Optimizing Biomass Conversion Routes for Sustainable Chemical Production

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Abstract

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Monali Patel

This research focuses on shifting vital chemical production from fossil fuels to renewable alternatives, particularly through biomass-based pathways. Promising methods using agricultural waste show potential for sustainable production, contributing to a resilient, resource-conscious future for the chemical sector and supporting climate targets through innovative bio-based solutions. The current research focuses on utilizing bio-based production routes, particularly biochemical pathways originating from agricultural biomass to derive bio-polyethylene. Six production pathways are analyzed base on different pretreatment methods: dilute acid, hot water, ammonia fiber explosion, steam explosion, organic solvent and alkaline. The primary objective is to provide a decision support system among the available process options and identify promising integrated production routes based on costs, resources, and energy demands inherent in these processes. This evaluation is conducted using mixed-integer linear programming modeling techniques, which enables the selection of technologies from a broader range of production routes and optimizes their integration. The results from this modeling indicate that the dilute acid pretreatment production route proves to be the most cost-efficient, followed by steam explosion. The findings offer valuable insights into variations in primary resource usage and energy demands based on the pretreatment methods employed to yield the final product. Investment costs associated with each process unit facilitate a comparative economic analysis and highlight avenues for potential cost reduction. This approach aids in assessing the feasibility and advantages of various bio-based processes toward industrial production, to be complemented by thorough environmental assessment in future work.

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Nomenclature

AA	Acetic Acid
AFEX	Ammonia Fiber Explosion
ALKALI	Alkaline
ATM	Atmospheric (pressure)
BM	Biomass
CAPEX	Capital Cost
CAT	Catalyst
CO_2	Carbon Dioxide
C_P	Specific Heat Capacity
CS	Corn stover
DAP	Dilute Acid Pretreatment
EtOH	Ethanol
GCC	Grand Composite Curve
GHG	Greenhouse Gas Emissions
H_2SO_4	Sulfuric Acid
HCl	Hydrochloric Acid
HMF	Hydroxymethylfurfural
HWP	Hot Water Pretreatment
K	Kelvin
KG	Kilogram
KJ	Kilojoule
KW	Kilowatt
LCB	Lignocellulosic Biomass
LCF	Lignocellulosic Feedstock
MILP	Mixed-Integer Linear Programming
NaOH	Sodium Hydroxide
NREL	National Renewable Energy Laboratory
OPEX	Operating Cost
ORC	Organic Rankine Cycle
ORGANO	Organosolvent
PE	Polyethylene
PT	Pretreatment
SE	Steam Explosion
ZN	Ziegler-Natta

1. Introduction:

The escalating energy crisis is a worldwide issue that significantly relies on petroleum, the primary energy source, meeting 36% of the United States energy needs, with a substantial 70% of this directed toward transportation [1]. Nevertheless, the annual rise in global petroleum consumption consistently intensifies, placing heightened strain on limited oil reservoirs. According to estimates, the world's recoverable oil reserves are dwindling at a substantial annual rate of 4 billion metric tons [2]. Even if we presume that this depletion continues at its current pace, projections indicate a complete exhaustion of these reserves by the year 2060 [2]. Consequently, it becomes imperative to seek alternative energy resources that are rooted in both renewability and environmental sustainability. The utilization of fossil fuels carries inherent ecological ramifications of significant concern. The combustion of these fuels results in the emission of approximately 21.3 billion metric tons of carbon dioxide (CO_2) and an array of other greenhouse gases (GHGs) annually [2]. The energy sector, primarily reliant on fossil fuels, contributes to approximately 73% of all greenhouse gas (GHG) emissions [3]. It is worth noting that natural processes can only treat half of this volume. As a result, there is an annual net increase of 10.65 billion metric tons of CO_2 in our atmosphere [2]. This underscores the pressing imperative to explore energy alternatives that are both renewable and ecologically benign [2].

In this context, there is a pressing demand for a viable, sustainable, and environmentally responsible means of producing fuels and chemicals. Attention now pivots toward the exploitation of biomass as a potential raw material for crafting substitutes for petroleum-based fuels and foundational components for biochemicals. Biomass is abundant, yet its utilization remains relatively limited. The notion of a biorefinery, a facility dedicated to converting biomass into biofuels and biochemicals, is still contending with the challenge of competing effectively against traditional petroleum refineries [4,5]. This thesis utilizes a Mixed-Integer Linear Programming (MILP) framework to optimize biomass (corn stover) conversion routes for polyethylene production emphasizing the attainment of economic efficiency, resource utilization and providing insights into energy consumption.

2. Literature Review:

The concept of "energy transition" refers to the shift away from reliance on fossil fuel-based energy sources such as coal, oil, and natural gas towards the adoption and utilization of renewable energy systems such as solar power, wind energy, biofuels, hydrogen, and other sustainable alternatives [6,7]. A significant and comprehensive overhaul of the world's energy system must occur within a tight 30-year window from today. This compressed timeline demands a strategic reorientation that goes beyond simply decarbonizing energy supply and consumption [8]. The manufacturing of various chemicals and synthetic polymers extensively depends on fossil fuels. Depletion of these resources, coupled with their alarming environmental impacts like global warming and waste accumulation, poses a significant threat to the polymer industry's future.

In the Planned Energy Scenario by IRENA (The International Renewable Energy Agency) [8], global demand for plastics is set to surge from 406 Mt in 2020 to 986 Mt by 2050, needing an additional 600 Mt of plastic supply annually. The sector's energy demand would reach 41 EJ (exajoule) yearly, mostly met by gas and oil. However, the 1.5°C Scenario by IPCC (Intergovernmental Panel on Climate Change) [9] aiming to limit global warming to 1.5°C also aims for reduced energy consumption in the chemical and petrochemical sector, projecting 26 EJ by 2030 and 36 EJ by 2050. This scenario targets a 12% decrease in energy use due to 3% annual efficiency improvements. Meeting these goals involves tailored actions within an energy transition that addresses the challenges faced by the chemical sector [10]. As part of this endeavor, numerous methods of production are being researched and proposed across various domains, aiming to alter either the techniques employed, or the raw materials utilized. This report primarily focuses on bioplastic production pathways that have potential to replace the traditional method or production routes.

During the early 1800s, Henry Ford proposed that adopting a bio-based economy is a sensible and essential choice for the advancement of any society [10,11,12]. Biopolymers can be categorized into three groups: those directly extracted from biomasses (e.g., modified starch, cellulose-derived polymers) [14], polymers generated by microorganisms (e.g., polyhydroxyalkanoates or PHAs) [14], and polymers produced using renewable materials via bio-intermediaries (e.g., polylactic acid or PLA, bio-polyethylene or BPE) [14].For the energy transition to succeed, biomass emerges as a prominently discussed and promising resource, having the potential to drive a robust economy during this shift. Biomass comprising of diverse forms such as wood and agricultural residues, holds promise as a crucial feedstock. Notably, lignocellulosic biomass stands out for its substantial potential in this context.

Plastic materials possess a wide array of advantageous characteristics including their lightweight nature, durability, ability to withstand corrosion, varied colors, transparency, and ease of handling during production [15]. These qualities make them highly advantageous compared to alternative materials in various applications. Furthermore, their versatility, affordability, and abundance have spurred their utilization in products that demand multifaceted performance attributes on a regular basis [15]. The majority of plastics fall under the category of thermoplastics, comprising linear polymer chains that enable reshaping through heat, commonly found in items like bottles and textiles. In contrast, certain polymers undergo crosslinking in their processing to create thermosets, which are more resilient than thermoplastics and maintain their shape regardless of temperature variations. These thermosets are utilized in products like car tires and epoxies [16] . Bioplastic earns its designation by differentiating itself from conventional plastic through the use of biological sources instead of fossil-based raw materials, marking a fundamental shift in its origin. Monomers, sourced from biomass compounds like plant sugars, undergo extraction or synthesis before being polymerized. This process aims to create direct substitutes for current plastics like polyethylene (PE) or polypropylene (PP). Biomass extraction

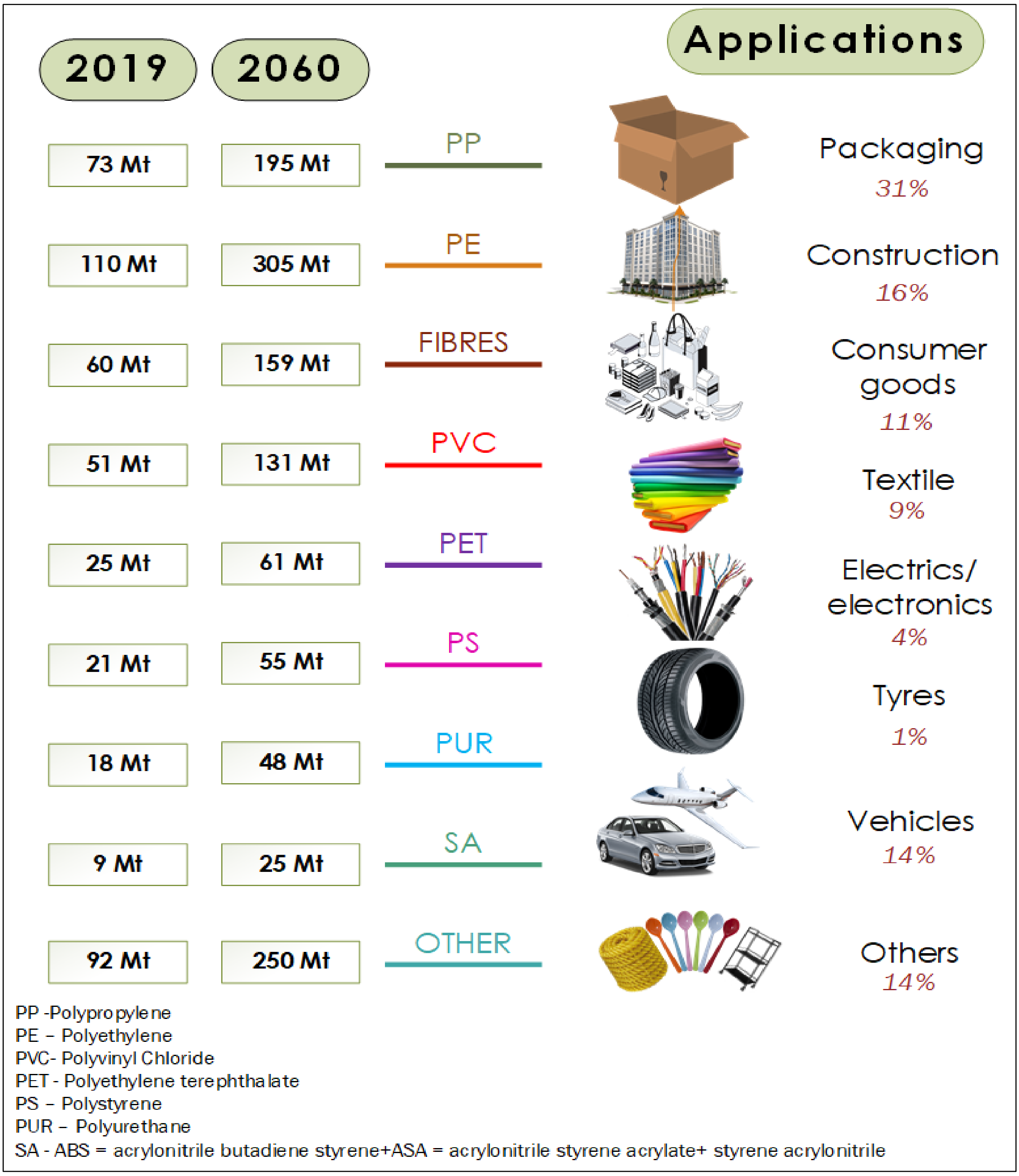

Figure 1 Different types of plastic consumption by 2060 [19]

can additionally produce natural polymers that are non-synthetic, including natural rubber and proteins. Biodegradability is a distinctive property shared by both fossil-derived and bio-derived polymers. While some fossil-derived polymers exhibit biodegradability, others do not. Similarly, certain bio-derived polymers from renewable sources are biodegradable, whereas others lack this property. Biodegradability refers to the ability of a substance to break down into simpler compounds through the action of microorganisms in the environment. It is specific to certain types of plastics capable of undergoing depolymerization by microorganisms. While some fossil-based plastics can be engineered to be biodegradable, this property isn't inherent to all of them. For instance, polyethylene (PE), a common fossil-based plastic, is not inherently biodegradable. Bioplastics, despite being derived from renewable sources like plant-based materials, do not universally possess biodegradability. Not all bioplastics naturally break down through microbial action; some require specific conditions or industrial processes to biodegrade. Therefore, the ability to biodegrade is a specific trait that varies among different types of plastics, irrespective of whether they are bioplastic or fossil-based [17,18]. biodegradable bioplastics can take anywhere from a few months to several years to fully degrade under suitable conditions, such as in a composting facility with the right balance of moisture, temperature, and microbial activity. However, the exact timeline can vary widely depending on the specific type of bioplastic and the environmental conditions it is exposed to.

The utilization of plastics is expected to rise across all polymer types as depicted in Figure 1, driven by the increasing demand for various applications requiring these materials. The connections between polymers and their diverse applications are intricate, as a single polymer can serve multiple purposes across different applications. By 2060, a significant surge in polymer usage for packaging is predicted despite efforts to reduce waste, which is entirely another concern, distinct from the focus of this thesis on producing polyethylene from biomass. Notably, low-density polyethylene (LDPE, including linear low-density polyethylene or LLDPE) usage in packaging is expected to triple by 2060 compared to 2019 [16]. Additionally, polypropylene (PP), high-density polyethylene (HDPE), and polyethylene terephthalate (PET), all employed in packaging, are projected to more than double by 2060 [16]. Polyvinyl chloride (PVC), primarily used in construction, is estimated to increase by 2.6 times [16]. Similarly, the use of fibers utilized in textiles is forecasted to triple. Furthermore, there is a substantial

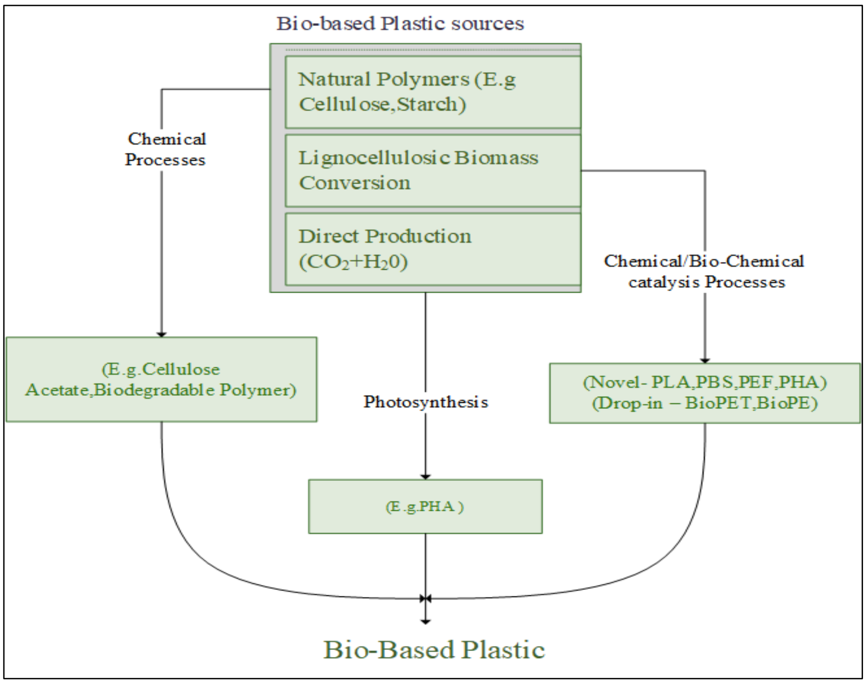

Figure 2 Sources of bio-based plastics [17]

projected increase in the use of polymers, particularly polypropylene (PP), for vehicle production [19]. Bio-based plastics can be derived through three primary methods as illustrated in Figure 2. The initial approach involves modifying natural polymers while largely retaining their original structure. This method is currently significant in creating starch and cellulose-based plastics, as well as various other bio-based polymers and fibers utilized in non-plastic and non-food applications.

The second method follows a two-step conversion process starting with the production of bio-based precursors (monomers) through biochemical or chemical transformation. These monomers are then

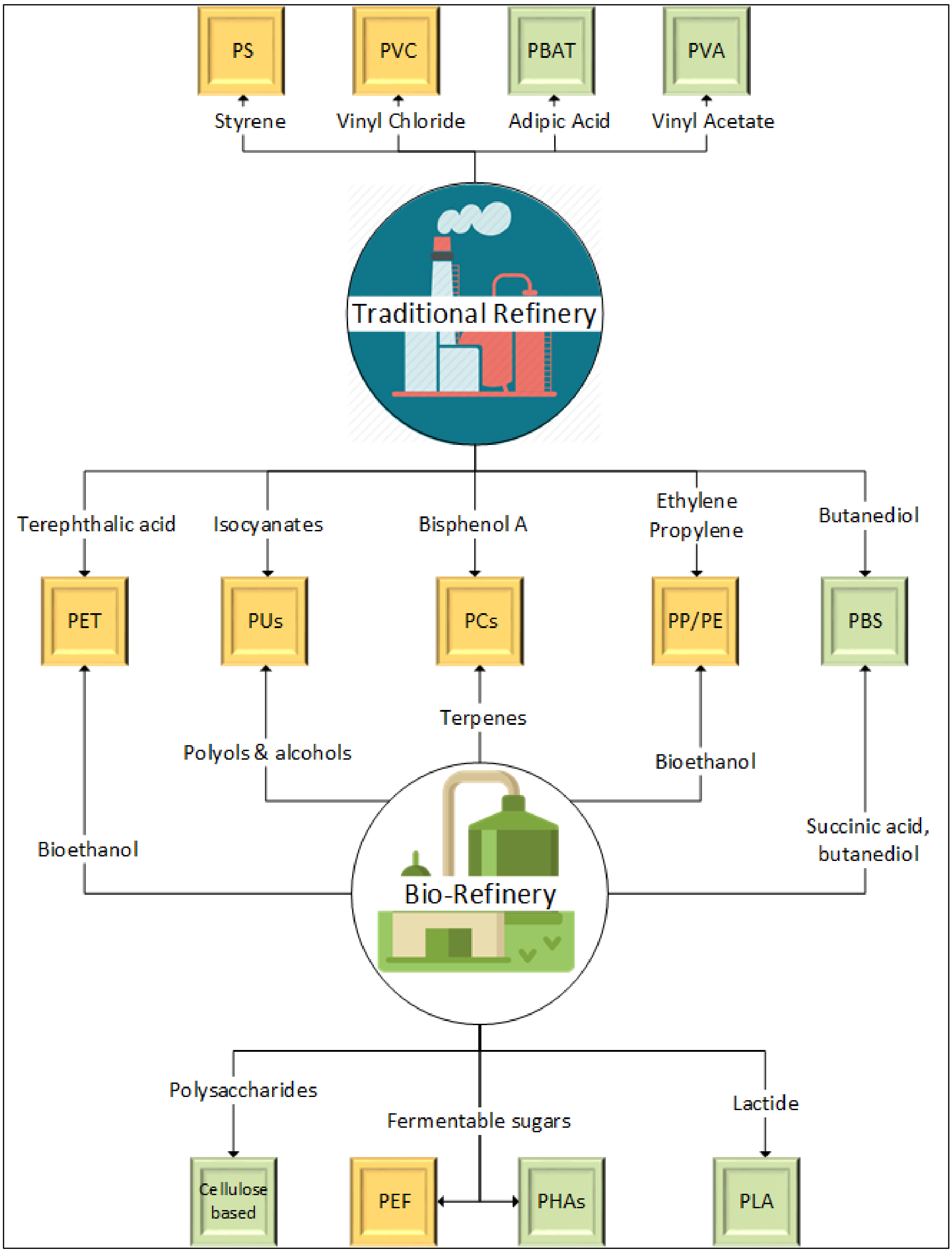

Figure 3 Fossil based vs bio-based routes for polymer synthesis [16]

polymerized in subsequent steps. When these obtained monomers mimic conventional ones, they are referred to as "drop-in" replacements. Plastics made using these drop-in monomers closely resemble their petrochemical counterparts in structure and performance, enabling their seamless integration into existing processing and recycling systems. For instance, bio-based polyethylene derived from bio-ethanol sourced ethylene exemplifies this. Alternatively, novel bio-based monomers with new structures or previously unused in markets are employed for plastic production. These "novel" bio-based plastics often exhibit distinct properties, potentially offering enhanced functionality compared to the plastics they might replace. However, unlike drop-in plastics, novel bio-based plastics necessitate the development of new recycling systems due to their unique properties. The second method is gaining significance owing to advancements in chemical and bio-technological production of monomers.

The third route involves creating a polymeric material directly in microorganisms or plants that can be utilized as plastic without additional modification. This method, although promising, relies on genetic engineering and biotechnology to transfer genes responsible for producing polymers like poly(hydroxyalkanoate) (PHA) from bacteria to crops. However, while direct production via photosynthesis seems advantageous, it presents complex environmental and regulatory challenges [17]. Figure 3 contrasts plastics manufactured by the traditional fossil-based industry with those potentially produced by the bio-based industry. Notably, certain plastics produced from biomass have the potential to replace their fossil-based counterparts. Moreover, plastics highlighted in green boxes indicate biodegradability, underscoring the environmental benefits of biomass-based alternatives. This comparison highlights the shift towards sustainable and eco-friendly plastic production methods. The conventional sources for the majority of commercial monomers and polymers, including those utilized in both durable and single-use applications (such as polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC), and polyethylene terephthalate (PET)), as well as certain fossil-based biodegradable polymers (like polybutylene adipate-co-terephthalate (PBAT) and polyvinyl alcohol (PVA)), are petrochemical feedstocks [16]. By utilizing renewable raw materials, first-generation and second-generation biomass (edible plant products and non-edible biowastes, respectively) into the same fundamental components as those derived from petroleum, as well as additional alternatives [20]. These monomers have the potential to undergo polymerization, resulting in various robust polymers (like bioPE and bioPET) and novel enduring polymers (such as polyethylene furanoate (PEF)). Additionally, they can form biodegradable polymers (such as polylactic acid (PLA) and bio-polybutylene succinate (bioPBS)) [16,21]. Moreover, Polyhydroxyalkanoates (PHAs) are produced in microorganisms via biochemical conversion from diverse feedstocks [16,22]. Plant-oil-based polyols can be utilized to produce bio-based non-isocyanate polyurethanes (PUs). Lignin, when separated, is commonly burned for energy retrieval; however, its phenolic structure can also be transformed into valuable chemicals. Polysaccharides obtained from plant biomass can be chemically processed to create plasticized starch and cellulose-based products. Some abbreviations used include BPA for bisphenol A, EG for ethylene glycol, FDCA for 2,5-furandicarboxylic acid, HMF for 5-hydroxymethylfurfural, PS for polystyrene, and TA for terephthalic acid [16]. The production of biopolymers and a wide array of plastics can be achieved using lignocellulosic biomass as a versatile and sustainable source.

2.1 Lignocellulosic Biomass as an alternative Feedstock:

Lignocellulosic Biomass and its derivatives are seen as highly promising alternatives [23,24]. These materials, formed through biological photosynthesis using CO_2, water, and sunlight, are considered the sustainable organic carbon source. Lignocellulosic biomass, the most abundant globally, holds immense potential for eco-friendly fuel and chemical production [25,26]. It's renewable, widely available, and touted as a carbon-neutral source, reducing net CO_2 emissions [27,28]. This biomass offers a viable substitute for crude oil, enabling the production of biofuels, biomolecules, and materials. Cellulose, a major component, is considered an excellent replacement for petroleum-based polymers due to its eco-friendly traits like renewability and biodegradability [29].

The viability of producing fuels and chemicals from biomass has triggered extensive discussions. For instance, there are substantial apprehensions about the sustainability of existing bioethanol production, which heavily depends on starch and sugar crops. The scarcity of these crops results in competition with food production. Lignocellulosic feedstocks possess pivotal benefits compared to other biomass sources because they consist of the inedible parts of plants, thus avoiding any impact on food supplies [30,31].Additionally, significant amounts of forestry, agricultural, and agro-industrial lignocellulosic wastes accumulate annually. These materials have the potential to be repurposed for manufacturing various high-value products [32].From an economic perspective, lignocellulosic biomass can be generated rapidly and at a reduced expense compared to other crucial biofuel sources in agriculture, like corn starch, soybeans, and sugar cane [33]. Conversely, the advancement of transforming lignocellulosic biomass into high-quality chemicals and polymers continues to pose a significant challenge [25]. Lignocellulose has naturally developed to withstand degradation. This intrinsic characteristic of lignocellulosic materials renders them resilient against both enzymatic and chemical breakdown processes [34]. To alter the characteristics of the lignocellulosic structure, pre-treating the biomass is necessary, but is a costly and energy-intensive process [35].Despite the abundance and typically low cost of lignocellulosic materials, the primary obstacle in converting them lies in achieving high yields of value-added chemicals at economical costs and with high selectivity [36].

2.2 Lignocellulosic Biomass Conversion Routes:

By exploring various pathways from biomass to bioplastics, this research endeavors to offer a comprehensive understanding of the most effective and sustainable methods for producing bioplastics on a significant scale. Figure 4 illustrates the primary available lignocellulosic biomass conversion routes, each yielding various products through distinct conversion processes. Notably, these routes also offer the additional benefit of generating significant heat or electricity, showcasing their considerable potential.

2.2.1 Thermochemical Routes:

Gasification and pyrolysis stand as two extensively studied methods in the realm of thermochemical biomass conversion. Gasification produces a combustible gas suitable for combustion or processing into further chemical products, whereas pyrolysis produces gaseous and liquid fuel mixtures that can serve as substitute for fossil fuels various heating or electricity generation applications.

