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Use of Photo Isomers to Enhance the Removal of Lignin From Woody Biomass Hydrolysate

Dipesh J. Karki
University of Maine, dipesh.karki@maine.edu

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by

Dipesh J. Karki

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Advisory Committee:

Peter Van Walsum, Professor of Chemical Engineering, Advisor

Sampath Gunukula, Assistant Reserach Professor of Chemical Engineering, Co-advisor

M. Clayton Wheeler, Professor of Chemical Engineering.

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Advisor: Dr. Peter van Walsum

Co-Advisor: Dr. Sampath Gunukula

An Abstract for the Thesis Presented

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In this investigation we propose a novel method to enable precipitation of desired solutes using photo-isomers in the extraction solvent. This photo-switchable solvent would enable dissolution or precipitation of desired components using alternating UV or visible light to modify the solubility of the compounds of interest. Three photo-isomers namely native azobenzene, diethoxy azobenzene and diethylamino azobenzene were studied in three different organic solvents: medium chain length alcohol, ethanol and acetone. It was found that among the different combinations of solvent and photo-isomer, acetone and the 4,4’-diethoxy azobenzene solution was most efficient at precipitating dissolved lignin in response to UV light exposure. This system was able to precipitate 20% of the initial amount of lignin added.

ACKNOWLEDGEMENT:

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I would also like to remember my late brother, Ligal Karki and my mother, Phul Maya Karki. Without your support none of this would have been possible.

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Chapter 1: Introduction and Literature Review:

1.1 Project Goal and Research Objectives:

This research project aims to introduce an innovative approach for the precipitation of desired solutes by leveraging the unique properties of photo-isomers within the extraction solvent. The conversion of lignocellulose into valuable biproducts and biofuels typically involves an initial hydrolytic pretreatment process, which plays a crucial role in breaking down the complex polymers present in biomass and generating a cellulose-rich pulp stream. However, it is equally important to extract the dissolved components from this hydrolysis stage in order to maximize the utilization of biomass constituents beyond cellulose.

Among the various components found in the hydrolysate, mildly hydrophobic substances like dissolved lignin and dehydration products such as furfural or levulinic acid are commonly recovered using a liquid-liquid extraction technique. Traditionally, the recovery of desired extracts from the solvent involves either distillation or back extraction, both of which often impose high energy requirements and introduce additional complexities to the overall process.

In this particular investigation, we propose a groundbreaking method that capitalizes on the phenomenon of photo-isomerization within the extraction solvent to facilitate the precipitation of the target solutes. By incorporating a photo-switchable solvent, we can dynamically control the dissolution or precipitation of the desired components by alternating between UV and visible light irradiation. This innovative approach holds the potential to revolutionize the overall operation, thereby offering a more sustainable and efficient solution for recovering valuable solutes from the lignocellulosic hydrolysate.

1.2 Lignocellulosic biomass as a resource:

The greatest challenge of the 21st century is to enable the transition from fossil resources to an economy based on renewable resources. The main source of functional carbon building blocks for the fuel, chemical, and polymer industries is largely based on fossil fuels. Unlike fossil fuels, lignocellulosic biomass is a well-known renewable and sustainable source of carbon. Lignocellulosic biomass is a natural, abundant, and renewable feedstock for production of fuels and chemicals. Lignocellulosic biomass, which mainly consists of cellulose, hemicellulose, and lignin, has received increased attention as a promising renewable and carbon-neutral feedstock for production of biofuels and platform chemicals due to its high availability, and low cost (Phitsuwan et al. 2013). However, the sustainable and cost-effective conversion of lignocellulosic biomass into valuable feedstock is significantly limited by the complex cross-linking between the components. Therefore, pretreatment and fractionation of lignocellulosic biomass are generally performed prior to its subsequent transformation.

Traditional processes that use acids, alkalis, and organic solvents have a lot of disadvantages such as requiring hazardous chemicals and requiring a large amount of energy as well as capital. The most critical problem is the derivatization in the physical as well as chemical properties of the components which occurs during extraction and separation (El Seoud et al., 2007). For instance, kraft pulping, the most frequently used method for lignocellulose fractionation, produces kraft lignin which contains sulfur, resulting in a negative effect for its use in the production of the value-added products (Mansouri and Salvadó, 2006). Thus, it is necessary to develop a green method to pretreat and fractionate lignocellulosic biomass which would cause minimum amount of variations to the physical as well as chemical structure of the desired products.

1.3 Lignin:

Lignin is the second most abundant renewable source of carbon behind cellulose. Lignin is composed of phenylpropanoid units that act as a glue to bind cellulose and hemicellulose, giving a remarkable resistance against chemical and microbial attacks. Lignin, which accounts for 20-30% of the lignocellulosic biomass has been attracting tremendous research interest in value-added applications that include adsorbent, sustainable construction materials, antioxidants, and carbon materials (Xu et al.,2019). As compared to other natural polymers, lignin is non-linear and manifests as an amorphous, three-dimensional copolymer of phenylpropanoid units linked by ether bonds and carbon-carbon bonds such as β-O-4′, β-β′, β-1′, β-5, and 5-5′ (Sun et al., 2021). An example of lignin structure is shown below:

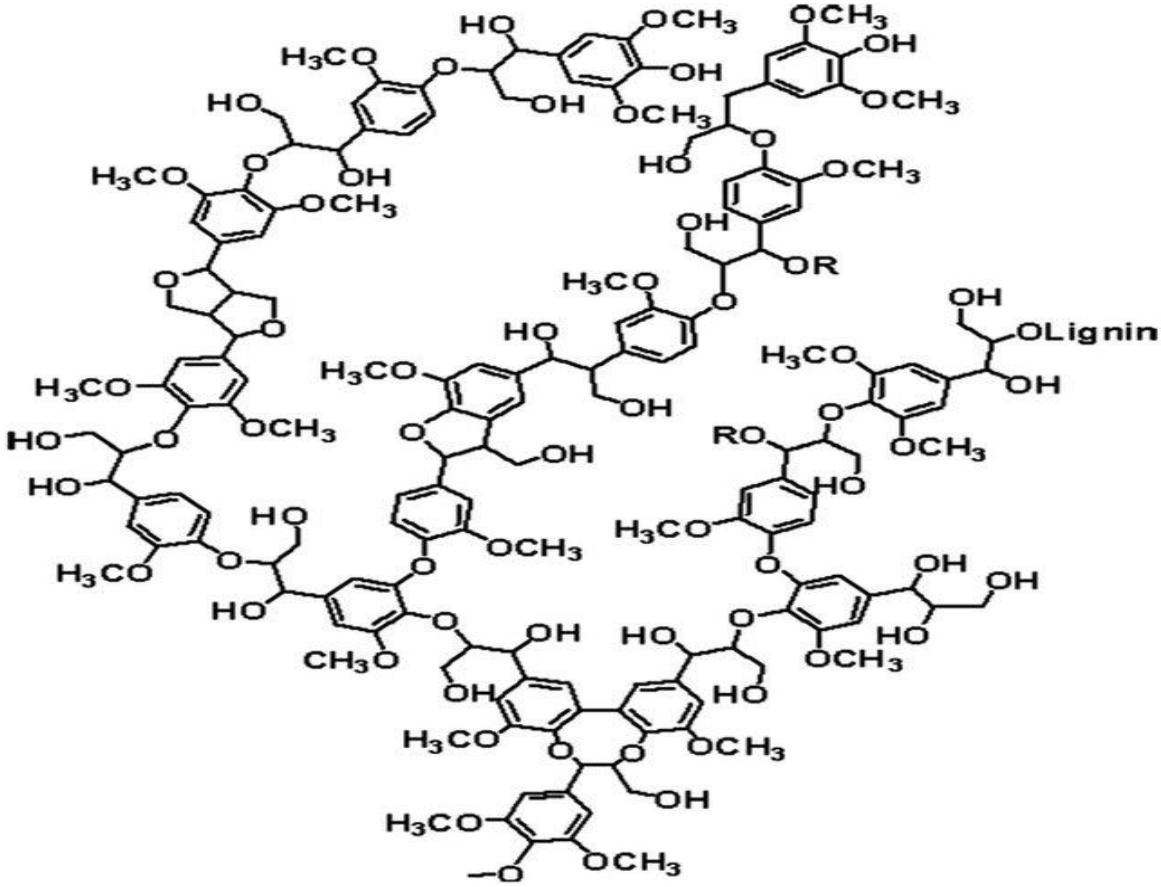


Figure 1: Chemical structure of lignin (source: lignoworks)

Resulting from this structure, lignin has antioxidant and anti-bacterial properties derived from its abundant aromatic structures and phenolic hydroxyl groups. This can be applied to high value-added products like medicine and cosmetic products (Sirviö et al.,2020).

1.4 Lignin Removal Process

There are several methods for lignin removal from biomass. The choice of lignin removal method depends on various factors such as the type of lignocellulosic material, the desired product, and the cost and environmental impact of the process. Some of the widely used methods are briefly explained below:

Kraft Pulping: It is a widely used method in the pulp and paper industry, where wood chips are treated with a mixture of chemicals (sodium hydroxide and sodium sulfide) under high temperature and pressure, resulting in the dissolution and removal of lignin. (Jun Liu et al.,2022).

Soda Pulping: This method is similar to kraft pulping but uses only sodium hydroxide without the sodium sulfide. The resulting pulp has lower strength but higher brightness than kraft pulp. (Jun Liu et al.,2022).

Sulfite Pulping: Usually conducted under acid or neutral conditions, sulfite pulping method uses sulfur dioxide and/or bisulfite ions to react with lignin to produce water-soluble sulfonated lignin. This method can be controlled to produce pulps over a wide range of lignin contents and pulp yields. (H.L. Hintz, 2001).

Organosolv pulping: It is a non-toxic and environmentally friendly process that uses organic solvents (such as ethanol, methanol, or acetone) and water at high temperature and pressure to remove lignin. (Jun Liu et al.,2022).

SO_2 steam explosion: This is a SO_2-catalyzed steam pretreatment method. This pretreatment substantially reduced the particle size of the feedstock (woodchips) eliminating any further need for grinding. The produced biomass has high heating values, low ash content and good overall carbohydrate recovery. (Toosyerkani et al.,2013)

SO_2 ,ethanol, water (SEW) pretreatment: This method provides high flexibility in the selection of the raw material, simple and efficient recovery of fractionation chemicals, absence of carbohydrate degradation (both cellulose and hemicelluloses), and high reaction rates. This process includes two-phase behavior. During the initial phase the hemicelluloses are removed together with lignin in the form of lignocarbohydrate complexes. The amount of sulfur bound to lignin is 2-3 times lower than that in acid sulfite cooking, and accounts for less than 1.1% on wood. The rest of SO_2 (95-97%) can be fully recovered by distillation. (Iakovlev et al.,2014)

Lime pretreatment: During this process, the biomass is pretreated with calcium hydroxide and water under different conditions of temperature and pressure. This method has been proven to be a useful method for selectively removing lignin without significant loss in carbohydrate. (Sierra et al.,2009)

Aqueous ammonia pretreatment: This method of pretreatment of lignocellulosic biomass uses aqueous ammonia. The main advantage of this method is delignification of biomass without significantly affecting the carbohydrate contents. It is a very effective method for substrates that have low lignin contents such as agricultural residues and herbaceous feedstock. The treated biomass retains cellulose as well as hemicellulose. (Kim et al., 2009).

Enzymatic Delignification: This method uses enzymes (such as laccases or peroxidases) to break down and remove lignin from plant materials. It is a promising method for lignin removal, but it is still in the research and development stage. (H.L. Hintz, 2001).

Ionic Liquid treatment: Ionic liquids are salts that are liquid at room temperature and have been shown to be effective at dissolving lignin. This method is still in the experimental stage but has shown promising results for removing lignin from plant materials. (An et al.,2015).

1.5 Organosolv Process:

The Organosolv process employs organic solvents like aromatic alcohols (phenols), acetone or aliphatic alcohols (e.g. ethylene glycol, methanol, ethanol, butanol, glycerol) as the cooking medium to treat lignocellulosic biomass. The purpose of this process is to separate lignin and to improve cellulose digestibility. Among the mentioned solvents, ethanol is the most preferred solvent for organosolv process because it is relatively inexpensive, has little toxicity, and is easy to recover. This process is usually performed in the presence of acidic catalysts such as H_2SO_4, HCl and $FeCl_3$ (Jun Liu et al.,2022). The processing temperature ranges from 140 to 220°C and the concentration of solvent in water ranges from 40% to 80% (Jun Liu et al.,2022). One of the major advantages of lignin produced via organosolv process is that it is sulfur-free as compared with kraft lignin and lignosulfonates. It is also of high purity, quality, and chemical reactivity, which makes it ideal for direct upgrading into high-value chemicals.

1.6 Current Separation Process at TRC:

The FBRI and its Technology Research Center (TRC) have been working to enhance the extraction of levulinic acid(LA) by removing lignin during a pre-conditioning process. Currently, LA is produced from wood cellulose using ~4% H_2SO_4 (mass basis) as a hydrolysis and dehydration catalyst. The mixture is heated up to ~180°C to convert the cellulose to levulinic acid and formic acid as a byproduct. Then the LA is separated from the aqueous phase by contacting

the aqueous phase with a hydrophobic medium chain length alcohol (MCL-OH). Part of the LA then moves from the aqueous phase to the MCL-OH phase. Lignin, being partly hydrophobic in the aqueous phase will also move into the alcohol phase. After the alcohol is separated from the aqueous phase, back-extraction is done on the alcohol to send the LA back to an aqueous phase, except this next aqueous phase is pure water and does not contain H_2SO_4. This is how LA is produced in clean water. The lignin in the solvent will partly return to the back extraction water, while some will remain in the alcohol.

1.7 Photo isomerization:

Conversion of one isomer to another isomer by light is known as photoisomerization, and the compounds that possess the properties to do so are known as photo isomers. The photoisomerization, also known as photochromism, is a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiation between two states, based on different absorption properties (Laurent and Dürr, 2001). Between the two isomers, one of them is more energetically stable and thus some external stimulus (light in this case) is needed to convert it to the next isomer.

For an organic compound like an alkene: light energy can unpair the electrons in the pi bond so that only a single bond holds their two carbon atoms together. This makes the resultant molecule very unstable. Since the free radical molecule has a C-C single bond, free rotation can occur about the C-C bond. After rotation through 180° the unpaired electrons can pair up again and thus another geometric isomer is formed. A simple mechanism is shown below in figure 2. The half arrows on the first step indicate unpairing of the pi electrons in the C=C bond, during which each one of the carbon atoms gets one electron. Both electrons are represented by a dot. The reduced single bond can undergo free rotation. After a few rotations, as indicated in step 3, half arrows point from the

electrons back into the bond. This re-creates a pi bond creating a new isomer of the same compound.

