Development of Process Configurations and Simulation of Biobutanol Production Using DWSIM

Développement des configurations de procédé et simulation de production de biobutanol à l'aide de DWSIM

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VÉRITÉ • DEVOIR • VAILLANCE
Truth • Duty • Valour
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ABSTRACT

Climate change resulting from extensive greenhouse gas (GHG) emissions and the depletion of finite fossil fuels have directed the scientific community to focus on exploiting biomass for sustainable production of bioproducts and bioenergy. In particular, biobutanol has been a focus in the area of biofuel research as the alternative renewable fuel due to its ability to act as a fuel additive and better compatibility with gasoline than bioethanol. However, low product yield and high substrate cost are the two major limiting factors in the industrialization of biomass-based products. Biobutanol production using lignocellulosic biomass as feedstock through acetone-butanol-ethanol (ABE) fermentation addresses the high substrate cost challenge and provides energy security since the supply and production can be done domestically. Nonetheless, this process is still under optimization for maximum fermentable sugar production and final product yield.

Process simulation has been used to facilitate the design of biobutanol production process. While commercial software is commonly used for process modeling, the accessibility and cost-free nature of open-source software present opportunities for effective simulation, particularly for small businesses.

The objective of this study is to develop suitable process configurations for biobutanol production and to demonstrate the viability of the open-source chemical process simulator, DWSIM, version 7.3.2, in modelling biobutanol production process and its ability to scale-up laboratory results.

An extensive literature review was conducted to establish process flowsheet and identify research papers with the required data to support process simulation. DWSIM was employed to model the fermentative production of biobutanol from five lignocellulosic feedstocks: hybrid poplar wood, elmwood, switchgrass, wheat straw, and pulp and paper mill side stream. The designed process consists of the following steps: pretreatment (autohydrolysis or dilute acid pretreatment), detoxification, enzymatic hydrolysis, fermentation, and distillation. In order to complete the simulation on DWSIM, additional compounds were imported into the software to represent the lignocellulose composition and the biomass pretreatment step. Chemical reactions were included to model feedstock pretreatment, hydrolysis and fermentation steps. Model validation was conducted against the results prior to configuration development. A total of six process configurations were developed with varying feedstock type and composition, pretreatment method and conditions, and content to be hydrolyzed. This study demonstrates the ability for DWSIM to simulate results from laboratory scale and estimate biobutanol production amount at an industrial level. The potential sites to locate biobutanol production plants in Canada were proposed. Finally, DWSIM performance was also analysed.

RÉSUMÉ

Le changement climatique résultant d'importantes émissions de gaz à effet de serre (GES) et de l'épuisement des combustibles fossiles limités a amené la communauté scientifique à se concentrer sur l'exploitation de la biomasse pour la production durable de bioproduits et de bioénergie. En particulier, dans le domaine des biocarburants, le biobutanol a fait l'objet de recherches, car c’est un carburant renouvelable alternatif qui a la capacité à agir comme additif et une meilleure compatibilité avec l'essence que le bioéthanol. Cependant, le faible rendement du produit et le coût élevé du substrat sont les deux principaux facteurs limitants de l’industrialisation des produits à base de biomasse. La production de biobutanol utilisant la biomasse lignocellulosique comme matière première par fermentation acétone-butanol-éthanol (ABE) répond au défi du coût élevé du substrat et assure la sécurité énergétique, puisque l'approvisionnement et la production peuvent être effectués au niveau régional. Néanmoins, ce procédé est toujours en cours d'optimisation pour une production maximale de sucres fermentescibles et un rendement élevé en produit final.

La simulation a été utilisée pour faciliter la conception du procédé de production de biobutanol. Alors que les logiciels commerciaux sont couramment utilisés pour la modélisation des procédés, l'accessibilité et la nature gratuite des logiciels « open source » offrent des opportunités de simulation efficace, en particulier pour les petites entreprises.

L'objectif de cette étude est de développer des configurations de procédé pour la production de biobutanol et de démontrer la viabilité du simulateur open source, DWSIM, version 7.3.2, dans la modélisation du procédé de production de biobutanol et sa capacité à faciliter la mise à l’échelle des résultats de laboratoire .Une revue approfondie de la littérature a été menée pour établir le diagramme de procédé et identifier les documents de recherche contenant les données requises pour la simulation. DWSIM a été utilisé pour modéliser la production de biobutanol par fermentation à partir de cinq matières premières lignocellulosiques : le bois de peuplier hybride, l'orme, le panic raide, la paille de blé et le courant secondaire des usines de pâtes et papiers. Le procédé développé comprend les étapes suivantes : prétraitement (autohydrolyse ou prétraitement acide dilué), détoxification, hydrolyse enzymatique, fermentation et distillation. Afin de compléter la simulation sur DWSIM, des composés supplémentaires ont été importés dans le logiciel pour représenter la composition lignocellulosique et l’étape de prétraitement de la biomasse. Des réactions chimiques ont été incluses pour modéliser les réactions qui ont lieu à chaque étape. Une validation du modèle a été effectuée avant le développement de la configuration. Au total, six configurations ont été développées avec différents types et composition de matières premières, méthodes et conditions de prétraitement et contenu à hydrolyser. Cette étude démontre la capacité du DWSIM à simuler des résultats de l’échelle laboratoire et à estimer la quantité de production de biobutanol au niveau industriel. Des sites potentiels pour implanter des usines de production de biobutanol au Canada ont été proposés. Finalement, la performance de DWSIM a également été analysée.

Table of Contents

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ABE	Acetone, butanol and ethanol
AH	Autohydrolysis
ASA	Accessible surface area
CS	Compound separator
CR	Conversion reactor
DP	Degree of polymerization
GHG	Greenhouse gas
LCB	Lignocellulosic biomass
SE	Steam explosion
HMF	5-hydroxymethylfurfural
SSF	Simultaneous saccharification and fermentation
SHF	Separate hydrolysis and fermentation
SLR	Solid to liquid ratio

1 INTRODUCTION

Over 80% of global energy demand relies on the finite fossil resources, predominantly petroleum (Soetaert and Vandamme, 2009) causing environmental concerns. Even though the recent COVID-19 pandemic in 2020 led to a 4.5% reduction in global energy consumption (bp, 2021), a rebound in energy demand was soon observed in 2021 following the lifting of the pandemic health measures (World Energy Council, 2022).

The petrochemical industry extensively relies on fossil fuels as raw materials for high-value products like polyester, epoxy, and commodities and fuels such as gasoline (Hopewell et al., 2009; Gary et al., 2007). Crude oil, owing to its low atomic oxygen to carbon ratio and high atomic hydrogen to carbon ratio, is a preferred source for cost-efficient chemical and oil production. Nevertheless, petroleum refining is an energy-intensive process with significant environmental impacts (Gary et al., 2007). Additionally, the dependence on fossil fuel poses energy security concern. Many countries, including those with significant energy needs, rely on petroleum imports from politically unstable countries like Russia, a top oil-producing nation worldwide (International Energy Agency, n.d.; Soetaert and Vandamme, 2009). Thus, most countries are dependent on potentially unstable sources for their oil supply.

The combustion of fossil fuels and the industrial production of petroleum-based products have contributed to fluctuating gasoline prices, climate change, and the depletion of these finite resources. Fossil fuel combustion leads to the generation of unburned hydrocarbons, particulate matter, carbon dioxide, and nitrogen oxide, all of which impact the environment (Obergruber et al., 2021). Specifically, carbon dioxide, along with other greenhouse gases (GHG), plays a major role in climate change effects (Ansari et al., 2023). Canada’s overall GHG emission in 2021 reached 670 megatonnes of carbon dioxide equivalent, marking a 1.8% increase from 2020 (Canada, 2023). The growing use of vehicles contributes significantly to both fossil fuel depletion and climate change. Moreover, transportation and power generation accounted for about a quarter of the global carbon dioxide emissions in 2020 (International Energy Agency, 2020). This increasing energy demand and the associated environmental impacts have directed scientific focus towards developing technologies or processes to efficiently produce chemicals from renewable resources, aiming to reduce reliance on non-renewable sources.

Utilizing renewable carbon resources as an alternative energy source reduces dependence on fossil fuels and aids in stabilizing atmospheric GHG levels (Liao et al., 2020). Hence, there is an increased focus on harnessing biomass to produce sustainable bioproducts such as enzymes, organic acids, antibiotics and bioenergy like biogas, biofuel, heat, electricity to mitigate climate change. Biomass as a renewable feedstock, can be sourced from various agricultural and forestry sources, dedicated energy crops, and waste residues (Williams et al., 2015). One of the products, renewable liquid biofuels have been increasingly integrated into the fuel mix for transportation each year due to their ability to reduce dependence on fossil fuels, lower exhaust emissions, and support local agriculture (Obergruber et al., 2021, Vertès 2010). For example, in 2021, the transportation sector in Canada relies on biofuel to meet 3.2% of its fuel demand (Pelkmans, 2021).

Lignocellulosic biomass (LCB) stands as second-generation biomass that doesn't compete with food cultivation, is abundant, and is considered carbon dioxide neutral since plant photosynthesis captures CO_2. Additionally, the technology for utilizing second-generation biomass is more mature than that for third-generation biomass (i.e. algae). LCB is a significant energy source besides coal, petroleum, and natural gas (Liu & Yu, 2021). The cellulose and hemicellulose components of LCB serve as substrates for various products such as xylitol, syngas, ethanol, butanol, and acetone, to name a few. Moreover, employing biomass as a raw material for bio-products and biofuel production reduces the costs related to fossil fuel import since biomass can often be grown domestically (Huang et al., 2013). Hence, converting lignocellulosic biomass to biofuel could mitigate both environmental and economic concerns. Canada is a country that has a great potential in local production of biofuel from woody biomass as it has abundant forest area.

While bioethanol has been extensively studied, biobutanol is a more promising candidate to be used as a drop-in liquid fuel due to its higher compatibility with gasoline. However, the current biobutanol production relies mainly on corn as feedstock. This substrate is an edible source and contributes to 60-70 % of the bioconversion production cost (Luo et al., 2021). Using lignocellulosic material can improve the economic feasibility of bioproduction of butanol. Yet, the utilization of lignocellulosic biomass for industrial biobutanol production encounters several challenges. These hurdles encompass high energy requirement for biobutanol separation, inhibitor formation during the production process, and economic feasibility (Guo et al., 2022b). The global market for n-butanol was valued at USD 6.4 billion in 2019 with projections to reach USD 7.6 billion by 2024 (Arsov et al., 2021).

Process simulation is an effective tool for predicting scale-up process from the laboratory (Trirahayu et al., 2022). Thus, it can be used to facilitate the design of biobutanol production process as it is still under development phase (Restiawaty et al., 2021). The cost-efficiency of computer simulations in providing deep insights towards processes is particularly attractive (Kellner et al., 2019). Computational process simulators have been implemented in plant design, identifying bottlenecks, and optimizing processes conditions (Andreasen, 2022). While software simulations are common in biobutanol production process (Liu et al., 2009), many studies have utilized commercial software such as Aspen Plus to model the process of biochemical production of biofuel (Lassmann et al., 2014; Quintero & Cardona, 2011; Sassner et al., 2008; Haigh et al., 2018). However, the accessibility and cost-free nature of open-source software encourage small businesses to incorporate simulations effectively. Additionally, open-source computer simulations enable the study of pilot plant behavior without the necessity of conducting experiments, resulting in a substantial reduction in experimental costs (Tangsriwong et al., 2020). To the author's knowledge, no study has conducted to model biobutanol production using the open-source simulator, DWSIM. Various feedstocks can be used to produce bioenergy. Examples of feedstock are microalgae, forestry feedstock such as wood chips and fire wood, municipal waste like paper and plastic, energy crops such as switchgrass, poplar wood, and fast-growing willow (Khan et al., 2023). In this study, the simulation focused on forestry biomass, algricultural feedstock, and pulp and paper mill side stream.

2 LITERATURE REVIEW

2.1 Lignocellulosic biomass

Biomass has been utilized to generate energy in the human history as early as when people burned wood for fire. In today’s world, biomass is a potential source of bioproducts, platform chemicals, and bioenergy. Biomass can be utilized through thermochemical processes like gasification, combustion, and pyrolysis, chemical conversion like transesterification, hydrogenation or biochemically via anaerobic digestion and fermentation. As illustrated in Figure 1, biomass is generally classified into first, second, and third generations. First-generation biomass comprises edible plant material, while second-generation biomass consists of non-edible lignocellulosic biomass. Algae is categorized as third-generation biomass.

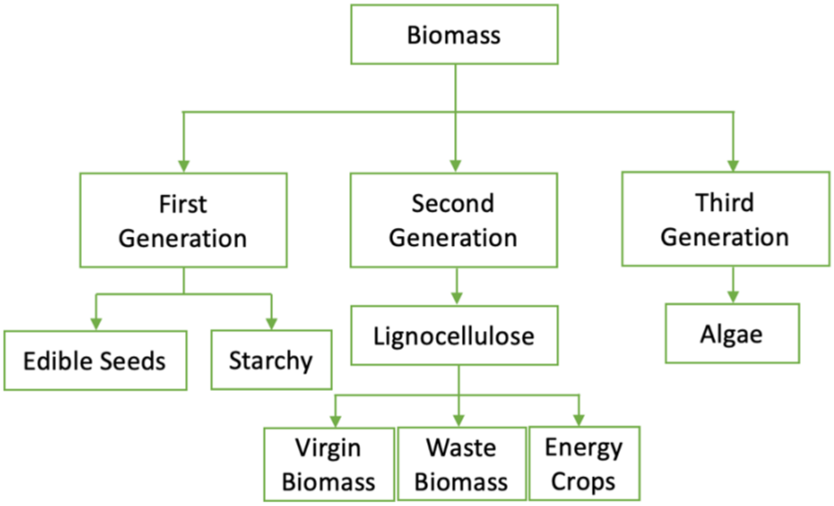


Figure 1. General classification of biomass. Adapted from Bardhan et al. 2015.

LCB is plant biomass that is abundant, carbon neutral, and solves the “food versus fuel” dispute that the first-generation biomass (i.e. edible material) creates in bioconversion. Additionally, the technology for converting LCB is more mature than the third-generation biomass (i.e. algae). Thus, there are abundant studies on biobutanol production investigating bioconversion from LCB. (Veza et al., 2021). The chemical composition of LCB typically comprises of 40-50% cellulose, 20-30% hemicellulose, and 10-25% lignin on average (Shinde et al., 2020). However, the specific ratio and composition of each lignocellulosic polymer vary based on the source of feedstock. Table 1 provides examples of the percentage of polymers of various lignocellulosic biomass.

Table 1. Composition of cellulose, hemicellulose, and lignin in various lignocellulosic biomass in % dry mass (adapted from Kumar et al., 2019).

Lignocellulosic material	**Cellulose (%)**	**Hemicellulose (%)**	**Lignin (%)**
Hardwood	40-50%	20-35%	16-25%
Softwood	40-50%	15-20%	23-33%
Straw	30-43%	22-35%	15-23%
Grass	25-40%	35-50%	10-30%
leaves	15-20%	80-85%	0%
Wheat straw	30%	50%	15%
Switchgrass	45%	31.4%	12%

2.1.1 Sources of lignocellulosic biomass

LCB can be categorized into three types: virgin biomass, waste biomass, and energy crops. Terrestrial plants and woody plants like trees and bushes fall under the classification of virgin biomass. Forestry residue, agricultural waste (e.g. bagasse, stover), paper mill by-residues (e.g. sawdust, wood chips, wood bark) are considered as waste biomass. Energy crops refer to dedicated crops used in second-generation biofuels production, such as switchgrass, miscanthus, giant reed (Yousuf et al., 2020& Broda et al., 2022). Examples of agricultural waste LCB include bagasse waste from sugar production, rice straw waste, and corn stover. All these biomass feedstocks can be used in biofuel production to make biofuels competitive to petroleum-based fuel (Adewuyi, 2022). The high content of cellulose and hemicellulose make LCB a promising source of cellulosic sugars for biofuel production (Ahorsu et al., 2018).

2.1.2 Lignocellulose structure and chemistry

Understanding the chemical composition of the lignocellulose is crucial in utilizing it in the bioconversion process. The primary chemical composition in LCB is lignocellulose, with trace amounts of ash, and extractives (Yousuf et al.,2020). Lignocellulose, found in plant cells walls, comprises well-organized polymers of cellulose, hemicellulose, and lignin. The composition and proportion of each polymer vary based on the source of the biomass. Carbohydrates, primarily C6 and C5 sugars, make up approximately 70% of the dry weight of LCB and serves as the most common building blocks for numerous bio-based products (Yousuf et al., 2020).

Cellulose is a linear polymer chain consisting of repeating *D*-glucose units linked via β-(1,4)-glucosidic bonds (Zoghlami & Paës, 2019). Within the structure of cellulose, cellobiose, a disaccharide of two glucose molecules is considered as the basic building block. Figure 2 provides a visual representation of the cellulose structure. The degree of polymerization (DP), indicating the number of glucose units in a molecular chain, varies in the cellulose chains depending on the type of biomass. For instance, the DP of cellulose can range from 9,000 to 15,000 in wood (Pettersen, 1984). These cellulose polymer chains can form microfibrils and fibrils with crystalline regions that exhibit intense hydrogen bonding interactions making the area resistant to chemical degradation. Conversely, the amorphous regions allow access for water or acid hydrolysis due to their less structured nature (Stephens et al., 2008). Only a small proportion of cellulose is amorphous (Kumar et al., 2009), rendering cellulose highly reluctant to degradation. In addition, the cellulose structure is thermodynamically stable due to van der Waals' forces, intermolecular hydrogen bonding, and intramolecular hydrogen bonding (Figure 2). The 1,4-glucosidic bonds within cellulose structure can break to yield glucose molecules through the action of enzyme or acid, (Kumar et al., 2009).

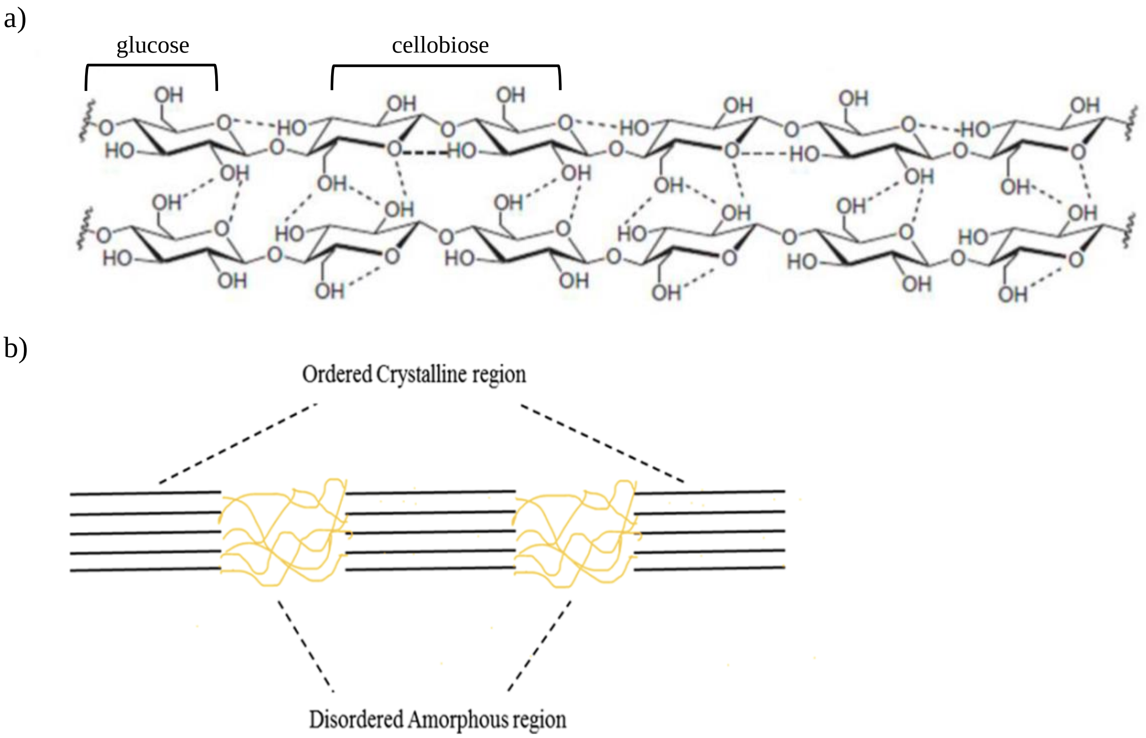


Figure 2. The structure of cellulose. a) The straight chain polysaccharides form cellulose microfibrils via hydrogen bonding (shown as dashed lines). b) Simple illustration of the crystalline and amorphous region of cellulose (Rajinipriya et al., 2018).

