extracting the sorbent from the flask, and a digital viscometer for measuring the sample viscosity.

#### **3.2 Raw Material preparation**

The air dried khat straw was collected from Khat Shop around Addis Ababa cultivated in SNNP region of Ethiopia. The khat straw flakes were first peeled before being placed on an

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oven dryer to dry. The dried khat straw was then mechanically pulverized using a laboratory mill. Figure 3-1 shows the process of raw material preparation.



**Figure 3-1: Peeling and crushing process of khat straw**

### **3.3 Synthesis of Biopolyol**

The method for the synthesis of biopolyol using the liquefaction process was adopted from previous studies with minor modifications (Y. Wang et al., 2009). The liquefaction process was carried out in reaction laboratory at Addis Abeba Institute of Technology (AAIT). The liquefaction process carried out under the following reaction parameters: a temperature of 160 °C, a glycerol/khat straw ratio of 5:1 (w/w), and a reaction time of 2 hours. The temperature and glycerol/khat ratio were taken as it was taken from the literature but the reaction time were dropped from 4hr to 2 hr because of the nature of the biomass. A 1000 ml flask with three necks, a temperature controller, and a heater made up the liquefaction apparatus. The motor-driven stirrer, thermometer, and reflux condenser were all attached to the three-neck flask. Ground khat straw was added to the flask after it had been preheated to 100 °C and filled with liquefying reagents (glycerol) and the catalyst sulfuric acid (10% wt., based on biomass load). The liquefaction process was run for two hours at 160 °C under reflux while being constantly stirred. To halt the liquefaction reaction, the flask was submerged in cold water following the presetting period. Table 3-1 and Figure 3-2 shows the compositions of the liquefaction system and grinding and liquefaction process of khat straw respectively.

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Table 3-1: Compositions of the liquefaction system.

Glycerol / khat (w/w)	Glycerol (g)	Khat straw (g)	Sulfuric acid(g)
5:1	50	10	1

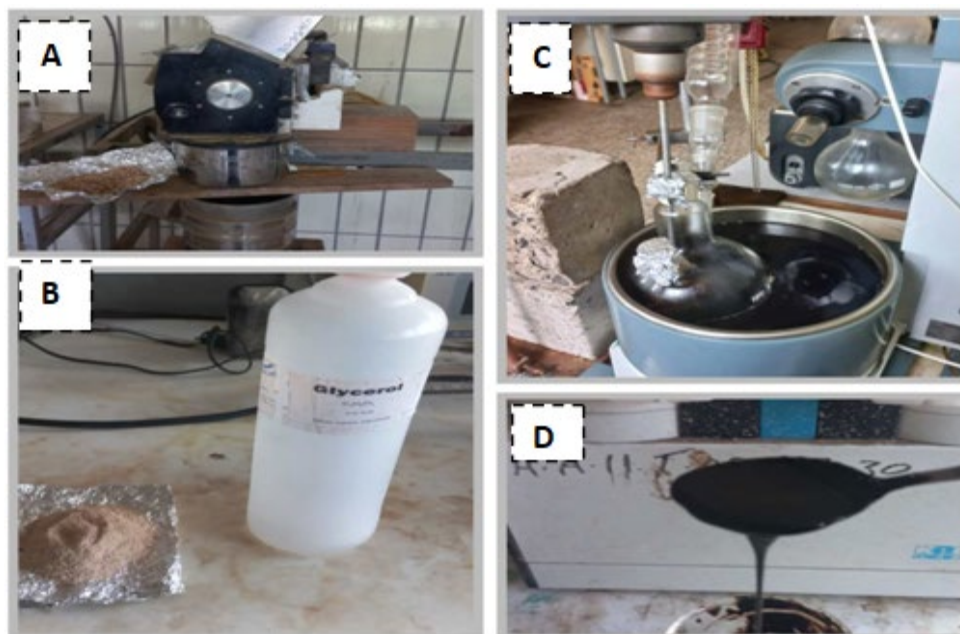


Figure 3-2: Shows A) Grinding, B) raw material preparation, C) liquefaction process of khat straw and D) biopolyols

### 3.4 Preparation of PUFs

Using the standard formulation, a two-shot method was used to prepare PUF based on biopolyol. After combining the polyol with the additives (biopolyol, catalyst, surfactant, and blowing agent) for five minutes at room temperature, all of the components were carefully combined by hand with an overhead stirrer to distribute the various proportions of the biopolyol content in the polyol. Subsequently, a specified amount of TDI was added to the plastic cup and vigorously mixed for 30 seconds at a high speed of 1000 rpm using a mixer. Following mixing, the foaming mixture is put into an open container and left to naturally expand at room temperature—a process referred to as "free-rise."

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The PUF without biopolyol (blank foam) was prepared as a control following the same procedure named, PUF-0. Finally, the foam was allowed to cure at ambient conditions for a minimum of 2 days. To prepare biopolyol-based PUFs, the quantities of biopolyol and polyol were determined based on various weight percentages of biopolyol to polyol: 25:75, 50:50, 75:25, and 100:0. These weight ratios corresponded to the samples named PUF-25, PUF-50, PUF-75, and PUF-100, respectively. For every proportion of polyol to biopolyols PUFs, three experiments were conducted. Table 3-2 summarizes the formulation for synthesis of PUFs.

Biopolyol content and remain reagents content were defined according to (1) and (2) respectively.

$$\text{Biopolyol content (w/w)} = \frac{W_{\text{biopolyol}}}{W_{\text{biopolyol}} + W_{\text{polyol}}} \times 100 \quad \dots\dots\dots (1)$$

**Where**  $W_{\text{biopolyol}}$  is the biopolyol weight, in g;

$W_{\text{Polyol}}$  is the polyol weight, in g;

$$\text{Reagent content (g)} = \text{pph of reagents} * \text{Mass of foam (g)} \quad \dots\dots\dots (2)$$

**Table 3-2: Reagents used in the synthesis of the PUFs, in parts per hundred parts of polyol (pph).**

Reagents	Parts per hundred (pph)
<b>Component A</b>	
Polyol	100
Water	4.2
Surfactant	1.01
Amine catalyst	0.182
Tin catalyst	0.2
<b>Component B</b>	
Isocyanate (TDI)	55

### **3.5 Characterization of Khat straw, Biopolyol, and PUFs**

#### **3.5.1 Characterization of Khat straw**

- **Moisture content**

1gram of khat straw sample was measured and taken in a crucible. It was spread nicely on the crucible and weighed (W1). It is heated then to 105 °C for 6 hrs. The crucible was left open during the heating process. After heating sample was removed, cooled in desiccators and then weighed until constant weight is obtained (W2).

The moisture content was determined by following equation:

$$\% \text{ moisture} = \frac{W_1 - W_2}{W_1} * 100 \dots\dots\dots (3)$$

Where: W1 = weight of sample and crucible before drying (gram).

W2 = weight of sample and crucible after drying (gram).

- **Ash content**

1 gram of sample was taken and weighted in a crucible (W1). It was then heated to 650 °C for 3 hr. During this test, the crucible was left open. After heating to the required temperature and time, the crucible was cooled in desiccators and then reweighed (W2).

The ash content was determined by following equation:

$$\% \text{ ash content} = \frac{W_2}{W_1} * 100 \dots\dots\dots (4)$$

Where: W1 = weight of dry sample before heating (gram).

W2 = weight of ash (gram).

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### **3.5.2 Characterization of Biopolyol**

- **Hydroxyl number**

In accordance with ASTM D284969, "Methods of Testing Urethane Foam Polyol Raw Materials," the following hydroxyl numbers were found in biopolyol: 25 ml of phthalate reagent and 1 g of biopolyol were heated to 110 °C for 20 minutes. 50 ml of pure 1,4-dioxane and 25 ml of distilled water were then added, and the mixture was titrated to the equivalency point using a 1M sodium hydroxide solution. The phthalate reagent was made up of a blend of 1000 g dioxane, 24.2 g imidazol, and 150 g phthalic anhydride (Silva et al., 2023).

- **Residue content**

The following procedure was used to determine the residue content: After weighing and diluting approximately 1 g of the liquefied product with 20 ml of an 80/20, v/v dioxane-water mixture, the dilution was thoroughly stirred for 4 hours. Filtered through folded filter paper, the filter residue was dried to a constant weight, and the residue content was computed (Jin et al., 2011).

- **Viscosity**

A digital viscometer (Brookfield viscometer LV DV-II + PRO, Brookfield Ameter, Middleboro, MA) was used to measure the viscosity of the biopolyol that was obtained.

- **Molecular weight distribution**

The ratio of the polyol's weight average ( $M_w$ ) to number average ( $M_n$ ) molecular weight is known as the molecular weight distribution. The method of gel permeation chromatography was used to determine the molecular weights of biopolyol. The device was made up of a Waters 410 RI detector, a Waters Ultrastyrigel 500A° column, and a Waters 515 pump. As the eluent, tetrahydrofuran was employed. The column was calibrated using a standard sample of narrowly distributed polystyrene.

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- **Functional group**

Fourier transform infrared spectroscopy (FTIR) was used to analyze the functional groups of PUFs and biopolyols. FTIR is an effective technique that produces an infrared absorption spectrum that resembles a molecular fingerprint, which is used to determine the type of chemical bond present in a molecule in the 4000-400  $\text{cm}^{-1}$  wavelength range. Using the KBr disks, FTIR spectra were obtained in a Perkin Elmer FTIR RX System with a resolution of 4  $\text{cm}^{-1}$  and 32 scans per sample. (Hernández-Ramos et al., 2023).

### **3.5.3 Characterization of PUFs**

- **Density**

Using ASTM D1622-03, the apparent densities of the PUFs were ascertained. The sample was measured in cubes that were 30 mm in length, 30 mm in width, and 30 mm in thickness. Five duplicate samples were tested for each density of PUFs, and an average value was determined.

- **Thermal behaviour**

By heating samples under carefully regulated conditions in an inert atmosphere, thermogravimetric analysis (TGA), is a technique for analyzing the thermal behavior of materials. The material's compositional stability and thermal characteristics are then revealed by plotting the data against time or temperature. A stable material will, at a given temperature range, show little loss of weight or breakdown (Santos et al., 2017). Using a simultaneous thermal analyzer (SDT Q600 TGA/DSC, TA Instrument), TGA experiments was conducted heating 10 mg of PUF sample under an inert nitrogen atmosphere to 600°C at a rate of 10°C/min (Darmadi et al., 2020).

- **Glass transition temperature (T<sub>g</sub>)**

Using DSC on a TA Instruments MDSC 2910 device (New Castle, DE 19720), the T<sub>g</sub> of each PUF was ascertained. The temperature at which a material transitions from a rigid, glassy state to a flexible, rubbery state is known as T<sub>g</sub>. It is the range of temperatures at which the mobility and behavior of the foam's polymer chains change. The PU foam becomes

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more flexible and elastic above the  $T_g$  and more rigid and brittle below the  $T_g$  (Hernández-Ramos et al., 2023). A 7–10 mg PUF sample was scanned to 100°C to remove the enthalpy relaxation effect, cooled to 50°C, and then scanned to 100°C once more. For every scan, a 50 ml/min dry nitrogen flow rate and a 10 oC/min heating or cooling rate were used. One-half of the total change in heat capacity ( $C_p$ ) over the transition region was used to define the  $T_g$  in the second scan (Rastegarfar et al., 2018).

- **Nuclear Magnetic Resonance (NMR) Spectroscopy**

Solid-state NMR analyses of the PU foams were carried out at 100 MHz on a Bruker Advances 400 spectrometer with MAS at 5 kHz. The pulse width was 1 $\mu$ s, and delay time is 2s. The number of scans is 5000. Approximately 40 mg of sample was packed in a zirconium sample tube.

- **Surface morphology of PUFs**

The Scanning Electron Microscope (SEM) Analysis has been a fundamental tool to obtain information on the morphology of the surface and for having insight into the morphology of the material. SEM is used to investigate the morphology and shape of the surface of PUFs (Arunagiri et al., 2021). The surface morphology of PUFs was investigated using a scanning electron microscope (FEI, INSPCT-F50, Germany). The characterizations were conducted in Adama Science and Technology University.

- **Compressive strengths**

A Zwick Universal Testing Machine Z005 was used to measure the mechanical tests of the foams under ambient conditions. The specimen measured 30 mm in length, 30 mm in width, and 30 mm in thickness. The crosshead movement rate was set at 2 mm/min for every sample. In accordance with ASTM D1621-10, compressive stress at 10% strain was carried out parallel to the direction of foam rise. Three duplicate specimens were tested for each compressive test of PUFs, and an average value was determined.

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## 3.6 Sorption capacity tests

The ASTM F726-99: Standard Test Method for Sorbent Performance of Adsorbents served as the foundation for the technique created to measure the sorbent's capacity to sorb water and oil. For each sorption test, three experiments were carried out in each PUFs proportion. The mean value was determined.

### 3.6.1 Oil sorption tests

50 ml of used Quartz 5000 20W-50 lubricant were added to a 100 milliliter beaker. After weighing and recording the value, the sorbent was submerged in the oil. Generally, the sorbent was removed and allowed to drain for  $30 \pm 3$  seconds after being submerged for  $30 \text{ min} \pm 28 \text{ s}$ . The saturated PUFs were then moved right away to a weighing bottle that had been pre-weighed and weighed.

The oil sorption of PUFs was calculated using the following equation:

$$\text{Oil sorption (g/g)} = \frac{st - s_0}{s_0} \text{-----} \quad (5)$$

Where  $s_0$  is the initial dry weight of PUFs and

$st$  is the weight of PUF with oil absorbed.

### 3.6.2 Water sorption tests

The PUFs were weighed before being added to a 250 ml Erlenmeyer flask that had 50 ml of water in it. After that, the sealed flask was shaken for 15 minutes plus or minus 20 seconds at 150 rpm in a shaker. Two minutes were given for the contents of the flask to settle. After removing the PUFs and letting them drain for  $30 \pm 3$  seconds, they were quickly moved to a weighing bottle that had been pre-weighed and weighed.

The water sorption was calculated using the following equation:

$$\text{Water sorption (g/g)} = \frac{S_{wt} - s_0}{s_0} \text{-----} \quad (6)$$

Where  $s_0$  is the initial dry weight of PUFs and

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$s_{wt}$  is the wet weight of PUFs (after water sorption).

### 3.6.3 Water/oil system sorption tests

100 ml of deionized water were placed in a 250 ml Erlenmeyer flask, and different amounts of used Quartz 5000 20W-50 lubricant were added. The oil film had a maximum thickness of 1 cm. The Erlenmeyer flask was first filled with the sorbent after it had been weighed. After that, the sealed flask was put in a shaker set to 150 rpm and shaken for 60 to 120 min. Every test was run at  $23 \pm 4$  °C. Two minutes were given for the contents of the flask to settle. After removing and weighing the sorbent, it was added to the petridish and dried at 100 °C to remove the water until the weight of the mixture remained constant.