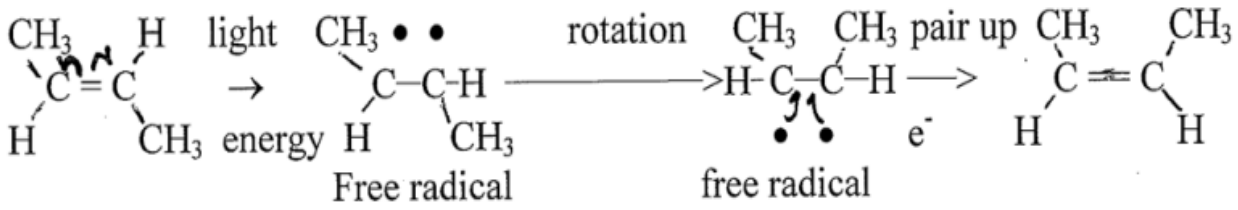


Figure 2: Mechanism of photo isomerization

Source:https://www.oit.edu/sites/default/files/document/chapter-3-4.pdf(accessed on 03/22/2022)

Organic photo-isomers like spiropyran, azobenzene, fulvalene diruthenium, and dithienylethene have been in a wide range of applications that include light-driven actuation, drug delivery, sensing, and optical memory. Among the above-mentioned photo-isomers, azobenzene(AB) has been extensively investigated due to its well-known shape. The planar structure is shown in figure 3. It has a molecular length of 9Å for trans, but only 5.5 Å for cis. The geometry in trans is planar, with the benzene rings tilted at 56° from each other, while in cis the molecule is nonplanar with a dihedral angle of 173.5°. The polarity of the isomers also changes, with a dipole moment of 0-1.2 D for trans and 3.1-4.4 D for cis. (Han et al. 2017)

Azobenzene can change from its trans configuration to cis-configuration while it is being irradiated by UV lights. Upon the irradiation of visible light on the cis form, the azobenzene isomerizes back to its trans isomer. In principle, isomerization can occur in azobenzene either through torsional motion around the N=N double bond or through inversion about one of the

nitrogen centers. This depends on the polarity of the solvent used. This is depicted in figure 4. In the first mechanism torsion around the N=N occurs and in the second mechanism the phenyl rings move in the plane of the molecule towards each other.(Tan et al. 2015)

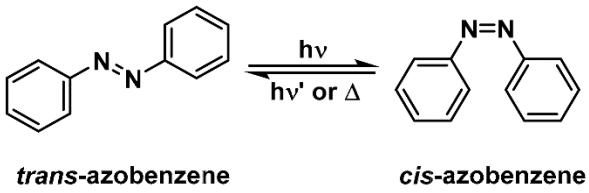


Figure 3: Planar (trans) and Nonplanar (cis) structures of azobenzene
Source: Xue et al. 2021

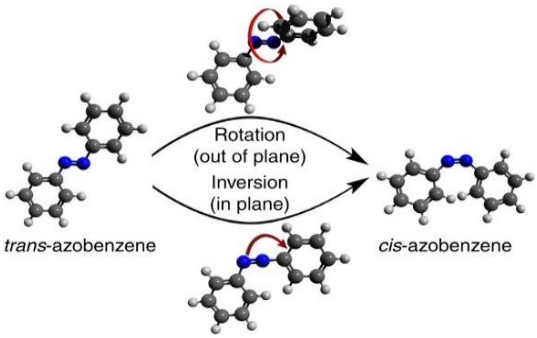


Figure 4: Isomerization pathways of trans-azobenzene
Source: Tan et al. 2015.

1.8 UV-Hypothesis:

Photo-isomers have found a wide range of applications. For instance, Han et al. used a C13 chain azobenzene dopant to lower the crystallization point of phase change molecules (PCM). The cis-isomer associated more closely with the liquid phase and stabilized the PCM in the liquid

phase. In so doing the PCM could store thermal energy at a temperature lower than its crystallization point. (Han et al. 2018). In this current study, we investigate the precipitation of lignin using a photo-switchable solvent with UV irradiation. We take advantage of changes in the polarity from the trans to cis isomer. Upon photoisomerization, the greater polarity of the cis form introduces a more significant dipole-dipole moment with the solvent, which changes the solubility of dissolved analytes such as lignin and thus precipitates them.

Chapter 2: Material and Methods:

2.1 Choice of Solvents:

For the production of levulinic acid from lignocellulosic feedstocks, the University of Maine Forest Bioproducts Research Institute (FBRI) Technical Research Center (TRC) made use of a medium chain length alcohol (MCL-OH) as an extraction solvent to recover the levulinic acid. Since lignin tended to contaminate the MCL-OH solvent, there was motivation to find way to remove lignin from the solvent system. Due to this reason, the initial idea of this study was to remove lignin from the MCL-OH extraction solvent being used. Along with the MCL-OH, in this investigation the solvents acetone and ethanol were also studied. Acetone and ethanol were chosen because they are the most commonly used organic solvents in lignin related extraction processes.

2.2 Choice of Lignin/Lignin monomers:

Alkaline lignin from TCI chemicals and Organosolv lignin from Sigma Aldrich were used. However, due to the complexity of the lignin polymer, three lignin monomers were also used: Vanillin, p-hydroxycinnamic acid (p-coumaric acid), and pyro-catechol. The complexity of lignin polymers makes analytical measurements difficult. HPLC and GC are commonly used instruments for composition analysis of biomass derived compounds. However, with lignin being a complex chain of monomers, performing concentrations analysis using either method was not viable, hence the approach of using defined lignin monomer molecules. The molecular structures of these three monomers are shown below:

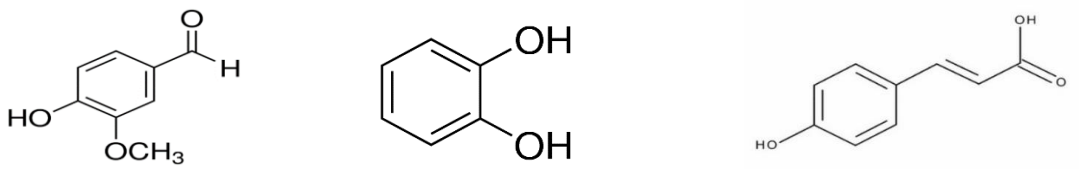


Figure 5: Molecular structure of vanillin, pyro-catechol and p-coumaric acid, left to right, respectively.

2.3 Choice of photo-isomers:

Three types of azobenzene were studied. Azobenzene in its native form without any added moieties, azobenzene with a diethylamino moiety attached asymmetrically to one of the benzene rings and azobenzene with two ethoxy moieties symmetrically attached to each of the aromatic rings. The isomerization products for all three azobenzenes are shown below:

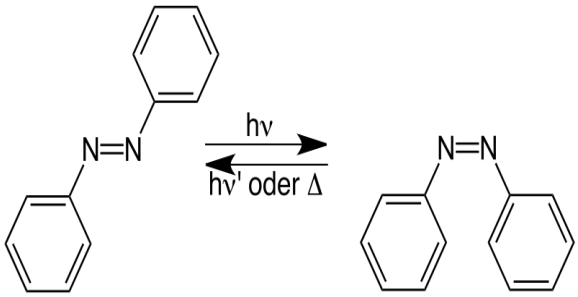


Figure 6(a) : Isomerization of native azobenzene

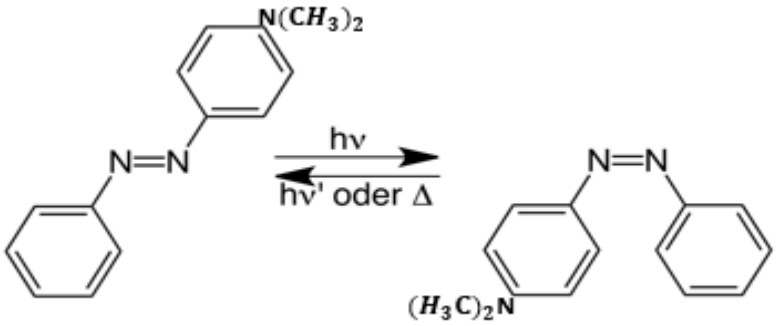


Figure 6(b) : Isomerization of diethylamino azobenzene

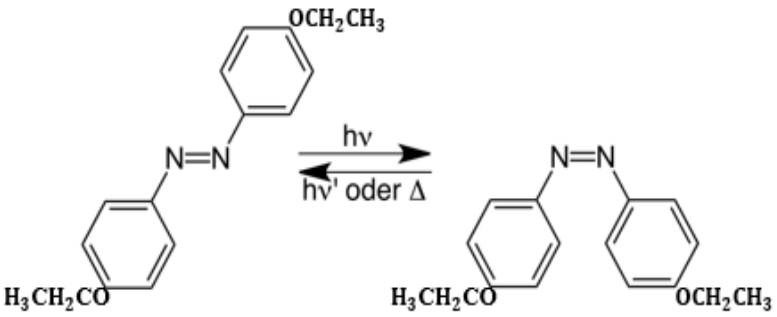
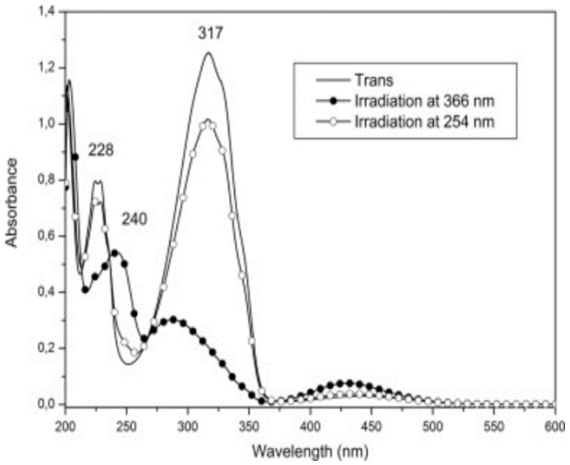


Figure 6(c) : Isomerization of diethoxy azobenzene

2.4 UV method on Photo-Isomerization:

The samples were irradiated using a Blak-Ray B-100AP/R (UVP) high intensity UV lamp (365 nm, 100 W, unfocused). To get insights on the isomerization of the photo isomers, an Evolution 100 UV-Visible Spectrophotometer Molecular spectroscopy from Thermo Fischer Scientific was used. The standard operating procedure for running a sample through the spectrophotometer is explained in Appendix: SOP-DK1. The isomers were irradiated for different periods of time and the corresponding UV-vis signal was studied.



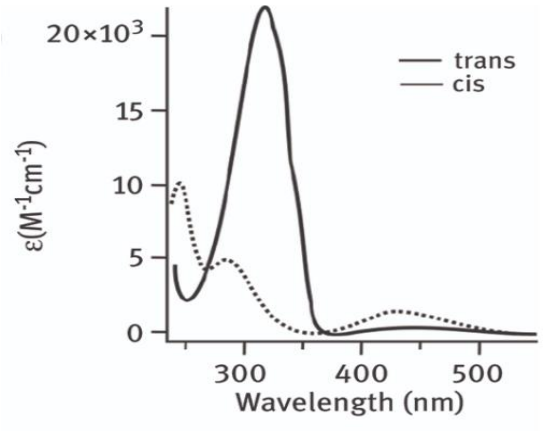


Figure 7 (a) and (b): Absorbance plot for acetonitrile and ethanol respectively.

Source: 7 (a) - Cicogna et al. 2016 and 7 (b) Beharry and Woolley, 2011.

Different papers have published absorbance data of azobenzene under UV irradiation in different solvents. The trans isomer shows a peak at 317nm in acetonitrile (Cicogna et al. 2016). Similarly, the trans isomer peaked at around 320nm in ethanol (Beharry and Woolley, 2011). The plots from both mentioned solvents are shown in figure 7 (a) and (b).

2.5 Filtration and analysis:

The precipitate obtained from the experimental process was separated using a carefully selected filter paper. The filter paper used in this study, with catalog number 09-790-4D, was procured from Fischer-brand. It has a fine porosity and Q2 quantitative rating, ensuring optimal filtration performance. This choice of filter paper was made to effectively capture and isolate the desired precipitate while minimizing any unwanted impurities or solid residues.

Following the filtration step, the resulting precipitate was then subjected to a dissolution process, whereby it was dissolved into a suitable solvent. To assess the characteristics and composition of the dissolved precipitate, a UV-Vis spectrum of the mixture was generated. This spectrum was subsequently compared to the UV-Vis spectrum of native lignin, serving as a benchmark to identify any significant deviations or changes in the chemical properties of the precipitate.

In addition to the UV-Vis analysis, further characterization of the dissolved precipitate was performed using Fourier Transform Infrared (FTIR) spectroscopy. The FTIR analysis was

conducted using a Nicolet iS20 FTIR instrument, following the standard operating procedure outline in Appendix: SOP-DK2. This analytical technique provided valuable insights into the molecular structure and functional groups present in the dissolved precipitate, facilitating a more comprehensive understanding of its chemical composition.

To ensure an accurate mass balance calculation, the remaining filtrate adhering to the glassware surfaces was carefully accounted for. The residual filtrate, containing any dissolved solutes that were not captured by the filtration process, was dried in an oven to evaporate the solvent, and obtain the solids residues. By including this step, the overall mass balance of the experiment could be maintained, accounting for any trace amounts of solutes that might have been present in the filtrate.

Considering the experimental setup and the use of relatively small quantities of solutes in most tests, it was recognized that any particles or residues adhering to the glassware, including the filtration funnel, could play a significant role in the overall mass balance. Therefore, to ensure a thorough mass balance closure, all the glassware components involved in the experimental process, including the funnel were carefully dried, eliminating any residual moisture or solutes that may have been present.

Chapter 3: Results and Discussions:

3.1 Solubility:

Since MCL-OH was the initial choice of solvent, the solubility of three lignin monomers along with the native azobenzene in MCL-OH was determined. For all cases, the solubility was checked at room temperature. Pyro-catechol was found to be most soluble at 43.02% by mass followed by vanillin at 17.38% and the least soluble monomer was found to be p-coumaric acid at 0.53%. Pristine azobenzene was found to be 15.46% soluble by mass. Along with lignin monomers, the solubility of Organosolv lignin was found to be 0.25% by mass in MCL-OH. Diethoxy azobenzene was found to be 0.01% by mass in MCL-OH. It was noticed that MCL-OH offered poor solubility for lignin and diethoxy azobenzene. Thus their solubilities were also determined in ethanol and acetone. Acetone offered the highest solubility for both solutes, with 5% by mass of Organosolv lignin and 2% by mass of diethoxy azobenzene. Ethanol also provided better results than MCL-OH, with 2% by mass of Organosolv lignin and 0.54% by mass of diethoxy azobenzene.

