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Determining the quality of novel polyols using potentiometric analysis for biodegradable thermoplastic polyurethanes (TPUs)

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UNIVERSITY OF CALIFORNIA SAN DIEGO

Determining the quality of novel polyols using potentiometric analysis for biodegradable  
thermoplastic polyurethanes (TPUs)

A Thesis submitted in partial satisfaction of the requirements  
for the degree Master of Science

in

Chemistry

by

Miheer Modi

Committee in charge:

Professor Robert S. Pomeroy, Chair  
Professor Michael D. Burkart  
Professor Stephen P. Mayfield

2022

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University of California San Diego

2022

## DEDICATION

The last two years have been filled with a whirlwind of life changing experiences that I was able to persevere through with the support of some very special people. My parents, who have been my biggest support and who nursed me back to health after an unexpected brain hemorrhage in July 2021. The medical staff at Jacobs Medical Center and Sharp Grossmont Rehabilitation Hospital, who not only saved my life but worked tirelessly to help me get back on my feet and pick up where I left off. My extended family, while physically apart, have remained as close knit as one can be. My friends, who jumped into action to support us and prayed relentlessly are another family I will always hold dear. Dr. Robert Pomeroy, Marissa Tessman and Anton Samoylov, who have been a blessing only a few can be lucky to grow under, have inspired me to be a better chemist and grow as a balanced individual. Lastly, this thesis is dedicated to my grandfather, Kantilal Modi, who we lost last year. His passing has left an enormous void that will never be filled but his vision of excellence, hard work and ambition is a tremendous driving force and the basis of our family's work ethic which I will carry on as best as I can.

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## VITA

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## PUBLICATIONS

Renewable low viscosity polyester-polyols for biodegradable thermoplastic polyurethanes  
Rajput, Bhausahab S. “Renewable Low Viscosity Polyester-Polyols for Biodegradable  
Thermoplastic Polyurethanes.” *Journal of Applied Polymer Science*, vol. 139, no. 43,  
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## FIELD OF STUDY

Biochemistry/ Chemistry

## ABSTRACT OF THE THESIS

Determining the quality of novel polyols using potentiometric analysis for biodegradable  
Thermoplastic polyurethanes (TPUs)

by

Miheer Modi

Master of Science in Chemistry

University of California San Diego, 2022

Professor Robert S. Pomeroy, Chair

Novel bio polyols made from different combinations of diacids, and diols were tested using potentiometric titrations to determine their hydroxyl number, total acid content and water content. These tests were in part accomplished by designing novel titration methods involving solvent substitutions which were verified to generate results within  $\pm 2\%$ . The second half of this thesis focused on the synthesis of a novel polyol made from the *Botryococcus braunii* using hydroboration-oxidation and epoxidation. Potentiometric analysis showed that the hydroboration-oxidation route was 13% more effective and supported by H NMR and FT-IR analysis. Future avenues with biodegradable adhesives could be explored.

## INTRODUCTION

Plastics have come to dominate the world of consumer goods in the years leading to the 21st century and have continued to persevere due to their applicability and ease of production. Plastic production surged after WWII, with plastic use overtaking conventional materials used in the automotive, packaging, and medical industries. The surge in plastic use rose from how they could be manipulated to suit different purposes. Plastics have become a major commercial commodity, opening new avenues for manufacturers to experiment with innovative and/or aesthetic designs. They have also helped manufacturers offer products at a friendly price point, enabling consumers to access a wider variety of products without compromising on quality. An example is diverse types of footwear. Access to plastics has enabled manufacturers to make options (rain boots, specialty orthopedic shoes, assorted formal shoes etc.) to suit various diverse needs, which have conversely driven consumer spending worldwide.



Figure 1- Footwear has changed drastically, with newer designs being made with synthetic materials such as thermoplastic polyurethanes, foams, and glues for enhanced durability

Variety is abundant in the market of cheap disposable plastics such as PET (polyethylene terephthalate), PVC (polyvinyl chloride), PVA (polyvinyl alcohol), and BPA (bisphenol A). These

all have different applications in consumer goods; PET is commonly used for convenience food and drink packages, PVA is commonly used as a convenient adhesive, and BPA is used to make baby bottles, reusable pitchers, and storage containers. The most versatile of plastics is PVC which is used for various uses ranging from window fittings, medical equipment, automotive furnishings, and footwear, to mention a few.








| Plastic Resin Identification Codes  |   |   |   |  |   |   |
|---|---|---|---|--|---|---|
|  |  |  |  |  |  |  |
| PETE  | HDPE  | PVC   | LDPE  | PP   | PS  | OTHER   |
| Polyethylene Terephthalate  | High-Density Polyethylene   | Polyvinyl Chloride  | Low-Density Polyethylene  | Polypropylene  | Polystyrene   | Other   |

Figure 2- The variety of commercially available plastic resins has opened many avenues for new products, designs, and innovation.

A common advantage of these plastics is that they are versatile and light, making it easy to tailor them to specific technical needs. BPA is unique in terms of its impact resistance and high optical clarity, which gives it glass-like visual qualities. These properties made BPA the first choice for baby bottles which may have to withstand rough use. PVA is still used as a sealer for construction as it quickly dries at room temperature and offers high bond strength.

While each plastic has its advantages and disadvantages, a common end-of-life concern is that these plastics do not biodegrade (if they do at all) at the same rate as when they are produced. Petroleum-based plastics are novel, and their end-of-life behavior is still being understood. The most recent finding was how microplastics had been found in the lungs. This is a disturbing finding as it suggests that plastics can become airborne as they break down over time and can settle in lung tissue. Microplastics have been linked to an increased risk of chronic respiratory diseases, with

polypropylene and PET being the most found in lower lung tissue when exposed by inhalation. This is a troubling revelation and opens research avenues on what needs to be done to limit airborne microplastic exposure and their long-term implications.

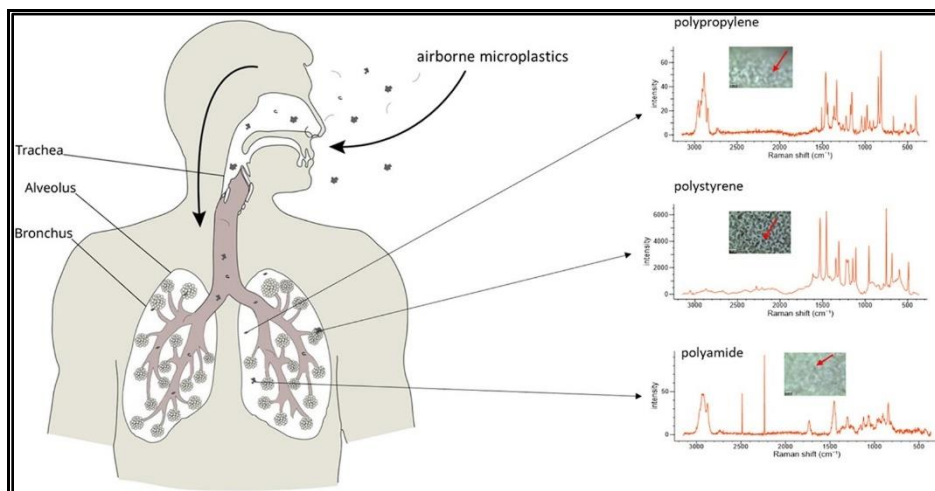


Figure 3- Airborne microplastics have been detected in human lungs in recent studies (autopsies). Inhalation and ingestion are two modes of entry. Further research needs to be done to understand the implications of microplastics in the human body.

Plastics are popular in various commercial spheres- the automotive, food and beverage, and footwear industries to name a few. An overarching idea that has made plastics such a lucrative material of choice in these industries is its versatility and ease of manufacture. Automobiles of the 1950s, as compared to modern cars, are a prime example. Advances in aerodynamics and environmental reforms, in addition to computer-aided design, have enabled engineers to create sleeker and safer vehicles with a lower drag coefficient as opposed to their predecessors, which were made from iron. Modern cars are lighter despite their increased size in each class and offer better crash protection. Manufacturers have access to several types of plastics used for body panels that weigh less and can crumple upon impact; these are some of the reasons that have cemented plastic use in the automotive industry.



Figure 4- A 2009 Chevrolet Malibu (left) and 1959 Chevrolet Malibu (right). The last 50 years have seen changes in automotive design which would not have been possible without the use of plastics.

Food and beverages have also become much more accessible at lower costs as plastic packaging enables suppliers to transport products easily and at lower prices. While this has made commercial products more accessible to consumers, it has also caused problems. Single-use plastic usage has skyrocketed, and proper disposal and recycling are becoming more challenging.

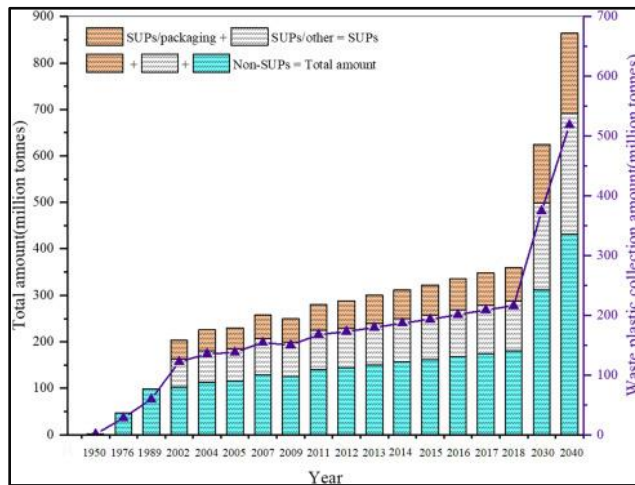


Figure 5- Single-use plastic usage has surged, and current production-consumption trends project a disturbing image of massive accumulation.



Plastic recycling is an imperative requirement now that plastics are so widely used in consumer goods. Plastic recycling is grossly insufficient in some of the significant plastic-polluting countries of the world, i.e., only 9% and 15% of plastic generated in the United States and Europe respectively is recycled. Plastic recycling is challenging because of contamination and high variability in the several types of waste that come into recycling centers. The second issue that deters plastic recycling is that traditional physical methods do not convert the starting material into its original form. Depolymerization can successfully break down certain plastics into simpler starting components, such as polyester and polystyrene but comes up short when dealing with more complex/ heterogeneous waste. As mentioned above, PET, which is commonly used for drink packaging, is of particular interest to recycling facilities as it is seen as a clean and homogeneous material, while other plastics such as polypropylene cups and mixed plastic pouches, are not. Recycling facilities will use optical sorters to select for PET, while other heterogeneous plastics are sent off to processors that attempt to extract plastics of value but mostly send them off to landfills. Economies of scale also bind traditional disposal methods. Extraction and recycling must be fiscally worthwhile; there needs to be enough of a particular type of clean plastic present with which to work. Not only is there a large amount of variability in the types of plastic that recycling centers receive, but plastics of interest (PET Number 1 and Number 2) are also often contaminated with food or grime which does not make them ideal for recycling. Lastly, plastics are unfortunately downcycled, i.e., recycled plastics are not able to maintain the exact specifications that their virgin counterparts had. For example, yogurt containers made from PET will not become yogurt containers again; they will be downgraded to lesser quality plastics such as carpet liners. Disposal methods of traditional plastics can extend their life to a certain extent but cannot eliminate plastic waste being added to existing waste in the environment.

Plastics are easier and cheaper to make and more sanitary, making them ideal for single use purposes, i.e., medical use catheters and syringes. However, there has been a massive rise in plastic pollution due to its chemical stability. Plastics are synthetic, and bacteria found in soil cannot effectively break down the chemical bonds in the different types of plastics used, i.e., polyethylene terephthalate, Styrofoam, polyvinyl chloride. This is because plastics are long chain polymers with large repeating units. Plastics are xenobiotic, i.e., unfamiliar to bacteria in nature, and the chemical bonds, like the long chain in plastics, bacteria have not yet evolved to break down. Naturally occurring materials such as cellulose (the primary constituent of paper bags) have a chemical structure that is significantly different and simpler than that of plastics, PET for explanation's sake. Cellulose is composed of linear long chain glucose units linked by  $\beta$ -1-4 glycosidic bonds. The glucan chains of cellulose aggregate themselves via hydrogen bonding and van der Waals forces to assemble into a long thread-like crystalline structure. In comparison, PET is built by polymerized units of ethylene terephthalate and repeating  $C_{10}H_8O_4$  units. PET is made by reacting ethylene glycol (diol) and terephthalic acid (dicarboxylic aromatic acid) under heated catalysis, which allows the hydroxyl and carboxyl groups to form ester groups.

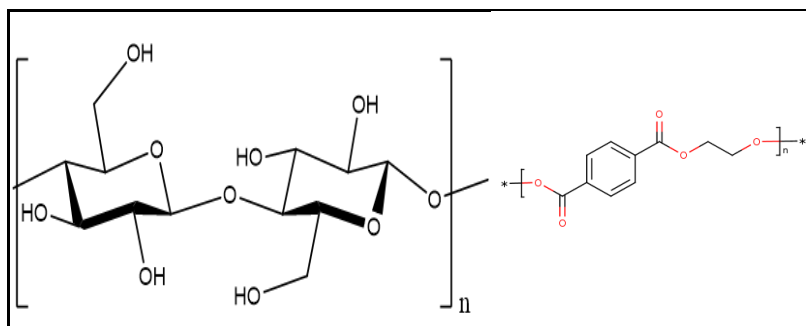


Figure 6- As seen in the picture above, the type of bonding seen in cellulose (left) is vastly different from what is seen in plastics. PET (right) is comprised of the terephthalate and ethylene monomers joined together by an ester linkage. Cellulose is held together by  $\beta$ -1-4, glycosidic bonds .

New research has taken advantage of chemical additives and biological techniques to help combat this problem by making the chemical chains more accessible to bacteria to break down into harmless organic compounds. As noted above, traditional plastics are xenobiotic so they cannot be chemically broken down by bacteria found in soil and aquatic bodies as they simply do not recognize these types of bonds. As a result, plastics stay in the environment and are subjected to conditions they were not designed for, i.e., high levels of physical stress and UV exposure. These conditions accelerate their breakdown into microplastics that find their way into human food chains.

Plastic pollution and microplastics have been a topic of discussion for the last 60 years. Microplastics can be up to 10 microns wide, making it quite easy for them to make it into the human body from food and beverage packing and cosmetics. Microplastic ingestion is a health hazard as it can cause cell death in the human body. Microplastics are also preserved, i.e., the body does not break them down before being excreted. Microplastics have even been found in placentas, suggesting a high maternal-fetal transmission rate. This is a concerning development, and it has been hypothesized that plastics carry chemicals that can disrupt the development of the immune system of a growing fetus. This is also dangerous as plastics that absorb and degrade with exposure to UV radiation release free radicals into the environment. While the full scale of free radical damage to the human body has not yet been fully understood, they have been linked to causing serious problems with cellular function. Some of the long-term effects can manifest as cell development problems, cancers, aging, and inflammatory diseases.

