Separation of Lignin from Lignocellulosic Hydrolyzates using Polymeric Flocculants and Fibrous Depth Filter Media

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SEPARATION OF LIGNIN FROM LIGNOCELLULOSIC HYDROLYZATES USING POLYMERIC FLOCCULANTS AND FIBROUS DEPTH FILTER MEDIA

By

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A thesis submitted in partial fulfillment of the requirements for the Master of Science Degree State University of New York College of Environmental Science and Forestry Syracuse, New York February 2020

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ABSTRACT


Lignocellulosic hydrolysates contain significant amount of colloidal lignin and its removal is vital since it inhibits fermentation, hinders oligomer hydrolysis and affects filtration. Flocculation of lignin prior to filtration is viable and previous research (Yasarla & Ramarao, 2012) demonstrated PEO’s ability to form complexes with lignin in the hydrolyzate. PEO viscosity was determined precisely to use as a control variable for flocculant quality. Flocculation efficiency of PEO in hydrolyzates was studied using parameters such as supernatant turbidity, sedimentation rate, filtration rate and cake permeability. Concentrations, dosages and molecular weights of PEO during flocculation were varied to study its effects. Multicomponent flocculation using APAM and p-DADMAC demonstrated better lignin removal than PEO flocculation. Addition of wood pulp as a filter media to PEO was based on incorporating both flocculation and filtration as a single operation. A depth filtration model was fitted using assumed parameters to obtain concentration profile and filter efficiency.

Keywords: Lignocellulosic hydrolyzate, lignin, flocculation, polymeric flocculants, PEO, flocculation parameters, depth filtration.
CHAPTER 1: INTRODUCTION

The global energy consumption has been growing significantly over the last few years and is spurred by economic growth and the rising demand. The total energy consumption in the United States reached a record high in 2018. In manufacturing countries like China, the energy consumption has been the highest due to its strong industrial demand and increasing fuel demand for transportation. Rise in population and increase in standard of living and modernization have also contributed to increase in energy consumption. According to the US EIA, the United States consumption of motor gasoline was about 3.4 billion barrels in 2018 [1]. The global energy data in 2018 based on the type of source gives us an idea of the current consumption, and oil is the largest source of energy being used while generated electricity and biomass are the least [2].

![Figure 1.1 Global energy consumption breakdown (2018)](image-url)
Fossil fuels include dry natural gas, crude oil, coal, and hydrocarbon gas liquids (HGL), and are still the leading source of energy among all other sources by about 72% of the total global energy [3]. Fossil fuel prices are also volatile during times such as natural calamities, political insecurities, etc. and therefore can place a significant strain in the global market. In the United States, hydraulic fracturing techniques in tight rock formations have yielded an increased production of natural gas and crude oil in 2017 and 2018. Global availability of this resource still remains limited and it is also not widely distributed among all consuming nations. It is also predicted to eventually run out over time, since it is a non-renewable source of energy and also because of the significantly rising demand. Although fracturing of shale increases the oil and gas supply, it uses significant amount of water and energy by itself and harmful chemicals that poison groundwater and environment [4].

Climate change due to carbon dioxide emissions from fossil fuels have brought in a negative impact to the environment by increasing the average global temperature and polluting the atmosphere and oceans. About 90% of global carbon emissions are from fossil fuels. Efforts to switch to alternative sustainable energy sources that provide clean fuel, are underway in most countries. They not only help alleviate climate change impact but also reduce the need for fossil fuels. Renewable resources are naturally replenished, and they are classified as biofuels, geothermal, solar, tidal, wind, wave and hydroelectricity. They also serve as great energy resources with almost zero emission of greenhouse gases [5].
Biomass is a renewable source of energy to produce carbon based fuels. They contain cellulose, hemicellulose and lignin. Biofuels are made from the conversion of these components through various chemical, thermochemical and biological processes. Biofuels such as ethanol and butanol have the ability to replace gasoline and diesel as fuel for transportation. This reduces the overall demand for traditional transport fuel [6-7]. Fuel such as E85 contains about 51 to 83% ethanol and is an alternative fuel to gasoline. Ethanol also burns cleaner than fossil fuels with almost zero emissions. Ethanol produced from biomass does not have any additional carbon footprint and also helps tackling the environmental impact of climate change [8].

Bioethanol is obtained from the cellulose fibers of plant cell walls and has the capability to play a big role as the fuel of the future. Any carbon based feedstock can be used for the production of ethanol. Currently agricultural feedstock such as corn are being used for bioethanol and other biofuel production. The only drawback of using agricultural feedstock as starting material for biofuel production is the increased food price. The problem can be solved by using agricultural wastes that are not used as food and sustainable forest resources for biofuel production. These fuels are termed as cellulosic biofuels. Different kinds of biomasses are found in Table 1.1.

Feedstocks that are starch or sugar based are relatively easier to produce ethanol than cellulose based. Corn is widely used as a starch based feedstock for ethanol production and accounts for about 90% of the total ethanol production in the United States. Sugars from the feed are extracted by milling and fermented to yield ethanol. Cellulosic
feedstocks such as grass, wood and crop residue follow a more elaborate process for ethanol production. The first biochemical pathway involves pretreatment to separate the hemicellulose, followed by hydrolysis to breakdown cellulose into sugars. The separated sugars are then fermented to yield ethanol. The second thermochemical pathway involves addition of heat and chemicals to produce syngas. The syngas when mixed with catalysts, reforms to ethanol and other products.

<table>
<thead>
<tr>
<th>Woody Biomass</th>
<th>Non-woody Biomass</th>
<th>Processed waste</th>
<th>Processed fuels</th>
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<tr>
<td>Trees</td>
<td>Sugarcane</td>
<td>Cereal husks and cobs</td>
<td>Charcoal</td>
</tr>
<tr>
<td>Shrubs</td>
<td>Cereal straw</td>
<td>Bagasse</td>
<td>Briquette</td>
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<tr>
<td>Forest sweepings</td>
<td>Cotton, Cassava</td>
<td>Nut shells</td>
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<tr>
<td>Bamboo</td>
<td>Grasses</td>
<td>Plant oil cake</td>
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<td>Soft stems, Pulses</td>
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<td></td>
<td>Swamp and Water plants</td>
<td>Papermill waste</td>
<td>Biogas</td>
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<td></td>
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<td>Industrial wood bark</td>
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*Table 1.1 Different types of biomass*

Cellulosic feedstocks have significant advantages over starch and sugar-based feedstocks. They are found abundantly in nature and require less energy to grow and get converted to ethanol. Selectively grown energy crops on marginal lands and waste byproducts can also be used to produce biofuels. Woody biomass specifically has higher density and one of the most sustainable and renewable sources for biofuels [9].
Biorefineries convert biomass not only into biofuel but also other beneficial bio-based products. They also help in valorization of agricultural and industrial waste and reduce emissions. Forest biorefineries process forest biomass such as wood from trees into biofuel and value-added forest byproducts such as biodegradable plastics. The paper and pulp industry are considered as the first industrialized biorefinery system. Lignocellulosic biomass contains cellulose, hemicellulose, lignin, aromatics and extractives. In a biorefinery, lignin and other particulates are separated, and cellulose and hemicellulose are pre-extracted. Hydrolysis of the resulting cellulose and hemicellulose yields acids and sugars. The sugars are further fermented to obtain ethanol, butanol and other beneficial byproducts. The separated lignin can be used for energy generation in biorefineries [10].

Figure 1.2 Generalized schematic of biorefinery processes
Although there are challenges involving cellulosic feedstock conversion to ethanol, such as high production cost and low yield, research is underway to find effective and affordable solutions. Research has been made in upstream processes like improving the hydrolysis to enhance cellulose extraction from the biomass, and optimizing enzyme loading which improves yield. Removal of lignin and other particulates are essential and can potentially affect fermentation of sugars [11].

A wide variety of separation techniques are used in the biorefinery industry to remove lignin from the biomass. Inefficient separation leads to the inhibition of fermentation, thereby affecting yield. Dead end filtration is commonly used but it poses challenges such as filter pore clogging as the particles are colloidal and cake formation causes resistance. Other methods such as centrifugation, etc. are not cost effective. Sequestering lignin from the lignocellulosic hydrolyzate using flocculation has been a promising method of separating the colloidal particles so far [12]. In this thesis, flocculation using polymeric flocculants have been studied and the significant separation of lignin was demonstrated. The use of pulp as a depth filter medium loaded with polymeric flocculant so as to combine both flocculation and depth filtration in a single step was investigated. A theoretical model to obtain the performance of a few depth filters were also fitted. The plots give an idea of the concentration profile and the capacity of a depth filter.
CHAPTER 2: BACKGROUND

2.1 Lignocellulosic Biomass Composition

Biomass is a renewable source of energy that is found naturally and in abundance. It is carbon neutral and therefore used for the production of biofuels and chemicals. The expression “lignocellulosic biomass” refers to woods or waste plants and amounts to 1.3 billion tons a year of global yield. The main components or lignocellulosic biomass are cellulose, hemicellulose and lignin and they are responsible for creating complex plant cell wall structure. Other components such as proteins, ash and pectin are found in minor quantities [13-14].