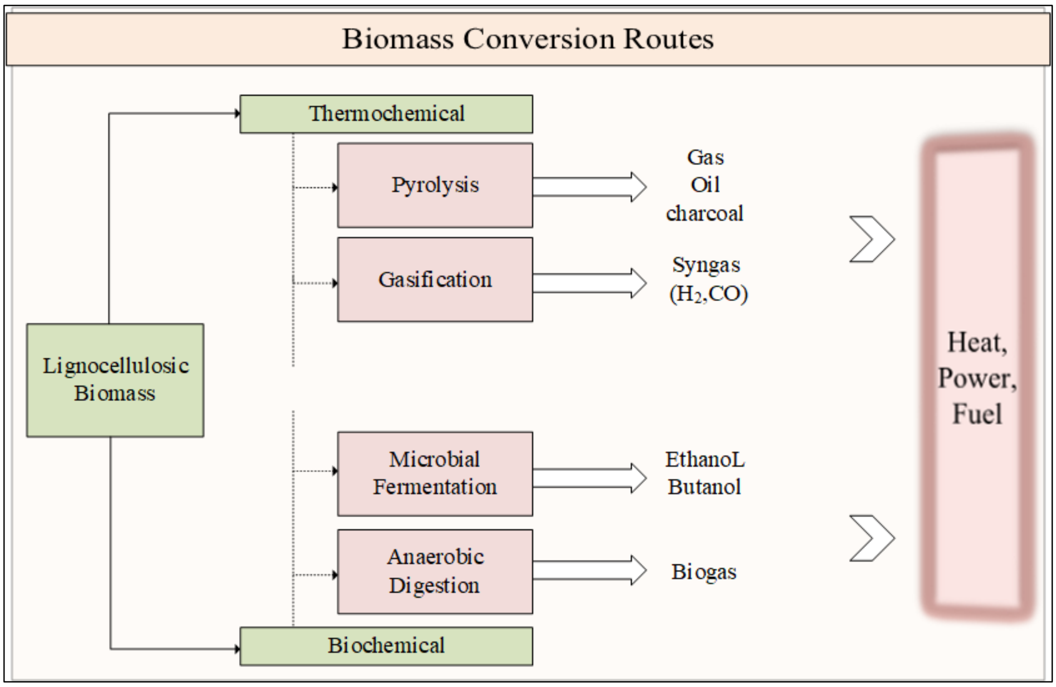

Figure 4 Primary routes for biomass conversion [38]

Gasification of carbon-based feedstocks into syngas occurs within a specialized reactor called a gasifier, typically operating at high temperatures ranging from 800 to 1500°C. Within this environment, the feedstock undergoes partial oxidation due to the presence of a stoichiometric level of oxygen. Oxygen necessary for the process is introduced via a gasifying agent or carrier, which could be air, pure oxygen, water vapor, or a combination thereof. While carbon dioxide can serve as a gasifying agent, its usage is less common. Additionally, the use of supercritical water stands out as an innovative technology that achieves high yields of hydrogen (H_2) without the need for pre-treatment, consequently reducing the production of tar and char. Gasification, compared to combustion, is the prevalent thermochemical route. Unlike biological or chemical hydrolysis in biochemical processes, gasification has the capability to convert the entire carbon content present in the biomass feedstock into gaseous compounds. This characteristic sets it apart, enabling a more comprehensive conversion of the carbon content than other methods like biochemical processes relying on hydrolysis [37]. At the conclusion of the complete process, two primary mixtures are obtained: a solid mixture and a gaseous mixture. The solid mixture comprises the organic fraction that hasn't undergone reaction along with inert components like tar and ash. The gaseous mixture consists primarily of syngas along with minor impurities such as light hydrocarbons (like ethane, ethylene, acetylene), hydrogen sulphide (H_2S), sulphur dioxide (SO_2), hydrogen chloride (HCl), nitrogen oxides (NO_X), nitrogen (N_2), and ammonia (NH_3) [38].

Pyrolysis, characterized by the thermal breakdown of a substance into smaller fragments due to heat in an oxygen-deprived environment, involves the thermal decomposition of a feed substance without the presence of oxygen [39].Pyrolysis refers to the thermal breakdown of organic matter in the absence of oxygen, typically occurring at temperatures between 400 to 500°C. This process is endothermic, meaning it absorbs rather than releases heat. When biomass is rapidly heated in an oxygen-deprived environment, it generates organic vapors containing fragments derived from cellulose, hemicellulose, and lignin polymers present in the biomass. These vapors can be condensed to form a flowing organic liquid known as bio-oil. The production of liquid bio-oil via pyrolysis holds promise for significantly contributing to the supply of liquid biofuels and serving as a source of various valuable chemicals. The gases that cannot be condensed exit the system and can be utilized to provide heat for sustaining the pyrolysis process. The remaining residue, rich in carbon, is referred to as bio-char [39,40].

2.2.2 Biochemical Routes:

Anaerobic digestion of biomass is a biological process where microorganisms break down organic materials in the absence of oxygen, producing biogas (mainly methane and carbon dioxide) and a nutrient-rich residue called digestate. This process occurs in a sealed vessel called a digester. Initially, biomass such as agricultural residues, food waste, or manure is loaded into the digester. Bacteria break down biomass through a series of steps, generating biogas that can be used for electricity production, heating, or further chemical processing. However, challenges like the need for optimal reactor operation, management of inhibitory compounds, fluctuations in feedstock composition, and maximizing methane yield while minimizing process inefficiencies remain significant issues in anaerobic digestion [41,42].

This research primarily utilizes the pathway of microbial fermentation, which involves various stages including biomass pretreatment and fractionation, enzymatic hydrolysis, saccharification, microbial fermentation, and the subsequent product separation and purification. These steps will be further discussed and explored in detail throughout the thesis.

2.3 Structure and Compositions of Lignocellulosic Biomass

Lignocellulosic materials primarily comprise three polymers: cellulose, hemicellulose, and lignin. These polymers form a heterogeneous matrix, interlinked to varying degrees and relative compositions. The specific association and proportions of these polymers within the matrix vary based on the type, species, and even the origin of the biomass [43]. Lignocellulosic biomass typically contains trace amounts of extractives, ash, proteins, and acids, the presence of which varies depending on the type of biomass. However, these constituents are generally present in relatively small quantities. Lignocellulosic biomass, the largest renewable organic material on Earth, includes agricultural residues (sugarcane bagasse, corn stover), energy crops (Miscanthus, switchgrass), and woody materials (forest residues, wood wastes from industries). A diverse range of sources forms the basis for biomass pretreatment, biorefineries, and the creation of potential products [44,45].

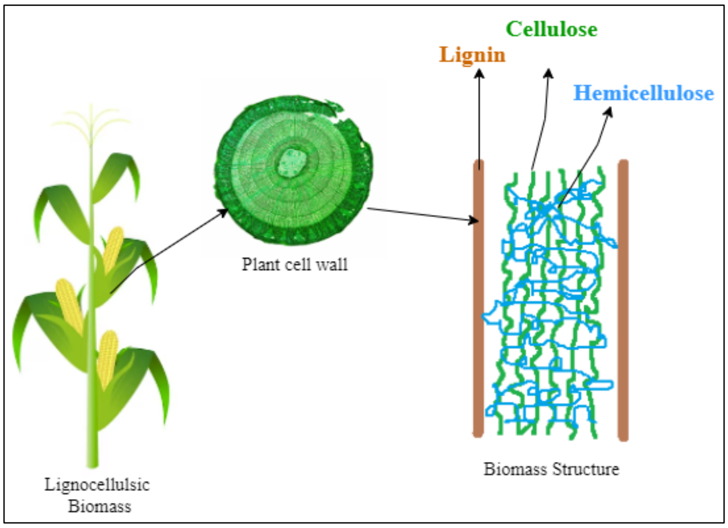

Figure 5 Biomass structure of cell wall [46]

One of the prominent and largest fractions of biomass structure is cellulose. Cellulose forms the structural backbone and is a linear polymer made up of glucose units tightly packed together, providing strength and rigidity to the cell walls. Hemicellulose, a heteropolymer composed of various sugar molecules, fills the spaces between cellulose fibrils, contributing to the flexibility and porosity of the biomass. Lignin, a complex and irregular polymer, acts as a binding agent (Figure 5), providing structural support and protection to the plant cells. These three components comprise 80-90% of biomass and the rest comprise moisture. The proportions and arrangements of these components vary among different types of biomasses, influencing the overall characteristics and suitability for various industrial processes including biofuel production, biorefining, and biopolymer synthesis. Understanding and manipulating these compositions are crucial in optimizing the extraction and conversion processes for desirable end-products from lignocellulosic feedstock [46].

Various types of lignocellulosic biomass exhibit differences in their structure and composition of lignin, cellulose, hemicellulose, and ash. Which can vary depending on their categories e.g. agricultural, forestry or woody biomass [47]. Table 2.1 below details the compositions of the most common lignocellulosic biomass found in agricultural categories.

Table 2. 1 Compositions of different LCB

Lignocellulosic Biomass	Lignin (%)	Hemicellulose (%)	Cellulose (%)	Ash (%)	References
Wheat straw	17-19	26-32	33-38	3.74	[48,49] [50]
Rice straw	12-14	23-28	28-36	19.8	[49] [51] [120]
Barley straw	14-19	27-38	31-45	-	[49] [120]
Rice husk	26-31	18-21	25-35	17	[48] [120]
Sugarcane bagasse	20-42	19-25	42-48	-	[49] [52] [120]
Sweet sorghum	14-21	18-27	34-45	-	[49] [120]
bagasse		24-26	38-40	6.8	[50] [49] [120]
Corn stover	7-19	30-50	5-20	5-6	[53,54]
Switch grass	10-40				

2.4 Ethanol Production from Lignocellulosic Biomass:

Ethanol (C_2H_5OH), derived from plant sugars or biomass, serves as a renewable, cleaner-burning fuel that reduces net greenhouse gas emissions. Its higher-octane rating improves engine efficiency, while its bendability with gasoline offers versatility in fuel mixtures, aiding energy security and reducing environmental impact. Ethanol can also be processed into a variety of higher-value chemicals. Historically, synthetic ethanol has been conventionally manufactured through the catalytic hydration of petroleum-derived substances like ethylene (C_2H_4). The ongoing exhaustion of non-renewable fuel and chemical resources has spurred exploration into alternative sources to replace fossil fuels and chemicals. Currently, among the significant biofuels in today's economy, bioethanol stands out as a crucial player, accounting for 65% of total biofuels production.

Large-scale industrial production of first-generation ethanol from sugarcane, corn, or beet sugar is widely established. In contrast, second-generation ethanol (2GE) is presently in the developmental phase, exploring various region-specific alternatives. Opinions on the economic feasibility and environmental impact of 2GE, particularly concerning its CO_2 footprint, vary significantly [55]. Hence, this thesis serves as a pivotal contribution towards the identification and comprehensive analysis of a biorefinery approach tailored specifically for the production polyethylene via production of ethanol, providing a platform to optimize alternative biomass conversion routes for plastic production.

The development of ethanol from lignocellulosic materials, such as agricultural industry's solid waste, remains a topic of ongoing research and is a subject of debate, particularly regarding technical and economic aspects. Nevertheless, utilizing solid residues has demonstrated itself as a viable alternative, alleviating competition for land and water resources between energy and food crop cultivation [56]. Ethanol produced from lignocellulosic biomass is seen as a highly promising liquid chemical, especially with the need to shift away from petroleum derived products. However, there's a growing focus on lignocellulosic biomass for bioethanol due to its abundant availability and low cost, suggesting its potential to become a significant feedstock in the medium to long-term [57]. Lignocellulosic biomass, plentiful in nature, does not compete with food sources [57]. The European Union's biofuels research advisory council suggested a plan to raise the utilization of biofuels in transportation to 25% by the year 2030 [58].Various commodity chemicals can be derived from the catalytic enhancement of bioethanol, lessening reliance on fossil resources and subsequently reducing the linked environmental repercussions [59].

2.5 Lignocellulosic Biorefinery – a holistic approach:

An oil refinery serves as a key industrial facility focused on refining oil into various products such as transport fuels (gasoline, jet fuel), high-value chemicals, and raw materials for petrochemicals. Emerged in the 1940s, refineries epitomize the dynamism of the chemical industry. Presently, 85% of the refined oil mass in these refineries comprises fuels, while the remaining 15% encompasses diverse chemical products. Biomass emerges as a promising alternative raw material, possessing the potential to be transformed into valuable products like fuels and chemicals through various conversion methods within a biorefinery. Biorefineries are essential for a bioeconomy's advancement, resembling petrochemical refineries but processing biomass sustainably into various marketable bio-based products and bioenergy. Multiple classifications based on technology, raw materials, and processes categorize these biorefineries [60]. Four common types of biorefinery systems frequently discussed in research and development include those focused on lignocellulosic feedstock, whole crops, green biomass, and the two-platform concept with syngas [61,62]. Among the potential large-scale industrial biorefineries, the lignocellulose feedstock (LCF) biorefinery seems to be in a prime position for considerable success. This is attributed to the abundance of available raw materials (such as straw, reed, grass, wood, paper-waste, etc.) and the favorable market prospects for its converted products in both traditional petrochemical and future biobased product markets [61]. The biorefinery concept offers several advantages over standalone processing methods. It enables the creation of diverse products, reducing production costs by optimizing sale prices through the generation of high-value coproducts alongside the primary product. This integrated approach allows for the cost-effective production of smaller market products and maximizes the utilization of raw materials, leading to increased feedstock value. Additionally, the interconnected processes in biorefineries facilitate mass and energy integration, optimizing resource utilization and meeting heat and power requirements. Combining common streams between processes, such as acid and enzymatic hydrolysis, allows for the production of fermentable sugars efficiently. Overall, biorefineries capability to yield various value-added products addresses market challenges like price fluctuations, mitigating the emergence of unprofitable products in some cases [63]. However, effective strategies are imperative to design biorefineries, considering numerous facets such as energy requirements, economic viability, environmental impacts, and resource utilization. Transitioning from a fossil-based economy to a bio-based economy necessitates a transitional phase guided by multifaceted considerations. These considerations encompass economic, political, environmental, demographic, agricultural, and food-related aspects.

The utilization of biomass for diverse product generation necessitates the establishment of a systematic methodology or model to discern the most optimal routes and products within a biorefinery. Extensive research in this domain has led to the identification of primary approaches, with prevailing emphasis on two methodologies: conceptual design and optimization. These methodologies, as mentioned by Moncada et al. [64], remain pivotal in the biorefinery domain. Conceptual design involves a comprehensive framework to structurally outline the biorefinery's elements and interconnections, facilitating informed decision-making in route and product selection. Conversely, optimization methods focus on refining and enhancing bioprocessing pathways through systematic analysis, aiming to maximize efficiency and output yield within the biorefinery context. These established methodologies serve as foundational pillars for strategic decision-making processes in biomass transformation.

2.5.1 Conceptual design of biorefinery:

The conceptual design approach for biorefineries incorporates various factors like feedstock diversity and regional development. It emphasizes a holistic view and involves technical, economic, and environmental analyses. Commercial software tools (e.g., Aspen Plus, ChemCad) aid in technical analysis through mass and energy balances, often integrated with economic evaluations using tools like Aspen Process Economic Analyzer. Environmental impact assessment employs algorithms like US-EPA's Waste Reduction (WAR) or LCA studies. This approach integrates mass and energy through software and methods like pinch analysis. Experimental data from literature inform simulations, enabling performance comparison to select the most favourable scenario. Stemming from chemical processes synthesis, this approach extends to complex biorefinery systems, employing three core concepts: hierarchy, sequencing, and integration. Hierarchy involves decomposing elements like feedstocks, products, and technologies, while sequencing establishes logical order and connections for transformation routes. Integration maximizes resource use, considering feedstock and processing route integration while emphasizing waste reduction through mass and energy integration. Various models and approaches have been documented in the literature for biorefinery design and evaluation, demonstrated by a range of studies. For instance, Moncada et al. [64] conducted a techno-economic analysis of a sugarcane biorefinery in Colombia, comparing diverse conversion pathways involving sugar, fuel ethanol, PHB, anthocyanins, and electricity production. They utilized Aspen Plus software for simulation procedures, showcasing the economic, environmental, and social viability of fuel ethanol and PHB production from combined cane bagasse and molasses. Other studies, exemplified by Sánchez & Cardona [65], explore biotechnological fuel ethanol production from diverse raw materials such as sucrose-containing feedstocks, starchy materials, and lignocellulosic biomass. These studies delineate technologies, analyze biomass processing complexities, discuss fermentation processes, present comparative indexes for fuel ethanol production, and conclude by highlighting current research and future trends in pretreatment and biological conversion methods for these feedstocks. Additionally, Gutiérrez et al [66] examines the integration of biodiesel and bioethanol production from palm oil biomass using simulation. It utilizes oil from fresh fruit bunches for biodiesel and proposes a method using in situ ethanol from empty fruit bunches and palm press fiber for transesterification. Analyzing various integration approaches, it illustrates that material flow integration reduces unit energy costs by 3.4%, while material and energy integration reduces costs by 39.8%. This integrated setup becomes feasible when biomass-based ethanol production costs align with those of grain or cane ethanol. Further contributions from studies by Santibanez-Aguilar et al. [67], El-Halwagi [68], Posada et al. [69], Kelloway and Daotidis [70], and Kokossis et al. [71] offer diverse perspectives on biorefinery analysis and design in the literature.

2.5.2 Optimization:

The methodological approach for biorefinery design via optimization involves tracking chemical species (products and raw materials), linking streams with processing technologies, and exploring various configurations simultaneously. This method explores numerous raw materials and products to achieve specific goals, swiftly scanning multiple alternatives for conceptual biorefinery designs and laying the groundwork for detailed techno-economic analysis. It encompasses diverse objectives such as maximizing yield, minimizing costs, waste, and environmental impact. The methodology unfolds in three pivotal steps: Initially, adopting a Process Systems Engineering (PSE) approach to comprehensively define the scope and complexity by exploring all potential transformation routes. Martin M [72] extensively examines the design of production processes for different biofuels sourced from various biomass origins. These employ mathematical programming to evaluate numerous technology options, aiming for economic viability and sustainability by optimizing resource utilization, particularly raw materials, energy, and water. Emphasizing integrated processes, the study underscores the potential for cost reduction and synergy benefits in future biorefineries. This aims to optimize value generation while accounting for environmental impact.

The second step is integrating modelling and experimental data, which involves leveraging simulation software like Aspen Plus, HYSYS, or Pro II to validate and optimize models for enhanced resource efficiency. This phase incorporates economic and environmental data gathering. In the final step, the biorefinery optimization phase merges model libraries and economic performance using numerical solvers like MILP (Mixed-Integer Linear Programming) and MINLP (Mixed-Integer Non-Linear

Programming). Its goal is to maximize economic gains while evaluating and refining environmental impact until achieving satisfactory outcomes. For example, a similar approach is undertaken in Rizwan et al. [73] which builds on prior research that optimized biodiesel production from microalgae. It expands this by including the processing of previously treated microalgae residue as part of a broader biorefinery framework. Using a mixed integer nonlinear programming (MINLP) model implemented in GAMS with an Excel-based database, the study aims to identify optimal biorefinery configurations with various objective functions. Economic sensitivity analysis is conducted to illustrate potential enhancements in overall economics and establish future viability targets for microalgal biofuels. Another example of this is Pham and El-Halwagi [68], in which the authors propose a new two-stage approach for designing biorefineries, addressing limitations in current biofuel research.

3. Introduction to MILP Modelling and Applied Methodology:

Biorefining involves utilizing biomass to generate chemicals and convert energy, offering a promising avenue for developing more sustainable industrial models. However, the sheer variety of biomass sources, diverse conversion technologies, and the array of potential end-products pose a significant challenge in designing efficient biorefineries due to their complexity. Exploring efficient production routes has become pivotal in contemporary industrial practices. One such exploration involves the transformation of lignocellulosic biomass into bioplastics-an essential endeavor in contemporary manufacturing. Leveraging mathematical programming stands as the most effective approach for efficiently addressing this task.

This thesis focuses on analyzing diverse lignocellulosic biomass types and evaluating various conversion technologies to derive targeted bioplastic products. The key methodology employed to navigate this intricate process is the utilization of Mixed-Integer Linear Programming (MILP). MILP serves as a powerful computational tool that enables the systematic optimization of these complex pathways. Through MILP modeling, intricate mathematical formulations are constructed to meticulously assess the most efficient routes for obtaining desired bioplastic products, accounting for factors such as biomass variations, conversion techniques, and optimal materials and energy required. This thesis aims to explore and enhance the most effective methods for producing bioplastics, specifically polyethylene, through the examination and optimization of corn stover as a feedstock. The models are generic and applicable to all types of feedstocks. However, corn stover serves as the basis for the numerical results presented later on.

This MILP modeling approach has been implemented using a platform called OSMOSE, which can efficiently solve typical process integration problems. Additionally, it can analyze, improve, and design energy systems by coupling with other simulation tools, optimization solvers, and post-analysis methods. The MILP modelling methodology employed in this research draws its foundation from the extensive work of Kantor et al. [74]. Their research provides a comprehensive mathematical framework aimed at optimizing the integration of intricate industrial systems, ranging from individual unit operations to entire processes and plants. Furthermore, it addresses the exploration of potential industrial symbiosis between different plants [74].

3.1 Methodology, objective, and problem formulation:

This approach employs mixed-integer linear programming (MILP) to optimize process integration, favouring it over mixed-integer non-linear programming (MINLP) due to its ability to swiftly attain globally optimum solutions. MILP's advantage lies in its rapid resolution, crucial for handling diverse solutions efficiently. Although specific integration problems, like designing heat exchanger networks, benefit from mixed-integer non-linear programming (MINLP) approaches, in the MILP framework, such complex units or operations are addressed either by linking with external flowsheeting software or by employing surrogate models, concepts discussed briefly in the paper by Kantor et al. [74]. MILP proves more efficient for generating quicker solutions, especially in larger, complex scenarios. The formulation in Kantor et al. [74] is inspired by previous research, particularly Maréchal and Kalitventzeff [75], expanding to consider material flows in industrial symbiosis. Additional insights from other studies are also summarized in the literature by Kantor et al. [74].

In process integration MILP problems, the fundamental objectives revolve around minimizing various costs and environmental impacts. This typically includes reducing operating costs and capital expenditure associated with setting up or enhancing process units. Another critical aspect involves mitigating environmental issues, often quantified by minimizing emissions or other ecological footprints. Additionally, a comprehensive view involves calculating the total cost, which combines efforts to minimize both operational and investment expenses. These objectives serve as pivotal metrics. Nonetheless, objectives can vary based on the unique requirements and priorities of individual users or specific applications. This thesis particularly employs a Mixed-Integer Linear Programming (MILP) framework to optimize polyethylene production routes derived from biomass, with a primary focus on achieving cost-effectiveness, resource utilization efficiency, and energy minimization.

To achieve these objectives or optimize the problem, constraints are imposed on the modelling. These constraints are formulated based on the specific objectives, system characteristics, and limitations within a given problem domain. Constraints are used to define the boundaries, limitations, or relationships among decision variables and aim to represent the real-world conditions that the model must adhere to while optimizing. The current MILP framework incorporates critical constraints like sizing and scheduling, ensuring units operate within specified capacities over time. Mass and energy balance constraints maintain physical requisites for material flows, while heat cascade constraints enforce energy conservation principles, pivotal for optimizing complex systems in diverse industrial applications. Sizing concerns determining the capacity or size of each unit within defined limits. This process uses continuous variables to specify the capacity factor, ensuring that if a unit exists in a specific time period, its capacity remains within the given boundaries. Scheduling involves managing the usage or operation of units over time. It defines usage factors, representing unit activation within defined limits, and ensures that the usage factors are within certain bounds for each time period. Maintaining mass and energy balances across the system is crucial. This entails ensuring that supply and demand of materials or energy is within each unit and in-between layers that are in equilibrium. The balance is closed for specific types of layers within clusters of units, preventing exchange between clusters for certain flows. Constraints related to the heat cascade impose the first and second laws of thermodynamics within the system. They ensure that energy balance within clusters is maintained, and that heat is transferred only from higher to lower temperature intervals within a cluster. Additionally, the formulation suggests ways to integrate with external software tools for tasks such as simulation, thermodynamic calculations, and flowsheeting. This integration allows for handling non-linearities and complex processes that might not be easily manageable within the MILP framework alone. The definitions such as “layers, clusters, units” are further explained with clear examples for better understanding. The MILP framework is constructed upon a combination of modeling languages and solvers for efficient formulation and resolution of optimization problems. It utilizes AMPL or GLPK as the modeling language to express constraints and objectives. It also utilizes solvers such as GLPSOL or CPLEX to effectively integrate and solve formulated models and derive optimized solutions. This integration establishes a comprehensive toolset for MILP modeling and optimization [74].

3.2 Case Study Examples of How Models Work:

To illustrate how the model can be applied to industrial symbiosis studies, it has been explained with examples as shown in this Figure 6, the case study comprises 12 process units and 2 utility units, with each process representing an industrial process from a different sector. The processes are depicted as simple rectangle boxes (green color) with basic inputs of raw materials and energy, and outputs of products, co-products, and waste. Despite the simplified models used for the illustrative case, the approach remains the same as for real applications but may vary in level of detail and complexity.

Each process unit is in its own cluster (yellow-colored boxes), which also connects to a utility unit common to all industrial processes. Raw materials for the processes, electricity, fuel for boilers, and water used as inputs by the process units are each supplied by a resource unit (blue colored boxes), all of which are regrouped in the ‘resources’ cluster. The outputs generated as waste or products are sent to units belonging to the ‘Products and Waste’ cluster. Total input and output streams connected with any process unit are also termed 'resource balance layers', indicating that streams of this type can be exchanged between clusters. For illustrating the discovery and optimization of industrial symbiosis, some products, co-products, or waste from process units can be used by others, either directly or indirectly (e.g., Pretreated Biomass from the AFEX process can be used by Hydrolysis (without Inhibitors)). Moreover, excess heat (hot stream) of one cluster can be sent to another cluster via the steam supply unit. Where it converts the cold stream into hot stream (steam) and itself turns into the cold stream, which again sent it to another cluster (to be used by hot stream to cool down) and converted into hot stream (Steam demand unit). The steam network is a closed loop, implying that all condensate is recovered and recycled. For further detailed explanation on the modelling framework refer to Kantor et al. [74].