3.2 Photo-isomerization information:

3.2.1 Azobenzene in MCL-OH:

Azobenzene in MCL-OH was the first system studied. The solubility of azobenzene was found to be 18% in the alcohol at room temperature (25°C). Since UV-Vis scan was the preferred method of analyzing isomerization information, this concentration was too high for the instrument range. Thus, the solution was diluted to a very low level of 0.05% by mass. With pure alcohol as a blank, the solution ran through the spectrophotometer and the corresponding absorbance data are shown in figure 8.

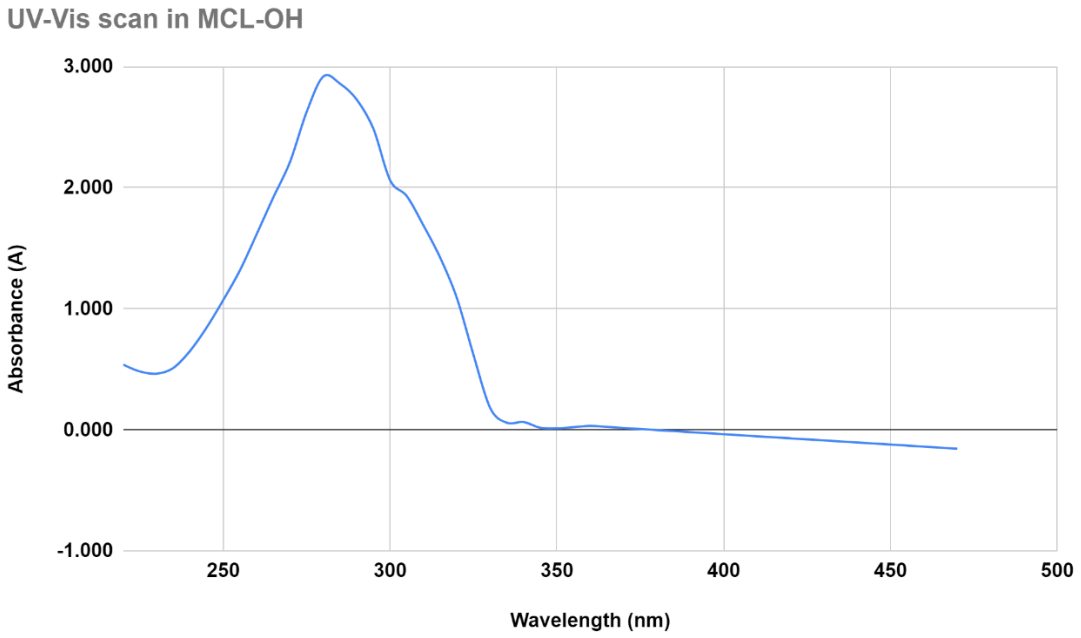


Figure 8: UV-Vis scan of Azobenzene in MCL-OH

The y-axis on the graph shows the absorbance in units of A and the x-axis reports wavelength in nm. This solution contains azobenzene without any excitation of any kind which means it is in trans-isomer state. 20 ml of this solution was irradiated using the UVA (365nm) lights. The irradiated samples under different periods of time were run through the UV-Vis scan and the corresponding plot is shown in figure 9.

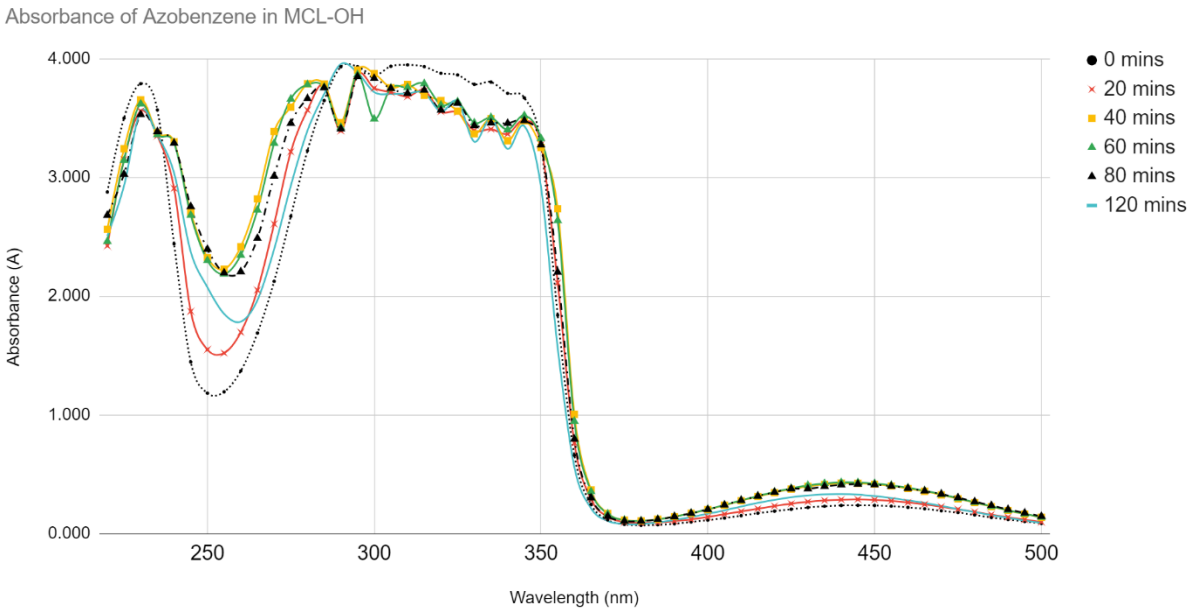


Figure 9: UV-Vis scan of Azobenzene in MCL-OH under different UV illumination time frame

Even after 12 hours of constant UV irradiation, there was little to no change in the spectrum. Moreover, there was no visual observation of color change seen in the solution. Typically, when a photo-isomer undergoes isomerization, it changes its color to a darker shade. This was not observed in this case. The initial reasoning was that the solution was dilute so it could not isomerize. Due to this reason, a literature review was done to check the concentration being used for UV-Vis spectrum. One study was found where an azobenzene derivative in acetonitrile was run through a UV-Vis spectrophotometer. Cicogna et. al used 4-(phenylazo)-benzoyl-2,2,6,6-tetramethylpiperidine-1-oxyl radical (AzO-TEMPO) in acetonitrile 50 μM. The concentration of azobenzene being used in MCL-OH was less than 1 μM and thus it was increased to 50 μM and it was again UV irradiated. However, the system still produced no significant variation. After

looking into literature, it was found that the native azobenzene results in poor film morphology due to crystallization, which prevents photoisomerization of the molecule (Cho et. al 2017).

However, Merino and Ribagorda (2012) stated that the trans-azobenzene easily isomerizes to the cis isomer by irradiation of the trans isomer with a wavelength between 320nm-370nm. The reaction is reversible and the conversion back to trans isomer is done with 400-450nm visual light irradiation or heat. They also included that for many azobenzenes, the two chemical conversions occur on the scale of picoseconds. To overcome all these issues, it was found that in most work; longer chained azobenzenes were being used in various experiments. For example, Han et. al(2017) were working with a C13-azobenzene dopant. In this study, two modified derivatives of azobenzene were bought from Fischer Scientific to overcome issues related to native azobenzene. 4-diethylaminoazobenzene and 4,4'-Diethoxyazobenzene were the two azobenzene selected.

3.2.2 Diethylamino and diethoxy azobenzene in MCL-OH:

Like the native azobenzene, solutions of the two azo-derivatives were created in MCL-OH and without any UV irradiation, they were run through the UV-Vis spectrophotometer to get their respective trans spectra. For both isomers a concentration of 50 μM was used. The resulting spectra alongside the spectrum of azobenzene is shown in figure 10(a). The FT-IR spectra of the three azobenzene are shown in figure 10(b).

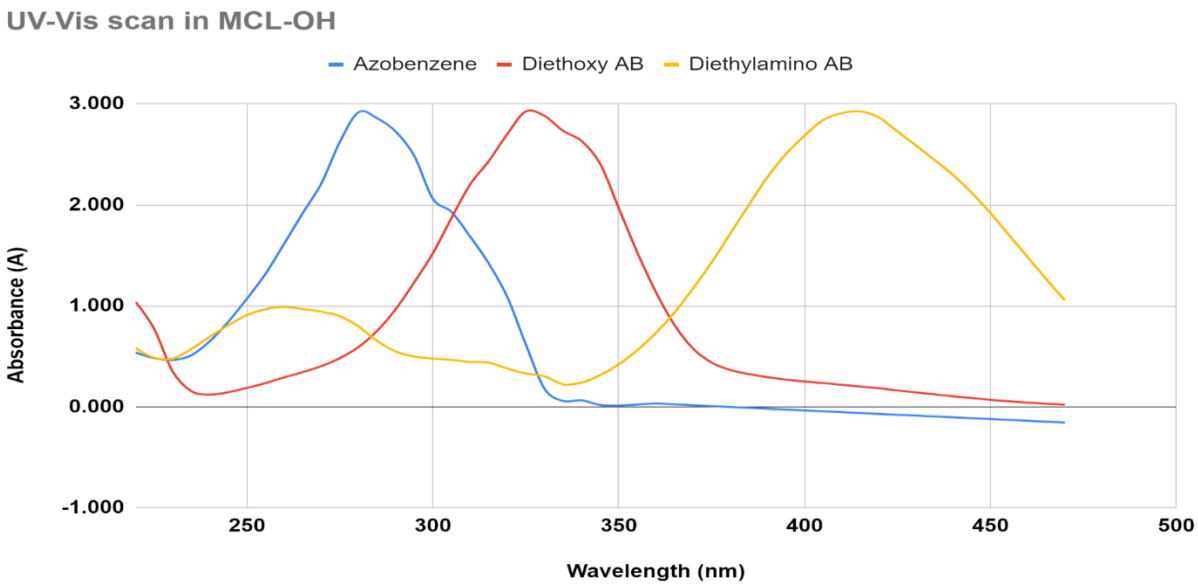


Figure 10(a): UV spectra of trans-isomer of Azo, Diethoxy Azo and Diethylamino Azo in MCL-OH.

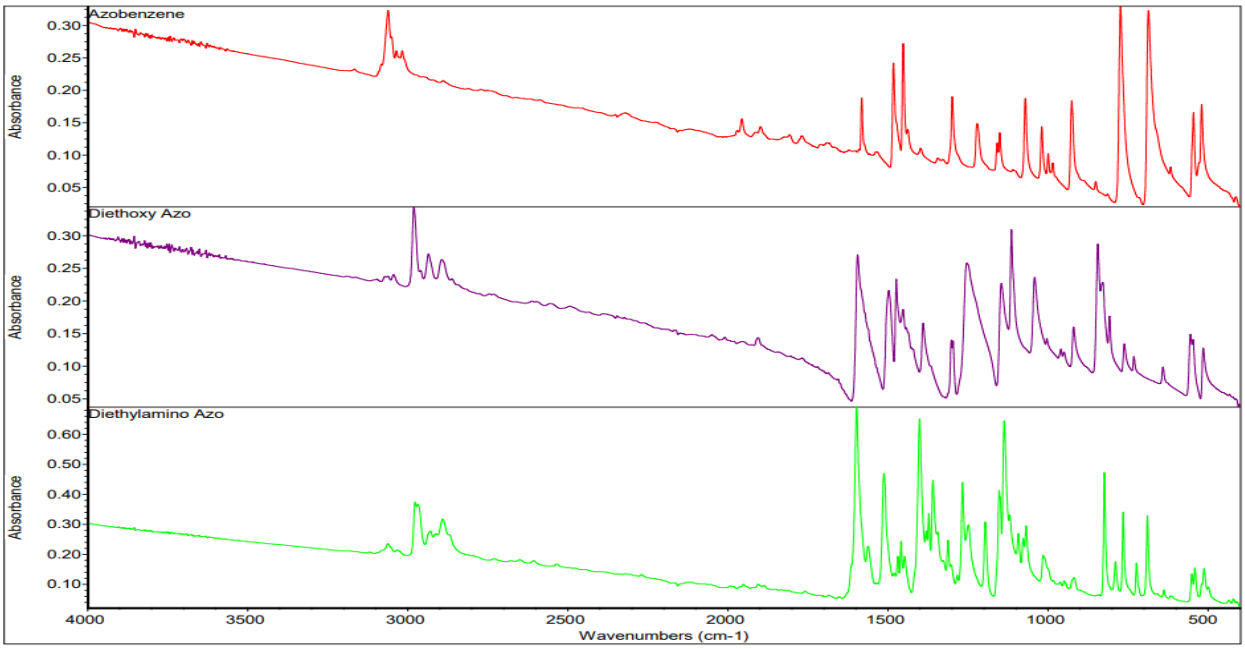
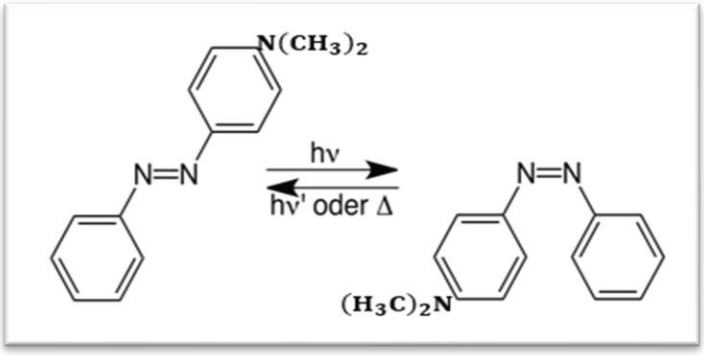


Figure 10(b): FT-IR spectra of trans-isomer of azo, diethoxy azo and diethylamino azo

3.2.3 Analysis of diethylamino azobenzene:

Five grams of 4-diethylaminoazobenzene (CAS-No: 2481-94-9) was bought from ThermoFischer Scientific. The molecular structure alongside the isomerization of diethylamino azobenzene is shown in figure 6b(reproduced below).