Cellulose is the most abundant polymer found in lignocellulosic biomass and accounts for about 30-60% of its composition. Cellulose is the main source of strength and structural integrity of the biomass, and it is a linear polysaccharide of D glucose molecules linked by β - (1,4) -glycosidic bonds. It serves as a versatile source for the production of fibers, films, composites, chemicals and fuels due its functional properties such as biocompatibility, stereoregularity, hydrophilicity, and reactive hydroxyl groups. Although it is generally insoluble in water under normal conditions, cellulose exhibits a certain degree of solubility at extreme pH levels and also with certain solvents. Cellulose is found in both crystalline and non-crystalline arrangement within the biomass, although, the crystalline structure account for two thirds of the total cellulose configuration.

Hemicelluloses are the second major component of lignocellulosic biomass and account for about 20-40% of the total mass. They are amorphous due to low degree of
polymerization, highly branched structure and presence of acetyl groups. Hemicelluloses are made up of polysaccharides such as xylan, galactomannan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan, held together by b-(1,4)- and/or b-(1,3)-glycosidic linkages. Unlike cellulose, hemicellulose is easily degradable and thus extremely advantageous in industrial applications such as cosmetics, hydrogels and as drug carriers.

Lignin covalently binds cellulose and hemicellulose and form a protective boundary against degradation. It accounts for 15-25% of the total lignocellulosic biomass composition. Lignin is a complex, three-dimensional, cross-linked polymer composed of phenylpropane monomers such as p-coumaryl, coniferyl, and sinapyl alcohols forming the three different p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units respectively. The ratio of occurrence of the S, G and H units depend on the type of biomass. Lignin is insoluble in water at normal conditions, but a degree of solubility can be observed a higher temperatures. Lignin produces energy when burned and therefore used a rich source of energy in biorefineries. Recently, lignin was also used to manufacture biodegradable plastics [15,16].
Figure 2.1 Main components of lignocellulosic biomass
2.2 Lignocellulosic Biomass Pretreatments in Biorefineries

Pretreatment of lignocellulosic biomass is vital for further processing into biofuels and value-added products. Factors such as cellulose crystallinity, degree of lignification and complexity of the components are responsible for biomass recalcitrance. Pretreatment aids in the collapse of this recalcitrance by breaking the lignin sheath, hemicellulose degradation and reduction of cellulose crystallinity and degree of polymerization. This step is significant in the biorefinery process. It is also the most expensive step and efforts to lower cost would increase process efficiency and help intensification of product recovery. Pretreatment of biomass is influenced by amount of feedstock, yield amount, minimizing waste and toxic products, effective removal of lignin, cost of equipment and energy source and finally the compatibility of the method with further processing. Pretreatment methods are classified as physical, chemical, physicochemical and biological [15-17].
Figure 2.2 Methods of pretreatment processes of lignocellulosic biomass
2.2.1 Physical Pretreatment

Physical pretreatments are always used prior to other treatments. It usually involves size reduction methods, thereby increasing the surface area and reducing the degree of polymerization and crystallinity. Milling, microwave assisted size reduction, extrusion and ultrasonication are the commonly prevalent methods of physical pretreatment.

2.2.1.1 Milling

Milling involves particle size reduction using motorized equipment. The different types of milling include two-roll milling, ball milling, rod milling, hammer milling, vibratory milling, colloid milling, and wet disk milling. The milling method used depends on biomass type, processing time, etc. Although it involves high capital cost and energy requirement, it does not result in any toxic or inhibitory compounds. It is a preferred and safe pretreatment method prior to further processing. Particle size reduction up to 0.2 mm can be achieved through milling [15,16,18].

2.2.1.2 Microwave assisted size reduction

Microwave method uses heat under an applied electromagnetic field for the pretreatment of lignocellulosic biomass. In this method, dielectric polarization creates molecular collisions that generate thermal energy, resulting in the disruption of the lignocellulosic structure. Although the method is non-conventional, it is energy efficient and quicker with minimal inhibitor formation. Several research experiments have proved
that this method is an assuring technique for fermentable sugar production from lignocellulosic biomass [15,16,19].

2.2.1.3 Extrusion

Extrusion is a commonly used physical pretreatment method that employs the use of high temperature and shear forces. The biomass is usually passed through a barrel with blades at high temperature (>300°C). The lignocellulosic degradation occurs due to high temperature and the shear forces of the rotating blades. Parameters such as blade design, rotation speed and barrel temperature control the efficiency of the extrusion process [15,16,20].

2.2.1.4 Ultrasonication

Ultrasonic radiation causes cavitation in this method of pretreatment. This cavitation causes shear forces to break the linkages between lignin, cellulose and hemicellulose. Ultrasound frequency, sonication power, duration and temperature influence this pretreatment method. Even though it is a viable method, it is not often chosen due to the fact that it is high energy demanding and the process parameters are yet to be optimized for large scale operations [15,16,21].

2.2.2 Chemical Pretreatment

Chemical pretreatments use either organic or inorganic chemicals to breakdown the linkages of lignin, hemicellulose and cellulose, thereby deconstructing the
lignocellulosic structure. Hydrolysis using alkali and acid, the use of ionic liquids and deep eutectic solvents, oxidizing agents and organosolv process purely fall under the chemical pretreatment category. Cellulose removal occurs in acid, alkali and oxidative pretreatment. Deep eutectic solvents and ionic liquids assist in hemicellulose removal. Except acid pretreatment, all other chemical pretreatments are involved in lignin removal [15,16].

Figure 2.3 Chemical pretreatment methods in biorefineries
2.2.2.1 *Alkaline Hydrolysis*

Alkaline hydrolysis is based on the solubilization of lignin in an alkali solution. It is one of the extensively studied chemical pretreatment methods. Alkaline reagents are usually hydroxides of sodium, potassium, calcium and ammonium and sodium hydroxide was proven to be the most effective among the rest. When alkali is introduced to the lignocellulosic biomass, a saponification reaction occurs. As a result, the intermolecular linkages between hemicelluloses and lignin are severed and solubilized in the alkali leaving behind cellulose. Cellulose swells up and causes a reduction in the degree of polymerization and its crystallinity, and therefore, becomes more available for downstream processing. Alkali recovery post pretreatment is a challenge and it is only favorable for biomass with lower lignin content [22,23].

2.2.2.2 *Acid Hydrolysis*

Pretreatment using acids are one of the most efficient methods of making cellulose more accessible for further processing. Hydrolysis of hemicellulose and condensation and precipitation of solubilized lignin are the two reactions that result during this treatment. Inorganic acids such as sulfuric, phosphoric, nitric and hydrochloric acid and organic acids such as formic, maleic and oxalic acid are used. Dilute acids are used at higher temperatures while concentrated acids are used at lower temperatures. The main disadvantage of this pretreatment is the corrosive and toxic nature of these acids, increasing the operational and maintenance costs. Therefore, dilute acids are preferred over concentrated acids in large scale operations. Undesired cellulose degradation occurs
to a certain degree and inhibitors such as furfurals, 5-hydroxy methyl furfural, phenolic acids and aldehydes are also formed [24].

2.2.2.3 Ionic Liquids

Ionic liquids are heterogenous structures containing inorganic anions and organic or inorganic cations. They are highly polar with high thermal stability and negligible vapor pressure. Ionic liquids exist in the form of molten salts at room temperature and pressure and their structure can be modified based on the requirements. When ionic liquids are introduced to lignocellulosic biomass, they disrupt the inter and intramolecular hydrogen bonds in cellulose and help in solubilizing cellulose and also lignin. Despite their distinctive chemical properties, ionic liquids are very expensive and toxic to enzymes and micro-organisms and therefore, are currently not economically feasible for large scale industrial operations [25].

2.2.2.4 Organosolv Process

Organosolv is a biomass pretreatment method that involves the addition of various organic solvents or their aqueous solutions to lignocellulosic biomass. As a result, the bonds between lignin and hemicellulose are fragmented, leaving behind porous cellulose of higher surface area for better saccharification. Organic solvents such as ethanol, methanol, acetone, organic acid, organic peracid and ethylene glycol or their aqueous solutions are used. A catalyst such as mineral acids, bases and some salts, is usually added afterwards to lower the process temperature and enhance delignification. The only
advantage of this pretreatment is the easy solvent recycle and recovery using distillation. Organic solvents are generally expensive to use and since they are highly volatile and flammable, the cost of maintenance and operation also goes up [26,27].

2.2.2.5 Deep Eutectic Solvents

Deep eutectic solvents are a newer generation of ionic fluids. They are made up of two or three components inter-linked through hydrogen bonding forming a eutectic mixture. DES have low melting points and exist as liquids at <100°C. DES as similar to ionic liquids in their physical and chemical properties but have a better biodegradability and lower cost than them. DES are made by mixing a quaternary ammonium salt with a metal salt or a hydrogen bond donor. A complex formation of the halide ion of the quaternary ammonium salt with the hydrogen bond donor occurs. Salts such as cholin chloride, CHCl is used along with hydrogen bond donors such as urea, glycerol, carboxylic acids and polyols. DES also enhances lignin and hemicellulose removal better than ionic liquids [28].

2.2.2.6 Oxidative Pretreatment

This method of chemical pretreatment involves an introduction of oxidizing agents such as ozone, hydrogen peroxide, oxygen or air. Removal of lignin in this process increases the availability of cellulose. Oxidation in non-selective, therefore cellulose and hemicellulose also gets degraded to a certain degree along with lignin. Delignification occurs through mechanisms such as electrophilic substitution, side chain displacement
and alkyl-aryl linkage disruption. This method is not suitable for large scale operations due to its extensive energy costs [29].