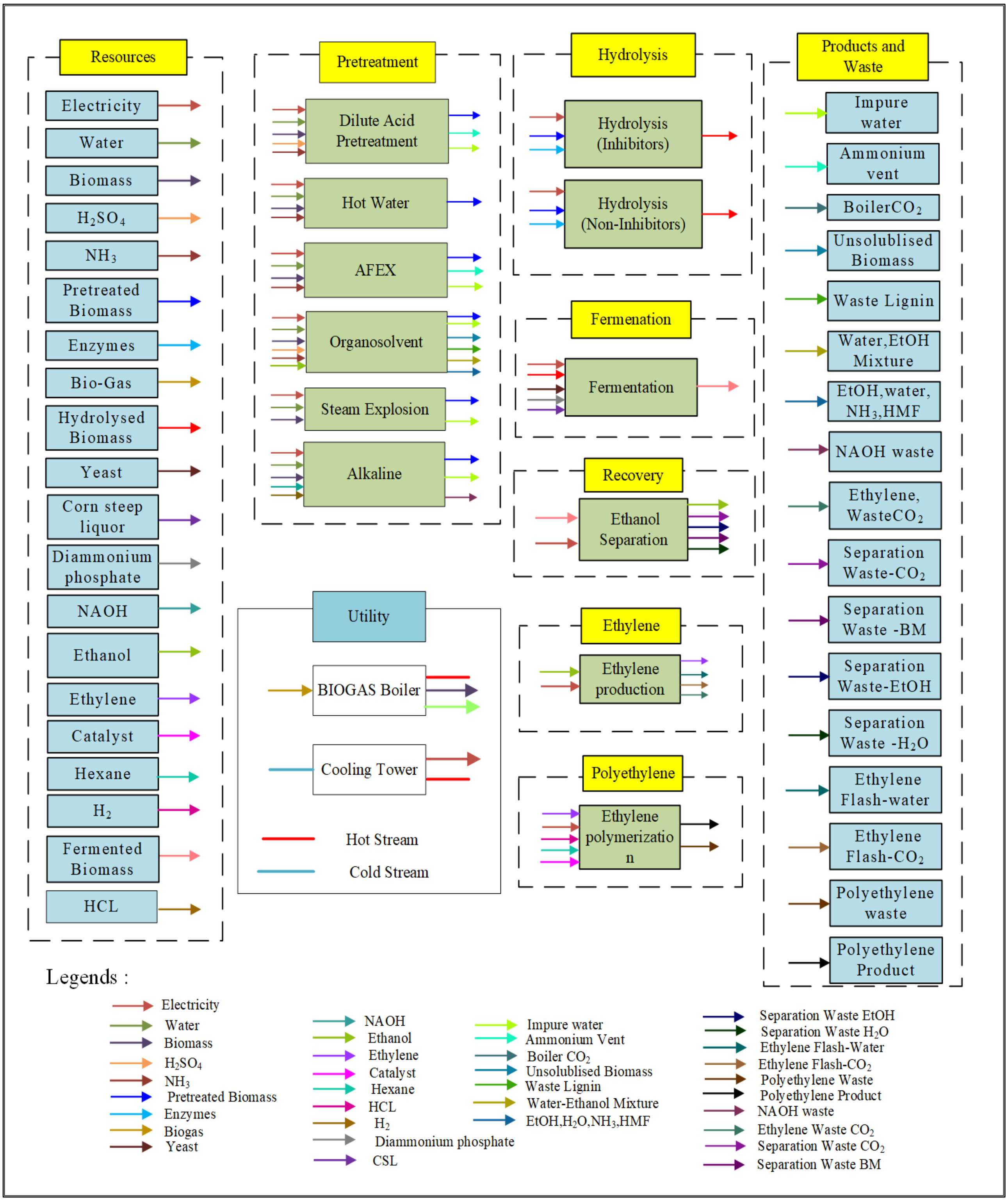

Figure 6 MILP framework

3.3 Problem Statement:

The pursuit of sustainable biomass-to-bioplastic/biochemical conversion methods necessitate a shift from conventional petroleum-based products towards environmentally friendly alternatives. Current research efforts have extensively explored various technologies for biomass conversion, yet there remains a significant challenge in systematically identifying the most viable routes from a holistic systems perspective while efficiently utilizing limited resources. The existing landscape of research predominantly revolves around individual technology assessments and comparative studies, often lacking an integrated systems view. While these studies contribute valuable insights into specific conversion pathways, they fall short in providing a comprehensive understanding of the interplay between diverse technologies, resource allocation, and societal needs.

To support this transition to sustainable practices, there is a need to provide a framework encompassing multiple biomass conversion routes to offer a decision support system that can compare and analyze various available options considering several aspects, particularly focusing on giving insight into the economic aspects, resource utilization across different pathways, and energy demand of technologies.The envisioned decision support system aims to equip stakeholders and decision-makers with a robust tool to navigate the complexities of technology prioritization. By offering insights into the most promising biomass conversion technologies that align with societal demands and optimal resource utilization, this research endeavours to facilitate informed decisions regarding technology selection to meet the evolving needs of society.

4. Process Implementation and Methodology:

The objective of the thesis is to compare and identify potential production path for biomass to bioplastic conversion. The primary approach is to design building blocks of an entire process pathway and then to connect them using MILP modelling software to generate results. Background data are required to quantify some chemical engineering aspects such as a calculation of mass and energy balances of the process, Chemical and energy utilization, costs, etc. Those calculations are initially carried out in separate excel sheet in detail; hence, throughout this thesis, discussions on the mass and energy balances of various processes, including their reaction energies, alongside other pertinent information primarily imported from these calculations. The calculations, such as mass and energy balances, are initially conducted based on their respective original references, which may vary in scale. However, during the final optimization steps, standardized scaling, specifically a flow rate of 10,000 kg/hr, is uniformly applied to ensure consistent results. During database implementation in MILP models, reactions and their conversion factors adhere to original references, determining the initial flow rate. However, it's important to note that the models allow for flexibility; if necessary, the reactions and conversion factors can be adjusted within the models, potentially altering the results accordingly. As the very first product obtained is bioethanol, the approach can be classified considering two sub-goal aspects: biomass to bioethanol and then bioethanol to polyethylene. From ethanol, ethylene can be produced via catalytic dehydration process, which is the most common, conventional, and widely used method. Further ethylene can be converted into polyethylene by polymerization. So, the later processes are approached as the original conventional processes. Therefore, modeling the initial processes from converting biomass to bioethanol is the most targeted effort in this research work. As research and development for bioethanol production from biomass has been underway for some time, there is sufficient data available on several process pathways and available pretreatment options.

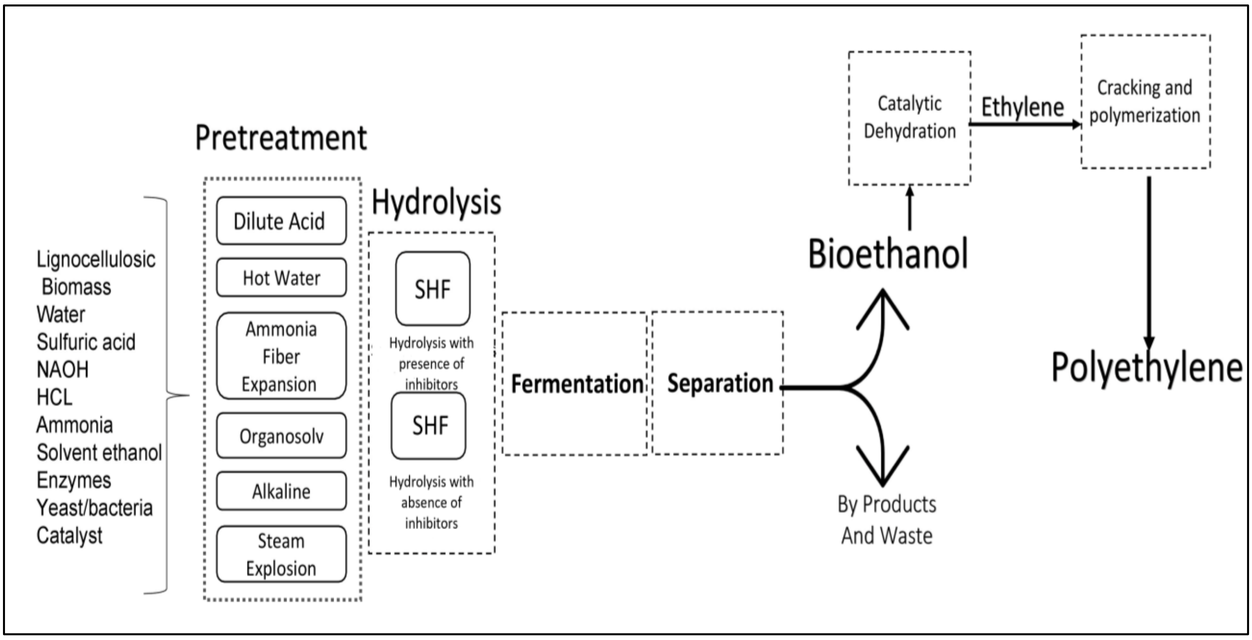

Figure 7 Process modelling blocks of LCB to PE

These have not yet been fully developed on an industrial scale basis, and thus most available data reports result from small-scale experiments. Initial data gathering steps are crucial and challenging. However, NREL (National Renewable Energy Laboratories) have done detailed research for bioethanol production on large scale for selected processes. So, it is helpful to take them as a reference to develop other processes as well. Throughout this research NREL [76] has been taken as a base reference to build the calculations and in selection of certain parameters. Figure 7 is a graphical representation of how the approach has been considered to conduct this research. The blocks represent each process in the production path. In e.g., pretreatment, there are several options to select from.

The first step to execute a typical modelling approach is to gather background data and evaluate primary parameters which are required by the model to put as an input. Hence, prior to evaluating those factors, extracting some reference data or previous experimental results must be completed for these pretreatments. For this research, several reference papers have been selected to evaluate pretreatment processes. After the pretreatment, the following unit operations of hydrolysis, fermentation and separation are majorly carried out based on NREL references [76]. Those parameters are to do detailed mass and energy balance of typical process flow diagrams and calculate electricity requirements of those processes. The MILP optimization is utilized here to interconnect various biomass conversion process pathways, rather than focusing on internal process optimization.

Table 4. 1 Comparisons of Different Pretreatment Types [77]

Types of Pretreatments	Pretreatment Methods	Advantages	Disadvantages
Biological	Fungi (brown, white) Bacterial	• Low energy Consumption • Environmentally Friendly • No chemical required	• Slow process • Possibility of Health Issues • Hydrolysis of hemicellulose is not effective
Physical Pretreatment	Mechanical extrusion Milling Microwave Ultrasound Pulsed electric field	• No Chemical use • Alters the crystallinity of hemicellulose (which makes effective hydrolysis) • Reduces the size of biomass	• High Energy consumption • No Breakdown of Lignin • No chemical use
Chemical	Diluted acid Alkaline Ozonolysis Organosolvent Ionic liquids	• Breakdown Lignin bond • Separate out hemicellulose, cellulose and lignin	• Chemicals are used • Formation of inhibitors and toxic compounds • May impact environmentally
Physicochemical	Steam explosion Liquid hot water Ammonia fiber expansion (AFEX) CO_2 explosion Wet oxidation	• Increases surface area and so improves hydrolysis • High conversion rate • Separate lignin, hemicellulose and cellulose • Suitable for industrial level	• High energy consumption • High temperature and pressure requirements. • Possibility of inhibitors.

4.1 Pretreatment of lignocellulosic Biomass:

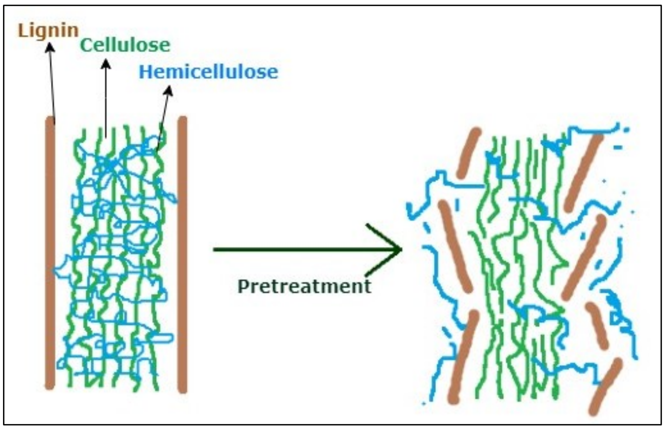

Figure 8 Impact of pretreatment on biomass structure [78]

Lignocellulosic biomass, if used directly as a substrate in fermentation, does not give a high production yield because it is difficult to break down the hard cell wall structure of biomass and hence its unbroken biomass will stay intact even in fermentation process. So, it is strongly necessary to break the structure of cell wall of biomass (Figure 8), which is basically removing bound lignin and releasing hemicellulose and cellulose to let enzymes and bacteria react with them. That process can be efficiently done by pretreatment which is why pretreatment is a necessary step in biomass conversion. Breaking the complex structure is energy-intensive, thus pretreatment is one of the costliest processes in the entire production pathway. Due to the complex structure of biomass and crystallinity of cellulose, pretreatment and enzymatic hydrolysis are the largest obstacles in establishing large-scale biorefineries [78]. The pretreatment stage stands out as a high-cost phase that significantly shapes the expenses involved in both preceding activities (e.g., reducing size) and subsequent processes (e.g., enzymatic hydrolysis and fermentation) [79]. The primary aim of pretreatment is to modify or eliminate structural and compositional barriers, enabling better enzymatic hydrolysis rates and enhancing the production yield of fermentable sugars derived from cellulose and hemicellulose [80]. Numerous affordable pretreatment methods have emerged to achieve elevated sugar yields from both cellulose and hemicellulose. Table 4.1 provides an overview and comparison of frequently employed pretreatment techniques [78]. Additionally, alternative approaches involving ozone, organic solvents, ionic liquids (ILs), and supercritical CO_2 have been researched [81].

The initial stage in the production pathway from biomass to bio-polyethylene involves the conversion of biomass into bioethanol, serving as the primary objective within this process. The process of transforming lignocellulosic biomass into ethanol involves several key stages: enzymatic breakdown of cellulose and hemicellulose into fermentable sugars, fermentation of sugars into ethanol, extraction of lignin residue, and ultimately, the retrieval and refinement of ethanol to further efficient polymerization [82]. Biomass must undergo a pretreatment process before being introduced into conversion systems for further processing. Different pretreatment techniques aim to break down, dissolve, and decompose biomass, segregating cellulose, hemicellulose, and lignin within lignocellulosic materials. These pretreatment methods are categorized into four primary types: physical, chemical, physico-chemical, and biological. Several physical pretreatment techniques like milling, chipping, grinding, freezing, and radiation are employed in treating lignocellulosic waste. These approaches aim to diminish particle size and augment the surface area of lignocellulosic materials [83]. Physico-chemical methods involve the utilization of severe conditions like high temperatures, pressure, and/or chemical substances. Conversely, biological pretreatments utilize natural microorganisms such as fungi, bacteria, and microbial combinations to disrupt the cell wall of lignocellulosic material. Biological pretreatment techniques, being environmentally friendly and chemical-free,facilitate the delignification of lignocellulosic biomass [84].In the urgent drive to achieve the energy transition goal by 2050, the selection of pretreatment methods prioritizes those with potential for rapid development and scalability, emphasis is placed on pretreatment capable of transitioning swiftly from pilot scale to practical application, facilitating the accelerated adoption of biobased industries and sustainable production practices.

In the research work, six different pretreatment processes are selected which can have the potential to establish on industrial scale. In the acid hydrolysis, dilute acid pretreatment is selected which has been designed for industrial scale development by NREL [76] and serves as a basis for several other processes. In hot water pretreatment, pressurized water has the ability to permeate biomass, hydrate cellulose, and eliminate hemicellulose along with a portion of lignin. The benefits include the absence of chemical additives and the elimination of the necessity for corrosion-resistant materials in hydrolysis reactors during this procedure [32]. AFEX pretreatment uses ammonia to treat biomass. Similarly, steam explosion, organosolvent, and alkaline pretreatments involve subjecting biomass to specific treatments—high-pressure steam, organic solvents, and alkaline solutions, respectively—to disrupt the biomass structure, dissolve lignin, and facilitate the separation of cellulose and hemicellulose components for subsequent processing.

4.1.1 Dilute Acid Pretreatment:

Dilute acid pretreatment (DAP) stands as the extensively employed commercial method, effectively disintegrating the lignocellulosic structure by disrupting its covalent bonds within the composite linkages. Acids utilized in this process include diluted sulfuric acid, nitric acid, and hydrochloric acid. Typically, DAP is conducted within temperatures ranging from 120°C to 210°C, using an acid concentration below 4 wt.%. [85].

Table 4.2 presents a comprehensive breakdown of the mass and energy balances in DAP, derived from modelling based on NREL data [76]. The process initiates with a feedstock handling unit that reduces biomass size before pretreatment and includes storage and transportation belts. In this report, although feedstock handling is not explicitly detailed, its electricity usage and capital cost are integrated within the pretreatment unit.

Throughout these pretreatments, corn stover serves as the chosen biomass for comparative analysis. Initially, biomass (corn stover) with 20% moisture undergoes size reduction in the feed handling unit for stock storage and processing. The assumed reduction in size is 0.19 inches for pretreatment cases. The subsequent step involves dilute acid pretreatment, aiming to convert the bulk of biomass into soluble sugars for enhanced conversion during hydrolysis and fermentation. Initially, biomass undergoes a presteaming phase to permeate its intricate structure, where hot water is added to keep the solid loading of biomass approximately 30 wt% in the slurry. It's then directed into the pretreatment reactor, introducing dilute sulfuric acid (21.1 mg/g dry biomass), operating at 158°C and 5.5 atm. The resulting conversions are tabulated in Table 4.3. A significant volume of acetic acid and furfural, known for their inhibitory effect during fermentation, is removed via water in the flash column post-pretreatment. In the subsequent phase, ammonia (4.8 g/liter of pretreated biomass) is introduced to the pretreated biomass, significantly elevating the pH to about 5 and aiding in the removal of acetic acid through ammonia reaction. The resulting slurry is now ready for further hydrolysis. Enthalpy calculations are conducted in kilowatts for the total hot and cold streams. To imply a separate building blocks in model, final in and out conditions of streams have kept same at an ambient temperature and pressure of 25°C and 1 atm. Furthermore, detailed energy calculations for reactions are executed in an Excel sheet, and summary is mentioned in Table 4.3.

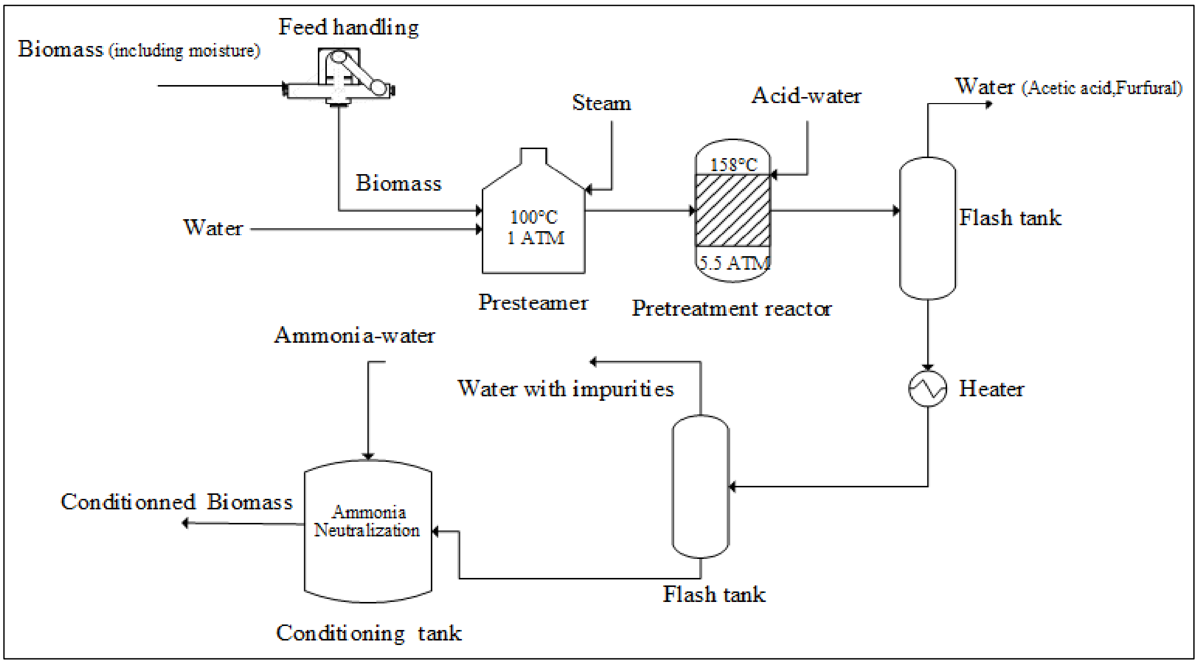

Figure 9 Process flow diagram of DAP [76]

Table 4. 2 Mass and Energy Balance of DAP [76]

Stream	**Total In/ out**	**Massflow (kg/hr)**	**C_P (kJ/kg*K)**	**T1 (K)**	**T2 (K)**	**Sensible Heat (kW)**	**Latent Heat (kW)**
BM moisture	In	20833	4.182	298.15	373.15	1815	-
Dry BM	In	83333	1.085	298.15	373.15	1883	-
Hot water	In	140850	4.182	298.15	373.15	12271	-
Heating steam		3490	1.996	298.15	541.15	825	1910.51
Steam to presteamer	In	3490	1.996	541.15	373.15	-507	-2001.82
Presteamed BM		248507	3.109	373.15	431.15	12448	-
Diluted acid water	In	38801	4.032	298.15	431.15	5780	-
Heating steam 2		24534	2.35	298.15	541.15	5802	13430
Steam to PT - reactor	In	24534	2.35	541.15	431.15	-1774	-14283
PT reactor exit slurry		311842	3.164	431.15	403.15	-7675	-
Water vapor (impurities)	Out	19782	4.129	403.15	298.15	-2382	-
Pretreated BM slurry		292060	3.254	403.15	298.15	-27725	-
BM to conditioning		292060	3.254	298.15	404.15	27986	-
Water (impurities)	Out	13866	4.147	404.15	298.15	-1693	-
Heated BM		278194	3.209	404.15	351.15	-13146	-
Ammonia water	In	151360	4.168	298.15	351.15	9288	-
Conditioned BM	Out	429554	3.543	351.15	298.15	-22410	-
Reaction energy required in PT-reactor						638	-
Reaction energy liberated in conditioning						-2074	-

Table 4. 3 Pretreatment Reaction – DAP [76]

Reactions	Conversion to Product	ΔH_f (cal/mol)
(Cellulose)n + n H_2O → n Glucose	0.099	1004
(Cellulose)n + n H_2O → n Glucolig	0.003	68232
(Cellulose)n → n HMF + 2n H_2O	0.003	-2941
Sucrose → HMF + Glucose + 2 H_2O	1	-55669
(Xylan)n + n H_2O → n Xylose	0.9	892
(Xylan)n + n H_2O → n Xyolig	0.024	68232
(Xylan)n → n Furfural + 2n H_2O	0.05	-2102
Acetate → Acetic Acid	1	26
Lignin → Soluble Lignin	0.05	0
NH_3+ CH_3COOH → CH_3COO^- + NH_4^+ (Conditioning)	1	-20746

4.1.2 Hot Water Pretreatment:

Liquid hot water (HW) pretreatment, or hydrothermal pretreatment, refers to a method that utilizes high temperatures (typically ranging between 130°C to 240°C) and elevated pressure to employ water as a heating agent while sustaining it in its liquid state, without having a need of any chemical additives [86,87]. Water exhibits acidic characteristics at elevated temperatures and can function as an acidic catalyst [88]. HW pretreatment helps in partial break down of hemicellulose and disturbs the structures of lignin and cellulose. Furthermore, it generates toxic inhibitors like HMF and furfurals during sugar degradation reactions, which can be effectively neutralized by maintaining the pH within a range of 5 to 7 [89].

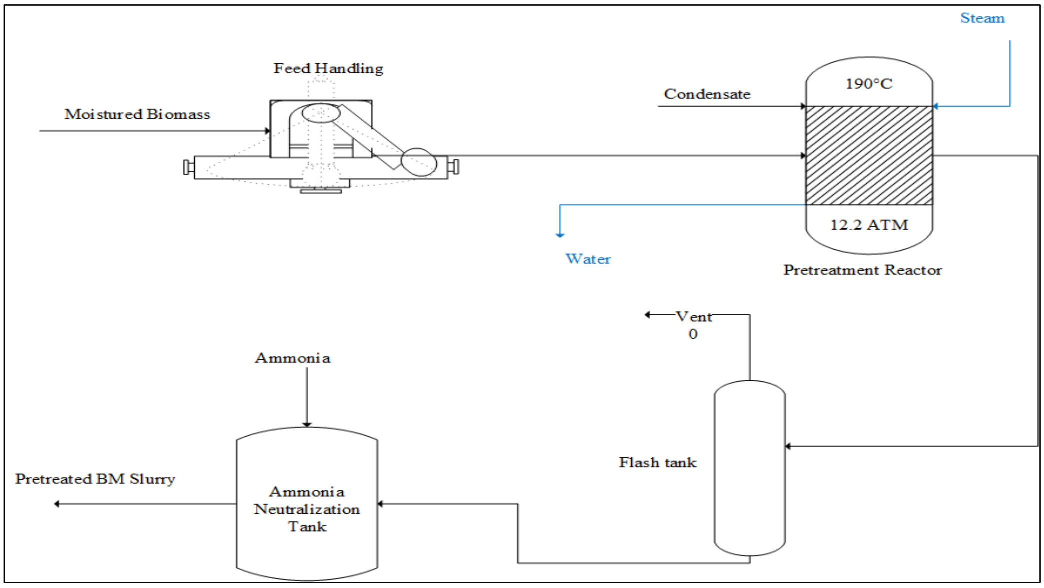

Figure 10 Process flow diagram of HWP [90]

This pretreatment method offers notable advantages by solely utilizing hot water within its pretreatment reactor. The illustrated HWP is referred from Kazi et al. [90]. Following the feed handling area, the biomass undergoes transfer to the pretreatment reactor, where hot water is introduced. Operating at 12.2 atm and 190°C, the reactions within this reactor significantly differ from those in diluted acid pretreatment. As hot water serves as the pretreatment medium without inducing a phase change, the subsequent summary does not involve latent heat considerations. After the pretreatment, the resulting slurry undergoes flashing at ambient pressure and subsequently cools down to 65°C. To neutralize the slurry and eliminate acetic acid, which acts as an inhibitor during fermentation, ammonia is introduced. A comprehensive mass and energy balance of the hot water pretreatment process is detailed in Table 4.5 Additionally, Table 4.4 contains the total number of reactions alongside their respective conversions. Furthermore, the process flow diagram can be observed in Figure 10.