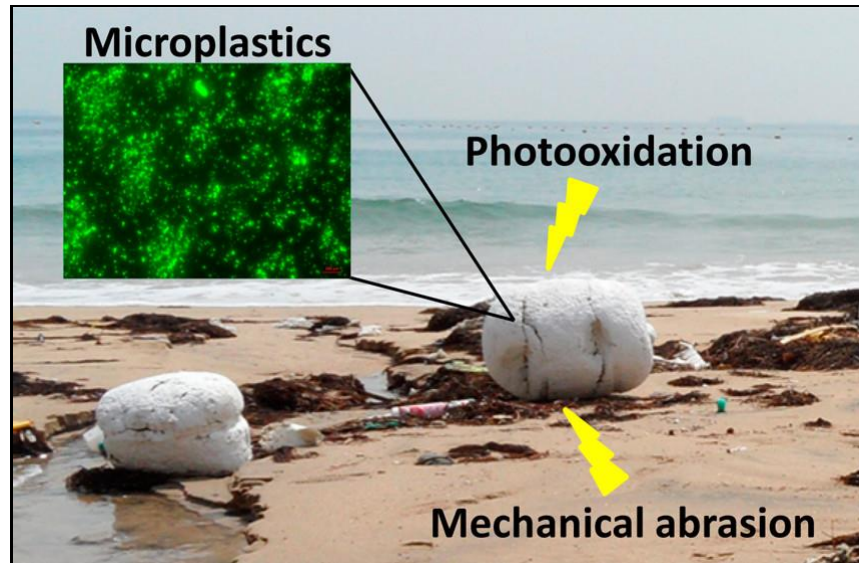


Figure 7- When exposed to UV radiation, synthetic plastics will undergo photooxidative degradation which will release microplastics and free radicals into the environment.

## CHAPTER 1

Some of the newer biobased polymers are made from polyols which are composed of different combinations of diacids and diols. These compounds are designed keeping in mind the traditional advantages of plastics such as moldability and rigidity. These compounds require extensive testing to determine which is the best formulation for biodegradation. Numerous metrics, both chemical and physical, are analyzed during formulation. Some chemical metrics such as water content, acid content and hydroxyl number help determine how well a polyol has been made.

As highlighted above, traditional plastics such as PVC, PET, BPA, etc., bring environmental and biological hazards and problems such as microplastic pollution and free radical formation when they enter the ecosystem and start to break down. Despite offering numerous industrial advantages in the consumer goods industry, health and marine welfare concerns have been pushing consumers to move away from petroleum-based plastics and, by extension, incentivizing manufacturers to adopt biodegradable alternatives. Bio-polyurethanes are particularly interesting as they are a versatile material with comparable properties and use-specific formulations. Renewable bio-based polymers sourced from succinic-sebacic and azelaic acid-based polyester polyols have been studied, i.e., their mechanical and chemical breakdown properties to assess how different compositions affect the properties mentioned above and biodegradability. Thermoplastic polyurethanes (TPUs) are segmented elastomers derived from polyols that function as soft segments, and hard segments are made up from diisocyanates and small molecule chain extenders.

TPUs offer significant advantages over traditional petroleum-based plastics as they have comparable properties while offering biodegradability. TPUs have mechanical strength compared

to traditional plastics, are resistant to abrasion and are versatile, i.e., they can be used for coatings, solvents, and adhesives. TPUs can have formulation specific properties and can range from soft/ elastic plastics or hard/ rigid plastics.

TPUs are made from polyols and diisocyanates. Depending on the desired end use of the product, the properties of the TPU can be altered, much like with traditional plastics. Different formulations can be applied to application-specific requirements, i.e., different tensile strengths and rigidity. A representative example of a TPU synthesis is shown below.

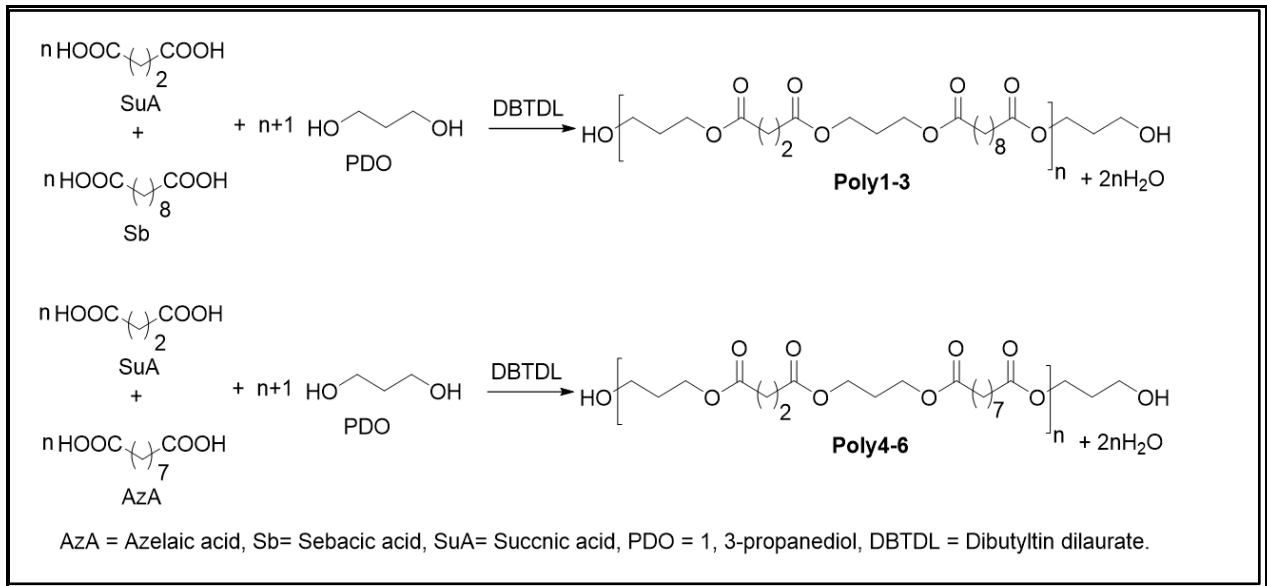


Figure 8- Polyol synthesis is done by reacting a diacid with a diol in the presence of an organometallic catalyst such as DBTDL. Different combinations of diacids and diols are used.

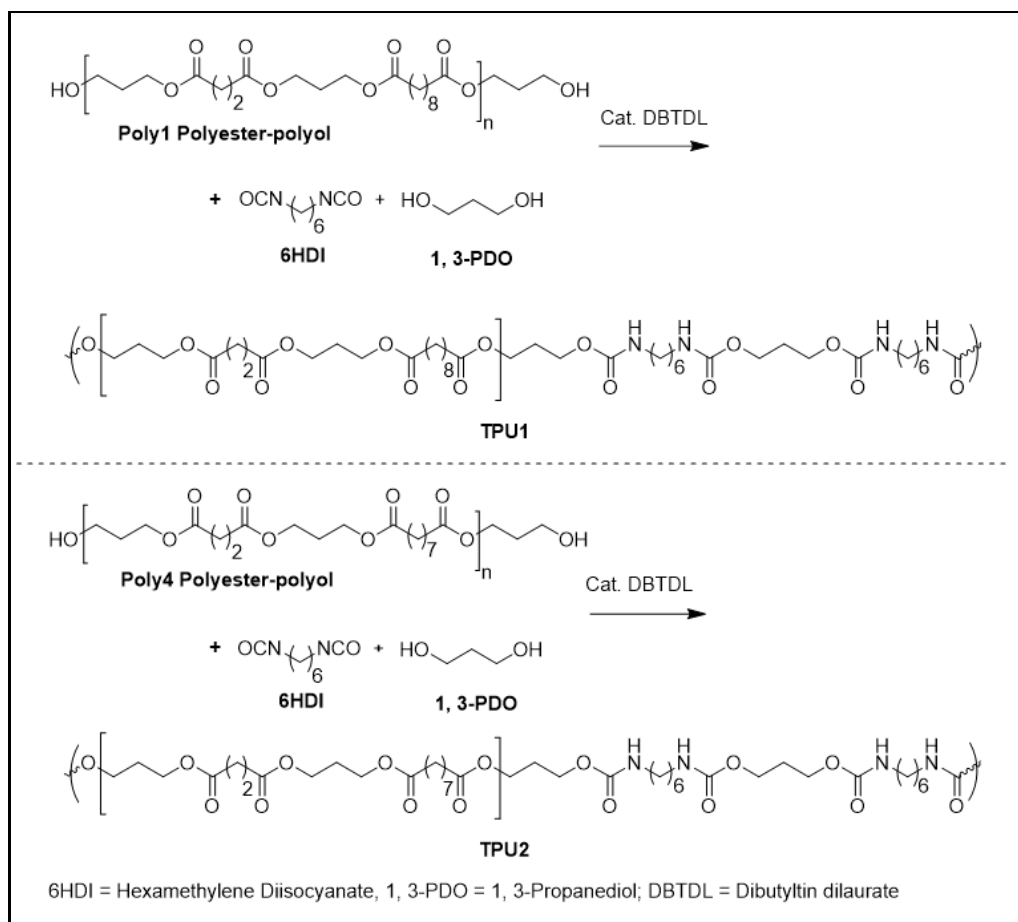


Figure 9- The polyol is reacted with a diol and isocyanate in the presence of DBTDL to make a TPU. The molar ratio of isocyanate, diol and polyol is calculated to optimize the reaction.

TPUs are biologically accessible as compared to traditional plastics (such as polyethers) as they are less resistant to hydrolysis. While this could be seen as a disadvantage at first, this increases the propensity of polyester-polyol TPUs to biodegrade when they reach their end of life. Hydrolysis is of interest as it means the polyester-polyol TPU will be able to break down into its constituents when exposed to water over an extended period.

TPUs would be favorable/ important in the industry as we have been grappling with the long-term implications of microplastic pollution and challenges associated with recycling plastic waste. Previous attempts at making biodegradable plastics from algae biomass have been

moderately successful but have hit problems with the cost of production and feedstock purity. Having access to biodegradable TPUs will help bypass problems associated with biomass feedstock procurement. In addition, lower viscosity polyols offer lower processing temperatures and decrease manufacturing time which results in lowered manufacturing costs. Lower viscosity polyester-polyols can also serve as drop-in replacements for existing equipment used in industrial applications, which can make adopting them easier.

TPU synthesis encompasses a wide array of analytical tests such as scanning electron microscopy (SEM) and respirometric analysis to study the biodegradation of the final product. Other analytical metrics such as H NMR, C NMR, thermogravimetric analysis as used to study the polyol's physical and chemical properties while potentiometric titration tests are used to evaluate formulation specific criteria i.e., hydroxyl number and acid number to assess reaction completion and Karl Fischer titration to determine water content.

As TPUs are formulation-specific, tracking metrics such as viscosity, working temperature, and diacid-diol composition are imperative. These metrics are essential as they correlate to mechanical properties and biodegradation analysis. Potentiometric tests such as acid number analysis, hydroxyl number analysis, and Karl Fischer water content analysis can help quickly and accurately determine these numbers with high accuracy.

Potentiometric titrations are based on electrochemical behavior to determine the concentration of a solute when potential is applied between one or two electrodes. Potentiometric titrations offer various advantages when determining the concentration of diol and diacids when performing polyester-polyol analysis. These tests do not need colored indicators like traditional pH tests and require small sample sizes to be run. These tests are also easy to perform and can be



run multiple times quickly, which makes conducting time-based trials possible, i.e., testing stability over time and assessing product stability. Lastly, potentiometric titration tests enable data determination within small error margins (<2%) which makes them a superior choice for evaluating polyol formulations.

### **Acknowledgements**

Chapter 2, in partial, is a reprint of the material as it appears in Renewable low viscosity polyester-polyols for biodegradable thermoplastic polyurethanes, Bhausahab S. Rajput, Thien An Phung Hai, Natasha R. Gunawan, Marissa Tessman, Nitin Neelakantan, Gordon B. Scofield, Jose Brizuela, Anton A. Samoylov, Miheer Modi, Jenna Shepherd, Amal Patel, Robert S. Pomeroy, Naser Pourahmady, Stephen P. Mayfield, Michael D. Burkart. The thesis author was the primary investigator and author of this paper.

## CHAPTER 2

Acid number analysis is an analytical metric used to determine the total acid content per gram of polyol. It is a useful metric used to determine how much acid is left in the sample and assess reaction completion in polyol synthesis. The acid number analysis is important as the synthesis of polyols and TPUs is dependent on a stoichiometric balance of acids and diacids respectively.

The polyol formulations used for TPU formation are varied which can affect different parameters such as operational temperatures, viscosity, and biodegradability. To better understand these metrics, acid number testing is performed. Material formulation of thermoplastic polyurethanes is an upcoming field which plays into biodegradable plastics and as bio-based polyols are being designed to serve as drop-in replacements in lieu of petroleum-based polyols, understanding their physical and chemical behavior is important.

Acid number analysis is typically performed using ASTM D664-18e2 and denoted by  $\frac{mg\ KOH}{g\ sample}$ . It is a single equivalence point potentiometric titration using a 50:48:2 mixture of toluene, isopropyl alcohol and deionized (DI) water respectively. This mixture is the titration solvent and is used as it is a combination of non-polar aprotic and polar protic solvents to dissolve the polyol synthesized. A predetermined quantity of sample is dissolved in the titration solvent and titrated against 0.05M potassium hydroxide in isopropyl alcohol (KOH in IPA).

Polyol and TPU synthesis is a catalyst driven process. One such catalyst used in bio-based polymer reactions is dibutyltin dilaurate (DBTDL). DBTDL is an organometallic catalyst which is a powerful base and a good reducing agent. Organometallic reagents will attack/ deprotonate acidic hydrogens and will attack the carbonyls on acids. Acids used in polyester polyol and TPU synthesis (azelaic, sebacic and succinic acid) are all classified as weak Bronsted acids which can

preferentially react with the catalyst rather than participate in the intended reaction. This can prevent the polyester-polyol reaction from going to completion.

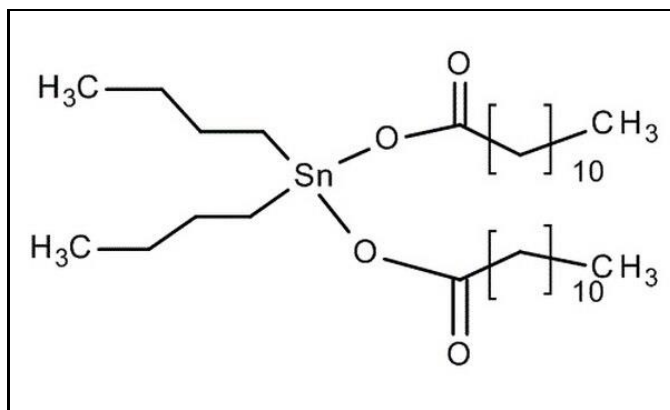


Figure 10- DBTDL is the catalyst of choice for both polyol and TPU synthesis. It is sensitive to excessively acidic conditions which can hamper its reactivity

The acid number titration starts by dissolving 0.15 g of KHP in 30 mL of deionized (DI) water. Concurrently, a 0.05M solution of KOH in IPA is prepared by dissolving solid KOH in HPLC grade isopropyl alcohol under heat (15pprox.. 60 °C); this solution is the titrant. The KHP solution is titrated with the titrant to determine its true molarity as KOH is only partially soluble in IPA. The following formula is used to calculate the true molarity.

*Molarity of titrant (M)*

$$= \frac{\text{Mass of KHP used (g)}}{1} \times \frac{1}{\text{Molar mass of KHP (g)}} \times \frac{1000 \text{ mL}}{\text{Volume of KOH (mL)}}$$

To verify and quantify the usability and expected error respectively of the reagents, a standardization test using benzoic acid is performed. Approximately 0.07 g of solid benzoic acid is dissolved in 60 mL of titration solvent and an acid number titration is performed. An expected endpoint (mL) is calculated using the formula

*Expected endpoint (mL)*

$$= \frac{\text{Mass of Benzoic acid used (g)}}{1} \times \frac{1}{122.12 \text{ g/mol}}$$
$$\times \frac{1000 \text{ mL}}{\text{Molarity of KOH (mol/ 1000 mL)}}$$

The expected endpoint is compared with the experimental endpoint and the percent error is calculated. Acid number analysis of polyols is performed by dissolving a variable mass of melted polyol sample (0.5-1.0g) in 60 mL of the titration solvent. The auto titrator dispenses the titrant at a rate of  $0.20 \frac{\text{mL}}{\text{second}}$  and plots pH changes as a function of volume of titrant dispensed. The first derivative of this plot is monitored and the volume at which the first derivative is highest is the equivalence point.