2.2.3 Physicochemical Pretreatment

Physicochemical methods involve both the physical changes and application of chemical effects to breakdown the lignocellulosic structure. They are therefore more effective in the biomass degradation. Usually, conditions such as high heat and/or pressure along with the addition of an inorganic compounds are employed for the disintegration of biomass for further processing. Steam, ammonia and CO₂ explosion and hydrothermal extraction are the physicochemical pretreatments presently available in the biorefinery industry [15,16].

2.2.3.1 Steam Explosion

Steam explosion is the most commonly applied pretreatment method due to its effectiveness. Water molecules penetrate the biomass structure when it is exposed to high temperatures (160-260°C) and high-pressure saturated steam (0.69-4.83 MPa). Once the pressure is rapidly released, the water molecules leave the biomass in an explosive manner, causing the biomass to split into fibers. Glycosidic bonds within cellulose and hemicellulose molecules are broken and cleavage of bonds between hemicellulose and lignin occur. Hemicellulose also gets hydrolyzed into glucose and xylose. This pretreatment method has hardly any chemical usage and therefore environmentally safe, uses less time and energy and higher sugar yield compared to conventional methods. Poor
lignin removal, possible inhibitor formation and reversal of hemicellulose into xylan are some of the drawbacks of steam explosion [30,31].

2.2.3.2 Ammonia Fiber Explosion

Ammonia fiber explosion or AFEX methodology is similar to steam explosion. The biomass is heated with liquid ammonia in 1:1 ratio to a temperature of about 60-100°C under high pressure conditions in a closed unit for about 5-30 min. As with steam explosion, the pressure is released rapidly. The lignocellulosic biomass swells under these conditions and the pressure release causes the biomass to structurally disintegrate and reduce cellulose crystallinity. The main advantage of this method is the negligible formation of inhibitors. Recovery and recycle of ammonia is required not only to minimize environmental damage, but also owing to its cost, corrosivity and its volatile nature [32].

2.2.3.3 Carbon dioxide Explosion

Supercritical CO₂ has the ability to diffuse through spaces like gas and also able to dissolve liquid materials. The CO₂ molecules under high pressure conditions penetrate into the biomass structure and disintegrates lignin and hemicellulose. Similar to steam and ammonia explosion methods, rapid release of pressure causes the biomass to split into fibers. CO₂ dissolves in water to form carbonic acid that allows for hemicellulose hydrolysis. For biomass with less to no moisture content, this pretreatment method is therefore not viable. Although this method has advantages such as low cost, low toxicity
and easy recovery, the high capital cost for employing CO₂ at high pressures is a hurdle for large scale industrial operations [33].

2.2.3.4 Hydrothermal Pretreatment Methods

Water without the presence of any other chemicals or catalysts, is used for the pretreatment of lignocellulosic biomass in the hydrothermal methods. They hydrothermal process are classified based on the operational temperature as: hot water extraction (HWE), liquid hot water pretreatment (LHW) and hydrothermal liquefaction (HTL). The employment of different temperatures is selected based on the end product requirement. The HWE process operates at low temperatures below 100°C and extracts pectin and tannin, the water-soluble biomass components. LHW is carried out at higher temperatures between 140 - 230°C. In this process, biomass structure is reduced due to the partial dissolution of hemicellulose and lignin. This is the most commonly used method of extracting lignocellulosic hydrolysates in this research as it involves less complexity and cost with the ability to provide desired material for this project. A biocrude oil like substance is formed when the biomass is subject to higher than 280°C during the HTL process. Water is maintained in its liquid state throughout the hydrothermal processes unlike steam explosion. High temperatures cause biomass recalcitrance disruption for further processing [16, 34].
2.2.4 Biological Pretreatment

Biological pretreatments use bacteria, fungi as whole cells or enzymes, that cause lignin degradation. This method of pretreatment is not only cost effective and eco-friendly, but also consumes lower energy and there is no inhibitor formation. They also have lower efficiency and longer residence periods, when used in isolation. Biological pretreatment can also remove antimicrobial components. Fungi such as white-rot, brown-
rot and soft-rot fungi are used for whole cell biological pretreatment of lignocellulosic biomass. Enzymes such as laccases, lignin peroxidase, manganese peroxidase, and versatile peroxidase cause disintegration of lignin [15,35].

2.3 Separations in Biorefineries

Hydrolysates from pretreatment of lignocellulosic biomass contain a significant quantity of negatively charged colloidal and particulate matter. These solids inhibit fermentation of sugars and interfere with other downstream processing. Therefore, it is necessary to separate these solids and its removal will help in the overall ethanol yield and economic viability of the bioconversion. Separation accounts for about two-thirds the total processing cost, therefore it is very vital that it not only be efficient but also less complex. Biorefinery processes are divided into three sections: pretreatment, separations and purification and downstream operations including hydrolysis and fermentation. Biomass becomes more amenable in the pretreatment stage. The output from pretreatment streams undergoes separation and purification where lignin, fermentation inhibitors and toxic compounds are removed in the second stage. Most of these separations in biorefinery processes are solid-liquid operations. Downstream processes such as fermentation and hydrolysis convert the biomass into ethanol and other value-added products. Process flow diagram of lignocellulosic biomass conversion to ethanol illustrates the current solid-liquid separation technologies in biorefineries.
Figure 2.5 Process flow diagram of conversion of biomass to ethanol in a biorefinery
Biomass liquor/hydrolysate from the pretreatment step usually contains a significant quantity of solids in particulate and colloidal form causing high turbidity. Therefore, clarification of these hydrolysates is essential. The method of solid-liquid separation used depends on the particle concentration and size distribution in the hydrolysate. Methods of solid liquid separations include centrifugation, filtration, flocculation and adsorption. In this research, primary separation of the colloidal solids from lignocellulosic hydrolysate is achieved through flocculation [36,37].

2.3.1 Centrifugation

Centrifugation separates suspended particles in a liquid medium, based on their physical characteristics such as density, size and shape. The hydrolysate is usually sent to a device known as a centrifuge with rotates at high speed to achieve sedimentation much faster than the rate of gravity. Centrifugal force is applied to each particle in suspension as the rotor of the centrifuge spins and separation is obtained. The separation is directly proportional to the amount of centrifugal force each particle experiences [38].

Figure 2.6 Centrifugation of a solid-liquid suspension
2.3.2 Filtration

Filtration is the one of the oldest and most common method of separation used in many industries. Solid-liquid separation occurs when the suspension is allowed to pass through a screen under the influence of a driving force such as pressure or vacuum, and solids are retained while the liquids pass through. The liquid stream is termed as filtrate and the solid layer is called the cake. The screens are usually membranes of different porosities and chosen based on the particle size required to be removed. Filtration maybe of two types: dead-end filtration and cross-flow filtration. The only difference between the two is the direction of flow of the suspension. If the direction of flow is parallel to the filter medium, it is considered to be a cross-flow filtration and when the flow is normal to the filter medium, it is s dead end filtration.

Figure 2.7 Comparison between filtration types, (i) dead-end filtration and (ii) cross-flow filtration
Dead-end filtration is considered a batch process. Formation of solid cake increases over time due to the accumulation of solids and creates a hydraulic resistance, decreasing the filtration rate. Some of the particles also clog the filter medium causing fouling. Cake removal and membrane fouling are the two constraints that can affect dead end filtration. In cross-flow or tangential filtration, maintaining the pressure between the flow and the membrane allows for liquid to permeate through the membrane. Solids are either swept along with the flow or collect near the membrane surface. Flux decay is observed with time due to membrane fouling. In both methods, filtration operation is ceased when the flux is negligible. Separation of lignin from hydrolysate can be done using filtration with a membrane of higher molecular weight cutoff. Flocculation is another method of solid-liquid separation and the use of this method prior to filtration helps membrane fouling reduction and thereby increases filtration efficiency [36].

2.3.3 Adsorption

Adsorption is a process of solid-liquid separation where the solids from the bulk fluid are bound to a solid surface. The solid phase is called the adsorbent and the adsorbed solids onto the surface is the adsorbate. Although the bulk fluid could be liquid or gas, in biorefinery separation processes, liquids are more often dealt with. Regeneration of the adsorbent is critical for the separation to occur. Adsorption occurs due attractive forces such as van der Waal’s forces, electrostatic forces and chemical bonding, between the adsorbent and the adsorbate. Adsorption technology in the biorefinery industry depends on the use of novel and robust adsorbents. Traditional adsorbents such as activated carbon, zeolites, ion-exchange resins and silica gel, and some modern adsorbents such as
polymeric resins, bio-based adsorbents and metal organic frameworks (MOF) have potential applications in biorefinery separation processes. Concentration of inhibitors in the pretreated hydrolysates can be reduced by used adsorption methods. Adsorbents can also be used after downstream processing for biofuel recovery [39].