Table 4. 4 Pretreatment Reactions – HWP [90]

Reactions	Conversion to Product	ΔH_f (cal/mol)
$(Cellulose)_n$ → n (Glucolig)	0.053	0
$(Cellulose)_n + n\ H_2O$ → n Glucose	0.0032	1004
$(Xylan)_n$ → n (Xyolig)	0.554	0
$(Xylan)_n + n\ H_2O$ → n Xylose	0.0239	892
$(Mannan)_n$ → n (Mannolig)	0.554	0
$(Mannan)_n + n\ H_2O$ → n Mannose	0.0239	1004
$(Galactan)_n$ → n (Galaolig)	0.554	0
$(Galactan)_n + n\ H_2O$ → n Galactose	0.0239	1004
$(Arabinan)_n$ → n (Arabolig)	0.554	0
$(Arabinan)_n + n\ H_2O$ → n Arabinose	0.0239	892
Acetate → Acetic Acid	1	26
$(Furfural)_n + 3\ H_2O$ → Tar	1	70334
$(HMF)_n + 3\ H_2O$ → 1.2 Tar	1	85853
Lignin → Soluble Lignin	0.05	0
$(Glucose)_n$ → n HMF + $2n\ H_2O$	0.5	64287
$(Mannose)_n$ → n HMF + $2n\ H_2O$	0.5	64287
$(Galactose)_n$ → n HMF + $2n\ H_2O$	0.5	64287
$(Xylose)_n$ → n Furfural + $2n\ H_2O$	0.5	65238
$(Arabinose)_n$ → n Furfural + $2n\ H_2O$	0.5	65238
$NH_3 + CH_3COOH \rightarrow CH_3COO^- + NH4^+$ (Conditioning)	1	-20746

Table 4. 5 Mass and Energy Balance of HWP [90]

Stream	**Total In/Out**	**Massflow (kg/hr)**	**C_P (kJ/kg*K)**	**T1 (K)**	**T2 (K)**	**Sensible Heat (kW)**
BM moisture	In	58482	4.182	298.15	463.15	11209
Dry BM	In	69768	1.085	298.15	463.15	3469
Condensate	In	415542	4.182	298.15	463.15	79649
Pretreated BM		543792	3.784	463.15	353.15	-62885
Ammonia	In	1333.33	2.2	298.15	353.15	45
Pretreated BM slurry	Out	545125	3.780	353.15	298.15	-31487
Reaction energy required in PT-reactor						439
Reaction energy liberated in conditioning						-3418

4.1.3 AFEX (Ammonia-Fiber Explosion Pretreatment):

Ammonia-based pretreatments, such as AFEX (Ammonia Fiber Expansion), represent a form of physico-chemical treatment where lignocellulosic biomass undergoes treatment with liquid ammonia at relatively moderate temperatures (ranging between 90 to 100°C) for a duration of 30 to 60 minutes. Subsequently, this treatment involves a swift release of pressure [91]. This procedure induces a rapid expansion of liquid ammonia, leading to the swelling and physical disruption of biomass fibres, along with a partial reduction in the crystalline structure of cellulose. AFEX specifically yields pretreated

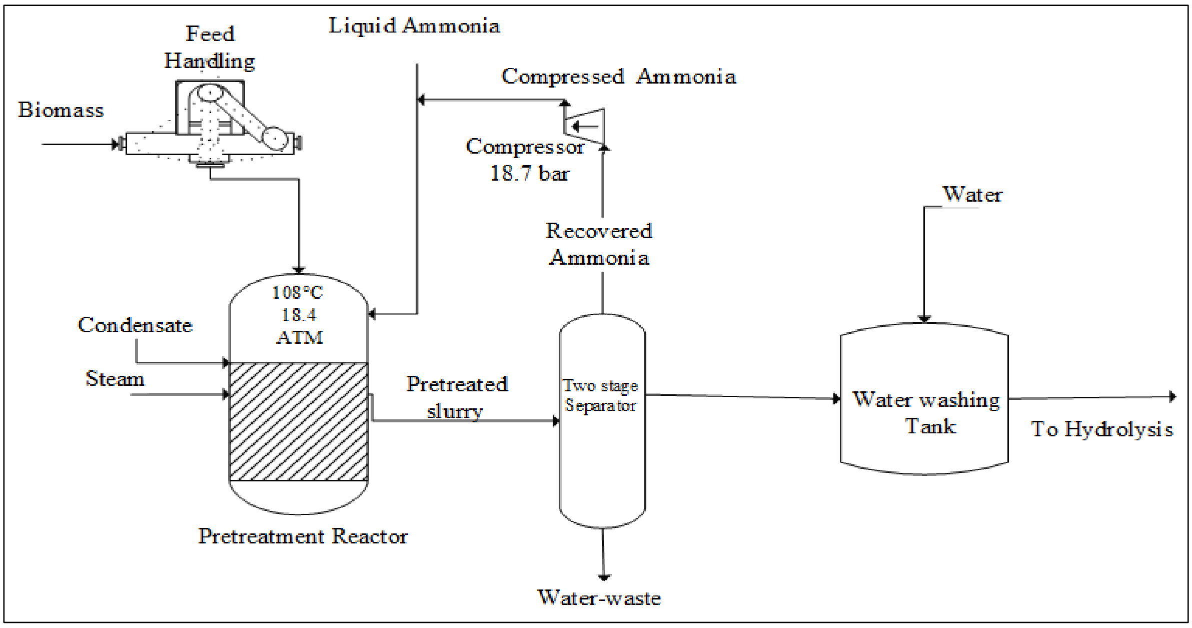

Figure 11 Process flow diagram of AFEX [90]

solid material and has the capability to either modify or significantly decrease the cellulose crystallinity and lignin fraction within lignocellulosic materials [92]. Herbaceous and agricultural residues tend to respond more effectively to AFEX pretreatment compared to woody biomass and other feedstocks with higher lignin content, for which its effectiveness is more limited [93]. The primary advantage of ammonia pretreatment lies in its ability to avoid the production of inhibitors for subsequent fermentation processes, eliminating the need for a water wash step [82].

Table 4. 6 Pretreatment Reactions of AFEX [90]

Reactions	**Conversion to Product**	**ΔH_f (cal/mol)**
(Xylan)$_n$ → n (Xyolig)	0.5	0
(Mannan)$_n$ → n (Mannolig)	0.5	0
(Galactan)$_n$ → n (Galaolig)	0.5	0
(Arabinan)$_n$ → n (Arabolig)	0.5	0
Lignin → Soluble Lignin	0.33	0

Table 4. 7 Mass and Energy Balance -AFEX [90]

Stream	**Total In/Out**	**Massflow (kg/hr)**	**C_P (kJ/kg*K)**	**T1 (K)**	**T2 (K)**	**Sensible Heat (kW)**	**Latent Heat (kW)**
BM moisture	In	59647	4.182	298.15	381.15	5751	-
Dry BM	In	68626	1.085	298.15	381.15	1717	-
Condensate	In	5075	4.182	298.15	381.15	489	-
Heating steam 1	In	62.50	1.996	298.15	541.15	16	34
Steam to reactor		62.50	1.996	541.15	381.15	-9	-33
Liquid ammonia	In	1675	4.27	298.15	381.15	165	-
Compressed ammonia	In	67115	2.2	767.75	381.15	-15856	-
Pretreated BM slurry		202201	2.473	381.15	338.15	-5973	-
Vent ammonia	Out	67115	2.2	338.15	767.75	17620	-
Pretreated BM		100093	1.954	338.15	298.15	-2174	-
Wastewater	Out	34992	4.186	338.15	298.15	-1628	-
Recycle water	In	335875	4.182	298.15	373.15	29263	-
Recycle water in		335875	4.182	373.15	298.15	-29263	-
BM slurry to hydrolysis	Out	435968	3.670	298.15	298.15	0	-
Reaction energy						0	-

AFEX here is referenced from Kazi et al. [90] involves subjecting biomass to anhydrous ammonia under high pressure conditions at 18.7 atm and 108°C. However, unlike several other pretreatment methods, only a limited portion of the hemicellulose structures are converted into oligomers in the AFEX process. Notably, cellulose does not undergo breakdown within the current AFEX process. Following pretreatment, the slurry is depressurized to ambient levels (Figure 11), causing the fiber to expand and rupture the carbohydrate structure. Subsequently, ammonia recovery takes place via a flash column, and the pretreated biomass is then directed to the hydrolysis stage for further processing. This method's approach to utilizing ammonia under specific high-pressure conditions results in a selective breakdown of hemicellulose structures while maintaining the cellulose integrity, necessitating subsequent steps for cellulose degradation during downstream processing. Detailed conversion reaction and mass and energy balance are summarized in Table 4.6 and 4.7 respectively.

4.1.4 Organosolvent Pretreatment:

Organosolvent pretreatment involves various combinations of organic or aqueous solvent mixtures, such as methanol, ethanol, acetone, ethylene glycol, and tetrahydrofurfuryl alcohol. These solvent mixtures are utilized to dissolve and solubilize lignin [94]. An advantageous aspect of organosolvent, in contrast to other pretreatment methods, is the potential to recover relatively pure lignin as a by-product [95]. Certainly, in this pretreatment method, it's crucial to remove the solvents because they could interfere with or impede the enzymatic process and fermentation [30]. Due to this reason, solvents

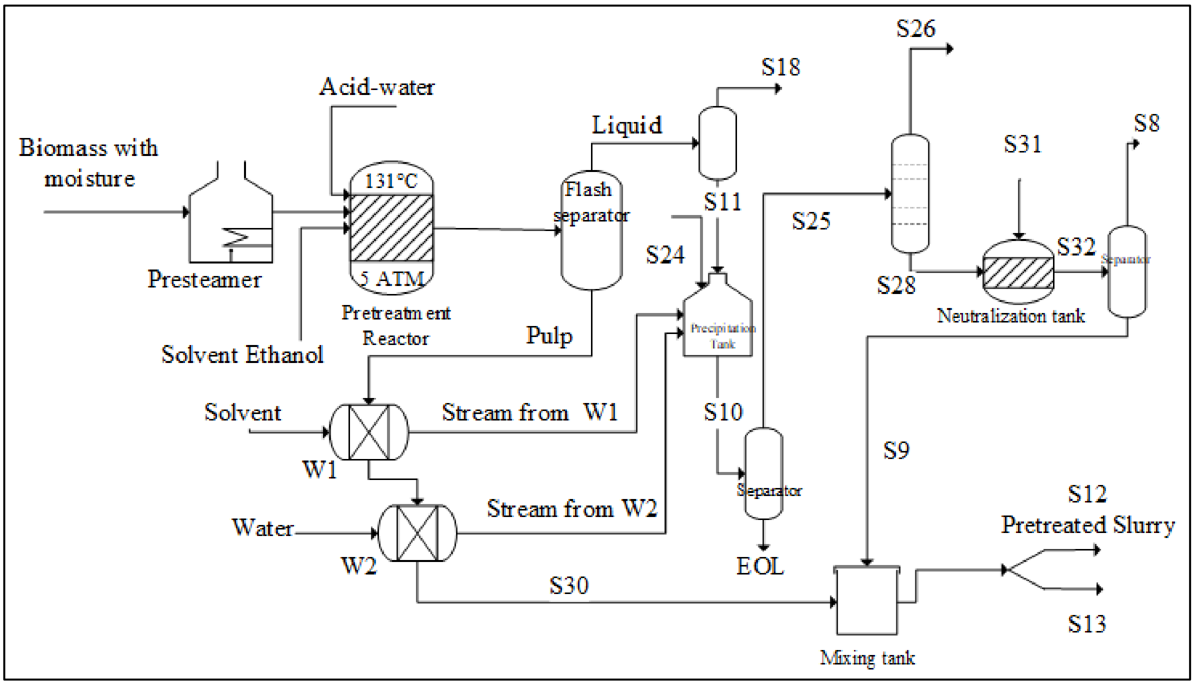

Figure 12 Process flow diagram of organosolvent [96]

like ethanol and methanol, which have low boiling points and are easier to remove, are preferred [95]
In the present organo-solvent process [96], the initial step involves presteaming biomass with moisture content at 130°C and 1 atmosphere pressure. This presteamed biomass is then directed to the pretreatment stage, where a 50% weight ethanol solution serves as the organic solvent. Dilute sulfuric acid with acid flowrate of 1548 kg/hr and water flowrate of 221366 kg/hr is utilized as a catalyst during the pretreatment reaction, conducted within the pretreatment reactor operating at 27.2 atm and 130°C. Details of the reactions occurring in the reactors are provided in Table 4.8, showing few similarities to dilute acid pretreatment reactions.

Table 4. 8 Pretreatment Reactions of Organosolvent [96]

Reactions [96]	**Conversion to Product**	**ΔH_f (cal/mol)**
$(\text{Cellulose})_n + n\ H_2O \rightarrow n$ Glucolig	0.0003	68232
$2\ (\text{Cellulose})_n + H_2O \rightarrow$ Cellobiose	0.0007	53732
$(\text{Cellulose})_n + n\ H_2O \rightarrow n$ Glucose	0.32	1004
$(\text{Xylan})_n + n\ H_2O \rightarrow n$ Xyolig	0.023	68232
$(\text{Xylan})_n + n\ H_2O \rightarrow n$ Xylose	0.767	892
$(\text{Xylan})_n \rightarrow n$ Furfural $+ 2n\ H_2O$	0.050	-2102
Lignin → Soluble Lignin	0.25	0
Acetate → Acetic Acid	1	26
$2\ NH_3 + H_2SO_4 \rightarrow (NH_4)_2\ SO_4$ (Conditioning)	1	-57141
$NH_3 + C_2H_4O_2 \rightarrow NH_4CH_3COO$ (Conditioning)	1	-19905

Following pretreatment, the resulting slurry undergoes separation into solid and liquid components. The solid biomass primarily comprises cellulose along with a portion of solvent and lignin. It undergoes a two-stage washing process: initially with the same ethanol solvent (50% by weight), followed by a second stage involving water wash to recover solvent and extract additional lignin. The washed pulp is then conveyed to a mixing tank for further processing.

Conversely, the liquid slurry mainly contains lignin, hemicellulose, and residual lignin after passing through a series of flash towers and distillation columns, aimed at recovering lignin and solvent. The remaining hemicellulose in this stream contains traces of acetic acid and sulfuric acid resulting from the reactions. These acids are neutralized by the addition of ammonia, similar to other pretreatment methods. The neutralized slurry is amalgamated with the solid stream in the mixing tank before advancing to subsequent hydrolysis process. In process flow diagrams (Figure 12), some streams are represented by numbers (same as original reference) instead of longer names to prevent confusion, especially when their components are identical or similar, thereby maintaining clarity and brevity in the diagram.

Table 4. 9 Mass and Energy Balance – Organosolvent [96]

Stream	Total In/Out	Massflow (kg/hr)	C_p (kJ/kg.K)	T1 (K)	T2 (K)	Sensible Heat (kW)
BM moisture	In	17700	4.182	298.15	403.15	2159
Dry BM	In	88500	1.085	298.15	403.15	2801
Prestreamed BM		106200	1.601	403.15	453.15	2362
Acidic water	In	222914	3.902	298.15	453.15	37457
Solvent ethanol	In	221250	2.891	298.15	453.15	27540
Pretreated BM		550364	3.051	453.15	404.25	-22812
Splitted liquid slurry		500515	2.790	404.25	358.15	-17883
S18 -Waste solvent ethanol	Out	193679	3.023	358.15	298.15	-9761
S11- Wastewater and BM		306836	3.347	358.15	338.05	-5735
S24 - Water	In	65500	4.182	298.15	338.05	3036
S10- Wastewater plus BM		571732	3.593	338.05	338.05	0
EOL - Soluble lignin	Out	4871	1.355	338.05	298.15	-73
S25 – BM and wastewater		566860	3.612	338.05	351.45	7623
S26 - Ethanol & wastewater	Out	141273	2.730	351.45	298.15	-5712
S28 – BM & wastewater		425587	3.938	351.45	368.15	7776
S31 - NH_3	In	1250	2.2	298.15	368.15	53
S32 – BM & water&waste		426836	3.891	368.15	373.65	2538
S08 - BM &wastewater	Out	225518	4.139	373.65	298.15	-19577
S09 - Water & BM waste		201317	3.613	373.65	370.65	-606
Splitted pulp solid		49849	1.13	404.25	301.65	-1605
Solvent in washer1	In	99690	2.891	298.15	301.65	280
Stream from washer 1 (washed solvent)		99690	2.891	301.65	338.05	2914
Pulp		49849	1.13	301.65	301.65	0
Water in washer 2	In	99706	4.182	298.15	301.65	405
Stream from washer 2 (washed water solvent)		99706	4.182	301.65	338.05	4216
S30 - Glucose sugars		49845	1.13	301.65	370.65	1080
S13 - Waste BM & water	Out	25111	3.120	370.65	298.15	-1578
S12 - Pretreated slurry to hydrolysis	Out	226051	3.120	370.65	298.15	-14207
Reaction energy required in PT-reactor						205
Reaction energy liberated in conditioning						-4973

4.1.5 Steam Explosion:

Steam explosion is a technique that involves using high-pressure steam to break the bonds between different components and decompressing rapidly to break down the lignocellulose structure. In this method, the lignocellulose material is exposed to high-pressure steam (160–260ºC) for a specific duration, followed by quick depressurization to return to atmospheric pressure [97]. The rapid decompression and elevated temperature lead to the breakdown of hemicellulose, which is extracted as a water-soluble fraction. Cellulose remains mostly unchanged in its original form, experiencing only minor depolymerization under milder reaction conditions. Lignin, however, undergoes depolymerization through the cleavage of β–O–4 linkages, followed by the condensation of fragments to create a more stable polymer [98]. Steam explosion stands out as one of the most energy-efficient and environmentally friendly methods for treating lignocellulose. Its appeal lies in the absence of organic solvents and corrosive chemicals, making it an attractive option for large-scale industrial applications [99,100].

Steam explosion, as described in Conde-Mejia et al. [101], utilizes high-pressure steam at 30 atm and 240°C. This process involves injecting high-pressure steam into the pretreatment reactor, leading to the explosion of biomass. Operating at 220°C, the reactor suddenly reduces pressure to 1 atm, aiding in biomass disruption. However, in comparison to a few other pretreatment methods considered from the reference sources, steam explosion (SE) pretreatment displays minimal conversion from cellulose to glucose and hemicellulose to xylose (Table 4.10), with most of the biomass remaining intact. After the reactor (Figure 13) water and steam is removed from slurry and remaining solid slurry is introduced with fresh water with ratio 1:9 (to solid slurry) to help solid through hydrolysis step. In the referenced method, however after the pretreatment solid and liquid part is separated, where converted xylose and glucose are separated out from solid. In this case, it is not separated because the hydrolysis after the whole pretreatment is going to be the same model for sake of comparison and to apply to the MILP model. After adding the freshwater, the total pretreated biomass is then sent to hydrolysis.

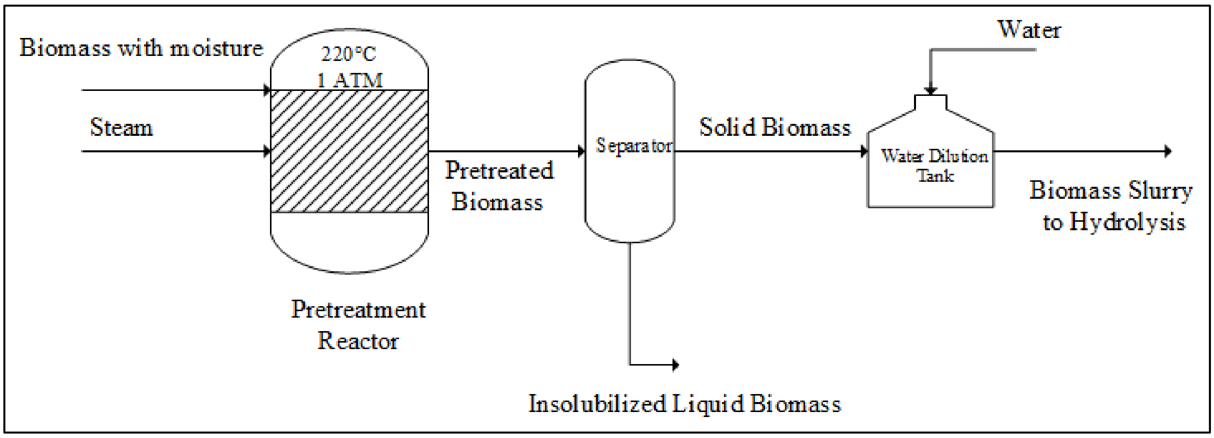

Figure 13 Process flow diagram of SE [101]

Table 4. 10 Pretreatment Reactions of SE [101]

Reactions [101]	**Conversion to Product**	**ΔH_f (cal/mol)**
$(Cellulose)_n + n\ H_2O \rightarrow n$ Glucose	0.0004	-9472
$(Xylan)_n + n\ H_2O \rightarrow n$ Xylose	0.0026	-9584

Table 4. 11 Mass and Energy Balance – SE [101]

Stream	**Total In/Out**	**M (kg/hr)**	**C_p (kJ/kg.K)**	**T1 (K)**	**T2 (K)**	**Sensible Heat (kW)**	**Latent Heat (kW)**
BM moisture	In	10886	4.182	298.15	493.15	2466	-
Dry BM	In	16329	1.085	298.15	493.15	960	-
Heating steam		27216	2.2	298.15	513.15	6761	13562
Steam in reactor	In	27216	2.2	513.15	493.15	-514	-17128
Pretreated BM		54431	2.261	493.15	377.4	-3959	-
Splitted solid		16329	1.085	377.4	298.15	-390	-
Splitted liquid	Out	38102	2.766	377.4	298.15	-232	-
Water	In	112486	4.182	298.15	298.15	0	-
Pretreated BM slurry to hydrolysis	Out	128816	3.789	298.15	298.15	0	-
Reaction energy required in PT-reactor						113	-

4.1.6 Alkaline Pretreatment:

Treating lignocellulosic biomass with alkali is advantageous because it operates at lower pressure and temperature than some other pretreatment methods, with its effectiveness often linked to the lignin content. However, this method requires longer retention times, ranging from hours to days. Calcium hydroxide and sodium hydroxide are considered effective and economically viable among the alkali agents. Furthermore, sodium, potassium, and calcium metals are also commonly used for alkali pretreatments [102]. During alkaline pretreatment, the process includes the dissolution of lignin by decreasing its degree of polymerization and breaking the bonds between lignin and other polymers.so lignin can be easily removed, and its structure is altered. However, the catalysts suitable for this process tend to be expensive. Also, comparatively lower amounts of inhibitors are produced during alkaline pretreatment [103].

Table 4. 12 Pretreatment Reactions of Alkaline [104]

Reactions [104]	**Conversion to Product**	**ΔHf (cal/mol)**
Lignin → Soluble Lignin	0.397	0
$HCl + NaOH \rightarrow NaCl + H_2O$ (Conditioning)	1	-8135

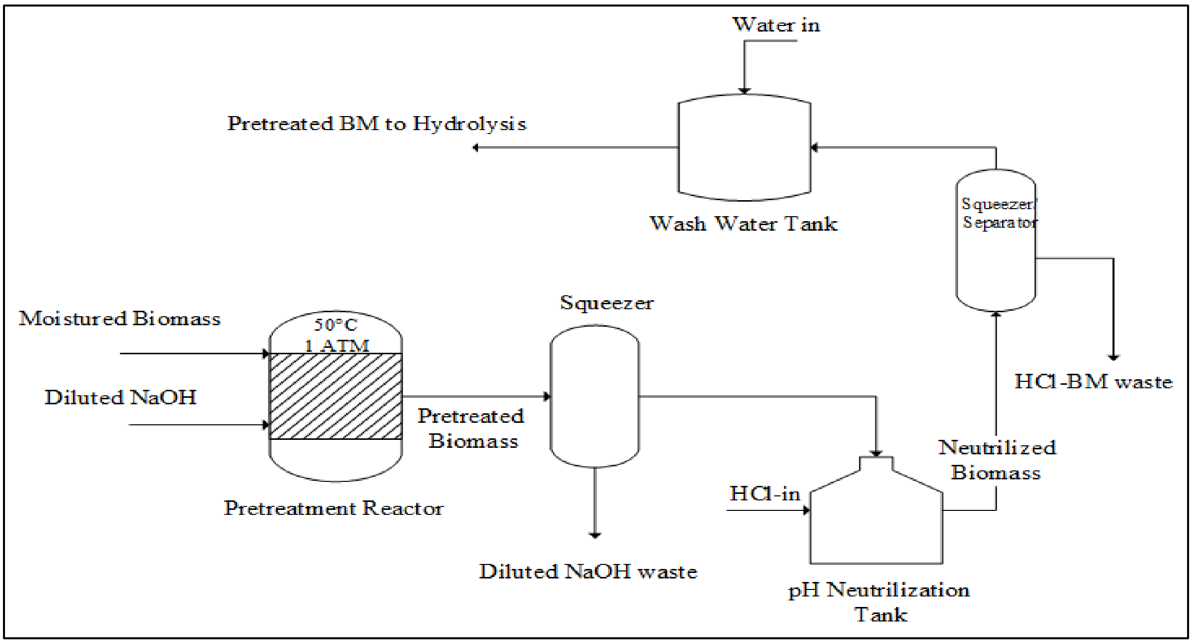

Figure 14 Process flow diagram of alkaline [104]

Table 4. 13 Mass and Energy Balance of Alkaline [104]

Stream	**Total In/Out**	**M (kg/hr)**	**C_p (kJ/kg. K)**	**T1 (K)**	**T2 (K)**	**Sensible Heat (kW)**
BM moisture	In	30	4.182	298.15	323.15	0.883
Dry BM	In	122	1.085	298.15	323.15	0.917
Diluted NaOH in	In	30	4.180	298.15	323.15	0.882
Pretreated BM		182	2.117	323.15	298.15	-2.681
Diluted NaOH out	Out	57	3.368	298.15	298.15	0
Squeezed BM		1254	1.346	298.15	298.15	0
Diluted HCl in	In	2.77	4.179	298.15	298.15	0
Conditioned BM		128	1.408	298.15	298.15	0
Acid -liquid BM	Out	17.11	3.499	298.15	298.15	0
BM separated (from acid)		111	1.085	298.15	298.15	0
Water in	In	886	4.182	298.15	298.15	0
Pretreated slurry to hydrolysis	Out	996.3	3.837	298.15	298.15	0
Reaction energy required in PT-reactor						0
Reaction energy liberated in conditioning						-0.078

Alkaline pretreatment here is referred from Le et al. [104]. In current pretreatment, moisture biomass is entered in the reactor under 50C and 1 atm. Diluted 1wt% NaOH is injected into the reactor with rate of 20g NaOH per 100 g Biomass. In the pretreatment reactor, the main reaction is delignification in which solid lignin is converted into solubilised lignin or liquid lignin (Table 4.12). Cellulose and hemicellulose mostly remain unreacted. Then the slurry is sent to the squeezer to separate alkaline liquid waste from solid slurry using filteration. The solid slurry still contains some amount of alkaline solution which is neutralized in a neutralization tank using 2 wt.% HCl in the tank and to keep the pH of the solution around 6. A further step involves passing the material through a squeezer to effectively separate any residual waste acid-alkaline solution along with a portion of liquid biomass from the solid slurry. The solid slurry is mixed with water to keep 17% solid loading in slurry. The resulting solid slurry is now prepared and ready to proceed to the subsequent hydrolysis step for further treatment. Mass and energy balance of alkaline pretreatment is summarized in Table 4.13.