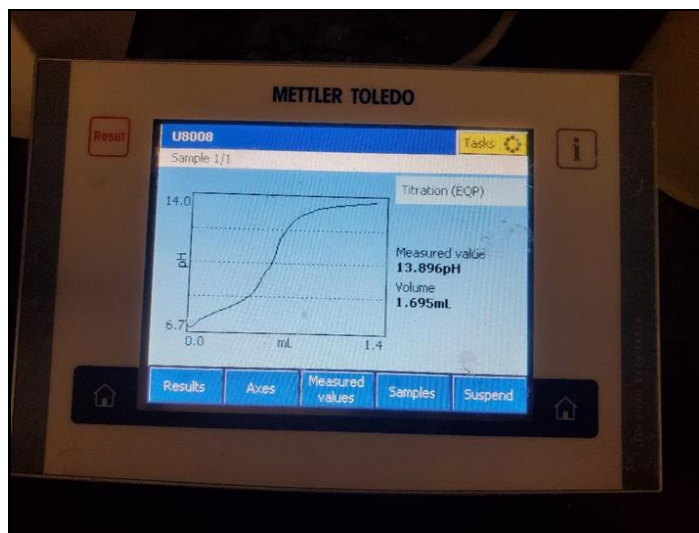


Figure 11- The equivalence point is where the slope is highest which is determined by the first derivative. The graph is generated by mapping the changes in pH as a function of titrant added.

The potentiometric acid number test has numerous advantages over other ASTM recognized titration methods. ASTM D974 Standard Test Method for Acid and Base Number by

Color-Indicator Titration and ASTM D8045 Standard Test Method for Acid Number of Crude Oils and Petroleum Products by Catalytic Thermometric Titration are two such reviewed methods.

ASTM D974 is at a distinct disadvantage as compared to the potentiometric method used as it is a qualitative method that does not quantify the amount of acid present in the polyol sample. It can be used to show large shifts in the polyol's acid concentration at a glance but does not provide valuable data when performing time-based trials on polyol stability.

On the other hand, ASTM 8045 (Catalytic Thermometric titration) is a quantitative method. A fixed mass of the sample is dissolved in a mixture of xylenes and propane-2-ol and titrated with a mixture of potassium hydroxide in propan-2-ol. The titration temperature is plotted as a function of the volume of titrant added, and a plot is generated. The rationale is that as the acid-base reaction occurs, the temperature increases. Once all the acidic constituents have been consumed, the slope of the plot will change; the point at which the slope changes is the inflection point.

A distinct disadvantage of this method is that it needs specialized equipment. It also has a much narrower range of operation than potentiometric titration. ASTM 8045 can provide precise acid number measurements between 0.1- 16 . In comparison, ASTM 664 can provide precise measurements between 0.1-150 . The potentiometric titration method has 8x the serviceable range as compared to thermometric titration method and is the superior analytical method. Experimental polyol formulations used for TPUs have regularly seen acid numbers greater than 50 and thermometric titrations would not be a compatible method. The first is being able to determine the percent error of the result. This is done by running a sample titration with a standard and setting a percent error cutoff. The standard of choice here is benzoic acid as it is highly soluble in the titration solvent as even though it has a polar carboxyl group on it, most of the molecule is

nonpolar. In addition, there are no internal stabilizing structures that will favor carboxylate ( $\text{COO}^-$ ) formation over carboxylic acid ( $\text{-COOH}$ ). This also means that benzoic acid is highly stable under normal storage conditions and will not pick up atmospheric water unlike one of the other standards used (potassium hydrogen phthalate (KHP)).

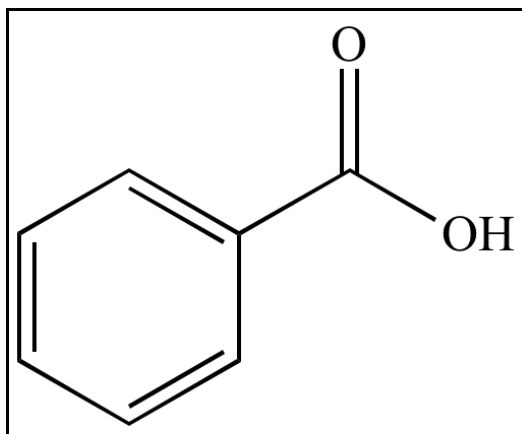


Figure 12- Benzoic acid is a reliable and robust compound that is not hygroscopic. Due to its chemical structure which makes it an ideal contender to be used as a standard in chemical tests.

When KHP becomes hydrated with atmospheric water, it becomes clumpy but can be baked for 2 hours at  $120\text{ }^{\circ}\text{C}$  to drive off the water it has absorbed to be used again without issues. Benzoic acid cannot be 'dried' as it sublimes at  $100\text{ }^{\circ}\text{C}$ . It is imperative that the standards used in the acid number tests be as dry as possible for optimal results.

Sample solubility in the titration solvent is a key factor in accurate polyol analysis. A common problem was that the polyol sample did not fully dissolve in the titration solvent. The standard polyol analysis method involved pouring polyol melted at  $45^{\circ}\text{C}$  into a titration cup and then adding 60 mL of titration solvent to dissolve the polyol. A frequent problem would be that many polyols would not completely dissolve, i.e., there would be visible chunks that would not dissolve despite stirring. In addition, the polyol would tend to accumulate in crevices. A proposed

idea was to heat the solvent to increase solubility; however, this was not done as the solvent was 50% toluene. The low boiling point of toluene, carcinogenicity and flammability did not make heating the titration solvent a viable option. A workaround was to heat the polyols to 65 °C (sometimes up to 90 °C depending on formulation) and pour the hot melted polyol into a premeasured quantity of solvent and mix immediately. This ensured that the sample dissolved well, and the results were as accurate and precise as could be.

If modified mixing methods did not address solubility issues, modifications in the solvent system were attempted. The standard mixture used was 50% toluene (non-polar aprotic), 48% 2-propanol (polar protic) and 2% DI water. Solvent substitutions were tried when the standard mixture did not work. The first solvent system substitution was attempted for polyol sample BSR-33-24 hr. (long chain polyol) as it did not dissolve in the toluene-based solvent. Chloroform (stabilized with ethanol) was chosen as it is also a non-polar aprotic solvent. However, careful attention had to be given to the unstable nature of chloroform and stabilizing agents had to be considered. Two types of stabilized chloroforms were available - chloroform with 2% amylenes and chloroform with 2% ethanol.

Chloroform is not routinely used in acid number analysis as it is an unstable compound compared to toluene. Chloroform needs to be chemically stabilized to prevent it from reacting with atmospheric oxygen and forming extremely toxic phosgene gas. Exposure to light (visible and UV) and catalytic contaminants hasten the formation of phosgene gas, dichloromethane, and unwanted acidic byproducts such as hydrochloric acid. This can severely hamper the acid number reaction and give unreliable data. While amylenes used for stabilization (2-methyl, 2-butane) do not interact with the titrant or polyol, they are not as effective as ethanol which can keep

chloroform stable for >5 years. Fresh reagents were used to ensure that reagent degradation was not a variable that would affect experimental accuracy and precision.

To start with, amylene stabilized chloroform was used in place of toluene to see if it is a suitable substitute. A 50:48:2 solvent mixture of amylene stabilized chloroform-IPA- MEQ was prepared and stored in a dark glass bottle to further slowdown chloroform degradation. To assess the viability of the solvent, a sample titration using was performed; approximately 0.08 g of benzoic acid was dissolved in 60 mL of solvent. Using the molar mass of benzoic acid and true molarity of the titrant, an expected endpoint was calculated. The expected endpoint and experimental endpoint were compared, and the percent error was calculated. Despite maintaining consistent stirring conditions in both toluene-based and chloroform-based (50% stir speed for 300 seconds), the average percent error and standard deviation were high. The error seen ranged from 10.9%-19.8% which indicated that the amylene stabilized chloroform was not a viable substitute. The ethanol substituted chloroform was the next option used.

Chloroform stabilized with ethanol is a far more viable reagent as compared to amylenes as amylenes have a short shelf life. Chloroform has a density of  $1.49 \frac{g}{cm^3}$  while ethanol has a density of  $0.80 \frac{g}{cm^3}$ . As a result, ethanol floats atop the chloroform and prevents it from reacting with atmospheric water and/or oxygen. Propanol has a similar density as ethanol and as it is a majority constituent of the solvent system, it can protect the chloroform from degrading.

Most polyols of interest were able to dissolve in the standard titration solvent used without issue. This can be attributed to the combination of solvents used to make the titration solution. The acid number titration solution is typically made as a 50:48:2 mixture of toluene: isopropanol: MEQ; this ratio is carefully monitored as the titration solution is made in 4L batches. Most samples



should dissolve without issue with this combination of non-polar aprotic, polar aprotic, and polar protic solvents. However, some polyols, particularly ones with large molecular weights or long chains struggled to dissolve. To combat this issue, a new titration solution using chloroform stabilized with ethanol was made and tests were performed with benzoic acid to develop a new titration protocol. In this protocol, the toluene was replaced with an equal volume of chloroform stabilized with 1% ethanol. This protocol was designed for polyol BSR-33, a long chain polyol which was unable to dissolve in acetonitrile, toluene or THF but dissolved easily in chloroform. Trials using MEK were not attempted due to its poor electrical conductivity and incompatibility with pre-existing equipment.

The molarity of the titrant (KOH in IPA) was determined by making a solution of KHP in MEQ. Approximately 0.1 g of dry KHP was dissolved in 30 mL of MEQ; the exact mass of the KHP used was recorded for calculations. The titrant was prepared by dissolving enough KOH in IPA to make a 0.05M solution. As KOH is not readily soluble in IPA, the solution was prepared by heating the isopropyl alcohol to 65 °C and dissolving the KOH in it; this is also why the titrant had to be prepared fresh every day. Initially, the acid number titration was performed with 0.1M KOH in IPA but this titrant did not provide consistent performance as it cooled. KOH precipitation was apparent which would often jam the titrator and clog lines. Due to solubility concerns, the molarity of the titrant was manually verified. The true molarity of the titrant was determined by using the formula below.

$$\text{True molarity (M)} = \frac{\text{Mass of KHP (g)} \times 1000}{204.23 \frac{\text{g}}{\text{mol}} \times \text{Equivalence point (mL)}}$$

The first trial was performed by dissolving approx. 0.08 g of benzoic acid pellets in 60 mL of the titration solution at 50% speed for 300 seconds. These were the same conditions used for

the toluene-based solution. For all subsequent trials, approx. 0.08 grams of benzoic acid was used. Exact masses were recorded to calculate percent error and determine optimal experimental conditions. The expected equivalence point was calculated using the formula below.

$$\text{Expected equivalence point (mL)} = \frac{\text{Mass of benzoic acid (g)} \times 1000}{122.22 \frac{\text{g}}{\text{mol}} \times \text{True molarity (M)}}$$

When the titration was performed, the pH probe tracked potential change as a function of the volume of titrant dispensed (mL). The true equivalence point (VEQ 1) was the point where the potential spiked, indicating that all the acid (KHP) has been neutralized. VEQ 1 and the expected VEQ were compared to determine the percent error of the method run. Experimental error in acid number analysis was determined by comparing the amount of titrant said quantity of benzoic acid would consume and how much titrant was consumed. Benzoic acid and KOH react in a 1:1 molar ratio which makes it easier to work with.

$$\text{Percent error (\%)} = \frac{\text{VEQ 1 (mL)} - \text{Expected VEQ (mL)}}{\text{Expected VEQ (mL)}} \times 100$$

With regards to the chloroform-based titration method, the KHP standardization showed that the titrant prepared had a true molarity of 0.570M. It was expected as excess KOH had been added to the IPA to account for insolubility. After the KHP standardization, the benzoic acid standards were performed, and titration conditions were varied to identify the combination that could result in the least amount of error. The combinations and the ideal condition identified are explained below.

The first run was performed exactly how benzoic acid standardizations using the toluene-based reagent were performed. Approximately 0.08g of benzoic acid pellets were dissolved in 60 mL of the 50% chloroform mixture at 50% speed and then titrated with the titrant. This approach

resulted in 1.537% error. While the maximum permissible error allowed, for our analytical tests is 2%, further modifications were explored to see if experimental error could be reduced. It was known that when exposed to air, chloroform is likely to form acidic byproducts such as HCl.

The second trial was performed with the same solution and benzoic acid pellets, but the stirrer speed was reduced from 50% to 35%. Identical titration procedures were followed. Error was successfully reduced from 1.537% to 1.206%. While the reduced stir speed was successful in reducing experimental error, the same trial was repeated by crushing the benzoic acid pellets. As the available surface area was increased, the total stir time was decreased from 300 seconds to 240 seconds and stir speed was reduced from 35% to 25%. These changes further reduced experimental error to 0.851%. The last modification was to further reduce stirring time from 240 seconds to 150 seconds at 25% speed while using crushed benzoic acid. The final modification further reduced error down to 0.145%.

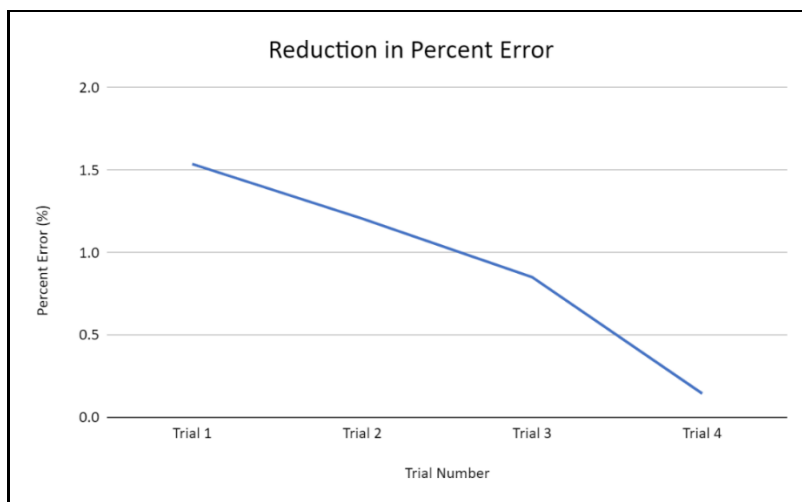


Figure 13- Reaction conditions were modified with each trial to determine the best possible conditions that would result in the lowest possible percent error. By using crushed benzoic acid, 25% stir speed and 150 seconds of pre-stirring, the percent error could be brought down to as low as 0.145%.

All these manipulations were done to reduce how much the chloroform was agitated during the titration. Reducing agitation was hypothesized to reduce the amount of solvent breakdown that would potentially interfere with accurate acid number values. The trials above show that chloroform stabilized with 1% ethanol can replace equal parts of toluene in the acid number solution without sacrificing accuracy or requiring extensive procedural modifications. However, chloroform is a more finicky compound as compared to toluene so preparing large batches and storing it for extended durations may not be wise. This solution when prepared in small batches and used quickly (< 500 mL) can provide reliable performance.

As both chloroform and toluene are non-polar aprotic compounds, they may be used interchangeably in certain situations. This can be attributed to the polarity of the two. Toluene has a relative polarity of 0.099 while chloroform has a relative polarity of 0.253. This can increase intramolecular interaction with the polyols being analyzed and allow them to dissolve.