Hemicellulose consists of branched heteropolysaccharide chains that link cellulose and lignin polymers via covalent bonding (Nashiruddin et al., 2020) and is often heavily acetylated (Zoghlami & Paës, 2019). Hemicellulose is composed of mostly pentoses (monosaccharide with five carbon atoms) like xylose and arabinose, hexoses (monosaccharide with six carbon atoms) such as glucose, mannose, rhmnose, and galactose (Boro et al., 2022) and some uronic acids (Kumar et al., 2009). The sugar composition of hemicellulose varies depending on the feedstcok, linear polymer composed of β-D-xylopyranosyl units linked by β-(1,4)-glycosidic bonds and substituted by 4-O-methyl-D-glucopyranosyluronic acid and acetyl groups. Glucuronoxylan is the main hemicellulose found in hardwood hemicellulose (Dou et al., 2021). The absence of crystallinity in the hemicellulose structure makes it more accessible to chemical attack than cellulose (Williams et al., 2015).

Contrary to cellulose and hemicellulose, which are made of carbohydrate units, lignin is a phenolic polymer composed of pheno-propane units: p-hydroxyphenol, guaiacyl, and syringyl units (Basile & Dalena 2019). In nature, lignin is the structural component that protects plants from microbial attack. This functional feature of lignin makes it difficult to chemically degrade when processing in the labratory. The units in lignin are connected by ether bond and carbon-to-carbon connections (Harmsen et al., 2010). Similar to hemicellulose, the exact composition of pheno-propane units varies among different feedstocks. For example, softwoods have guaiacyl lignin but hardwoods are rich in guaiacyl-syringyl lignin. Since lignin has no carbohydrate content, its removal is an important aspect of biofuel production. However, lignin removed in fermentative biofuel conversion can be converted into energy through combustion, other high-value compounds (e.g. cardon fibres, adhesives, vanillin), or synthetic gas via pyrolysis/gasification.

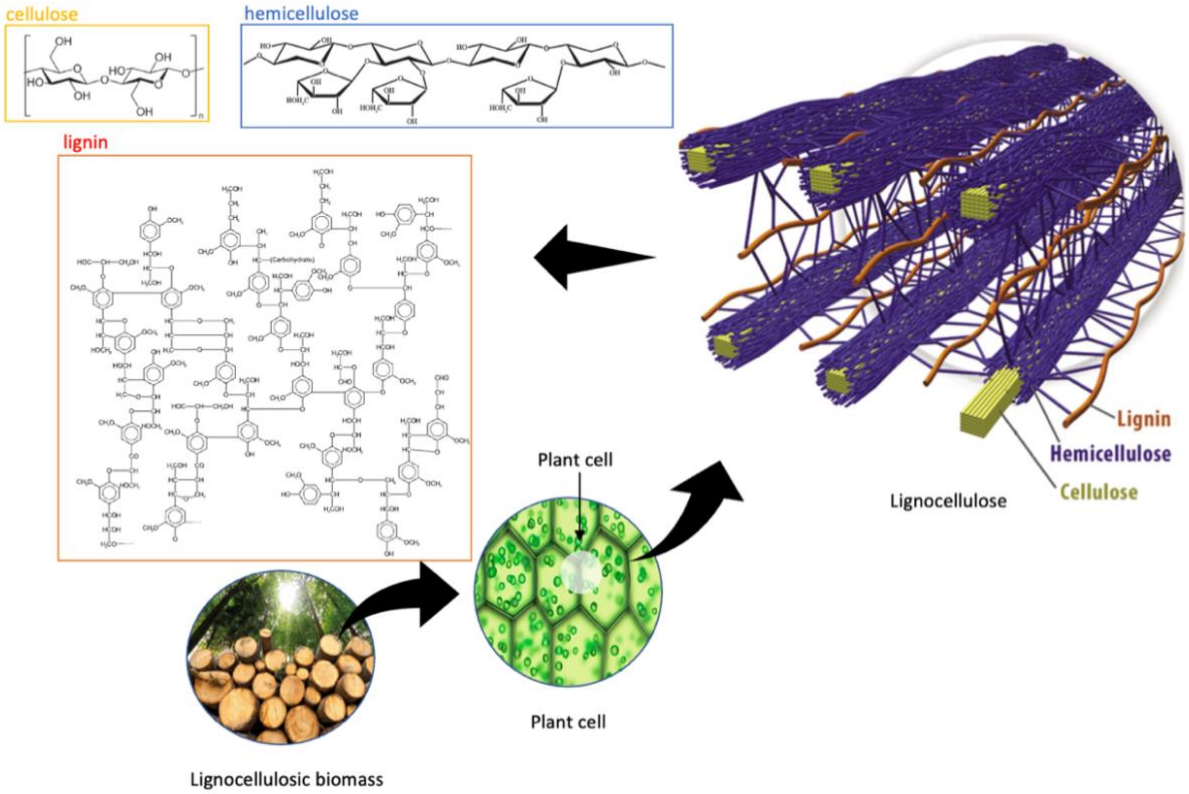


Figure 3. The structure and composition of lignocellulosic biomass.

2.2 Biomass pretreatment

The recalcitrant nature of LCB to chemical and enzymatic degradation makes utilization of this material challenging. Specifically, the physical and chemical characteristics of LCB contribute to its resistance to hydrolysis. Physical characteristics of lignocellulose such as crystallinity, particle size, pore size and accessible surface area (ASA) are some of the contributors to this resistance to catalytic degradation (Zoghlami & Paës, 2019). As depicted in Figure 3, the polymers present in lignocellulose form a microfibril structure that is well-organized via various bonding interactions. Cellulose within the lignocellulose matrix is recalcitrant to enzymatic degradation due to its structural integrity (Zoghlami & Paës, 2019). Hemicellulose forms intermolecular and intramolecular hydrogen bonds with cellulose. Ester and ether bonds are formed between hemicellulose and lignin in addition to the hydrogen bonding interactions (Yousuf et al., 2020). To counter this issue, the bioconversion process employs a step called pretreatment to disrupt the structural integrity of lignocellulose and to increase the accessibility of polysaccharides to acid or enzymatic hydrolysis.

Pretreatment is a necessary step in the conversion of lignocellulosic material to biofuel. As illustrated in Figure 4, pretreatment opens the organized lignocellulosic structure to expose cellulose for enzymatic hydrolysis by breaking down hemicellulose and lignin (Kundu et al., 2021). Pretreatment is crucial for the overall efficiency of biomass conversion. Treating biomass can lead to a 3-10 fold increase in rate of enzymatic hydrolysis (Nauman Aftab et al., 2019). Furthermore, pretreatment affects the crystallinity of cellulose, degree of polymerization, the structure of lignin, solubilization of hemicellulose, and the cellulose digestion in the feedstock (Zoghlami & Paës, 2019). Pretreatment must achieve the following criteria: generate monomeric sugars or enhances sugar production of the subsequent hydrolysis, preserve polysaccharide, avoid or minimize the production of inhibitory compounds and be cost-effective (Kumar et al., 2009). The source of LCB impacts the requirement of pretreatment method. Wang et al. 2021 compared the effect of dilute sulfuric acid pretreatment on birch, spruce, and aspen wood. The pretreatment resulted in a higher glucose yield from enzymatic saccharification in birch than in spruce. Conversely, aspen wood demonstrated less resistance to enzymatic degradation, as the dilute acid treated aspen and untreated aspen resulted in similar glucose conversion enzymatically (Wang et al., 2021).

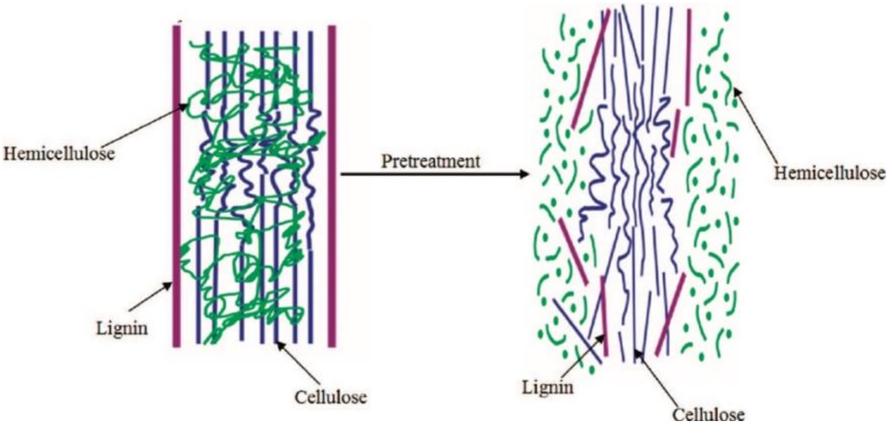


Figure 4. The effect of pretreatment on lignocellulose structure. Pretreatment disrupts the structural integrity of lignocellulose, reduces cellulose crystallinity, and degrades lignin to enable enzymatic hydrolysis (Kumar et al. 2019).

Biomass pretreatment can be categorized into physical, chemical, and thermochemical pretreatment. Various pretreatment methods have been developed to address the compositional and structural variation among LCB (Figure 5). Mechanical milling, dilute acid pretreatment, steam explosion, autohydrolysis, and alkaline pretreatment are some examples of pretreatment methods.

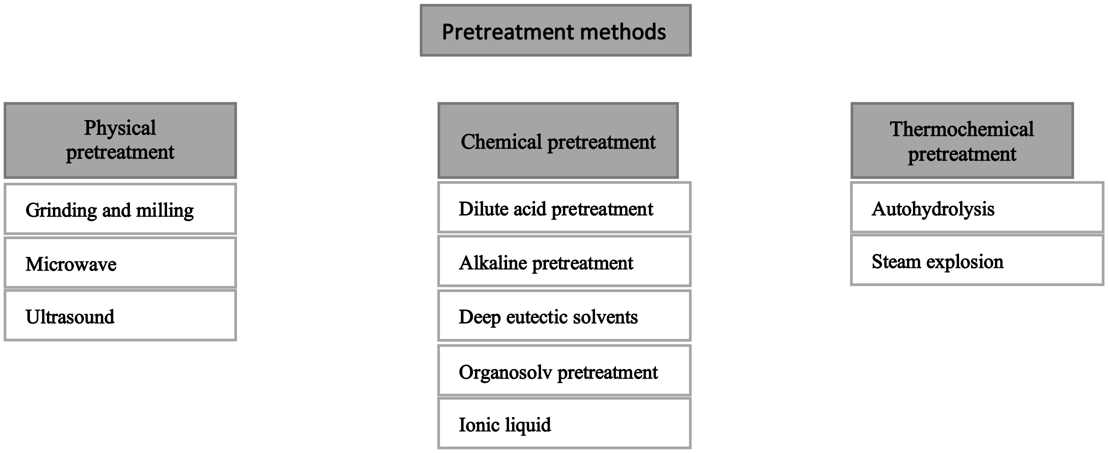


Figure 5. An overview of biomass pretreatment methods.

The main advantages and disadvantages of different pretreatment methods are briefly summarized in Table 2. It is important to note that one pretreatment method is not effective to treat all feedstock types. Many studies have been carried out to determine the optimal conditions for pretreatment to process biomass feedstock and maximize sugar yield during saccharification. Wang et al. (2020) studied the chemical and structural changes of switchgrass using 12 different pretreatment methods to provide a comprehensive understanding of the most effective pretreatment for switchgrass at a laboratory scale. It was concluded that nitric acid, sodium hydroxide alkaline treatment, and organosolv pretreatment using ethanol were the most effective for switchgrass, inducing more morphological alterations to the lignocellulose structures.

Table 2. Advantages and disadvantges of biomass pretreatment methods (adapted from Brodeur et al. 2010).

Pretreatment method	Advantages	Disadvantages
Milling and grinding	- Simple operation - Can process large biomass volumes - No chemicals added - Generates no inhibitors	- High energy consumption - Often require additional pretreatment step
Acid	- High sugar yield - Solubilizes hemicellulose - Effective on different types of biomass	- High cost of acids - Generates inhibitors - Requires anticorrosive equipment
Alkaline	- Efficient removal of lignin - Low inhibitor formation	- Cost of alkaline catalyst - Does not hydrolyze hemicellulose
Autohydrolysis	- No additional catalyst - Hydrolyze hemicellulose - Generation of inhibitors is minimized	- High energy/water requirement
Steam explosion	- Cost effective - Suitable for hardwoods	- Generates inhibitors - Acid catalyst needed for efficient processing

2.2.1 Physical pretreatment

The main aim of physical pretreatment is to reduce the particle size of LCB to increase the rate of hydrolysis and form polymer chains (Banu J et al., 2021). Physical pretreatment methods include mechanical treatment, ultrasonic treatment, or microwave irradiation. This type of pretreatment offers several advantages: it reduces the crystallinity index, minimizes waste chemical production, and increases the surface area for enzymatic actions (Yousaf 2020; Basile & Dalena, 2019). For example, hybrid poplar wood underwent mechanical pretreatment by chipping to obtain a particle size of less than 1 cm^3 and was subsequently subjected to chemical pretreatment (Wang et al., 2021).

Mechanical treatments, such as chipping, grinding, or milling, reduce the size of biomass material, ranging from centimeters to micrometers (Barakat et al., 2014). For instance, chipping can achieve a particle size ranging from 10 to 30 mm, while milling can produce finer biomass sizes of up to 0.2 mm (Kumar and Sharma, 2017). Milling facilitates the processing of LCB by also reducing the DP of cellulose and cellulose crystallinity (Amin et al., 2017). Various milling instruments, including hammer mills, knife mills, ball mills, and centrifugal mills, are used (Barakat et al., 2014). Wet disk milling has become a preferred method due to its low energy consumption (Kumar & Sharma, 2017) and the absence of inhibitor generation (Hideno et al., 2009). Hideno et al. 2009 compared wet disk milling and dry ball milling on rice straw as the sole pretreatment before enzymatic hydrolysis. The sugar yield (glucose, xylose, and arabinose) from enzymatic hydrolysis was slightly higher when rice straw underwent dry ball milling for 60 min compared to 10 repeated wet disk milling operations. However, chipping is preferred for hardwood feedstock (Banu J et al., 2021).

Moreover, physical pretreatment alone is often insufficient and is typically combined with chemical or thermochemical pretreatment (Yousuf et al., 2020). For instance, Wi's group grounded rice straw with a wet-disk mill to reduce the particle size to 0.7 cm before hydrogen peroxide acetic acid pretreatment (Wi et al., 2015). Similarly, Ruiz et al. 2008 reduced the particle size to less than 10 mm by milling sunflower stalks with a hammer mill before steam explosion treatment.

Microwave pretreatment applies heat to break the connection of lignin to the polysaccharides, facilitating lignocellulose digestibility (Indriani et al., 2021). Parameters such as microwave intensity, substrate concentration, and irradiation duration are crucial in microwave pretreatment (Ma et al., 2009). Ma's group found that under optimal conditions, microwave pretreatment significantly improved the enzymatic digestibility of rice straw. Similar to mechanical pretreatment, microwave radiation is often combined with other pretreatment methods to enhance the solubility of LCB (Yousuf et al., 2020).

Ultrasounication is another type of physical pretreatment that employs high-intensity ultrasound to alter biomass structure (Banu J et al., 2021). It is commonly used in pretreating agro-industrial biomass to produce value-added bioproducts and can be used to treat agricultural biomass to produce bioethanol (Sabaruddin et al., 2023). Zeynali et al. (2017) demonstrated that ultrasonic pretreatment on fruit and vegetable wastes can significantly increase the biogas and methane yield.

2.2.2 Chemical pretreatment

The objective of chemical pretreatment such as acid pretreatment and alkaline pretreatment is to remove lignin and hemicellulose, thereby facilitating cellulose hydrolysis (Adewuyi, 2022). Acids, alkalis, and organic solvents are used to hydrolyze LCB by disrupting the glycosidic bonds connecting hemicellulose to cellulose (Guo et al., 2022a). Acid pretreatment involves concentrated or dilute acids. However, dilute acid pretreatment is more common as it is less corrosive and generates less inhibitors. This process chemically solubilizes hemicellulose and lignin (Awoyale & Lokhat, 2021), enhancing the release of fermentable sugars during enzymatic hydrolysis (Nauman Aftab et al., 2019). The acidic conditions dissolve intra- and inter-chain hydrogen bonds within the amorphous region of cellulose, enabling more effective enzymatic hydrolysis (Li et al., 2010). Dilute sulfuric acid, at concentrations below 4 wt%, is the most commonly used method due to its proven effectiveness and cost efficiency (Kumar et al., 2009). However, nitric acid (Zhang et al., 2010), hydrochloric acid (Yan et al., 2021), phosphoric acid (Yan et al., 2021), and acetic acid (Wang et al., 2020) are also utilized.

Dilute acid pretreatment employs low concentrated acids (0.75-5 wt%) at high temperatures (120-200 ℃). These conditions promote dissolution of hemicellulose into monosaccharides and partial breakdown of cellulose. The exact temperature, reaction time and acid concentration vary based on the type of biomass being treated (Loow et al., 2016). While dilute sulfuric acid is cost-effective and efficient, it also produces inhibitory compounds alongside carbohydrate monomers. For instance, treating wheat straw with 10 dm^3/m^3 sulfuric acid at 140 °C for 30 min resulted in an 89% glucose yield and a 47% xylose yield from subsequent enzymatic hydrolysis, with a small number of inhibitors such as formic acid, acetic acid, and furfural generated (Rajan & Carrier, 2014). Partial delignification using acid-chlorite before dilute sulfuric acid pretreatment on poplar wood was found to enhance the subsequent glucose yield from enzymatic hydrolysis compared to full lignin removal (Sun et al., 2014).

Alkaline pretreatment uses bases like sodium hydroxide, ammonia, and calcium oxide at lower temperatures (60-85℃) and requires longer residence times (48-192h). Although it results in limited hemicellulose dissolution, alkaline pretreatment is effective in delignifying biomass (Awoyale & Lokhat, 2021). This method improves the digestibility of residual cellulose and hemicellulose in the pretreated solid (Mosier et al., 2015). Other chemical pretreatment methods include the use of organosols and ionic liquids. Ionic liquid pretreatment enhances switchgrass digestibility by causing more aggressive structural disruption, significantly reducing saccharification time (Li et al., 2010).

Pretreatment has limitations in its application and further research is required to enhance the economic viability of biomass conversion. The chemicals and energy involved in pretreatment add additional cost to the overall operation of the conversion process (Lim & Wang, 2013). For instance, pretreating LCB alone can contribute to 40% of the total biofuel production cost (Awoyale & Lokhat, 2021). Moreover, the creation of inhibitory compounds, during pretreatment, that are toxic to microbial growth also needs to be considered.

2.2.3 Thermochemical pretreatment

Chemical pretreatment modifies the structure of the biomass in the presence of acids, bases, or solvents whereas thermochemical pretreatment uses heat and pressure to alter the structure of biomass. Thermochemical pretreatment includes autohydrolysis (hot water wash) and steam explosion that releases a mixture of monosaccharides and disaccharides (Obergruber et al., 2021). Both methods operate at high temperature condition.

Autohydrolysis (AH) is also known as hydrothermolysis or hot water extraction that is particularly effective in breaking down hemicellulose with a high recovery of lignin and cellulose in the solid fraction of pretreated slurry (Carvalheiro et al., 2016). Additionally, AH does not require any chemical addition, making AH a popular pretreatment method in fractionating LCB content (Wang et al., 2020). AH partially dissolves hemicellulose using only water as a reagent. The breakdown of acetyl groups from beta-(1-4)-linked xylan backbone forms acetic acid, which acts as an additional catalyst for the hydrolysis reaction (Gütsch et al., 2012). AH generates mostly oligomeric sugars and minimum amount of inhibitors in the autohydrolysate liquid. Additionally, AH is cost-effective and more environmentally friendly then chemical hydrolysis (Chen et al., 2010). This pretreatment method generally operates at around 160-240℃ for a variable amount of time, from mins to several hours (Nashiruddin et al., 2020). Rigual et al. (2018) conducted an AH at 200 ℃ for 30 min and achieved the highest glucan digestivity in *E. globulus*, a hardwood species. Two distinct streams of products are obtained from autohydrolysis pretreatment: a liquid phase containing hydrolysable hemicellulose sugars, and a solid fraction containing mostly cellulose and lignin (Yousuf et al., 2020).