2.4 Flocculation

Flocculation is a novel separation technology and involves the process of destabilizing and aggregating colloidal and particulate matter into porous and loosely assembled larger aggregates known as flocs. Colloidal particles with sizes in the range of 20 to 2000 Å can be flocculated effectively. The reagent that brings about the formation of flocs is knows as a flocculating agent. Selection of flocculating agent is based on the type of colloid/particles present in the solution. Polymeric flocculants are best suited for the flocculation of lignocellulosic hydrolysates, thereby making the separation easier by sedimentation and reducing membrane fouling during filtration. It also reduces the hydrolysate toxicity during the fermentation step. Flocculation depends on the polymer molecular size in solution and after adsorption, charge density, polymer concentration, the presence of other electrolytes and the mode of addition. In this study polymeric flocculants such as polyethylene oxide (PEO), cationic polyacrylamide (CPAM), anionic polyacrylamide (APAM) and poly-diallyldimethylammoniumchloride (p-DADMAC) were used. Flocculation occurs due to different mechanisms: charge neutralization, patch, and bridging flocculation. Complex flocculation occurs when more than one mechanism is used, as in the case of multicomponent flocculation [40-44].
2.4.1 Charge Neutralization

Stable colloidal particles are usually anionic and carry negative charges. Flocculants with high positive charges are introduced to the suspension and they are adsorbed onto the surface of the negatively charged colloids. The flocculant penetrates the diffuse electrical double layer around the particles, making them thinner and smaller in volume, enabling the particles to move closer and stick to each other as flocs [45].
2.4.2 Patch Flocculation

Patch flocculation occurs when branched polyelectrolytes are used as the flocculating agent. The flocculant adsorbs onto the surface of the oppositely charged colloidal particles, giving a non-uniform charge distribution across the particle surface. This leads to the formation of “patches” with excess localized polymer charges. Electrostatic attraction between these patches and the particles of opposite charge causes floc formation [46].

2.4.3 Bridging Flocculation

Bridging flocculation is the simplest and widely used industrial method. In this mechanism, a segment of the polymeric flocculant chain adsorbs onto the surface of more than one particle causing a three-dimensional network formation among the particles. Sufficient adsorption sites on a particle are required for the polymer chains with other particles to adhere to it. Increase in the molecular weight of the polymer results in longer chains thereby improving flocculation. Lignocellulosic hydrolysate flocculation using PEO follows this mechanism. PEO complexes with lignin allowing for an increase in the extent of dewatering, i.e., solid-liquid phase separation processes such as sedimentation and filtration [47].

2.5 Depth Filtration

Depth filtration is novel separation technology used for removal of solids from a fluid medium with the help of a filter media. A porous filter media is packed into a tubular
structure forming a bed, and particles in the flowing suspension are trapped along the length of the depth filter. Surface or membrane filtration filters suspensions by size exclusion while depth filters capture particles within their pore structure. Therefore, membrane filters have a more defined cut-off for particle size. Since depth filters remove particles of almost all sizes, they are more beneficial in high contaminant removal [48,49].

![Diagram of Depth Filtration and Surface Filtration](image)

*Figure 2.9 Comparison of depth filtration and surface filtration*

### 2.5.1 Mechanism

Depth filter media maybe be of two types: granular and fibrous. Fibrous filter media have a higher void fraction of 80-90% and therefore have larger surface area resulting in a greater rate of adsorption. Clarification occurs in the filter media through mechanisms such as surface retention, depth straining, interception and adsorption. Particles that are larger than the pore size are retained and do not pass through the filter. When the particles are intercepted by the fibrous composition, they lose momentum and
are not able to pass through the tortuous path while crossing the depth of the filter. This energy loss experienced by the particle traps it within the filter. Depth straining occurs when the pore size narrows within the filter and does not allow the larger particle to go through because of its size. Adsorption of particles within the filter occurs due to the attraction forces such as van der Waal’s forces, chemical attraction and electrostatic attraction between the particle surface and the surface within the depth of the filter [50-53].

![Depth filtration mechanism](image)

*Figure 2.10 Depth filtration mechanism*

### 2.5.2 Mathematical model

Modeling of fibrous filters and granular filters proceeds in a similar fashion, except that the single collector efficiency is now the single fiber efficiency in fibrous filtration. Particle collection occurs due to inertial impaction, electrostatic attraction, interception, gravity and Brownian diffusion. The total single fiber efficiency, \( \eta_f \) is a function of single fiber efficiencies of the different mechanisms. Capture due to diffusion decreases with an
increasing particle size, and impaction and interception mechanisms work better with larger particles. Therefore, the overall filter efficiency has a drop in the diffusion regime [54].

![Particle size vs filtration efficiency](image)

*Figure 2.11 Particle size vs filtration efficiency*

The total single fiber efficiency, $\eta_F$ is given by,

$$\eta_F = 1.6 \left( \frac{1-\alpha}{Ku} \right)^{1/3} Pe^{-2/3} + 0.6 \left( \frac{1-\alpha}{Ku} \right) \frac{N_R^2}{1+N_R^2}$$  \hspace{1cm} (2.1)

Where, $Ku$ is the Kuwabara flow factor, $Pe$ is the Peclet number, $\alpha$ is the packing number and $N_R$ is the interception number which is the ratio of particle to fiber diameter. The pressure $\Delta P$, drop across the fibrous filter media is given by Darcy’s law,

$$u_s = \frac{K \Delta P}{\mu L}$$  \hspace{1cm} (2.2)

Where, $L$ is the length of the filter, $u_s$ is the superficial velocity and $K$ is the permeability.
The dynamic performance of a depth filter is an analytical solution and function of position and time. The conservation equation for the suspended particles is given by,

\[ \varepsilon \frac{\partial c}{\partial t} + u_s \frac{\partial c}{\partial z} + \frac{\partial \rho' q}{\partial t} = 0 \] .... (2.3)

Since the filter bed is initially devoid of any particles, the following initial and boundary conditions can be applied.

\[ c(\theta = 0, z) = 0 \] ..... (2.4)
\[ c(\theta, z = 0) = c_i \] ..... (2.5)

The rate law is given by,

\[ \frac{\partial c}{\partial z} = -\lambda c \] ..... (2.6)

The coefficient \( \lambda \) in the above equation is known as the 'filter coefficient' and expressed as,

\[ \lambda = \lambda_0(1 - k\sigma) \] ..... (2.7)

The scaling parameter, \( \lambda_0 \) is usually taken to be the coefficient when the bed is clean without particle deposition, i.e. at the initial condition. \( \lambda_0 \) is known as the 'clean' or 'initial' filter coefficient. Also, \( \lambda = n/L \). The concentration profile changes with time and position as given by the following equation.

\[ \frac{c}{c_i} = \frac{\exp[u_s\lambda_0 c_i k\theta]}{\exp[\lambda_0 z]+\exp[u_s\lambda_0 c_i k\theta]-1} \] ..... (2.8)

Most often though, one is interested in the variation of the exit concentration, \( c_e \) as a function of time. For a depth filter of length \( L \), the above equation can be rewritten as below (setting \( z = L \)).
\[
\frac{c_e}{c_i} = \frac{1}{1 + \exp[u_s\lambda_0 c_i k\theta_L \{\exp[\lambda_0 L] - 1\}]} \quad \text{..... (2.9)}
\]

The filter efficiency is given by,

\[
E(t) = 1 - \frac{c_e}{c_i} = 1 - \frac{1}{1 + \exp[u_s\lambda_0 c_i k\theta_L \{\exp[\lambda_0 L] - 1\}]} \quad \text{..... (2.10)}
\]

The throughput is calculated by determining \(t_{\text{max}}\), the time taken when \(c_e = 0.05 c_i\). The value of \(u_s\theta\) obtained from the above correlation helps to calculate the throughput volume,

\[
V = u_s t = \epsilon L + u_s\theta \quad \text{..... (2.11)}
\]

Experimental data are fitted to this model to analyze depth filter performance [55-58].
CHAPTER 3: PROJECT OBJECTIVES

Lignocellulosic hydrolysates are in a particulate suspension despite the method of production and pretreatment. The suspended particulates mostly contain lignin and are either colloidal or macroscopic. Cake and centrifugal filtration are currently the methods of solid-liquid separation in the biorefinery industry. Flocculation is a very promising separation technique for removing colloidal particles in suspension. It is based on charge neutralization of particles, thereby disintegrating the electrical double layer and eliminating the electrostatic repulsions between the particles. Flocculants such as alum, and high charge density cationic polymers such as p-DADMAC and PEI have been investigated successfully on lignocellulosic hydrolysates by Duarte, Yasarla and Ramarao. Application of non-ionic polymers such PEO depends on the hydrogen bonding capability of the ether oxygen linkages within the polymer to the phenolic components of lignin and its derivatives. Novel flocculation of lignocellulosic hydrolysates using PEO was investigated by Yasarla, Gnanavel and Ramarao. Polymer dosage, pH and temperature sensitivity, re-floculation, polymer degradation, flocculation comparison with other flocculants and multicomponent flocculation were some of the studies conducted on PEO flocculation.