As explained in Sun et. al (2019), diethylamino azobenzene falls under the amino-azobenzene type. This means that the π-π* absorption band of the trans isomer is bathochromatically shifted to 400-450 nm, partially overlapping with the n-π* absorption band.

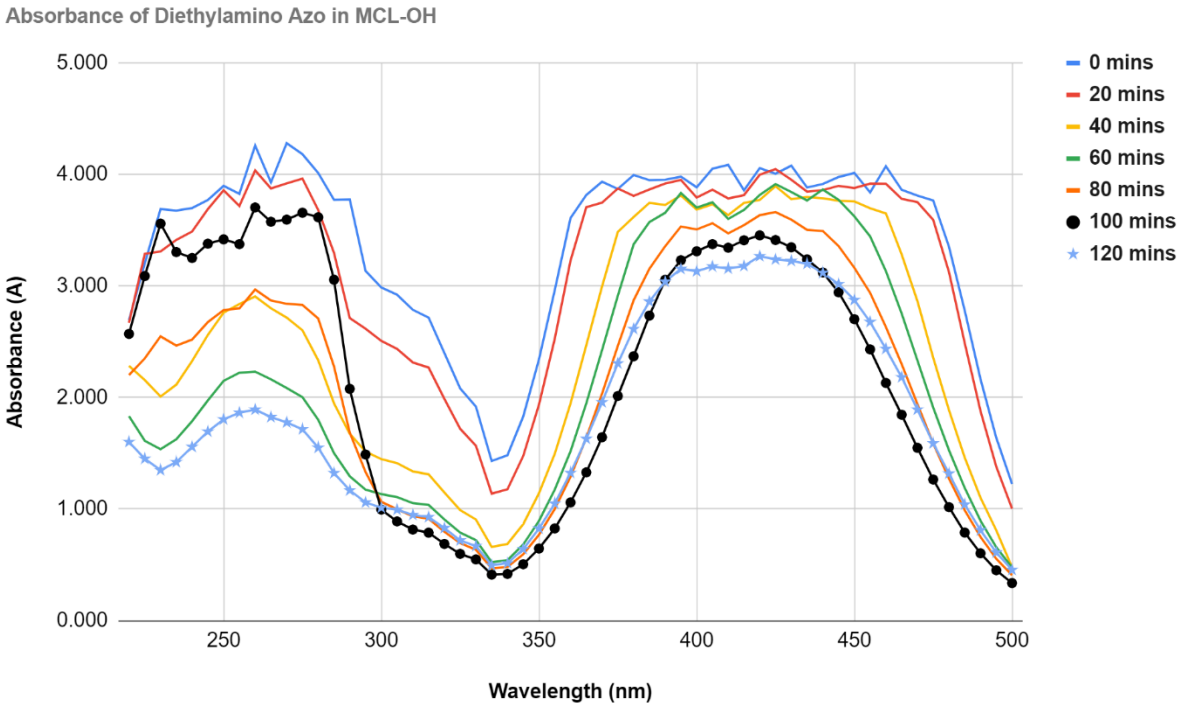


Figure 11: UV-Vis spectra of Diethylamino azobenzene in MCL-OH.

Due to this reason, both the trans as well as the cis isomer have peaks at same range i.e. 400-450 nm, unlike other azobenzene types which have different peaks for the two isomers. This is seen in figure 11. The UV spectra of diethylamino azobenzene in MCL-OH under different irradiation period is shown in figure 12. The spectrum shows its peak around same range (400-450 nm) for all different irradiation periods. A highly concentrated cis-isomer containing sample would give the same spectrum as that of a diluted trans-isomer, thus studying qualitative isomerization would not be feasible.

3.2.4 Analysis of Diethoxy Azobenzene:

Five grams of 4,4'-diethoxy azobenzene (CAS-No: 588-52-3) was bought from ThermoFischer Scientific. Like previous azobenzenes, a solution of diethoxy azobenzene was made in the MCL-OH and the UV-vis spectra was generated under different periods of UV irradiation. The spectrum is shown in figure 12.

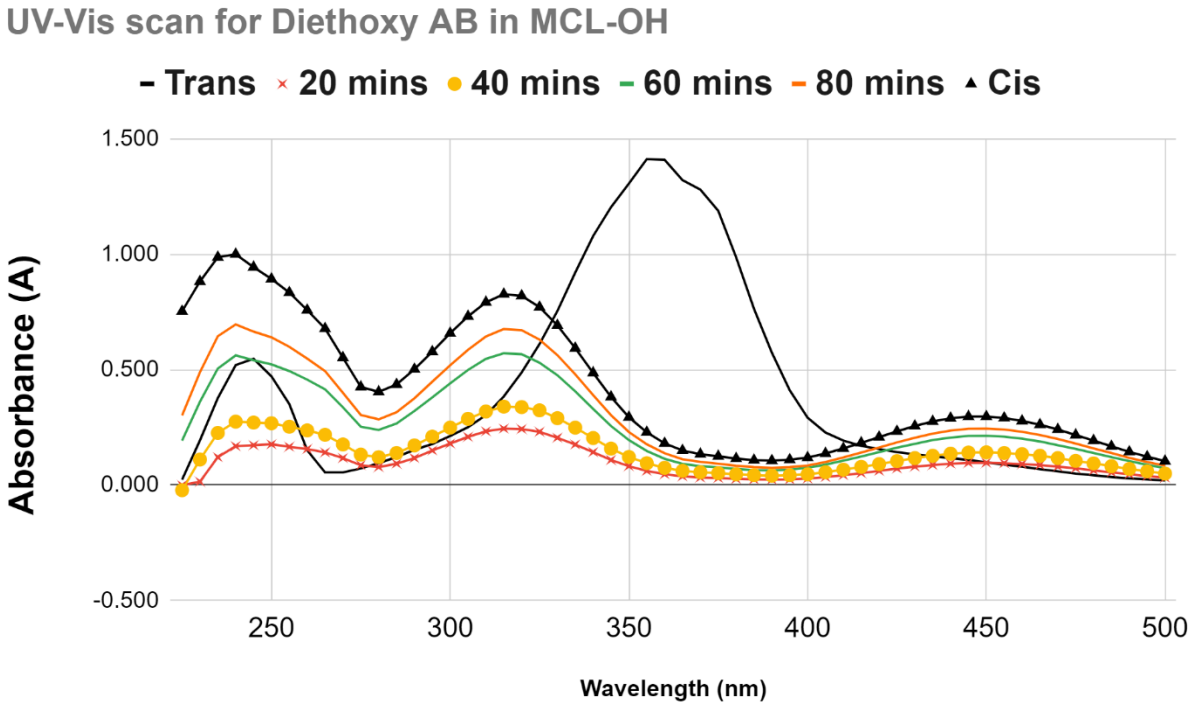


Figure 12: UV charging of Diethoxy Azobenzene in MCL-OH.

We start with an unirradiated (trans) solution and upon UV charging, there is change in the signal. We expected to see a trend as we go from trans to cis. After 20 mins, the trans signal has gone significantly down and after every 20 minutes of UV charging, the signal is growing more and more towards the cis signal. The solution reaches pure cis-form after 100 minutes and

further charging does not change the spectra. After getting the charging information, the UV light was turned off and the solution was discharged using ambient light. The discharging spectra is shown in figure 13.

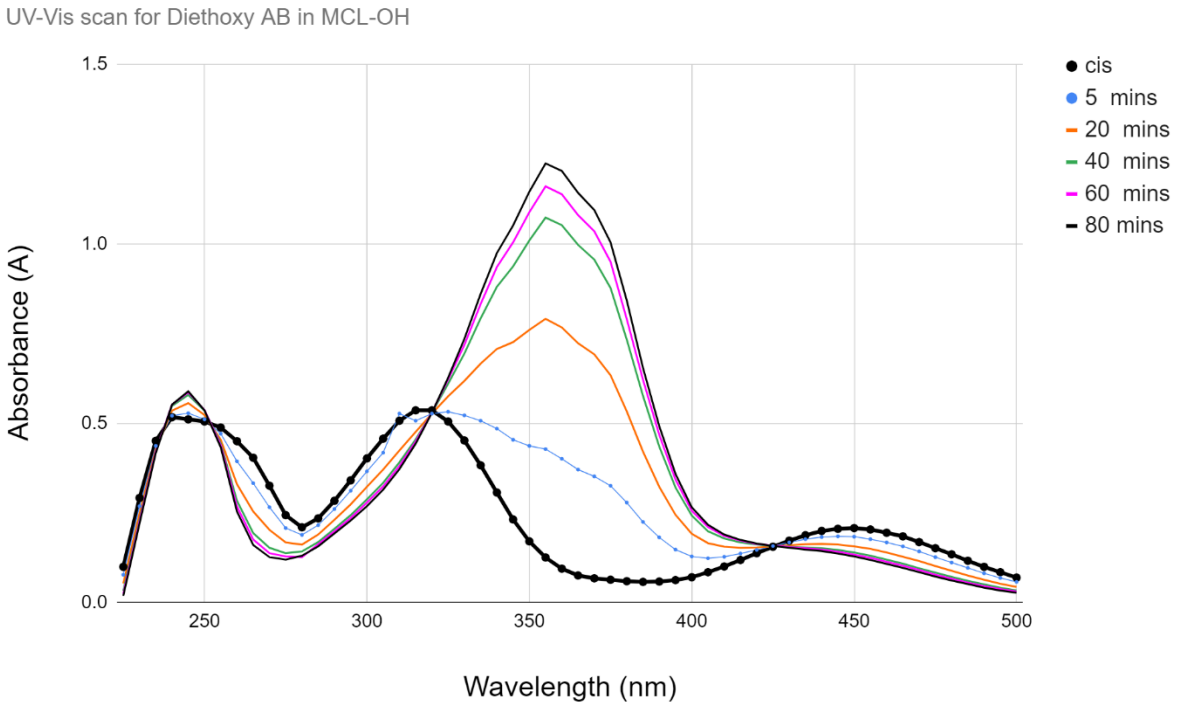


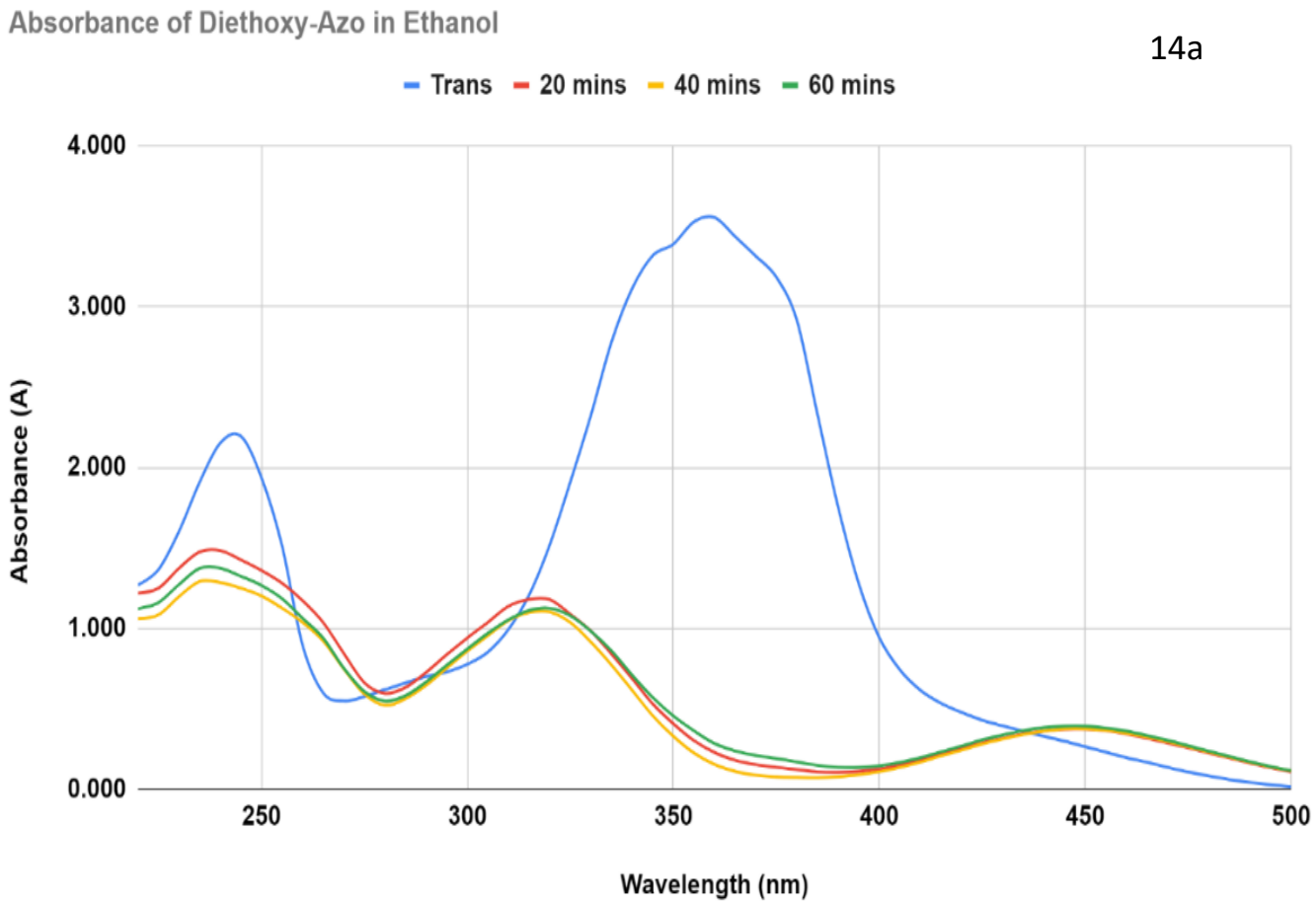
Figure 13: Ambient light dis-charging of Diethoxy azobenzene in MCL-OH

As shown in the figure 13, the cis-isomer reverts back to trans-isomer in about 80 minutes. The solution was re-charged, and the solution was kept in an ice bath to see if the relaxation period to trans can be decreased. However, similar spectra were observed once again with the total duration of 80 minutes. This suggests that relaxation is not temperature dependent.

3.2.5 Diethoxy Azobenzene in Ethanol and Acetone:

The charging with UV of diethoxy azobenzene was studied in ethanol and acetone as well. These solvents were chosen because of their wide industrial applications and also because they were able to solubilize more lignin and azobenzenes than the MCL-OH. The charging of diethoxy azobenzene in ethanol is shown in figure 14a and that in acetone is shown in figure 14b.