The amount of water absorbed can be calculated as:-

$$\text{Water sorption} = M_f - M_i \quad \text{-----} \quad (8)$$

Where  $M_f$  – weight of sorbent (after placed in drying oven)

$M_i$  - weight of sorbent (before placed in drying oven)

Lastly, the following equation was used to determine the oil sorption in the water-oil system:

$$\text{Oil sorption} = \frac{M_t - M_0}{S_0} \quad \text{-----} \quad (9)$$

Where  $M_0$  is the constant weight Petri dish,  $S_0$  is the initial dry weight of sorbent.

$M_t$  is the weight of constant weight petridish with absorbed oil and

### 3.7 Investigating effect of process parameters on oil sorption capacity

One-factor-at-a-time (OFAT) were conducted for the testing of process factors once at a time rather than multiple factors simultaneously, to demonstrate the effect of only one parameter and to select parameter ranges for optimization trials. In this test the effect of one factor was investigated by keeping all the other factors at constant value. In every PUF proportion, three experiments were conducted for every sorption test. The mean value was determined. Table 3-3 shows the Factors and their study level for the OFAT experiment.

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Table 3-3: Factors and their study level for the OFAT experiment.

Biopolyol content (%)	Oil type	Contact time (min)
PUF-O	Quartz 5000 20W	30
PUF-25	Quartz 5000 20W	30
PUF-50	Quartz 5000 20W	30
PUF-75	Quartz 5000 20W	30
PUF-100	Quartz 5000 20W	30
PUF-25	Quartz 5000 20W	60
PUF-25	Quartz 5000 20W	90

### ➤ Characterization of Wastewater

The wastewater was characterized to determine its properties, which included the examination of various parameters and tested as per ASTM. The parameters examined in this study were oil and grease concentration, pH level, conductivity, and temperature.

### 3.8 Experimental Design

In this research, the Response Surface Methodology (RSM) employing the Box Behnken Design (BBD) was utilized to design the experimental setup. Three factors were selected for investigation as shown in Table 3-4. This methodology is commonly employed in engineering problem-solving scenarios to optimize and develop solutions. The Design Expert software 13.0.0 was used to design the trials and study the oil sorption capacity of PUFs on oil/water system. The biopolyol content (0% - 50%), oil to water percentage (15 – 25, v/v %), and contact time (60min – 120min) were chosen as process variables, and the working range was determined by the results of OFAT tests. BBD provides a balanced design by ensuring an equal number of experiments at various levels of the factors. This balanced distribution is critical because it allows for better estimation of main effects and interactions, resulting in more reliable optimization results. By providing a balanced representation of the

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experimental conditions, BBD aids in the reduction of biases caused by uneven factor distribution.

**Table 3-4: Level and code of variables used for RSM.**

Factors	Unit	Coded symbol	Level	
			Low	High
Biopolyol content	%	A	0	50
Oil to water percentage	%	B	15	25
Contact Time	Min	C	60	120

**Table 3-5: BBD experimental design**

Std	Run	Biopolyol content %	Oil to water percentage (v/v %)	contact time (min)
1	2	0	15	90
2	9	50	15	90
3	14	0	25	90
4	1	50	25	90
5	16	0	20	60
6	11	50	20	60
7	12	0	20	120
8	15	50	20	120
9	4	25	15	60
10	7	25	25	60
11	8	25	15	120

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12	13	25	25	120
13	17	25	20	90
14	5	25	20	90
15	10	25	20	90
16	6	25	20	90
17	3	25	20	90

## **4 Results and Discussion**

### **4.1 Physicochemical Characterization of Khat straw and Biopolyol**

#### **4.1.1 Moisture content**

Three samples of khat straw were examined and three different measurements were taken to determine its moisture content. Subsequently, the moisture content of each sample was calculated using equation (1), yielding an average value of  $11 \pm 0.833\%$ . According to various studies, the moisture content of various straw types when measured on a dry basis ranges from 0% to 10% (Gabriel et al., 2021). Biomass used for liquefaction should have a low moisture content to reduce the amount of energy required for drying and prevent steam formation during the process.

#### **4.1.2 Ash content**

The ash content of khat straw was determined using equation (2) and three samples' values were recorded. While existing literature suggests that khat straw has an ash content of 3.40% (Gabriel et al., 2021), the average value obtained from this experiment was 5.27%, indicating that the ash content is slightly higher than reported in the literature.

#### **4.1.3 Hydroxyl number, Molecular weight distribution, and Residue content of Biopolyol**

The synthesis of biopolyols involved the liquefaction of Khat straw, employing specific reaction conditions consisting of a glycerol-to-Khat straw ratio of 5:1, a temperature of 160°C, and a reaction time of 2 hours. These procedures were replicated five times, ensuring that the same reaction conditions were maintained throughout each repetition.

The hydroxyl number and molecular weight distribution of biopolyol are the two important parameters in preparing the PUFs. The biopolyol samples derived from the synthesis process exhibited an average hydroxyl number of 411 mgKOH/g and a molecular weight distribution of 1.29, as determined through standard testing methods. These values indicate that the synthesized biopolyol possesses suitable characteristics in terms of hydroxyl value and

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molecular weight distribution, making it a viable polyol option. Consequently, this type of biopolyol shows promise as a potential alternative resource for the production of PUFs. The average residue content observed in the five biopolyol samples was 4.1%.

### **4.1.4 Viscosity**

The biopolyol, obtained from the liquefaction of khat straw, demonstrated an average viscosity of 1.71 Pa.s across the five samples. In comparison, the viscosity of petroleum-based polyol was measured to be 1.85 Pa.s. Thus, the viscosity of the biopolyol falls within a feasible range for the production of PUFs.

### **4.1.5 Fourier Transform Infrared Spectroscopy (FTIR) Analysis of Biopolyol**

The functional group of biopolyol were analysed as shown on Figure 4-1. Due to hydroxyl groups, the FTIR spectra exhibit a strong bond stretching band at 3428  $\text{cm}^{-1}$ . This band corresponds to the -OH stretching vibration and is linked to free  $\text{H}_2\text{O}$  and the -OH groups of non-bonded polyol. This peak's existence suggested that there were a lot of -OH groups in the biopolyol. At 1731  $\text{cm}^{-1}$ , a stretching band was seen, suggesting the presence of esters, or carbonyl groups. In addition, there is a stretching peak at 1100  $\text{cm}^{-1}$ , which suggests the existence of C-O bonds. The synthesis of biopolyol from pure glycerol was successfully confirmed by the presence of expected characteristic structures. The functional groups that were found in the liquefied khat straw's FTIR spectrum are summarized in Table A-1.

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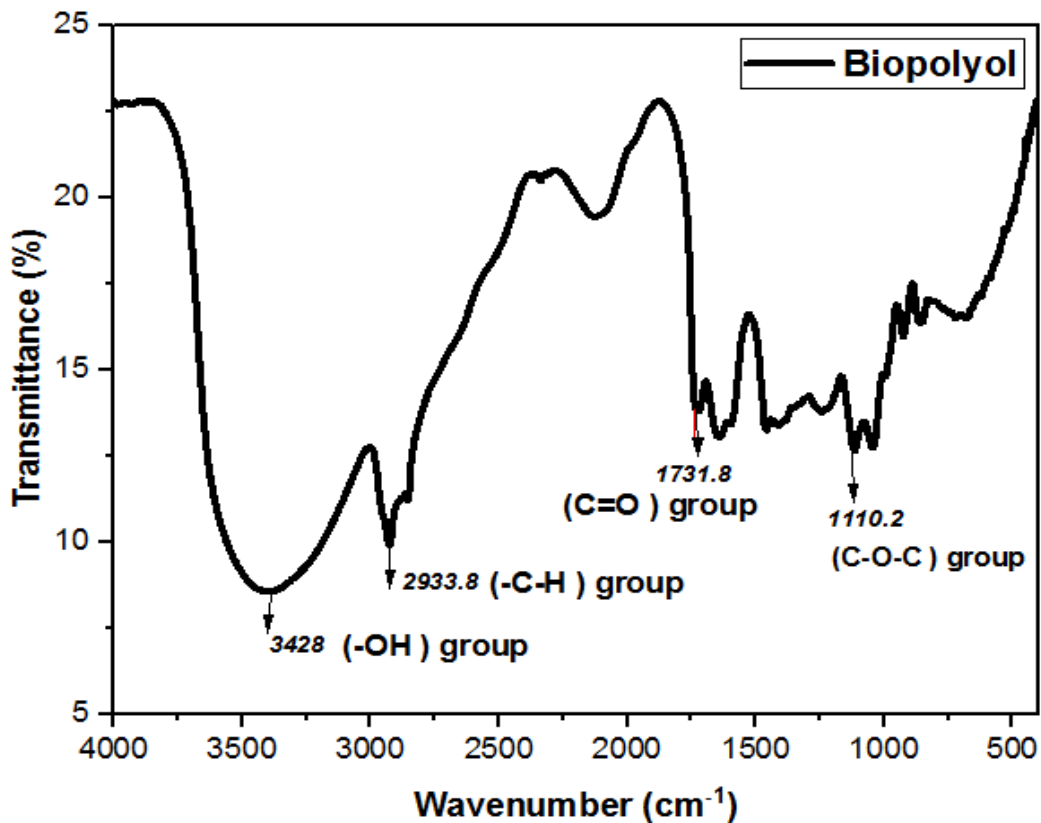


Figure 4-1: FTIR analysis of Biopolyol

### 4.2 Effects of biopolyol/polyol proportion on PUFs

Using the two-shot technique, blank and biopolyol-based PUFs were created using different ratios of petroleum-based polyol and biopolyol. The cream time, gel time, and rise time were found to be longer when the biopolyol content was increased in the PUF preparation laboratory experiment. The duration required for the polyol and isocyanate mixture to transition from a clear to a creamy color is known as the "cream time." The initial reaction between the polyol and isocyanate takes place during the cream time, forming a thicker, more viscous mixture. The rise time is the amount of time required for the foam to fully expand and solidify, and the gel time is the amount of time required for an infinite network to form (Cinelli et al., 2013). In Table 4-1 show the composition of the chemicals and the values of cream time, gel time, and rise time measured.

Based on the provided table, it can be observed that a higher quantity of biopolyol in the foam leads to an increase in cream time, gel time, and rise time, implying slower reaction kinetics. This implies that the foam's expansion kinetics may be influenced by the quality of

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the biopolyol and how it interacts with other components. Moreover, as the biopolyol content increases from 0% to 100%, there is a color transition in the PUFs from white to dark brown, potentially attributed to the color of the biopolyol itself. Figure 4-2 shows PUFs produced using different biopolyols percentage.

**Table 4-1: Formulations (grams) used for synthesis of PUs and values of cream time and rise time (s).**

	Weight % of Biopoyol content				
	0%	25%	50%	75%	100%
<b>Biopolyol (g)</b>	0	3.725	7.47	11.175	14.9
<b>Polyol (g)</b>	14.94	11.175	7.47	3.725	0
<b>Water (g)</b>	0.628	0.628	0.628	0.628	0.628
<b>Surfactant (g)</b>	0.152	0.152	0.152	0.152	0.152
<b>Amine catalyst (g)</b>	0.028	0.028	0.028	0.028	0.028
<b>Tin catalyst (g)</b>	0.03	0.03	0.03	0.03	0.03
<b>Isocyanate (g) (TDI)</b>	8.22	8.22	8.22	8.22	8.22
<b>Cream time (s)</b>	10	15	45	65	115
<b>Gel time (s)</b>	15	20	70	100	125
<b>Rise time (s)</b>	20	30	100	120	140

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Figure 4-2: PUFs produced using different biopolyols percentage.

### 4.3 Physicochemical Characterization of PUFs

#### 4.3.1 Scanning Electron Microscope (SEM) Analysis, Density, and Mechanical Property of PUFs

The surface morphology of the five PUFs samples is shown in Figure 4-3 below. The pore surface of PUF-0 and PUF-25 exhibited a predominantly regular and smooth appearance. The cellular structure of the biopolyol-based PUFs was found to be influenced by the amount of biopolyol present in the PU matrix. As the bio polyol content increased, the cellular shape became more irregular and heterogeneous, resulting in the formation of larger cells. This change in cell morphology is likely attributed to the impact of biopolyol on the process of cell nucleation during the preparation of PU foams. Furthermore, it was observed that the cell structure of PUF-75 and PUF-100 differed from that of PUF-25 and PUF-50. This discrepancy is likely due to the poor dispersion of biopolyol within the PU foam matrix when the bio polyol content exceeded 50%.

The experimental data presented in Table 4-2 indicates a positive correlation between the percentage of biopolyol and foam density. As the percentage of biopolyol increases from 0% to 100%, there is a corresponding increase in the density of the foam from 29.28 kg/m<sup>3</sup> to 289.75 Kg/m<sup>3</sup>. This relationship can be attributed to the thickening effect caused by the addition of biopolyol. When biopolyol is added to the foam formulation, it introduces additional unliquefied residue into the system, as evidenced by the measured residue content

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of 4.1% in the biopolyol. These residues can contribute to an overall increase in the mass or packing of the foam material.