The first intent of the present work consists of further PEO flocculation investigation. Intrinsic viscosity analysis of PEO of varying concentrations and molecular weights at different temperatures were used as a control variable for the conformation of PEO thereby making the flocculant solution reproducible. Degradation of PEO occurs with time and therefore it becomes an ineffective flocculating agent. This was previously
studied by Vignesh (2015). Settling velocity of the flocs at different temperatures were studied to see if a drastic increase in settling rate could be achieved. Flocculation comparison based on turbidity was done using a non-ionic polymer PEO, anionic polymer APAM and cationic polymer CPAM. Flocculation of hydrolysates using different molecular weights and concentrations were carried out at different dosages to obtain optimum separation. Parameters such as turbidity, filtration time, sedimentation rate and solid permeability were analyzed at different PEO dosage to help improve the filtration process that follows flocculation. Multicomponent flocculation involving the addition of two polymers one after another using APAM and then p-DADMAC was carried out and compared with PEO flocculation.

The second part of the research involves the addition of wood pulp along with PEO for flocculation of lignocellulosic hydrolysates. The idea behind that was to incorporate wood pulp as a depth filter medium, loaded with flocculant, thereby integrating two separation steps, flocculation and depth filtration as a single operation. Wood pulp was considered due to its low cost and abundance. Both bleached and unbleached pulps were used and parameters such as particle size of supernatant and lignin adsorption were compared. A depth filter performance model was fitted for different depth filters based on assumed parameters. This could help identify the exact depth filter needed for a particular operation [59-61].
CHAPTER 4: METHODS AND MATERIALS

4.1 Preparation of Lignocellulosic Hydrolyzates

The biomass used for the hydrolyzates was sugar maple wood chips. Hydrolyzates were also made on a bench scale 4 L M&K digester using hot water extraction method. Sugar maple (*Acer saccharum*) wood chips were obtained from SUNY ESF Heiberg forest in Tully, NY. They were screened, air dried and were loaded into the digester along with DI water at a 4:1 weight ratio of water to wood chip. The digester run was performed for 2 hours at 160°C and around 95psi corresponding to maximum dissolved solids. Hydrolyzates were collected using a heat exchanger. The hydrolysates contain lignin in colloidal form.

Additional wheat straw and Aspen hydrolyzates were also analyzed. These were obtained either from NREL or from an industry producing them using the Biogasol process.

4.2 Polymer Flocculant Preparation System

The polymer mainly used for flocculation studies was Polyethylene Oxide (PEO) (Alfa Aesar, Ward Hill, MA) had molecular weights ranging from 0.1 MDa to 8 MDa*. Polyethylene Oxide (PEO) solution was made in the laboratory by dissolving the dry

* 1 MDa = 1x10^6 Da
polymer powder in de-ionized water at a ratio of 1:1000 by weight in a 250 mL beaker. The de-ionized water was kept under agitation around 500 RPM using a magnetic stirrer (Thermo-Scientific Inc.) and PEO was added slowly and carefully to avoid the formation of lumps leading to non-uniform concentration. Fresh batch of polymer solutions were made everyday due to its degradation. Polymeric solutions can be prepared by this technique up to about 1 liter in volume. While mixing, it is important that the depth of the vertex from the free liquid surface should be greater than ½ the stationary level value (i.e. $h_1/h_0 \geq 1/2$). The other polymers used were poly-Di-Allyl-Di-Methyl-Ammonium-Chloride (0.001N p-DADMAC) from Ecolabs, Napierville, IL, Anionic polyacrylamide (APAM) and Cationic polyacrylamide (CPAM) from Kemira. P-DADMAC was readily available in liquid form. Preparation of other polymeric flocculants such as: CPAM and APAM, followed the same method as PEO.

![Figure 4.1 Stirring setup for polymer preparation](image)
4.3 Intrinsic viscosity measurements

Intrinsic viscosities of PEO with varying molecular weights were measured at 20°C, 40°C and 60°C using a Cannon-Fenske viscometer immersed in a temperature-controlled water bath. The molecular weights used were 0.1 MDa, 0.3 MDa, 0.4 MDa, 1 MDa, 5 MDa and 8 MDa. There was also an unknown molecular weight PEO that was tested. The time taken for the PEO solution to travel from point A to point B in the viscometer corresponds to its kinematic viscosity. It is given by the following equation,

\[ v = ctd \]

where, \( v \) is the viscosity (mPa s), \( c \) is the viscometer constant, \( d \) is the density of liquid and \( t \) is the time taken for the polymer to pass from the upper to the lower mark [61].

![Figure 4.2 Cannon-Fenske viscometer](image-url)
The specific viscosities were calculated and then plotted in the Huggins equation, to solve for $\eta$, the intrinsic viscosity.

\[ \frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c \] \hspace{1cm} ..... (4.1)

Where, $k_H$ is the Huggins constant. The Mark-Houwink-Sakurada equation represents the relation between the intrinsic viscosity, $[\eta]$ and molecular weight, M. It was used to obtain the molecular weight of unknown PEO using viscosity data for each temperature. The relationship is represented as,

\[ [\eta] = KM^\alpha \] \hspace{1cm} ..... (4.2)

Where, K and $\alpha$ are the Mark-Houwink constants [62].

### 4.4 Turbidity Measurements

Aspen hydrolyzate was flocculated with PEO of different molecular weights (1 MDa, 5 MDa and 8 MDa) with varying dosages. The turbidity of their supernatant after flocculation was measured in Nephelometric turbidity units (NTU). The removal of lignin by flocculation shows a color change with flocculant dosage. Since the non-flocculated hydrolyzate control was out of the turbidimeter range, it was diluted twice to obtain a concentration of 25% in DI water. The same procedure was followed for samples after flocculation and before turbidity measurements. All turbidity data measured were for 25% concentration of the hydrolysates. Turbidity was also measured for flocculation using CPAM and APAM and compared to PEO.
4.5 Settling Velocity and Temperature Dependence in Flocculation

A volume of 100 mL of Aspen hydrolyzate was taken in a 250 mL beaker and 10 mL of 0.1% PEO solution was added while stirring at 500 rpm and 20°C. Once flocculated, the magnetic stirrer was removed, and the contents were rapidly transferred into a 100 mL measuring jar and a timer was started. The sediment height was measured over time till it became constant. The same experiment was repeated at 45°C and 65°C.

4.6 Filtration parameters for the purpose of optimization

Lignocellulosic hydrolyzates were obtained from NREL. LCH was allowed to thaw and flocculation was performed at 20°C. A volume of 5 mL of the hydrolyzate was weighed in an oven safe dish and weighed and was left overnight at 105°C. The weight of the dish with the solids alone was weighed and the solid content of the LCH was determined.

A volume of 50mL of the LCH was mixed with 50mL of DI water to dilute the LCH in half. The total 100mL of the diluted LCH was taken in a 250mL beaker and stirred in a magnetic stirrer and the flocculant was added. Flocculation experiments were conducted with PEO with varying dosages: 10, 25 and 50ppm. The flocculated LCH was transferred to a graduated 250mL cylinder and allowed to sediment. The sedimentation time and height (volume in mL) were noted. The LCH after sedimentation was vacuum filtered to obtain the cake solids and the clear supernatant. The filtration time was noted.
The supernatant was collected, and its turbidity was performed using a turbidimeter. A volume of 100mL of DI water was allowed to pass through the filter cake to assess its permeability and the time was noted.

### 4.7 Multicomponent Flocculation Studies

A volume of 100 mL of the Aspen hydrolyzate was taken in a 250 mL beaker and heated to about 45°C using a hot plate with magnetic stirring at around 500 RPM. When it reached the desired temperature, 7 mL of the p-DADMAC solution was pipetted into the beaker and allowed to mix well. A volume of 3 mL of the APAM solution was then pipetted into the beaker. The stirring and heating were turned off once flocculation was observed. The contents were vacuum filtered using a Buchner funnel setup and the supernatant was collected. Flocculation was conducted for 100 mL using 10 mL of PEO solution and the supernatant was taken as a control. The pH and turbidity were measured for both the supernatants. The same experiment was performed at 20°C (room temperature) and at 60°C.

### 4.8 Flocculation using Polymeric Flocculant and Depth Filter Media

The idea behind suspending wood pulp in PEO solution and then introducing it to the hydrolysates to remove lignin, was based on trying to combine two processes in one step. Pulp would be considered a depth filter medium due to its adsorbing properties, abundant availability and cost [60, 63, 64]. Flocculation and depth filtration could be combined into a single step process if the filter medium were to be loaded with a
flocculant. A flocculation setup was made by introducing a combination of wood pulp and polymeric flocculant to lignocellulosic hydrolysates. The two pulps used were Eucalyptus bleached Kraft pulp and Aspen unbleached Kraft pulp. Sugar maple hydrolyzate with a pH of 3 was used and PEO was the flocculant. A suspension of pulp and polymer was made by mixing 0.5g of wood pulp with 10mL of 0.1% PEO solution. Pulp fibers were added in increments of 0.5g for each run while PEO amount remained constant. It was then introduced to 100mL of hydrolyzate and allowed to flocculate. Lignin was observed to bind to the polymer loaded pulp as floccules. The adsorption spectrum of the filtrate was measured using a UV-Vis spectrometer and its particle size was also measured using a particle size analyzer.