4.2. Hydrolysis:

4.2.1 Enzymes:

Enzymatic hydrolysis stands as a pivotal process in the conversion of LCB into fermentable sugars, offering significant potential for advancing bioethanol production. Among the enzymes utilized in this process, cellulases play a prominent role in converting cellulose into simpler sugar forms. There are primarily two enzyme categories: cellulases, which effectively break down glucan or cellulose in biomass, and hemicellulases, which catalyze the hemicellulose or xylan components of biomass. Commonly used cellulolytic enzymes in industry are derived from various bacteria and fungi, including Cellulomonas, Clostridium, Bacillus, Thermomonospora, Ruminococcus, Bacteriodes, Sclerotium rolfsii, Phanenerochate chrysosporium, and species within the genera Trichoderma, Aspergillus, and Penicillium. Notably, Trichoderma and Aspergillus genera, particularly Trichoderma reesei, exhibit significant capabilities in enzymatic hydrolysis [105].

Cellulase, a diverse group of enzymes derived from bacterial and fungal species, exhibits activity across a spectrum of aerobic and anaerobic conditions, and functions effectively within a specific temperature range [106]. These enzymes catalyze the breakdown of ß-(1,4)-glycosidic linkages within cellulose chains, facilitating the transformation of cellulose into readily fermentable simple sugars [107]. Enzymatic hydrolysis stands out as a promising technique for breaking down biomass into its constituent sugars, enabling their conversion into biofuels by microorganisms [108].When compared to conventional acid hydrolysis, enzymatic hydrolysis operates under milder conditions (typically around 40–50°C and pH 4–5), requiring less energy. Consequently, its advantages over acid saccharification include reduced toxicity, minimal degradation and corrosion, lower operational costs, absence of inhibitory by-products, and no environmental harm [105].

The costliness of enzymes necessitates evaluation of enzyme loading, which refers to the quantity of enzymes applied. The required amount of enzymes for the pretreated slurry depends on several factors, including the substrate's composition, its accessibility to enzymes, the efficiency of the enzymes used, the specific characteristics of the biomass, the operating conditions such as temperature and pH, the desired yield, and the duration of hydrolysis, among other variables. Optimizing enzyme loading involves considering this multitude of factors to strike a balance between maximizing conversion efficiency and minimizing operational costs in biomass processing. Hence, this aspect stands as a pivotal challenge in establishing biorefineries, primarily due to the inherent complexity and variability associated with determining these factors. The diverse nature of biomass feedstocks, coupled with variations in enzyme efficiency, substrate accessibility, and the interplay of numerous operational parameters like temperature and pH, underscores the intricate and often unpredictable nature of this process. The task of optimizing enzyme loading becomes a significant concern as it necessitates a delicate balance between multiple variables, making it a crucial aspect in the quest for efficient and cost-effective biorefinery operations.

Also, in the biomass pretreatment phase, particularly chemical treatments, the process generates various toxic degradation byproducts like phenolics, furans, aliphatic acids, and inorganic compounds. These compounds pose a challenge as they have the potential to hinder or deactivate the activity of cellulolytic enzymes. For instance, compounds like acetic acid, furfural, and hydroxymethylfurfural (HMF) are known to inhibit enzyme activity. Acetic acid (AA) can alter the pH conditions, affecting enzyme stability, while furfural and HMF can interfere with enzyme function by binding to active sites or altering enzyme structure, thereby reducing their effectiveness in breaking down biomass [105,109]. In our ongoing research, certain pretreatment methods result in the production of inhibitory compounds such as acetic acid and furfurans. Hence, considering the results of the current pretreatment on the biomass slurry, enzyme loading for the hydrolysis is simplified based on 'Inhibitor' factor. enzyme loading is adjusted based on the presence of inhibitors to get the maximum glucose yield. So, for the hydrolysis phase, the process remains largely similar, but the enzyme loading varies between pretreatments that generate inhibitory compounds such as AA, HMF, and furfurans, and those that do not include these inhibitory toxic compounds. Studies consistently demonstrate that pretreatments lacking inhibitors yield higher glucose output with a reduced enzyme quantity compared to those containing inhibitors [109].

4.2.2 Enzymatic Hydrolysis Types:

Enzymatic hydrolysis has become the preferred method for biomass conversion, offering two primary strategies: separate hydrolysis and fermentation (SHF) and simultaneous saccharification and fermentation (SSF). SHF involves distinct stages where hydrolysis and subsequent fermentation occur separately, allowing for precise control of conditions in each phase. On the other hand, SSF integrates these processes, enabling enzymes and microorganisms to work simultaneously, potentially enhancing overall efficiency. Despite these distinct approaches, the differences in resulting biofuel yield between SHF and SSF tend to be marginal, with the main contrast lying in capital costs. SHF, with its requirement for separate equipment in hydrolysis and fermentation, generally incurs higher initial expenses [110,111]. In contrast, SSF demands fewer units since enzymes and microorganisms' function together, reducing equipment costs. However, the choice between SHF and SSF is not solely dictated by capital costs. Factors such as process efficiency, the unique characteristics of the utilized biomass, enzyme effectiveness, and microorganism adaptability to conditions also influence the selection. Presently, SHF is often preferred due to its clearer operational guidelines, as suggested by entities like NREL. Nevertheless, a comprehensive evaluation considering these factors is crucial to determine the optimal method for biofuel production.

4.2.3 Implemented Hydrolysis Process (NREL based):

In the hydrolysis process designed by NREL [76], enzymes are produced at the facility. However, the consideration for enzyme manufacturing units, in this thesis, is not included in the calculations rather purchased from market. The main focus of this study is centered on the original contributing process manufacturing units. A cellulase enzyme preparation constitutes a blend of various enzymes that collaborate to decompose cellulose fibres into cellobiose and soluble gluco-oligomers, eventually resulting in the formation of glucose monomers. The glucose and other sugars derived from the hydrolysis of hemicellulose during pretreatment are subjected to fermentation processes to produce ethanol.

The approach implemented as per NREL [76], is designed separate (or sequential) hydrolysis and fermentation (SHF). Enzymatic hydrolysis begins while the mixture remains at an elevated temperature after pretreatment and conditioning. However, in this thesis work, as discussed earlier, the total inlet and outlet conditions of each process has been kept at an ambient temperatures and pressures so that it can address the problem of different pretreated slurry leaving at different temperature. Also, it eases in combining processes in MILP framework. This higher temperature of 48°C enhances enzyme activity, resulting in quicker conversion and necessitating a reduced quantity of enzymes. After the cellulose-to-glucose conversion is finished, the mixture is cooled to the fermentation temperature before being directed to the fermentation reactor. Unlike SHF, in the simultaneous saccharification and fermentation (SSF) method, the temperature of the pretreated slurry is reduced to an optimal fermentation temperature, initiating fermentation before the enzymatic hydrolysis is entirely finished. Within SSF, despite fermentation commencing, the enzymes continue to break down cellulose. As fermentation progresses and consumes sugars, serving as a "sugar sink," it encourages enzymatic hydrolysis reactions to prioritize the production of glucose.

4.2.4 Enzyme loading calculations for Pretreatments with and without inhibitors:

Enzyme loading for hydrolysis is segmented into two categories—those with and without inhibitors—as previously discussed. Dilute acid and hot water pretreatments have been observed through experimental data to yield toxic compounds such as acetic acid and furfural. Consequently, AFEX, steam explosion, Alkaline, and Organosolvent processes are classified as non-inhibitor processes. While alkaline and organosolvent pretreatments may sometimes yield inhibitors, result of this research indicates that alkaline treatment does not produce inhibitors, and organosolvent generates minimal furans, deemed negligible. However, the formation of inhibitory compounds in these processes is significantly influenced by factors such as biomass composition, the quantity of solvent or alkaline used, and operating conditions. Therefore, each pretreatment's determination can be influenced by a multitude of factors. The current classification is based on the outcomes derived from the considered and calculated pretreatment techniques and their results in the present study.

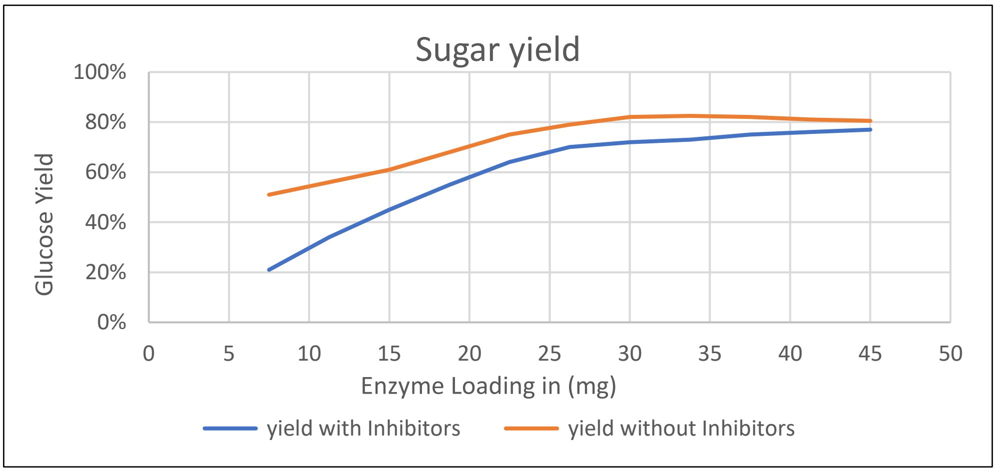

Figure 15 Enzyme loading vs sugar conversion

Through experimental studies comparing 'enzyme loading vs glucose yield' in two distinct pretreatment methods—AFEX and SE—the literature reveals that steam explosion is associated with inhibitor production, whereas AFEX does not yield inhibitors [112]. Consequently, in this research endeavor, the determination of processes generating inhibitors is predicated on the data derived from steam explosion [112].Conversely, AFEX pretreatment serves as the model for processes not producing inhibitors. Above is depicted graph (Figure 15) with xylan to glucose yield based on different enzyme loading. In this case, cellulase is used to hydrolyse both cellulose and xylan together, the xylose yield is calculated based on enzyme loading required for the glucose yield. The maximum theoretical yield achieved for both hydrolysis case including all six pretreatments is calculated and mentioned in Table 4.15. The graphical representation clearly indicates a distinct divergence between the two categories: those with inhibitors and those without inhibitors, showcasing notable differences in both glucose yield and enzyme consumption. Through the graphical data analysis employing polynomial regression, a formula has been formulated to establish the correlation between enzyme loading and sugar yield shown in Table

4.14 enzyme loading is based on enzyme mg/g of cellulose. Additionally, mass composition of hydrolysed slurry for all different pretreatment is further mentioned in Tables 4.16-4.21. The equation of calculating enzyme loading for sugar yield is nonlinear here and is computed separately before applying MILP optimization to address its nonlinearity.

Table 4. 14 Enzyme Loading of Different Pretreatment

Pretreatments	**Relationship between enzyme loading and sugar yield**	**Maximum Yield**
Pretreatment with Inhibitors		
DAP HWP	$Y= -0.0006\times X^2+0.0438\times X-0.0785$ $Z= -0.0002\times X^2+0.0217\times X+0.1885$	Y = 72% X = 36.5 mg Z = 71%
Pretreatments without Inhibitors		
AFEX Alkaline Organosolvent Steam Explosion	$Y = -0.0004\times X^2+0.0282\times X+0.2984$ $Z= -0.0002\times X^2+0.0158\times X+0.5029$	Y=79% X = 35 mg Z = 81%
	Y = Glucose yield (in fraction)	
	Z = Xylose yield (in fraction)	
	X = Enzyme loading in mg(milligram) per gram of cellulose	

Table 4. 15 Hydrolysis Reaction

Pretreatment	**Reactions**	**Conversions**	**ΔHf (cal/mol)**
Dilute Acid	$(\text{Cellulose})_n + n\ H_2O \rightarrow n$ Glucose $(\text{Xylan})_n + n\ H_2O \rightarrow n$ Xylose	0.72 0.71	1004 892
Hot Water	$(\text{Cellulose})_n + n\ H_2O \rightarrow n$ Glucose $(\text{Xylan})_n + n\ H_2O \rightarrow n$ Xylose	0.72 0.71	1004 892
AFEX	$(\text{Cellulose})_n + n\ H_2O \rightarrow n$ Glucose $(\text{Xylan})_n + n\ H_2O \rightarrow n$ Xylose	0.79 0.81	1004 892
Organosolvent	$(\text{Cellulose})_n + n\ H_2O \rightarrow n$ Glucose $(\text{Xylan})_n + n\ H_2O \rightarrow n$ Xylose	0.79 0.81	1004 892
Steam Explosion	$(\text{Cellulose})_n + n\ H_2O \rightarrow n$ Glucose $(\text{Xylan})_n + n\ H_2O \rightarrow n$ Xylose	0.79 0.81	1004 892
Alkaline	$(\text{Cellulose})_n + n\ H_2O \rightarrow n$ Glucose $(\text{Xylan})_n + n\ H_2O \rightarrow n$ Xylose	0.79 0.81	1004 892

Table 4. Component flowrates at the hydrolysis boundary - DAP

Pretreatment	Pretreated Slurry (kg/hr)	Hydroslysed Slurry (kg/hr)
Water	341063	341063
Cellulose	26138	7296
Xylan	423	121
Glucose	3550	22391.6
Xylose	16476	16778
Furfural	705	705
Rest BM	4119	41198
Enzymes	0	954
Total	429553	430507

Table 4. 16 Component flowrates at the hydrolysis boundary - HWP

Pretreatment	Pretreated Slurry (kg/hr)	Hydroslysed Slurry (kg/hr)
Water	474024	474024
Cellulose	22013	6145
Xylan	6526	1866
Glucose	37	15905
Xylose	185	4845
Furfural	272	272
Rest BM	42068	42068
Enzymes	0	803
Total	545125	545929

Table 4. 17 Component flowrates at the hydrolysis boundary – AFEX

Pretreatment	**Pretreated Slurry (kg/hr)**	**Hydroslysed Slurry (kg/hr)**
Water	367343	367343
Cellulose	22942	4694
Xylan	7604	1438
Glucose	0	18248
Xylose	0	6166
Furfural	0	0
Rest BM	38081	38081
Enzymes	0	803
Total	435969	436772

Table 4. Component flowrates at the hydrolysis boundary – ORGANO

Pretreatment	**Pretreated Slurry (kg/hr)**	**Hydroslysed Slurry (kg/hr)**
Water	147568	147568
Cellulose	25401	5197
Xylan	2734	517
Glucose	11549	31753
Xylose	13491	15708
Furfural	49	49
Rest BM	25259	25259
Enzymes	0	889
Total	226051	226940

Table 4. 18 Component flowrates at the hydrolysis boundary – SE

Pretreatment	**PretreatedSlurry (kg/hr)**	**Hydroslysed Slurry (kg/hr)**
Water	112486	112486
Cellulose	6270	1283
Xylan	3263	617
Glucose	261	5249
Xylose	1146	3792
Furfural	0	0
Rest BM	5389	5389
Enzymes	0	219
Total	128816	129035

Table 4. 19 Component flowrates at the hydrolysis boundary – ALKALI

Pretreatment	**Pretreated Slurry (kg/hr)**	**Hydroslysed Slurry (kg/hr)**
Water	886	886
Cellulose	44	9
Xylan	25	5
Glucose	0	35
Xylose	0	20.50
Furfural	0	0
Rest BM	42	42
Enzymes	0	2
Total	996	998

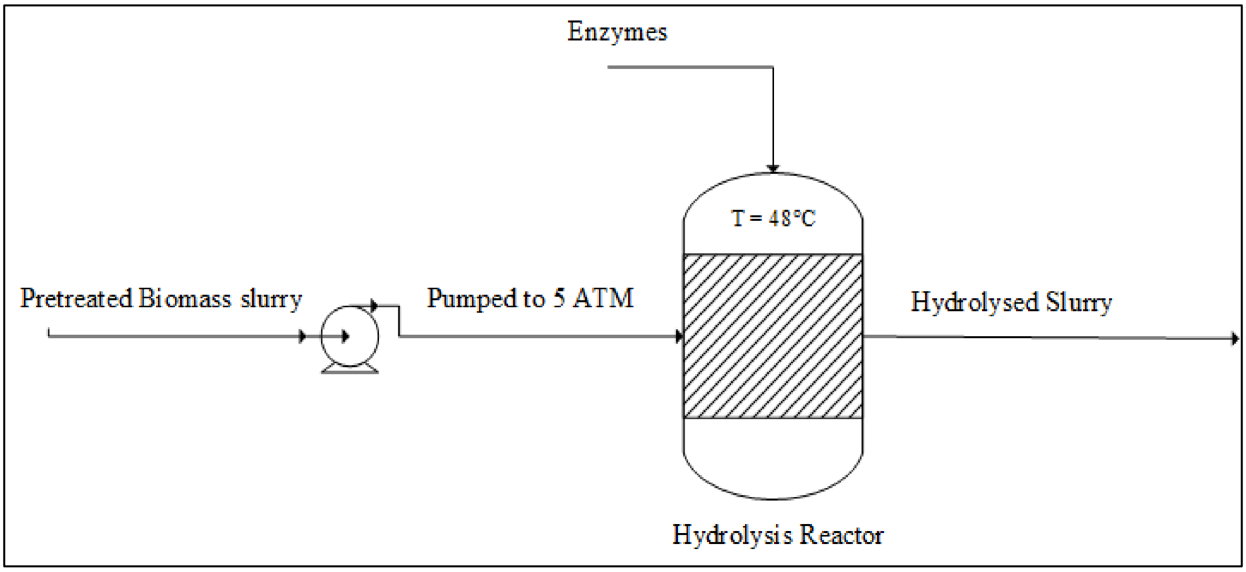

Figure 16 Hydrolysis unit [76]

In this hydrolysis process, the unit is modelled as a single reactor where the pretreated slurry is introduced, and enzymes are additionally added into the reactor. The outlet is also depicted as a single point, showcasing both converted glucose and unconverted biomass slurry mixed with water, as illustrated in Figure 16. The slurry undergoes pressurization to nearly 5 atm before being directed to the hydrolysis reactor, where cellulase enzymes act under 1 atm and controlled temperature of 48°C. The specified hydrolysis time, as per NREL [76], is 84 hours, varies across different literature or experimental datasets. However, in the present work, explicit consideration of residence time is omitted, as the primary goal is to showcase the potential of these processes in terms of bioplastic production from lignocellulosic biomasses. The reactions (Table 4.15) are conversion of glucose and xylose from cellulose and xylan respectively.

Table 4. 20 Mass and Energy balance of Hydrolysis

Stream	Massflow (kg/hr)	C_p (kJ/kg.K)	T1 (K)	T2 (K)	Heat (kW)
DAP					
Pretreated slurry in Enzymes added Hydrolysed slurry out Reaction heat	429553 954 430507	3.543 1.083 3.538	298.15 298.15 321.15	321.15 321.15 298.15	9725 6.7 -9732 138
HWP					
Pretreated slurry in Enzymes added Hydrolysed slurry out Reaction heat	545125 803 545929	3.780 1.083 3.776	298.15 298.15 321.15	321.15 321.15 298.15	13167.5 5.6 -13173 151
AFEX					
Pretreated slurry in Enzymes added Hydrolysed slurry out Reaction heat	435969 803 436772	3.670 1.083 3.665	298.15 298.15 321.15	321.15 321.15 298.15	10224 5.6 -10229 180
ORGANO					
Pretreated slurry in Enzymes added Hydrolysed slurry out Reaction heat	226051 889 226940	3.120 1.083 3.112	298.15 298.15 321.15	321.15 321.15 298.15	4507 6 -4513 163
SE					
Pretreated slurry in Enzymes added Hydrolysed slurry out Reaction heat	128816 219 129035	3.789 1.083 3.784	298.15 298.15 321.15	321.15 321.15 298.15	3119 2 -3120 57
ALKALINE					
Pretreated slurry in Enzymes added Hydrolysed slurry out Reaction heat	996 2 998	3.837 1.083 3.833	298.15 298.15 321.15	321.15 321.15 298.15	24 0.010 -24 0.41

4.3 Fermentation:

Once the sugars (glucose and xylose) are obtained through enzymatic hydrolysis, fermentation takes place. Microorganisms like yeast or bacteria are employed to convert these sugars into ethanol and carbon dioxide. Certain bacteria strains, like some species of the genus Zymomonas or genetically engineered bacteria, possess the ability to ferment sugars into ethanol. This makes them suitable for the fermentation of a broader range of sugars present in biomass. Saccharomyces cerevisiae stands out as the preferred organism for large-scale ethanol production in industry. It represents the most extensive biotechnological application of yeast. This choice is under pinned by a range of favourable industrial characteristics exhibited by Saccharomyces cerevisiae, including rapid growth, effective anaerobic metabolism of glucose, exceptional ethanol productivity, high yield, and robust tolerance to various environmental stressors like ethanol, low pH, and limited oxygen availability. Moreover, yeasts, including Saccharomyces cerevisiae, generally display resilience against bacteriophage infections, which holds particular significance in sizable industrial processes relying on bacteria as the primary production microorganism [113]. Fermentation research at NREL primarily focuses on utilizing the recombinant co-fermenting bacterium Zymomonas mobilis. This microorganism possesses the ability to simultaneously ferment glucose and xylose into ethanol. Additionally, other co-fermenting ethanologens, like engineered strains of Saccharomyces cerevisiae, are being explored both at NREL and in other research settings. Three fundamental fermentation methods employed for ethanol production are batch, fed batch, and continuous fermentation, each possessing distinct advantages and disadvantages. The most commonly utilized fermentation approach is batch fermentation, where a substantial amount of the initial substrate is transformed into a concentrated product before initiating a new batch [114].