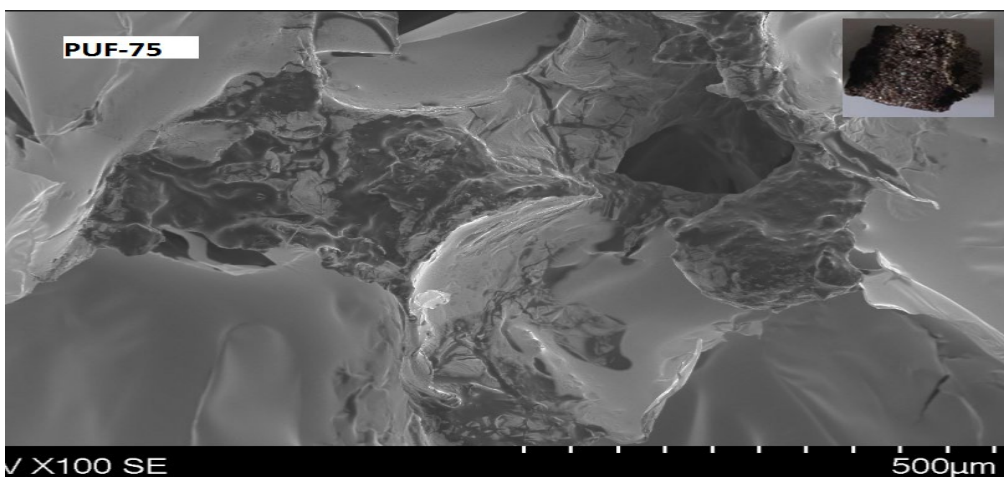
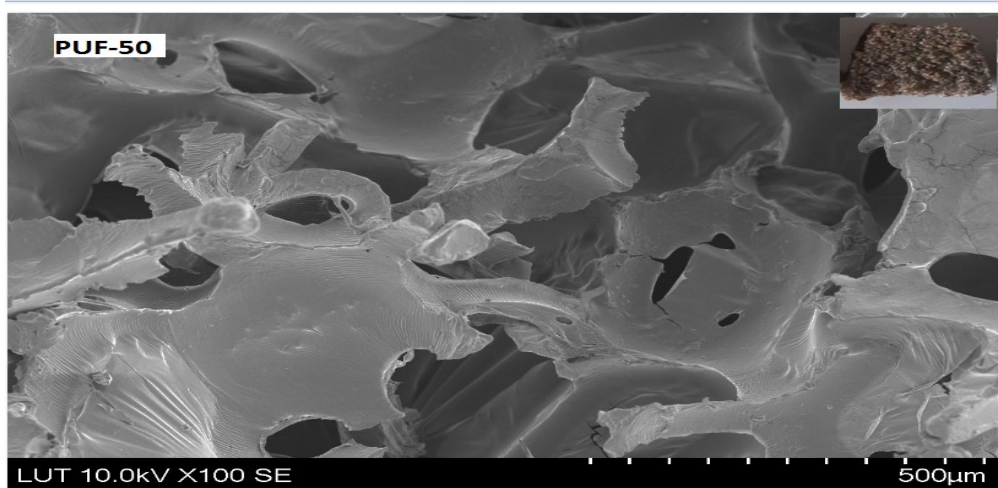
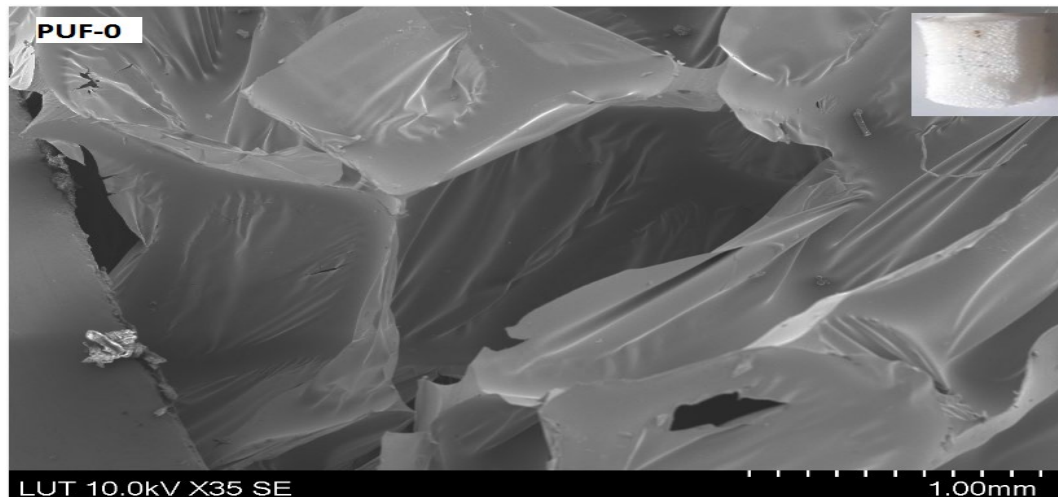
The compressive strength of the foams based on biopolyols decreased significantly as the biopolyol content increased in comparison to blank PUFs. As the biopolyol content rose from 25% to 100%, the compressive strength of the foams based on biopolyol fell from 288 to 90 KPa. When compared to pure polyol, the biopolyol-based foams had a lower cross-linking density and compressive strength because of the relatively small amount of hydroxyl groups in the biopolyol.

**Table 4-2: Density and Compressive strength of PUFs.**

<b>No</b>	<b>PUFs</b>	<b>Density (Kg/m<sup>3</sup>)</b>	<b>Compressive strength (KPa)</b>
1	PUF-O	29.28175	291
2	PUF-25	54.853	288
3	PUF-50	94.467	260
4	PUF-75	167.541	100
5	PUF-100	289.75	90

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**Figure 4-3:** SEM pictures of various PUFs' cross section

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### **4.3.2 Fourier Transform Infrared Spectroscopy (FTIR) Analysis**

Figure 4-4 shows the FTIR analysis performed on PUF-0 (blank foam) and biopolyol-based foams (PUF-25, PUF-50, and PUF-75), which indicates that there were no significant differences observed in the chemical structure of the PUFs when biopolyol was added as a substitute for petroleum-based polyol.

The FTIR spectra show characteristic absorption bands that are indicative of the presence of specific chemical groups in the foam samples. A strong absorption band at  $3432.4\text{ cm}^{-1}$  corresponds to the N-H group, which is a characteristic feature of urethane structures. Additionally, an absorption band at around  $1742.8\text{ cm}^{-1}$  indicates the presence of carbonyl groups (C=O) of urea linkages in the urethanes (Cinelli et al., 2013; Santos et al., 2017). The presence of these specific absorption bands in the FTIR spectra confirms that the PUFs samples contain urethane structures, regardless of the incorporation of biopolyol. This suggests that the chemical integrity and formation of urethane bonds were preserved in the foam samples, even with the addition of biopolyol. Another notable absorption band observed between  $2880\text{-}2890\text{ cm}^{-1}$  represents C-H stretching, which is characteristic of hydrocarbon groups. This further supports the presence of PU materials in the foam samples (Santos et al., 2017). In contrast to other PUF-25 and PUF-75 samples, they exhibited weaker absorption at  $2360\text{ cm}^{-1}$ , indicating the presence of a small quantity of unreacted isocyanate (-NCO group). This can be attributed to the steric hindrance caused by the biopolyol structure, and a strong peak at  $1045.6\text{ cm}^{-1}$  was observed, indicating the deformation of C-O and C-O-C bonds, respectively.

The FTIR spectra show the expected FTIR characteristic structures, such as urethane-specific bands, confirming the successful synthesis of PUFs with biopolyol as a substitute for petroleum-based polyol. These findings show that the chemical structure of the foam was preserved, and biopolyol incorporation did not cause significant changes in the PU composition. Common peaks and associated functional groups that are usually seen in the FTIR graph of polyurethane foam are summarized in Table A-2.

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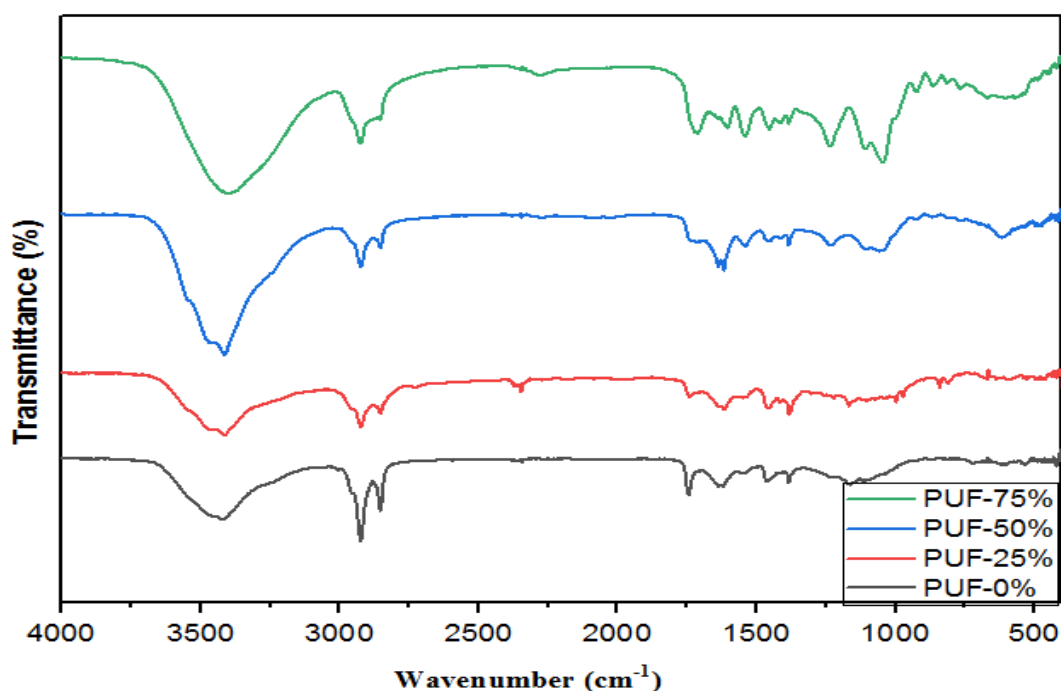


Figure 4-4: FTIR analysis of blank and biopolyol based PUFs.

### 4.3.3 Nuclear Magnetic Resonance (NMR) Analysis

Figure 4-5 illustrated the H-NMR spectrum analysis of the blank foam and biopolyols based PUFs. The spectrum provided important information about the relative signals and chemical shifts of the various protons present in the PUFs. On the blank foam curve, the formation of urethane linkages—more precisely, NHCOO—was confirmed by the presence of a single peak at 8.76 ppm. Furthermore, the protons in the methoxy group and the aromatic protons were identified as the source of a single peak at 3.87 ppm and multiplet peaks ranging from 7.53 to 6.99 ppm, respectively. The polyol's aliphatic chain was found to be between 1.23 and 1.64 ppm in concentration. In PUFs based on biopolyol, the amine proton of the urethane linkage was identified as the peak at 3.1 ppm, and the isomannide methylene protons were identified as the signals that occurred between 3.5 and 5.2 ppm. It should be noted that due to the quality of the biopolyols, there may be additional side reaction peaks in the NMR analysis of biopolyol-based PUFs. These consistent and prominent peaks observed in both FTIR and NMR analyses provide strong evidence that the reaction between the materials took place and successfully led to the preparation of PUFs.

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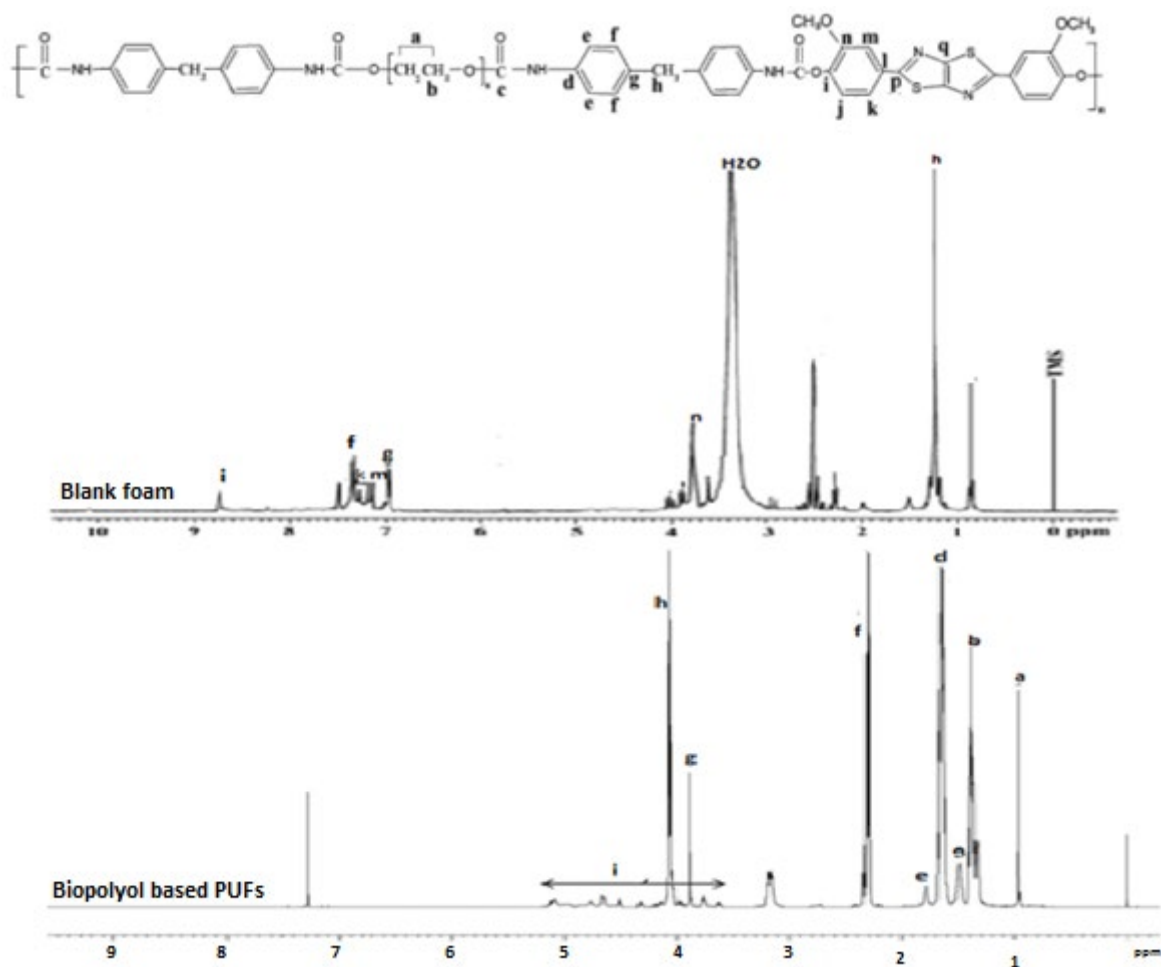


Figure 4-5: NMR analysis graph

### 4.3.4 Thermogravimetry (TGA) and Differential Scanning Calorimetric (DSC) analysis

Figure 4-6 shows degradation and rate of weight loss TGA, and DTGA curves of the blank and biopolyol-based PUFs. The weight loss curves for PUF-0 to PUF-50 samples had similar shapes, with the exception of PUF-75. PUF samples ranging from PUF-0 to PUF-50 exhibit a slight reduction in weight below 200°C, which is attributed to the evaporation and removal of adsorbed and surface water present in the PUFs. The TGA revealed major two stages of weight loss in the PUF-0 to PUF-50 samples. The initial mass loss between 200 and 350°C is attributed to the decomposition of the urethane group, while a second mass loss between 400 and 600°C is associated with the breakage of C-C bonds and the decomposition of the remaining materials from the first stage of thermal degradation (Oribayo et al., 2017; Zilouei

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& Asadinezhad, 2015). The reduction in thermal stability is reflected in the decrease in  $T_{\text{onset}}$ , which indicates the temperature at which the foam starts to undergo significant decomposition (H. Wang et al., 2011; Zilouei & Asadinezhad, 2015). The lower  $T_{\text{onset}}$  observed with higher biopolyol concentrations indicates that the foam is more susceptible to thermal degradation at lower temperatures, as the weakened cross-linking structure allows for easier breakage of chemical bonds and degradation of the polymer matrix. Additionally, the mass loss between 200 and 350°C for the biopolyol-based foam is slightly higher compared to the blank PUFs. This can be attributed to the thermal decomposition of the unliquefied biomass attached to the foam's skeletons. According to (Javni et al., 2000), the first stage, which occurred between 200°C and 300°C, involved the dissociation of urethane linkages to form isocyanates, alcohols, amines, and olefins, resulting in the release of CO<sub>2</sub>. Urethane bonds, which are commonly found in thermally unstable materials, decompose between 150 and 220°C, depending on the substituent present on the isocyanate and polyol sides.

In the case of PUF-75, the first stage of weight loss begins before 58°C, indicating that it is a less stable material than the other samples. This lower stability is due to a higher proportion of biopolyol content replacing petroleum-based polyol in the foam formulation. As a result, the critical reaction between the polyol and isocyanate that forms the urethane bond may not have occurred to the expected extent. This substitution of biopolyol content appears to affect the foam's stability and thermal behaviour, resulting in an earlier onset of weight loss.