Steam explosion (SE) treats biomass with saturated high-pressure stream followed by a rapid reduction in pressure to achieve explosive decompression (Hendriks and Zeeman, 2009). The pressure can range from 0.7 to 4.8 MPa and the operation temperature ranges between 160 ℃ and 260 ℃. This process can be catalyzed by sulfuric acid, ammonia, sulfur dioxide. SE is effective in partial lignin depolymerization (Ruiz et al., 2008) and hemicellulose solubilization and minimizes formation of inhibitors (Basile & Dalena, 2019). Advantages are short reaction time, low energy requirement, no additional chemicals required (Basile & Dalena, 2019). SE is another frequently used technique to pretreat LCB (Ruiz et al., 2008). Ruiz et al examined the effect of SE on enzymatic hydrolysis of sunflower stalks. It was found that maintaining the temperature at 220 ◦C for 5 min before depressuring the reactor vessel resulted in the optimal sugar yield in enzymatic hydrolysis. A 72% enzymatic hydrolysis sugar yield was obtained and the authors suggested this pretreatment condition on sunflower stalks as a promising method for bioethanol production (Ruiz et al., 2008). SE has its disadvantages: inhibitors like organic acids, furfural, HMF can be generated (Cantarella et al., 2008). Futhermore, xylan is partially lost thus reducing the efficiency of pretreatment (Kang et al., 2014).

2.2.4 Biomass-derived inhibitors

Although pretreatment reduces the recalcitrant nature of LCB, depending on the type of pretreatment and conditions, pretreatment can generate compounds that disrupt enzymatic hydrolysis and inhibit microbial growth and metabolism in fermentation. Figure 6 illustrates some of the most common inhibitors generated from lignocellulosic biomass. Inhibitors like 5-hydroxymethylfurfural (HMF), 2-furaldehyde (furfural), phenolic compounds, formic acid, and acetic acid are toxic to microbial growth. Some of the xylose and other monosaccharides can be further hydrolyzed into furfural during the pretreatment process (Mosier et al., 2015). Lou et al studied the effect of inhibitors on clostridial metabolism. It was found that the presence of lignin-derived phenolic acids and aldehydes in the fermentation feed significantly decreased the intracellular reducing power (NADH level) and increased reactive oxygen species concentration leading to a reduction in butanol production in wild type *C.*

acetobutylicum ATCC 824 strains (Luo et al., 2021). Additionally, these pretreatment by-products reduce sugar yield from lignocellulosic material (Jönsson & Martín, 2016). Acetic acid is especially relevant when considering pretreatment of hardwood biomass because it is formed through hydrolysis reaction of acetyl groups on xylan that is a major component in hardwood and annual plant hemicellulose (Jönsson & Martín, 2016; Cho et al., 2011). Jung & Kim found that HMF impacted cellulase catalytic efficiency during enzymatic hydrolysis of the pretreated lignocellulose. The amount and type of inhibitors generated vary with the severity of pretreatment and type of biomass feedstock. Cho et al. 2012 reported significant reduction in total ABE production of *C. acetobutylicum* when 11.7 g/L of acetic acid was added and in the presence of 1.0 g/L formic acid, total ABE concentration was reduced to 25%. The growth of *C. acetobutylicum* was completely inhibited when furfural concentration reaches 1.2 g/L in the fermentation medium (Liu et al., 2017). In the presence of furfural or HMF, microbial consumption of xylose and glucose were delayed (Liu et al., 2017; Liu et al., 2004).

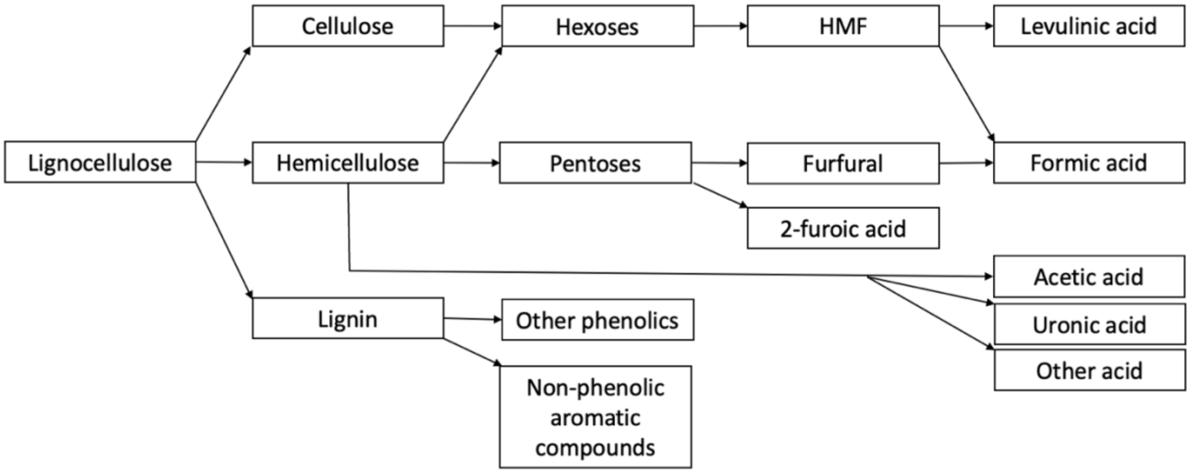


Figure 6. Degradation pathway of lignocellulose in inhibitor formation. Adapted from Jönsson & Martin. 2016

The toxic effects of inhibitors can be alleviated through a detoxification step, aiming to remove the inhibitors and enhance the fermentability of the hydrolysate. Detoxification can be done by physical separation using membranes such as nanofiltration to remove HMF, furfural, and acetic acid (Sun&Liu, 2012). Other detoxification techniques encompass various methods such as charcoal adsorption (Guan et al., 2018), overliming (Sun&Liu, 2012), activated carbon (Zhang et al., 2018), deionized water rinse (Rajan & Carrier, 2014), enzymatic treatment with laccase or peroxidase, liquid-liquid extraction, liquid-solid extraction (Jönsson et al., 2013).

Overliming has the advantage in operating cost and is commonly employed to detoxify dilute acid-pretreated liquid hydrolysate (Sun & Liu, 2012). This method, utilizing calcium hydroxide

($Ca(OH)_2$) or calcium oxide (CaO) to effectively eliminate undesirable inhibitors like furans and HMF, may result in a loss of carbohydrates in the hydrolysate (Martinez et al., 2000). Overliming detoxification involves adding an alkali to elevate the pH of the hydrolysate. After incubation under high pH level, the pH of the reaction mixture is then lowered to around 6.7, facilitating the removal of precipitates containing inhibitory compounds (Guan et al., 2018). A combination of overliming and activated carbon detoxification of poplar prehydrolysate from 1.0% (w/v) sulfuric acid pretreatment, produced a butanol yield comparable to glucose control *C. saccharobutylicum* fermentation (Zhang et al., 2018). Sun and Liu observed a ten-fold increase in biobutanol yield when dilute acid hydrolysate was treated with $Ca(OH)_2$ for detoxification (Sun & Liu, 2012). Additionally, Dou et al. 2021 performed steam explosion on hybrid willow wood and detoxified the resulting hydrolysate obtained from enzymatic hydrolysis using activated charcoal. The microorganism, *C. acetobutylicum* NRRL B-527 produced 8.5 g/L of butanol through fermentation of the detoxified hydrolysate.

2.3 BIOBUTANOL

The U.S. Energy Information Administration defines biofuels as liquid fuels and blending components produced from biomass materials (EIA, 2024). Examples of biofuels include bioethanol, biobutanol, and biodiesel, which can be produced from feedstock such as starchy biomass, LCB and algae (Sandesh & Ujwal, 2021). Generally, bioconversion of LCB into biofuels is commonly carried out biochemically with the assistance of enzymes and microorganisms and thermochemically with the aid of high temperature and chemicals (Yousuf et al., 2020; Inyang et al., 2022). According to Advanced Biofuels Canada, the expansion of biofuel facilities creates more clean energy-related occupations, increases the availability of fuel, and helps mitigate GHG emissions (Advanced Biofuels Canada, 2023). Biofuel refers to fuel produced from renewable sources and can be classified as primary biofuels, which are fuels derived from the direct combustion of raw materials to provide energy or heating, or as secondary biofuels, which are obtained through chemical, thermochemical, or biochemical conversion (Basile & Dalena, 2019)

Among the fuel alcohols used in the transportation sector, butanol is the superior option given that it performs better as a motor fuel when used in spark-ignition engines (Kukharonak et al., 2017). Due to its high production cost, biobutanol (C_4H_9OH) has only recently attracted interest as an alternative transportation fuel. However, technological advancements are making the biobutanol production process more cost-efficient, providing biobutanol the potential to surpass bioethanol in production (Kukharonak et al., 2017). Biobutanol emerges as a promising next-generation biofuel, offering several advantages over ethanol. Compared to ethanol, biobutanol boasts higher energy content, lower volatility, and a reduced tendency to absorb moisture. Additionally, with a double number of carbon atoms compared to ethanol, butanol holds approximately 30% more energy (Ndaba et al., 2015).

2.3.1 Properties of biobutanol

The molecule butanol exists in 4 isomeric forms: n-butanol, 2-butanol, iso-butanol, and tert-butanol. Isobutanol is the isomer form for commercial use in transport section due to its more effective blending potency with gasoline according to the Department of Energy of the USA (Nandhini et al., 2023). As seen in Table 3, butanol's physical and chemical properties resemble gasoline more than ethanol. Butanol has higher calorific value, is less hydrophilic, more compatible with car engines, less corrosive, and more stable when mixed with gasoline (Liu et al., 2022). Additionally, it exhibits reduced corrosiveness and is better suited for distribution via current petrol pipelines (Ndaba et al., 2015). Butanol finds its applications not only as a fuel but also as a solvent in rubber production (Liu et al., 2022), eluent for chromatography (Liu et al., 2022), extractant (Mahapatra et al., 2017), and plasticizer (Mascal, 2012).

Table 3.Property comparison between gasoline, butanol, and ethanol, adapted from Bharathiraja et al. 2017.

Properties	Gasoline	Butanol	Ethanol
Calorific value (MJ/L)	32.3	30.8	23.5
Octane index	85-94	87	112 to 114
Oxygen content (%)	Close to 0	22	36
Melting point (℃)	-57.1 to -56.6	-89.3	-114
Auto-ignition temperature (℃)	246-280	343-345	422
Solubility in 100g of water	immiscible	immiscible	miscible

2.3.2 Conversion of lignocellulosic biomass to biobutanol

The process of biobutanol production from LCB can be summarized into four main stages: pretreatment, hydrolysis, fermentation, and purification/separation. Pretreatment is the preliminary step to reduce the recalcitrant nature of LCB, while hydrolysis converts polysaccharides into monomeric sugars. Subsequently, fermentation metabolizes sugars into acetone, butanol, ethanol. The final stage involves the separation/purification process to recover butanol from the fermentation broth.

Following the pretreatment step that exposes cellulose and hemicellulose, enzymatic hydrolysis further breaks down the polysaccharide fractions into fermentable monomer sugars for microorganisms to utilize for metabolism. Enzymatic hydrolysis, also known as saccharification, can be performed simultaneously with fermentation in the same bioreactor (termed simultaneous saccharification and fermentation - SSF) or separately prior to fermentation (known as separate hydrolysis and fermentation - SHF) (Pendse et al., 2023). Enzymatic hydrolysis uses glycosyl hydrolases, which include cellulase (e.g., endoglucanases, exoglucanases, glucosidases) to breakdown cellulose into glucose molecules and noncellulosic polysaccharides (e.g., xylanase, mannanases, glucuronidases, xylosidases, mannosidases) to enable the degradation of the cellulose main chain backbone and side chain constitutes (Vertès, 2010). The reaction of glucan and xylan with water can be represented as (Kang et al., 2014):

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6 \text{ (for cellulose)}$$

$$(C_5H_8O_4)_n + nH_2O \rightarrow nC_5H_{10}O_5 \text{ (for hemicellulose)}$$

Most sugars produced from hydrolysis in a hydrolysate are glucose, sucrose, xylose, and arabinose. Within these carbohydrates, glucose molecules are the preferred carbon source of Clostridia sp. for biobutanol production (Amiri&Karimi, 2018). The concentration of sugar molecules generated from hydrolysis varies depending on the type of lignocellulosic feedstock. For example, hydrolysis of hardwood hemicellulose results in a higher concentration of pentoses, while a higher quantity of hexoses is observed for softwood hydrolysis (Jönsson & Martín, 2016). A notable advantage of enzymatic hydrolysis is that it does not generate additional inhibitors (Jegatheesan et al., 2020). Furthermore, enzymatic hydrolysis operates under mild conditions, resulting in low energy requirements (Jegatheesan et al., 2020).

On the contrary, enzymatic hydrolysis has its flaws. Despite its low energy requirement for operation, the high production cost of enzymes contributes significantly to the overall biobutanol production cost. Since cellulases are used as catalyst, competitive inhibition of the hydrolysis products by enzymes (e.g., glucose, cellobiose, xylose) limits the effectiveness of hydrolysis. Typically, enzymatic hydrolysis occurs under mild conditions (temperature of 45-50 °C and pH level 4-5 (Paul & Chakraborty, 2019). To optimize hydrolysis, tight monitoring of operating conditions like pH, temperature, concentrations of substrate, and enzyme levels is essential. The majority of hydrolytic products from LCB are composed of glucose and xylose so the efficiency of xylose and glucose conversion is paramount (Jiang et al., 2014).

ABE fermentation was first introduced for industrial acetone production in the 1910s (Moon et al., 2016). This process rapidly declined in the 1950s due to the lack of feedstock and competition with the petrochemical industry. Later, the ABE fermentation gained more attention mostly for the butanol production during the oil crisis in 1970s (Birgen et al., 2019). ABE fermentation is biphasic process utilizing bacteria from the *Clostridium* genus and it can be conducted using three different processes: batch, fed-batch, or continuous. *Clostridial* ABE fermentation involves: acidogenesis phase that converts sugars into acetic acid and butyric acid and solventogenesis phase that produce the solvents (acetone, butanol, and ethanol) from acids (Buehler & Mesbah, 2016). These bacteria are the commonly used strains due to their ability to metabolize a variety of carbon sources, including monosaccharides (pentose and hexose), disaccharides (lactose, sucrose, and cellobiose), and polysaccharide (starch) (Williams et al., 2015). *Clostridium acetobutylicum*, *Clostridium beijerinckii*, *Clostridium saccharoperbutylacetonicum*, and *Clostridium saccharobutylicum* produce higher levels of butanol and are widely employed in research studies and industrial applications (Lin et al., 2023). An advantage of *Clostridial* species is that they are able to utilize multiple carbon sources such as hexose, pentose, disaccharide for fermentation

(Bharathiraja et al., 2017). The efficiency of sugar utilization (rate of consumption, solvent production and yield) of *C. acetobutylicum* from high to low is glucose, arabinose, mannose, xylose and cellobiose (Jiang et al., 2014). A study conducted by Jiang et al. 2014 examined the effect of pH control on *C. acetobutylicum* ATCC 824 fermentation, finding improvements in microbial growth, xylose utilization, and total solvent production when the pH was controlled between 4.5 to 5.0 compared to uncontrolled pH (below 4.0 to 5.0) (Jiang et al., 2014). Acetone-butanol-ethanol is produced in a molar ratio of 3:6:1 (Sarangi & Nanda, 2018). Nonetheless, from the perspective of butanol production, the simultaneous formation of acetone and ethanol limit the production of butanol (Sandesh & Ujwal, 2021).

Figure 7 provides an overview of the biochemical pathway of ABE fermentation. During fermentation, glucose and xylose are metabolized into pyruvate through distinct pathway. Glucose first undergoes phosphorylation to glucose-6-phosphate (G6P) and further gets converted into pyruvate via Embden-Meyerhof-Parnas (EMP) pathway. On the other hand, xylose is converted into fructose-6-phosphate through the pentose-phosphate pathway (PPP) before being converted into pyruvate. Pyruvate is then further metabolized into acetyl-CoA and subsequently into solvents (Ndaba et al., 2015). The utilization of a mixed sugar feed as a substrate for *Clostridial* fermentation is an efficient method to sufficiently utilize lignocellulosic material (Birgen et al., 2019). However, a phenomena known as carbon catabolite repression (CCR) occurs in solventogenic bacteria such as *C.acetobutylicum* (Delarouzée et al., 2023), *C. tyrobutyricum* (Fu et al., 2022), and *Clostridium beijerinckii*, where the utilization of other carbohydrates is inhibited in the presence of preferred carbon source such as glucose) (Bruder et al., 2015). Thus, CCR affects the efficiency of carbohydrate utilization by bacteria when a sugar mixture is available. With the appropriate fermentation conditions and the right sugar ratio, sugar mixture can be used effectively to produce ABE. Jiang et al. 2014 elucidated that when the ratio of glucose is lower than xylose in a glucose/xylose sugar mixture feed for *C. acetobutylicum* ATCC 824 under a controlled pH environment, xylose consumption is significantly enhanced. The study concluded that the presence of a small amount of glucose enhances the xylose utilization and solvent production of ABE. Furthermore, the CCR effect can be reversed through gene inactivation involved in glucose and xylose metabolism (Fu et al., 2022).

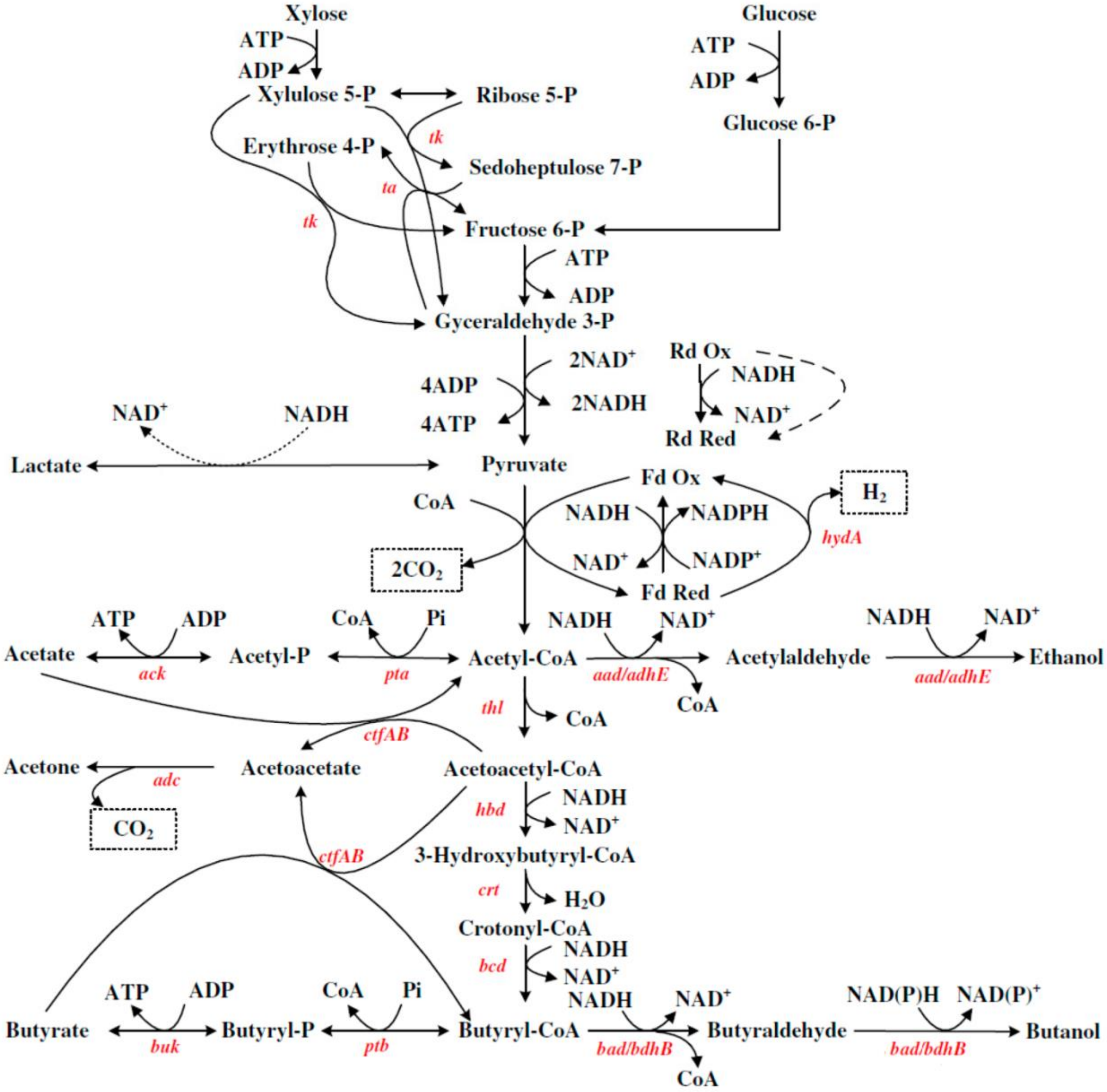


Figure 7. ABE fermentation pathway of Clostridia species (Lin et al., 2023).