4.9 Dynamic performance of depth filters

Modelling of depth filter performance was done using MS-Excel. Parameters such as the column length, column diameter and the flow are generally user defined. Inlet concentration and column porosity are measurable parameters. Based on the filter used, the filter bed parameters such as clean bed filter coefficient and linear filter decay coefficient are evaluated. Since depth filter experiments weren’t experimentally conducted to obtain these parameters, the dynamic performance of depth filters were fitted to the model using assumed parameters given in Table 4.1.
<table>
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</table>

Table 4.1 Assumed Depth Filter Parameters

The depth filter performance for different filters (variation of λ₀) were analyzed. The throughput is given by

\[ V_{max} = q_1 t_{max} \]

..... (4.3)

where \( q_1 \) is the flow rate per unit filter area.
CHAPTER 5: RESULTS AND DISCUSSION

5.1 Intrinsic Viscosity Analysis

Intrinsic viscosity of a polymer is related to the its molar mass according to the Mark-Houwink-Sakurada correlation. Therefore, to find out the unknown molar mass of a polymer, known molar masses of the same polymer were investigated. In our case, the polymer was PEO. The average viscosity of the solution of known molecular weights (0.1 MDa, 0.3 MDa, 0.4 MDa, 1 MDa, 5 MDa and 8 MDa) of PEO were obtained from viscometer studies. These were performed for various concentrations: 1, 2, 3, 4 and 5g/L. The relative viscosity was calculated as,

\[ \eta_{rel} = \eta / \eta_0 \]  

here, \( \eta_0 \) is the viscosity of the solvent and in our case, it was DI water, and \( \eta \) is the average viscosity obtained from viscometer studies. The specific viscosity was calculated as,

\[ \eta_{sp} = \eta_{rel} - 1 \]  

The reduced viscosities were calculated as,

\[ \eta_{red} = \eta_{sp} / c \]  

The reduced viscosities were plotted as \( \eta_{red} \) vs \( c \) using the Huggins equation. The intercept obtained from linearizing the data points gave the intrinsic viscosity, \([\eta]\). The intrinsic viscosities were plotted against the molecular weights as \( \log[\eta] \) vs \( \log M \) and the Mark Houwink constants, \( \alpha \) and \( K \) were obtained. Standard error was determined to obtain a 95% confidence interval for the data. The intrinsic viscosity analysis was performed at three different temperatures, 20, 40 and 60°C.
Intrinsic viscosity analysis at 20°C - Huggins equation

Figure 5.1 Intrinsic viscosity analysis at 20°C using Huggins equation
Figure 5.2 Intrinsic viscosity analysis at 40°C using Huggins equation
Figure 5.3 *Intrinsic viscosity analysis at 60°C using Higgins equation*

Figures 5.1, 5.2 and 5.3 show the intrinsic viscosity profiles measured at different temperatures. The intrinsic viscosities of PEO at 20°C for molecular weights \( \leq 1 \text{MDa} \) shows a slight increase with concentration. With increasing temperatures, i.e. at 40°C and 60°C, the contribution of PEO to the solution viscosity barely increases with
concentration. PEO degrades at higher temperatures and therefore the viscosities reduce and this in turn can affect the rate of flocculation. For molecular weights greater than 1 MDa, the solution viscosity increases with concentration, but they are also slightly affected by increased temperatures. The Mark Houwink plot in Figure 5.4 shows the variation of the intrinsic viscosity – molecular weight relationship with temperature. The contribution of molecular weight to the intrinsic viscosity of PEO decreases with increasing temperatures.

**Figure 5.4 Mark Houwink plot**
The Mark-Houwink constants $\alpha$ and $K$ were evaluated from the plot and are helpful in ascertaining the relationship between the intrinsic viscosity and molecular weight relationship for PEO solutions. This relationship is meaningful when it comes to reproducing PEO solutions for flocculation experiments as the intrinsic viscosity refers to a conformation variable of PEO. The constants $\alpha$ and $K$ were used to evaluate a sample of an unknown molar mass of PEO.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\alpha$</th>
<th>$\alpha \pm 2\text{s.e.}$</th>
<th>Log K</th>
<th>Log K $\pm 2\text{s.e.}$</th>
<th>Molar mass (MDa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.4697</td>
<td>0.0893</td>
<td>-3.0421</td>
<td>0.5350</td>
<td>5.1868</td>
</tr>
<tr>
<td>40</td>
<td>0.6254</td>
<td>0.1954</td>
<td>-4.4118</td>
<td>1.1692</td>
<td>5.0269</td>
</tr>
<tr>
<td>60</td>
<td>0.5756</td>
<td>0.1408</td>
<td>-4.2256</td>
<td>0.8427</td>
<td>5.0837</td>
</tr>
</tbody>
</table>

*Table 5.1* Molar mass of unknown PEO at different temperatures

Based on the intrinsic viscosity data and the Mark-Houwink constants from Table 5.1, average molar mass of the unknown PEO sample was calculated to be 5.0991MDa, and was safely assumed to be 5 MDa.

### 5.2 Turbidity Measurements

Turbidity measurement of the supernatant after flocculation is an important parameter of flocculation. Lower turbidity values mean that there is a reduction of colloidal particles in the hydrolyzate due to floc formation. In the first set of experiments, turbidity was measured and compared between the different polymeric flocculants: PEO, APAM and CPAM. Figure 5.5 shows a comparison of the original hydrolyzate to the
supernatants of the hydrolyzate after flocculation with CPAM, APAM and PEO.

![Figure 5.5 Hydrolyzate supernatants, (i) Control, (ii) Flocculation with CPAM, (iii) Flocculation with APAM and (iv) Flocculation with PEO](image)

Although the supernatants after flocculation look visually the same for all flocculants, PEO had the lowest turbidity among the three flocculants and was chosen to perform further experiments with. Table 5.2 shows turbidity data for the supernatants of each flocculant.

<table>
<thead>
<tr>
<th>Polymeric Flocculant</th>
<th>Turbidity (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td>2.62</td>
</tr>
<tr>
<td>APAM</td>
<td>3.24</td>
</tr>
<tr>
<td>CPAM</td>
<td>4.13</td>
</tr>
</tbody>
</table>

*Table 5.2 Turbidity of flocculated LCH with a 10ppm dosage*
From Table 5.3, optimal polymer dosage is around 25 ppm. A plot of supernatant turbidity measurements from flocculation experiments of sugar maple hydrolyzate involving different molecular weights of PEO is shown in Figure 5.6. Turbidity decreases sharply with addition of 1MDa PEO to the hydrolyzate. Turbidity also decreases with 5MDa and 8MDa PEO, but the numbers are slightly higher than 1MDa PEO. Any PEO with molecular weight under 1MDa either does not flocculate at all or barely flocculates. Turbidity drops with increasing molecular weight until 1MDa and with molecular weight increase to 5MDa, turbidity slightly increases and remains almost constant with further molecular weight increase as in the case of 8 MDa. Turbidity data corresponds to 25% supernatant dilution.

![Turbidity measurements vs PEO Molecular weight](image.png)

*Figure 5.6 Turbidity measurements of supernatants with PEO molecular weight*

Flocculation varies with dosage and this can be seen visually and using turbidity measurements. Turbidity of the supernatants drop with increasing dosage and also vary
with different PEO molecular weights. For sugar maple hydrolyzates, turbidity data was measured from flocculation experiments using PEO of 5 MDa and 8 MDa molecular weights. Figure 5.7 shows the turbidity decreases with increasing dosage although around 25 ppm, it starts to remain constant. It is also observed that the turbidity is lower with 5 MDa molecular weight than 8 MDa.

Figure 5.7 Turbidity measurements of supernatants from flocculation with varying PEO dosage

5.3 Settling Velocity and Temperature Dependence

Settling velocity is caused by drag force due to the motion of particle through the fluid and a primary force such as gravity. This is an important factor for the sedimentation of the flocs after flocculation. Flocculation of Aspen hydrolyzate with 0.1% PEO solution and immediate transfer into a graduated cylinder allowed for the measurement of sedimentation height of the flocs with respect to time. The sediment height was measured
till it became constant. The plot of height vs. time shows two parts – one where there is rapid settling of flocs and one where a plateau is seen. The slope of the rapid settling area in the plot gives us the settling velocity of the flocs. The settling velocities calculated at 20°C, 45°C and 65°C were 5.234E-06 m/s, 5.517E-06 m/s and 5.8E-06 m/s. In Figure 5.8, we can notice that as the temperature increases, the viscosity of water reduces, the floc sizes reduce due to PEO conformation changes and the rate of settling of flocs increases. Floc size also affect sediment height as observed in Figure 5.8. From the settling velocities, it is evident that temperature is a driving force for settling time.

![Settling Velocity - Height of Sediment vs. Time](image)

*Figure 5.8 Height of Flocs vs. Time of Settling*
5.4 Filtration Parameters with Varying PEO Dosage

For the Aspen hydrolyzate, the dry weight of the solids was 3.6 g for 5mL of the hydrolyzate and therefore the solids content of the LCH was 720g/L or about 72% solids. Therefore, the hydrolyzates were diluted with equal parts of DI water for conducting flocculation experiments. Dosage of PEO was also maintained accordingly. For example, a flocculation experiment with 10 ppm PEO (0.1% solution) would require 5 mL of PEO for 100 mL of diluted hydrolyzate. PEO was added in dosage of 10ppm, 25ppm and 50ppm and three flocculation experiments were carried out followed by turbidity measurement, filtration time, floc sedimentation rate and solids (cake) permeability. The sedimentation volume and time were used to obtain the sedimentation rate. Time required for 100 mL of DI water to flow through the cake was used to get the solid permeability of the flocs. Table 5.3 shows the variation of filtration parameters for the flocculated hydrolyzates with varying dosages.