During the TGA analysis, the foams PUF-0, PUF-75, and PUF-50 demonstrated decreasing levels of mass loss, with PUF-0 having the greatest mass loss, followed by PUF-75, and then PUF-50. In contrast, PUF-25 showed a lower mass loss. This suggests that PUF-25 is more thermally stable foam than PUF-0, PUF-75, and PUF-50. PUF-25 is less prone to significant mass loss when exposed to high temperatures, indicating greater thermal stability than the other foam compositions.

Figure 4-7 shows the Dsc curve of PUFs samples. The foam material exhibited a glass transition temperature ( $T_g$ ) of around 50°C up to 80 °c. The DSC curves obtained for the different PUF samples with varying proportions of biopolyol did not show a significant change. This suggests that the addition of biopolyol did not have a substantial effect on the thermal transitions observed in the DSC analysis. However, there was one notable difference

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observed in the DSC curves. The samples labeled PU-25 up to PUF-75, which had a biopolyols composition, exhibited a  $T_g$  approximately  $50^\circ\text{C}$  higher than the other PUF samples. This indicates that the addition of biopolyol in this specific proportion resulted in a significant increase in the  $T_g$  of the foam. Additionally, no hard segment endotherm was observed in any of the DSC curves. Hard segments in polyurethane foams typically exhibit an endothermic peak due to their crystalline nature. However, the absence of this peak in the DSC curves suggests that the addition of biopolyol led to a lower degree of crystallinity in the hard segment of the PUFs.

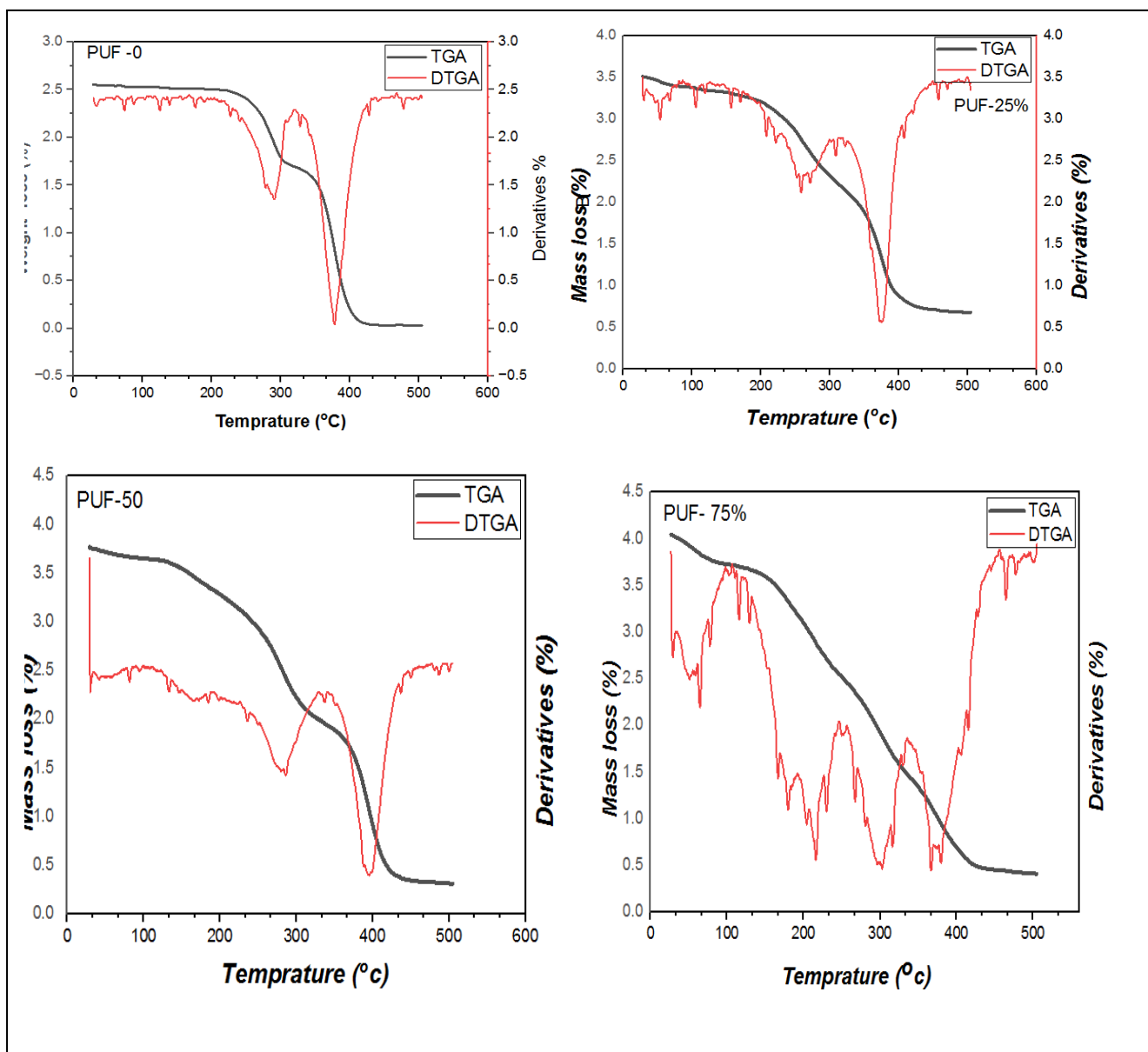
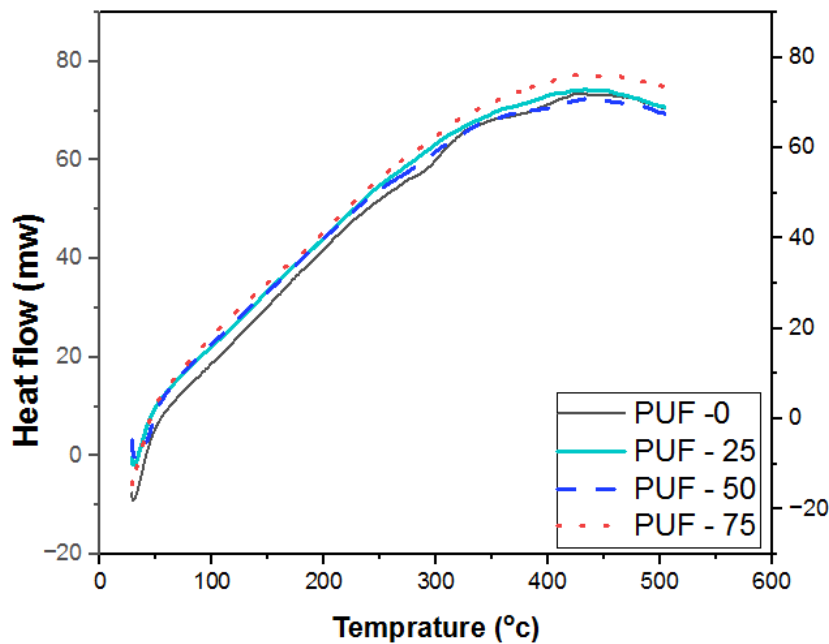


Figure 4-6: TGA and DTGA curves of blank and biopolyol-based PUFs.

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**Figure 4-7: DSC curves of blank and biopolyol based PUFs.**

### ➤ Characteristics of used oil

Quartz 5000 20W-50 are type of oil that are commonly used as lubricant for internal combustion engines in cars, motorcycles, and other vehicles. According to the information provided from Table 4-3, Quartz 5000 20W-50 has high viscosity and density. These properties may have an impact on foam's sorption efficacy.

**Table 4-3: Measured value of RubiaTir 7400 15W-40 and Quartz 5000 20W-50.**

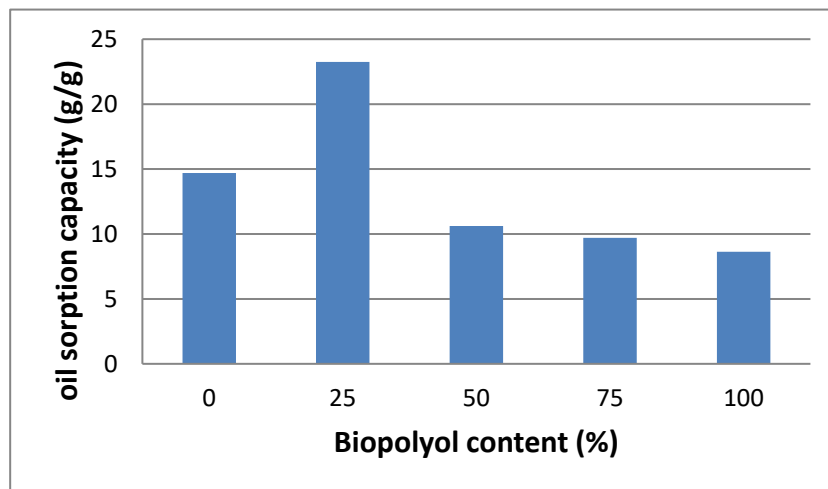
Oil type	Viscosity (m pa.s) @17°C	Density kg/m <sup>3</sup>
Quartz 5000 20W-50	444	859.47

### 4.4 Effect of biopolyols content and contact time on oil sorption capacity

As one-factor-at-a-time (OFAT) experiments investigated whether the biopolyol content varied on the formation of PUFs had an effect on oil sorption capacity on Quartz 5000 20W-50 oil, there was a decrease in sorption capacity while increasing the biopolyol content of the foam. Oil sorption capacity varies primarily due to viscosity, density, and surface tension. In general, the higher the density and viscosity of an oil, the better its sorption capacity (J. Wang & Geng, 2015; Y. Yang et al., 2015). It took a few minutes for reached maximum sorption

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uptake in a low-viscosity organic solvent (Quartz 5000 20W-50). The maximum sorption capacity of PUF-25 in Quartz 5000 20W-50 oil was 23.54 g/g, this means the PUF-25 foam was excellent oil sorbent with a sorption capacity of 23.54 times its own weight. The sorption capacity of PUF - 0 for Quartz 5000 20W-50 oil were 14.6 g/g. Based on this observation, the working range of biopolyol content for optimization analysis was selected as 0–50 wt% biopolyol because, above this percentage, the foam oil sorption capacity decreased. Figure 4-8 shows effect of biopolyol content and Quartz 5000 20W-50 on oil sorption capacity of PUFs.



**Figure 4-8: Effect of biopolyol content and Quartz 5000 20W-50 on oil sorption capacity of PUFs.**

Contact time had a positive effect on the oil absorption capacity. The oil sorption capacity of PUF-25 increased from 24.69 to 28.55 g/g, while contact time increased from 30 to 90 min in Quartz 5000 20W-50 oil. Depending on those results, the working range of contact time for optimization analysis was fixed at 60–120 min because sorption capacity increases as time increases, so the previous time range was modified.

Biopolyol content vs. water sorption shows an inverse relationship between biopolyol content and water sorption capacity. Water sorption capacities of PUF-0, PUF-25, PUF-50, PUF-75, and PUF-100 at constant contact time were obtained 2.38, 4.39, 3.82, 0.49, and 0.21 g/g, respectively. As the biopolyol content rises, the water absorption capacity decreases. This observation suggests that increasing the biopolyol content increases the foam's hydrophobic properties, which makes the foam more unlikely to absorb or retain water. The foam's

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hydrophobic nature is useful in applications involving oil-water separation because it allows it to selectively absorb oil while repelling water. However, this does not necessarily imply an increase in the foam's oilophilic (oil-absorbing) properties. Although the hydrophobic property of the foam is important for oil-water separation via sorption, foams containing more than 50% biopolyol have a low oil sorption capacity, making them unsuitable for the intended use.

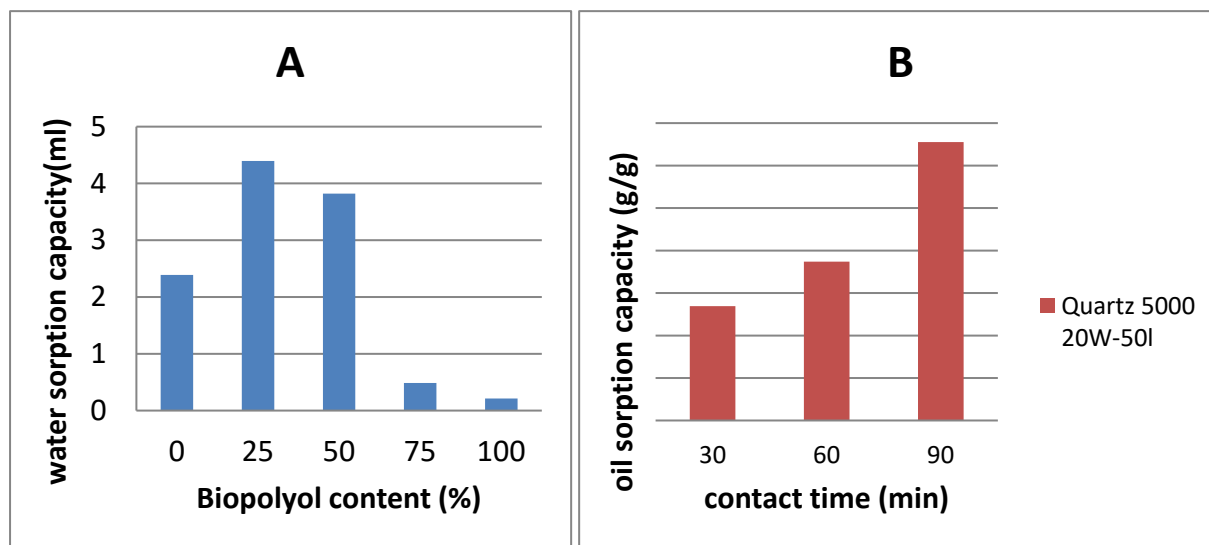


Figure 4-9: A) Biopolyol content Vs water sorption capacity and B) Contact time Vs oil sorption capacity.

### 4.5 Statistical Analysis of the Experimental Results

#### 4.5.1 Experimental Data

The Box-Behnken design (BBD) was chosen with a three-level, three-factor design that addressed the biopolyol content (0 – 50%), oil to water percentage (15–25, v/v%), and the contact time (60–120 min) to optimize the oil sorption capacity of biopolyol/polyol based polyurethane foam. Based on the BBD experimental design, these experimental parameters and their outcomes are presented in Table 4-4. Design-Expert 13 software was used to conduct 17 planned experiments and analyze the data using multiple regressions.

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**Table 4-4: The value of experimental data and predicted data at selected parameter values.**

<b>Std</b>	<b>Run</b>	<b>Biopolyol content %</b>	<b>Oil to water percentage (v/v%)</b>	<b>contact time (min)</b>	<b>Actual:- oil sorption capacity (g/g)</b>	<b>Predicted: oil sorption capacity g/g</b>
1	2	0	15	90	15.04	15.00
2	9	50	15	90	13.42	13.82
3	14	0	25	90	16.75	16.35
4	1	50	25	90	14.12	14.16
5	16	0	20	60	14.90	15.19
6	11	50	20	60	14.27	14.12
7	12	0	20	120	14.21	14.36
8	15	50	20	120	12.36	12.07
9	4	25	15	60	23.61	23.35
10	7	25	25	60	26.94	27.05
11	8	25	15	120	24.88	24.77
12	13	25	25	120	22.51	22.76
13	17	25	20	90	22.08	22.48
14	5	25	20	90	22.64	22.48
15	10	25	20	90	22.43	22.48
16	6	25	20	90	22.12	22.48
17	3	25	20	90	23.12	22.48

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### 4.5.2 Model Summary Statistics

The software recommended utilizing the Quadratic model for this task. By applying RSM, a practical connection can be found between the response function and the independent variables, leading to successful outcomes. Table 4-5 shows suggested model for design.