14a



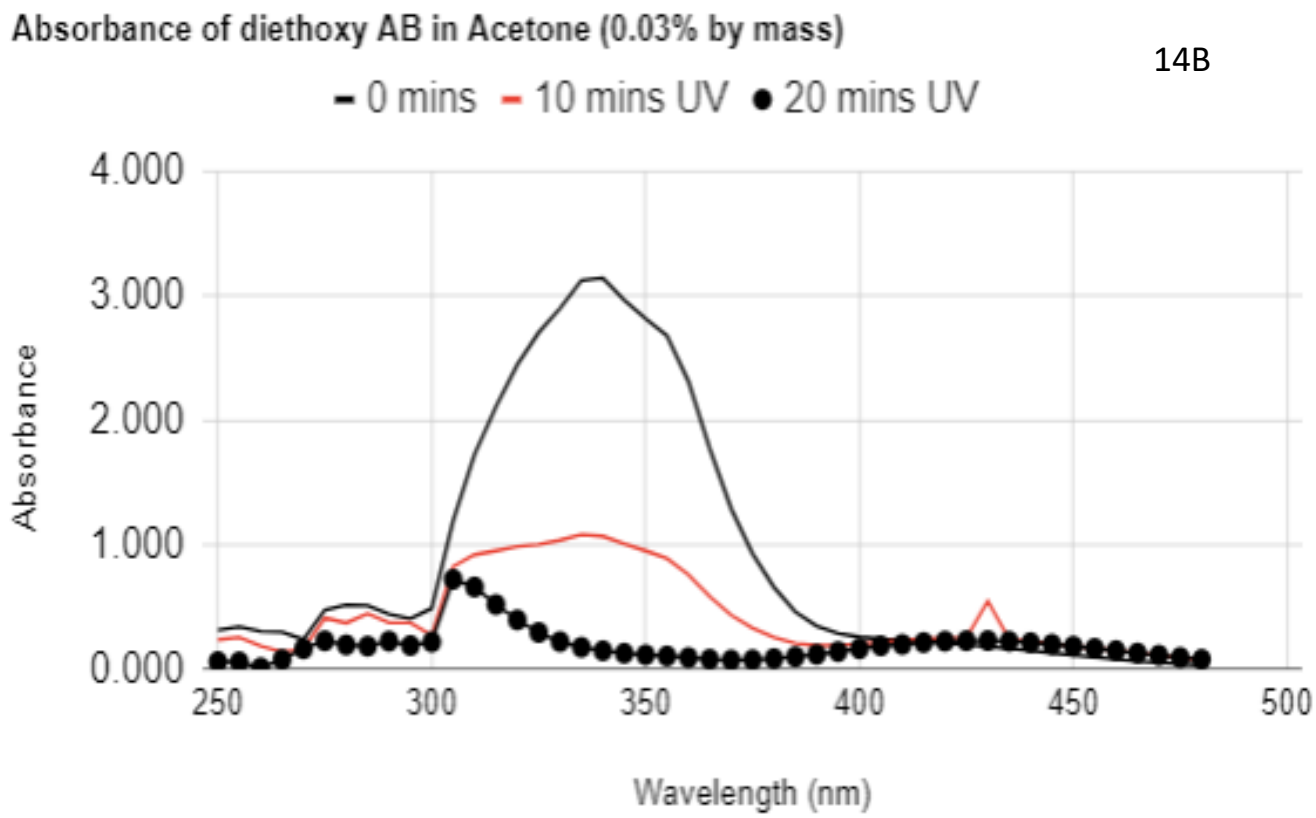
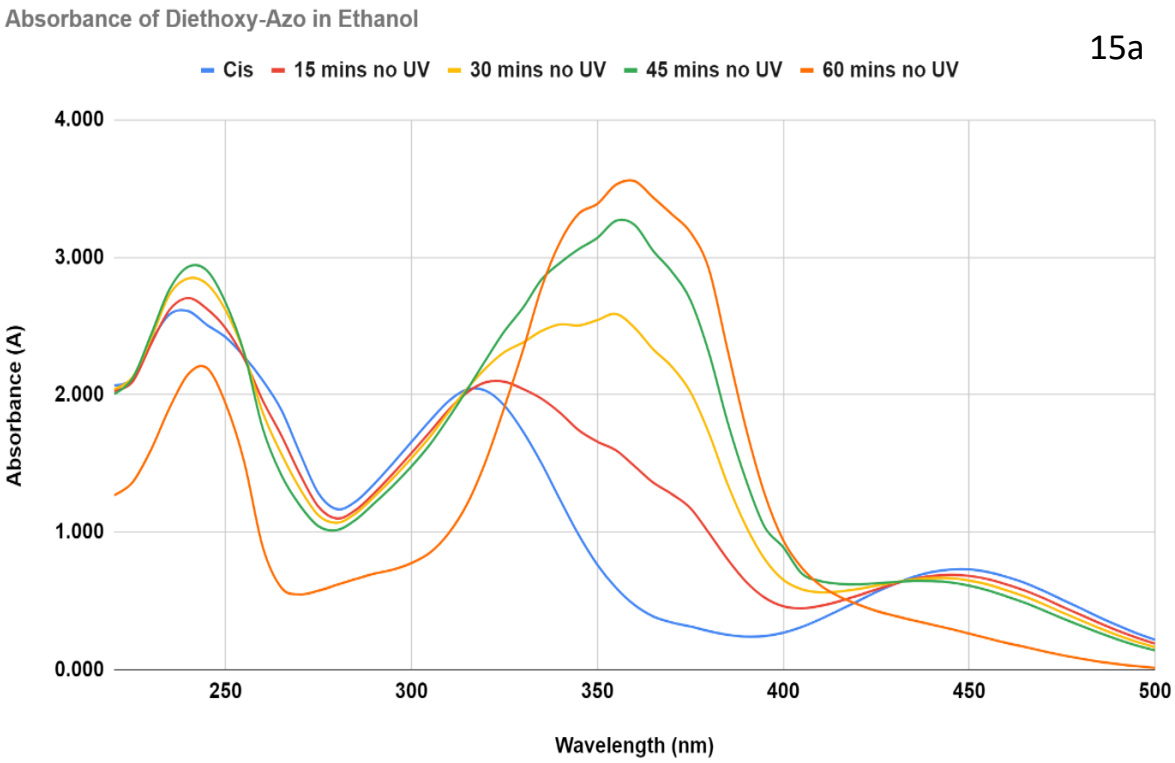


Figure 14: UV charging of diethoxy azobenzene in ethanol (top) and acetone(bottom)



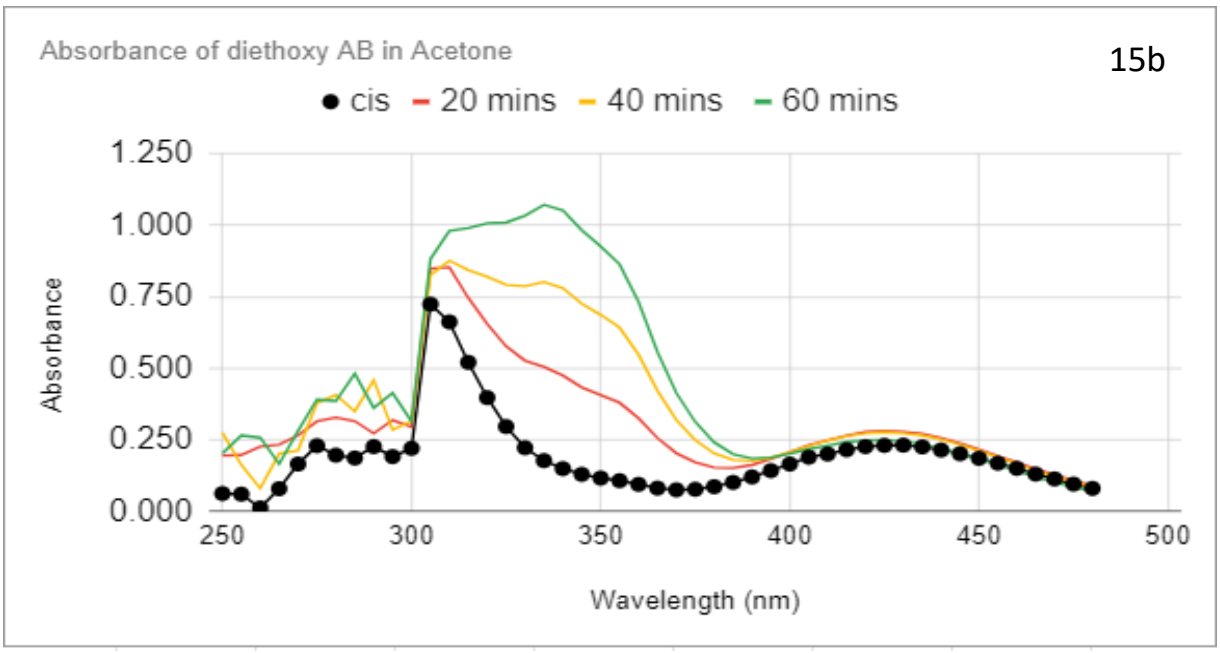


Figure 15: Ambient light discharging of diethoxy azobenzene in ethanol (top) and Acetone(bottom)

The charging period in MCL-OH was found to be around 100 minutes, however in ethanol, the signal attains saturation for cis level after just 20 minutes. Similarly, in acetone as well the solution reaches cis level after 20 minutes of irradiation. The discharging spectra of diethoxy azobenzene in both ethanol and acetone are shown in figure 15.

In ethanol, the cis isomer reverts back to its trans state in about sixty minutes of discharging with ambient lights. Meanwhile in acetone, the signal has only returned back to 1/3rd of the original trans state (3A absorbance) after sixty minutes of discharging. As compared to MCL-OH and ethanol, acetone provides faster charging and slower discharging. This suggests that the cis-isomer interacts better with acetone.

3.3 Initial Runs:

3.3.1 Lignin monomers:

Since, native azobenzene only has a cis life of pico to milliseconds and diethylamino azobenzene shows trans/cis peaks at same range of wavelength, diethoxy azobenzene was the preferred photo isomer. An individual solution of lignin monomers in MCL-OH at half the saturation level was made. Similarly, diethoxy azobenzene was also added to those solutions at half the saturation level. The final solutions were irradiated with UV lights for different periods of time. After prolonged irradiation (more than 6 hours), no precipitation was seen in any of the three solutions. It was concluded that the lignin monomers were too soluble for the photo isomer to precipitate out. Due to this reason, we started using Organosolv lignin instead of the lignin monomers. Organosolv lignin being a much larger molecule was expected to precipitate more easily if the solubility of the solution changed.

3.3.2 MCL-OH Solutions:

Two different solutions were made in MCL-OH at room temperature. 0.25% by mass of Organosolv lignin and 0.03% of unirradiated (trans) diethoxy azobenzene in MCL-OH. 5ml of each solution was mixed and the final solution was irradiated with UV lights for different periods of time. The visual observations at different time periods are shown in figure 16.

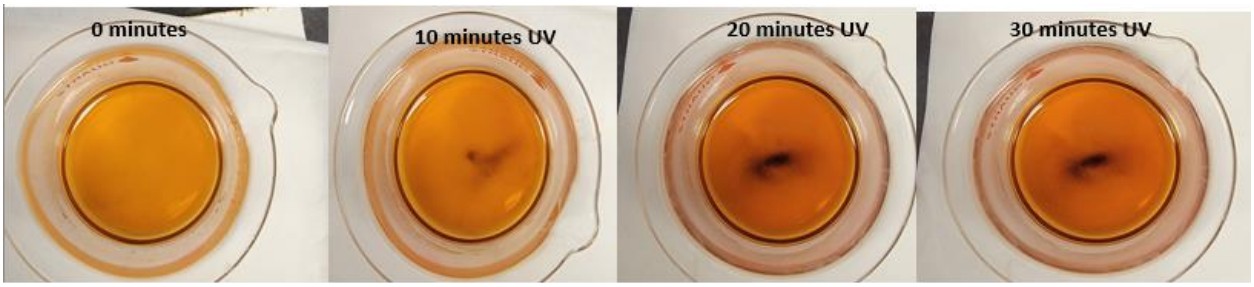


Figure 16: Visual Observation for different irradiation periods of 5ml MCL-OH, Organosolv lignin and diethoxy azobenzene each

Initially, the solution was clear. At 10 minutes of UV exposure a small amount of precipitate can be seen forming at the bottom of the beaker. Upon further irradiation, the precipitate increased and after 30 minutes we achieved the same amount of precipitation as we had at 20 minutes. The solution was stirred again, and it was left exposed to ambient light but without UV irradiation for 30 minutes to determine if any precipitation occurred with time. No precipitation was observed during this period which concludes that UV excitation was responsible for precipitation.

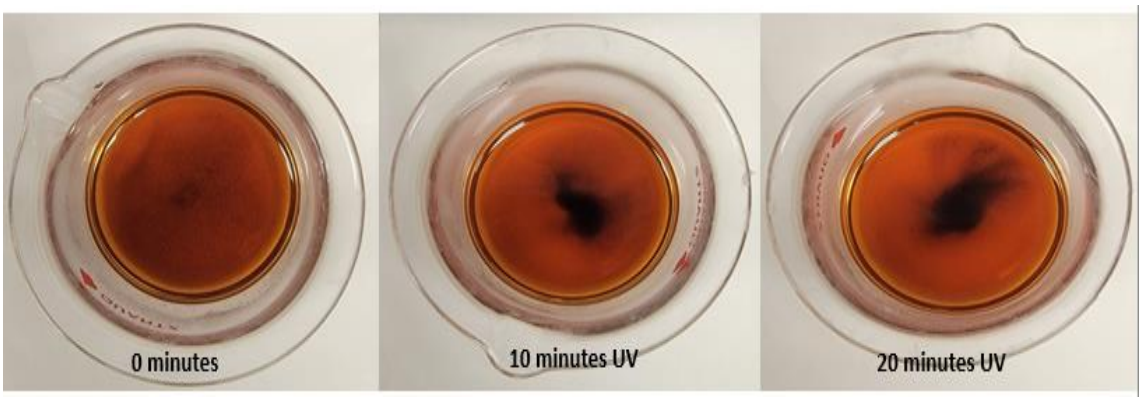


Figure 17: Visual Observation for different irradiation periods of Organosolve lignin dissolved in, and precipitated out of 6 ml MCL-OH with diethoxy azobenzene under UV irradiation

Then 5ml of the diethoxy azobenzene solution was mixed with 6 ml of lignin solution. This is represented in figure 17. Since we got the same amount of precipitation for 20 and 30 minutes, we started using 20 minutes as the standard irradiation period. As seen in figure 17(b), the amount of precipitation has significantly increased at 20 minutes. However, the low solubility offered by MCL-OH made it difficult to do any quantitative analysis on the precipitate. Less than 0.01 gram of lignin was dissolved in the setup and thus filtering the precipitate and doing any further analysis had a higher probability of error. For this reason, we moved to a solvent that provided better lignin solubility. In our case, acetone provided the highest solubility for both lignin as well as diethoxy azobenzene and thus acetone was used for further analysis.