The final step of biobutanol production is the separation and purification step which recovers biobutanol from the fermentation broth. The effectiveness of separation is critical for the final yield of butanol. The low volatility nature of biobutanol (Oh et al., 2021) and the low biobutanol concentration within the fermentation broth makes the recovery process energy demanding (Karimi et al., 2024). This is a major limitation to the commercialization of biobutanol production through ABE fermentation (Chen et al., 2018). Separation by distillation is the most common method to separate products of ABE fermentation based on the difference in boiling points. However, this method of biobutanol purification is energy intensive. Other separation methods such as adsorption, gas stripping, membrane distillation, vacuum pervaporation, reserve osmosis (Kujawska et al., 2015) and liquid-liquid extraction-assisted distillation (Sanchez-Ramirez et al., 2018) were explored by the scientific community. A newer and more environmentally friendly method to separate biobutanol from the fermentation broth is perstraction. Perstraction is a method of membrane separation technique that transfers biobutanol from an aqueous phase through a polymeric membrane to an extractant of selection to purify biobutanol (Cabezas et al., 2022). Liquid extraction using an additional extractant is also an alternative biobutanol recovery method. This purification technique is less energy demanding but requires careful selection of extractant (Oh et al., 2021).

2.3.3 Process simulation

Process simulation plays a pivotal role in assessing technical feasibility and estimating costs during the plant's process design stage. It also facilitates analyses aimed at optimizing operations within existing plants. Process simulation software falls into two main categories: commercial and open-source. Features of some of the commonly used software simulators are presented in Table 4. Examples of open-source simulators include DWSIM, COCO, and ASCEND. The software packages can be downloaded onto a user’s computer without requiring the purchase of a license. The relevance of open-source platforms heightened during the pandemic, fostering increased utilization.

Table 4. Comparison of the common process simulation software.

Name of simulator	Type	Features
Aspen Plus	Commercial	- dynamic simulation for most processes - user-defined compounds are available
UniSim	Commercial	- dynamic simulation for most processes - user-friendly process design software (Kasani et al., 2022) - can conduct steady-state and dynamic simulations
ProSim	Commercial	- dynamic simulation for 2 processes only - offers low-cost academic course on the simulator
ChemCAD	Commercial	- dynamic simulation for most processes - integrates chemical process simulation with chemical engineering workflow and process efficiency (Ureta & Salvadori, 2022)
DWSIM	Open-source	- user-friendly interface - can conduct steady-state and dynamic simulations
COCO	Open-source	- sequential simulation software (Zalazar-Garcia et al., 2022) - can conduct steady-state simulation
ASCEND	Open-source	- solve non-linear systems of equations (ASCEND) - can conduct steady-state and dynamic simulations (ASCEND)
OpenModelica	Open-source	- Modelica language-based simulator - can conduct steady-state and dynamic simulations

Contrarily, commercial simulators such as Aspen Plus, Aspen Hysys, ChemCAD, UniSim, among others, dominate the market. While this software boasts a larger database (Tangsriwong et al., 2020), they typically entail substantial licensing fees. Notably, open-source simulation software often yields results comparable to those obtained from commercial simulators. For instance, Tangsriwong et al. 2020 compared simulation results between DWSIM and Aspen Plus in the context of offshore petroleum production processes, finding consistency with actual plant data.

Similarly, Nayak et al. conducted simulations using OpenModelica and compared the outcomes with data obtained from DWSIM and Aspen Plus. Their findings revealed agreement in various chemical processes, including methanol-water distillation, ethylene glycol production from ethylene oxide and water, and the esterification reaction of acetic acid (Nayak et al., 2019). Omar et al. employed DWSIM to model the PRICO LNG process, comparing the results with Aspen Plus simulations. The slight deviation observed in the coefficient of performance (COP) values indicated a comparable performance between DWSIM and Aspen Plus (Omar et al., 2018).

Moreover, Hassan and Manji successfully simulated combined cycle and gas turbine power plants using DWSIM, generating results aligned with predictive models. DWSIM, known for its user-friendly interface and sequential modular structure, possesses the capability to simulate intricate chemical processes (Chantasiriwan, 2023). For instance, Bahrun et al. 2022 utilized DWSIM to develop a deodorization process consisting of three stages: pre-stripper, deodorizer, and vacuum scrubber, effectively removing fatty acids from bleached palm oil.

In this study, the biobutanol production process was simulated using DWSIM version 7.3.2, aligning with previous studies performed at a laboratory scale. DWSIM is created by Daniel Wagner Oliveira de Medeiros (Andreasen, 2022). It can be downloaded for free and is compatible with various platforms such as Windows, Linux, macOS, Android and IOS. In addition to being freely available to the community, DWSIM's open-source nature enables research communities and professionals to contribute to the software development by sharing their simulation work and providing suggestions and solutions to simulation cases.

Biobutanol production is currently undergoing research and development, with studies conducted primarily at the laboratory level. Simulation serves as a crucial intermediary, facilitating the transition of laboratory results to predictions of industrial-scale production. However, despite the wealth of studies simulating the biofuel production process, there is a notable deficiency in the utilization of open-source simulators, as previous research heavily relied on commercial counterparts. Additionally, the majority of research efforts have concentrated on incorporating a singular biomass feedstock or specific sections of the entire conversion process, such as conducting pretreatment exclusively on one biomass type without further exploration of the fermentation process, as opposed to considering multiple feedstocks.

Consequently, comprehensive investigations covering the entirety of the biobutanol production process are infrequent. Thus, this study was motivated to establish a preliminary simulation research to demonstrate the feasibility of bioprocess simulation using an open-sourced simulation software.

2.4 Objectives

This study is designed to achieve three objectives: (1) the primary objective of this study is to investigate the process modeling feasibility of biobutanol production from a lignocellulosic material using an open-source simulator, DWSIM, (2) the secondary goal is to evaluate different configurations for butanol production based on feedstock composition and the type of pretreatment method and compare biobutanol yield between different feedstocks, (3) the tertiary objective is to predict the biobutanol production in a plant setting from laboratory-scale results.

2.5 Process description

The overall methodology of this study is illustrated in Figure 8. Further literature review was conducted to establish a flow diagram outlining the essential steps involved in the biological conversion from LCB. The resulting flow diagram facilitated the initial development of flowsheet on DWSIM. After reviewing the settings of DWSIM flowsheet, relevant experimental data was gathered from research studies. The criteria for selection of literature was focused variety of different category of LCB, employed autohydrolysis or dilute acid pretreatment, sufficient data to calculate conversion rate for each step and it needs to conduct the full process from pretreating feedstock to ABE fermentation. The collected experimental data were then used to develop different configurations. Lastly, results were evaluated and locations of biobutanol plant sites based biomass availability were suggested.

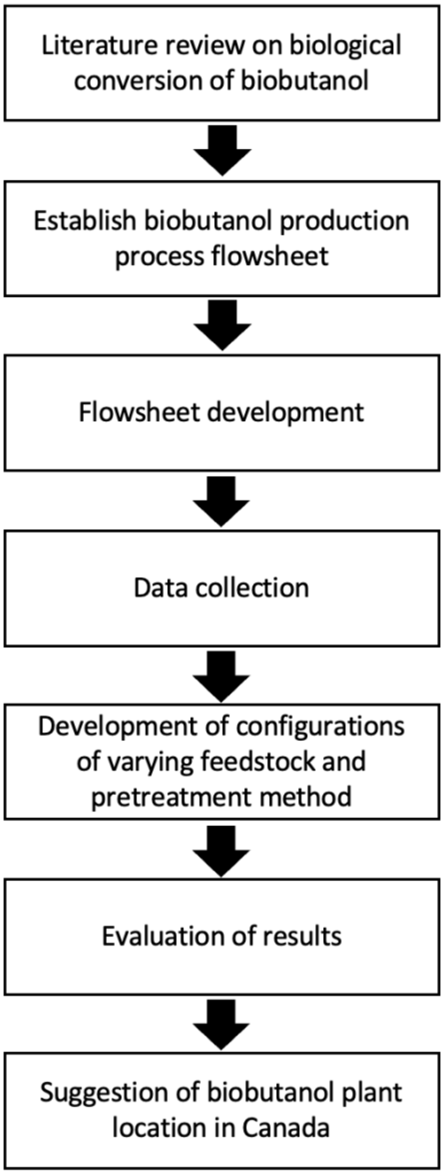


Figure 8. Overview of the methodology of the biobutanol production simulation process.

Figure 9 summaries the fermentative biobutanol production process, which can be generally categorized into the following stages: (1) pretreatment of the biomass feedstock; (2) separation to remove liquid from the pretreated solid; (3) detoxification to minimize the effect of inhibitors on the subsequent steps; (4) enzymatic hydrolysis to convert polysaccharides into monomeric sugars (5) fermentation to metabolize sugars into ABE, acids, and gas; and (6) distillation to recover butanol. Subsequently, a simulation model was constructed based on the main steps established in Figure 9 and was validated using experimental data from the literature. Various types of feedstock and pretreatment methods for biobutanol production were used to development multiple configurations.

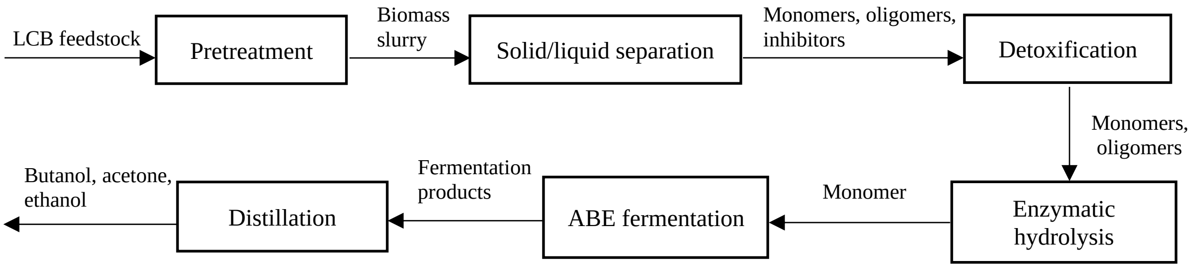


Figure 9. Schematic representation of steps involved in biobutanol production from lignocellulosic biomass.

3 DWSIM SIMULATION DEVELOPMENT

3.1 Compound selection and creation in DWSIM

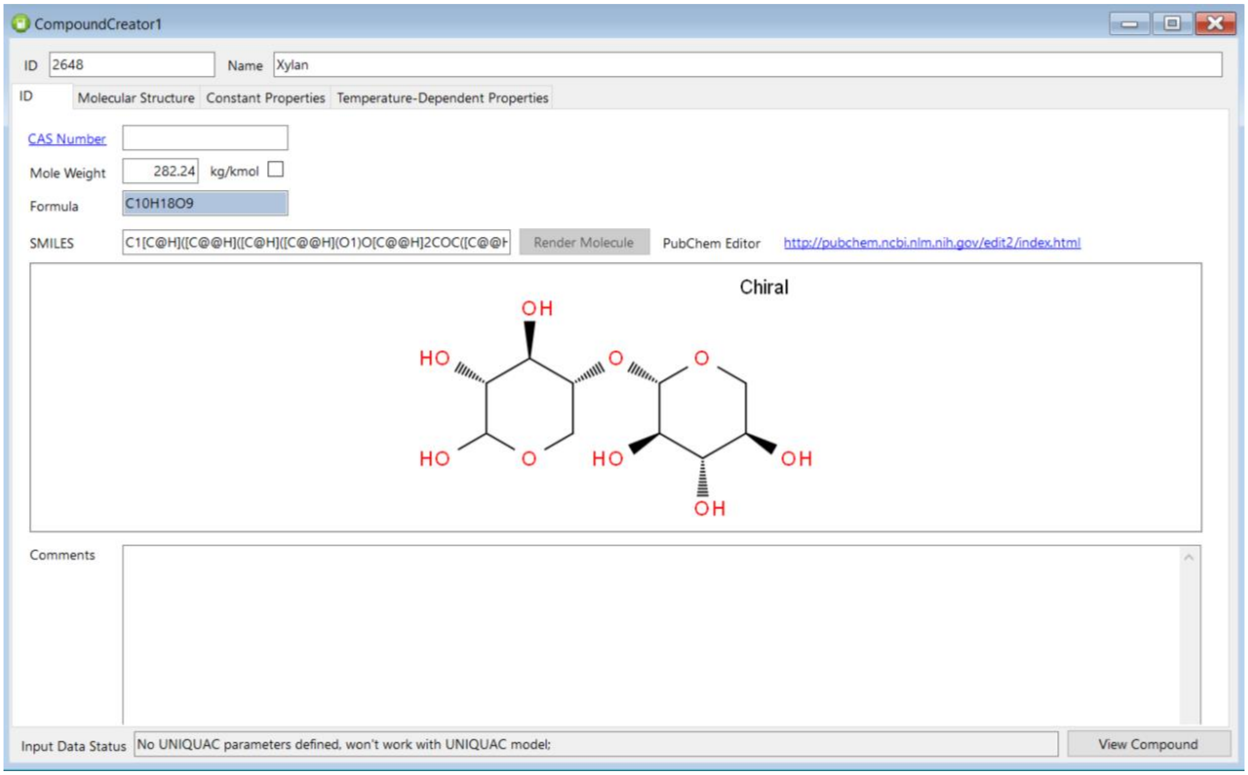
As shown in Table 5, not all required compounds are available in the DWSIM compound database. Hence, the development of the simulation began with the creation of compounds absent in the DWSIM database. These molecules were generated using the ‘compound creator’ function within the ‘user compound creation’ tool, utilizing information sourced from PubChem and UNIFAC group assignments from the Dortmund Data Bank. Figure 10 provides an example of the software interface of the compound creater function in DWSIM. Each compound was downloaded as a JSON file and was then imported into DWSIM.

Table 5. List of compounds used in DWSIM model for this simulation.

Compound	Molecular Formula	Available in DWSIM
Cellulose	$C_{12}H_{11}O_{11}$	✗
Xylan	$C_{10}H_{18}O_9$	✗
Lignin	$C_{10}H_{12}O_3$	✗
Acetate	$C_2H_3O_2$	✗
Glucolig	$C_{12}H_{22}O_{11}$	✗
Xylolig	$C_{10}H_{18}O_9$	✗
Lignin soluble	$C_{10}H_{12}O_3$	✗
Glucose	$C_6H_{12}O_6$	✓
Xylose	$C_5H_{10}O_5$	✓
Furfural	OC_4H_3CHO	✓
1-butanol	$CH_3(CH_2)_3OH$	✓
Acetone	CH_3COCH_3	✓
N-butyric acid	$CH_3CH_2CH_2COOH$	✓
Acetic acid	CH_3COOH	✓
Water	HOH	✓
Carbon dioxide	CO_2	✓
Hydrogen	H_2	✓

Cellobiose, xylobiose, and coniferyl alcohol were chosen to represent the three primary components. Cellobiose served as the representative molecule for cellulose and was denoted as cellulose. Xylobiose was included and labeled as xylan to portray hemicellulose because xylose is the major component of hemicellulose. Coniferyl alcohol, being the most prevalent unit in hardwood lignin, was used to represent lignin within the database.

The primary focus of this simulation was to illustrate the conversion of glucose and xylose to biobutanol, given that they constitute the major sugar units in cellulose and hemicellulose, respectively. No reactions were introduced for the other C5 and C6 sugars. Similarly, acetate was added to represent acetate, ash, and unknown components found in biomass. Glucose-oligosaccharide (glucolig) and xylose-oligosaccharide (xylolig) were integrated to mimic short-chain polymers to allow simulation of the generation of polysaccharides during pretreatment and the subsequent conversion of these polymers into monomeric sugars during enzymatic hydrolysis. Additionally, soluble lignin was included to represent inhibitory compounds derived from lignin.



ID: 2648
Name: Xylan
Mole Weight: 282.24 kg/kmol ☐
Formula: C10H18O9
SMILES: C1[C@H]([C@@H]([C@H]([C@@H](O1)O[C@@H]2COC([C@@
PubChem Editor: http://pubchem.ncbi.nlm.nih.gov/edit2/index.html
Input Data Status: No UNIQUAC parameters defined, won't work with UNIQUAC model;

Figure 10. Example of the compound creation panel on DWSIM for xylan.

3.2 General settings of process units

Raoult’s law was selected as the thermodynamic property package for this process. The calculation mode for these conversion reactors was set to be isothermic, simulating a constant temperature condition throughout the reaction duration. For pressure calculation, the inlet average was selected when multiple streams were combined using a mixer. CS was instrumental in simulating solid/liquid separation for the pretreated slurry, detoxification, decanter operations, and other compound removal processes. Finally, shortcut columns were incorporated to simulate the purification of fermentation products through distillation.

3.3 Data collection

The primary focus of this study lies in analyzing AH and dilute acid hydrolysis while examining variations in feedstock. During data collection phase, specific information needs to be extracted from literature to aid in the development of flowsheets. This includes: (1) feedstock composition, (2) operating conditions for pretreatment, (3) prehydrolysate sugar composition, (4) enzymatic hydrolysis conditions, (5) hydrolysate sugar concentration. Autohydrolysis and dilute acid pretreatment were the targeted pretreatment methods in data collection from literatures as they are the commonly employed pretreatment methods for lignocellulosic feedstock (Lee et al., 2010). One of the challenges during the literature research process was identifying research papers that provided a comprehensive dataset encompassing all aspects, particularly detailed information for the pretreatment phase.

3.4 Assumptions

Several assumptions were considered during the flowsheet development in DWSIM: i) The feedstock compositions reported in literature varied considerably. Lignocellulose composition was presented either in terms of cellulose, hemicellulose and lignin percentages or as carbohydrate mass percentages (e.g. glucan, xylan, arabinan, mannan, galactan). When the lignocellulose composition is presented in the cellulose, hemicellulose and lignin format, it was assumed the entire mass of hemicellulose consisted of xylan and cellulose is composed of cellubiose; ii) Some studies implemented simultaneous saccharification and fermentation (SSF). To ensure consistency, separate conversion reactors were used for saccharification and fermentation instead of combining them into a single reactor. iii) As previously discussed, *Clostridial* species exhibit carbon catabolite repression (CCR) when fermenting mixed sugar. In the fermentation reaction setup, it was assumed that the conversion of xylose into fermentation products was as efficient as that of glucose.; iv) In instances where specific data for certain compounds during pretreatment was not provided in the literature, it was assumed that no conversion of these compounds occurred. and v) Most studies involved physical pretreatment methods such as chipping and milling, which were not integrated into the flowsheet during the modeling process.

3.5 Flowsheet development for biomass conversion modelling

3.5.1 Operating units

The flowsheet development was connected through streams and various units. Conversion reactor (CR), module illustrated in Figure 11 was essential for the development of this simulation. The CR was involved in modeling pretreatment, enzymatic hydrolysis, and fermentation processes. It was utilized to facilitate chemical and biochemical reactions, characterized by the conversion of reactants as a function of temperature. The setting for CR allows for specifying the percentage conversion of the limiting reagent with respect to temperature, as determined by the user. CR in DWSIM had two product streams by default.

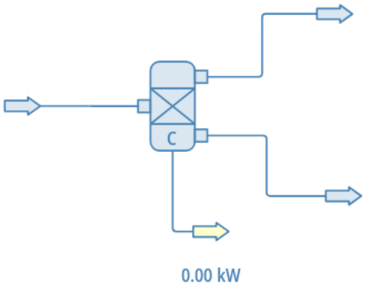


Figure 11. Conversion reactor unit with inlet and outlet streams and an energy stream.

Compound separator (CS) module, visualized in Figure 12 was chosen to model liquid/solid separation after pretreatment and detoxification to remove inhibitors. The setting enables users to specify the percentage of compounds within one inlet stream.

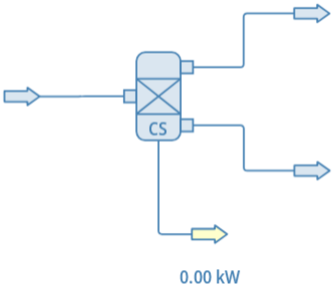


Figure 12. Compound separator with inlet and outlet streams and an energy stream.

Shortcut column module (Figure 13) was used specifically in the last step of the production process, separation and purification of biobutanol through distillation.

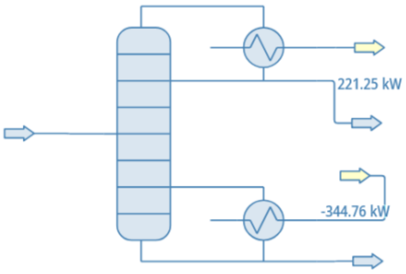


Figure 13. Shortcut column used in this simulation.

Other ancillary units (Figure 14) involved are stream mixers, coolers, heaters. Stream mixer was employed to simulate the combination of biomass and water or dilute acid solution. This unit was used when the entirety of the products in both outlet streams needed to be collected for further processing.

Heaters and coolers were used to represent change in the operating conditions such as increase and decrease in temperature.

Figure 14. Ancillary units used in this simulation.

3.5.2 Reaction sets

The conversion process is divided into three reaction sets: (a) reactions for pretreatment that convert a portion of hemicellulose and cellulose into monomers and oligomers, (b) enzymatic hydrolysis to break down oligomers into their monomeric form, and (c) reactions that metabolize C5 and C6 sugars into fermentation products, modeling Clostridium saccharobutylicum metabolism.