**Table 4-5: Suggested model for the design.**

Source	Sequential p-value	Lack of Fit p-value	Adjusted R <sup>2</sup>	Predicted R <sup>2</sup>	
<b>Linear</b>	0.9378	< 0.0001	-0.1937	-0.8848	
<b>2FI</b>	0.9680	< 0.0001	-0.5143	-3.2581	
Quadratic	<b>&lt; 0.0001</b>	<b>0.4000</b>	<b>0.9913</b>	<b>0.9674</b>	<b>Suggested</b>
<b>Cubic</b>	0.4000		0.9922		<b>Aliased</b>

### 4.5.3 Analysis of variance (ANOVA)

Analysis of variance (ANOVA) for the oil sorption capacity obtained using Box Benken Design (BBD) is shown in Table 4-6. Sum of squares is Type III – Partial. The Model F-value of 204.07 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, BC, A<sup>2</sup>, B<sup>2</sup>, C<sup>2</sup> are significant model terms. The biopolyol content (A) is highly significant parameters relative to others with F-value of 27.92, followed by contact time (C) with F-value of 20.48 and oil to water percentage (B) with F-value of 7.07 and the interaction effect between oil to water percentage and contact time (BC) is highest with F-value of 40.13. This shows the oil sorption capacity of PUF affected by all process variables and the interaction between oil to water percentage and contact time. Compared to the pure error, the Lack of Fit shows up to be insignificant, as indicated by the F-value of 1.26 for the Lack of Fit. This significant Lack of Fit F-value has a 40.00% probability of being noise-related. A low degree of inconsistency is acceptable.

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**Table 4-6: Analysis of Variance (ANOVA) for quadratic model.**

Source	Sum of squares	Df	Mean Square	F -value	p-Value	
Model	372.48	9	41.39	204.07	< 0.0001	Significant
A-Biopolyol content	5.66	1	5.66	27.92	0.0011	
B-Oil to water percentage	1.43	1	1.43	7.07	0.0326	
C-Contact time	4.15	1	4.15	20.48	0.0027	
AB	0.2543	1	0.2543	1.25	0.2997	
AC	0.3767	1	0.3767	1.86	0.2151	
BC	8.14	1	8.14	40.13	0.0004	
A <sup>2</sup>	348.40	1	348.40	1717.91	< 0.0001	
B <sup>2</sup>	8.86	1	8.86	43.69	0.0003	
C <sup>2</sup>	1.30	1	1.30	6.41	0.0392	
Residual	1.42	7	0.2028			
Pure Error	0.7297	4	0.1824			

#### 4.5.4 Model Adequacy Checking

The variation of oil sorption capacity as fraction of process variables is described by checking adequacy of the model. It is performed by using  $R^2$ , Adj  $R^2$ , Pred  $R^2$  and Adeq Precision.

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**Table 4-7: Model adequacy check.**

<b>Std. Dev.</b>	<b>0.4503</b>	<b>R<sup>2</sup></b>	<b>0.9962</b>
<b>Mean</b>	9.14	<b>Adjusted R<sup>2</sup></b>	0.9913
<b>C.V. %</b>	2.35	<b>Predicted R<sup>2</sup></b>	0.9674
		<b>Adeq Precision</b>	43.3879

The correlation between experimental and predicted responses can be accurately evaluated by the regression coefficient ( $R^2$ ), as demonstrated in Table 4-7. The results of  $R^2 = 0.9962$  and  $Adj-R^2 = 0.9913$  indicate a strong agreement between the predicted and experimental values. Since the ideal range for  $R^2$  is between 1 and 0, a value closer to 1, such as 0.9962, suggests a high-quality fit between the model equation and experimental data. This is further supported by the results of this investigation, where an  $R^2$  value of 0.9962 was obtained, indicating a strong correlation between the experimental and predicted data. The predicted  $R^2$  of 0.9674 is in reasonable agreement with the adjusted  $R^2$  of 0.9913, i.e., the difference is less than 0.2. Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 43.388 indicates an adequate signal. This model can be used to navigate the design space.

#### **4.5.5 The Regression Model Equation**

The following is the model equation that describes how the response to independent variables relates to actual factors:

The final equation in terms of Actual factor is:

$$\text{Oil sorption capacity} = 23.85506 + 0.771231L - 1.33014V + 0.065300R - 0.002017LV - 0.000409LR - 0.009509VR - 0.014554L^2 + 0.058026V^2 + 0.000617R^2$$

Where; L- Biopolyol content,

V- Oil to water percentage,

R- Contact time.

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The equation in terms of actual factors can be used to make predictions about the response at given levels of each factor. The intercept term represents the expected oil sorption capacity when all factors are set at their zero levels, while the coefficients indicate the impact of each factor on the oil sorption capacity. Positive coefficients signify an increasing effect, whereas negative coefficients imply a decreasing effect. The quadratic terms capture the curvature of the response surface, and the interaction terms denote the combined effects of factors. Overall, the equation provides valuable insights into the influencing factors and their interactions on the oil sorption capacity of PUFs.

### 4.5.6 Diagnostic Plot

The generated model's adequacy was assessed using graphical analyses such as expected vs. actual yield, residual vs. predicted yield, and a residual normal plot.

#### 4.5.6.1 Normal plot of residuals

Figure 4-10 displays a linear plot comparing the normal probability distribution to the externally standardized graph. The majority of data points align closely along the straight diagonal line, indicating a strong correspondence between observed and expected values. However, there are a few residual points that deviate from this pattern. The graph suggests that there are no high-leverage data points, which are outliers that have a substantial impact on the model.

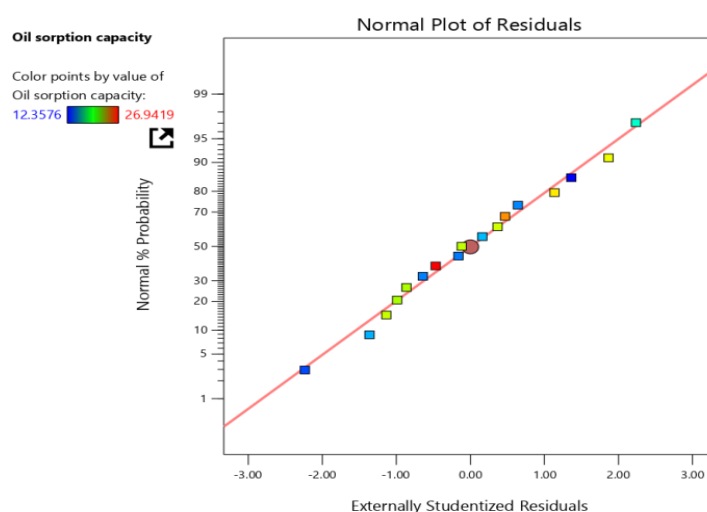


Figure 4-10: Normal plots of residuals for oil sorption capacity.

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## 4.5.6.2 Residual Vs Predicted

The scatter plot of residuals versus predicted yield provides valuable insights into the accuracy and reliability of the model. The scattered distribution of residuals suggests the absence of systematic errors within the model. When the residuals are randomly scattered around zero with no discernible pattern or trend, it indicates that the model is capturing the underlying relationships between the predictors and the response variable effectively. This suggests that the model is not biased towards overestimating or underestimating the yield consistently. The absence of systematic errors in the residuals strengthens the reliability of the model's predictions. It implies that the model is providing unbiased estimates of the yield and that its predictions are not systematically skewed in one direction. This is crucial for making reliable decisions based on the model's output.

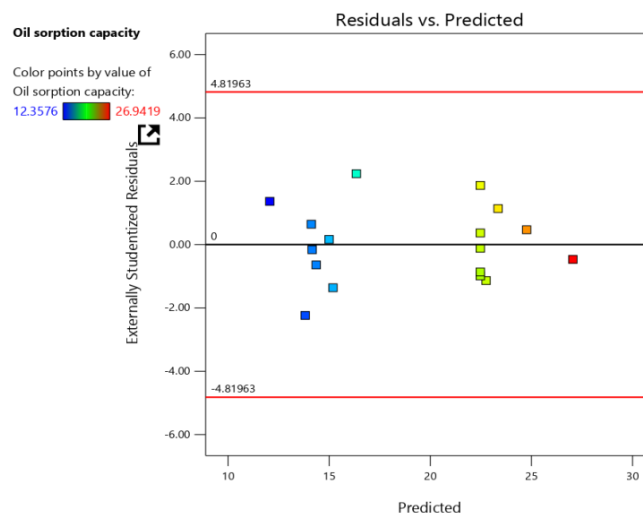


Figure 4-11: Plot of residuals versus predicted for sorption capacity.

## 4.5.6.3 Predicted vs. Actual

The linear diagonal alignment of data points in the predicted versus actual graph shows that the predicted and actual values are very close. The predicted values are estimates generated by a statistical tool using initial input values, whereas the actual values are the observed sorption capacity of biopolyol-based PUFs derived from laboratory experiments. Figure 4-12 shows that the predicted and actual values have a linear relationship, with points closely following the diagonal line. This suggests that the laboratory results are consistent with the

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model's predictions. As a result, the model equation can be considered reliable and appropriate for predicting future outcomes in subsequent research.

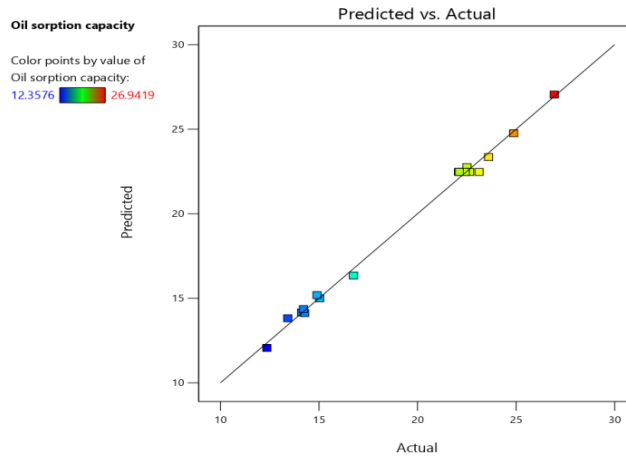


Figure 4-12: Plot of the predicted versus actual sorption capacity.

## 4.5.6.4 Residual Vs Run

Figure 4-13 shows that none of the residual vs. run values are outside the two boundary lines. This means that residuals are acceptable as long as they do not influence run treatment values. The graph's two boundary lines are drawn at 4.81963 and -4.81963 of external residuals, whereas the values of residual versus run are at the center line, connected by a zigzag line on the boundary line, and no outline was found.

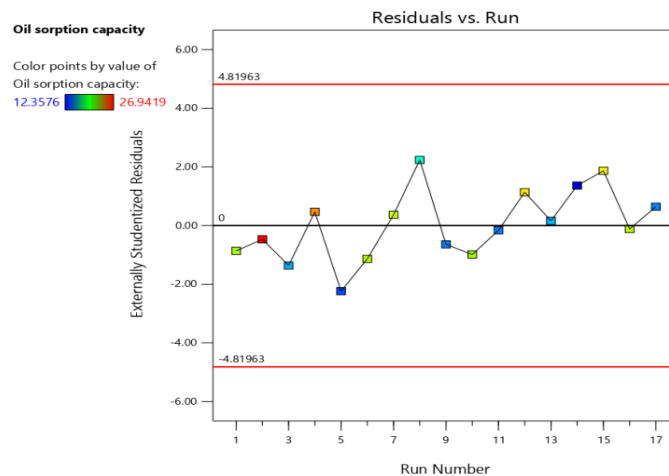


Figure 4-13: Plot of the Residual versus Run sorption capacity.

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### **4.5.7 Effect of Process Parameters on oil sorption capacity**

Based on analysis of variance (ANOVA), process variables (biopolyol content, oil-to-water percentage, and contact time) highly influenced the sorption capacity, and the interaction between oil-to-water percentage and contact time was also significant. The effects of individual process variables are discussed below.

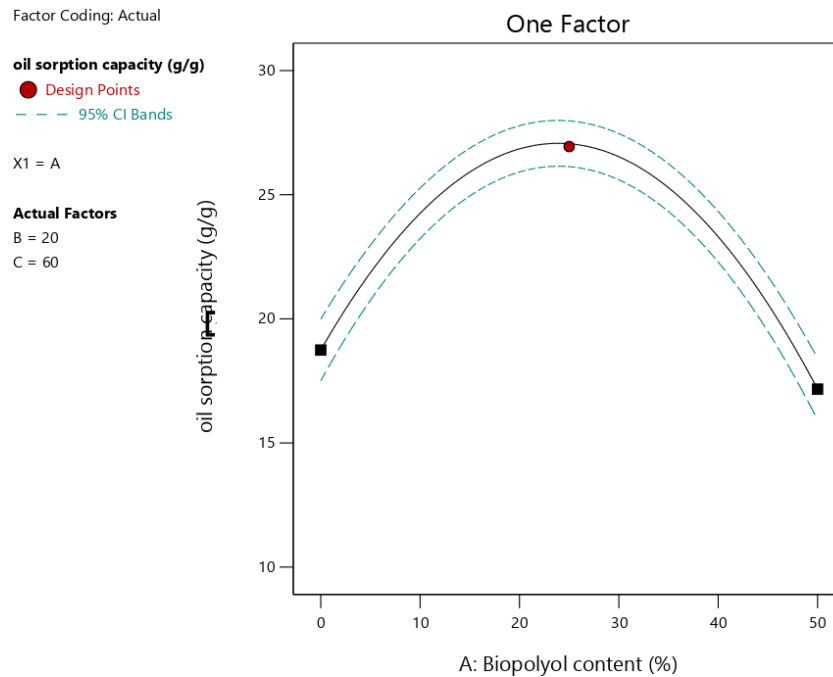
#### **4.5.7.1 Effects of biopolyols content**

Biopolyol-based foams exhibited better oil sorption in the PUF/oil/water system than the blank system, indicating that biopolyol has a positive influence on oil sorption. According to research conducted by (Santos et al., 2017), lignin reduces the hydrophobic character of modified foams due to the polar groups in the structure, but it also contains aromatic groups that can aid in the sorption of organic compounds. Contrary to what is reported in the literature, incorporating biopolyol in different weight proportions actually enhances the hydrophobic nature of biopolyol-based PUFs while reducing their capacity for oil sorption. This effect may be attributed to the presence of 4.1% residue content in the biopolyol, which potentially obstructs the foam's pores and limits the available space for oil absorption. Furthermore, some impurities may undergo chemical reactions with the foam components, altering the foam's properties and decreasing its affinity for oil. This can further reduce the foam's ability to absorb and retain oil.