3.3.3 Acetone Solutions:

For background analysis: 133.3 milligrams of Organosolv lignin, without any diethoxy azobenzene, were dissolved into 25ml of acetone. The solution was stirred to make it a homogenous mixture. It was irradiated with UV light for 30 mins, and no precipitation was seen in the beaker. However, over time precipitation was observed due to the evaporation of acetone (0.66% mass per minute). Evaporation of acetone was quite pronounced under the high energy of the UV light. Appendix SOP-DK3 describes how this evaporation rate was evaluated. Briefly, acetone in a beaker identical to the one used for the precipitation experiments, with the same ambient temperature and applied UV radiation, was monitored for the loss of mass over time. At around 120 minutes, the solution reached a saturation level of 4% (Organosolv lignin in acetone) at room temperature and we can see some precipitation on the bottom of the glassware. The different mass fractions of lignin were quantified and added together to confirm a mass balance. The results of this mass balance is depicted in figure 18.

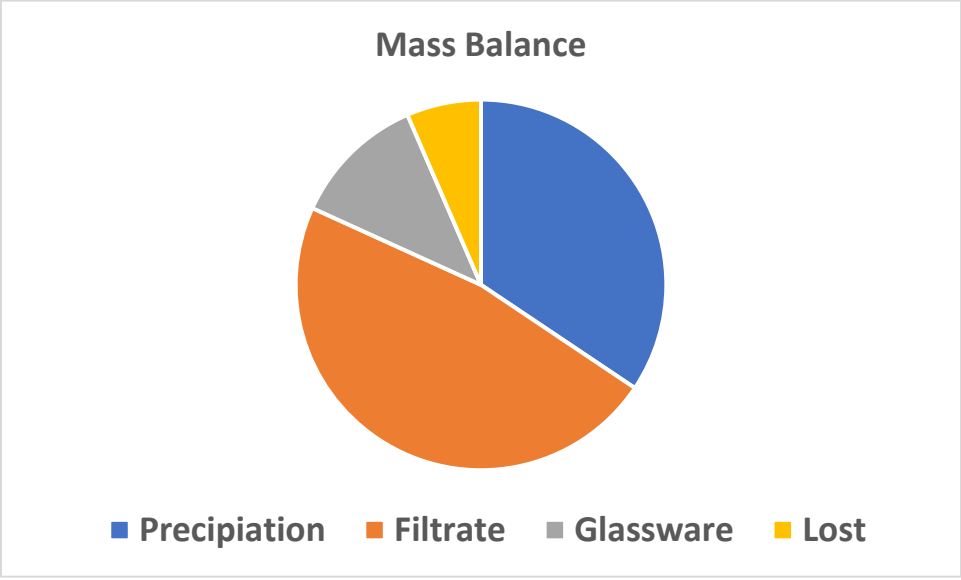


Figure 18: Mass balance of the precipitation test.

3.4 **Precipitation Results:**

For the final analysis: 242.5 milligrams of Organosolv lignin were added to sixty ml of acetone. Then 63.6 milligrams of diethoxy azobenzene was added and dissolved. The mixture was then charged under UV light for 20 minutes. The experimental setup and the filtration mechanism is shown in figure 19. IN the figure on the left, the UV light was shone directly on top of the beaker using a lamp funnel. On the right side, a filter paper is shown collecting precipitate from the solution. Since a finer filter paper was used, the filtration time required was about twenty minutes for sixty ml of solution. In order to diminish the chance of reverting back to trans, the solution was irradiated with UV during the filtration process. The blue film seen on the top of the solution is the UV light shining on the top layer of the solution.

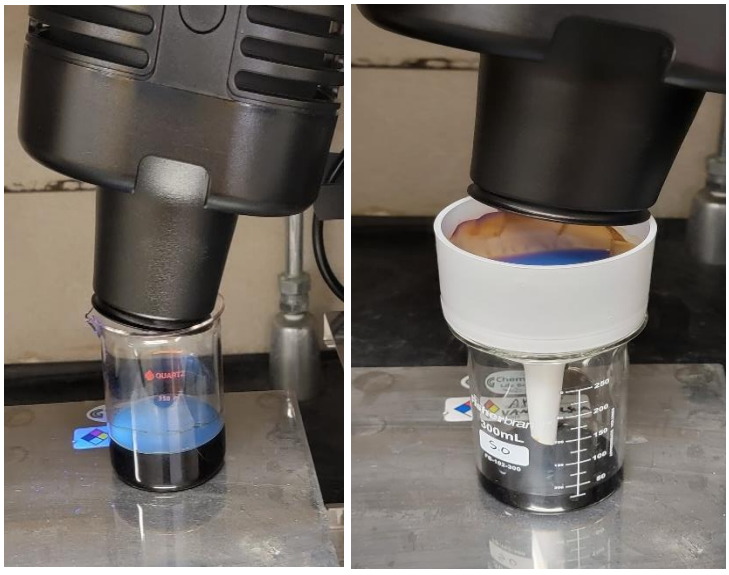


Figure 19: Experimental Setup

The trans molecule isomerizes to cis in 20 minutes and changes the solubility of the mixture, and thus, lignin particles start precipitating. The solution along with the precipitate was poured into a funnel with filter paper, and the filtrate was caught in a beaker below the funnel. The filtrate was evaporated inside an oven at 60°C for 30 minutes to quantify dissolved materials. The precipitate captured by the filter paper amounted to 34.4% of the total added solute (lignin and azobenzene), 47.4% was recovered by evaporating the filtrate solution, and 11.7% was found on the glassware wall bringing the total to 93.5% from the original mass added.

3.5 UV-Vis scan of Precipitate:

The collected precipitate on the filter paper was redissolved and run through a UV spectrophotometer to check for any presence of diethoxy azobenzene. The scan is shown in figure 20. The spectrum was compared to that of Organosolv lignin in acetone without any azobenzene. The difference looks minimal, and thus it was concluded that the majority of the precipitate was lignin with minor alteration to its structure. Inspection of the solids caught on the filter paper did not identify any crystals of diethoxy azobenzene, which when present, are a bright red color and detectable.

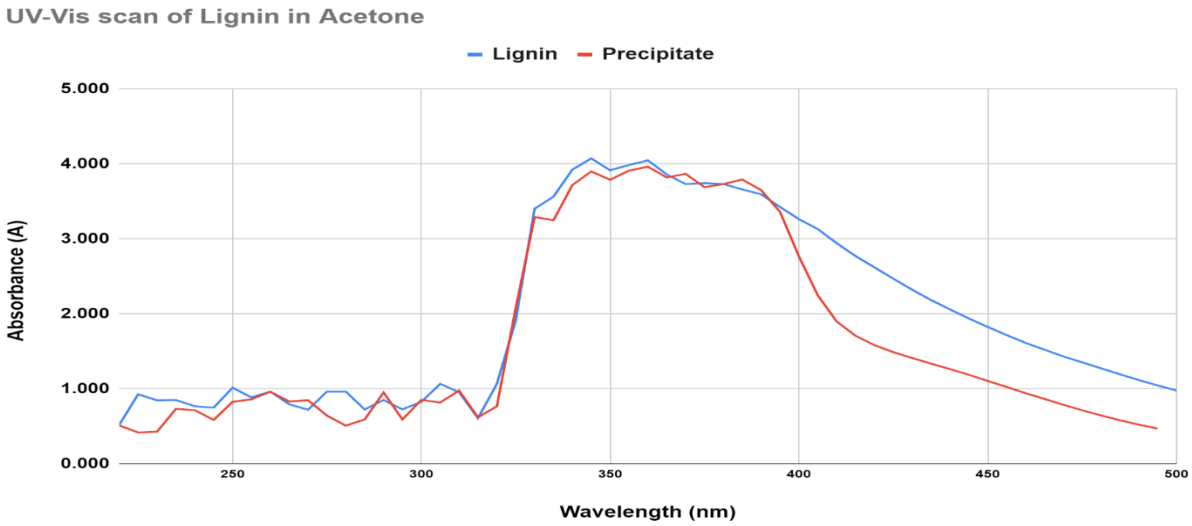


Figure 20: UV-Vis scan of Organosolv Lignin and precipitate both in Acetone

3.6 Different ratios:

3.6.1 Acetone as solution:

Next, the amount of diethoxy azobenzene was varied to further understand its influence on precipitation. Two hundred milligrams of Organosolv lignin were added to fifty ml of acetone, and the precipitation amount collected by the filter paper was tabulated. Figure 21 shows three replicates of the runs. The recovered amounts of lignin that that had zero milligrams of diethoxy azobenzene correspond to lignin that was adsorbed, but not precipitated, on the filter paper.

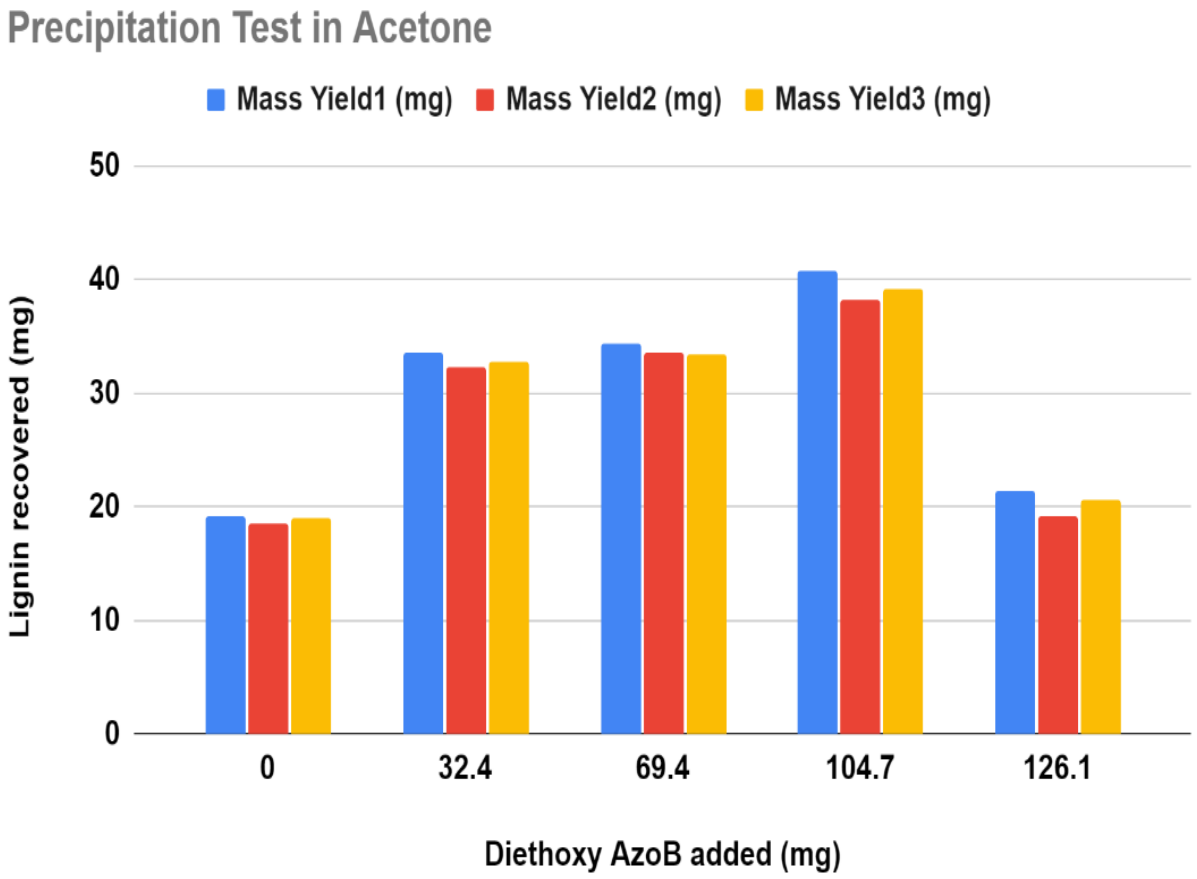


Figure 21: Precipitated lignin recovered at different amounts of diethoxy azobenzene.

3.6.2 Ethanol as solvent:

Ethanol was also used as a solvent. For ethanol, one hundred thirty milligrams of Organosolv lignin were added in fifty ml of ethanol, and the amount of diethoxy azobenzene was varied. Since the solubility was slightly lower than that in acetone, only two sets of experiments were performed. The duplicate results in ethanol are depicted in figure 22.

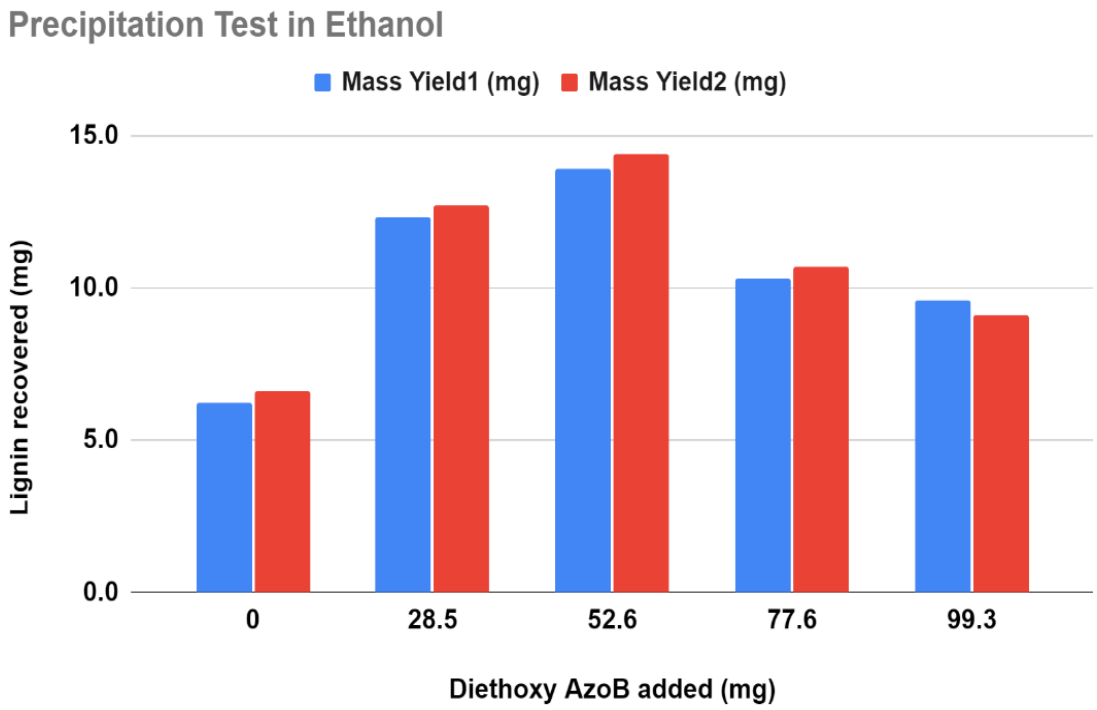


Figure 22: Precipitated lignin recovered at different amounts of diethoxy azobenzene in ethanol.