<table>
<thead>
<tr>
<th>PEO Dosage (ppm)</th>
<th>Turbidity (NTU)</th>
<th>Filtration time (sec)</th>
<th>Sedimentation rate (mL/sec)</th>
<th>Solids permeability (sec/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.62</td>
<td>442</td>
<td>0.1755</td>
<td>10.88</td>
</tr>
<tr>
<td>25</td>
<td>1.52</td>
<td>411</td>
<td>0.1325</td>
<td>9.63</td>
</tr>
<tr>
<td>50</td>
<td>3.20</td>
<td>1241</td>
<td>-</td>
<td>13.72</td>
</tr>
</tbody>
</table>

Table 5.3 Flocculation parameters with dosage variation

At 50ppm the given LCH did not flocculate very well with hardly any floc formation and therefore the sedimentation rate was unable to be determined. At 10 ppm,
flocculation was observed but the parameters show that a better performance was seen at 25 ppm. At some dosage level between 25 and 50 ppm, flocculation in hindered due to the fact that the particles could have reversed charges. A minimum dosage of 10 ppm was required to achieve flocculation. Turbidity decreases with better flocculation and the filtration time is lesser. Higher cake permeability is seen with 25ppm dosage. The lower sedimentation rate can be explained as a result due to better and bigger flocs that require time to settle in a narrow cylinder. Polymer dosage influences turbidity, filtration time, sedimentation rate and cake permeability.

5.5 Multicomponent Flocculation - Comparison with PEO

Multicomponent flocculation involved the addition of more than one flocculant and in this case, it was p-DADMAC, a cationic polymer followed by APAM, an anionic polymer. Cationic p-DADMAC with its high charge density must have formed patches on the negatively charged colloids with excess of positive charge. Instantaneous flocculation is observed after the addition of APAM. APAM with its negative charge and polymer length sticks to these positive charges and forms flocs. The flocculated Aspen material using multi-component flocculation appeared to have bigger floc formation and clearer supernatants than single component flocculation upon visual examination as seen in Figure 5.8.
The contents in each beaker were vacuum filtered and the supernatants were obtained. The filtrate from the multi-component flocculation showed a lighter color visually than the single component flocculation as seen in Figure 5.10. This proves that the p-DADMAC and APAM flocculant combination removes lignin more effectively than just PEO alone.
The pH and the turbidity in NTU were measured for the two types of flocculation. Table 5.4 shows that the pH remains the same for both the single and multi-component flocculation while the turbidity data suggests that p-DADMAC and APAM removes lignin slightly better than PEO.

<table>
<thead>
<tr>
<th>Turbidity</th>
<th>PEO</th>
<th>p-DADMAC + APAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.91</td>
<td>4.92</td>
</tr>
<tr>
<td>NTU</td>
<td>1.31</td>
<td>1.01</td>
</tr>
</tbody>
</table>

*Table 5.4 pH and NTU measurements of supernatant using single and multi-component flocculation*

Another advantage of this multi-component flocculation is that it is independent of temperature while the PEO flocculation is temperature dependent as observed from previous research. Table 5.5 shows the variation of turbidity at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Turbidity (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.64</td>
</tr>
<tr>
<td>45</td>
<td>0.75</td>
</tr>
<tr>
<td>60</td>
<td>0.54</td>
</tr>
</tbody>
</table>

*Table 5.5 Turbidity measurements of supernatant using multicomponent flocculation at different temperatures*
5.6 PEO and Pulp Flocculation

A visual comparison of flocculation with and without pulp shows that the flocs are smaller with pulp and lignin was observed to bind to the polymer loaded pulp as floccules. Therefore, this combination could be positive for the construction of a depth filter made of pulp and loaded with a polymeric flocculant.

Figure 5.11 A. Flocculation with PEO, B. Flocculation with Pulp + PEO, C. Flocculation with PEO. (i) wood pulp (ii) wood pulp in suspension with PEO (iii) flocculated hydrolyzate with pulp suspension (iv) control flocculation with PEO
Both bleached and unbleached pulp were used for the flocculation of lignocellulosic hydrolyzate along with PEO and their adsorption capacities were compared. The zeta potential of bleached kraft pulp, unbleached kraft pulp and hydrolyzate were measured. This could mean that the unbleached kraft pulp could have a better flocculating capacity than bleached pulp.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignocellulosic hydrolyzate</td>
<td>-9.16</td>
</tr>
<tr>
<td>Bleached pulp</td>
<td>-28.58</td>
</tr>
<tr>
<td>Unbleached pulp</td>
<td>-22.34</td>
</tr>
</tbody>
</table>

*Table 5.6 Zeta potential measurements of hydrolyzate, bleached and unbleached pulp*

*Figure 5.12 Flocculation using Pulp and PEO. (Left) Lignocellulosic Hydrolyzate (control), (Center) Filtrate using PEO and bleached pulp and (Right) Filtrate using PEO and unbleached pulp.*
Visually, the supernatants of both bleached and unbleached pulp and PEO flocculation looks similar, but in comparison to the hydrolyzate, a great separation of lignin is seen.

The supernatants from PEO and pulp flocculation with varying pulp amounts for both bleached and unbleached pulp were measured for absorbance using a UV-Vis spectrometer. The concept of Beer’s law was used to establish the relationship between absorbance and concentration of lignin in the supernatant.

\[ A = a \times b \times c \] ..... (5.3)

Where, \( A \) is the absorbance, \( a \) is a constant, \( b \) is the path length and \( c \) is the concentration.

\[ \text{Figure 5.13 UV-Vis spectrum of flocculated hydrolysate using PEO and unbleached pulp} \]
UV-Vis spectrum of lignin in hydrolyzate presented a typical adsorption peak near 280 nm due to phenolic groups, a shoulder at 230 nm and a maximum adsorption at 200-208 nm due to conjugated C=C bond [66]. Unbleached pulp also shows a lower absorbance compared to bleached pulp. Since a linear relationship exists between the absorbance and concentration, a conclusion can be made that unbleached pulp adsorbs more lignin than the bleached pulp.

Langmuir isotherm was plotted for the adsorption of lignin. The general form of the isotherm is given as:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad \ldots (5.4)$$

**Figure 5.14 UV-Vis spectrum of flocculated hydrolyzate using PEO and bleached pulp**
Where, \( q_e \) is the amount of adsorbate in the adsorbent at equilibrium (g/g), \( c_e \) is the adsorbate initial concentration (g/L), \( q_m \) is the quantity of adsorbate adsorbed in a single monolayer (g/g) and \( b = \text{rate of adsorption} \ (k_a) / \text{rate of desorption} \ (k_d) \). Upon linearization, the above equation becomes,

\[
\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_m c_e} \quad \text{..... (5.5)}
\]

A plot of \( 1/q_e \) vs \( 1/c_e \) yields a slope of \( \frac{1}{bq_m} \) and an intercept of \( \frac{1}{q_m} \) [67].

![Figure 5.15 Adsorption of lignin onto bleached and unbleached pulp](image)

From the isotherm, \( q_m = 0.0179 \text{ g/g} \) for unbleached pulp and \( q_m = 0.0123 \text{ g/g} \) for bleached pulp. The equilibrium constant, \( b = 1.389 \) for unbleached pulp and \( b = 1.358 \) for bleached pulp. The maximum adsorption capacity of the media hasn’t been reached yet and that would be vital in the construction of the depth filter bed. Unbleached pulp shows higher adsorption of lignin than bleached pulp.
Lignin particle size in the filtrate was measured using a particle size analyzer. The hydrolyzate had an initial particle size of 1795 nm and was used as control. A drop of \(~70\%\) in the particle size was observed with the addition of 0.5 g of pulp and the particle size dropped further with increase in pulp amount. There was about an 8-10\% difference in particle size with unbleached pulp compared to bleached pulp. Therefore, unbleached pulp seems to adsorb larger particles than bleached pulp.

![Figure 5.16 Comparison of lignin particle size in filtrate using bleached and unbleached pulp](image)

**Figure 5.16 Comparison of lignin particle size in filtrate using bleached and unbleached pulp**

### 5.7 Depth Filter Performance Model

The analytical solution of depth filtration as a function of position and time is,

$$\frac{c}{c_i} = \frac{\exp[u_s\lambda_0 c_i k\theta]}{\exp[\lambda_0 z] + \exp[u_s\lambda_0 c_i k\theta] - 1}$$  \hspace{1cm} ..... (5.6)
Where, $\theta$ is the corrected time, $\lambda_0$ is the initial filter coefficient assumed to be 50 m$^{-1}$, $c_i$ is the inlet concentration assumed to be $8.8 \times 10^{-5}$ g/L, $c$ is the particle concentration, $z$ is the downstream or axial position, $k$ is the rate of decay assumed to be 12.5 and $u_s$ is the superficial velocity. Since the column length is assumed to be 0.4, position along the bed is considered from 0 to 0.4 m (L) and $\Delta z = 0.02$ m. Therefore, the data points selected were between 0 to 0.4 m with increments of 0.02 m. Similarly, the corrected time, $\theta$ varied from 0 upwards from position $z = 0$ and $\Delta t = 10$ h. Three profiles were considered at 10, 20 and 30 hours for each position $z$ along the filter bed depth. The superficial velocity, $u_s$ is calculated using the filtrate flow rate divided by the column area and is $1.443 \times 10^{-3}$ m/s. The corrected time was given by

$$\theta = t - (\varepsilon z / u_s) \quad \ldots (5.7)$$

and was calculated for $\Delta t = 10$ h and $z = 0$ to 0.4 m. The concentration profiles, $c/c_i$ were then calculated using the above equation. They were repeated for 20 and 30 h. The three concentration profiles were then plotted over the position along the filter bed depth, i.e. $c/c_i$ vs $z$.