Figure 4-14 illustrates that the oil sorption capacity of the PUF material increases gradually from 16.7 g/g to 26.9 g/g as the weight percentage of biopolyol in the PUFs preparation rises from 0% to 25%. However, as the biopolyol content further increases from 25% to 50%, the oil sorption capacity decreases from 26.9 g/g to 14.3 g/g. These findings indicate that incorporating biopolyol into the PUF material can significantly enhance its oil sorption capacity; particularly when up to 25% biopolyol is added. According to a study by (J. Wang & Geng, 2015), they found that pristine sponge can absorb 20.1g of n-hexane, 28.3g of toluene, 36.9g of chloroform, 18.9g of linseed oil, 14.7g of paraffin oil, and 17.8g of crude oil per gram of sponge. But when they modified the sponge, it could absorb even more oil - 27.1g of n-hexane, 35.3g of toluene, 46.8g of chloroform, 23.6g of linseed oil, 19.8g of paraffin oil, and 25.6g of crude oil per gram of sponge. So basically, the treatment made the sponge way better at soaking up oil.

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As a result, these new biopolyol-based sponges are way better at absorbing oil compared to other similar materials like microporous polymers (6–23 times), graphene aerogels (12–27 times), and PU sponges (13–26 times). The biopolyol probably adds more spots for absorbing oil or changes the structure of the sponge, making it better at soaking up oil.



**Figure 4-14: Effects of biopolyol content on the oil sorption capacity of PUFs.**

### 4.5.7.2 Effects of oil to water percentage

Figure 4-15 demonstrates the relationship between the oil-to-water percentage and the sorption capacity of the sorbent. It shows that as the oil-to-water percentage increases within the range of 15%, 16.5%, and 20%, the sorption capacity of the sorbent also increases. This suggests that higher concentrations of oil in water discourage water sorption by the foam and instead promote greater sorption of oil by the polymer material. However, there is a point at which the sorption capacity starts to diminish with further increases in the oil-to-water percentage. This decrease is expected because it indicates that the foam becomes saturated when the oil adsorption process reaches equilibrium. At this point, the foam can no longer absorb additional oil, resulting in a decrease in the overall sorption capacity.

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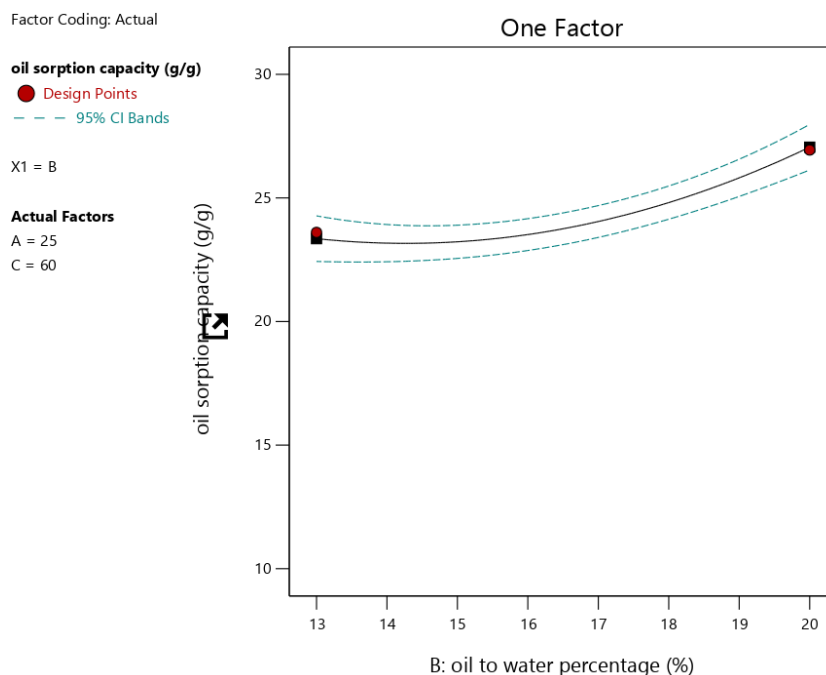


Figure 4-15: Effects of oil-to-water percentage on oil sorption capacity of PUFs.

### 4.5.7.3 Effects of contact time

According to the previous study, the adsorption process of oil in the PUF material can be divided into two distinct phases: a primary rapid phase and a slow phase (Abdul Hamid et al., 2016). The primary rapid phase of PUF adsorption occurs when the contact time between the material and oil increases, indicating active sites that enable oil molecules to bind effectively. However, this phase slows down as active sites become clogged with oil molecules, resulting in fewer available adsorption sites for further oil binding. In terms of specific results, for the PUF-0 sample, the oil sorption capacity demonstrates a continuous increasing pattern, reaching a maximum sorption capacity of 16 g/g. In the PUF-25 sample, the highest oil sorption capacity recorded is 26.9 g/g. In the PUF-50 sample, the highest oil sorption capacity is 14.3 g/g.

(Abdul Hamid et al., 2016) state that the rate of oil and grease removal increased with longer contact times. As the contact time increased from 20 to 80 minutes, the percentage removal of raw sugarcane bagasses (RSB) increased from 17.2 to 56%, and the percentage removal of raw banana pith (RBP) increased from 20.29 to 97%.

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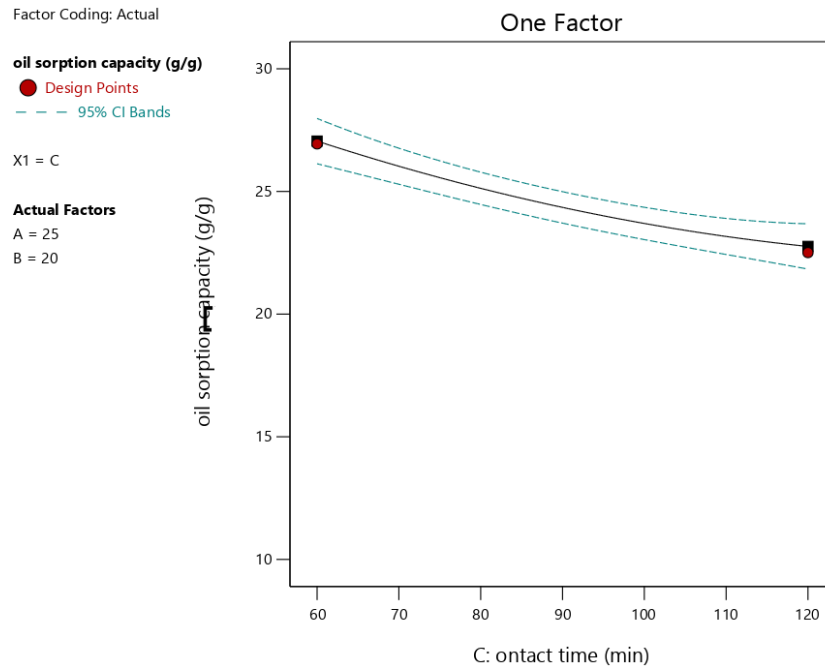
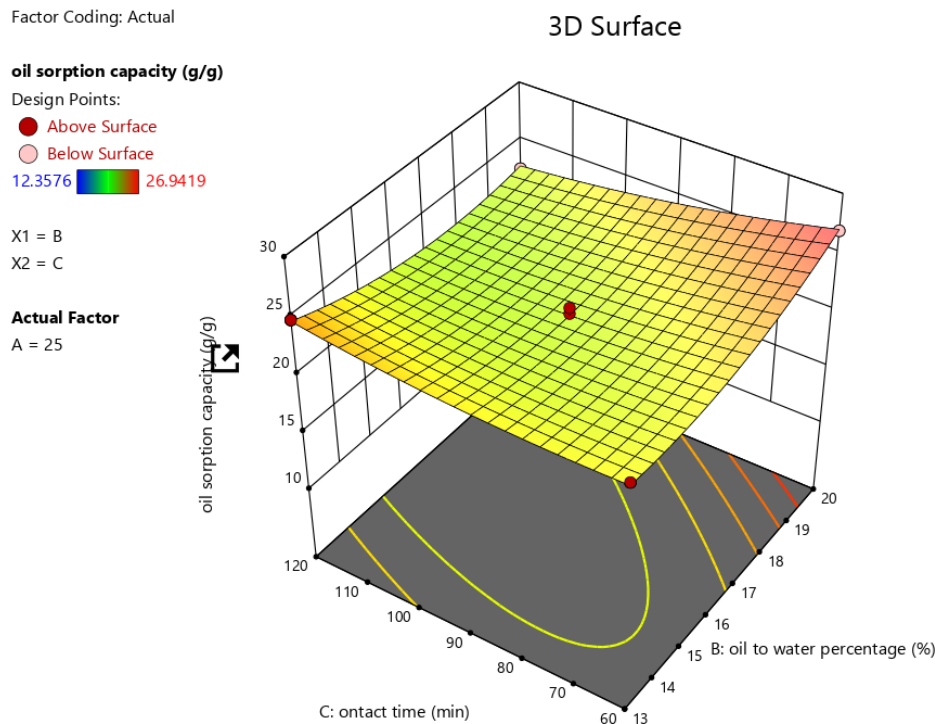


Figure 4-16: Effects of contact time on the oil sorption capacity of PUFs.

## 4.5.8 Interaction effects between oil to water percentage and contact time

Oil sorption capacity is significantly impacted by the interaction effects between the percentage of oil to water and the duration of contact. The response surface of a 3-D graph displaying the impact of contact time and oil to water percentage at a fixed biopolyol content is displayed in Figures 4–17. There is a set amount of biopolyol—25%. As demonstrated in both figures, an increase in the oil to water percentage from 15 to 25% and a 60-minute contact time resulted in an increase in the oil sorption capacity from 23.35 g/g to 26.9 g/g. However, as the contact time increased from 60 to 120 minutes, as depicted in both figures, the oil sorption capacity decreased. The oil to water ratio of 20% and the contact time resulted in the lowest oil sorption capacity of 120 minutes. Whereas the maximum oil sorption capacity was observed at percentage of 20% and 60 minutes of contact time.

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**Figure 4-17: The 3D graph of oil to water percentage and contact time interaction effect on sorption capacity.**

### 4.5.9 Optimization of Process Parameters for oil sorption capacity

By using BBD, the ideal process parameters for the oil to water percentage, contact time, and biopolyol content were found. The parameters were maintained within a certain range and the oil sorption capacity was maximized in order to conduct the analysis. Numerical optimization results in combinations of process parameters that yield the highest response, as shown in Table 4-8. To optimize any combination of one or more goals, numerical optimization was applied. The optimal process variable values were those that the operating process variables were putting on the range, according to the model that could predict the maximum oil sorption capacity.

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Table 4-8: Adjusted process parameters in range to maximize the yield.

Name	Goal	Lower limit	Upper limit	Importance
<b>A:Biopolyol content</b>	is in range	0	50	3
<b>B: oil to water percentage</b>	is in range	13	20	3
<b>C:Contact time</b>	is in range	60	120	3
<b>Oil sorption capacity</b>	Maximize	12.36	28.94	3

The BBD numerical analysis yielded 41 potential solutions, each with a desirability rating of 88.7%. Among these solutions, the highest oil sorption capacity recorded was 27.071 g/g. This optimal result was achieved using a biopolyol content of 23.9%, oil to water percentage of 20%, and a contact time of 60 minutes.

### 4.5.10 Model Validation

The RSM results indicated that a biopolyol content of 23.9 weight percent, an oil to water percentage of 20%, and a contact time of 60 minutes were the ideal process conditions for the oil sorption capacity. A confirmation experiment using the triplicate set was carried out at the precise ideal process conditions that the model predicted in order to validate the validity of the RSM model results. The average yield was then determined. It was discovered that the average oil sorption capacity was 26.987g/g. This demonstrates that the model was validated since the experimental values were discovered to be fairly near to the predicted values. As a result, the model helped to forecast PUFs' oil sorption capacity.

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### **4.5.11 Characterization of Actual Wastewater and Verification of Optimum Operation Parameters on Real Wastewater**

Table 4-9 shows the results of the characterization of wastewater collected from garages waste disposal. Based on the experimental results, the oil concentration in the wastewater was found to be 128.79 g/l, indicating a high level of oil contamination.

**Table 4-9: Wastewater Characteristic.**

<b>Parameter</b>	<b>Value</b>
<b>Oil and Grease</b>	128.79 g/l
<b>pH</b>	6.39
<b>Temperature</b>	25.9 <sup>0</sup> C

Biopolyol-based PUFs was used to remove oil from wastewater. The sorption capacity obtained during the cleanup of garage wastewater was 24.98 g/g. Even though this value is slightly lower than the optimization process's predicted value of 27.071 g/g, it is still regarded as acceptable. This sorption capacity demonstrates that the biopolyol-based PUF-25 foam extracts oil from wastewater. The observed sorption capacity during wastewater cleanup was lower than the value obtained from the laboratory-prepared wastewater sorption test. Several factors can contribute to this disparity. One possible explanation is the mixing of different types of oil in the wastewater, which can impair the foam's ability to absorb oil efficiently. Furthermore, the presence of other impurities in the wastewater, such as suspended solids or chemicals, might interfere with the sorption process and impair the foam's performance. The pH of the wastewater can also have an impact on sorption capacity because extreme pH levels can change the structure of the foam and affect its interaction with oil molecules.

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## **5 CONCLUSIONS AND RECOMMENDATION**

### **5.1 Conclusion**

In conclusion, this study successfully synthesized biopolyol-based PUFs using liquefied khat straw as a substitute for petroleum-based polyol. The optimization of foam preparation for oil cleanup from water was achieved through the BBD of the RSM. The average oil sorption capacity obtained by using the BBD softwares suggested process parameters is 26.987 g/g for laboratory-prepared waste water and 24.98 g/g for actual garage waste water sorption tests. The ANOVA analysis confirmed the significance of the model, with a high  $R^2$  value of 0.9962 and a significant F-value of 204.07. The key factors influencing the foam properties were determined to be the biopolyol content, oil to water percentage, contact time, and the interaction effect between oil to water percentage and contact time.

The resulting foams were evaluated by their chemical structure, cellular structure, density, compressive strength, and thermal property. The FT-IR and NMR spectra indicated that typical urethane linkages in biopolyol-based PUFs were formed. SEM results showed that the cell shape is significantly affected by the biopolyol content, which resulted in inhomogeneous, irregular, and large cell shapes. Mechanical results suggested that the compressive strength of the biopolyol-based PUFs decreased with the increase in biopolyol content. TGA analysis revealed that the onset temperature of the foams decreased with increasing biopolyol concentration, indicating alterations in thermal stability. Significantly, the modified foams exhibited improved oil sorption capacity in a PUF/oil/water system, with the PUF-25 foam displaying the highest sorption capacity of 26.9 g/g at 20% of oil to water percentage and 60 minutes of contact time.

Overall, these findings highlight the potential of biopolyol-based PUFs as effective oil adsorbents for oil cleanup from water. The utilization of liquefied khat straw as a renewable resource for the production of PUFs offers a promising solution for environmentally friendly oil spill remediation strategies. Further research and development in this area can contribute to the advancement of sustainable materials for environmental protection applications.