3.6.3 Precipitation test with diethylamino azobenzene:

Two hundred milligrams of organosolv lignin were dissolved in 50 ml of acetone. Thirty-five milligrams of diethylamino azobenzene were added to the solution. The final mixture was UV irradiated for 20 minutes. Precipitate was seen forming on the bottom of the beaker, so the solution was passed through a filter paper (same porosity as before). The amount of precipitate collected was thirty-six milligrams. Then, the precipitate was re-dissolved in acetone, and it was run through the UV spectrophotometer. The spectrum is shown in figure 23.

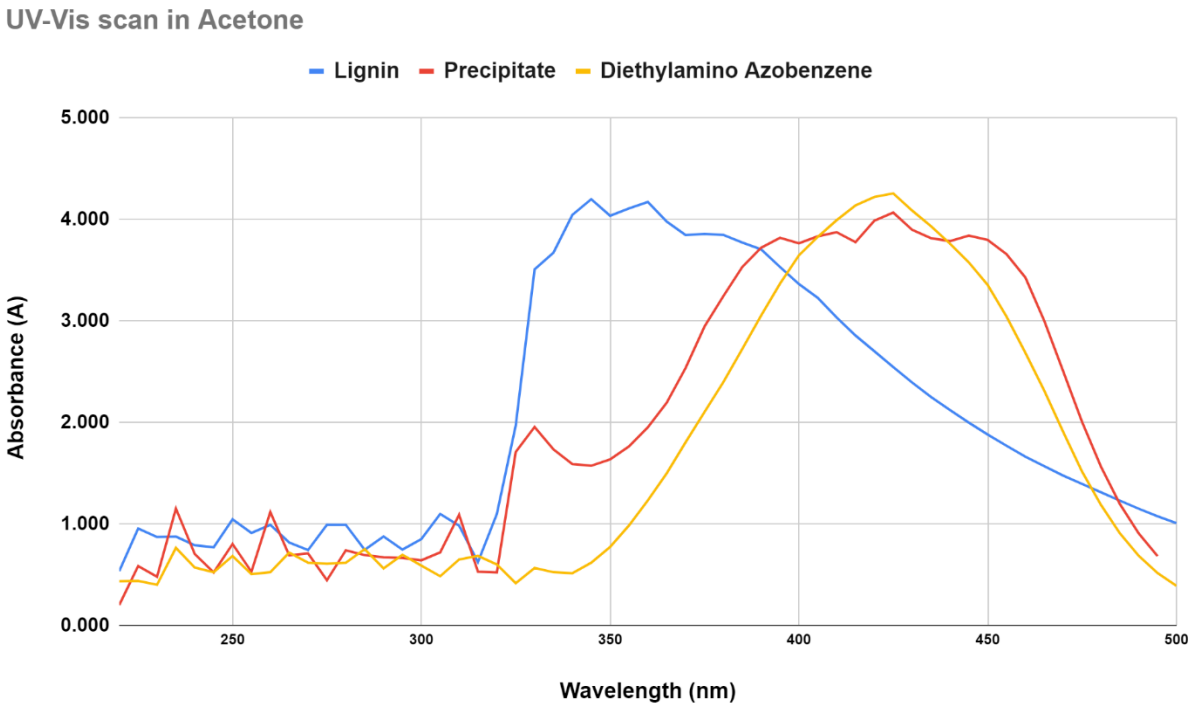


Figure 23: UV spectra of Organosolv lignin and diethylamino azobenzene in Acetone.

It was observed that most of the precipitate was diethylamino azobenzene itself and lignin was not precipitated. It was concluded that diethylamino azobenzene is not effective at precipitating lignin out of solution.

Chapter 4: Conclusions:

4.1 Discussion:

Figures 21 and 22 show that the precipitation increases with an increased amount of photo-isomers until a certain point, after which precipitation appears to decline. We hypothesize that as more azobenzene is added to the solution, a shading effect comes into play, and thus isomerization becomes limited. As more photo-isomer is added to the solution, the isomers at the top of the solution, closer to the source of UV light, start blocking the absorption of UV light by the isomers sitting at the bottom of the solution, diminishing their ability to precipitate the lignin.

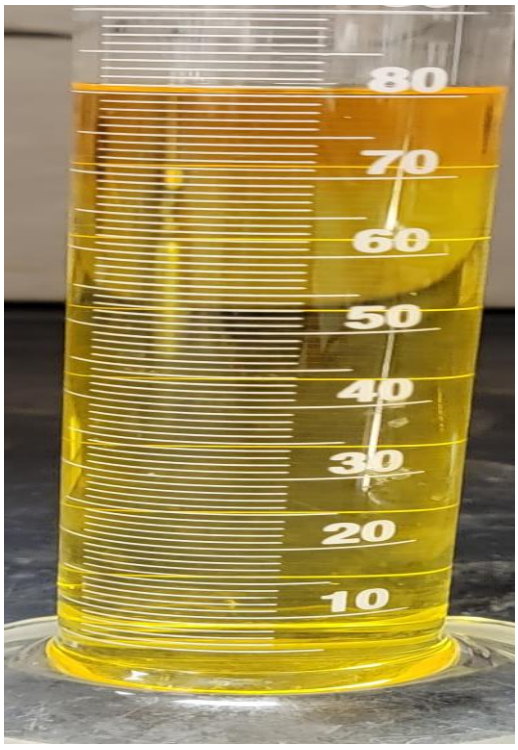


Figure 24: Shading effect as seen in a tall, graduated cylinder.

This shading effect was investigated by irradiating the photo-isomer solution from the top of a vertical 100 mL graduated cylinder. This shading effect was indicated by a waning intensity of the pink color of the solution, with the hue diminishing from the top towards the bottom of the solution while under UV radiation. Liquid samples of the irradiated cylinder were collected from the top and middle of the graduate cylinder. The UV-Vis scans of these samples were compared to the spectrum of the trans isomer.

The solution after the irradiation is shown in figure 24. The top layer has changed to a darker shade whereas below that layer, no change is seen at all. Figure 25 shows the UV-vis comparison and the apparent reduction in isomerization at a depth farther from the source of UV light.

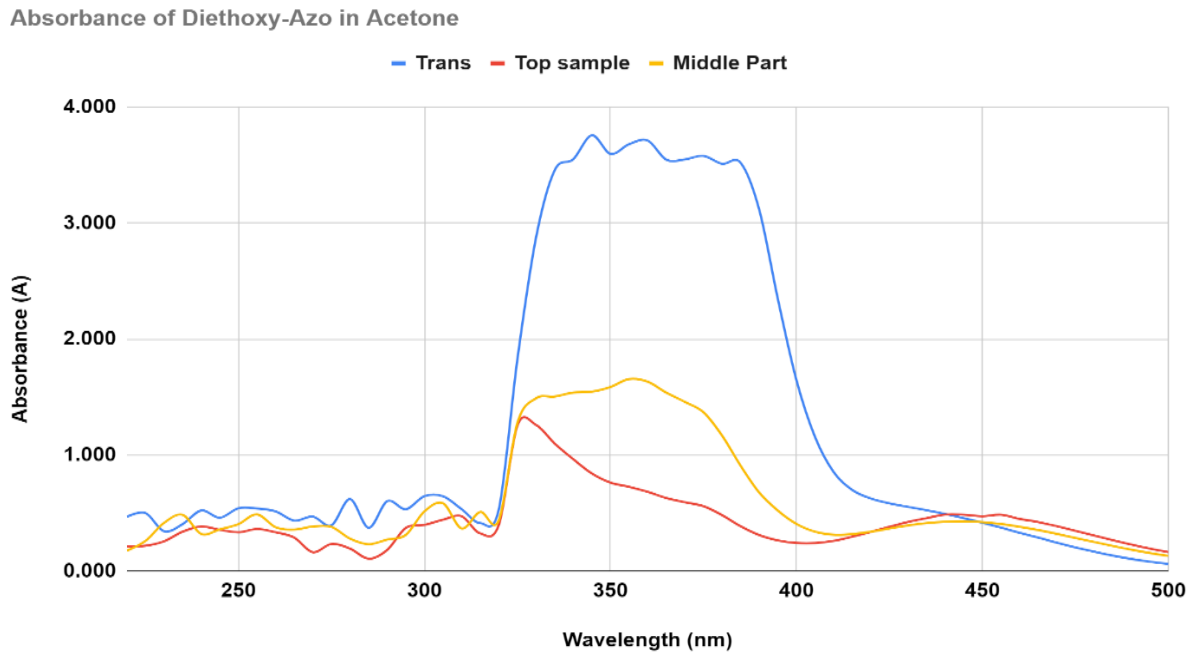


Figure 25: UV-Vis comparison of Diethoxy Azobenzene in Acetone at different height.

4.2 Hypothesis Success:

In this experimental work, we successfully validated our hypothesis regarding the development of a switchable solvent system that utilizes UV light for activating a switch in solvent activity. This achievement provides a solid foundation for further exploration and potential advancements in separation processes.

One noteworthy aspect of our research is the utilization of diethoxy azobenzene, which demonstrated positive results in our experiments. By highlighting the effectiveness of this compound, we can emphasize the potential of utilizing photo isomers, such as azobenzenes, in the development of separation processes. The exploration of different solvents and photo isomers holds great potential for expanding the scope and versatility of this approach. Furthermore, the application of this proof of concept to other solutes beyond lignin could potentially unlock opportunities for novel separations in various industries.

Given the promising results obtained thus far, it is anticipated that our proof of concept will generate significant interest and inquiries within the scientific community. Researchers may be inspired to delve deeper into this approach, exploring alternative solvents, photo isomers, and target solutes. The potential for this method to revolutionize separations will require further investigation and collaboration among experts in the field.

4.3 Shading Effect Analysis:

It is crucial to address the shading effect that arises when a higher concentration of photo-isomers is added to the solution. The shading effect occurs as the isomers at the top of the solution, closer to the source of UV light, hinder the absorption of UV light by the isomers

situated at the bottom of the solution. Consequently, this limitation diminished the ability of the bottom isomers to precipitate the lignin effectively.

To tackle the shading effect and enable the scaling process, several approaches can be considered:

Optimal Equipment Selection: One way is to utilize open or glass process equipment, preferably made of quartz. Quartz equipment allows better transmission of UV light throughout the solution, minimizing shading effect. It is important to choose materials that have high UV transparency to ensure efficient activation of the switchable solvent system.

Stirring or Mixing: Implementing a stirring or mixing mechanism within the system could help distribute the photo-isomers more evenly throughout the solution. By promoting thorough mixing, the shading effect can be minimized, as the isomers will be continuously dispersed and prevented from settling at the top of the solution. However, with stirring we could end up diminishing the formation of precipitates, or possibly enabling redissolution.

Light Diffusion: Employing light diffusers or diffraction techniques can assist in spreading the UV light more evenly across the solution. This helps to overcome the shading effect by ensuring a more uniform distribution of light, thereby enabling effective isomerization and precipitation throughout the solution. Likewise, multiple light sources could also be used to evenly irradiate the solution.

However, there could be some potential regarding the shading effect. It could be explored as a means to control the rate of precipitation in a system. Strategically manipulating the distribution of photo-isomers and the exposure to UV light, it might be possible adjust the

precipitation process according to specific requirements. This aspect requires further investigation and experimentation to fully understand the implications and potential applications of the shading effect in the separation process.

4.4 Conclusion:

The experimental work validated our hypothesis that a switchable solvent system could be developed that makes use of UV light as the means of activating a switch in solvent activity. This work shows that a photo isomer can help in precipitating lignin with UV irradiation. Diethoxy azobenzene in ethanol was able to reach a maximum precipitation of 14 mg out of 130 mg added, which relates to roughly 11%, whereas in acetone, it was able to reach a maximum of 42 mg out of 200 mg added. The number in acetone relates to more than 20% of the original amount. Thus, it was concluded that among all the systems studied, 4,4'-diethoxy azobenzene with acetone was found to be most efficient at precipitating Organosolv lignin in response to UV light exposure.

4.5 Future Directions:

4.3.1 Organosolv Process:

A next step in our analysis of this approach to separation is to replicate the Organosolv process. The Organosolv process involves cooking lignocellulosic materials with organic solvents at elevated temperature. Likewise, it would be interesting to perform our process with an aqueous mixture of solvents at higher temperature. At higher temperature, we would be able to dissolve more lignin into the solution. However, we are not sure of the isomerization information in aqueous mixture nor in elevated temperatures. Thus, the first thing to determine will be isomerization information.

4.3.2 Green Solvents:

A second approach could be a chain of experiments that could be done with green solvents like ionic liquids or deep eutectic solvents. These solvents are described as green because they have a low impact on the environment. They are developed to address concerns related to toxicity, volatility, flammability, and their potential to contribute to air pollution and waste generation. They minimize the use of hazardous chemicals, reduce energy consumption, and promote safer and more sustainable practices in various industries, including pharmaceuticals, chemicals, coating, and cleaning products. Since they are typically derived from renewable resources, they exhibit properties such as low toxicity, low volatility, biodegradability, and low environmental persistence.

Chapter 5: References:

- Phitsuwan, P., Sakka, K., Ratanakhanokchai, K., 2013. Improvement of lignocellulosic biomass in planta: a review of feedstocks, biomass recalcitrance, and strategic manipulation of ideal plants designed for ethanol production and processability. Biomass Bioenergy 58, 390–405.

- El Seoud, O.A., Koschella, A., Fidale, L.C., Dorn, S., Heinze, T., 2007. Applications of ionic liquids in carbohydrate chemistry: a window of opportunities. Biomacromolecules 8, 2629–2647.