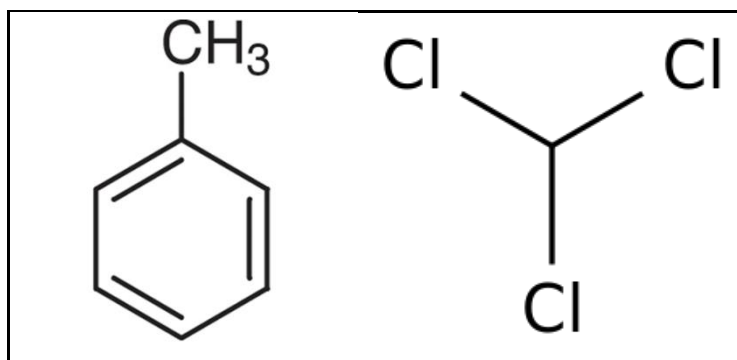


Figure 14- Toluene (left) is vastly different from Chloroform (right) given the functional groups present. The asymmetric distribution of chlorine can be attributed to the increased polarity that helped dissolve BSR-33 in the modified titration solvent used for acid content analysis.

As substitution was a successful exercise, the next step was to see if the acid number test could be successfully run if certain components were entirely removed. Toluene is a carcinogenic chemical that needs careful handling. It is not as much of a safety concern when being handled in

smaller quantities by few people but when in a teaching laboratory, it is not safe. With learning exercises, it would be ideal if toluene and/or chloroform could be eliminated. Isopropyl alcohol is the next largest constituent in the acid number solvent used. The toluene was replaced in equal volume with IPA to make a 98:2 mixture of IPA: MEQ. Benzoic acid was used to standardize the IPA- MEQ mixture, and this was successfully done within  $\pm 1\%$  error. The next step was to run the new solvent on the biodiesel. The first test was to assess solubility, and this was done by comparing relative polarity. Both biodiesel and IPA are non-polar molecules but do have small polar regions. Biodiesel is a long chain alkyl ester, and the ester groups make the molecule slightly polar.

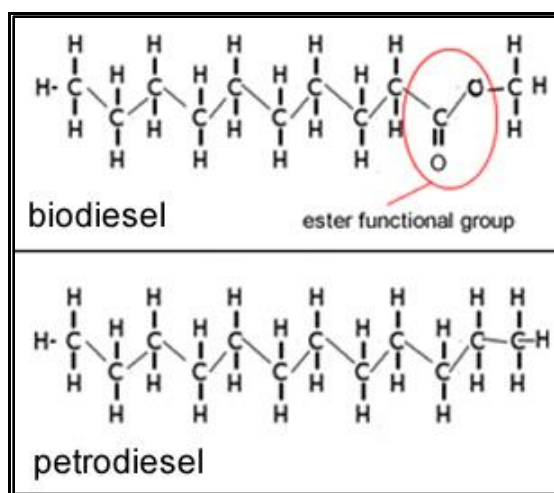


Figure 15- Biodiesel is also a long chain hydrocarbon like petrodiesel except for the presence of an ester function group. The ester group contributes to the slightly polar character of the biodiesel.

Ester groups are polar as oxygen is more electronegative compared to carbon, but the long chain dominates the non-polar character of the molecule. Similarly, isopropyl alcohol is a non-polar molecule. Its intermolecular bonds do not include hydrogen bonding and the molecules

cannot stick to one another despite having a polar -OH group on each molecule. The similar non-polar properties of biodiesel and IPA provide the backing that solubility should not be an issue.

The challenge was to design a method that was safer but did not sacrifice experimental reliability and the quality of the data acquired as a result. The mixture of 2% MEQ in IPA was tested using benzoic acid for accuracy and biodiesel for precision. Biodiesel acid content is an important metric to assess as biodiesel is typically made with used vegetable oil. This used oil often has acidic components that can make it into the biodiesel. The components, when in excess of  $0.500 \frac{mg\ KOH}{g\ sample}$ , can cause damage to engines and generators that run on this type of fuel.

To begin with, general standardizations were performed i.e., KHP to determine titrant molarity and benzoic acid to quantify percent error. The titrant's true molarity was calculated to be 0.052M following which, the benzoic acid standardization was performed. Benzoic acid was used as a standard again due to its stability and compatibility with the modified titration solvent. Percent error using benzoic acid standardization was remarkably low; errors within  $\pm 1\%$  were seen. There were no visible issues observed with solubility either. This reagent was then tested with biodiesel to determine the biodiesel's acid content.

The next step was to determine how much biodiesel could dissolve in the new mixture. The first trial was performed by dissolving 0.5 g of biodiesel in 60 mL of the new solution. While there were no visible solubility issues, the sample size was too small for any measurable data. The equivalence point was not registered.

The acid number value of the biodiesel was calculated using the formula below. The blank (0.1 mL) is the acid number of the solution.

$$\text{Acid number } \left( \frac{\text{mg KOH}}{\text{g sample}} \right) = \frac{(\text{VEQ } 1 - 0.1) \times 56.1 \times \text{Molarity of titrant (M)}}{\text{Mass of sample (g)}}$$

The next trial had a much larger sample size, approximately 5g of biodiesel was used with no solubility problems observed. This increase was useful as the titration moved beyond the blank (0.1 mL) and allowed an equivalence point to be determined. Further trials were performed to determine the maximum amount of biodiesel that could be dissolved in the solvent. This quantity was determined to be approximately 10 g keeping in mind the physical constraints of the equipment available. The quantity of biodiesel used was limited to 10g to ensure the titration cup would not be overfilled and cause spills or accidents. Additionally, it was seen that increasing the quantity of biodiesel from 5 g to 10 g did not affect the precision of results. Thus, any quantity between 5 g-10 g was acceptable for this method.

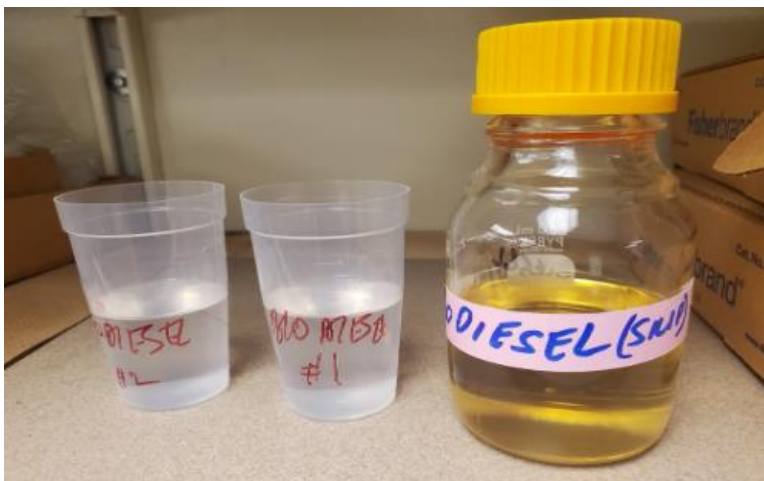


Figure 16- Eliminating toluene from the acid content titration made the process safer without sacrificing accuracy or precision. This new titration method was also compatible with titration equipment in use.

The 2% MEQ in IPA method to determine the acid number of biodiesel was used in a teaching lab as part of the curriculum for CHEM 100B - Instrumental Analysis. The advantage of this method was that it was much safer than the previous method that used toluene. IPA, unlike

toluene, is not a carcinogen and accidental spills are benign. In addition, this solvent elimination also made storage and waste disposal easier and safer.



## CHAPTER 3

Hydroxyl number titration is an analytical method to determine the number of free -OH groups present in a compound. Commonly, the hydroxyl number is denoted by units of mg base/g sample, i.e., milligrams of strong base required to neutralize the acetic acid taken up by the acylation of one gram of compound. This test provides valuable metrics to monitor reaction completion, polyol stability and can help modify experimental procedures and/or setups. There are several types of hydroxyl tests approved by ASTM International when working with polyurethane materials. Some are acylation using acetic anhydride and pyridine, pressure bottle phthalate and reflux phthalate using distilled phthalic anhydride and potentiometric titration using tetrabutylammonium hydroxide. The goal of each method is the same but equipment and reagent availability, user familiarity and waste disposal restrictions are all potential limitations to each method's applicability and adoption.

Acylation using acetic anhydride is a potential method suitable for a variety of polyester and polyether precursors that requires the sample to be either finely ground up or melted and for the sample to be dry (<0.2% water). The sample is acylated in a solution of acetic anhydride in pyridine in a 98 °C water bath for 2 hours. This acylated mixture is titrated using sodium hydroxide and phenolphthalein to its endpoint to determine the hydroxyl number of the polyol. A few drawbacks of this method are the reagents used, the time involved and the inherent inaccuracy when using a visual method. It is difficult to work with and it is easy to miss visual endpoints. In addition, water can easily destroy the acylation reagent, making titration unreliable.

Phthalate is also a route for hydroxyl number determination - either pressure bottle or reflux. In both methods, the sample is dried (<0.2% water), transferred to a reaction vessel using a hypodermic syringe and reacted with phthalic anhydride for two hours. The final product is then

titrated using sodium hydroxide and phenolphthalein to determine its endpoint and, consequently, hydroxyl number. A similar drawback as with the acylation with acetic anhydride is that this method takes a long time to complete and uses visual indicators which cannot offer the same level of accuracy and precision as a potentiometric method.

The method of choice for our novel polyol analysis is reacting the sample in acetonitrile (ACN) with p-toluene sulfonyl isocyanate (p-TSI) and titrating that with n-tert butyl lithium hydroxide (n-Bu<sub>4</sub>NOH). The titration is done using an auto titrator and monitored using a pH probe. The pH probe monitors changes in potential (mV) to determine equivalence points.

The p-TSI-based method has several advantages as opposed to the acylation and phthalate methods proposed:

1. The p-TSI method can be performed in a fraction of the time required. A polyol sample can be reacted with p-TSI and titrated with n-Bu<sub>4</sub>NOH in less than 15 minutes, as opposed to the 2+ hours required for the potential alternatives above.
2. The p-TSI method can be performed with an auto titrator and pH probe for easier, more accurate and more precise analysis. The p-TSI based method is done potentiometrically wherein the titration's endpoints can be accurately tracked, and it is easy to have error margins within  $\pm 2\%$ . The p-TSI method can also be performed at room temperature; it does not require any heating, pressure or reflux which makes the titration much safer.
3. The p-TSI based test used safer solvents and can be performed with small quantities of reagents which makes it safer to perform and to dispose of.

However, a common pitfall as with the others is moisture contamination. Excessive water can negatively affect the p-TSI by preferentially reacting with it and prevent it from reacting with the

polyol. This can skew the calculated hydroxyl number of the sample. We can mitigate these issues as best as possible by storing the p-TSI under a bed of nitrogen after use and preparing it in small batches of approx. 500 mL. The other reagents involved (n-Bu<sub>4</sub>NOH, ACN and 2-propanol) are stable and do not need special storage accommodations.

The low viscosity polyols in question here are precursors of thermoplastic polyurethanes (TPUs). They are made from polyester polyols and diisocyanates. These two components are reacted with a catalyst (DBTDL) and a diol. The polyester polyol and diol both contain hydroxyl groups, while the final product (TPU) does not contain any hydroxyl groups. In this context, a lower hydroxyl number would be indicative of greater reaction completion as it shows that the reactants have successfully formed a product of interest. A high hydroxyl number could indicate that the TPU synthesis was not complete due to a variety of factors such as insufficient starting materials, expired catalyst, or improper reaction conditions.

However, when making the polyester polyols (the precursor), a diacid is reacted with a diol and catalyst (DBTDL) and water is removed as the reaction progresses. Here, the final product should have a high hydroxyl number as it indicates reaction completion. In this context, a low hydroxyl number could be indicative of poor reaction completion caused by a variety of factors such as insufficient starting material, improper reaction conditions or the catalyst being denatured by the diacid. Organometallic catalysts such as DBTDL are incompatible with acids, and insufficient catalyst available can also affect final polyol yield.

The hydroxyl number test is thus an important metric to assess reaction progress and make necessary modifications to the synthesis to maximize yield. A deterrent to industrial adoption for

biobased polyols is equipment incompatibility and working out manufacturing hiccups will only make industrial adoption easier.

Hydroxyl numbers are not supposed to be time sensitive as the polyols produced (and TPUs by extension) are theorized to be stable. However, the -OH test is an important metric to verify that, as when making novel polyols, changes in -OH values over time can be detrimental to the TPU that is made from them.

The -OH test using p-TSI was started by determining the true molarity of the n-Bu4NOH in 2-propanol. The titrant is prepared by dissolving 0.1L of n-Bu4NOH in methanol into 0.9L of 2-propanol to make a 0.1M solution. n-Bu4NOH is chosen for this titration as opposed to other inorganic bases such NaOH and KOH as these are poorly soluble in organic solvents at room temperature; they typically have a solubility of  $\approx \frac{14 \text{ g}}{100 \text{ mL}}$  at room temperature. Typically, these inorganic bases will dissolve in 2-propanol only when heated but will start to crash out when the solution cools. This poses a severe hazard to the auto titrator as the solution cools, it will clog dispensing lines and burettes, which can cause equipment damage and unnecessary delays. Lastly, given the sensitivity of the p-TSI to water, it would be detrimental to use a hygroscopic inorganic base such as NaOH/KOH. Water introduced through the inorganic bases would react with the p-TSI and skew -OH values. The true molarity of the n-Bu4NOH is determined by titrating it with KHP (dissolved in MEQ); the molarity is required to calculate -OH values.

Through working experience with KHP, it has been demonstrated that even under vacuum storage when not under use, it is a highly hygroscopic salt and will easily pick up atmospheric water, a problem more commonly seen during humid summers. The salt would turn clumpy and

had a distinct sheen on it which indicated it was hydrated. However, this can be easily worked around by heating the salt at 120 °C for 3-4 hours and storing it under vacuum overnight.

After determining the molarity of the n-Bu<sub>4</sub>NOH in 2-propanol, an octanol standard test is performed. The octanol standard test is crucial to verify the viability of the p-TSI and n-Bu<sub>4</sub>NOH. The p-TSI is extremely sensitive to changes in atmospheric humidity as moisture can very quickly render the reagent useless. The n-Bu<sub>4</sub>NOH, while significantly more stable and robust as compared to p-TSI, also needs to be checked routinely. 1-octanol is a stable standard of choice as it is not volatile, insoluble in water and highly soluble in organic solvents used in the titration such as acetonitrile and isopropanol.