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### **5.2 Recommendation**

Considering results obtained in this thesis the following recommendations are suggested for future works;

- ❖ In future studies, it is important to investigate the effects of different types of blowing agents, isocyanates, and catalysts on the properties of PUFs.
- ❖ It is recommended to examine the interaction between the insoluble residues of biopolyol and other reagents during the preparation process. This investigation will shed light on the formation of polymers and their morphology, which may have an impact on the nature and performance of PUFs derived from biopolyol. To ensure accurate analysis, it is advisable to employ glass filter paper to remove impurities and study the properties of PU prepared from pure biopolyol.
- ❖ It is recommended to examine the influence of factors such as sorbent dosage, pH of wastewater, and working temperature on the sorption capacity of PUF. By conducting experiments that manipulate these variables, researchers can gain a better understanding of their effects on the sorption capabilities of PUF. This information will contribute to the development of optimized PUF materials for efficient and effective treatment of contaminated water or other relevant applications.
- ❖ Further study can be needed to study the reusability of the PUFs.
- ❖ The economic feasibility of the PUFs should be studied.

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---

## Reference

- Abd El-Gawad, H. S. (2014). Oil and Grease Removal from Industrial Wastewater Using New Utility Approach. *Advances in Environmental Chemistry*, 2014, 1–6.  
<https://doi.org/10.1155/2014/916878>
- Abdul Hamid, N. S., Che Malek, N. A., Mokhtar, H., Mazlan, W. S., & Mohd Tajuddin, R. (2016). Removal of oil and grease from wastewater using natural adsorbents. *Jurnal Teknologi*, 78(5–3), 97–102. <https://doi.org/10.11113/jt.v78.8519>
- Ahmad, A. L., Sumathi, S., & Hameed, B. H. (2005). *Residual oil and suspended solid removal using natural adsorbents chitosan , bentonite and activated carbon : A comparative study*. 108, 179–185. <https://doi.org/10.1016/j.cej.2005.01.016>
- Ahvazi, B., Wojciechowicz, O., Ton-That, T. M., & Hawari, J. (2011). Preparation of lignopolyols from wheat straw soda lignin. *Journal of Agricultural and Food Chemistry*, 59(19), 10505–10516. <https://doi.org/10.1021/jf202452m>
- Akindoyo, J. O., Beg, M. D. H., Ghazali, S., Islam, M. R., Jeyaratnam, N., & Yuvaraj, A. R. (2016). Polyurethane types, synthesis and applications-a review. *RSC Advances*, 6(115), 114453–114482. <https://doi.org/10.1039/c6ra14525f>
- Aniceto, J. P. S., Portugal, I., & Silva, C. M. (2012). Biomass-based polyols through oxypropylation reaction. *ChemSusChem*, 5(8), 1358–1368.  
<https://doi.org/10.1002/cssc.201200032>
- Annunciado, T. R., Sydenstricker, T. H. D., & Amico, S. C. (2005). *Experimental investigation of various vegetable fibers as sorbent materials for oil spills*. 50, 1340–1346. <https://doi.org/10.1016/j.marpolbul.2005.04.043>
- Arunagiri, V., Prasannan, A., Udomsin, J., Lai, J. Y., Wang, C. F., Hong, P. Da, & Tsai, H. C. (2021). Facile fabrication of eco-friendly polycaprolactone (PCL)/Poly-D, L-Lactic acid (PDLLA) modified melamine sorbent for oil-spill cleaning and water/oil (W/O) emulsion separation. *Separation and Purification Technology*, 259(September), 118081. <https://doi.org/10.1016/j.seppur.2020.118081>

## **Study on the sorption capacity of biopolyol (derived from khat straw) based polyurethane foam for removal of oil from wastewater.**

---

- Basar, I. A., Liu, H., Carrere, H., Trably, E., & Eskicioglu, C. (2021). A review on key design and operational parameters to optimize and develop hydrothermal liquefaction of biomass for biorefinery applications. *Green Chemistry*, 23(4), 1404–1446. <https://doi.org/10.1039/d0gc04092d>
- Bontaş, M. G., Diacon, A., Călinescu, I., & Rusen, E. (2023). Lignocellulose Biomass Liquefaction: Process and Applications Development as Polyurethane Foams. *Polymers*, 15(3). <https://doi.org/10.3390/polym15030563>
- Brandão, P. C., Souza, T. C., Ferreira, C. A., Hori, C. E., & Romanielo, L. L. (2010). Removal of petroleum hydrocarbons from aqueous solution using sugarcane bagasse as adsorbent. 175, 1106–1112. <https://doi.org/10.1016/j.jhazmat.2009.10.060>
- Burnard, S. (2019). Background and general introduction. In *Understanding and Managing Learning Behaviour*. <https://doi.org/10.4324/9780429346644-1>
- Cinelli, P., Anguillesi, I., & Lazzeri, A. (2013). Green synthesis of flexible polyurethane foams from liquefied lignin. *European Polymer Journal*, 49(6), 1174–1184. <https://doi.org/10.1016/j.eurpolymj.2013.04.005>
- Cui, S., Liu, Z., & Li, Y. (2017). Bio-polyols synthesized from crude glycerol and applications on polyurethane wood adhesives. In *Industrial Crops and Products* (Vol. 108). <https://doi.org/10.1016/j.indcrop.2017.07.043>
- Darmadi, Lubis, M. R., Saputra, R., Alfarabi, M. D., Sarah, S., & Adisalamun. (2020). Characterization of modified polyurethane foam adsorbents for mercury adsorption applications. *IOP Conference Series: Materials Science and Engineering*, 845(1). <https://doi.org/10.1088/1757-899X/845/1/012002>
- de Medeiros, A. D. M., da Silva Junior, C. J. G., de Amorim, J. D. P., Durval, I. J. B., de Santana Costa, A. F., & Sarubbo, L. A. (2022). Oily Wastewater Treatment: Methods, Challenges, and Trends. *Processes*, 10(4), 1–20. <https://doi.org/10.3390/pr10040743>
- de Rezende, S. C., Pinto, J. A., Fernandes, I. P., Leimann, F. V., & Barreiro, M. F. (2018). Oxypropylation of brazilian pine-fruit shell evaluated by principal component analysis.

## Study on the sorption capacity of biopolyol (derived from khat straw) based polyurethane foam for removal of oil from wastewater.

---

*Journal of Renewable Materials*, 6(7), 715–723.

<https://doi.org/10.32604/JRM.2018.00028>

Doherty, W. O. S., Mousavioun, P., & Fellows, C. M. (2011). Value-adding to cellulosic ethanol: Lignin polymers. *Industrial Crops and Products*, 33(2), 259–276.

<https://doi.org/10.1016/J.INDCROP.2010.10.022>

Dong, T., Wang, F., & Xu, G. (2015). Sorption kinetics and mechanism of various oils into kapok assembly. *Marine Pollution Bulletin*, 91(1), 230–237.

<https://doi.org/10.1016/j.marpolbul.2014.11.044>

Duong, H. T. T., & Burford, R. P. (2006). Effect of foam density, oil viscosity, and temperature on oil sorption behavior of polyurethane. *Journal of Applied Polymer Science*, 99(1), 360–367. <https://doi.org/10.1002/app.22426>

Environ, E. (2012). *Environmental Science fabricated using a facile dip coating method †*.

7908–7912. <https://doi.org/10.1039/c2ee21848h>

Gabriel, T., Wondu, K., & Dilebo, J. (2021). Valorization of khat (*Catha edulis*) waste for the production of cellulose fibers and nanocrystals. *PLoS ONE*, 16(2 February), 1–20.

<https://doi.org/10.1371/journal.pone.0246794>

Gama, N. V., Ferreira, A., & Barros-Timmons, A. (2018). Polyurethane foams: Past, present, and future. *Materials*, 11(10). <https://doi.org/10.3390/ma11101841>

Ge, J., Ye, Y. D., Yao, H. Bin, Zhu, X., Wang, X., Wu, L., Wang, J. L., Ding, H., Yong, N., He, L. H., & Yu, S. H. (2014). Pumping through porous hydrophobic/oleophilic materials: An alternative technology for oil spill remediation. *Angewandte Chemie - International Edition*, 53(14), 3612–3616. <https://doi.org/10.1002/anie.201310151>

Geissen, V., Mol, H., Klumpp, E., Umlauf, G., Nadal, M., van der Ploeg, M., van de Zee, S. E. A. T. M., & Ritsema, C. J. (2015). Emerging pollutants in the environment: A challenge for water resource management. *International Soil and Water Conservation Research*, 3(1), 57–65. <https://doi.org/10.1016/j.iswcr.2015.03.002>

Grancharov, G., Atanasova, M., Kalinova, R., Tuleshkov, P., Petrov, P. D., Marinova, M. K.,  
Addis Ababa Institute of Technology (AAIT)

## Study on the sorption capacity of biopolyol (derived from khat straw) based polyurethane foam for removal of oil from wastewater.

---

Ravutsov, M. A., & Simeonov, S. P. (2023). *Incorporation in Rigid Polyurethane Foams*.

Hayase, G., Kanamori, K., Fukuchi, M., Kaji, H., & Nakanishi, K. (2013). Facile synthesis of marshmallow-like macroporous gels usable under harsh conditions for the separation of oil and water. *Angewandte Chemie - International Edition*, 52(7), 1986–1989.  
<https://doi.org/10.1002/anie.201207969>

Hernández-Ramos, F., Alriols, M. G., Antxustegi, M. M., Labidi, J., & Erdocia, X. (2023). Valorisation of crude glycerol in the production of liquefied lignin bio-polyols for polyurethane formulations. *International Journal of Biological Macromolecules*, 247(April 2023). <https://doi.org/10.1016/j.ijbiomac.2023.125855>

Hu, S., & Li, Y. (2014). Two-step sequential liquefaction of lignocellulosic biomass by crude glycerol for the production of polyols and polyurethane foams. *Bioresource Technology*, 161, 410–415. <https://doi.org/10.1016/j.biortech.2014.03.072>

Hu, S., Luo, X., & Li, Y. (2014). Polyols and polyurethanes from the liquefaction of lignocellulosic biomass. *ChemSusChem*, 7(1), 66–72.  
<https://doi.org/10.1002/cssc.201300760>

Hu, S., Wan, C., & Li, Y. (2012). Bioresource Technology Production and characterization of biopolyols and polyurethane foams from crude glycerol based liquefaction of soybean straw. *Bioresource Technology*, 103(1), 227–233.  
<https://doi.org/10.1016/j.biortech.2011.09.125>

Jin, Y., Ruan, X., Cheng, X., & Lü, Q. (2011). Liquefaction of lignin by polyethyleneglycol and glycerol. *Bioresource Technology*, 102(3), 3581–3583.  
<https://doi.org/10.1016/j.biortech.2010.10.050>

Kadier, A., Al-Qodah, Z., Akkaya, G. K., Song, D., Peralta-Hernández, J. M., Wang, J. Y., Phalakornkule, C., Bajpai, M., Niza, N. M., Gilhotra, V., Bote, M. E., Ma, Q., Obi, C. C., & Igwegbe, C. A. (2022). A state-of-the-art review on electrocoagulation (EC): An efficient, emerging, and green technology for oil elimination from oil and gas industrial wastewater streams. *Case Studies in Chemical and Environmental Engineering*,

## Study on the sorption capacity of biopolyol (derived from khat straw) based polyurethane foam for removal of oil from wastewater.

---

6(November). <https://doi.org/10.1016/j.cscee.2022.100274>

Kataoka, L. F. de M. S., Hidalgo Falla, M. D. P., & Luz, S. M. Da. (2021). The Influence of Potassium Hydroxide Concentration and Reaction Time on the Extraction Cellulosic Jute Fibers. *Journal of Natural Fibers*, 19(13), 6889–6901.

<https://doi.org/10.1080/15440478.2021.1934934>

Keshavarz, A., Zilouei, H., Abdolmaleki, A., & Asadinezhad, A. (2015). Enhancing oil removal from water by immobilizing multi-wall carbon nanotubes on the surface of polyurethane foam. *Journal of Environmental Management*, 157, 279–286.

<https://doi.org/10.1016/j.jenvman.2015.04.030>

Laurichesse, S., Huillet, C., & Avérous, L. (2014). Original polyols based on organosolv lignin and fatty acids: New bio-based building blocks for segmented polyurethane synthesis. *Green Chemistry*, 16(8), 3958–3970. <https://doi.org/10.1039/c4gc00596a>

Lee, A., & Deng, Y. (2015). Green polyurethane from lignin and soybean oil through non-isocyanate reactions. *European Polymer Journal*, 63(November), 67–73.

<https://doi.org/10.1016/j.eurpolymj.2014.11.023>

Lee, S. H., Yoshioka, M., & Shiraishi, N. (2000). Liquefaction of corn bran (CB) in the presence of alcohols and preparation of polyurethane foam from its liquefied polyol. *Journal of Applied Polymer Science*, 78(2), 319–325. [https://doi.org/10.1002/1097-4628\(20001010\)78:2<319::AID-APP120>3.0.CO;2-Z](https://doi.org/10.1002/1097-4628(20001010)78:2<319::AID-APP120>3.0.CO;2-Z)

Li, B., Liu, X., Zhang, X., Zou, J., Chai, W., & Lou, Y. (n.d.). *Rapid adsorption for oil using superhydrophobic and superoleophilic polyurethane sponge*.

<https://doi.org/10.1002/jctb.4646>

Li, H., Liu, L., & Yang, F. (2012). Hydrophobic modification of polyurethane foam for oil spill cleanup. *Marine Pollution Bulletin*, 64(8), 1648–1653.

<https://doi.org/10.1016/j.marpolbul.2012.05.039>

Li, K., Zeng, X., Li, H., & Lai, X. (2014). *RSC Advances Facile fabrication of a robust superhydrophobic / superoleophilic sponge for selective oil absorption*. 23861–23868.

## Study on the sorption capacity of biopolyol (derived from khat straw) based polyurethane foam for removal of oil from wastewater.

---

<https://doi.org/10.1039/c4ra01227e>

Ma, X., Chen, J., Zhu, J., & Yan, N. (2021). Lignin-Based Polyurethane: Recent Advances and Future Perspectives. *Macromolecular Rapid Communications*, 42(3), 1–13.

<https://doi.org/10.1002/marc.202000492>

Mahmood, N., Yuan, Z., Schmidt, J., & Xu, C. (2016). Depolymerization of lignins and their applications for the preparation of polyols and rigid polyurethane foams: A review.

*Renewable and Sustainable Energy Reviews*, 60, 317–329.

<https://doi.org/10.1016/j.rser.2016.01.037>

Nadányi, R., Ház, A., Lisý, A., Jablonský, M., Šurina, I., Majová, V., & Baco, A. (2022).

Lignin Modifications, Applications, and Possible Market Prices. *Energies*, 15(18), 1–16.