- Mansouri, N.-E.E., Salvadó, J., 2006. Structural characterization of technical lignins for the production of adhesives: application to lignosulfonate, kraft, soda-anthraquinone, organosolv and ethanol process lignins. Ind. Crops Prod. 24, 8–16.

- G. Xu, Z. Shi, Y. Zhao, J. Deng, M. Dong, C. Liu, V. Murugadoss, X. Mai, Z. Guo, Structural characterization of lignin and its carbohydrate complexes isolated from bamboo (dendrocalamus sinicus), Int. J. Biol. Macromol. 126 (2019) 376–384.

- S. Sun, H. Yang, J. Yang, Z. Shi, J. Deng, Revealing the structural characteristics of lignin macromolecules from perennial ryegrass during different integrated treatments, Int. J. Biol. Macromol. 178 (2021) 373–380.

- J.A. Sirviö, M.Y. Ismail, K. Zhang, M.V. Tejesvi, A. Ämmälä, Transparent lignin-containing wood nanofiber films with UV-blocking, oxygen barrier, and anti-microbial properties, J. Mater. Chem. A 8 (2020) 7935–7946.

- Han, G., Li, H., Grossman J. C. (2017) Optically-controlled long-term storage and release of thermal energy in phase-change materials. Nat. Commun. 8(1).

- Cicogna, F., Domenichelli, I., Coiai, S., Bellina, F., Lessi, M., Spiniello, R., Passaglia, E. (2016). Structural, thermal and photo-physical data of azo-aromatic TEMPO derivatives before and after their grafting to polyolefins. Data in brief. 6:562-570.

- Prieur B., Meub, M., Wittemann, M., Klein, R., Bellayer, S., Fontaine, G., Bourbigot, S., (2017). Phosphorylation of lignin: characterization and investigation of thermal decomposition. RSC advances. 7(16866).

- An, Y., Zong, M., Wu, H., Li, N. (2015). Pretreatment of lignocellulosic biomass with renewable cholinium ionic liquids: Biomass fractionation, enzymatic digestion and ionic liquid reuse. Bioresource Technology. 192: 165-171.

- Cho, E., Zhitomirsky, D., Han, G., Liu, Y., Grossman, J (2017). Molecularly engineered Azobenzene Derivatives for High energy Density solid-state Solar Thermal Fuels. ACS Applied Materials and Interfaces. 9(10): 8679-8687

- Beharry, A.A., Woolley, G.A. (2011) Azobenzene photo switches for biomolecules. Chem. Soc. Rev. 40:442-4437.

- Merino, E. and Ribagorda, M. (2012) Control over molecule motion using the cis-trans photoisomerization of the azo group. Beilstein Journal of Organic Chemistry. 8:1071-1090.

- Sun, S., Liang, S., Xu, W., Xu, G., Wu, S. (2019) Photo responsive polymers with multi-azobenzene groups. Polymer Chemistry. 10(32): 4389-4401.

- Liu, J., Xiang, L., Li, M., Zheng, Y.(2022) Lignin biorefinery: Lignin source, isolation, characterization, and bioconversion. Advances in bioenergy. 7:211-270.

- Hintz, H.L. (2001) pulping and Bleaching. Encyclopedia of Materials: Science and Technology. 6707-6711.

- Tooyserkani, Z., Kumar, L., Sokhansanj, S., Saddler. J., Xiaotao, T. B., Lim, C.J., Lau, A., Melin, S. (2013) SO_2-catalyzed steam pretreatment enhances the strength and stability of softwood pellets. 130: 59-68.

- Sierra, R., Granda, C. B., & Holtzapple, M. T. (2009). Lime pretreatment. *Methods in molecular biology (Clifton, N.J.)*, *581*, 115–124.

- Iakovlev, M., You, X., van Heiningen, A. *et al.* SO_2–ethanol–water (SEW) fractionation process: production of dissolving pulp from spruce. *Cellulose* **21**, 1419–1429 (2014).

- Kim TH, Gupta R, Lee YY. Pretreatment of biomass by aqueous ammonia for bioethanol production. *Methods Mol Biol*. 2009;581:79-91.

- Xue, L., Pan, Y., Zhang, S., Chen, Y., Yu, H., Yang, Y., Mo, L., Sun, Z., Li, L., Yang, H. (2021). Fluorescent Azobenzene-Containing Compounds: From Structure to Mechanism. Crystals. 11(7): 840.

Chapter 6: Appendix:

University of Maine Standard Operating Procedure
Department of Chemical and Biomedical Engineering
5337 Jenness Hall
Orono, ME, 04469

SOP File ID: CHE SOP#DK-1 rev. 0
Date: 06/27/2023

Prepared by: Dipesh J. Karki	Date: 06/27/2023
Reviewed by: PvW	06/30/2023
Approved by: PvW	06/30/2023

SOP History:

rev	Description	Date
0	Running a sample through the spectrophotometer to generate UV-Vis scan.	06/27/2023
1		
2		
3		
4		
5		
6		

1. **Summary of the Method**
   Samples are put in a UV-cuvette and run through the spectrophotometer to generate UV-Vis scan which is essential in finding key isomerization information.

2. **Scope + Application**
   10.1 Determining trans charging and cis discharging information for photo-isomers.
   10.2 Comparing spectra of an unknown sample to a known sample and predicting the unknown sample.

10.3 Determining concentration using a calibration curve.

3. Exclusion + Interferences

The cuvette should be cleaned properly with Kim wipes and no impurities should be present.

4. Safety Alerts

4.1 Require equipment: gloves, safety glasses.

4.2 Solvent (water, ethanol, among others) could be hazardous.

5. Required apparatus

10.1 Gloves

10.2 Pipette

10.3 Chemglass Life Sciences UV-Cuvette, Semi-Micro

6. Reagents and Materials

10.1 Sample

10.2 Solvent (water, ethanol, among others)

7. Documents Referenced: none

8. Procedure

10.1 Turn on Evolution 100 UV-Visible Spectrophotometer, it takes couple of minutes to start the lamp.

10.2 Select General test. From the drop-down menu, choose: scanning.

10.3 Set the criteria such as starting wavelength, stop wavelength and the desired interval.

10.4 Select run test.

10.5 In the case of a solute dissolved inside a solvent, use the pure solvent as the blank. Use a pipette to add 1ml of pure solvent into a cuvette.

10.6 Place the cuvette into the blank holder, make sure the arrow inscribed on one of the four sides of the cuvette is facing towards the beam/light source.

10.7 To measure a sample, add 1 ml of that sample into a cuvette using a pipette.

10.8 Place the cuvette into no.1 position of the holder, make sure the arrow inscribed on one of the four sides of the cuvette is facing towards the beam/light source.

10.9 To generate spectrum for a pure solvent, leave the blank holder inside the spectrophotometer empty.

10.10 Repeat 8.7 and 8.9.

9. Quality Control

Wearing gloves would prevent impurities getting onto the wall of the cuvettes.

10. Comments

10.1 SOP rev 0 still under construction

University of Maine Standard Operating Procedure
Department of Chemical and Biomedical Engineering
5337 Jenness Hall
Orono, ME, 04469

SOP File ID: CHE SOP#DK-2 rev. 0
Date: 06/27/2023

Prepared by: Dipesh J. Karki	Date: 06/27/2023
Reviewed by: PvW	06/30/2023
Approved by: PvW	06/30/2023

SOP History:

Rev	Description	Date
0	Generating FTIR spectra	06/27/2023
1		
2		
3		
4		
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1. **Summary of the Method**
    a. Samples were run through a FTIR to get valuable information into molecular structure and functional groups present in the dissolved precipitate.

2. **Scope + Application**
    a. FTIR spectra generation for various samples.
    b. FTIR spectra can help in facilitating a comprehensive understanding of chemical composition.

3. **Exclusion + Interferences**
    a. The sample holder should be cleaned thoroughly before and after taking a sample.

4. Safety Alerts

a. 4.1 Require equipment: gloves, safety glasses.
b. 4.2 Solvent (water, ethanol, among others) could be hazardous.

5. Required apparatus

a. Sample
b. Tweezers
c. Pipette

6. Reagents and Materials

a. Samples

7. Documents Referenced: none

8. Procedure

8.1 Turn on the computer. Log in password is Ober 1234. The FTIR machine should already be on; it always stays on, do not turn it off. If for some reason it is off, turn it on.

8.2 Open OMNIC software.

8.3 Remove dust cover(s) and turn pressure peg to side. Clean diamond plate (tiny circle at center

8.4 of stainless-steel circle at center top of FTIR instrument) gently using isopropyl alcohol (IPA) and a Kim wipe. Be aware that the IPA will need some time to evaporate off the diamond plate completely; if you don't give enough time, there will be spectral peaks for IPA. It's often good to clean with ethanol and/or DI water after the IPA, and dab with a Kim wipe gently, to be sure the IPA is cleaned off and to keep the diamond plate extra clean and dry. Count to 30 slowly to allow time for full drying.

8.5 Run a background by clicking "Collect Background" on the instrument or in the software or under "Collect -> Collect Background". Wait while the scans are completed. The background tells the instrument what to subtract from each subsequent scan, as it represents moisture in

8.6 the air, etc., not the sample. The instrument will prompt you for a new background every two

8.7 hours (or as you set in the Experiment setup), as humidity will often change during the day.

8.8 Run your sample by clicking "Collect Sample" on the instrument or in the software or under

8.9 "Collect -> Collect Sample". The software will prompt you to name your sample. You can use the default name based on date/time or enter your sample name. Click "OK" and then the instrument will prompt you to prepare your sample. Place your sample on the diamond plate.

8.10 For solids: place the pressure peg over the sample and turn the pressure peg knob clockwise until you feel the knob "slip" meaning it is at its correct pressure.

8.11 For liquids: leave the pressure peg turned off to the side as for background collection. If your sample will not evaporate off the diamond plate in the time it takes to do the scans, simply place a drop of liquid over the diamond plate to cover the entire diamond.

8.12 For highly volatile liquids: you may place the liquid sample cover disc (rubber gasket side down) over your sample and then apply the pressure peg onto the disc as you would a solid sample; this will help minimize evaporation during sampling.

8.13 Click to run the sample. Wait while the sample scans are completed. Add the spectrum to your active Window. Save/analyze/annotate/compare from there.

8.14 If you used the pressure peg, release the pressure by turning the knob counterclockwise. IT IS IMPORTANT TO AVOID RAISING THE PRESSURE PEG MORE THAN ABOUT 1 INCH ABOVE THE DIAMON PLATE. The pressure peg will sometimes stick in the uppermost position if it is raised too high, and it is quite difficult to release it back down to normal operation. Please don't raise the pressure peg more than about an inch. Turn it to the side if it is in your way or unused.

8.15 Using a Kim wipe, gently pick/absorb the majority of your sample from the diamond plate and the pressure peg tip or cover disc, if used. Use the wash bottle(s) to further clean the diamond plate and pressure peg tip or disc, as applicable. End with ethanol and/or water and count slowly to 30 to allow dry time after dabbing dry with another clean Kim wipe.

8.16 Complete steps 5 to 7 for each sample. When finished, after cleaning according to step 7, turn the pressure peg so it is over the diamond plate and no more than about 1" above the plate. Return the dust cover(s) into place.

9. Quality Control

a. Always clean the instrument before and after use, aim to leave it in better condition than before you arrived.

10. Comments

a. 10.1 SOP rev 0 still under construction

University of Maine Standard Operating Procedure
Department of Chemical and Biomedical Engineering
5337 Jenness Hall
Orono, ME, 04469

SOP File ID: CHE SOP#DK3 rev. 0
Date: 06/27/2023

Prepared by: Dipesh J. Karki	Date: 06/27/2023
Reviewed by: PvW	06/30/2023
Approved by: PvW	06/30/2023

SOP History:

Rev	Description	Date
0	Evaporation rate calculation for a solvent	06/27/2023
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1. **Summary of the Method**
    a. The evaporation rate of acetone was obtained by measuring the mass under different time periods and temperature.

2. **Scope + Application**
    a. Estimation of acetone evaporation under different time periods and temperature.

3. **Exclusion + Interferences**
    a. The same beaker should be used for all mass measurements.

4. Safety Alerts

a. 4.1 Required equipment: gloves, safety glasses.
b. 4.2 Solvent (acetone, ethanol, among others) could be hazardous.

5. Required apparatus

5.1 50 ml Pyrex beaker
5.2 Balance-> 200 * 0.001 gm
5.3 Pipette -> 10ml - 1ml
5.4 Stopwatch
5.5 Hot plate
5.6 Thermometer -> 0°C - 100°C

6. Reagents and Materials

a. Acetone

7. Documents Referenced: none

8. Procedure

8.1 Measure the mass of the beaker using the balance.
8.2 Add acetone to the beaker using the pipette.
8.3 Measure the total mass again.
8.4 Subtract the mass of beaker from total mass to get initial mass of acetone.
8.5 Leave the beaker uncovered so that acetone can evaporate off.
8.6 Measure the mass three times in intervals of 20 minutes-40 minutes- 60 minutes
8.7 Subtract the mass of beaker from total mass to get final mass of acetone.
8.8 Subtracting the final mass from the initial mass will give the amount of acetone evaporated.
8.9 Plotting this mass difference with respect to time will give the evaporation rate as a function of time.
8.10 For higher temperatures, follow 8.1 to 8.4
8.11 Place the beaker on a hot plate and set the hot plate at desired temperature.
8.12 Place a thermometer inside the beaker to measure the actual temperature of the solution.
8.13 Then repeat 8.5 to 8.9.

9. Quality Control

a. The beaker should never be completely filled with acetone as there is always risk of spilling it over and the same beaker should be used for all calculations.

10. Comments

10.1 SOP rev 0 still under construction

Chapter 7: BIOGRAPHY OF THE AUTHOR:

Dipesh Karki was born in Pokhara city of Kaski district, Nepal on November 12, 1998. He was raised in Kathmandu, capital city of Nepal and graduated from Trinity International Higher Secondary School in 2016. He attended the University of Southern Maine and graduated in 2021 with a bachelor's degree in mechanical engineering. He jumped ship from mechanical and joined Chemical Engineering graduate program at The University of Maine in fall of 2021. After receiving his degree, Dipesh will work in the industry for a couple of years. After some valuable industry experience, Dipesh desires to further pursue PhD . Dipesh is a candidate for the Master of Science degree in Chemical Engineering from the University of Maine in August 2023.