The mass of the sample used for -OH number analysis needs to be precalculated to prevent missing/ overshooting endpoints. The approximate mass of sample used is calculated using -

$$\text{Mass of sample (g)} = \frac{40}{\text{Expected Hydroxyl Number}}$$

1-octanol should have a theoretical hydroxyl number of approximately 430.8 ; the 1-octanol standard test calculates the experimental value which quantifies error and assess reagent viability. Error margins of ± 2% are permissible (values between 422.2 to 439.4 ) and the calculated experimental error from the standard test is applied to proceeding samples. Using the expected hydroxyl number, a sample size is calculated to avoid overloading the system. This is calculated using the formula –

$$\text{Mass of sample (g)} = \frac{40}{\text{Expected hydroxyl number}}$$

$$\text{Mass of 1-octanol (g)} = \approx 0.09 \text{ g}$$

Approximately 0.09g of 1-octanol is dissolved in 40 mL of ACN to which 10 mL of 0.02M p-TSI in ACN is added. Another advantage of using 1-octanol is that as it is a liquid, it is much easier to dispense small quantities that will readily dissolve. The titration cup is sealed to limit the amount of moisture reacting with the p-TSI and the mixture is stirred for five (5) minutes. The p-TSI added is in excess to prevent it from being a limiting reagent in the titration process. Post reaction, 0.5 mL of MEQ water is added to neutralize the excess p-TSI. This mixture is then titrated with the 0.1M n-Bu4NOH titrant and the equivalence points are determined by drops in potential; the -OH test should show two distinct points. These two points (VEQ1 and VEQ2) are used to calculate the experimental -OH value using the formula

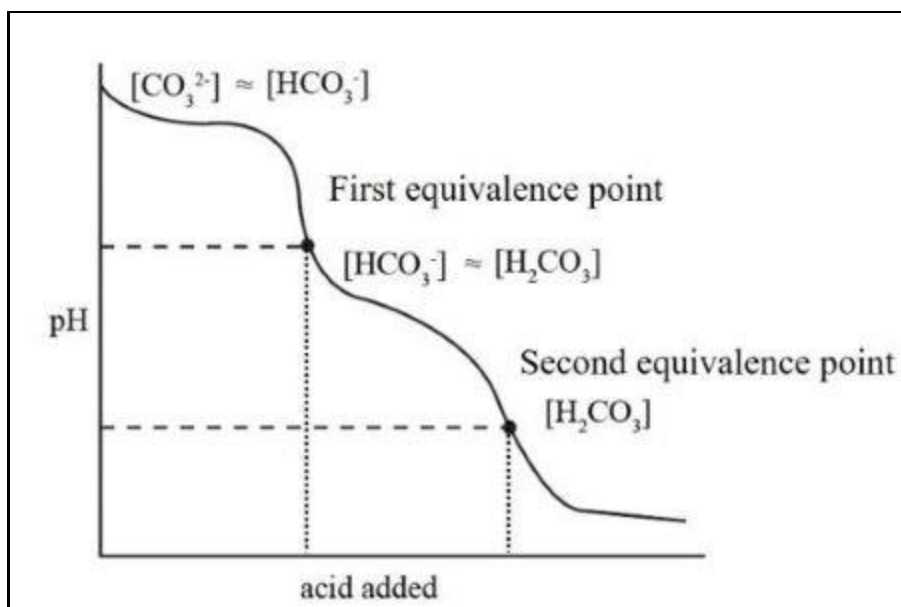


Figure 17- A representative image of how the potentiometric titration curve of a hydroxyl titration test would look. For our tests, potential (mV) is tracked as a function of the volume of base (n-Bu4NOH) added. The equivalence points are where the potential shows the steepest decrease.

$$\text{OH Number } \left( \frac{\text{mg } n\text{-Bu}_4\text{NOH}}{\text{g sample}} \right) = \frac{(\text{VEQ2} - \text{VEQ1}) \text{ mL} \times \text{Molarity of } n\text{-Bu}_4\text{NOH (M)} \times 56.1}{\text{Mass of sample (g)}}$$

The standardization using 1-octanol is also important to show that while reagents containing -OH groups are involved (2-propanol, methanol, and water), they do not interfere with the titration. The 2-propanol and methanol used do not artificially inflate -OH values as they are simply inert solvents. The water added post reaction with the p-TSI will also not affect the -OH value calculated as it neutralizes the p-TSI by forming p-TSA (p-toluene sulfonyl acid) which is a chemically inert substance and carbon dioxide. p-TSA will not react with other isocyanate groups and forms insoluble ureas. As a result, it does not play any role in the titration.

A source for an increase in the -OH number can be attributed to the polyol picking up water. It is entirely possible that a novel formulation can be hygroscopic and pick up atmospheric water as time goes by. It is possible that this attribute be exacerbated by environmental conditions. This is an important consideration to make when attempting to use novel polyols as drop-in replacements. Many plastic production facilities are in humid parts of the world, and if a particular polyol formulation is unstable in humid climates, it is less likely to be adopted. These changes can be prevented by storing the polyol of interest in a vacuum oven at 60 °C. The vacuum ovens accessible can generate a vacuum of up to 600 mm Hg; at the pressure, water can evaporate at 60 °C. The vacuum oven is used so that water is drawn out of the polyol as best as possible without exposing it to elevated temperatures that can damage it and cause unwanted side effects. For this reason, polyols are stored under vacuum during testing and dried overnight if suspected to not have been stored properly.

Excess water in samples is problematic as it can skew the true -OH value output of the polyol. At first, the water in the sample will react with the p-TSI and form p-TSA. This has been observed during experimental handling of bottles of 1.0M p-TSI in methanol (stock). A 0.02M

solution of p-TSI in ACN is used for -OH titrations which is prepared by pouring the stock (20 mL) into ACN (480 mL). A white powdery residue (p-TSA) was visible shortly after on the stock bottle's rims after being left out. Excess p-TSI is typically added (10 mL) when analyzing samples to account for minor water contamination resulting from pipetting, transfer and stirring but the excess does not consider water contamination from highly hydrated samples. However, the reason water is so problematic is because of the solvent's dipole moment and dielectric constant make it easy for water to dissolve in it. Given how sensitive potentiometric methods are – especially the one using p-TSI, careful attention needs to be paid to ensure proper polyol dehydration and storage.

It is possible that the polyol of interest is not soluble in the solvent used in the -OH number titration (ACN). While ACN can dissolve most organic compounds, substitutions may need to be made when working with polyols that have large OH numbers. This has been observed when working with some of the botryococcene polyols with theoretical -OH values greater than 400 . The polyol's solubilities were tested in multiple solvents - THF, MEK, chloroform, ACN and acetone. The polyol dissolved in all the solvents albeit it struggled with acetonitrile, which is why an alternative test needed to be designed. Acetone was not used due to concerns over pH probe damage and its high volatility. The remaining three choices - THF, MEK and chloroform were tested.

Chloroform was an unlikely choice as the solvent was stabilized using ethanol. A 100% chloroform blank and 10% chloroform-90% ACN blank were tested. The 100% chloroform blank did not register the endpoints as predicted , so a 10% (by volume) blank was tested which returned data. The quantity of ethanol used was small (1% v.v) and easily accounted for, for which additional p-TSI was added. However, unusually high hydroxyl values were seen during titrations



with 1-octanol. A blank titration could not account for the huge disparities seen and it was evident that chloroform was not a suitable choice and would not provide reliable data. Further investigation was not performed due to poor solvent behavior and other avenues were explored instead.

MEK was also discovered to not be a suitable choice as unlike chloroform, the pH probe was unable to detect distinguishable changes in potential. This was further investigated, from which it was seen that ACN is more conductive than MEK and that the pH probe used was not designed for MEK. Applications using this solvent were not investigated further as a result.

The last option explored was THF. There were initial concerns regarding the use of THF as it has the possibility of forming explosive peroxides with age. Careful attention was given to the solvent's age to ensure safety and viability. THF has the propensity to auto-oxidize when exposed to oxygen and form a peroxide (which has an OH group on it) even when fresh. Thus, a blank -OH test was run to determine the inherent -OH number of the solvent before use. When testing THF as a potential replacement, it was substituted neat, unlike the chloroform trial, where a mixture of acetonitrile and chloroform was used. The sample was dissolved in 20 mL of neat THF, stirred and when the sample had fully dissolved, the sample-containing mixture was topped up with an additional 20 mL of THF. A 1-octanol standard was then performed to see if the solvent could work with it. Unlike the chloroform, there was no unusual behavior seen and the blank was able to account for the spike in -OH number seen when running a 1-octanol standard. The -OH test using neat THF was determined to be a suitable replacement if necessary for certain polyols.

The polyol for which this titration method was developed was synthesized by Anton Samoylov and Miheer Modi for their botryococcene project. The polyol of interest struggled to dissolve in ACN but readily dissolved in THF which is why this approach was designed. The

project is elaborated upon in a later chapter. With -OH titrations, the solvent of choice is especially crucial as it needs to be compatible with the p-TSI i.e., the solvent should not react with it or be excessively hygroscopic. Trials using THF were done to verify its compatibility with the p-TSI. THF is a particularly tricky compound to use as it has the tendency to auto-oxidize in the presence of oxygen and form a peroxide. This peroxide has an -OH group on it which will react with the p-TSI and can artificially inflate the hydroxyl value of the sample being tested. This is demonstrated in the schematic below.

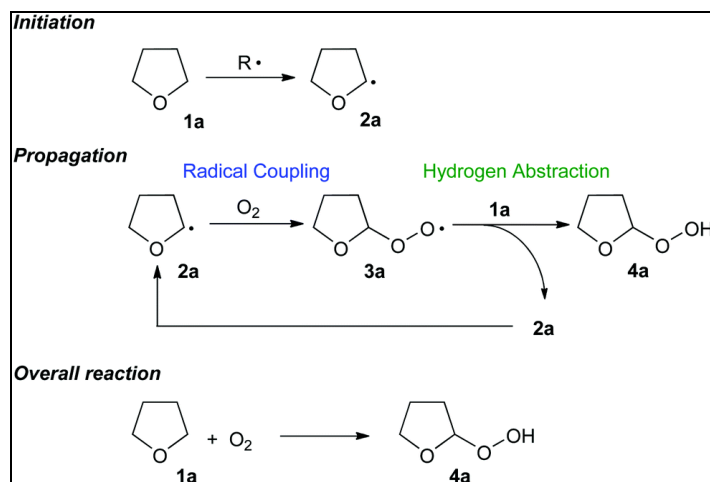


Figure 18- THF can rapidly undergo photooxidative degradation which can result in the formation of a -OH group. This is problematic as it can react with the p-TSI and invalidate results.

The titration method was first attempted by using a 50:50 (v.v) mixture of fresh THF and ACN titration mixture. A combination of two solvents was used to see if the pH probe is compatible with THF. Before the standard test was performed, a 3-point pH probe calibration as prescribed by the manufacturer was performed using pH4, 7 and 10 buffers. An acid-base titration using KHP was also performed to verify the molarity of the n-Bu<sub>4</sub>NOH titrant.

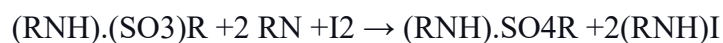
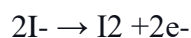
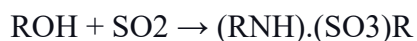
A standard -OH test was run with 40 mL of the titration mixture and approximately 0.1 g of the 1-octanol standard using the same protocol as with other polyols. As this was a novel approach to polyol synthesis and -OH analysis, the permissible error margin was increased from  $\pm 2\%$  to  $\pm 5\%$ . The 50:50 mixture was able to easily dissolve the polyol, but it did not pass the 1-octanol standardization. This approach failed as the 1-octanol standardization resulted in extremely high errors. The expected -OH number with the 1-octanol standard was 430.8 with an acceptable range 409.26 to 452.34 . The 1-octanol standard saw -OH values in excess of 500 were seen which resulted in % errors of 22.75%, significantly higher than the permissible upper limit of 452.34 . The inflated errors were not able to be accounted for when a blank titration was performed on the solvent. This showed that there was some incompatibility and the approach needed to be re-evaluated.

The next attempt was performed by eliminating ACN completely. ACN was entirely substituted with THF, and a 1-octanol standard was performed. As seen with the previous 50:50 mixture, the -OH value was inflated, the standard showed a -OH value of 476 . A blank titration was performed to determine the inherent -OH value of THF, this was calculated to be 37 . The difference was the true -OH value which was calculated to be 439 sample which is 1.59% error. This was promising as the solvent was compatible with the equipment available, errors were accounted for, and the percentage error calculated was well below the  $\pm 5\%$  limit allowed. THF does require greater care and attention as compared to acetonitrile. Given its propensity to form explosive peroxides with age and carcinogenic risk in addition to general handling hazards, THF is a riskier alternative to ACN. However, given that the substitution works without sacrificing accuracy and precision, this method can be used for polyols that may struggle to dissolve in ACN.

## CHAPTER 4

As shown, excess water content is detrimental to experimental accuracy by introducing an unwanted variable into the analyses. Water can skew chemical metrics of synthesized polyols and affect the physical properties of the TPUs made from them. To determine the amount of water present in a sample, another potentiometric method is used known as the Karl Fisher titration. This is a useful method to determine the water content of a sample quickly, accurately, and precisely.

This method was developed by scientist Karl Fisher and works on the principle of oxidation between iodine and sulfur dioxide. This method can be done as a volumetric titration or coulometric titration; the method used for our polyols is coulometric. This is done for ease, safety, and better compatibility with the type of samples being used. In this type of titration, iodine is generated electrochemically from iodide and the amount of water present in the sample is determined by measuring the amount of iodine generated. The following reaction schematic explains the process.



The reagents used are part of a prepackaged product sold as Hydranal Coulomat A which consists of a solvent alcohol (ROH- methanol), a base (imidazole), iodide and sulfur dioxide. The potentiometric titration is performed in a special Karl Fisher cell which has three frosted glass prongs in which the electrodes fit. The frosted glass increases surface area for a tighter seal. The electrodes are sealed with vacuum grease to prevent atmospheric water from exhausting the coulomat and causing excessive drift. Typically, the cell is furnaceed at 450 °C for 1 hour and allowed to cool overnight in the furnace. The cell is cooled as such to prevent it from being shocked

with an abrupt temperature change which could potentially shatter it. Once the cell has been cooled and taken out of the furnace, it is stored under vacuum until ready for use.

When the cell is ready for use, it is rinsed with acetone, dried and a special Teflon coated stir bar is placed into it. The greased electrodes (measuring electrode and generator electrode with platinum diaphragm) are fitted into the cell and necessary quantity of Coulomat A is added. On average, 150 mL is added to ensure that the probes are submerged, but more can be added if more samples need to be processed. The cell is quickly closed with a rubber septa and a pretitration cycle is run. During this process, water picked up during setup is titrated off to prepare the cell for samples. The pretitration cycle is run daily before sample analysis. Usually, a thin syringe is used to avoid making large holes in the septa. This allows the septa to last longer. Polyol samples are also heated to temperatures between 65 °C and 90 °C for easier injection and solubility.

Before a sample is analyzed, the coulomat's health is assessed by checking the potential and drift. Viable coulomat should have a potential greater than 100 mV and a drift of less than 10 mV. If the potential is lower than 100 mV, it is indicative of exhaustion. Consistent drifts greater than 10 mV could indicate a poor seal of the joints but this is usually remedied with grease. After verifying coulomat health, the sample is pulled into a syringe which is weighed. The sample is injected into the cell and the empty syringe is reweighed (double balance method). The mass difference between the full and empty syringe is the total quantity of sample injected into the cell. This mass difference is entered into the titrator which then calculates the water content of the sample.



Figure 19- The Karl Fisher cell is a highly specialized piece of glassware that can hold up to 200 mL of Hydranal Coulomat A with the probes in place. The gray probe measures potential and the blue probe is the generator electrode. The injection site is sealed with a rubber septa (white).

The instrument used (Mettler Toledo DL 39) can track coulomat health and potential which is used to calculate water content (ppm) of the sample being tested. The polyols tested while not being very viscous, struggled to dissolve in the coulomat if not heated enough. Heating the polyols has two advantages- the significantly decreased viscosity allowed a narrow bore syringe to be used and allowed the polyol to dissolve with more ease in the coulomat. The titration cell is designed to accommodate a magnetic variable speed stirrer which along with a potent polar organic solvent (methanol) can overcome solubility problems and easily dissolve all polyols of interest with ease. Additionally, the cell can easily accommodate between 150-200 mL of coulomat with the electrodes in. This can allow for approximately fifty samples to be analyzed before the coulomat

is exhausted, i.e., it needs to be replaced with fresh solution and the cell needs to be re-furnaced. This makes the method economical and well-suited for time-based trials. Time based metrics were important to track when making novel formulations as it helped understand and optimize reaction conditions for different diacid and diol combinations. Water is a byproduct of polyol synthesis, and while reactions running at temperatures upwards of 150 °C can theoretically drive off all water, it is wise to track water content in the event of unusual behavior. Lastly, the system is automated, so if the coulomat is viable and the mass of the sample is accounted for, the system can calculate water content (in ppm) depending on changes in potential. The system used also tracks potential and drift in real-time which are crucial for high quality analysis.