<https://doi.org/10.3390/en15186520>

Nikkhah, A. A., Zilouei, H., Asadinezhad, A., & Keshavarz, A. (2015). Removal of oil from water using polyurethane foam modified with nanoclay. *Chemical Engineering Journal*,

262, 278–285. <https://doi.org/10.1016/j.cej.2014.09.077>

Okiel, K., El-Sayed, M., & El-Kady, M. Y. (2011). Treatment of oil–water emulsions by adsorption onto activated carbon, bentonite and deposited carbon. *Egyptian Journal of Petroleum*,

20(2), 9–15. <https://doi.org/10.1016/j.ejpe.2011.06.002>

Olszewski, A., Kosmela, P., & Piszczyk, Ł. (2022). Synthesis and characterization of biopolyols through biomass liquefaction of wood shavings and their application in the preparation of polyurethane wood composites. *European Journal of Wood and Wood Products*,

80(1), 57–74. <https://doi.org/10.1007/s00107-021-01755-6>

Oribayo, O., Feng, X., Rempel, G. L., & Pan, Q. (2017). Synthesis of lignin-based polyurethane/graphene oxide foam and its application as an absorbent for oil spill clean-ups and recovery. *Chemical Engineering Journal*, 323, 191–202.

<https://doi.org/10.1016/j.cej.2017.04.054>

Pan, H., Zheng, Z., & Hse, C. Y. (2012). Microwave-assisted liquefaction of wood with polyhydric alcohols and its application in preparation of polyurethane (PU) foams.

## **Study on the sorption capacity of biopolyol (derived from khat straw) based polyurethane foam for removal of oil from wastewater.**

---

*European Journal of Wood and Wood Products*, 70(4), 461–470.

<https://doi.org/10.1007/s00107-011-0567-6>

Pan, Y., Zhan, J., Pan, H., Wang, W., Tang, G., Song, L., & Hu, Y. (2016). Effect of Fully Biobased Coatings Constructed via Layer-by-Layer Assembly of Chitosan and Lignosulfonate on the Thermal, Flame Retardant, and Mechanical Properties of Flexible Polyurethane Foam. *ACS Sustainable Chemistry and Engineering*, 4(3), 1431–1438. <https://doi.org/10.1021/acssuschemeng.5b01423>

Peyrton, J., & Avérous, L. (2021). Structure-properties relationships of cellular materials from biobased polyurethane foams. *Materials Science and Engineering R: Reports*, 145(March). <https://doi.org/10.1016/j.mser.2021.100608>

Pham, V. H., & Dickerson, J. H. (2014). *Superhydrophobic Silanized Melamine Sponges as High Efficiency Oil Absorbent Materials*.

Pulat, M., & Babayigit, D. (2001). Surface modification of PU membranes by graft copolymerization with acrylamide and itaconic acid monomers. *Polymer Testing*, 20(2), 209–216. [https://doi.org/10.1016/S0142-9418\(00\)00026-X](https://doi.org/10.1016/S0142-9418(00)00026-X)

Rahmat, S. N., Mohd Ali, A. Z., Wan Ibrahim, M. H., & Alias, N. A. (2016). Oil and grease (O&G) removal from commercial kitchen waste water using carbonised grass as a key media. *MATEC Web of Conferences*, 87. <https://doi.org/10.1051/mateconf/20178701010>

Rastegarfar, N., Behrooz, R., & Barikani, M. (2018). Characterization of polyurethane foams prepared from liquefied sawdust by crude glycerol and polyethylene glycol. *Journal of Polymer Research*, 25(7). <https://doi.org/10.1007/s10965-018-1516-4>

Sanghamitra, P., Mazumder, D., & Mukherjee, S. (2021). Treatment of wastewater containing oil and grease by biological method- a review. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*, 56(4), 394–412. <https://doi.org/10.1080/10934529.2021.1884468>

Santos, O. S. H., Coelho da Silva, M., Silva, V. R., Mussel, W. N., & Yoshida, M. I. (2017).

## Study on the sorption capacity of biopolyol (derived from khat straw) based polyurethane foam for removal of oil from wastewater.

---

Polyurethane foam impregnated with lignin as a filler for the removal of crude oil from contaminated water. *Journal of Hazardous Materials*, 324, 406–413.

<https://doi.org/10.1016/j.jhazmat.2016.11.004>

Shimizu, T., Koshiro, S., Yamada, Y., & Tada, K. (1997). Effect of cell structure on oil absorption of highly oil absorptive polyurethane foam for on-site use. *Journal of Applied Polymer Science*, 65(1), 179–186. [https://doi.org/10.1002/\(sici\)1097-4628\(19970705\)65:1<179::aid-app21>3.0.co;2-y](https://doi.org/10.1002/(sici)1097-4628(19970705)65:1<179::aid-app21>3.0.co;2-y)

Silva, E. R., Barros Neto, E. L., Nascimento, P. F. P., Oliveira, H. N. M., Medeiros, G. G., & Duarte, L. J. N. (2023). Liquefaction of Coffee Biomass With Residual Glycerin: a Study of Renewable Fuel Production. *Brazilian Journal of Petroleum and Gas*, 17(4), 169–177. <https://doi.org/10.5419/bjpg2023-0011>

Tansel, B., & Pascual, B. (2011). Removal of emulsified fuel oils from brackish and pond water by dissolved air flotation with and without polyelectrolyte use: Pilot-scale investigation for estuarine and near shore applications. *Chemosphere*, 85(7), 1182–1186. <https://doi.org/10.1016/j.chemosphere.2011.07.006>

Thakur, V. K., Thakur, M. K., Raghavan, P., & Kessler, M. R. (2014). Progress in green polymer composites from lignin for multifunctional applications: A review. *ACS Sustainable Chemistry and Engineering*, 2(5), 1072–1092. <https://doi.org/10.1021/sc500087z>

Vasilachi, I. C., Asiminicesei, D. M., Fertu, D. I., & Gavrilescu, M. (2021). Occurrence and fate of emerging pollutants in water environment and options for their removal. *Water (Switzerland)*, 13(2), 1–34. <https://doi.org/10.3390/w13020181>

Wang, C. F., & Lin, S. J. (2013). Robust Superhydrophobic/superoleophilic sponge for effective continuous absorption and expulsion of oil pollutants from Water. *ACS Applied Materials and Interfaces*, 5(18), 8861–8864. <https://doi.org/10.1021/am403266v>

Wang, H., Ni, Y., & Jahan, M. S. (2011). *Stability of cross-linked acetic acid lignin-containing polyurethane*. 293–302. <https://doi.org/10.1007/s10973-010-1052-x>

## Study on the sorption capacity of biopolyol (derived from khat straw) based polyurethane foam for removal of oil from wastewater.

---

- Wang, J., & Geng, G. (2015). Highly recyclable superhydrophobic sponge suitable for the selective sorption of high viscosity oil from water. *Marine Pollution Bulletin*, 97(1–2), 118–124. <https://doi.org/10.1016/j.marpolbul.2015.06.026>
- Wang, Y., Wu, J., Wan, Y., Lei, H., Yu, F., Chen, P., Lin, X., Liu, Y., & Ruan, R. (2009). Liquefaction of corn stover using industrial biodiesel glycerol. *International Journal of Agricultural and Biological Engineering*, 2(2), 32–40. <https://doi.org/10.3965/j.issn.1934-6344.2009.02.032-040>
- Wang, Y., Wyman, C. E., Cai, C. M., & Ragauskas, A. J. (2019). *Lignin-based Polyurethanes from Unmodified Kraft Lignin Fractionated by Sequential Precipitation*. *Lignin-based Polyurethanes from Unmodified Kraft Lignin Fractionated by Sequential Precipitation*. <https://doi.org/10.1021/acsapm.9b00228>
- Williams, J. B., Clarkson, C., Mant, C., Drinkwater, A., & May, E. (2012). Fat, oil and grease deposits in sewers: Characterisation of deposits and formation mechanisms. *Water Research*, 46(19), 6319–6328. <https://doi.org/10.1016/j.watres.2012.09.002>
- Wu, D., Fang, L., Qin, Y., Wu, W., Mao, C., & Zhu, H. (2014). Oil sorbents with high sorption capacity, oil/water selectivity and reusability for oil spill cleanup. *Marine Pollution Bulletin*, 84(1–2), 263–267. <https://doi.org/10.1016/j.marpolbul.2014.05.005>
- Xu, J., Jiang, J., Hse, C. Y., & Shupe, T. F. (2014). Preparation of polyurethane foams using fractionated products in liquefied wood. *Journal of Applied Polymer Science*, 131(7), 1–7. <https://doi.org/10.1002/app.40096>
- Yang, C., Wang, S., Yang, J., Xu, D., Li, Y., Li, J., & Zhang, Y. (2020). Hydrothermal liquefaction and gasification of biomass and model compounds: A review. *Green Chemistry*, 22(23), 8210–8232. <https://doi.org/10.1039/d0gc02802a>
- Yang, Y., Yi, H., & Wang, C. (2015). *Oil Absorbents Based on Melamine/Lignin by a Dip Adsorbing Method*. <https://doi.org/10.1021/acssuschemeng.5b01187>
- Yao, Y., Yoshioka, M., & Shiraishi, N. (1996). Water-absorbing polyurethane foams from liquefied starch. *Journal of Applied Polymer Science*, 60(11), 1939–1949.

## Study on the sorption capacity of biopolyol (derived from khat straw) based polyurethane foam for removal of oil from wastewater.

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Yu, F., Le, Z., Chen, P., Liu, Y., Lin, X., & Ruan, R. (2008). Atmospheric pressure liquefaction of dried distillers grains (DDG) and making polyurethane foams from liquefied DDG. *Applied Biochemistry and Biotechnology*, 148(1–3), 235–243. <https://doi.org/10.1007/s12010-007-8040-z>

Zhao, C., Zhou, J., Yan, Y., Yang, L., Xing, G., Li, H., Wu, P., Wang, M., & Zheng, H. (2021). Application of coagulation/flocculation in oily wastewater treatment: A review. *Science of the Total Environment*, 765, 142795. <https://doi.org/10.1016/j.scitotenv.2020.142795>

Zhou, X., Zhang, Z., Xu, X., Men, X., & Zhu, X. (2013). Facile fabrication of superhydrophobic sponge with selective absorption and collection of oil from water. *Industrial and Engineering Chemistry Research*, 52(27), 9411–9416. <https://doi.org/10.1021/ie400942t>

Zhu, J., Sun, H., Yang, B., & Weng, Y. (2024). Modified Biomass-Reinforced Polylactic Acid Composites. *Materials*, 17(2). <https://doi.org/10.3390/ma17020336>

Zhu, Q., Pan, Q., & Liu, F. (2011). Facile removal and collection of oils from water surfaces through superhydrophobic and superoleophilic sponges. *Journal of Physical Chemistry C*, 115(35), 17464–17470. <https://doi.org/10.1021/jp2043027>

Zilouei, A. K. H., & Asadinezhad, A. A. A. (2015). Impregnation of polyurethane foam with activated carbon for enhancing oil removal from water. *International Journal of Environmental Science and Technology*. <https://doi.org/10.1007/s13762-015-0908-9>

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### Appendix

#### Appendix A: Result obtained from FTIR analysis.

**Table A.1- Functional groups identified in biopolyol according to the FTIR analysis**

Functional groups	Wave numbers /cm <sup>-1</sup>	Type of vibration
-OH (Hydroxyl groups)	3200 – 3600	Stretching
-C-H (Alkanes)	2800 – 3000	Stretch
C=O (Carbonyl groups)	1650 -1800	Stretching
C=C (aromatic)	1450 – 1600	Stretching
C=O (carboxylic acid)	1725- 1700	Stretching
C-O-C (Alcohols, ethers, esters, carboxylic acids)	1100 – 1300	stretching

**Table A.2- The main characteristic bands observed for polyurethane foams (Pulat & Babayigit, 2001).**

Functional groups	Wave numbers /cm <sup>-1</sup>	Type of vibration
N-H	3300 – 3600	Stretching
Aliphatic bonds (C-H)	2800 – 3000	Stretching
Isocyanate group (NCO)	2250 – 2270	Stretching
Urethane group (NHCOO)	1600–1740	Stretching
Carbonyl group (C=O)	1650–1715	Stretching
	1510	N H deformation
	1215–1050	C O and C O C deformation

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### Appendix B: Results from Design Expert

#### Coefficients in Terms of Coded Factors

When all other factors are held constant, the coefficient estimate shows the expected change in response for each unit change in factor value. The total average response of all the runs is the intercept in an orthogonal design. Based on the factor settings, the coefficients represent adjustments made around that average. VIFs are 1 when the factors are orthogonal; VIFs greater than 1 denote multi-collinearity; the higher the VIF, the stronger the factor correlation. VIFs of less than 10 are generally acceptable.

**Table B.1: Coefficients in Terms of Coded Factors**

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	22.48	1	0.2014	22.00	22.95	
A-biopolyol content	-0.8413	1	0.1592	-1.22	-0.4648	1.0000
B-oil to water percentage	0.4232	1	0.1592	0.0467	0.7997	1.0000
C-Contact time	-0.7205	1	0.1592	-1.10	-0.3440	1.0000
AB	-0.2522	1	0.2252	-0.7846	0.2803	1.0000
AC	-0.3069	1	0.2252	-0.8393	0.2256	1.0000
BC	-1.43	1	0.2252	-1.96	-0.8939	1.0000
A <sup>2</sup>	-9.10	1	0.2195	-9.62	-8.58	1.01
B <sup>2</sup>	1.45	1	0.2195	0.9317	1.97	1.01
C <sup>2</sup>	0.5555	1	0.2195	0.0365	1.07	1.01

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Appendix C: Some pictures from laboratory work.

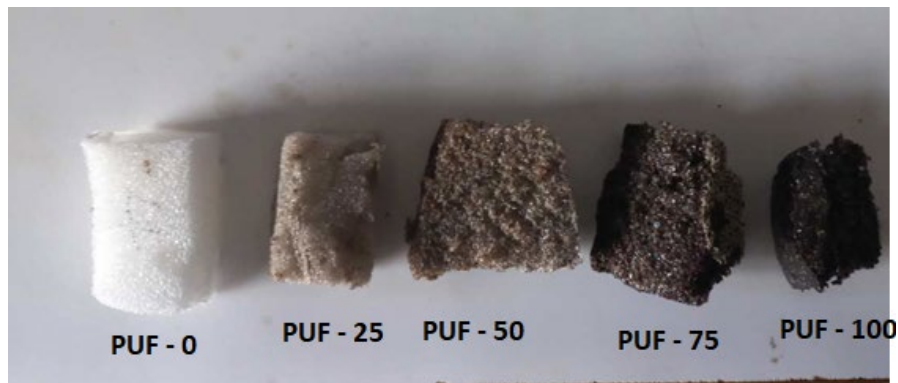


Figure C-1: Production process of Pure and biopolyols- based PUFs



Preparation of raw material for sorption capacity test

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Placing the prepared oil/water/sorbent system on shaker    Taking out the sorbent from flask



Measuring weight of oil/water/sorbent



Putting the oil/water/sorbent on drying oven

**Figure C-2: Pictures showing the lab test of measuring the oil sorption capacity of PUFs foam in Quartz 5000 20W-50/ water system.**