The percent conversion in pretreatment reactions was calculated based on the experimental data from the literature. Reactions converting xylan into furfural and acetic acid, as well as lignin into lignin soluble, were included to represent the generation of inhibitors. The generation of glucolig, glucose, xylolig and xylose were included in the pretreatment because some cellulose and hemicellulose are hydrolyzed into monomeric sugars and sugar oligomers. However, literature lacked sufficient experimental data to calculate conversion for certain compounds. For instance, Amiri and Karimi's paper in 2015 (used in the development of configuration 2) primarily focused on the generation of sugars in the liquid hydrolysate after autohydrolysis, without presenting data regarding inhibitory compounds. Therefore, data was lacking in this aspect.

In terms of enzymatic hydrolysis reactions, a total of four reactions were considered to represent the breakdown of the pretreated solid or prehydrolysate liquid via enzymatic hydrolysis. Reactions of cellulose and xylan represented the hydrolysis of pretreated solid, while the conversion of glucolig and xylolig into monomers were used to represent enzymatic hydrolysis of the liquid. However, due to variations in enzymatic hydrolysis methods, glucolig and xylolig conversion were only included when the liquid prehydrolysate was involved in the enzymatic hydrolysis.

3.5.3 Flowsheet development

Six distinct flowsheet configurations were developed, each distinguished by factors such as feedstock composition, pretreatment conditions, and feed for enzymatic hydrolysis. In configuration one, the approach involved simultaneous saccharification and fermentation of charcoal-detoxified hybrid poplar liquid hydrolysate. Elmwood was used for configuration two, undergoing autohydrolysis pretreatment, followed by enzymatic hydrolysis of the solid. The resulting hydrolysate was then used for fermentation. Both configurations three and six used switchgrass as the feedstock, employing similar operating conditions for pretreatment and SSF, differing pretreatment methods; configuration three used autohydrolysis, while configuration six used dilute acetic acid pretreatment. Configuration four entailed the dilute sulfuric acid pretreatment of wheat straw, followed by enzymatic hydrolysis of the pretreated solid. Finally, configuration five involved dilute sulfuric acid treatment of pulp and paper side-stream, followed by SSF of the resulting pretreated solid.

The conversion rates for each reaction in pretreatment and enzymatic hydrolysis are summarized in Table 6.

Table 6. Chemical reactions and extent of reactions in percentage for pretreatment and enzymatic hydrolysis in each configuration. Cellulose and xylan conversion signify the hydrolysis of pretreated solid. Glucolig and xylolig conversions were included when the liquid prehydrolysate was utilized for enzymatic hydrolysis. References: [1] Guan et al. 2018. [2] Amiri & Karimi, 2015. [3] Wang et al. 2019. [4] Rajan & Carrier, 2014. [5] Sander et al., 2020. [6] Wang et al. 2019.

	Config 1[1]	Config 2[2]	Config 3[3]	Config 4[4]	Config 5[5]	Config 6[6]
Pretreatment Reactions						
$Cellulose + H_2O \rightarrow Glucolig$	4.07 %	19.15 %	10.96 %	n/a	0 %	11.8 %
$Cellulose + H_2O \rightarrow 2\ Glucose$	1.5 %	7.3 %	2.8 %	3 %	0 %	4.49 %
$Xylan + H_2O \rightarrow Xylolig$	32.86 %	1.76 %	36.98 %	n/a	0 %	49.48 %
$Xylan + H_2O \rightarrow 2Xylose$	6.5 %	12.3 %	3.1 %	45.13 %	0 %	4.17 %
$Xylan + H_2O \rightarrow 5H_2O + 2\ Furfural$	1.9 %	n/a	3.65 %	n/a	1.3 %	4.17 %
$Xylan + H_2O \rightarrow 5Acetic\ acid$	10.16 %	n/a	12.5 %	n/a	0.19 %	27.9 %
$Lignin \rightarrow Lignin\ soluble$	2.255 %	n/a	27.4 %	n/a	n/a	25.5 %
Enzymatic Hydrolysis Reactions						
$Cellulose + H_2O \rightarrow 2Glucose$	-	96.1 %	77.7 %	89.25 %	47 %	71 %
$Xylan + H_2O \rightarrow 2\ Xylose$	-	26.7 %	78 %	47.18 %	30 %	78 %
$Glucolig + H_2O \rightarrow Glucose$	77.7 %	-	77.7 %	-	-	71 %
$Xylolig + H_2O \rightarrow Xylose$	38 %	-	78 %	-	-	78 %

For fermentation reactions, the chemical reactions and extent of reactions described by Meramo-Hurtado et al. 2021 (Table 7) were used for all configurations. This consistency provides more accurate comparison of the amount of butanol produced from different feedstock and pretreatment methods. The fermentation reactions were chosen to convert glucose and xylose because the two monosaccharides are the major sugar components in a lignocellulosic hydrolysate.

Table 7. Fermentation reactions and % conversion (Meramo-Hurtado et al. 2021).

Fermentation Reactions	Conversion (%)
$Glucose \rightarrow Butanol + 2CO_2 + H_2O$	57
$Glucose + H_2O \rightarrow Acetone + 3\ CO_2 + 4H_2$	27.4
$Glucose \rightarrow 2\ Ethanol + 2\ CO_2$	7.4
$Glucose \rightarrow Butyric\ acid + 2C\ O_2 + 2\ H_2$	4.3
$Glucose \rightarrow 3\ Acetic\ acid$	3.2
$6\ Xylose \rightarrow 5B\ utanol + 10\ CO_2 + 5\ H_2O$	50.0
$Xylose \rightarrow Acetone + 2\ CO_2 + 2\ H_2$	30.0
$3\ Xylose \rightarrow 5\ Ethanol + 5\ CO_2$	15.0
$2\ Xylose \rightarrow 5\ Acetic\ acid$	1.0

The flowsheet begins with a mixer combining either water stream or a dilute acid stream with biomass feedstock stream to achieve the desired solid to liquid ratio (SLR). The resulting stream is then heated with a heater to obtain the desired temperature for pretreatment before feeding into the conversion reactor. After the reactor, the pretreated slurry stream is then fed into a cooler to reduce the temperature to 25 ℃. A compound separator is used to simulate the separation of prehydrolysate liquid and preteated solid.

Detoxification was represented by adding a CS unit to separate inhibitory compounds from the prehydrolysate liquid.

In enzymatic hydrolysis, the common practice involves discarding the prehydrolysate liquid that typically lacks a sufficient sugar content for effective fermentation (Wang et al., 2019) and focusing solely on treating the pretreated solid, which harbors the bulk of polysaccharides. However, it is possible to hydrolyze both solid and liquid phases or just the prehydrolysate liquid for further fermentation. This study encompasses all these scenarios. Depending on the methodology of the study, the flowsheet incorporated streams from i) liquid prehydrolysate, ii) pretreated solid, or iii) a combination of both into the conversion reactor for enzymatic hydrolysis. Notably, conversions of glucolig and xylolig were only included when the prehydrolysate liquid was part of the enzymatic hydrolysis process.

The output stream from enzymatic hydrolysis was fed to a compound separator to create a stream containing only glucose, xylose, and water for fermentation. Before distillation, fermentation gases and acids were separated from the fermentation products.

For the recovery and purification of butanol from the fermentation broth, three shortcut modules were utilized to represent distillation columns, and a separator was employed as a decanter. The order of product separation was determined based on the boiling point of the fermentation products. At atmospheric pressure and temperature of 364.6 K, 1-butanol forms a heterogeneous azeotropic complex with water with a composition of 76.33 mol % water (Luyben, 2008). Kujawska et al. 2015 detailed the conventional ABE separation via distillation. An azeotrope represents a mixture of two liquids maintaining a constant mole fraction composition in the vapor phase (Anderson, 2012) and cannot be separated by a conventional distillation (Baral et al., 2016). The presence of azeotropes involving butanol and water in the fermentation broth necessitates a decanter unit to disrupt these interactions. Because the azeotrope formed between water and n-butanol is heterogenous, a two-column distillation is used for separation. In addition to azeotropic distillation, membrane distillation, reverse osmosis, and extractive distillation are also possible method to separate water from biobutanol (Gai et al., 2018).

The distillation process for ABE product recovery was elucidated by Kujawska et al. 2015. Initially, the material stream containing solvents and water underwent distillation to extract acetone, achieving a high removal percentage of 99.5 wt%. The resulting stream then underwent a second distillation to remove a fraction of ethanol from the mixture. Subsequently, a decanter was introduced to disrupt the azeotropic interactions within the butanol-water mixture. The decanter generated a butanol-rich stream (comprising 23 wt% water) and a butanol-lean stream (containing 9.5 wt% butanol). The butanol-rich stream was further processed in a column for the final purification of butanol. The simulation input for distillation is facilitated by the boiling point differences between fermentation products listed in Table 8.

Table 8. Boiling point of fermentation products (Basile & Dalena. 2019).

Compound	Boiling point (°C; at 1.013 bar)
Acetone	56.14
Ethanol	78.31
n-Butanol	117.8
Water	100.0
Acetic acid	118.0
n-Butyric acid	163.3

3.6 Model validation

The results from DWSIM were compared against experimental data obtained by Amiri & Karimi, who conducted autohydrolysis on elmwood at 180 ℃ for 60 min by mixing 40 g of biomass and 400 g of deionized water (1:10 SLR) in a high-pressure stainless-steel reactor. The prehydrolysate liquid was separated from pretreated slurry through cheesecloth. Enzymatic hydrolysis was done on the pretreated solid. The resulting hydrolysate, containing 13.2 g/L of C6 sugars and 5.0 g/L C5 sugars was then fermentated by *C. acetobutylicum* NRRL B-591.

In the flowsheet, the feedstock composition used for elmwood was 51.8% cellulose, 22.7% xylan, 25.1% lignin and 0.4% acetate (Amiri & Karimi, 2015). The mass flow of the biomass stream was 40 kg/h and it was mixed with 400 kg/h of water to reflect the 1: 10 SLR. The mixed stream was then heated to 180 ℃. The heated stream was sent to the RC for autohydrolysis reaction. The output streams from autohydrolysis were combined and the resulting stream was then introduced into a cooler and a CS to model separation of liquid from solid. The majority of water was incorporated into the solid stream from the CS and was then heated to 45 ℃ to reflect the operating conditions of enzymatic hydrolysis. The stream was fed to a cooler and CS to obtain a stream containing glucose, xylose, and water, which was then fed to fermentation reactors. The fermentation products, butyric acid, acetic acid, carbon dioxide, hydrogen gas, and some water were removed using CS before distillation.

The conversation percentage for each of the reaction in the setting was calculated from the data provided by the literature. For model validation, the concentration of compounds in prehydrolysate liquid, sugar feed for fermentation, and ABE products in g/L in the material streams were compared against the data presented in the paper. As shown in Table 9, the concentration of compounds on DWSIM were similar to the values provided in the reference.

Table 9. Data comparison between flowsheet results from configuration 2 and experimental data presented by Amiri and Karimi (2015).

Component	Prehydrolysate Liquid	Reference
	Concentration (g/L)	
Glucose	3.6	3.8
Xylose	2.7	2.8
Glucolig	9.0	10
Xylolig	0.36	1.0
	Sugar feed for Fermentation (g/L)	
Glucose	14.2	13.2
Xylose	2	5
	Fermentation product (g/L)	
Butanol	4.7	4.4
Ethanol	0.9	0.5
Acetone	1.8	1.8
ABE	7.4	6.7

4 RESULTS

This section presents the results obtained from DWSIM for each configuration, detailing a flowsheet for each feedstock/pretreatment combination. First, the variation in feedstock composition is discussed, followed by a comparison of fermentation product concentrations between configurations. To evaluate biobutanol production between different feedstocks and to obtain a more comprehensive representation of butanol production at industrial level, the final mass flow of butanol was compared by increasing the initial mass flow of biomass to 4000 kg/h.

4.1 Feedstock

Many studies have been conducted to investigate the optimal pretreatment conditions for a specific LCB feedstock (Lima et al., 2013; Pu et al., 2011; Li et al., 2019; and Nitsos et al., 2016). Different feedstocks were examined to further explore the effectiveness of DWSIM in simulating biobutanol production. The data were gathered from various references focused on either autohydrolysis or dilute acid pretreatment on the LCB material. A diverse feedstock was selected to encompass the variety of feedstock: woody biomass, agricultural biomass, and waste biomass. In this study, a total of six configurations were created in DWSIM with different feedstock composition as detailed in Table 10.

Configuration one involved the use of hybrid poplar as the feedstock that was pretreated by autohydrolysis. Configuration two utilized elmwood, a hardwood species, which also underwent autohydrolysis. Both configuration three and six utilized switchgrass as a feedstock. Configuration three employed autohydrolysis as the pretreatment method, while configuration six incorporated acetic acid pretreatment for switchgrass. Notably, configuration five involved the utilization of wheat straw as a feedstock.

Table 10. Feedstock composition of each lignocellulosic material used in the simulation.

Compound	Hybrid poplar (Config 1)	Elmwood (Config 2)	Switchgrass (Config 3 & 6)	Wheat straw (Config 4)	Side stream (Config 5)
Cellulose	45.4 %	51.8 %	35.6 %	38.4 %	61.26 %
Xylan	19.2 %	22.7 %	19.2 %	19.7 %	7.5 %
Lignin	27.5 %	25.1 %	22.6 %	16.9 %	19.01 %
Acetate	7.9 %	0.4 %	22.6 %	25 %	12.23 %

4.2 Flowsheet configurations

Six configurations were developed based on the data reported in literature. The parameters used for each configuration are outlined in Table 11 and were used for the development of each configuration. These configurations encompassed three pretreatment methods: autohydrolysis, dilute sulfuric acid, and dilute acetic acid.

Table 11. Parameters for all configurations.

Parameter	Configuration 1	Configuration 2	Configuration 3	Configuration 4	Configuration 5	Configuration 6
Feedstock	Hybrid poplar	Elmwood	Switchgrass	Wheat straw	Pulp and paper side stream	Switchgrass
Pretreatment method	AH	AH	AH	Dilute sulfuric acid	Dilute sulfuric acid	Dilute acetic acid
Pretreatment conditions	SLR of 1:5 at 170 °C for 60 min	SLR of 1:10 at 180 °C for 60 min	SLR of 1:10 at 170 °C for 10 min	SLR of 1:10 at 140 °C for 30 min with 10 dm3/m3 sulfuric acid	SLR of 1:10 at 180 °C for 10 min with 0.2% sulfuric acid	SLR of 1:10 at 170 °C for 10 min with 3 g/L acetic acid
Solid/liquid separation	Vacuum filtration	Cheesecloth	Vacuum filtration	Centrifugation	Vacuum filtration	Vacuum filtration
Enzymatic hydrolysis	Prehydrolysate	Treated solid	Both prehydrolysate and solid	Treated solid	Treated solid	Both prehydrolysate and solid
Hydrolysis temperature	36 °C	45 °C	30 °C	50 °C	30 °C	30 °C
Hydrolysis method	SSF	SHF	SSF	Saccharification only	SSF	SSF
Detoxification	Charcoal adsorption	Not specified	Activated carbon adsorption	Water wash	Not specified	Activated carbon adsorption
Microbe	*C. acetobutylicum* ATCC 824	*C. acetobutylicum* NRRL B-591	*C. saccharoperbutylacetonicum*	Not specified	*C. acetobutylicum* DSM 1731	*C. saccharoperbutylacetonicum*
Unused material	Pretreated solid stream	Remaining unconverted solid	Remaining unconverted solid	Remaining unconverted solid	Remaining unconverted solid	Remaining unconverted solid
Reference	Guan et al. 2018	Amiri & Karimi, 2015	Wang et al. 2019	Rajan & Carrier, 2014	Sander et al. 2020	Wang et al. 2019

4.2.1 Configuration 1 – Autohydrolysis on hybrid poplar wood

Configuration 1 (Figure 15) involved the mixing of 50 kg/h of hybrid poplar, with a mass fraction of the stream input consisting of 45.4% cellulose, 19.2% xylan, 27.5% lignin, and 7.9% acetate, with 250 kg/h of water in a mixer, MIX-101. Subsequently, the resulting stream with a mass flow of 300 kg/h was heated to an outlet temperature of 170 °C. This heated stream was then introduced into R-101, where pretreatment reactions took place. In R-101, 4.07% of cellulose was converted into glucolig, 1.5% of cellulose into glucolig, 32.9% of xylan into xylose. In addition, 6.5% of xylan into furfural, 10.2% of xylan into acetic acid and 2.26% of lignin was converted into soluble lignin to represent the formation of inhibitory compounds. The output streams from R-101 were combined in MIX-102 because products are generated in both streams, followed by cooling to 25 °C. CS was employed to separate the solid components (cellulose, xylan, lignin, acetate) from the pretreated slurry. CS produces a solid and a liquid stream and only the liquid stream was further utilized in the configuration. The resulting stream (labeled as 09-Prehydrolysate) was then directed to V-102, where 14.2% of glucolig, 90.3% of soluble lignin, 3.6% of xylolig, 14.2% of glucose, 3.6% of xylose, 43.2% of acetic acid, and 66.7% of furfural were removed from the liquid, yielding detoxified stream 11. This step emulates detoxification by charcoal adsorption.

R-102 and R-103 were utilized to represent the conversion of xylolig to xylose at a conversion rate of 38% and glucolig to glucose at a conversion rate of 77.7%, respectively. Stream 17 exiting R-103, and containing monomers, oligomer, sugars and the remaining inhibitory compounds was cooled using E-104 to a temperature of 25 ℃, resulting in stream 18. Stream 18 was subsequently passed through V-103 to obtain a stream containing glucose, xylose, and water prior to the fermentation reactions in R-104 and R-105, as detailed in Table 7. Notably, the composition of stream 25 consists of 9.5 g/L of butanol, 4.7 g/L of acetone, 2.9 g/L of ethanol, 0.77 g/L of acetic acid, and 0.31 g/L of butyric acid. It is essential to highlight that the ABE concentration in stream 25 reflects a production ratio of 3 parts acetone, 6 parts butanol, and 1 part ethanol. V-104 and V-105 were used to remove butyric acid, acetic acid, carbon dioxide, hydrogen gas, glucose, and xylose from the fermentation products before distillation.

The 28-ABE, water stream was fed into T-101 to remove acetone in the distillate stream by setting acetone as the light key compound. The bottom stream was then directed to T-102 to remove ethanol in the distillate stream. Stream 33, the bottom stream, was introduced into V-106 to simulate a decanter, disrupting the azeotropic mixture between butanol and water. V-106 was set to generate a butanol-rich stream and a butanol-lean stream. The butanol-rich stream is composed of 23 wt% water and 77 wt% butanol, which was processed in T-103 to purify butanol.

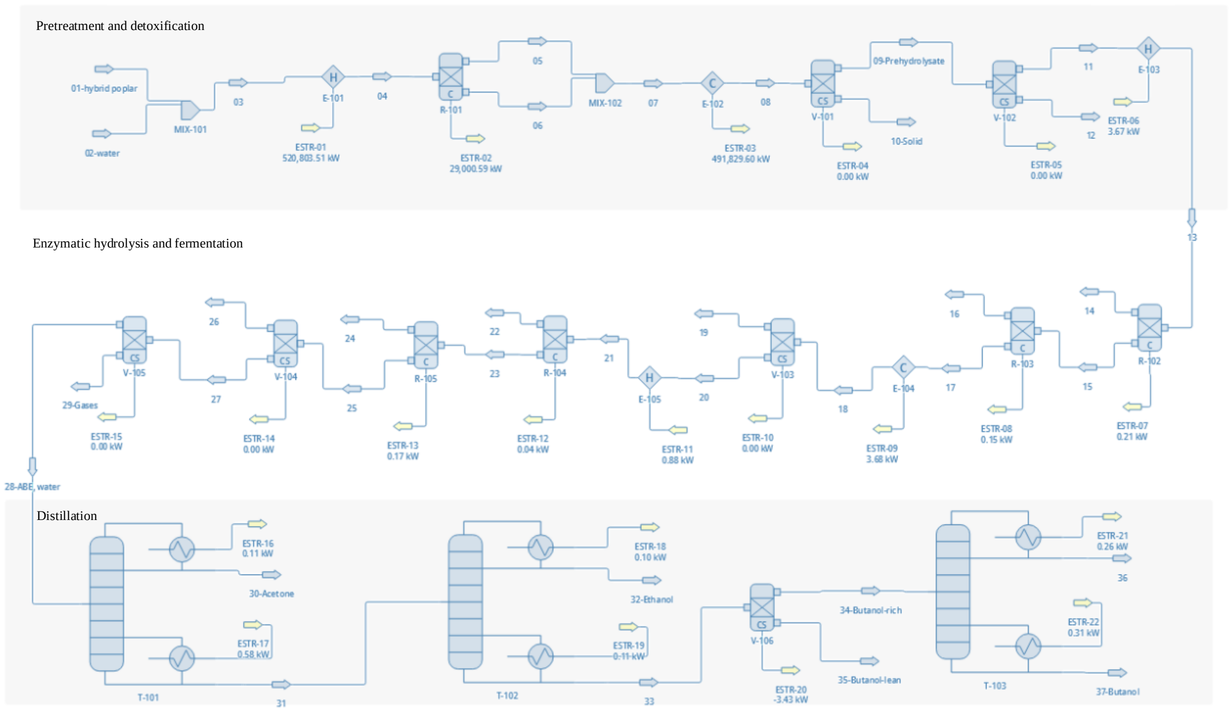


Figure 15. Flowsheet for configuration one modelling biobutanol production using hybrid poplar as feedstock and pretreated through autohydrolysis.