![Figure 5.17 Concentration profile inside the depth filter at different times](image)
The exit concentration, \(c_e\) from the filter was calculated by setting \(z = L = 0.4 \text{ m}\) and using the following equation.

\[
\frac{c_e}{c_i} = \frac{1}{1 + \exp[u_s\lambda_0 c_i k\theta][\exp[\lambda_0 L] - 1]}
\]

... (5.8)

The last value of \(c/c_i\) at \(z = 0.4 \text{ m}\) is \(c_e/c_i\) and it was plotted against time (h). A slight increase of \(c_e/c_i\) is seen at 20 h compared to a significant increase at 30 h. As time increased, the filter reaches maximum adsorption capacity, therefore, it became less effective and the exit concentration increased over time.

![Figure 5.18 Exit concentration from the filter](image)

Five filter samples were considered with different inlet concentrations. Each concentration was assumed to have a step difference of \(8.8 \times 10^{-5} \text{ g/L}\). So basically, the concentrations were multiples of the original \(c_i\). The time taken when the exit concentration reached 5% of the inlet concentration gave \(t_{\text{max}}\). The maximum throughput volume,

\[
V_{\text{max}} = t_{\text{max}}u_s
\]

... (5.9)

was calculated using the relation,
\[ \theta = t - (\varepsilon z / u_s) \] 

\[ \text{..... (5.10)} \]

The throughput was calculated for various \( c_i \) for \( \lambda = 50 \text{ m}^{-1}, 100 \text{ m}^{-1} (2\lambda), 150 \text{ m}^{-1} (3\lambda) \) and \( 8 \text{ m}^{-1} (0.16\lambda) \). The value of \( \lambda_0 = 8 \text{ m}^{-1} \) corresponds to 16% of \( \lambda_0 = 50 \text{ m}^{-1} \), which is similar to untreated filter surfaces.

As the filtration proceeds, the filter co-efficient, \( \lambda \) increases as a function of the initial filter co-efficient, \( \lambda_0 \) by the following relationship,

\[ \lambda = \lambda_0 F(\sigma) \] 

\[ \text{..... (5.11)} \]

Where \( F(\sigma) \) is the function of the extent of adsorption within the bed of the filter. Variation of the inlet concentration, \( c_i \) with variation of \( F(\sigma) \) was plotted, i.e., different throughput was obtained for different \( F(\sigma) \) for a given \( c_i \). The increase in \( c_i \) was plotted against the throughput volume, \( V \), to predict the performance of the depth filter for various \( \lambda_0 \).

![Depth Filter Performance](image)

*Figure 5.19 Predicted depth filter performance with inlet concentration*
CHAPTER 6: CONCLUSION

This thesis focused on separation of lignin in the colloidal phase using flocculation and depth filtration media. A significant separation of lignin from the hydrolysates was observed in all the methods. The precipitated PEO-lignin can be used for further research and has various applications. An intrinsic viscosity analysis of PEO was performed since the molecular weight of the flocculating polymer influenced the outcome of flocculation. The Mark-Houwink constants were analyzed to help in the reproducibility of the polymer solution. Molecular weight of an unknown PEO was also found to 5 MDa using the Mark-Houwink relationship.

The turbidity measurements of the supernatant after flocculation of hydrolyzates helped to assess the extent of flocculation. Based on this data, PEO had a lower turbidity and therefore chosen for the majority of flocculation studies. Turbidity data showed that flocculation rate increases with increasing molecular weight until 1MDa and then slightly decreases with increasing MW and remains constant around 8 MDa. Flocculation also varies with dosage and with increase in dosage, turbidity decreases and remains constant after a dosage of around 25ppm.

Rate of settling of flocs immediately following flocculation, seemed to be temperature dependent. Higher temperatures yielded a relatively faster settling rate and a smaller sediment height. Flocculation efficiency using PEO as the flocculant was determined using filtration parameters such as supernatant turbidity, filtration rate,
sedimentation rate and solid permeability. The flocculation seemed to have hindered between 25 and 50 ppm due to the fact that the particles could have reversed charges.

Multicomponent flocculation using APAM + p-DADMAC removes lignin better than just PEO alone and it was observed visually and using turbidity data. Both the PEO and APAM + p-DADMAC flocculation were independent of pH, but PEO was temperature dependent unlike APAM + p-DADMAC.

A bench scale setup of flocculation using PEO as the polymeric flocculant loaded onto wood pulp as the depth filter media seemed to be promising for further research in the construction of a depth filter bed loaded with flocculant. Although visually similar, but based on particle size analysis, UV-Vis analysis and adsorption rate analysis, unbleached pulp has a slightly better lignin removal rate than bleached pulp. A depth filter performance model was fitted with assumed values of parameters to find an analytical solution. A concentration profile along the depth of the filter bed was plotted. The exit concentration filter helps to identify the maximum adsorption capacity of the filter. The depth filter performance could be predicted based on the maximum throughput for the given filter at a particular inlet concentration.

Further studies are to be done to obtain the maximum adsorption capacity of the filter media. The filtration efficiency and pressure drop are to be determined both mathematically and by constructing and designing a fibrous depth filter.
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EDUCATION
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Bachelor of Technology in Chemical Engineering (GPA 3.9/4.0) May 2009


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Diploma in Software Engineering

CHEMICAL/BIOTECHNOLOGY EXPERIENCE
Bioprocess Engineering Research Assistant, SUNY - ESF (Syracuse, New York) Jan 2013 – Feb 2020
- Performed flocculation of lignocellulosic hydrolyzates with flocculants for improving lignin separation
- Improved the process by varying flocculant dosage, multistage and multi-component flocculation
- Modeled the dynamic performance of depth filters using macroscopic equations

Biofilm Engineering Research Associate (GLP), Syracuse University (Syracuse, New York) Sep 2010 – Aug 2012
- Improved the process and optimized the conditions for the isolation of P. aeruginosa planktonic persister cells
- Constructed an electrochemical cell for the treatment of P. aeruginosa persister cells under the influence of weak electric currents
- Succeeded in proving that the persister cells treated with antibiotics and weak electric current combination was most effective
- Engineered P. aeruginosa biofilm and their associated persister cells treatment resulted in a similar pattern as their planktonic cells
- Contributed to bio-medical research that helps in devising a patient tolerable instrument to treat infection more effectively

Synthesis of Fluorescent SaposinB with Terbium for Cellular Imaging, Syracuse University (Syracuse, New York) Jan 2011 – May 2011
- Engineered SaposinB genetically from E. coli, purified it with FPLC and dialysis and characterized it by MALDI-TOF
- Optimized the reaction of SaposinB with Terbium metal and proved the complex formation
- Fluorescent SaposinB-Tb complex was engineered to see its interaction with cancerous cells for the purpose of cellular imaging

- Processed animal skin to leather using the chrome-tanning procedure and collected effluents at the end of each step
- Performed conventional methods to treat tannery effluent and their COD, BOD and TKN were determined
- Designed a bench top electrochemical reactor that made use of solar energy from panels to treat the tannery effluents
- Proved that the electrochemical reactor was 35% more efficient than other conventional methods

Enzyme Technology Intern, Sangene Biotech Ltd. (Bengaluru, India) Jun 2007 – July 2007
- Performed enzyme separation from various sources using homogenization and centrifugation
- Learned to conduct enzyme purification techniques like ammonium sulfate precipitation and gel filtration chromatography
- Measured the purification using methods like SDS-page, Western blot, specific activity determination and purification table

WORK EXPERIENCE
Teaching Assistant, SUNY ESF (Syracuse, New York) Jan 2013 – Dec 2015
- Computing Methods for Engineers & Scientists
- Fluid Mechanics
- Pulping and Bleaching Processes Laboratory
- Paper properties
- Engineering Design Economics

Front Desk Clerk, Office of Disability Services at Syracuse University (Syracuse, New York) Jan 2016 – May 2016
- Performing secretarial and administrative work, providing customer service, data processing and record keeping

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Programming Languages: C, C++, HTML, SQL, JAVA, VB
Software: Matlab, AfterMath, MS Project, MS Office

HONORS AND AWARDS
- Received graduate assistantship offered by State University of New York Aug 2013 – May 2018
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- Earned 14th rank among 400 candidates graduated with the Bachelor’s degree in Chemical Engineering Sep 2005 – May 2009
- Awarded scholarship for academic performance at St. Joseph’s College of Engineering, Chennai, India Sep 2006 – Sep 2008

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Member, American Institute of Chemical Engineers (AIChE) Jan 2010 – Present
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- Guided the new Indian Students who came to Syracuse University and provided temporary accommodation and housing
- Organized events for festivals to spread awareness of Indian culture and traditions to the greater Syracuse University community
- Conducted general body meetings, provide community service and interact with other student organizations