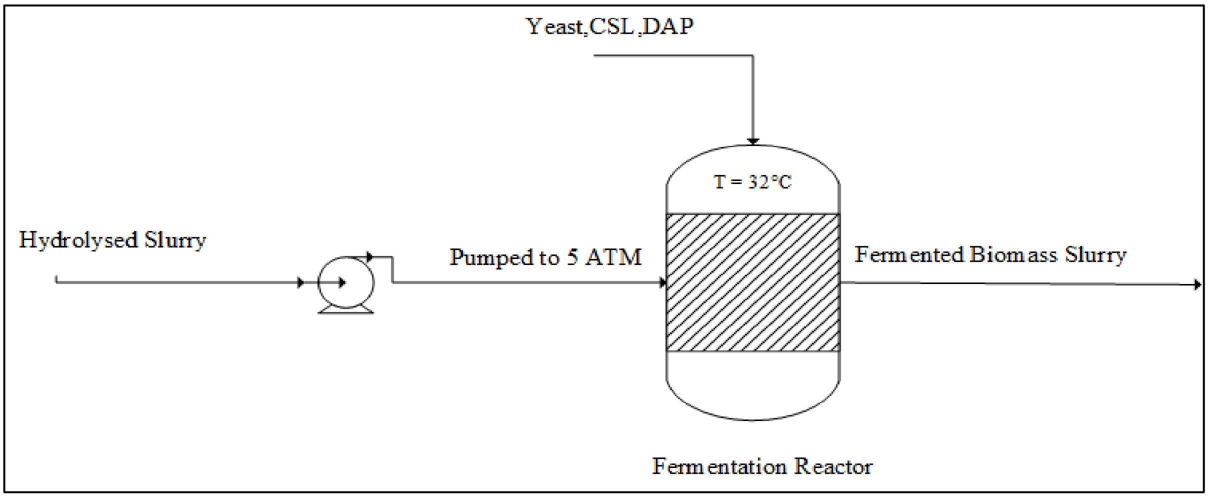

Figure 17 Fermentation unit [76]

Table 4. 21 Reactions and Yeast Loading of Fermentation [76,101]

Reactions [101]	**Conversions**	**ΔHf (cal/mol)**
$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$ $3\ C_5H_{10}O_5 \rightarrow 5\ C_2H_5OH + 5\ CO_2$	0.95 0.60	-20104 -17563.2
Fermentation Input Material	**Loading**	
Corn Steep Liquor Diammonium Phosphate Yeast Broth	0.25% per 1 kg flowrate (hydrolysed slurry) 0.33 g/L of flowrate 0.01% per 1 kg flowrate	

Table 4. 22 Composition of Stream -Fermentation

Stream	**DAP**	**HWP**	**AFEX**	**ORGANO**	**SE**	**ALKALI**
Water	341063	474024	367343	147568	112486	886
Ethanol	16026	9214	10757	20246	3713	23
CO_2	15309	8802	10276	19341	3547	22
Rest BM	59766	55903	50038	40395	9725	70
Total	432164	547943	438414	227549	129472	1001

Reaction (Table 4.23) demonstrates the fermentation of glucose into ethanol with an efficient conversion rate of 95%. Subsequently, fermentation of xylose, which occurs at a slower pace and exhibits a lower yield of approximately 60% [115]. The NREL-based document reports an 85% ethanol yield from xylose fermentation. However, the choice to adopt a 60% yield is based on a comprehensive analysis of numerous experimental studies and diverse pretreatment methodologies [101]. This 60% value aligns more closely with commonly observed outcomes and aims for an optimal target yield. The reason for not selecting the 85% yield from the NREL data stems from the methodology employed in their analysis. The NREL approach doesn't encompass the conversion of xylan to xylose within their hydrolysis stage, although it exists as a realistic component of the process. Instead, this conversion is accounted for within the pretreatment phase. To ensure a more balanced and adaptable perspective, a commonly observed or realistic conversion rate has been chosen. This selected rate can be universally applied to fermentation processes following various pretreatment methods. The utilized model specifically targets the conversion of xylose and glucose to ethanol, maintaining consistency by leaving other components unchanged. Also, in the fermentation process involving yeast, byproducts like succinic acid, glycerol, or xylitol can indeed be produced, although typically in minor quantities compared to ethanol. in this work, when the primary objective is ethanol production, the reactions are often simplified to focus on glucose and xylose conversion to ethanol. Other reactions are either omitted or assumed negligible to streamline the process towards maximizing ethanol yield. This approach facilitates ease of application across different pretreatment scenarios, ensuring the model's adaptability and reliability in evaluating ethanol production. To support microbial growth and the process of ethanol fermentation effectively, it is customary to Fermentation process at a lower temperature range, typically between 30–34 °C [116].The processed slurry, post-hydrolysis, is chilled to a temperature of 32°C to facilitate the fermentation process. A genetically modified strain of Zymomonas mobilis bacteria serves as the ethanologen. This specific Zymomonas mobilis strain possesses the capability to ferment both glucose and xylose concurrently into ethanol. In this scenario, the design focuses solely on modeling a fermentation reactor where the hydrolyzed slurry and yeast are introduced together into the same reactor. In typical industrial-scale operations, including those outlined in the NREL approach, the hydrolyzed slurry is usually bifurcated into two streams for effective cost saving from yeast loading. Approximately 10% of this slurry flow is diverted into seed fermentors, while the remaining fraction is directly channeled to the production vessel. The 10% slurry diverted to the seed fermentors serves as a fermentation base where the ethanologen culture, such as yeast, is introduced and allowed to ferment for a designated period, usually around 24 hours. Overall yeast loading is considered to be 1 g/L [117] of inoculum volume which is in included in yeast culture (ethanologen). This fermentation process occurs in a series of 4 to 5 batch vessels or reactors. The initial vessel is inoculated with yeast, initiating the fermentation process. Subsequently, the fermented broth is transferred to the next reactor, allowing for larger volumes of slurry to undergo fermentation. This cycle continues through the subsequent reactors. Once the 10% slurry in all 5 reactors has completed the fermentation process effectively, it is consolidated and introduced into the larger production vessel as a broth. This fermented broth then acts as the fermenting agent for the remaining hydrolyzed slurry. This multi-step approach significantly enhances efficiency by requiring less ethanologen for the overall fermentation process. Although the calculations are conducted here considering a single reactor, the methodology follows an industrial-based strategy that involves additional seed fermentation.

The estimate of capital costs also considers this industrial-oriented approach for enhanced efficiency in ethanol production. The interaction between the hydrolysed slurry and yeast leads to the conversion of glucose and xylose into ethanol, as described earlier. Additionally, this reaction yields CO_2 alongside ethanol. A summarized overview of the mass and energy balance for this process is provided in Table 4.25. The fermented slurry, comprising ethanol, requires extraction from water, CO_2, and any residual unfermented biomass. Thus, it is directed towards a separation procedure to segregate and extract the ethanol from these constituents.

Table 4. 23 Mass and Energy Balance -Fermentation

DAP	**Streams**	**Massflow (kg/hr)**	**C_p (kJ/kg.K)**	**T1 (K)**	**T2 (K)**	**Heat (kW)**
	Hydrolysed in	430507	3.538	298.15	305.15	2962
	CSL/bacteria/DAP in	1666	1.083	298.15	305.15	4
	fermented out	432164	3.528	305.15	298.15	-2965
	Reaction Heat					-3444
HWP	Hydrolysed in	545929	3.776	298.15	305.15	4009
	CSL/bacteria/DAP in	2015	1.083	298.15	305.15	4
	fermented out	547943	3.766	305.15	298.15	-4013
	Reaction Heat					-2100
AFEX	Hydrolysed in	436777	3.665	298.15	305.15	3113
	CSL/bacteria/DAP in	1644	1.083	298.15	305.15	3
	fermented out	438414	3.656	305.15	298.15	-3117
	Reaction Heat					-2439
ORGANO	Hydrolysed in	226940	3.112	298.15	305.15	1374
	CSL/bacteria/DAP in	916	1.083	298.15	305.15	2
	fermented out	227549	3.108	305.15	298.15	-1376
	Reaction Heat					-4488
SE	Hydrolysed in	129035	3.784	298.15	305.15	950
	CSL/bacteria/DAP in	438	1.083	298.15	305.15	0.92
	fermented out	129472	3.775	305.15	298.15	-951
	Reaction Heat					-800
ALKALI	Hydrolysed in	998	3.833	298.15	305.15	7
	CSL/bacteria/DAP in	3	1.083	298.15	305.15	0.007
	fermented out	1001	3.824	305.15	298.15	-7
	Reaction Heat					-5

4.4 Separation:

The separation process comprises a sophisticated, multi-unit configuration, as per the NREL [76] design specifications. This involves a series of distillation columns, recycling streams, and supplementary units aimed at extracting ethanol. The schematic representation, illustrated in figure 18, showcases the simplified nature of the separation system.

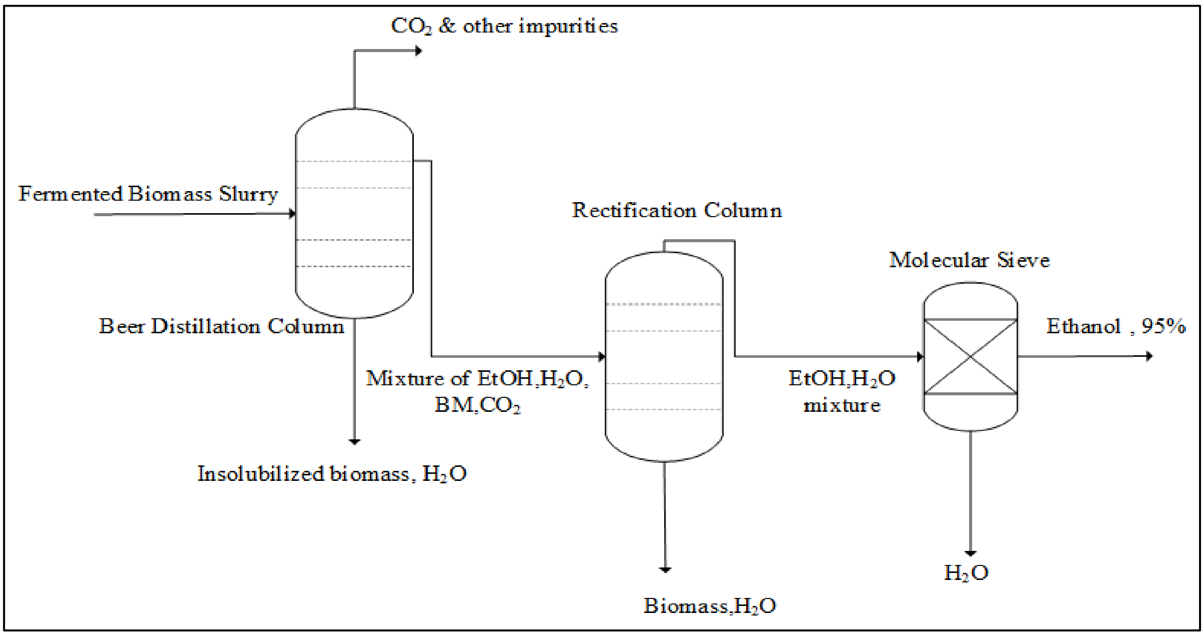

Figure 18 Separation unit [76]

The initial phase involves the beer distillation column, where a significant portion of the insoluble biomass, CO_2, and approximately half of the water content are segregated through distinct lower and upper outlets. The residual mixture is subsequently directed to the rectification column for further refinement. Within this secondary column, a substantial fraction of residual water and remaining biomass constituents are further separated. These consecutive distillation columns collectively yield an ethanol product with an approximate purity range of 75% - 85% for various pretreatments. About 1.22% of the ethanol is lost during its passage through the separation units. In the ethanol separation process, due to the azeotropic nature of the ethanol-water mixture, residual water alongside trace amounts of CO_2 remains post-rectification. To achieve further purification, the ethanol undergoes a dehydration step employing molecular sieve adsorption. Molecular sieves, with tailored pore dimensions, selectively capture larger water molecules while enabling smaller ethanol molecules to pass through. This process, exploiting the molecular size disparity, retains water within the sieve pores while allowing ethanol to pass, yielding ethanol purity ranging from 94% to 95%. These purity levels differ based on various pretreatment stages, rendering the ethanol suitable for subsequent applications, notably in the ethylene production process. The separation ratio of different streams is kept consistent across all pretreatment pathways, resulting in nearly the same proportional amounts of product and waste generated. Therefore, the energy required is calculated accordingly. The separation process, including various pretreatments, is summarized in Tables 4.27-4.32, illustrating mass and energy balances.

Table 4. 24 Separation Fractions of Different Streams and Components

Stream	**Ethanol**	**Water**	**CO_2**	**Rest BM**
Beer distillation column	0.0083	0.9028	0	0.996
CO_2 impurities	0.0030	0.00005	0.950	0
Mix. of EtOH, water, BM, CO_2	0.9886	0.0970	0.049	0.003
Ethanol water mixture	0.9991	0.0589	1	0
Rectification column	0.0008	0.9410	0	1
Ethanol	1	0.05	1	0
Water	0	0.95	0	0

Table 4. 25 Separation Mass and Energy Balance -DAP

Stream	**Mass flow (kg/hr)**	**C_p (kJ/kg*K)**	**T1 (K)**	**T2 (K)**	**Sensible Heat (kW)**	**Latent Heat (kW)**
Fermented BM slurry	432164	3.75	298.15	376.15	35187	
CO_2 impurities	14624	1.14	376.15	333.15	-201	2332
Beer distillation column	367633	3.78	376.15	320.15	-21670	
Mix. of EtOH, water, BM, CO_2	49905	2.45	376.15	390.15	476	23244
Ethanol water Mixture	18533	2.55	390.15	364.15	-342	
Rectification Column	31372	2.38	390.15	387.15	-62	19595
Ethanol	16680	2.56	364.15	311.15	-630	3540
Water	1853	2.38	364.15	311.15	-65	1157
CO_2 impurities	14624	1.14	333.15	298.15	-163	
Beer distillation column	367633	3.78	320.15	298.15	-8513	
Rectification column	31372	2.38	387.15	298.15	-1847	
Water	1853	2.38	311.15	298.15	-16	
Ethanol	16680	2.56	311.15	298.15	-155	

Table 4. 26 Separation Mass and Energy Balance -HWP

Stream	Mass flow (kg/hr)	C_p (kJ/kg*K)	T1 (K)	T2 (K)	Sensible Heat (kW)	Latent Heat (kW)
Fermented BM slurry	547943	3.75	298.15	376.15	44614	
CO_2 impurities	8424	1.14	376.15	333.15	-116	1343
Beer distillation column	483776	3.78	376.15	320.15	-28516	
Mix. of EtOH, water, BM, CO_2	55742	2.45	376.15	390.15	531	25963
Ethanol water mixture	12244	2.55	390.15	364.15	-226	
Rectification column	43498	2.38	390.15	387.15	-86	27168
Ethanol	9669	2.56	364.15	311.15	-365	2052
Water	2575	2.38	364.15	311.15	-90	1608
CO_2 impurities	8424	1.14	333.15	298.15	-94	
Beer distillation column	483776	3.78	320.15	298.15	-11203	
Rectification column	43498	2.38	387.15	298.15	-2560	
Water	2578	2.38	311.15	298.15	-22	
Ethanol	9669	2.56	311.15	298.15	-90	

Table 4. 27 Separation Mass and Energy Balance -AFEX

Stream	Mass flow (kg/hr)	C_p (kJ/kg*K)	T1 (K)	T2 (K)	Sensible Heat (kW)	Latent Heat (kW)
Fermented BM slurry	438415	3.75	298.15	376.15	35696	
CO_2 impurities	9825	1.14	376.15	333.15	-135	1566
Beer distillation column	381623	3.78	376.15	320.15	-22494	
Mix. of EtOH, water, BM, CO_2	46966	2.45	376.15	390.15	448	21875
Ethanol water mixture	13231	2.55	390.15	364.15	-244	
Rectification column	33735	2.38	390.15	387.15	-67	21070
Ethanol	11236	2.56	364.15	311.15	-425	2385
Water	1995	2.38	364.15	311.15	-70	1246
CO_2 impurities	9825	1.14	333.15	298.15	-110	
Beer distillation column	381623	3.78	320.15	298.15	-8837	
Rectification column	33735	2.38	387.15	298.15	-1986	
Water	1995	2.38	311.15	298.15	-17	
Ethanol	11236	2.56	311.15	298.15	-104	

Table 4. 28 Separation Mass and Energy Balance – Organosolvent

Stream	Massflow (kg/hr)	C_p (kJ/kg*K)	T1 (K)	T2 (K)	Sensible Heat (kW)	Latent Heat (kW)
Fermented BM slurry	227549	3.75	298.15	376.15	18527	
CO_2 impurities	18459	1.14	376.15	333.15	-253	2943
Beer distillation column	173661	3.78	376.15	320.15	-10236	
Mix. of EtOH, water, BM, CO_2	35429	2.45	376.15	390.15	338	16502
Ethanol water mixture	21793	2.55	390.15	364.15	-402	
Rectification column	13635	2.38	390.15	387.15	-27	8516
Ethanol	20992	2.56	364.15	311.15	-793	4455
Water	802	2.38	364.15	311.15	-28	501
CO_2 impurities	18459	1.14	333.15	298.15	-206	
Beer distillation column	173661	3.78	320.15	298.15	-4021	
Rectification column	13635	2.38	387.15	298.15	-803	
Water	802	2.38	311.15	298.15	-7	
Ethanol	20992	2.56	311.15	298.15	-195	

Table 4. 29 Separation Mass and Energy Balance – SE

Stream	Mass flow (kg/hr)	C_p (kJ/kg*K)	T1 (K)	T2 (K)	Sensible Heat (kW)	Latent Heat (kW)
Fermented BM slurry	129472	3.75	298.15	376.15	10542	
CO_2 impurities	3391	1.14	376.15	333.15	-47	-541
Beer distillation column	111285	3.78	376.15	320.15	-6560	
Mix. of EtOH, water, BM, CO_2	14796	2.45	376.15	390.15	141	6892
Ethanol water mixture	4486	2.55	390.15	364.15	-83	
Rectification column	10311	2.38	390.15	387.15	-20	-6440
Ethanol	3875	2.56	364.15	311.15	-146	-822
Water	611	2.38	364.15	311.15	-21	-382
CO_2 impurities	3391	1.14	333.15	298.15	-38	
Beer distillation column	111285	3.78	320.15	298.15	-2577	
Rectification column	10311	2.38	387.15	298.15	-607	
Water	611	2.38	311.15	298.15	-5	
Ethanol	3875	2.56	311.15	298.15	-36	

Table 4. 30 Separation Mass and Energy Balance – ALKALI

Stream	**Mass flow (kg/hr)**	**C_p (kJ/kg*K)**	**T1 (K)**	**T2 (K)**	**Sensible Heat (kW)**	**Latent Heat (kW)**
Fermented BM slurry	1001	3.75	298.15	376.15	82	
CO_2 impurities	21	1.14	376.15	333.15	-0.29	-3
Beer distillation column	870	3.78	376.15	320.15	-51	
Mix. of EtOH, water, BM, CO_2	110	2.45	376.15	390.15	1	51
Ethanol water mixture	29	2.55	390.15	364.15	-0.53	
Rectification column	81	2.38	390.15	387.15	-0.16	-51
Ethanol	24	2.56	364.15	311.15	-0.91	-5
Water	5	2.38	364.15	311.15	-0.17	-3
CO_2 impurities	21	1.14	333.15	298.15	-0.24	
Beer distillation column	870	3.78	320.15	298.15	-20	
Rectification column	81	2.38	387.15	298.15	-5	
Water	5	2.38	311.15	298.15	-0.04	
Ethanol	24	2.56	311.15	298.15	-0.22	

4.5 Bioethanol to Bio-Ethylene:

Ethylene is derived from ethanol through a process known as catalytic dehydration. Ethylene is produced from ethanol through a process involving its conversion in catalytic reactors with the help of a Syndol catalyst. This conversion yields ethylene along with water as a by-product, and some unreacted ethanol might remain. To obtain high-quality ethylene suitable for polymer production, the resulting mixture undergoes a purification process that aims to remove most of the ethanol, water, and other impurities, such as carbon dioxide, from the final ethylene product [118]. The process initiates by vaporizing ethanol from the separation unit and elevating its temperature to 425°C.

Table 4. 31 Reaction of Bioethanol to Bio-Ethylene [118]

Primary Reaction	**Overall conversion**	**ΔH_f(cal/mol)**
$C_2H_5OH \rightarrow C_2H_4 + H_2O$	0.97	10920

Table 4. 32 Stream flowrates of different PT Pathways

Stream	DAP (kg/hr)	HWP (kg/hr)	AFEX (kg/hr)	ORGANO (kg/hr)	SE (kg/hr)	Alkaline (kg/hr)
Ethanol from separation (in)	16680	9669	11236	20992	3875	24
Water (out)	5668	3285	3818	7133	1316	8
Water, byproducts (out)	483	280	326	608	112	0.70
CO_2, water, byproducts (out)	1251	725	843	1575	291	2
Pure Ethylene (out)	9278	5378	6250	11676	2155	13

Table 4. 33 Energy Balance of Bioethanol to Bio-Ethylene Unit

Process	Total Heat (kW)
DAP	-10919 9182 3813 (Reaction Energy)
HWP	-6330 5324 2210 (Reaction Energy)
AFEX	-735 6186 2568 (Reaction Energy)
ORGANOSOLVENT	-13741 11554 4799 (Reaction Energy)
SE	-2536 2133 886 (Reaction Energy)
ALKALINE	-16 13 6 (Reaction Energy)

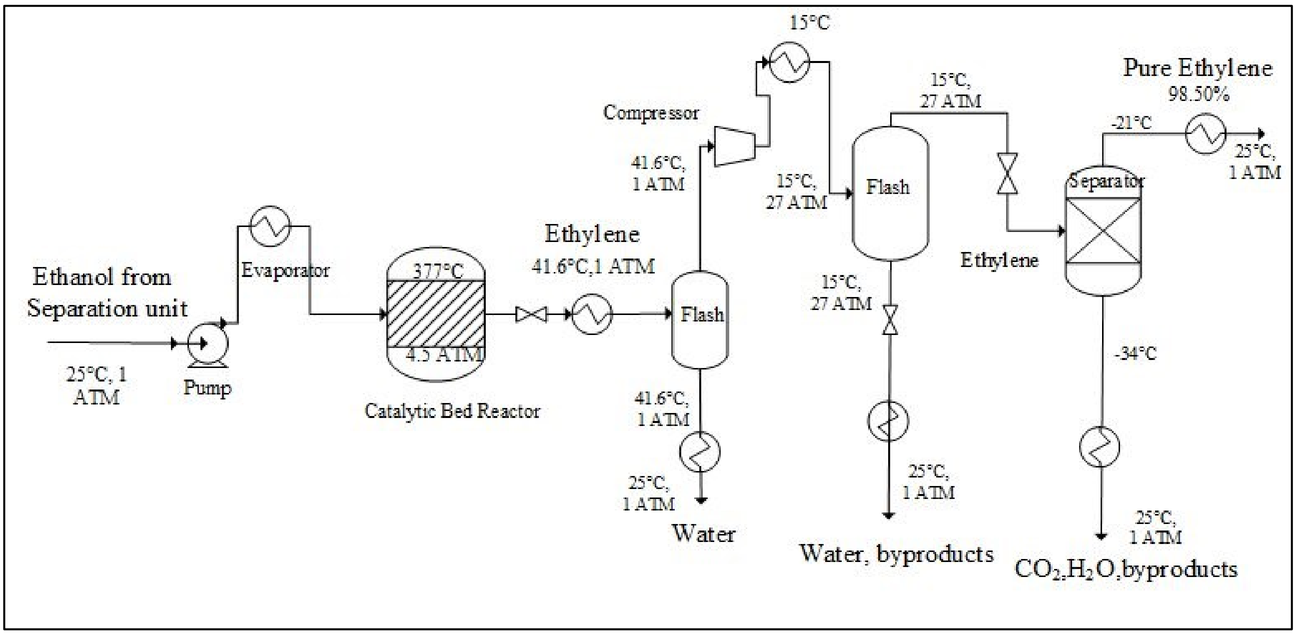

Figure 19 Catalytic dehydration of ethanol [118]

The prepared ethanol is then directed into a fixed-bed catalytic reactor maintained at 377°C and 4.5 atm pressure, where the syndol catalyst facilitates the conversion of ethanol into ethylene. The primary reaction (Table 4.33) achieves an impressive 97% conversion of ethanol into ethylene, while minor side reactions are considered but not written explicitly since it is negligible. Although its energy requirement to do the reaction is considered. After the reactor, the outlet stream undergoes pressure reduction to 1 atm and temperature adjustment to 41°C before entering a flash unit. The process includes separating a significant amount of water and specific by-products that are formed during the reactions.

Further purification involves the pressurization of the remaining water and CO_2 to approximately 27 atm. This pressurized stream is directed through a series of separation columns to primarily remove water. Traditionally, CO_2 removal is executed through a caustic wash column using NaOH. However, in this instance, a simpler separation column is employed to achieve the same goal of CO_2 removal, albeit differently from the literature data. However, the capital cost is determined based on the original plant case, thus incorporating the expense of the CO_2 absorber. Concluding this purification process, nearly pure ethylene, ranging from 98% to 99% purity, is obtained. This highly purified ethylene is now suitable for the conversion into polyethylene.

4.6 Bio-Ethylene to Bio-Polyethylene:

Ethylene polymerization is a chemical process where ethylene molecules are bonded together to form polymer chains, creating polyethylene. This reaction is typically catalyzed by specific catalysts or catalyst systems.

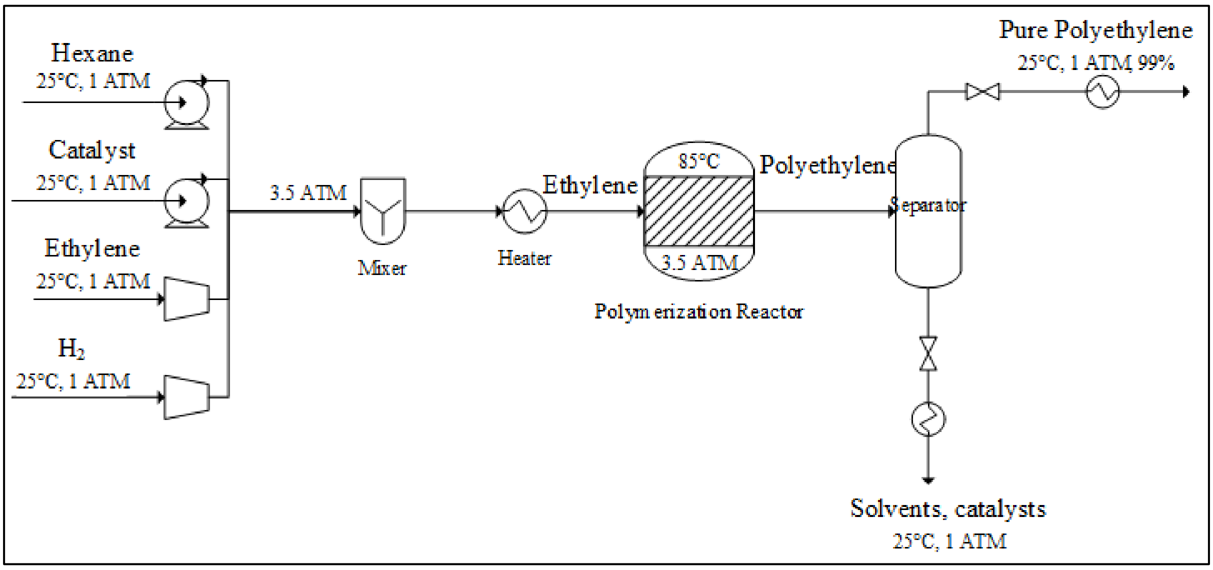

Figure 20 Ethylene polymerization [119]

Ethylene, a simple hydrocarbon gas, undergoes a chain-growth polymerization reaction where the double bond in the ethylene molecule is broken, allowing the carbon atoms to link together in long chains. This reaction can occur using various methods and catalysts, resulting in different types of polyethylene with varying properties and applications, such as high-density polyethylene (HDPE) or low-density polyethylene (LDPE), widely used in the production of plastics, packaging materials, and various other products due to their flexibility, durability, and versatility.