4.2.2 Configuration 2 – Autohydrolysis on elmwood

Configuration two (Figure 16) begins with a stream of elmwood with a mass flow of 40 kg/h consisting of 51.8% cellulose, 22.7% xylan, 25.1% lignin, and 0.4% acetate was mixed with a mass flow of 400 kg/h water. The resulting combined stream, with a mass flow rate of 440 kg/h was then subjected to heating at 180 °C. Subsequently, this heated stream was introduced into R-101, where pretreatment reactions occurred. In R-101, 19.2% of cellulose was converted into glucolig, 7.3% of cellulose into glucose, 1.76% of xylan into xylolig, 12.3% xylan into xylose, 1% of xylan into furfural, and 1% of xylan into acetic acid. Additionally, 1% of lignin was converted into soluble lignin. The output streams from R-101 were mixed to collect products in both output streams. The merged stream, referred to as stream 07 was then cooled to 25 °C.

To further process the components, V-101 was employed to separate cellulose, xylan, lignin, acetate into the solid stream, while the remaining portion was designated as 09-Prehydrolysate. Only the solid stream is heated to 45 and subsequently introduced into R-102 for enzymatic hydrolysis. In R-102, cellulose was converted into glucose at a rate of 38.44%, and xylan into xylose at a rate of 10.68%. Stream 13 was cooled to 25 °C using E-104, resulting in stream 14. Stream 14 was then directed through V-102 to generate a stream containing only glucose, xylose, and water for the fermentation reactions in R-

103 and R-104. The specifics of these reactions and their respective conversion percentages are detailed in Table 7.

In stream 21, the composition of solvents and acids are as followed: 4.96 g/L of butanol, 1.96 g/L of acetone, 0.96 g/L of ethanol, 0.63 g/L of acetic acid, and 0.40 g/L of butyric acid. V-103 was employed to separate butyric acid, acetic acid, carbon dioxide, hydrogen gas, glucose, and xylose from the fermentation products before undergoing distillation. The 22-ABE, water stream was fed into distillation column T-101 to separate acetone into the distillate stream. The residual stream, denoted as stream 24 was then introduced into T-102 to remove ethanol in the distillate stream. Stream 26 is processed through V-104, yielding the 27-Butanol-rich stream with a mass fraction of approximately 77% of butanol and 23% of water. Finally, the butanol-rich stream is fed into T-103 to purify biobutanol.

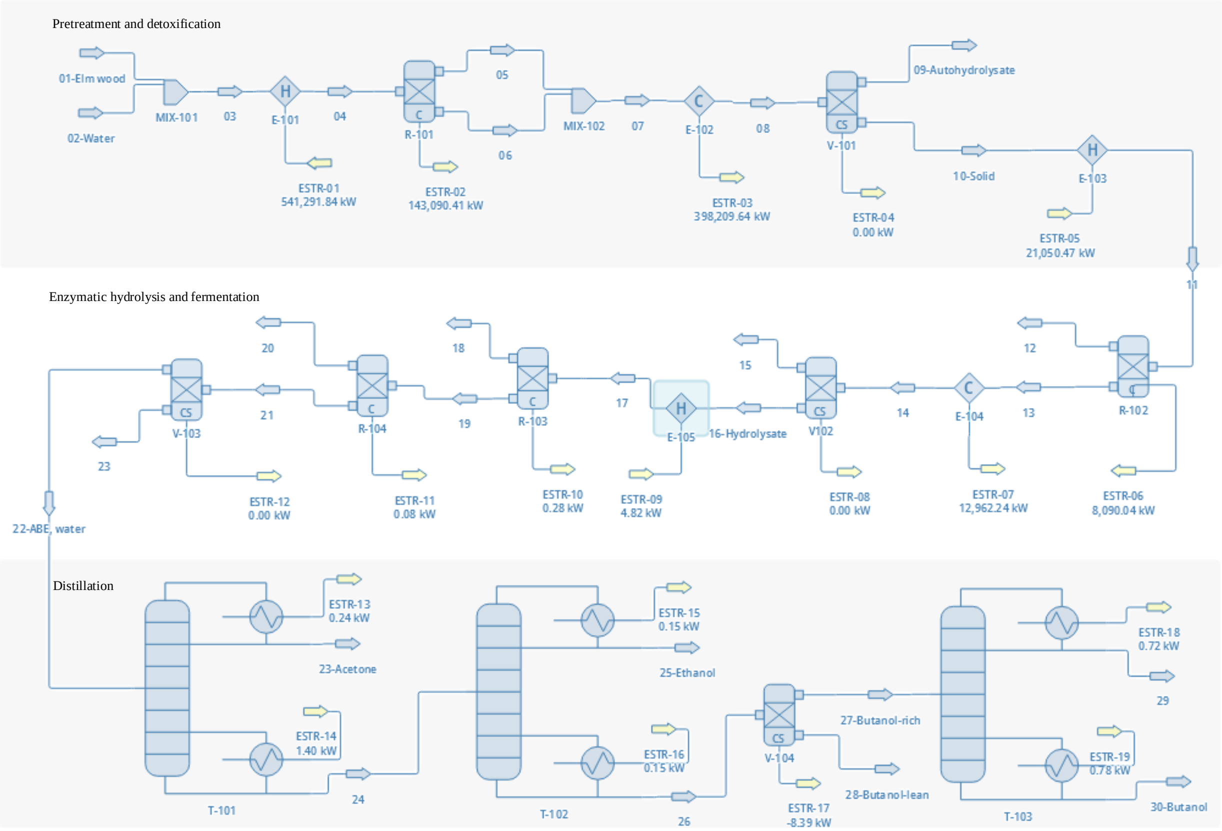


Figure 16. Flowsheet for configuration two modelling biobutanol production using elmwood as feedstock pretreated through autohydrolysis.

4.2.3 Configuration 3 – Autohydrolysis on switchgrass

The biobutanol production utilizing switchgrass as a feedstock is represented in Figure 17. The mass flow input for 01-Switchgrass was 10 kg/h, with a mass fraction of 35.6% cellulose, 19.2% xylan, 22.6% lignin, and 22.6% acetate. This stream was mixed with a mass flow of 100 kg/h water, and the resulting mixture was subjected to heating to attain a temperature of 170 °C. Subsequently, the heated stream was fed to R-101 for autohydrolysis pretreatment. In R-101, the following reactions occurred: 10.0% of cellulose was converted into glucolig, 2.8% of cellulose into glucolig, 36.0% of xylan into xylolig, 3.1% xylan into xylose, 3.65% of xylan into furfural, and 12.5% of xylan into acetic acid. Moreover, 27.4% of lignin was converted into soluble lignin. The two outlet streams from R-101 were combined into stream 07 to collect all products, which was then subsequently cooled to 25 °C.

The separation of cellulose, xylan, lignin, acetate into the solid stream was achieved using V-101, with the remainder designated as stream 09-LPF. The 09-LPF stream was fed into V-102 to separate some inhibitors and sugar to model activated carbon adsorption detoxification. The amount of compound separated was calculated based on the experimental data presented in the literature. The detoxified stream was then combined with the solid fraction, heated to 50 °C and fed to R-102. In R-102, cellulose and glucolig was converted into glucose at a 77.7% conversion rate. R-103 subsequently converted xylan and xylolig into xylose at a rate of 78%.

The output stream from R-103, stream 18 was cooled to 25 °C, resulting in stream 19. Stream 19 was then directed through V-103 to generate a stream containing only glucose, xylose, and water for fermentation reactions in R-104 and R-105, with specific conversion percentages detailed in Table 7. Fermentation products in stream 26 included 4.96 g/L of butanol, 1.96 g/L of acetone, 0.96 g/L of ethanol, 0.63 g/L of acetic acid, and 0.40 g/L of butyric acid. V-104 and V-105 were used to produce the 30-ABE, water stream containing solvents and water.

The 30-ABE, water stream was introduced into distillation column T-101 to separate acetone into the distillate stream. The remaining stream, denoted as stream 32, underwent ethanol removal in T-102. Stream 34 was then processed through V-106, resulting in the 27-Butanol-rich stream with a mass fraction of approximately 77% of butanol and 23% of water. Finally, the butanol-rich stream is fed into T-103 for the purification of biobutanol.

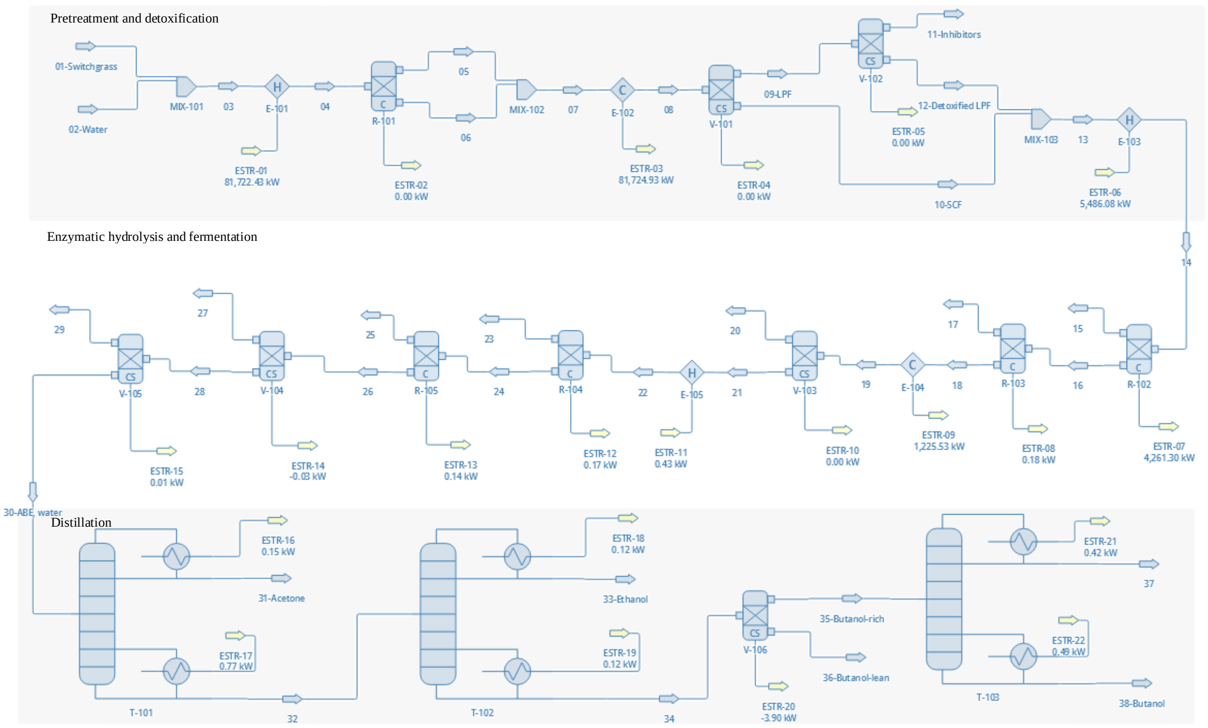


Figure 17.Flowsheet for configuration 3 modelling biobutanol production using switchgrass as feedstock and pretreated through autohydrolysis.

4.2.4 Configuration 4 – Dilute sulfuric acid pretreatment on wheat straw

In configuration 4, dilute sulfuric acid pretreatment of wheat straw was employed to produce biobutanol. The flowsheet for this configuration is visualized in Figure 18. A stream of 10 kg/h wheat straw stream consisting of 38.4% cellulose, 19.7% xylan, 16.9% lignin, and 25% acetate was mixed with a dilute sulfuric acid stream containing 99 % mass fraction of water and 1% mass fraction of sulfuric acid. The resulting combined stream, stream 03 underwent heating to generate stream 04, which was then directed to R-101 for pretreatment reactions. In R-101, cellulose to glucose at 3% conversion xylan was converted to xylose at 45.1%, xylan to furfural, xylan to acetic acid, and lignin to lignin soluble at 1%. Streams 05 and 06 were mixed, cooled and subsequently fed in to V-101, which served to separate the liquid from solid components.

To achieve enzymatic hydrolysis of the solid fraction only, stream 10-solid was heated to a temperature of 50 °C. Stream 11 was then introduced into R-102 to hydrolyze 89.3% of cellulose into glucose and 47.2% of xylan into xylose. All materials exiting R-102 were consolidated into stream 13, which was cooled down to room temperature and directed to V-102. V-102 produced stream 16 comprising only glucose, xylose, and water, intended for fermentation. This stream was subsequently fed into R-103 for fermentation, and the outlet stream, stream 19 was fed into V-103 and V-104 to isolate solvents and water from other compounds. The resulting 23-ABE, water stream is then fed into T-101 to separate acetone out of the mixture. Then ethanol is removed in T-102. V-105 produced butanol-rich and butanol-lean streams. Finally, T-103 column was utilized to purify butanol from the butanol-rich stream.

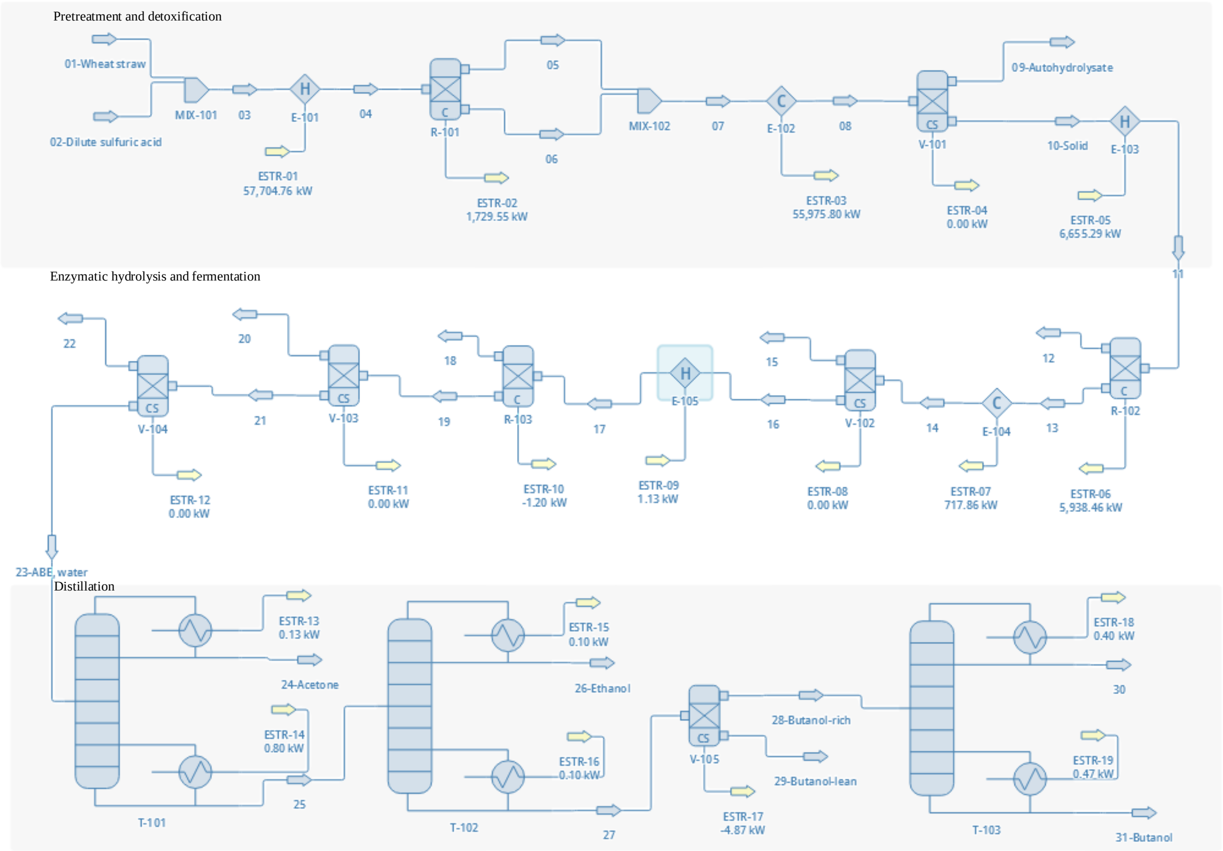


Figure 18. Flowsheet modelling biobutanol production using wheat straw as feedstock and pretreated through dilute sulfuric acid.

4.2.5 Configuration 5 – Dilute sulfuric acid pretreatment on pulp and paper side-stream

In configuration 5, dilute sulfuric acid pretreatment was applied on pulp and paper sides-tream waste to produce biobutanol. The pulp and paper side stream was combined with a dilute sulfuric acid stream containing 2% sulfuric acid and 98% water. The resulting stream was then fed into a heater to heat the stream to 180℃. This heated stream was directed into R-101 for pretreatment reactions. Streams 05 and 06 were combined to consolidate all pretreatment products. The resulting combined stream was cooled to 25 ℃ and then introduced into V-101 to facilitate the separation of liquid from solid components. The solid fraction underwent heating and was introduced into R-102 for enzymatic hydrolysis reactions, resulting in the conversion of 47% of cellulose to glucose and 30% of xylan to xylose.

R-102 produced two outlet streams: 12 and 13. However, only stream 13 contained contents and was subsequently cooled and directed into V-102 to produce stream 16, consisting solely of glucose, xylose, and water. This stream was then heated to 37 °C and introduced into R-103 for fermentation reactions. Fermentation reactions are detailed in Table 7. The output stream from R-103, stream 19, underwent separation in V-103 to eliminate unconverted sugars, gases, and acids, leaving stream 20 containing only water and solvents.

For further separation by distillation, stream 20 was fed into T-101 to initially separate acetone from the mixture. Subsequently, the remaining stream was introduced to T-102 to remove ethanol in the distillate stream. Stream 24 was then directed into V-104, simulating a decanter and producing a butanol-rich stream and a butanol-lean stream. Finally, the butanol-rich stream underwent purification in T-103, representing the final stage of butanol separation and purification.

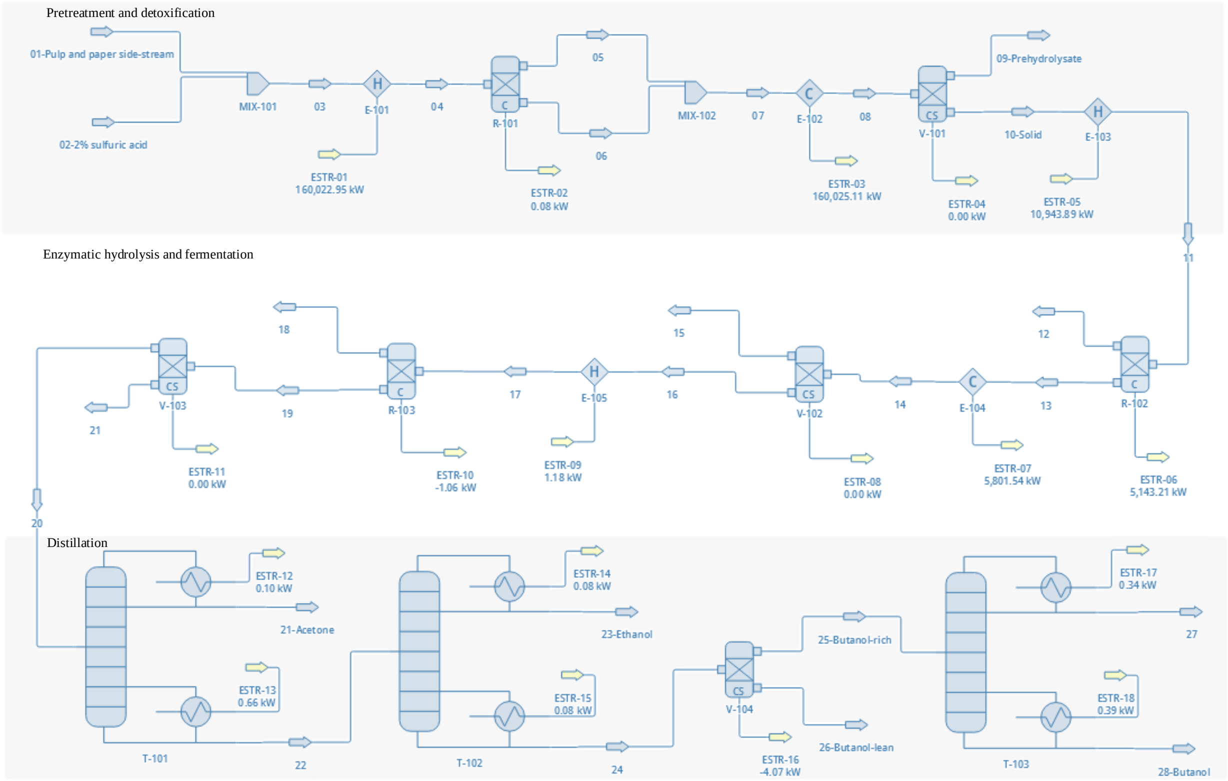


Figure 19. The flowsheet modelling biobutanol production using pulp and paper side-stream as feedstock and treated through dilute sulfuric acid.