Water content analysis is a crucial metric as the polyols synthesized are part of a linear synthetic chain to make TPUs. TPUs are made by reacting said polyols with diacids and isocyanates in the presence of DBTDL. The isocyanates are of particular importance as it has been observed that they are sensitive to water. This has been seen during -OH number analysis and NCO content analysis. The -OH analysis was performed with p-toluene sulfonyl isocyanate (p-TSI), and NCO content analysis was performed with methylene diphenyl diisocyanate (MDI). Both classes of compounds showed decreased reliability exposed to moisture. If the polyols were excessively hydrated, the diisocyanate would not be able to fully participate in the TPU synthesis. This could lead to poorly synthesized TPUs. By extension, this would lead to subpar physical metrics when performing tests such as DSC, TGA, GPC, tensile strength, and dog bone analysis.

High water content is a problem when performing polyol analysis as it will interfere with the proceeding stoichiometric balances needed for TPU formulations unless accounted for. Typically, water content is determined in ppm by the titrator, and this value is manually converted

to % mass; formulations are generally preferred to be under 500 ppm/ 0.05% water. An important metric related to the water content is the hydroxyl number which is done through a delicate potentiometric titration that determines the number of -OH groups present per gram of polyol. The -OH number is crucial as it is used to calculate the equivalent weight of the polyol and the molecular weight of the polyol, both of which are done using the equations below.

$$\text{Equivalent weight} \left( \frac{g}{eq} \right) = \frac{56,100}{OH \text{ value}} \left( \frac{g}{eq} \right)$$

$$\text{Molecular weight} \left( \frac{g}{mol} \right) = \frac{56,100}{OH \text{ value}} \times (fn) \left( \frac{g}{mol} \right)$$

(fn) is the nominal functionality of the polyol. It refers to the number of chemically active groups present per molecule for the proceeding reaction. If a sample has a (fn) of 4, it will mean (in this case) that there are 4 -OH groups available. As shown above, the polyol's molecular weight is dependent on the hydroxyl value of the sample. If a sample is excessively hydrated, the p-TSI will be neutralized, and a lower hydroxyl value will be calculated which can have negative implications on the TPU made from it.

For example, if a polyol's true hydroxyl value is 500 and it has a nominal functionality value of 4 (there are 4 -OH groups present), the molecular weight would be –

$$\text{Molecular weight(gmol)}=(4) \rightarrow 561.0$$

However, if the same polyol was excessively hydrated and as a result returned an artificially lower hydroxyl value of 400 , the molecular weight would be calculated to be –

$$\text{Molecular weight(gmol)}= (4) \rightarrow 448.8$$

As seen, a 20% reduction in -OH value would result in a 20% reduction in molecular weight as well. This type of artificial deflation would spill over into calculating the total weight of isocyanate needed for TPU synthesis.



However, -OH numbers are not the only metric affected by excessive water. Polyol analysis needs water content analysis as numerous other metrics can be affected by water. In our case, DSC (differential scanning calorimetry), TGA (thermogravimetric analysis) and GPC (gel permeation chromatography) are metrics that will be affected if the total water content of the polyol is not accounted for.

Differential Scanning calorimetry (DSC) is a means of measuring the rate of change in heat flow to a sample as compared to a reference sample. Both samples are subject to a controlled temperature program and the heat transfer is measured in (J/s). DSC is an essential method to understand the characteristics of a polyol which can be used to study oxidation and other chemical reactions. The presence of water can be severely detrimental to accurate analysis. Water has a high specific heat capacity of 4.184 and this can significantly impede heat transfer through a sample by retaining energy. Unless the water content of the sample is properly accounted for, the artificially inflated transition temperatures can skew other important metrics.

Thermogravimetric analysis is another analytical metric to study polyols. This analytical method involves heating a substance to constant changes in temperature over time to induce a thermal reaction. Resulting changes in mass are observed to assess numerous parameters such as rate of oxidation and decomposition, material purity, and the thermal cracking point of base fluids. TGA is especially useful for polyol analysis as these compounds need to withstand high reaction temperatures upwards of 150 °C. TGA analysis can help test the polyol's thermal resistance as well as quality and stability parameters.

Gel Permeation Chromatography (GPC) is an analytical method used to study the molecular weight, size, and structure of a polymer. The method separates the macromolecules of

interest using a column packed with material of a certain pore size. Larger molecules will not be able to interact with the material packed in the column whereas smaller molecules will. This interaction determines the elution time wherein larger molecules will elute faster as compared to smaller molecules that are entrapped within the column material. As GPC is dependent on a range of factors such as matrix choice, packing material, and eluent, unaccounted water content may cause unwanted interactions between the stationary and mobile phase and the polyol, which can negatively affect the final data obtained.

When a polyol is excessively hydrated, it is more likely to exhibit unstable behaviors over time. Different polyol samples synthesized by Dr. Naser Pourahmady were analyzed wherein their water content and hydroxyl value over time were evaluated. Their hydroxyl values over time were tracked and graphed. The trend line was mapped, and the equation of that line was determined. The equation followed the format below (equation of a straight line).

$$y=mx+b$$

Here,  $m$  (slope) is of importance as is the rate of hydroxyl drift over time. In some polyols, the hydroxyl value was negative, while in others, it was positive. When the slope was positive, it indicated that the hydroxyl value increased with time and when the slope was negative, the hydroxyl value decreased with time. The water content and absolute value of the slope was then graphed. The absolute value of the slope was used as we wanted to see if there was a definitive correlation between hydration and stability. Stability was evaluated as absolute change over time, not in terms of hydroxyl value increase or decrease.

It was seen that in four out of the five polyols analyzed, as the water content (ppm) increased, the absolute slope also increased.

**Polyol Name**

**Water content**

**Slope**

AZEG- 1500 with Emery

298

0.1806

AZA-NPG 1000

584

0.2333

AZA-EP 1000

905

0.4303

Emerox 14550

1391

1.2226

AGEZ- 1000 with Emery

1401

0.2919

The polyols were analyzed for their water content and hydroxyl stability over time. This data was graphed to see if there was a correlation between the two.

Polyol AZEG-1500 with Emery was the least hydrated at 298 ppm with an absolute slope value of 0.1806. This indicates that as a polyol becomes more hydrated, the hydroxyl drift over

time will also increase. A likely explanation is that existing water will attract more water as time passes and this will interfere with the hydroxyl analysis. Inaccurate hydroxyl analysis will have dire implications on TPU formulations as explained below.

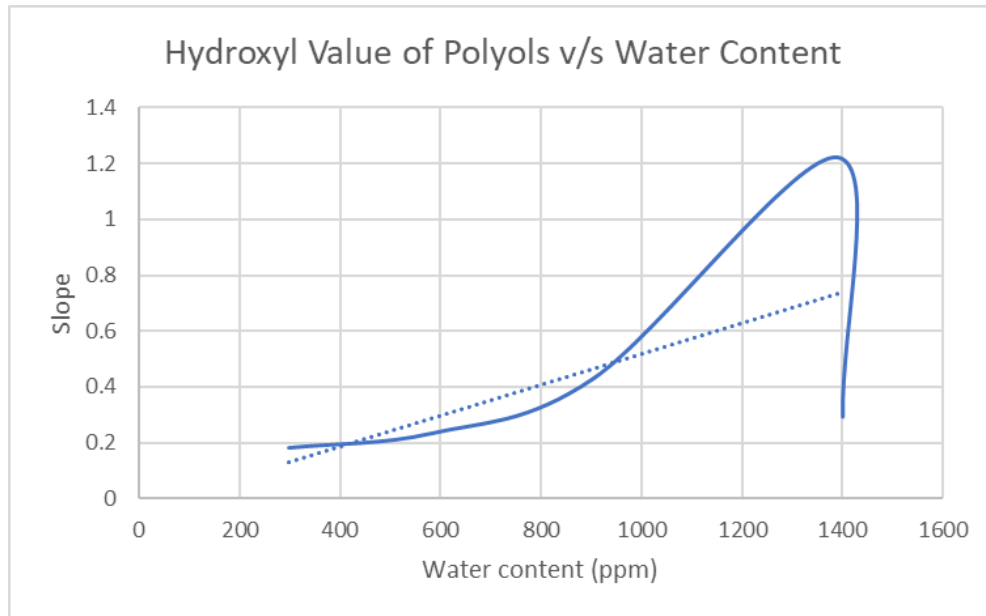


Figure 20- As polyols became more hydrated, their absolute hydroxyl drift also increased. The trendline also supports this idea. A likely explanation can be that water present would attract more water from air and as a result, cause the polyol to become hygroscopic

As polyols became more hydrated, their absolute hydroxyl drift also increased. The trendline also supports this idea. A likely explanation can be that water present would attract more water from air and as a result, cause the polyol to become hygroscopic.

Polyols are reacted with isocyanates (NCO) to make polyurethanes. The isocyanate (NCO) group reacts with a hydroxyl (OH) group in a 1:1 ratio. This ratio is known as the index. The index is crucial to determine the exact quantity of isocyanate required for the TPU synthesis to happen. The equation used to calculate the total weight of MDI (isocyanate) required for a complete reaction is shown below.

Total weight of MDI (g) = Index × MDI equivalent weight (g) × f(n)

$$= \frac{\text{Weight fraction (polyol)}}{\text{Equivalent weight (polyol)}} + \frac{\text{Weight fraction (water)}}{\text{Equivalent weight (water)}}$$

The equation above considers the weight fraction and equivalent weight of water present in a polyol of interest as well. This is done to ensure that the isocyanate is not exhausted by unaccounted water and a limiting factor in accomplishing as close to complete a reaction as possible. Accurate water content analysis is imperative to synthesize TPUs of high quality as incomplete synthesis can result in TPUs that may be excessively porous and weak. This can compromise structural integrity and durability of products made from them. Additionally, under-synthesized TPUs may also not be able to meet industrial biodegradation metrics as foams may behave in ways not expected. Thus, for high quality TPUs that meet industrial standards and consumer expectations, water content needs to be carefully monitored and adjusted.

## CHAPTER 5

Botryococcene is an algae derived oil which can be used to make high functionality polyols. It is obtained from the B-race of green algae *Botryococcus braunii*. What makes botryococcene special is that 80% of its dry weight is lipids. The strain of interest- Bot-22, produces a thirty-four carbon (C-34) molecule. This oil's alkene bonds would be converted into primary -OH bonds that would then be used to make polyols. These polyols could be used to make rigid foams. This molecule is isolated, purified and used in our experiments. The botryococcene algae oil used was acquired from Tsukuba University (Japan).

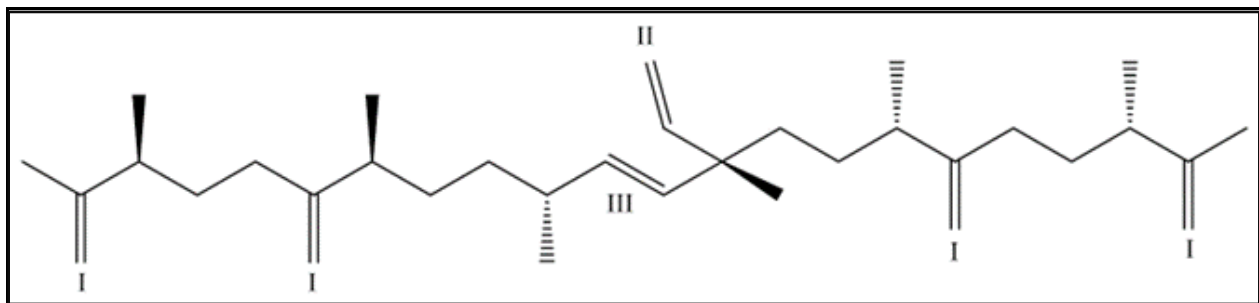


Figure 21- The chemical structure of C-34 botryococcene with labeled double bonds (roman numerals). (I) are vinylidenes, (II) is a monosubstituted alkene and (III) is a sterically hindered trans-disubstituted alkene.

There has been a global shift in consumer awareness and the implications of petrochemical based plastics currently in the market. The dangers of said plastics have been highlighted with major concerns regarding pollution, damage to marine life and microplastics, to mention a few fueling a transition to biopolymers. As a result, study and demand of bio-based alternatives has grown in recent years, and algal oil has been a contender. It is a favorable bio alternative due to its higher lipid content as opposed to crop-based sources. Additionally, relying on crops can be problematic in the event of crop failure as demand for biopolymers and food crops coinciding could have disastrous implications. For example, soybean oil has a high enough oil content to be used as a bio alternative, but this could have negative repercussions on food supply chains. Algal

sources are a more sustainable alternative as not only do they have higher lipid content, but they also will not compete with other food sources as algae is not part of any human diet.



Figure 22- *Botryococcus braunii* is used to make the algae oil that can be functionalized to make polyols

What makes botryococcene an interesting contender for future development is that the molecule is easier to work with as compared to other options such as soybean and rapeseed oil. Botryococcene oil by nature is a symmetrical molecule as compared to soybean oil which has a highly asymmetric comb-like structure. In soybean oil, the functionalized fatty acids are affixed onto a glycerol backbone unlike in botryococcene where the molecule exists as individual chains. Additionally, botryococcene polyols tend to exist as monomers like other biobased polyols, i.e., they do not form long chains made from numerous linked units. However, what makes botryococcene a tricky molecule to work with is it is available in limited quantities. It is a biomacromolecule which cannot be grown at large scales yet like crops.

The botryococcene molecule is a triterpene and the alkenes are distributed which means they can be functionalized through anti-Markovnikov chemistry. This is necessary as it enables the formation of primary hydroxyl groups. Primary hydroxyl groups are of particular importance

as these are the groups that can participate in reactions with isocyanates. Studies have shown that secondary hydroxyl groups do not exhibit the same kind of reactivity seen by primary hydroxyl groups and tertiary groups exhibit even lower reactivity. The botryococcene molecule has three different types of double bonds - 4 vinylidenes, 1 centrally located double bond and 1 internal olefin. The presence of 6 available sites for functionalization makes it a viable contender. Bio-based oils need to show high levels of functionalization with average hydroxyl values in the range of 200-600 mg KOH/ g sample. These have been achieved through existing hydroxyl groups or through a combination of epoxidation and transesterification of the unsaturated fatty acids.

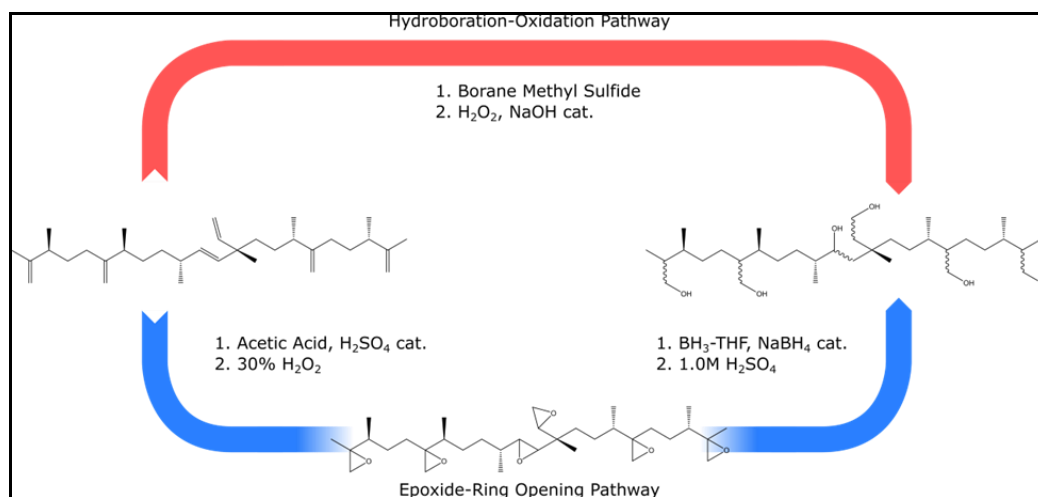


Figure 23- The botryococcene algae oil can be functionalized using two pathways. The hydroboration-oxidation pathway is a one step process. The epoxide-ring opening pathway is a two-step process. Both methods should theoretically yield the same amount of polyol.