The ethylene polymerization process, particularly the HDPE slurry phase reaction, usually involves using a sequence of reactors such as CSTRs or PFRs, dividing the slurry between them. However, this simplified model aims to conduct fundamental mass and energy balances without delving into detailed process design. The flow diagram in Figure 20 is modelled to just for simple representation derived from Zhang et al [119] which originally differs from actual processes.

In this process, pure ethylene is combined with catalysts, co-catalysts, solvent hexane, and reaction agent hydrogen. One catalyst-co-catalyst pair involves a Ziegler-Natta catalyst, a blend of $TICl_4$ and TEA (triethylaluminium) in a 50% proportion. These components are pressurized to 3.5 atm and 85°C, meeting the reactor's required conditions, and then directed into the reactor for polymerization—a chain reaction.

Due to the chain reaction of the polymerization mechanism and its specific approach, it is not explicitly modelled here, its complexity is acknowledged. Nevertheless, the primary goal remains centered on basic mass and energy requirements/balances. Following the reaction, a flash process separates a small amount of solvent and catalyst used, yielding pure polyethylene as the final products. However, the average energy released in an exothermic reaction is determined by the heat of reaction (ΔH_f=22285 cal/mol) associated with the polymerization of ethylene [120].

Table 4. 34 Mass and Energy Balance of Bio-Polyethylene

PT	Stream (In/out)	Massflow (kg/hr)	Heat (kW)
DAP	Ethylene	9278	-437 416 -8572 (Reaction energy)
	Catalyst	238	
	H_2	3	
	Hexane	43.14	
	Polyethylene	9278	
	Waste	284	
HWP	Ethylene	5378	-253 241 -4969 (Reaction energy)
	Catalyst	138	
	H_2	1.50	
	Hexane	25	
	Polyethylene	5378	
	Waste	165	
AFEX	Ethylene	6250	-294 280 -5774 (Reaction energy)
	Catalyst	160	
	H_2	2	
	Hexane	29	
	Polyethylene	6250	
	Waste	191	
ORGANO	Ethylene	11676	-550 523 -10788 (Reaction energy)
	Catalyst	300	
	H_2	3	
	Hexane	54	
	Polyethylene	11676	
	Waste	357	
SE	Ethylene	2155	-101 97 -1991 (Reaction energy)
	Catalyst	55	
	H_2	0.60	
	Hexane	10	
	Polyethylene	2155	
	Waste	66	
ALKALI	Ethylene	13	-0.63 0.60 -12 (Reaction energy)
	Catalyst	0.35	
	H_2	0.004	
	Hexane	0.06	
	Polyethylene	13	
	Waste	0.41	

4.7 Process Economics:

The total capital investment (TCI) for the plant is primarily determined using the reference and methodology provided by the National Renewable Energy Laboratory (NREL) [76]. This comprehensive calculation includes both variable and fixed capital costs, along with variable operating costs, which are essentially the prices of raw materials. The TCI is predominantly derived from the Installed Equipment Cost based on relative references. Equipment costs are calculated using a scaling formula [121] based on flowrate:

$$CB = CA \times \left(\frac{S_B}{S_A}\right)^{0.6} \tag{1}$$

Where *CB* represents the estimated cost of the current plant. *CA* represents the known cost of the reference plant. S_B represents the flow rate capacity of the current plant. S_A represents the flow rate capacity of the reference plant. Furthermore, historical prices are adjusted using the CEPCI (Chemical Engineering Plant Cost Index) index. This serves as a benchmark for adjusting historical capital costs associated with constructing chemical plants to current values, considering fluctuations in inflation and deflation [122]. The capital costs of the plant reflect substantial investments in advanced machinery and automation, illustrating a capital-intensive approach. Fixed operating expenses (fixed OPEX) are considered negligible due to the significant economies of scale achieved at this production level. Additionally, the plant's focus on operational efficiency and automation has shifted the cost structure towards capital expenditures, diminishing the relative importance of ongoing fixed operating expenses. As a result, this distinctive cost profile underscores the significance of capital costs and variable operating expenses (variable OPEX) in shaping the overall financial landscape of the large-scale production facility. In the context of our large-scale production plant model, the capital costs primarily revolve around ISBL (Inside Battery Limits) expenditures, encompassing core process units and associated infrastructure directly contributing to production. ISBL costs include equipment, piping, instrumentation, and control systems necessary for the core production process. ISBL is essential for accurately estimating the total cost of constructing and operating a plant, providing a comprehensive understanding of the financial requirements and ensuring effective budgeting and planning throughout the project lifecycle [123]. Auxiliary units such as storage tanks and boilers, while essential for supporting operations, are typically excluded from ISBL costs as they are not directly involved in the core production process.

In evaluating the raw material costs for the polyethylene production process, a meticulous approach was undertaken to ensure accuracy and reliability. Initially, raw material costs sourced from the National Renewable Energy Laboratory (NREL) were updated to reflect the year 2023 using the Producer Price Index (PPI) where applicable. In cases where PPI data was unavailable, adjustments were made based on inflation rates to provide a rough estimate. Additionally, to supplement the data, raw material costs were cross-referenced and validated through reputable online sources such as ChemAnalyst [124].

Waste disposal costs were estimated using guidelines outlined in "Analysis, Synthesis and Design of Chemical Processes" by Richard Turton et al [121], recognized for its comprehensive coverage of chemical process engineering principles. Enzymes are cost-influencing factor due to their high cost. To adjust for this cost from the base year to recent prices, NREL reference is utilized [90], incorporating the Producer Price Index (PPI) for agriculture/corn prices.

Table 4. 35 Capital Cost Evaluation [76]

Types of Costs		**Calculations of Cost**
Total Equipment Cost (TEC)	Pretreatment	Installed Equipment Cost
	Hydrolysis	Installed Equipment Cost
	Fermentation	Installed Equipment Cost
	Separation	Installed Equipment Cost
	Boiler	Installed Equipment Cost
	Storage	Installed Equipment Cost
ISBL cost	Sum of installed equipment cost of (PT, Hydrolysis, Fermentation, Separation)	
Sum of ISBL cost	Warehouse	4% of ISBL cost
	Site Development	9% of ISBL cost
	Additional Piping	4.5% of ISBL cost
Total Direct Cost (TDC)	TEC + sum of ISBL cost	
Total Indirect Cost (TIC)	Proretable Expenses	10% OF TDC
	Field Expenses	10% OF TDC
	Home Office & Construction Fees	20% OF TDC
	Project Contingency	
	Other Cost (Startup Permits Etc.)	10% OF TDC
		10% OF TDC
Fixed Capital Investment (FCI)	TDC + TIC	
Working Capital (WC)		5% of FCI
Total Capital Investment (Variable CAPEX)	FCI+WC	
Fixed CAPEX	Cost of Land	

Table 4.37 contains applied methodology to calculate capital costs whereas Table 4.38 contains summary of capital costs calculated using methodology (Table 4.37) for referenced feedstock capacity.

Table 4. 36 Summarized Capital Cost

DAP	Feedstock – 104167 (kg/hr) $ MM	SE	Feedstock - 27215 (kg/hr) $ MM
PT	170.10	PT	53.32
Hydrolysis	46.80	Hydrolysis	20.92
Fermentation	46.80	Fermentation	20.92
Separation	79.80	Separation	35.67
HWP	Feedstock - 128250 (kg/hr) $ MM	Alkaline	Feedstock -152 (kg/hr) $ MM
PT	101.87	PT	2.37
Hydrolysis	53.02	Hydrolysis	0.93
Fermentation	53.02	Fermentation	0.93
Separation	90.41	Separation	1.59
AFEX	Feedstock – 128273 (kg/hr) $ MM	Organosolvent	Feedstock - 106200 (kg/hr) $ MM
PT	173.48	PT	168.74
Hydrolysis	53.03	Hydrolysis	47.35
Fermentation	53.03	Fermentation	47.35
Separation	90.42	Separation	80.73
Ethylene Production Unit	Feedstock – 16680 (kg/hr)	Polyethylene Production Unit	Feedstock – 2280 (kg/hr)
	23.25 $ MM		0.747 $ MM
Boiler (Utility)	Capacity - 222.32 MW 67.34 $ MM		

Table 4. 37 Summarized Raw Material & Waste Cost [76,125,126]

Raw Material	Price (USD/kg)
Feedstock (Wet) / Corn Stover	0.069
Sulfuric Acid	0.090
93% Ammonia	0.415
Corn Steep Liquor	0.5
DAP (Diammonium Phosphate)	0.51
Makeup Water	0.00026
Ethanol Solvent	0.591
HCl	0.13
NaOH	0.57
Enzymes	0.849
Electricity	0.168
Yeast	8.91
Zigler Natta Catalyst	2.03
Hexane	1.17
H_2	1.26
Biogas Methane	0.0038
Syndol Catalyst	24.17

Categorised Waste	Price (USD/kg)
Hazardous Waste	0.358
Waste Water with Chemicals	0.00007697
Waste Water with Minor Toxicity	0.00010024
Primary Wastewater	0.00007339
Non-Hazardous Waste	0.06444

4.7.1 Methodology for Minimum Selling Price (MSP) Determination:

To calculate the minimum selling price (MSP) of polyethylene, we employ a methodology that involves various financial metrics [127]. The product revenue (PR) include income from polyethylene sales is determined at the breakeven point, where it equals the total cost of the plant. Total revenue encompasses the income generated from the sale of the product, polyethylene. The total cost comprises operating costs, return on investment (ROI), and income tax. The ROI is computed using the following formula [127]:

$$ROI = \frac{DR \times (1+DR)^{ELS}}{(1+DR)^{ELS}-1} \times TCI \tag{2}$$

Here, the discount rate (DR) is assumed to be 6.74%, and the equipment life span (ELS) is 20 years, using the same assumptions as the NREL models [76]. Operating costs (OC) of pretreatments are further given in Table 5.1-5.6. After computing the ROI, revenue is determined using the following equations. Income tax (IT) is calculated assuming a tax rate (TR) of 35%.

$$IT = TR \times (PR - OC - DC) \tag{3}$$

$$PR = OC + ROI + IT \tag{4}$$

Depreciation cost (DC) is computed using the basic formula [128]:

$$Depreciation = \frac{fixed\ capital\ inverstment - salvage\ value}{Equipment\ life\ span\ (years)} \tag{5}$$

In the present case, the decision to set salvage value as zero is based on the understanding that salvage value constitutes a negligible fraction compared to the Fixed Capital Investment (FCI) [121]. Then, using the breakeven point formula, minimum selling price (MSP) is calculated and reported further in results and evaluations.

5. Results and Evaluations:

The database containing various pretreatment methods and their associated calculations of material and energy balance, and estimated cost was imported into the MILP framework to facilitate Mixed Integer Linear Programming (MILP) modelling. Initial tests were conducted to verify the functionality of the tool, utilizing actual flow rates obtained from different references for accurate simulation. Subsequently, the models were tested to achieve a consistent product flow rate of 10,000 kg/hr of polyethylene. Six distinct pathways were analyzed, each differing primarily in their pretreatment unit. Material and energy consumption data for each process was recorded during testing shown in Table 5.1-5.6. Additionally, the Grand Composite Curve (GCC) data depicting the energy integration potential of the different pretreatment models is provided below, illustrating their respective efficiencies and contributions to the overall process.

5.1 Material Usage and Waste Generation Across Pathways from MILP results:

Table 5. 1 Flow Input and Output of Polyethylene Production via DAP

Raw material (kg/hr)		Products and Waste (kg/hr)		Cost	$ USD
Biomass	90685	Polyethylene	10000	CAPEX	416 MM
Water	410042	Waste	497219	OPEX	165 MM/yr
H_2SO_4	2193	CO_2 emission (Boiler)	13614		
Ammonia	1143	Waste water (Boiler)	11136		
Enzymes	1038				
Yeast	149				
DAP	493				
CSL	1171				
Catalyst Syndol	80				
Hexane	46.53				
H_2	2.81				
CAT	257				
Energy (kW)					
Electricity	22383				
Bio Gas (Boiler fuel)	23649				

Table 5. 2 Flow Input and Output of Polyethylene Production via HWP

Raw material (kg/hr)		Products and Waste (kg/hr)		Cost	$ USD
Biomass	130979	Polyethylene	10000	CAPEX	592 MM
Water	889907	Waste	1018984	OPEX	263 MM/yr
Ammonia	2503	CO_2 emission (Boiler)	5426		
Enzymes	1508	Waste water (Boiler)	4439		
Yeast	284				
DAP	937				
CSL	2562				
CAT	257				
Hexane	46.53				
H_2	2.81				
Catalyst Syndol	80				
Energy (kW)					
Electricity	55975				
Bio Gas (Boiler fuel)	9426				

Table 5. 3 Flow Input and Output of Polyethylene Production via AFEX

Raw material (kg/hr)		**Products and Waste (kg/hr)**		**Cost**	**$ USD**
Biomass	110869	Polyethylene	10000	CAPEX	629 MM
Water	647288	Waste	755122	OPEX	211 MM/yr
Ammonia	2706	CO_2 emission (Boiler)	4835		
Enzymes	1297	Waste water (Boiler)	3955		
Yeast	208				
DAP	685				
CSL	1764				
CAT	257				
Hexane	46.53				
H_2	2.81				
Catalyst Syndol	80				
Energy (kW)					
Electricity	31813				
Bio Gas (Boiler fuel)	8399				

Table 5. 4 Flow Input and Output of Polyethylene Production via Organosolvent

Raw material (kg/hr)		**Products and Waste (kg/hr)**		**Cost**	**$ USD**
Biomass	76423	Polyethylene	10000	CAPEX	336 MM
Water	487675	Waste	582597	OPEX	240 MM/yr
H_2SO_4	1337	CO_2 emission (Boiler)	9618		
Ammonia	1079	Waste water (Boiler)	7867		
Enzymes	768				
Yeast	70				
DAP	231				
CSL	490				
Solvent-Ethanol	24225				
Hexane	46.53				
H_2	2.81				
CAT	257				
Catalyst Syndol	80				
Energy (kW)					
Electricity	5297				
Bio Gas (Boiler fuel)	16707				

Table 5. 5 Flow Input and Output of Polyethylene Production via SE

Raw material (kg/h)		Products and Waste (kg/h)		Cost	$ USD
Biomass	76511	Polyethylene	10000	CAPEX	690 MM
Water	705576	Waste	775472	OPEX	152 MM/yr
Enzymes	1028	CO_2 emission (Boiler)	50153		
Yeast	126	Waste water (Boiler)	41025		
DAP	416				
CSL	1511				
CAT	257				
Hexane	46.53				
H_2	2.81				
Catalyst Syndol	80				
Energy (kW)					
Electricity	4146				
Bio Gas (Boiler fuel)	87122				

Table 5. 6 Flow Input and Output of Polyethylene Production via Alkali

Raw material (kg/h)		Products and Waste (kg/h)		Cost	$ USD
Biomass	91194	Polyethylene	10000	CAPEX	4364 MM
Water	711533	Waste	796982	OPEX	143 MM/yr
HCl	41	CO_2 emission (Boiler)	4833		
Enzymes	1145	Waste water (Boiler)	3953		
Yeast	154				
DAP	511				
CSL	1870				
Hexane	46.53				
H_2	2.81				
CAT	257				
NaOH	228				
Catalyst Syndol	80				
Energy (kW)					
Electricity	5654				
Bio Gas (Boiler fuel)	8396				

In this study, a Mixed Integer Linear Programming (MILP) model was developed to optimize the production of polyethylene from plastic, targeting a production flow rate of 10,000 kg/hr of polyethylene. All values are presented in USD dollars. A comparison of the capital expenditure (CAPEX) and operational expenditure (OPEX) revealed notable differences among the pathways. Among the six pathways evaluated for polyethylene production from biomass. DAP pathway has promising results of

$ 416 MM CAPEX and $ 165 MM/yr OPEX.HWP and AFEX pathways exhibit intermediate CAPEX figures $592 MM and $629 MM respectively. HWP has a higher operational cost of $ 263 MM/yr compared to other pathways. The operational cost of AFEX is $211 MM/yr. Organosolvent exhibits economical CAPEX of $ 336 MM and operating expenditure of 240 MM/yr. Alkaline demonstrates the most economical operational expenditure at $143 MM/yr, closely followed by SE ($152 MM/yr), while capital cost of alkali is $4364 MM and SE is $ 690 MM However, it's crucial to note that SE and Alkali pathways may require further refinement and analysis due to their disproportionately high CAPEX figures, as no data were available for units at industrial scale.

In terms of biomass feedstock consumption to produce 10,000 kg/hr of ethanol, organosolvent and steam explosion processes exhibit the lowest utilization, requiring 76,423 kg/hr and 76,511 kg/hr, respectively. Following closely, the DAP process ranks third with a consumption rate of 90,685 kg/hr, while the alkali process requires slightly more at 91,194 kg/hr. Moving up the scale, the AFEX process necessitates 110,869 kg/hr of feedstock, while the highest consumption is observed in the HWP process at 130,979 kg/hr. From an economic standpoint, when considering the minimum feedstock utilized, organosolvent and steam explosion methods emerge as the most economical options, whereas HWP stands out as comparatively costly. This diverse range of feedstock requirements across various pretreatment methods not only highlights their distinctive efficiencies but also offers valuable insights into decision-making regarding pathway selection based on feedstock availability or pricing dynamics.

5.2 Minimum Selling Price (MSP) of Product Polyethylene:

Table 5. 7 Minimum Selling Price of Polyethylene

Process	Cost (USD/kg)
DAP	2.69
HWP	4.14
AFEX	3.63
ORGANO	3.39
SE	3.07
ALKALI	10.07

From the results, it's evident that the Minimum Selling Price (MSP) is lowest for the DAP pathway compared to all other pathways. This is calculated at the breakeven point, where the total revenue equals the total cost of the plant. Thus, the total cost or revenue for the DAP pathway is approximately $236 MM/yr, which translates to 2.69 USD/kg, considering operational yearly hours of 8760 for the 10,000 kg/hr of product PE. Starting with SE (3.07 USD/kg) as the second most affordable option, the sequence progresses with Organosolvent and further down to AFEX, HWP, and lastly alkali, which represents the highest MSP among the considered pathways.

5.3 Capital Cost Analysis:

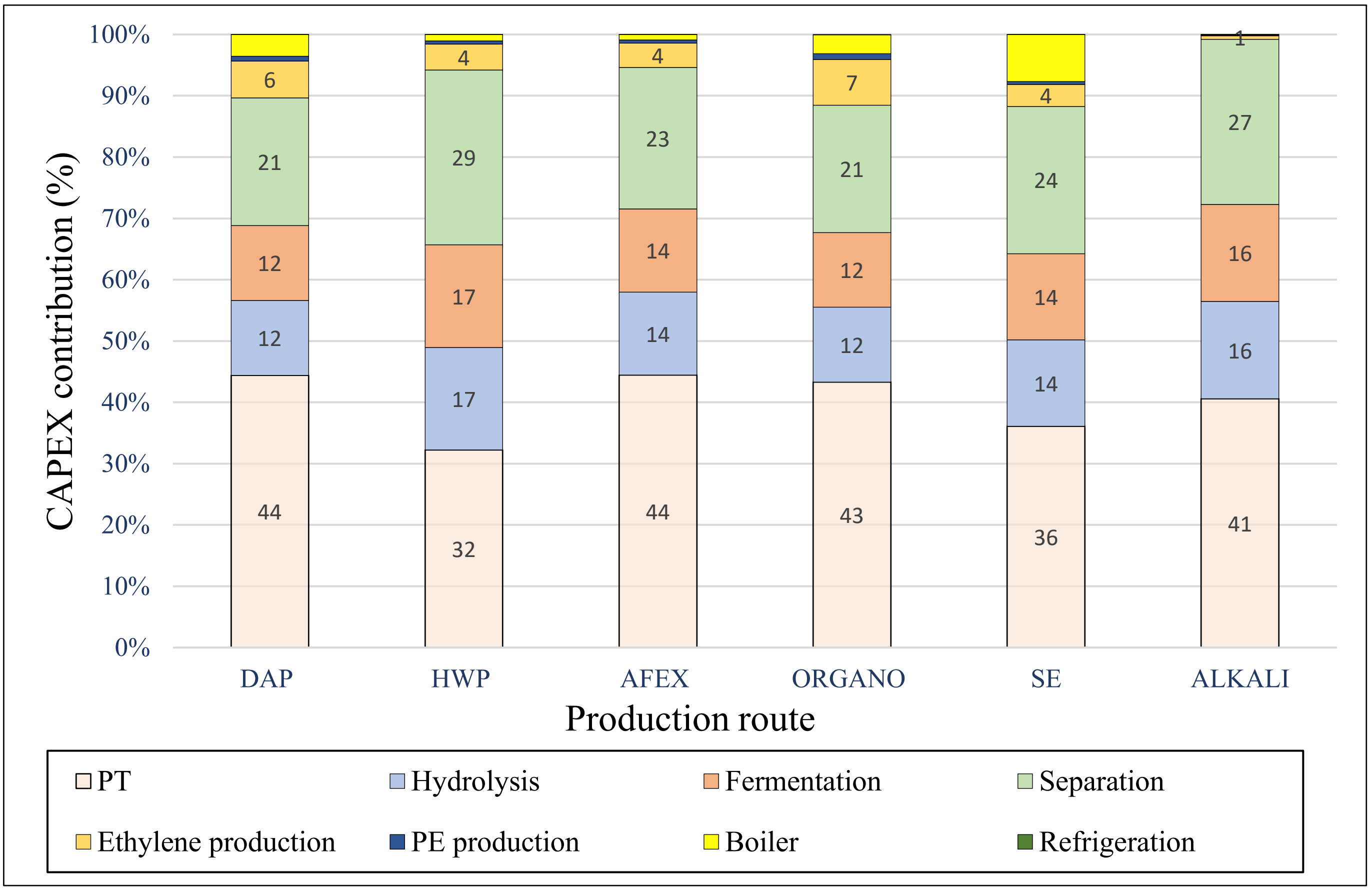

Figure 21 CAPEX contribution by production route

The capital costs for the production of polyethylene at a scale of 10,000 kg/hr exhibit (Figure 21) a consistent trend is observed across most pretreatment pathways, with pretreatment and subsequent separation dominating the majority of expenses. Notably, HWP and SE pretreatments exhibit lower CAPEX contributions at 32% and 36%, respectively, compared to other pathways. Conversely, AFEX and DAP allocate nearly 44% each of their total capital expenses to pretreatment, showcasing highest pretreatment expense among all options. Hydrolysis and fermentation, being unit operations with similar layouts, primarily differ in the supply of enzymes or yeast. Consequently, both are designed using separate hydrolysis and fermentation (SHF) processes, leading to similar capital costs. The capital cost of utilities, particularly boiler expenses, varies significantly across different pathways, ranging from 0.12% for alkaline to 7.64% for SE. DAP, HWP, and organosolvent allocate 3.51%, 1%, and 3.11% of their CAPEX, respectively, to boiler expenses. Refrigeration also demonstrates its contribution, in minor percentages ranging from 0.02% to 0.002%, depending on the specific pretreatment pathway. Breaking down capital costs by utility units provides a detailed understanding of where investments are concentrated within each pretreatment pathway. This breakdown helps in identifying potential areas for cost optimization, comparing and selecting potential pathways, and improving economic viability.

5.4 Operating Cost Analysis:

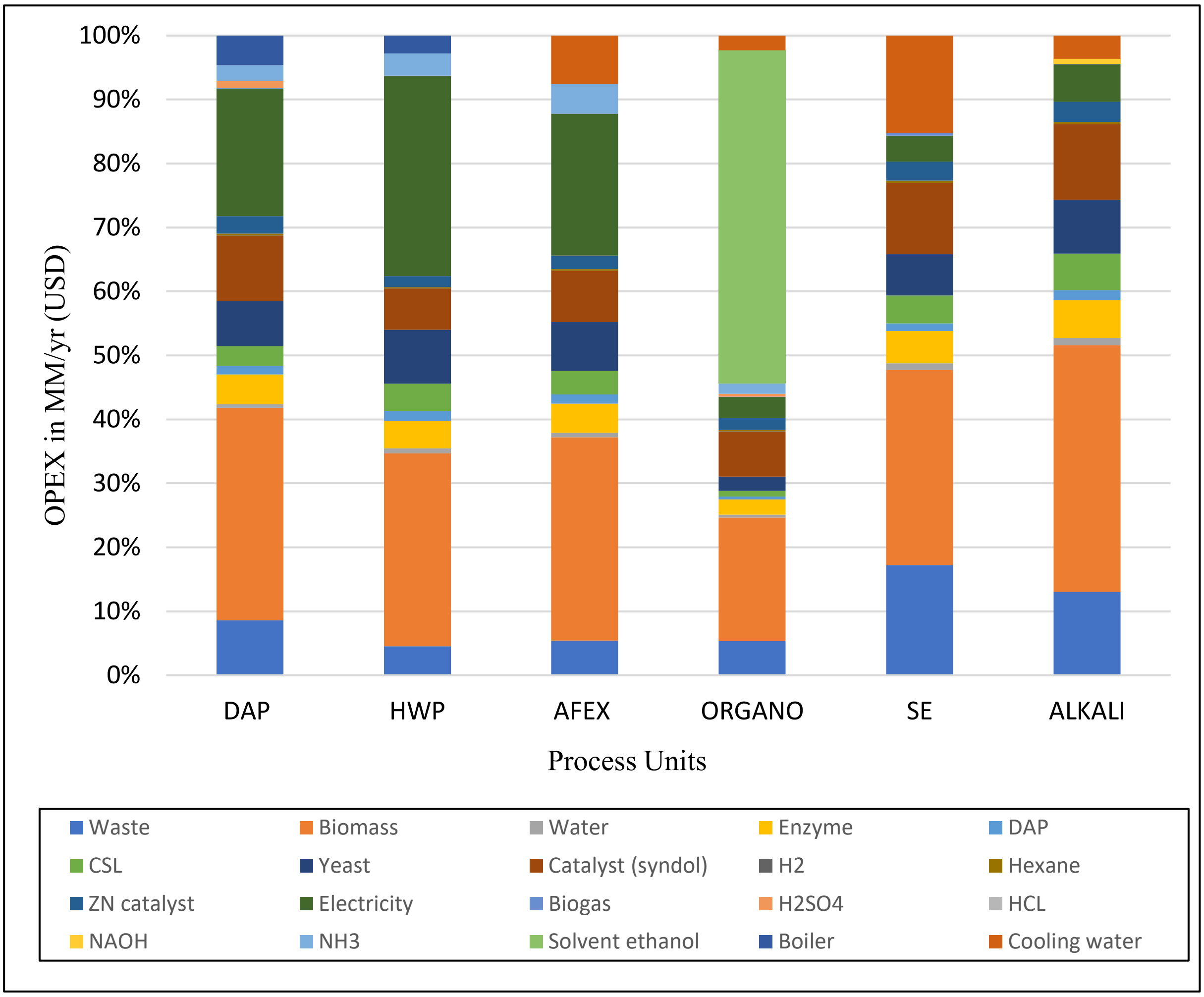

Figure 22 OPEX contribution by production route

Figure 22 illustrates the distribution of operating cost contributions for each feedstock. Across various pretreatment pathways, biomass feedstocks typically account for approximately 30% of the operating cost, except for organosolvent, where it comprises 19% of the total operating expenditure. Following biomass, costs associated with catalysts like syndol, yeast, enzymes, and CSL can also constitute a considerable percentage of the overall expenditure, although these proportions vary from one process to another. Furthermore, the graph highlights the operating costs for utilities, including boiler usage and cooling water accounting for different proportions depending on the process. Additionally, it aggregates the expenses related to waste product disposal under the label "waste," which typically represents a contribution ranging from 8 to 15% of the total operating cost, depending on the chosen pretreatment pathway. Considering that the separation yields the same amount of product, the feedstock required for ethanol and ethylene production remains constant across all six pathways. However, the electricity price contribution varies significantly among these pathways, with HWP utilizing 31% of its operating expenditure (OPEX) for electricity, the highest among them, while SE consumes the least electricity, contributing only 4% of its OPEX. This disparity in feedstock price contribution facilitates informed decision-making regarding feedstock selection, contributing to more effective resource allocation and improved economic analysis.