4.2.6 Configuration 6 – Dilute acetic acid pretreatment on switchgrass

As illustrated in Figure 20, the flowsheet for configuration 6 models the process of biobutanol production from acetic acid-pretreated switchgrass. A 10 kg/h of switchgrass stream consisting of 35.6% cellulose, 19.2% xylan, 22.6% lignin, and 22.6% acetate, was mixed with a 100 kg/h of 3 g/L acetic acid comprised of 0.3% of acetic acid and and 99.7% of water. The resulting combined stream was heated to 170 °C and directed into R-101 for pretreatment reactions. The pretreatment reactions that took place in

R-101 are as followed: 11.8% of cellulose converted to glucolig, 4.49% to glucose, 46.0% of xylan into xylolig, 4.17% of xylan into xylose, 4.17% of xylan into furfural, 27.9% lignin into soluble lignin, 12.5% of xylan into acetic acid.

The resulting outlet streams, denoted as stream 05 and 06, were combined to consolidate all the products, resulting in stream 07. This combined stream was cooled to 25 ℃ and fed to V-101 to separate prehydrolysate liquid (09-LPF) from solid (10-SCF). The 09-LPF stream underwent processing in V-102 to remove certain inhibitors and sugars, producing a detoxified stream, which was then combined with 10-SCF into stream 13-SCF and LPF. This combined stream was heated to 50 ℃ and then fed into R-102, converting 78% of xylan and 78% of xylolig to xylose. The stream is then introduced to R-103 converting 71% of cellulose and 71% of glucolig into glucose.

After enzymatic hydrolysis in R-102 and R-103, stream 18 was cooled to 25 ℃ and fed into V-103 to isolate glucose, xylose, and water into stream 21. This stream was then heated to 30 ℃ and fed into R-104 for fermentation reactions. The chemical reactions and extent of reactions for fermentation are described in Table 7. The output stream of R-104, stream 24 was introduced into V-104 to remove unconverted sugars, acids, gases, and most of the water. The remaining solvents and water stream was further processed to extract butanol from solvents and water.

This stream was first introduced to T-101 to remove acetone. Subsequently, the remaining stream was fed into T-102 to extract ethanol into the distillate stream. The residual stream from T-102 was subjected to V-105 to obtain a butanol-rich and a butanol-lean stream. The butanol-rich stream with 23 wt% water and 77 wt% butanol underwent final purification in T-103, resulting in purified 34-Butanol stream.

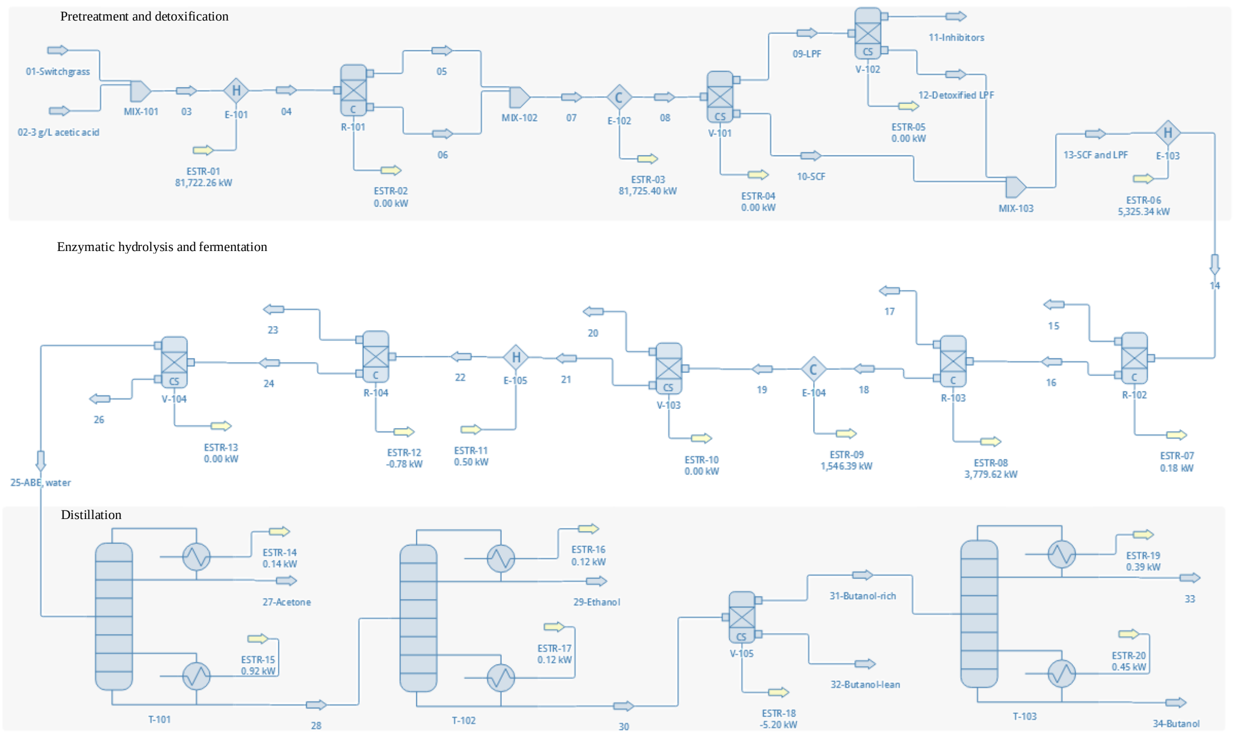


Figure 20. Flowsheet modelling biobutanol production using switchgrass as feedstock and pretreated through dilute sulfuric acid.

4.2.7 Fermentation products

Figure 21 shows the product concentration (in g/L) in the outlet stream from the fermentation RC for each configuration. It is observed that the butanol, acetone, and ethanol concentrations were relatively comparable across all configurations, except for configuration one and two, which displayed a significantly lower value. These two configurations were reviewed to investigate the discrepancy. Configuration one is the only one that uses liquid prehydrolysate alone to proceed with enzymatic hydrolysis and fermentation, which means it has a low availability of fermentable sugars and resulting in a lower concentration of ABE. As for configuration two, low enzymatic conversion rate (cellulose to glucose conversion rate of 38.44%, and xylan into xylose conversion rate of 10.68%) could contribute to the low product yield. It is noted that the ratio of solvents roughly follows the 3:6:1 acetone-butanol-ethanol ratio. Configuration three, which employed autohydrolysis to pretreat switchgrass, had the highest performance in ABE conversion because it had a wealth of sugars for fermentation. Configuration three utilized both prehydrolysate sugars and the pretreated solid for hydrolysis and fermentation. Additionally, this configuration had a high enzymatic hydrolysis rate (cellulose and glucolig were converted into glucose at a 77.7% conversion rate, and xylan and xylolig into xylose at a rate of 78%), which further increases the amount of carbon source available for fermentation.

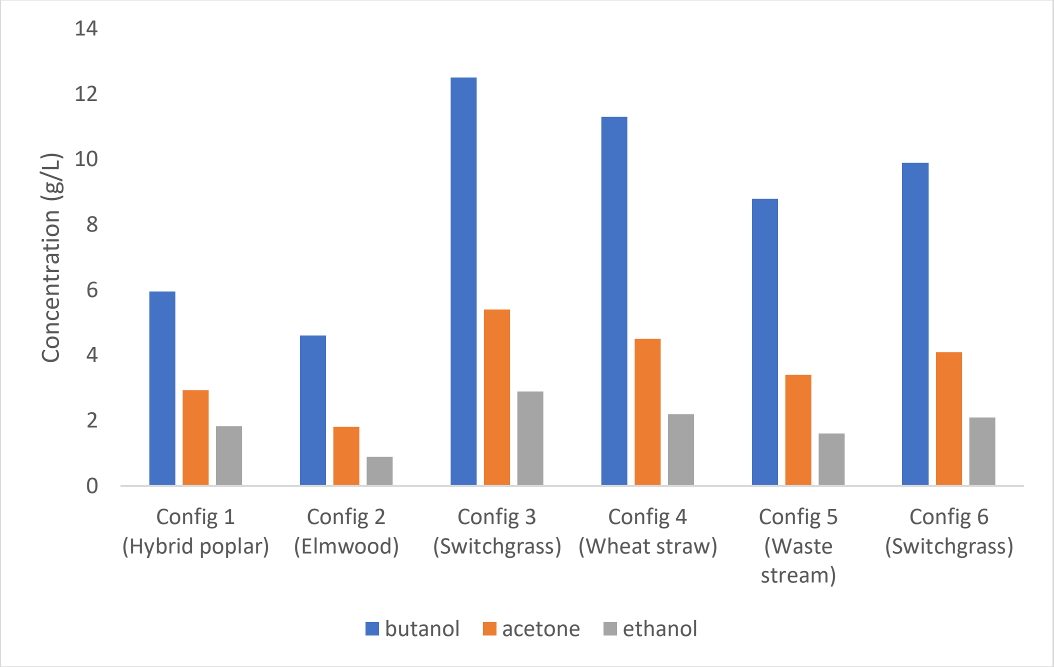


Figure 21. Concentration of acetone, butanol, and ethanol in g/L from fermentation for configuration one to six.

4.2.8 Increased initial feedstock mass flow

To evaluate the potential of DWSIM in predicting higher scale biobutanol production based on laboratory results, the initial biomass feed was increased to assess the simulated biobutanol production. As shown in Figure 22, upon increasing the mass flow of feedstock in each configuration to 4000 kg/h, the production of butanol is estimated to range from 401.7 ODT/year in configuration one to 3073 ODT/year in configuration three. The observed mass flow of butanol in configuration one, which utilized hybrid poplar, is notably lower in comparison to the other five configurations. This discrepancy might result from the selective hydrolysis of sugars exclusively with the liquid prehydrolysate, consequently reducing the available amount of reducing sugars for fermentation. As of configuration two, the enzymatic hydrolysis conversion rate was less efficient (cellulose to glucose at 38.44% xylan to xylose at 10.68%) when compared to other.

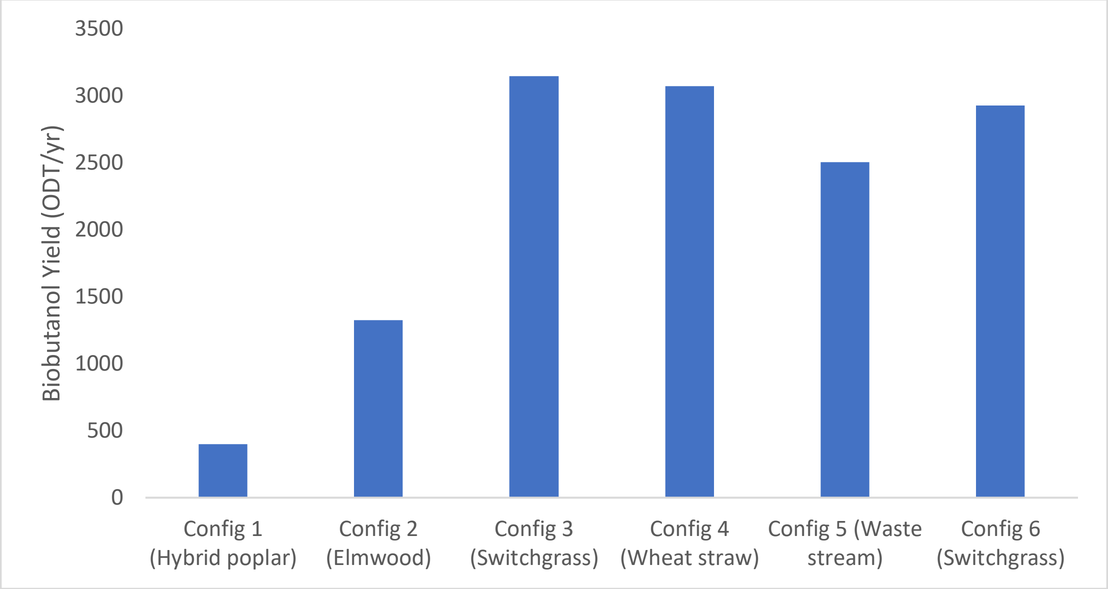


Figure 22. Butanol production in tonnes/year with an initial biomass input of 4000 kg/h.

5 DISCUSSION

5.1 Potential biorefinery locations in Canada

To further elucidate the potential of industrial-level biobutanol production and the location of the developed configurations in Canada, Agriculture and Agri-Food Canada's Biomass Inventory Mapping and Analysis Tool (BIMAT)[1] was explored to assess biomass availability in different regions. BIMAT is an interactive mapping application that maps out biomass inventory data of a variety of biomass sources such as agricultural biomass, waste forestry biomass, and municipal solid waste, which enables the analysis of the availability of the hardwood species (hybrid poplar wood and elmwood) and wheat straw from the simulation studies. Furthermore, BIMAT can calculate the amount of biomass in a specified area or to determine the area to be covered in order to secure a specified amount of biomass.

The mass flow of feedstock required was increased to 4000 kg/h in the simulation to represent industrial level of biobutanol production. This biomass amount is equivalent to 35080 oven-dried tonnes (ODT)/year because the moisture content was not included in the biomass composition in this simulation. BIMAT calculated the required area to satisfy the demand for 35080 ODT of biomass, including (i) hardwood residue (roadside harvest residue, mill wood residue, and mill bark residue) and (ii) wheat straw. From there, potential locations for biobutanol production plant can be inferred. A total of 5 sites are identified, two sites are for hardwood biomass and three sites are for wheat straw. The exact locations and required areas to satisfy the demand are listed in Table 12.

Table 12. Location in longitude and latitude of the identified sites and area requirement in km^2 for hardwood and wheat straw biomass.

	Hardwood biomass		
	Site 1	Site 2	
Longitude and Latitude	+46.698931 -70.876572	+45.481278 -72.073673	
Area requirement (km^2)	400	700	
	Wheat straw biomass		
	Site 1	Site 2	Site 3
Longitude and Latitude	+51.520299 -112.729126	+50.301202 -105.126587	+49.849958 -97.875611
Area requirement (km^2)	700	700	800

Figure 23 displays a map resulting from BIMAT that illustrates the optimal sites discovered to satisfy the required hardwood biomass demand. Initially, 9 sites with area ranging from 400 to 1400 km^2 were identified. Then the sites that require more than 1000 km^2 were excluded to reduce the transportation cost and subsequent CO_2 emissions. As a result, a total of two sites, denoted by the X sign and labeled as Site 1 and Site 2 on Figure 23 are recommended as the potential location for biobutanol production plant. Both Site 1 and Site 2 are located within the southern part of the province of Quebec. Site 1 is located just northeast of Quebec City, while Site 2 is located in the west of Sherbrooke. BIMAT

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[1] https://www.agr.gc.ca/atlas/apps/aef/main/index_en.html?emafapp=bimat_ocib&mode=release&iframeheight=800

also provided the breakdown of the type of biomass available. Within 400 km^2 radius of Site 1, BIMAT calculated 2884 ODT of roadside harvest residue, 31181 ODT of wood mill residue, and 10066 ODT of bark mill residue that will in total satisfy the biomass demand. BIMAT calculated that within a 700 km^2 radius of Site 2, 16434 ODT of roadside harvest residue and 58684 ODT of bark mill residue are available. The proposed biobutanol production plant at Site 1 can be integrated and co-located with a pulp and paper mill to reduce operation costs.

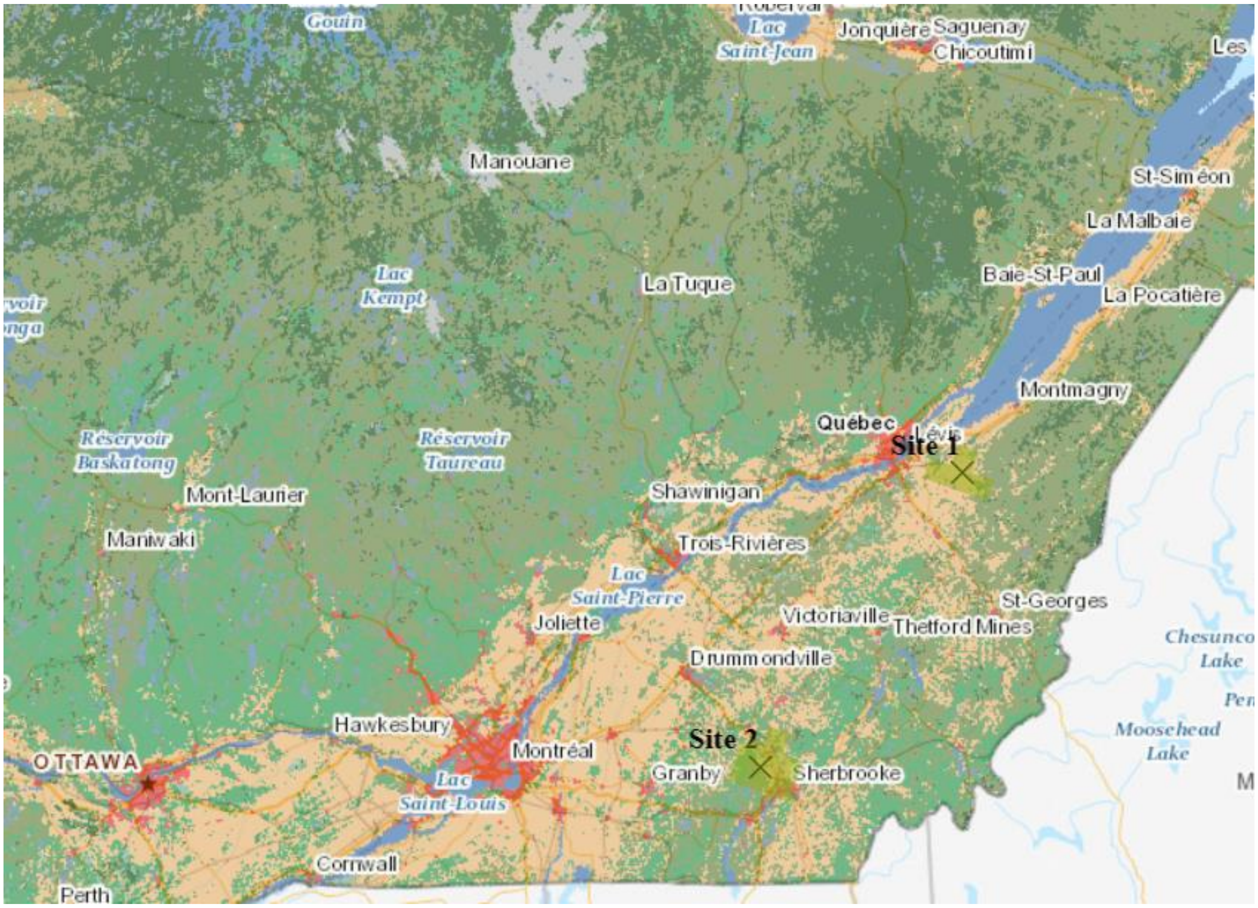

Figure 23. Map of province of Quebec from Biomass Inventory Mapping and Analysis Tool outlining the location of sites to supply 35080 tonnes/year of hardwood biomass.

Figure 24 illustrates the distribution of the identified potential locations (marked by X) for a biobutanol plant requesting 35080 ODT of wheat straw biomass. Sites that require more than 1000 km^2 were again excluded to minimize the requirement for transportation cost and associated CO_2 emissions. A total of three sites were determined: Site 1 that requires 700km^2, Site 2 with 700 km^2 area requirement and Site 3 with 800 km^2. Notably, these sites are exclusively located in regions covered by cropland, depicted with light orange color. The identified locations are: Site 1 in Drumheller, Alberta, Site 2 near Drinkwater, Saskatchewan, and Site 3 is located near Elie in Manitoba. A stand-alone biobutanol production plant is recommended if wheat straw is used as the sole feedstock.