The goal of this project was to investigate two synthetic pathways to functionalize C-34 botryococcene, both being involved to maximize the number of primary hydroxyl groups present. The first route was to use catalyzed hydroboration-oxidation and the second was to use anti-Markovnikov ring opening on highly substituted epoxides. As most of the alkenes on the botryococcene molecule are distributed, Anti-Markovnikov chemistry is required to form the most



number of primary hydroxyl groups. Comparative analysis would be done to evaluate the effectiveness of each method, i.e., how well the alkene groups were converted to functional -OH groups using borane complexes. The ability to form multiple potential hydroxyl groups make C-34 botryococcene an interesting point of research for further polyol synthesis or prepolymer mixes. The findings of this project can also be linked to novel rigid polyurethanes and their mechanical properties can be studied. For the scope of this project, the resulting polyols were purified and analyzed. Qualitative analysis was done using NMR (nuclear magnetic resonance) and FTIR (Fourier transform infrared spectroscopy). Quantitative analysis was done via hydroxyl number titrations to determine the polyol's functionality.

The hydroboration-oxidation method was first explored by Herbert Brown in 1959. This synthetic route opened avenues into the kinetic routes of borane complexes used in hydroboration. Borane methyl sulfide complex was identified as a stable participant for the hydroboration reactions. It is to be noted that most primary hydroxyl groups would be added to the botryococcene molecule via an Anti-Markovnikov reaction using hydroboration-oxidation; this process would create up to five primary hydroxyl groups. The monosubstituted alkene and sterically hindered trans-disubstituted alkene would show markedly reduced reactivity as compared to the vinylidenes due to steric hindrance. However, the reactivity of the vinylidenes is predicted to be like other triterpenes.

The procedure used was done in keeping in mind the high reactivity of Borane-THF and sodium borohydride. If the reagents available are not fresh, greater quantities may need to be used to compensate. The reaction was performed in a round bottom flask rinsed with THF. The flask

was flushed with nitrogen gas to create an inert atmosphere to which, a Teflon coated stir bar, 5 g of botryococcene and 228 g THF were added.

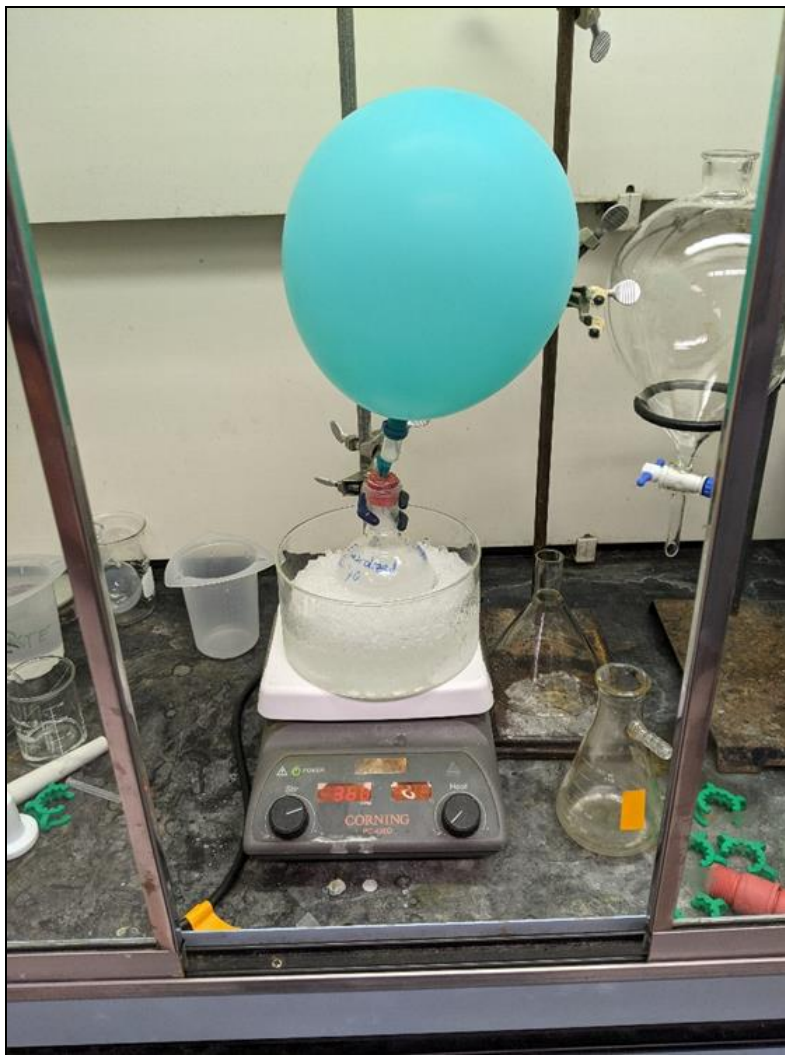


Figure 24- A nitrogen balloon was put in place to maintain an inert atmosphere for the hydroboration-oxidation reaction. The balloon was periodically refilled to ensure viability. On average, the balloon would need to be refilled every 30 minutes.

The flask was cooled in ice water and 32 mL of BMS was added dropwise. This was done to avoid having a violent exothermic reaction. The reaction was allowed to come to room temperature and allowed to react for two hours. The second phase of the reaction was started after the bubbling stopped; 5 mL of 3M NaOH catalyst was added along with 8 mL of cold H<sub>2</sub>O<sub>2</sub>

(dropwise). This process can be exothermic which is why it was done slowly. The contents of the flask were allowed to react for an additional two hours for a total of 4 hours of reaction time from start. Product extraction was done by transferring the contents of the reaction mixture into a separatory funnel and adding 1M sulfuric acid until the solution turned acidic. This was done to neutralize the NaOH catalyst and form an aqueous salt. A liquid-liquid extraction was performed using 150 mL of MtBE over 3 rounds. The organic phase was saved from each wash, combined, and dried with sodium sulfate. The MtBE removal is detailed below as that procedure was tweaked through trial and error.

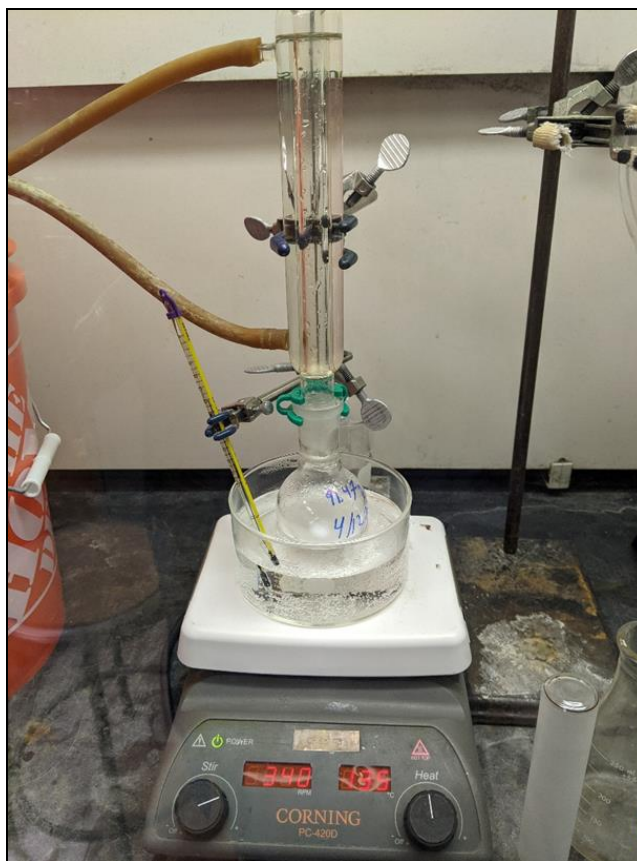


Figure 25- The reflux reaction was performed in a 65°C-water bath. The condenser was connected to a circulating water reservoir and a silicone oil trap.

The epoxide ring-opening method is a two-step process that involves using a mineral acid catalyzed epoxidation and anti-Markovnikov ring opening with  $\text{BH}_3$  catalyzed by  $\text{NaNH}_4$ . This approach was investigated by Brown and Yoon which was shown to produce primary hydroxyl groups on trisubstituted epoxides. This approach is predicted to target the epoxide rings formed on the vinylidenes but its effectiveness on the other rings will be investigated.

The first step of this process was to epoxide the double bonds of the botryococcene using a mineral acid. This was done by combining 5.0 g of botryococcene oil with 1.929 g of glacial acetic acid (1:2 molar ratio of double bonds to acid). Unlike the hydroboration-oxidation reaction, this reaction was not performed on ice. While stirring, 0.424 g of 18M phosphoric acid was dripped in (2% of total reaction weight accounting for 30%  $\text{H}_2\text{O}_2$ ). The reaction was heated up to 65C in a water bath and once the contents of the flask came up to temperature, 14 g of 30%  $\text{H}_2\text{O}_2$  was added. This was done to have a 2:1 ratio between the peroxides and unsaturated double bonds. The contents present were allowed to react for 2 hours and monitored by increasing viscosity and opacity. The epoxidized oil was separated using a liquid-liquid extraction of MtBE and MEQ water. In a separatory funnel, 80 mL of MTBE was added to the reaction contents and agitated. The bottom aqueous layer was discarded, and the layer was washed until it was near neutral pH. The organic phase was dried over sodium sulfate and the MtBE was rotovapped. The oil was then analyzed for quality.

The next stage of the process was to open the epoxide rings under an inert nitrogen atmosphere. The flask was kept on ice and to this cooled setup, 0.5g of  $\text{NaBH}_4$  dissolved in 100 mL THF and 50 mL of 1M  $\text{BH}_3$  in THF were added.



Figure 26- The sulfuric acid catalyst will turn the epoxide mixture a chestnut brown color; this type of color change was not observed with other acid catalysts. The brown mixture turned clear upon the addition of hydrogen peroxide.

The MtBE solvent removal process had to be tweaked for proper product extraction. In prior trials, the solvent was removed by rotovapping it out, but this approach was causing a white powdery precipitate to become entrapped within the polyol. This would prevent it from redissolving in the solvent and rendering the product unusable. Further investigation showed that the white precipitate was boric acid/ borane complexes. To work around this issue, the product removed from the reaction mixture was rinsed with acidified water (pH 3-4). This would remove boric acid. The dried organic phase was dried with sodium sulfate and passed through Amberlite IRA 743. This is a free base resin packed into a column to remove residual borane containing compounds which would become entrapped in the polyol. The free base resin was certified to remove the borane compounds without interfering with the polyol of interest. Out of caution, extra

MtBE was passed through the column to release any entrapped polyol. The column filtration process was repeated for optimal results. The organic washes were dried over sodium sulfate and the product was rotovapped at 25 °C to obtain the ring-opening product.



Figure 27- The ion-resin exchange column shown above was used to purify the botryococcene polyol. The resin used (Amberlite IRA 743) was specifically chosen for borane complex removal. Vacuum pressure was not required but can be used for accelerated filtration.

A hypothetical -OH number was calculated to estimate how well the botryococcene had been functionalized. The hypothetical -OH number is dependent on the number of double bonds converted - as there are 6 double bonds out of which 4 are easily accessible, we can expect the



following levels of functionalization. The expected hydroxyl number is also a crucial metric to calculate as best as possible the sample size needed for the test. If the sample size is too large, the endpoints could easily be overshoot, and the valuable product could be lost without reason.

If 4 of the 6 double bonds (vinylidenes) had been successfully functionalized, the expected -OH would be calculated as below.

The molar mass of botryococcene is 466.8 and the molar mass of KOH is 56.1. If a sample were to have four hydroxyl groups, the expected hydroxyl number would be -

$$4 \text{ -OH groups} = 480.8$$

If a sample were to have shown total functionalization with six hydroxyl groups formed, the expected hydroxyl number would be calculated as follows -

$$6 \text{ -OH groups} = 721.2$$

Using these hypothetical -OH values, the maximum sample sizes would be calculated as below-

$$\text{Sample size with 4 -OH groups} = 0.0929 \text{ g}$$

$$\text{Sample size with 6 -OH groups} = 0.0555 \text{ g}$$

The hydroxyl analysis of the botryococcene polyol would use a sample size between 0.0555g to 0.0929g.

The products of both reactions were analyzed using Fourier Transform Infrared Spectroscopy (FTIR) over a 600-400 nm range; 16 scans were performed to enhance the signal to noise ratio. The samples were applied to the anvil without any modifications. The noise from the IR spectra was processed using MATLAB using the X smooth function to the nth degree. The data was exported and reformatted using the Veusz data plotting software.

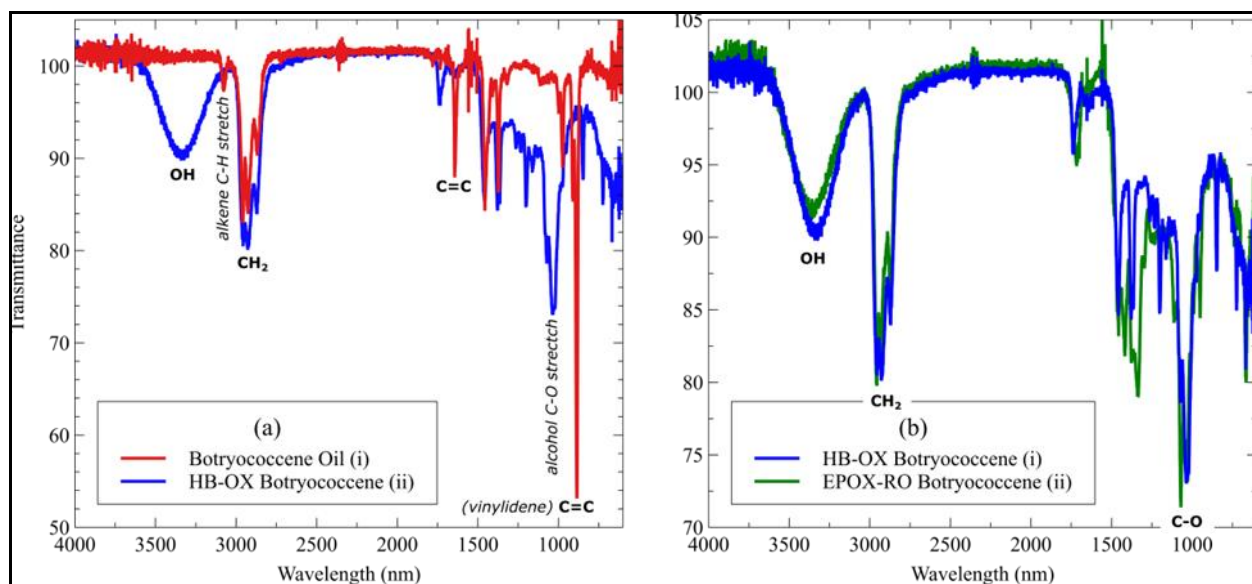


Figure 28- The FTIR spectra of the botryococcene oil and products. (a-i) is the hydroboration-oxidation product. (b-i and b-ii) are comparative spectra of the hydroboration-oxidation and Anti-Markovnikov epoxidation-ring opening products.

The goal of this paper was to evaluate the effectiveness of two synthetic routes to obtain the same product. The original botryococcene oil and polyol are both analyzed using FTIR. The IR spectra of the (a.i) unsaturated oil and (a.ii) hydroboration-oxidation product showed a marked change with the formation of hydroxyl groups in the product molecule. This was seen by the evident peak broadening between 3020-3700 nm on (a.ii). Additionally, the disappearance of the unsaturated -C bond peaks between 3000-3100, 880-900 and 1600-1700 nm seen on spectrum (a.i) show that there are no unsaturated bonds left unreacted. Several peaks corresponding to C-H bonds in the 1250-1500 and 2750-3000 nm region remain unchanged. This suggests that the product did not undergo major degradation during the functionalization of the unsaturated bonds.