5.5 Analysing MSP Sensitivity to Variable Electricity Cost:

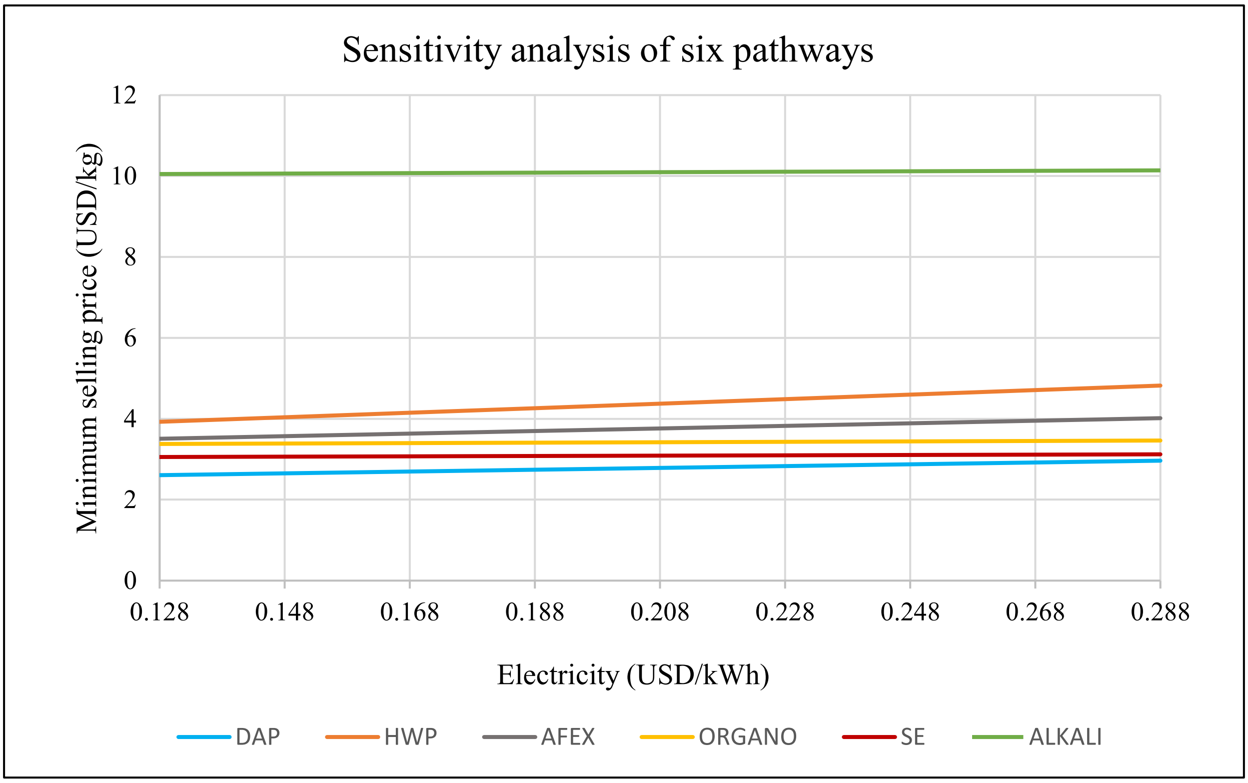

Figure 23 MSP sensitivity to electricity cost

Sensitivity analysis assesses how changes in input parameters affect the output of a model or system. In this study, it evaluates the impact of varying electricity costs on the Minimum Selling Price (MSP) across different production pathways. The sensitivity analysis conducted on MSP versus electricity cost (Figure 23) reveals significant insights into the economic dynamics of six different production pathways. As depicted in Figure 23, increasing electricity prices correspond to a steady and linear increase in MSP across all six pathways. The DAP pathway exhibits the lowest MSP, ranging from 2.60 USD/kg at an electricity rate of 0.128 USD/kWh to 3.12 USD/kg at 0.288 USD/kWh. Conversely, the alkaline pathway demonstrates the highest MSP, ranging from 10.04 to 10.14 USD/kg. The trends observed for other pathways follow a similar pattern, with SE showcasing the second cheapest MSP, followed by organosolvent, AFEX positioned in the middle, and HWP emerging as the second highest

MSP pathway after alkaline. This analysis showcases the importance of electricity costs in determining price of product for each production pathway; however, several pathways show higher sensitivity to electricity price than others according to the different process needs. Additionally, the variability in MSP based on electricity prices at different locations underscores the importance of considering regional energy dynamics in production planning and decision-making processes.

5.6 Pathway Heat Integration Using GCC Curves:

In the field of chemical engineering, the Grand Composite Curve (GCC) serves as a vital tool for analysing the heat dynamics within a process. These are obtained through the heat cascade formulation embedded in the MILP model, encompassing all process units and providing the theoretical minimum for energy required for the process. These GCC curves serve as powerful tools to analyze and optimize the thermal performance of each pathway variant, considering the diverse pretreatment methods employed. Through analysis, the results derived from the integrated GCC curves offer valuable insights into the efficiency and effectiveness of heat integration strategies, thereby informing decision-making processes and guiding further advancements in polyethylene production technologies. The GCC provides a clear depiction of heat sources and sinks. In this study on optimizing polyethylene production from biomass, the GCC reveals that all the pathway technologies generate excess heat, indicating an exothermic nature. This surplus heat presents opportunities for optimizing energy usage through connections with other biorefinery processes or with nearby heat demands. As we examine the GCC curves specific to each pretreatment technology, we aim to identify regions where excess heat is available. These "heat pockets" represent potential areas for integrating heat engines to convert thermal energy into mechanical work or heat pumps to elevate temperatures for various process requirements. The GCC graphs suggest opportunities for heat integration, although not implemented in this thesis. Investigating these prospects in future work could yield valuable insights for optimizing energy usage and improving process efficiency.

5.6.1 DAP Pathway:

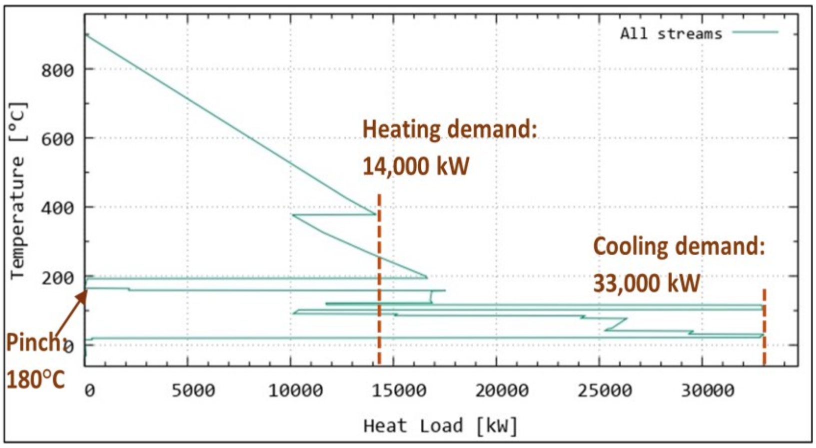

Figure 24 Grand composite curve of DAP pathway

The Grand Composite Curve (GCC) for dilute acid pretreatment, depicted in Figure 22 outlines the process' energy requirements and opportunities for heat integration. The graph reveals a minimum heating requirement of 14,000 kW, provided by a boiler operating at 900°C, and a cooling requirement of 33,000 kW, met by cooling water around 25°C. Notably, the pinch point, situated at approximately 180°C, exhibits a distinctive nose-like shape, with a secondary point at 200°C. This configuration offers a compelling opportunity for energy savings, particularly in providing substantial heating and cooling demand for a small temperature differential. Implementation of a heat pump within the temperature range of 180°C to 200°C could effectively capitalize on this potential. Additionally, the exothermic nature of the process, with a heat source of approximately 33,000 kW at above 25°C, presents an opportunity for utilizing an Organic Rankine Cycle (ORC) to harness waste heat and convert it into electricity. The generated electricity could then be used within the process or sold to another process sectors, thereby offering significant cost savings and enhancing economic viability.

5.6.2 HWP Pathway:

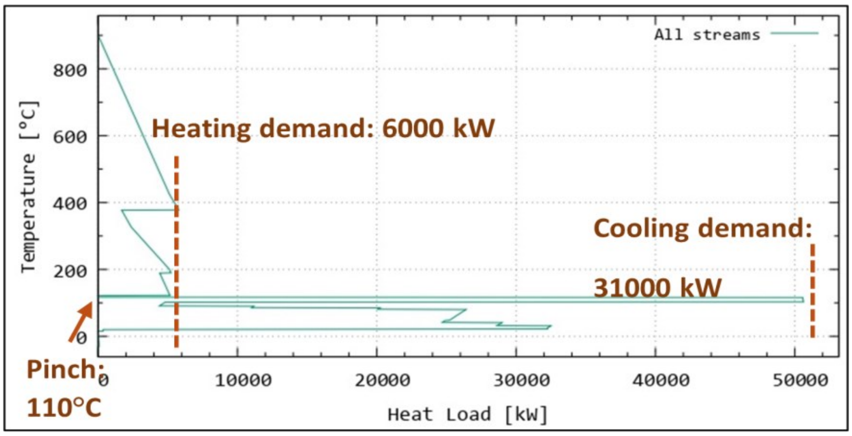

Figure 25 Grand composite curve of HWP pathway

The GCC of the HWP process (Figure 23) reveals a minimum cooling requirement of 31,000 kW and a heating requirement of approximately 6000 kW. The presence of self-sufficient pocket above the pinch point, particularly in the temperature range from 110°C to 380°C, suggests endothermic heat sink requirements are internally met without external heating sources. Below the pinch point on the GCC graph, a heat pump can be strategically placed to upgrade heat from 100°C to 110°C using a small amount of electricity, which would reduce both heating and cooling requirements by approximately 1000 kW. Further opportunities for heat integration are limited to low temperatures, which could be suitable for space heating in nearby installations.

5.6.3 AFEX Pathway:

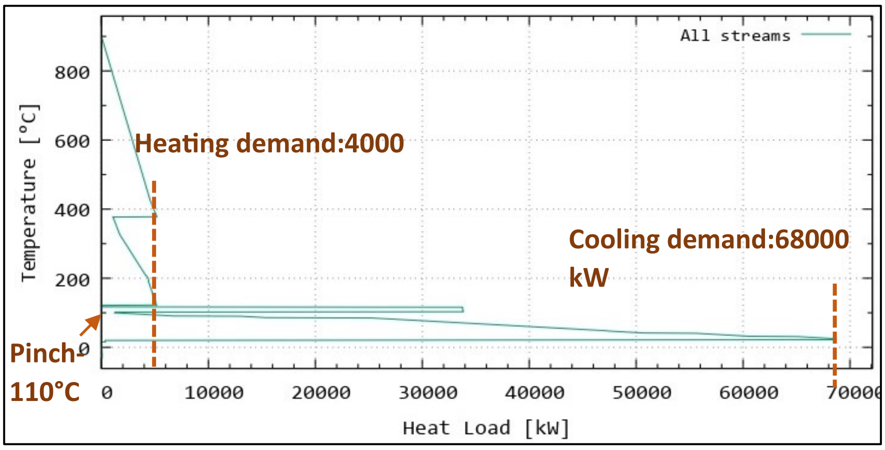

Figure 26 Grand composite curve of AFEX pathway

From the GCC for biomass to PE using AFEX Pretreatment (Figure 24), it's evident that the process is highly exothermic, with a minimum heating requirement of 4000 kW and a substantial cooling requirement of 68000 kW. In the self-sufficient pocket identified between temperatures of upper 400°C to 180°C on the GCC graph, endothermic (heat sink) requirements can be internally met without external heating sources. Additionally, for excess cooling demand, such as the significant cooling requirement of 68000 kW observed in the process, integrating an ORC could prove beneficial. An ORC system could utilize the excess heat for electricity generation, thereby reducing operational costs, ultimately contributing to its overall efficiency, sustainability, and economic viability.

5.6.4 ORGANO Pathway:

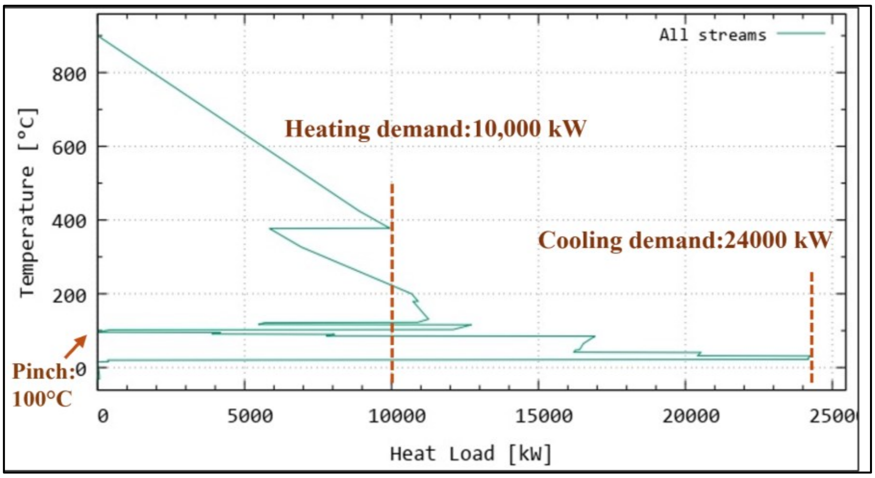

Figure 27 Grand composite curve of organosolvent pathway

In the presented GCC graph (Figure 25), the process exhibits a cooling demand of 24000 kW, satisfied by cooling water at 25°C, alongside a heating requirement of 10000 kW fulfilled by a boiler operating at 900°C. The pinch point exists at 100°C. Parallel lines extending from this pinch point indicate a region where effective heat transfer occurs with minimal temperature differences, presenting an opportunity to optimize energy usage through heat pumping. A small amount of electricity could be used to upgrade the heat from below to above the pinch temperature, saving approximately 5 MW of both heating and cooling utility. Additionally, a triangular self-sufficient pocket from 380°C to 110°C suggests the possibility of an ORC with more complex architecture, leveraging the 5500 kW of heat in this region for generating electricity. Significant heat is also available below the pinch point and above 25°C, which could be leveraged for low-temperature processes or space heating applications.

5.6.5 SE Pathway:

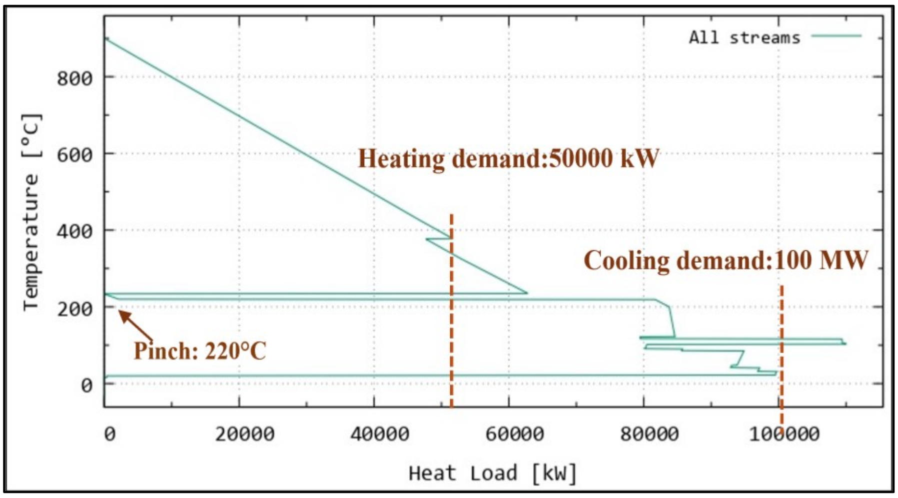

Figure 28 Grand composite curve of SE pathway

The GCC graph in Figure 26 illustrates a steam explosion pretreatment integrated process featuring a minimum heating requirement of 50000 kW from a boiler and a minimum cooling demand of 100000 kW managed by cooling water. A pinch point at 220°C signifies critical heat exchange optimization. Within the process, a self-sufficient pocket spanning from 220°C to 380°C, accommodating energy needs between 49000 kW to 62000 kW, indicates efficient internal heat recovery. Placing a heat pump along the parallel lines from 220°C to 210°C could increase the process efficiency; however, such technologies are not yet available. Additionally, excess cooling demands could be utilized through an ORC system for maximal energy utilization.

5.6.6 ALKALI Pathway:

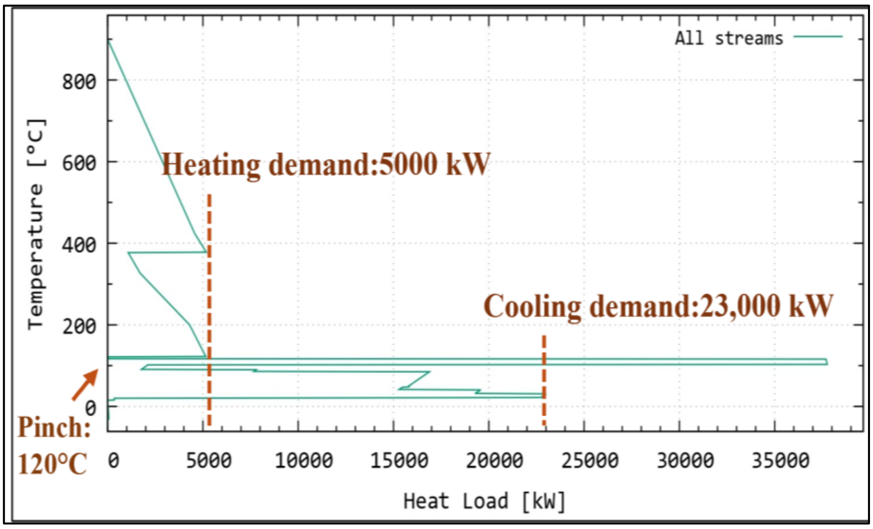

Figure 29 Grand composite curve of alkaline pathway

The GCC graph for the alkaline process (Figure 27), indicates a cooling demand of 23000 kW managed by cooling water and a heating requirement of 5000 kW supplied by a boiler, with a pinch point at 120°C. Excess heat of 23000 kW can be repurposed for either space or building heating applications using heat exchangers or heat pumps. The temperatures are too low for an efficient ORC; but remains a possibility if this heat could not be valorized for heating purposes. These options not only enhance energy efficiency but also contribute to environmental sustainability by reducing reliance on fossil fuels for heating or electricity generation.

5.7 Conclusion

Lignocellulosic biomass presents a promising avenue for transitioning away from fossil fuel, given its abundance and non-competition with food supplies. Various conversion processes for lignocellulosic biomass are actively researched, with a focus on pretreatment pathways. In this thesis, MILP modelling was employed to evaluate six different pretreatment pathways for the production of polyethylene, specifically from an economic perspective. The objective was to identify the most economically viable route among the options considered under current market conditions. Among these pathways, dilute acid pretreatment emerged as the most cost-efficient option in economic terms, considering its total cost and minimum selling price of product. This analysis demonstrates the potential of such models as decision-support tools for pathway selection and related factors, contributing to the advancement of sustainable alternatives to fossil fuels. This work also provides a piece in the broader biorefinery design and optimization framework, providing several fundamental building blocks for biochemical transformation of biomass to products. Future work in this domain can utilize this work and expand on it for larger system integration, design, and optimization.

5.8 Assumptions and Limitations:

In the modeling of biomass to biopolyethylene conversion pathways, our objective was to develop a screening tool for sustainable production approaches rather than conducting detailed process design. To facilitate this, several simplifying assumptions were made, which may introduce uncertainties into the results. While efforts were made to acquire quality data, reliance on available sources and discrepancies in data dates may impact the accuracy of the findings. Moreover, certain complexities inherent in the biomass conversion process were simplified or omitted in this study. For instance, considerations such as reaction time and solid loading in hydrolysis and fermentation were overlooked to streamline the analysis and provide a comparative framework. Similarly, detailed analyses on the types of enzymes and yeast were not conducted, leaving room for future investigations into kinetics and reaction design. Assumptions regarding the similarity of specific heat capacities (C_P) across the separation section to the polyethylene production stage were made same to ensure consistency in applying the process units across all six pretreatment methods in the MILP framework model. These simplifications and assumptions, while necessary for the study's objectives, may introduce limitations and uncertainties into the analysis. They highlight areas for future research to refine and expand upon our findings. All inlet and outlet streams of process units are standardized to ambient temperature and pressure (25°C and 1 atm) to ensure energy balance within each unit. Although this is not the case in taken references, but This ensures that when the model connects to subsequent processes, it doesn't introduce discrepancies in heat transfer, thereby maintaining consistency and accuracy throughout the system. Units such as fermentation and catalytic hydrations are simplified to do mass and energy balance over detailed design considerations. In such cases, side reactions may be ignored to focus on the main product. Additionally, equipment like CO_2 absorbers may not be explicitly designed but rather integrated into other units, such as separation columns, with their associated expenses still accounted for in capital expenditure assessments. Conversions for reactions are derived from relevant references and adjusted accordingly. However, it's important to note that reaction conversions can vary within the same type of pretreatment in different references due to numerous influencing factors.

5.9 Future work

While significant progress has been made in elucidating the pathways for biomass-to-bioplastic conversion, the journey towards achieving optimal efficiency, sustainability, and economic viability is ongoing. This section outlines potential avenues for future research and development, aimed at further enhancing the performance and applicability of biomass conversion technologies. Despite the progress made in this study, opportunities for enhancing decision-making processes through advanced modelling techniques remain, highlighting the need for continued exploration and innovation in the field. By addressing these challenges and embracing emerging opportunities, we can accelerate the transition towards a more sustainable and circular bioeconomy.

Conducting a comprehensive sensitivity analysis on the costs of feedstock and energy inputs is essential for understanding the economic viability of biomass-to-bioplastic pathways under varying market conditions. By systematically evaluating the impact of fluctuations in feedstock prices and energy costs, we can identify key factors influencing overall process economics and explore strategies for cost mitigation and optimization. Additionally, the best process options may change with varying market conditions and therefore would provide a comprehensive assessment of the appropriate technologies to pursue under various economic predictions, increasing the power of this approach.

Expanding the scope of biorefinery operations to encompass integration with other sectors presents promising opportunities for resource optimization and waste valorisation. Given that the biomass-to-bioplastic processes are exothermic, there is potential to utilize excess heat generated during these processes to meet the energy demands of neighbouring industries. For instance, excess heat could be transferred to urban areas for district heating purposes or utilized in drying or cleaning operations, where thermal energy is required. Such integration can enhance overall energy efficiency and reduce environmental footprint.

Future work entails maximizing the utilization of lignin, constituting 15-30% of lignocellulosic biomass. This involves exploring efficient methods to convert lignin waste into renewable fuels and value-added products, potentially integrating with other sectors and leveraging innovative technologies to enhance economic and environmental sustainability.

Further research is needed to explore additional biomass conversion routes and technologies for integrating various fine chemicals and intermediate chemicals. By investigating diverse biomass feedstocks and optimizing process integration, we can expand the range of sustainable products derived from biomass, enhancing overall efficiency and economic viability. This exploration will advance our understanding of biomass applications, contributing to the development of a bio-based economy. Additionally, the process integration approach used here can find improved economic and environmental solutions when additional integration opportunities are made available. This aligns well with the biorefinery concepts from literature and creates an ecosystem of processes and production routes that can be integrated to improve the overall system performance and reduce costs for all products from the biorefinery.

Refining the current models to address challenges associated with economic scale-up, particularly for smaller units, is also required for future research. By incorporating scaled-up designs, more nuanced scaling factors and accounting for variations in capital expenditures across different production scales, we can improve the accuracy and reliability of economic assessments for biomass-to-bioplastic pathways starting from small-scale production data.

In future work, exploring the environmental implications of chemicals like acids, sodium hydroxide or ammonia in pretreatment pathways is crucial. Utilizing MILP modelling, conducting a comprehensive life cycle assessment (LCA) can offer insights into environmental impacts, guiding sustainable polyethylene production strategies. Incorporating environmental considerations is essential for responsible industrial practices. It is important to note this analysis is limited to cost evaluation. However, expanding future research to include environmental assessments would provide a more detailed understanding, facilitating informed decision-making and promoting eco-friendly practices in the industry.

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