A final comparison of the FTIR spectra of the hydroboration-oxidation product and epoxide ring opening product was useful in a qualitative analysis of the synthesis. Spectra (b.i) and (b.ii) both showed significant overlap which suggested that the two reaction pathways produce near-identical products. The characteristic hydroxyl peaks around 3020-3700 nm showed that the



compounds have similar intensities which suggested similar rates of functionalization. Lastly, there is a discrepancy seen in the fingerprint regions around 400-1900 nm, but this could be due to contaminants the reagents may have picked up during transfer rather than a result of the reaction pathway used.

While FTIR analysis is a useful tool to qualitatively assess the synthesis, NMR (nuclear magnetic resonance) is an excellent tool to confirm hydroxyl group formation and functionalization of the unsaturated bonds of the botryococcene.

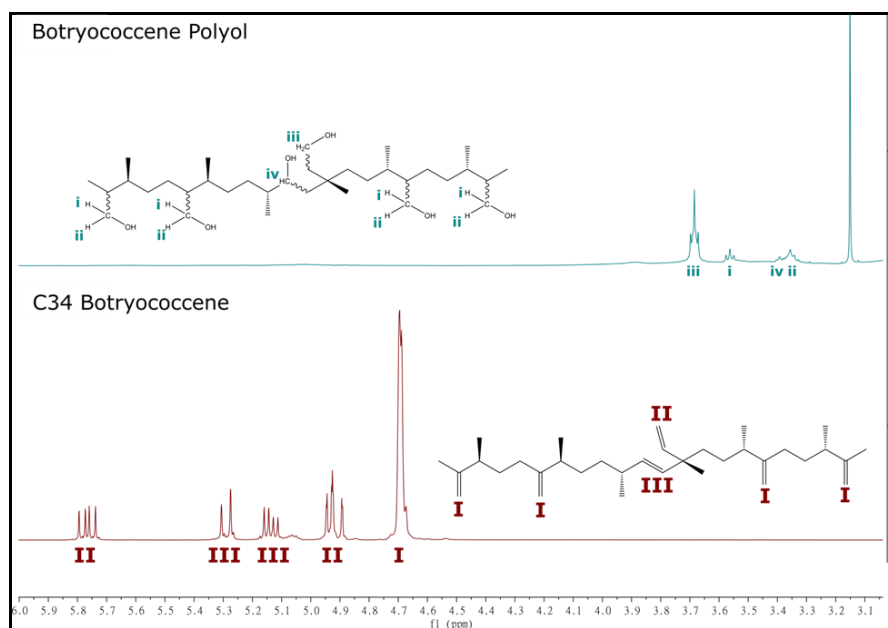


Figure 29- NMR spectra of the synthesized botryococcene products. The peak intensities were re-scaled for identification. The alpha carbon-hydrogens to each hydroxyl group were identified within the polyol. In the original C-34 botryococcene, each peak was correlated with the appropriate alkene. In the synthesized polyol, the hydroxyl hydrogen peak was seen at 3.15.

As seen in the figure above (side-by-side comparison of the botryococcene oil and polyol product), double bond elimination is evident with the disappearance of alkene hydrogens between 4.75-6.00 ppm. A large alkane peak at 1.15 ppm was seen in the C-34 botryococcene spectra which

was not seen in the functionalized polyol spectra. As analysis progressed, it was more effective to identify and analyze the hydrogens on the alpha carbon of the hydroxyl group. Alpha hydrogens form triplets as well as close clusters of doublets. NMR was also useful in helping identify the shifts belonging to the alpha carbons which also contributed to the idea that all 6 alkenes on the terpenoid had been functionalized. This idea was tested and confirmed with APCI-MS (atmospheric pressure chemical ionization - mass spectroscopy). The m/z (mass/charge) values were observed for all six levels of functionalization. Quantitative analysis was done using hydroxyl analysis detailed below.

The hydroxyl test was an important metric to quantify the functionalization of the double bonds to hydroxyl bonds. This method was imperative to quantify the success of both methods. Hydroxyl values (OH number) were determined using the ASTM-E 1899-16 method which used 0.2M p-toluene sulfonyl isocyanate (p-TSI) in acetonitrile as an acylation agent. A 1-octanol standard was used to calibrate the system. Calibration was brought within a  $\pm 2\%$  error margin before sample processing. The polyol sample was dissolved in HPLC-grade acetonitrile and reacted with excess p-TSI. The excess p-TSI was quenched with DI water after reacting with the polyol sample and the acylated polyol was titrated with 0.1M n-butyl ammonium hydroxide (n-Bu<sub>4</sub>NOH). The pH probe was used to measure potential difference as the titrant was added. The potentiometric differences were used to determine two equivalence points that were used to calculate the hydroxyl value in units of mg n-Bu<sub>4</sub>NOH per gram of sample.

The process needed to be modified slightly to account for solubility issues when analyzing the polyol made from the hydroboration-oxidation route. The polyol was solid at room temperature and needed to be coaxed to dissolve in the ACN. This was done by heating the solvent in a 65 °C

oven for 45 minutes. This encouraged the polyol to fully dissolve; the mixture was stirred occasionally as well. Once the polyol had fully dissolved, the hydroxyl number titration was performed without any issues. Solvent substitutions were not attempted in this trial as a result. Solubility issues may have stemmed up due to the formation of borane complexes when the reagents are exposed to air. Borane-complex formation cannot be avoided but can be minimized by storing the reagents in as cold an environment as possible and limiting contact with air through careful handling. The hydroxyl number test did not need to be modified when working with the epoxide- ring opening product.

The hydroxyl data observed shone valuable insight into the effectiveness of each method. The hydroboration-oxidation method's polyol was processed in triplicates after running a 1-octanol standard. The average of the trials was 416.665 . This was promising to see as this value suggested substantial functionalization. This value was also in line with the data obtained from the APCI-MS which suggested four out of six alkenes had fully reacted. The hydroxyl data from the epoxidation-ring opening ring opening showed a value of 361.118 which is 13.3% lower than the hydroxyl value obtained from the hydroboration-oxidation route. The qualitative data shows evidence of both synthetic routes being effective methods of functionalization. However, quantitative analysis showed that as the hydroboration-oxidation route can bring about functionalization, it would be a better choice.

The trickiest aspect of this reaction lies in the complete extraction of borane complexes/ boric acid from the polyol as if residual borane complexes do become entrapped in the polyol during the rotovapping stage, the polyol will be unable to dissolve in any solvent. Borane complexes will rapidly react with oxygen to form boric acid, which if not removed will cause

irreversible problems. The dissolved polyol in MtBE needs to be run through IRA 743 Amberlite multiple times to avoid this problem. Maintaining an inert nitrogen atmosphere during the reactions is key to reducing boric acid formation. This was done by using a septa and attaching a nitrogen filled balloon to it. This balloon was periodically refilled to ensure that as little oxygen reacted with the reactants as possible.

The advantages of using botryococcene based plastics is in the source itself. Algae is not part of any human food so there is no risk of it impeding on the global food supply chains. Also, it is a major source of concern for aquatic bodies as algae can draw out oxygen from water and cover it as they grow. This can starve water bodies of the oxygen their inhabitants need to survive, and the looming algae will prevent aquatic plants from being able to photosynthesize. By putting algae to use in plastic production, not only will a harmful and invasive plant be used to make a high demand commodity, but it will also allow for avenues of growth that will not be hampered by potential food insecurity.

The biggest limitation to using botryococcene to make plastics is its lack of availability. Botryococcene oil is derived from a specific strain of algae and has exclusively been worked on by Tsukuba University (Japan). This has severely restricted potential research avenues and work that can be done to develop botryococcene polyols.

The botryococcene polyol made was hypothesized to serve as a contender for bioplastics. It could be a viable option if not for the viscosity of the polyol. The polyol was extremely viscous, which made it difficult to dissolve in a solvent like acetonitrile. It would struggle immensely in its current state if it were used as a substitute in polyurethane synthesis. However, it could be interesting to study how the compound could be used to make bio adhesives. Commercially sold

adhesives such as PVA (polyvinyl acetate) glue are synthetic routes that will not be able to biodegrade. Given the preliminary physical properties of the botryococcene polyols, it could be an interesting route for future research.

## REFERENCES

- Amato-Lourenço, Luís Fernando. "Presence of Airborne Microplastics in Human Lung Tissue." *Journal of Hazardous Materials*, Elsevier, 24 May 2021, <https://www.sciencedirect.com/science/article/pii/S0304389421010888>.
- Borunda, Alejandra. "Most Shoes Are Made with Lots of Plastic. Can That Change?" *Science*, National Geographic, 3 May 2021, <https://www.nationalgeographic.com/science/article/shoes-sneakers-plastic-problem>.
- Carniel, Adriano. "A Comprehensive and Critical Review on Key Elements to Implement Enzymatic Pet Depolymerization for Recycling Purposes." *Biotechnology Advances*, vol. 52, 2021, p. 107811., <https://doi.org/10.1016/j.biotechadv.2021.107811>.
- Chemistry-Bio Fuels-Comparing Biodiesel and Petrodiesel*, <http://www.dynamicsscience.com.au/tester/solutions1/chemistry/organic/diesels.html>.
- Chen, Yuan. "Single-Use Plastics: Production, Usage, Disposal, and Adverse Impacts." *Science of The Total Environment*, Elsevier, 19 Aug. 2020, <https://www.sciencedirect.com/science/article/pii/S0048969720353018>.
- Chuang, Shien C., and Joseph W. Bozzelli. "Conversion of Chloroform to Hydrochloric Acid by Reaction with Hydrogen and Water Vapor." *Environmental Science & Technology*, vol. 20, no. 6, 1986, pp. 568–574., <https://doi.org/10.1021/es00148a004>.
- Datta, Janusz, and Paulina Kasprzyk. "Thermoplastic Polyurethanes Derived from Petrochemical or Renewable Resources: A Comprehensive Review." *Polymer Engineering & Science*, vol. 58, no. S1, 2017, <https://doi.org/10.1002/pen.24633>.
- "Different Types of Plastics." *Plastics Facts*, <https://www.plasticsfacts.com/new-page-1>.
- España, C. "Determination of Potassium Hydrogen Phthalate Purity by Coulometric Titration System: Validation Study and Uncertainty Estimation." *Journal of Physics: Conference Series*, vol. 1119, 2018, p. 012019., <https://doi.org/10.1088/1742-6596/1119/1/012019>.
- Illustrated Glossary of Organic Chemistry - Benzoic Acid; Benzoate; Benzoate Group*, [http://www.chem.ucla.edu/~harding/IGOC/B/benzoic\\_acid.html](http://www.chem.ucla.edu/~harding/IGOC/B/benzoic_acid.html).
- Li, Penghui. "Characteristics of Plastic Pollution in the Environment: A Review." *Bulletin of Environmental Contamination and Toxicology*, vol. 107, no. 4, 2020, pp. 577–584., <https://doi.org/10.1007/s00128-020-02820-1>.
- Mahajan, Sonam. "Determining the Acid Number of Biodiesel." *Journal of the American Oil Chemists' Society*, vol. 83, no. 6, 2006, pp. 567–570., <https://doi.org/10.1007/s11746-006-1241-8>.

- Matsubara, Hiroshi. “An Ab Initio and DFT Study of the Autoxidation of THF and THP.” *Organic & Biomolecular Chemistry*, The Royal Society of Chemistry, 12 Mar. 2015, <https://doi.org/10.1039/c5ob00012b>.
- “Microcrystalline Cellulose Chemical Characterization Services.” *Excipia*, 23 Feb. 2022, <https://www.excipia.eu/microcrystalline-cellulose/>.
- O’Brine, Tim, and Richard C. Thompson. “Degradation of Plastic Carrier Bags in the Marine Environment.” *Marine Pollution Bulletin*, vol. 60, no. 12, 2010, pp. 2279–2283., <https://doi.org/10.1016/j.marpolbul.2010.08.005>.
- Phung Hai, Thien An. “Flexible Polyurethanes, Renewable Fuels, and Flavorings from a Microalgae Oil Waste Stream.” *Green Chemistry*, vol. 22, no. 10, 2020, pp. 3088–3094., <https://doi.org/10.1039/d0gc00852d>.
- Pérez, J. “Biodegradation and Biological Treatments of Cellulose, Hemicellulose and Lignin: An Overview.” *International Microbiology*, vol. 5, no. 2, 2002, pp. 53–63., <https://doi.org/10.1007/s10123-002-0062-3>.
- Rajput, Bhausaheb S. “Renewable Low Viscosity Polyester-Polyols for Biodegradable Thermoplastic Polyurethanes.” *Journal of Applied Polymer Science*, vol. 139, no. 43, 2022, <https://doi.org/10.1002/app.53062>.
- Rongpipi, Sintu. “Progress and Opportunities in the Characterization of Cellulose – an Important Regulator of Cell Wall Growth and Mechanics.” *Frontiers in Plant Science*, vol. 9, 2019, <https://doi.org/10.3389/fpls.2018.01894>.
- Ruetschi, P., and R. F. Amlie. “Solubility of Hydrogen in Potassium Hydroxide and Sulfuric Acid. Salting-out and Hydration.” *The Journal of Physical Chemistry*, vol. 70, no. 3, 1966, pp. 718–723., <https://doi.org/10.1021/j100875a018>.
- Song, Young Kyoung. “Combined Effects of UV Exposure Duration and Mechanical Abrasion on Microplastic Fragmentation by Polymer Type.” *Environmental Science & Technology*, vol. 51, no. 8, 2017, pp. 4368–4376., <https://doi.org/10.1021/acs.est.6b06155>.
- “Standard Test Method for Acid and Base Number by Color-Indicator Titration.” *Digital Object Identifier System*, <https://doi.org/10.1520/d0974-21>.
- “Standard Test Method for Acid Number of Crude Oils and Petroleum Products by Catalytic Thermometric Titration.” *Digital Object Identifier System*, <https://doi.org/10.1520/d8045-17e01>.
- “Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration.” *Digital Object Identifier System*, <https://doi.org/10.1520/d0664-18e02>.

- “Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration.” *Digital Object Identifier System*, <https://doi.org/10.1520/d0664-18e02>.
- “Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration.” *Digital Object Identifier System*, <https://doi.org/10.1520/d6304-20>.
- “Standard Test Method for Hydroxyl Groups Using Reaction with P-Toluenesulfonyl Isocyanate (TSI) and Potentiometric Titration with Tetrabutylammonium Hydroxide.” *Digital Object Identifier System*, <https://doi.org/10.1520/e1899-16>.
- “Standard Test Methods for Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols.” *Digital Object Identifier System*, <https://doi.org/10.1520/d4274-21>.
- “Standard Test Methods for Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols.” *Digital Object Identifier System*, <https://doi.org/10.1520/d4274-21>.
- “Take Online Courses. Earn College Credit. Research Schools, Degrees & Careers.” *Study.com*, <https://homework.study.com/explanation/during-the-titration-of-sodium-carbonate-with-h-cl-the-dissolved-carbonate-ion-will-exist-in-three-different-forms-co-3-2-h-co-3-1-and-h-2-co-3-during-which-part-of-the-titration-initial-first-equivalence-point-or-second-equivalence-point-w.html>.
- Team, EBI Web. “Chebi.” *Poly(Ethylene Terephthalate) Macromolecule (CHEBI:53259)*, <https://www.ebi.ac.uk/chebi/searchId.do?chebiId=53259>.
- Top Gear. “Crash Test News - Malibu Slammer - 2009.” *Top Gear*, Top Gear, 24 Feb. 2021, <https://www.topgear.com/car-news/crash-test-news-malibu-slammer-2009>.
- Zhu, Kecheng. “Formation of Environmentally Persistent Free Radicals on Microplastics under Light Irradiation.” *Environmental Science & Technology*, vol. 53, no. 14, 2019, pp. 8177–8186., <https://doi.org/10.1021/acs.est.9b01474>.