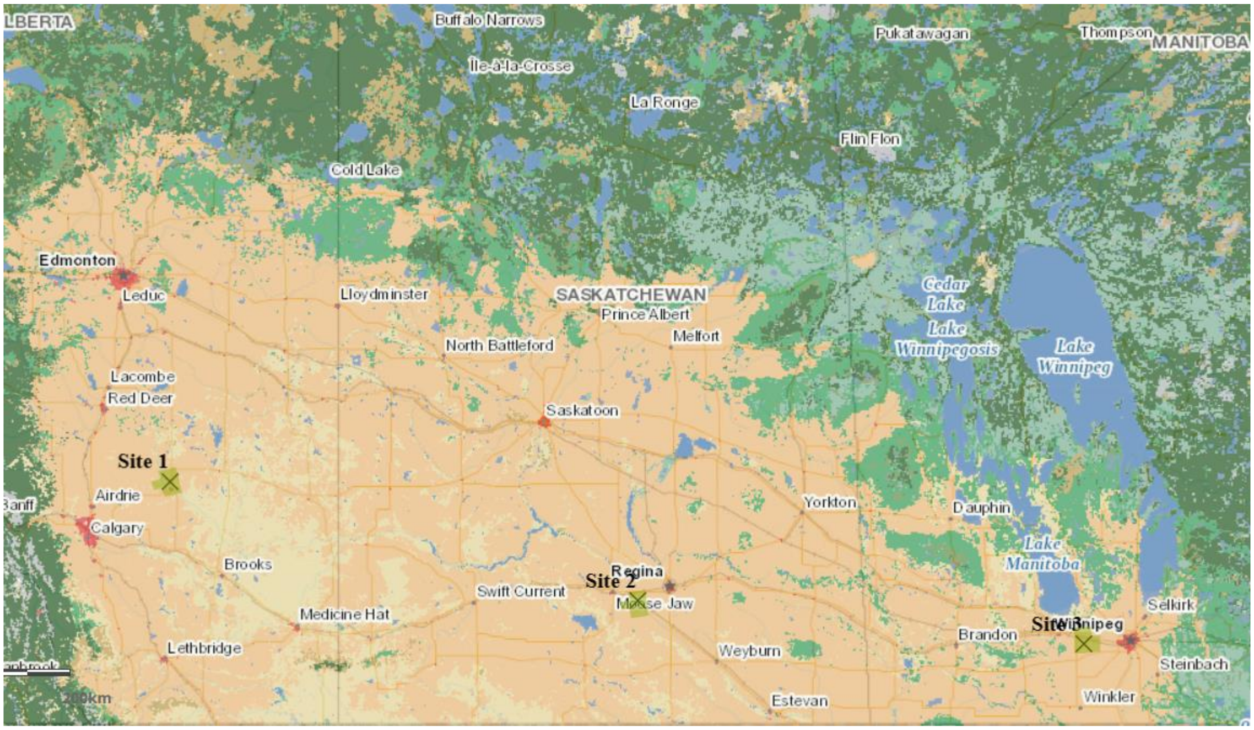

Figure 24. Map of Alberta, Saskatchewan, and Manitoba from Biomass Inventory Mapping and Analysis Tool that outline the sites with high availability of biomass to supply 35080 tonnes/year of wheat straw biomass.

5.2 Lignin applications in a biorefinery context

The focus of this study was to convert the hemicellulose and cellulose components of biomass. However, lignin exists abundantly within the lignocellulose structure, and its utilization is key for a sustainable and economic biorefinery. Typically, the lignin-rich stream resulting from the pretreatment step is burned to generate heat or electricity in a biofuel production process (Liakakou et al., 2019). However, this is a less effective usage of lignin, as it can be used as a feedstock for the production of fine chemicals such as vanillin, dimethyl sulfoxide (Wang et al., 2018), and *p*-hydroxybenzoic acid (Alherech et al., 2021). The presence of functional chemical groups, considerable antioxidant capacity, and the inherent biodegradability of lignin position it as a highly promising raw material for creating enhanced-value bioproducts using the biorefining process (Zhou et al., 2022). Through gasification, lignin is converted into syngas, which can be used to produce chemical products and liquid fuels (Liakakou et al., 2019).

Integrated biorefineries utilize biomass feedstock to convert it into biofuels as well as value-added chemicals through various conversion pathways (Ng et al., 2015). Simultaneous production of high-value products with biofuels or co-locating biofuel production plants with existing facilities are potential solutions that can reduce the cost of biofuel production (Biddy et al., 2020). Integrating the conversion of lignin to high-value products with biobutanol production enhances the economic viability of the biofuel production plant (Cotana et al., 2014). Each configuration in this simulation work has a stream rich in lignin, separated from cellulose and hemicellulose after pretreatment or enzymatic hydrolysis. This stream can be redirected to convert lignin into value-added products. This is an important aspect for future studies to consider, aiming to improve the economic viability of the biorefinery.

In the configurations considered in this study, the lignin component of the biomass goes unprocessed and simply discarded after pretreatment or enzymatic hydrolysis. However, as illustrated in Table 13, there is a substantial amount of lignin that can be utilized to generate energy, produce high-value chemical, and sell for further processing. The lignin-rich stream can be burned to provide heating for pretreatment that will significantly reduce the energy requirement to heat up biomass flurry for pretreatment. From the biorefinery aspect, the biobutanol production plant can simultaneously produce lignin-derived high value chemicals. Lastly, if the plant does not have the capability to convert lignin into high-value products, the discarded lignin-rich slurry can be sold for profit. It is recommended to dry out the lignin-rich stream to minimize moisture content and consequently shipping cost.

Table 13. Amount of unprocessed lignin for each configuration in kg/h and point of separation.

	Config 1	Config 2	Config 3	Config 4	Config 5	Config 6
Unprocessed Lignin (kg/h)	1075.2	1004.0	656.3	676.0	752.8	651.8
Source	Separation after pretreatment	Separation after hydrolysis	Separation after hydrolysis	Separation after hydrolysis	Separation after hydrolysis	Separation after hydrolysis

5.3 DWSIM Software Performance

Since this work is one of the first studies that employed the open-source software, DWSIM, to simulate fermentative biobutanol production from lignocellulosic materials, it is important to assess the experience during simulation development from the user’s perspective. This will enable potential improvements to the software and will allow other researchers interested in simulating biorefinery configurations to evaluate whether DWSIM is a viable software to use.

On the positive side, DWSIM is user-friendly and can be easily manipulated by users with limited experience in simulations. The advantages of DWSIM are as follows: the interface is intuitive and clear, the settings are easy to navigate, the simulator contains enough operating units to simulate the process, inputs of the operating units and conditions are easy to manipulate, and compounds that do not exist in the database can be easily included using the compound creator function.

However, some aspects of the DWSIM software need further improvement. For instance, the number of conversion reactions seems to impact the accuracy of conversion percentages. In some flowsheets, the reactions for fermentation required two conversion reactors, whereas in others, one conversion reactor could accommodate all reactions. Therefore, the conversion reactor exhibited inconsistency regarding the number of conversion reactions that could be included. Additionally, when user-created compounds were added after the flowsheet was developed, the operating units were unable to accept the newly added compounds, rendering the flowsheet inactive.

6 CONCLUSION AND RECOMMENDATIONS

A complete process model was developed and proposed using the open-source chemical process simulator, DWSIM, to simulate the biological conversion of lignocellulosic feedstocks to biobutanol. This study, among the first to utilize the open-source software DWSIM for simulating fermentative biobutanol production from lignocellulosic materials, demonstrates the capability of open-source simulators in computational modeling of biobutanol conversion processes from lignocellulosic biomass. Based on the developed configurations, it can be concluded that DWSIM provides flexibility in varying the feedstock composition, pretreatment conditions (operating temperature, SLR), pretreatment methods (dilute acid pretreatment, autohydrolysis), and other parameters that are usually considered in experimental studies, such as enzymatic hydrolysis content (pretreated solid, prehydrolysate liquid, and a combination of prehydrolysate liquid and pretreated solid).

From the simulation results, utilizing at least the pretreated biomass solid for further processing yielded higher biobutanol yields than using solely liquid prehydrolysate. Additionally, enzymatic hydrolysis efficiency impacted the overall biobutanol yield in the developed models. Increasing the initial biomass feed in DWSIM revealed biobutanol production estimates ranging from 401.7 to 3073 ODT/year across configurations. This demonstrates that DWSIM has the potential to predict industrial-level production of biobutanol from laboratory-scale results. Five potential sites for biobutanol plants utilizing hardwood biomass or wheat straw as feedstock are proposed across Canada, aimed at minimizing transportation costs and emissions. Specifically, these sites include two locations in Quebec and three in Alberta, Saskatchewan, and Manitoba, utilizing wheat straw biomass.

While DWSIM offers user-friendly features such as intuitive interfaces and easy manipulation of inputs, challenges include inconsistent accuracy of conversion percentages based on the number of conversion reactions and difficulties integrating user-created compounds into existing flowsheets, rendering them inactive.

With respect to future studies, several recommendations emerge:

1. The range of compounds created on DWSIM in addition to xylose and xylooligomer can be expanded to better reflect the breakdown of hemicellulose.
2. It is recommended to conduct a comparative analysis of DWSIM performance with a commercial simulator, particularly in biobutanol production, could further prove the effectiveness of this software.
3. Separating the xylose conversion and glucose fermentation reactions into two distinct reactors is advised. This segregation can mitigate potential errors in the flowsheet, which may arise when both reactions are accommodated within a single conversion reactor.

4. Adapt the biorefinery concept to co-locate biobutanol plant with existing pulp and paper mill to reduce energy consumption and cost. This will also facilitate access to pulp and paper mill residues to be used as part of the feedstock for biobutanol production.
5. In addition, co-production of value-added products from lignin can also be considered and simulated to increase revenues.
6. Future work can attempt to conduct economical comparison between configurations with varying parameters such as pretreatment method and conditions on the same type of feedstock.

7 REFERENCES

Adewuyi, A. (2022). Underutilized lignocellulosic waste as sources of feedstock for biofuel production in developing countries. Frontiers in Energy Research, 10. https://doi.org/10.3389/fenrg.2022.741570

Advanced biofuels. Advanced Biofuels Canada. (2023, May 4). https://advancedbiofuels.ca/net-zero/

Ahorsu, R., Medina, F., & Constantí, M. (2018). Significance and challenges of biomass as a suitable feedstock for bioenergy and biochemical production: A Review. Energies, 11(12), 3366. https://doi.org/10.3390/en11123366

Alam, M. S., & Tanveer, M. S. (2020). Conversion of biomass into biofuel: A cutting-edge technology. Bioreactors, 55–74. https://doi.org/10.1016/b978-0-12-821264-6.00005-x

Alherech, M., Omolabake, S., Holland, C. M., Klinger, G. E., Hegg, E. L., & Stahl, S. S. (2021). From lignin to valuable aromatic chemicals: Lignin depolymerization and monomer separation via centrifugal partition chromatography. ACS Central Science, 7(11), 1831–1837. https://doi.org/10.1021/acscentsci.1c00729

Amin, F. R., Khalid, H., Zhang, H., Rahman, S. u, Zhang, R., Liu, G., & Chen, C. (2017). Pretreatment methods of lignocellulosic biomass for anaerobic digestion. AMB Express, 7(1). https://doi.org/10.1186/s13568-017-0375-4

Amiri, H., & Karimi, K. (2015). Autohydrolysis: A promising pretreatment for the improvement of acetone, butanol, and ethanol production from Woody Materials. Chemical Engineering Science, 137, 722–729. https://doi.org/10.1016/j.ces.2015.07.020

Amiri, H., & Karimi, K. (2018). Pretreatment and hydrolysis of lignocellulosic wastes for butanol production: Challenges and perspectives. Bioresource Technology, 270, 702–721. https://doi.org/10.1016/j.biortech.2018.08.117

Andreasen, A. (2022). Evaluation of an open-source chemical process simulator using a plant-wide oil and gas separation plant flowsheet model as basis. Periodica Polytechnica Chemical Engineering, 66(3), 503–511. https://doi.org/10.3311/ppch.19678

Ansari, S. A., Shakeel, A., Sawarkar, R., Maddalwar, S., Khan, D., & Singh, L. (2023). Additive facilitated co-composting of lignocellulosic biomass waste, approach towards minimizing greenhouse gas emissions: An up to date review. Environmental Research, 224, 115529. https://doi.org/10.1016/j.envres.2023.115529

Arsov, A., Petrov, K., & Petrova, P. (2021). How to outwit nature: Omics insight into butanol tolerance. Biotechnology Advances, 46, 107658. https://doi.org/10.1016/j.biotechadv.2020.107658

Ashani, P. N., Shafiei, M., & Karimi, K. (2020). Biobutanol production from Municipal Solid Waste: Technical and Economic Analysis. Bioresource Technology, 308, 123267. https://doi.org/10.1016/j.biortech.2020.123267

Bahrun, M. H., Battak, N., Tan, W.-H., & Bono, A. (2022). Process simulation of steam stripping of bleached palm oil deodorization for removing free fatty acids using DWSIM. Journal of Physics: Conference Series, 2314(1), 012016. https://doi.org/10.1088/1742-6596/2314/1/012016

Banu J, R., Sugitha, S., Kavitha, S., Kannah R, Y., Merrylin, J., & Kumar, G. (2021). Lignocellulosic Biomass Pretreatment for enhanced Bioenergy Recovery: Effect of lignocelluloses recalcitrance and enhancement strategies. Frontiers in Energy Research, 9. https://doi.org/10.3389/fenrg.2021.646057

Bardhan, S. K., Gupta, S., Gorman, M. E., & Haider, M. A. (2015). Biorenewable Chemicals: Feedstocks, technologies and the conflict with food production. Renewable and Sustainable Energy Reviews, 51, 506–520. https://doi.org/10.1016/j.rser.2015.06.013

Baruah, J., Nath, B. K., Sharma, R., Kumar, S., Deka, R. C., Baruah, D. C., & Kalita, E. (2018). Recent trends in the pretreatment of lignocellulosic biomass for value-added products. Frontiers in Energy Research, 6. https://doi.org/10.3389/fenrg.2018.00141

Basile, A., & Dalena, F. (2019). Second and third generation of feedstocks: The Evolution of Biofuels. Elsevier.

Batalha, L. A., Han, Q., Jameel, H., Chang, H., Colodette, J. L., & Borges Gomes, F. J. (2015). Production of fermentable sugars from sugarcane bagasse by enzymatic hydrolysis after autohydrolysis and mechanical refining. Bioresource Technology, 180, 97–105. https://doi.org/10.1016/j.biortech.2014.12.060

Biddy, M. J., Davis, R., Dutta, A., Singh, A., Tao, L., Tan, E. C. D., Jones, S. B., Collett, J. R., Snowden-Swan, L. J., Webb, E., Kass, M., Langholtz, M., Dunn, J., Negri, C., Mishra, S. K., Quinn, J. J., Thompson, D. N., Hoover, A., Hartley, D. S., … Lamers, P. (2020). (rep.). Integrated Strategies to Enable Lower-Cost Biofuels. Department of Energy. Retrieved December 17, 2023, from https://www.energy.gov/eere/bioenergy/articles/integrated-strategies-enable-lower-cost-biofuels.

Birgen, C., Dürre, P., Preisig, H. A., & Wentzel, A. (2019). Butanol production from lignocellulosic biomass: Revisiting fermentation performance indicators with exploratory data analysis. Biotechnology for Biofuels, 12(1). https://doi.org/10.1186/s13068-019-1508-6

Boro, M., Verma, A. K., Chettri, D., Yata, V. K., & Verma, A. K. (2022). Strategies involved in biofuel production from agro-based lignocellulose biomass. Environmental Technology & Innovation, 28, 102679. https://doi.org/10.1016/j.eti.2022.102679

Brodeur, G., Yau, E., Badal, K., Collier, J., Ramachandran, K. B., & Ramakrishnan, S. (2011). Chemical and physicochemical pretreatment of Lignocellulosic Biomass: A Review. Enzyme Research, 2011, 1–17. https://doi.org/10.4061/2011/787532

Buehler, E. A., & Mesbah, A. (2016). Kinetic study of acetone-butanol-ethanol fermentation in continuous culture. PLOS ONE, 11(8). https://doi.org/10.1371/journal.pone.0158243

Cabezas, R. A., Riquelme, C. A., Merlet, G., Quijada-Maldonado, E., & Romero, J. R. (2022). Separation of Biobutanol from Fermentation Solutions by Perstraction using [P6,6,6,14][Tf2N] as Receiving Phase: Phase Temperature Analysis. Chemical Engineering Transactions, 96, 265-270. https://doi.org/10.3303/CET2296045

Cantarella, M., Cantarella, L., Gallifuoco, A., Spera, A., & Alfani, F. (2008). Effect of inhibitors released during steam-explosion treatment of poplar wood on subsequent enzymatic hydrolysis and SSF. Biotechnology Progress, 20(1), 200–206. https://doi.org/10.1021/bp0257978

Capolupo, L., & Faraco, V. (2016). Green methods of lignocellulose pretreatment for biorefinery development. Applied Microbiology and Biotechnology, 100(22), 9451–9467. https://doi.org/10.1007/s00253-016-7884-y

Carvalheiro, F., Duarte, L. C., Gírio, F., & Moniz, P. (2016). Hydrothermal/Liquid Hot Water Pretreatment (autohydrolysis). Biomass Fractionation Technologies for a Lignocellulosic Feedstock Based Biorefinery, 315–347. https://doi.org/10.1016/b978-0-12-802323-5.00014-1

Chantasiriwan, S. (2023). Simulation and Optimization of Vapor Absorption Refrigeration System Using DWSIM. Chemical Engineering Transactions, 100, 613–618. https://doi.org/10.3303/CET23100103

Chen, X., Lawoko, M., & Heiningen, A. van. (2010). Kinetics and mechanism of autohydrolysis of Hardwoods. Bioresource Technology, 101(20), 7812–7819. https://doi.org/10.1016/j.biortech.2010.05.006

Cotana, F., Cavalaglio, G., Nicolini, A., Gelosia, M., Coccia, V., Petrozzi, A., & Brinchi, L. (2014). Lignin as co-product of second generation bioethanol production from Ligno-cellulosic biomass. Energy Procedia, 45, 52–60. https://doi.org/10.1016/j.egypro.2014.01.007

DeMartini, J. D., Foston, M., Meng, X., Jung, S., Kumar, R., Ragauskas, A. J., & Wyman, C. E. (2015). How chip size impacts steam pretreatment effectiveness for biological conversion of Poplar Wood into fermentable sugars. Biotechnology for Biofuels, 8(1). https://doi.org/10.1186/s13068-015-0373-1

Dou, J., Chandgude, V., Vuorinen, T., Bankar, S., Hietala, S., & Lê, H. Q. (2021). Enhancing biobutanol production from biomass willow by pre-removal of water extracts or bark. Journal of Cleaner Production, 327, 129432. https://doi.org/10.1016/j.jclepro.2021.129432

Foston, M., & Ragauskas, A. J. (2010). Changes in lignocellulosic supramolecular and ultrastructure during dilute acid pretreatment of populus and switchgrass. Biomass and Bioenergy, 34(12), 1885–1895. https://doi.org/10.1016/j.biombioe.2010.07.023

Full report – statistical review of world energy 2021. (n.d.). https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2021-full-report.pdf

Gai, H., Lin, K., Feng, Y., Xiao, M., Guo, K., & Song, H. (2018). Conceptual design of an extractive distillation process for the separation of azeotropic mixture of N-butanol-isobutanol-water. Chinese Journal of Chemical Engineering, 26(10), 2040–2047. https://doi.org/10.1016/j.cjche.2018.05.003

Gao, K., & Rehmann, L. (2016). Combined detoxification and in-situ product removal by a single resin during lignocellulosic butanol production. Scientific Reports, 6(1). https://doi.org/10.1038/srep30533

Garita-Cambronero, J., Paniagua-García, A. I., Hijosa-Valsero, M., & Díez-Antolínez, R. (2021). Biobutanol production from Pruned Vine shoots. Renewable Energy, 177, 124–133. https://doi.org/10.1016/j.renene.2021.05.093

Guo, H., Zhao, Y., Chang, J.-S., & Lee, D.-J. (2022a). Inhibitor formation and detoxification during lignocellulose biorefinery: A Review. Bioresource Technology, 361, 127666. https://doi.org/10.1016/j.biortech.2022.127666

Guo, Y., Liu, Y., Guan, M., Tang, H., Wang, Z., Lin, L., & Pang, H. (2022b). Production of butanol from lignocellulosic biomass: Recent advances, challenges, and prospects. RSC Advances, 12(29), 18848–18863. https://doi.org/10.1039/d1ra09396g

Gütsch, J. S., Nousiainen, T., & Sixta, H. (2012). Comparative evaluation of autohydrolysis and acid-catalyzed hydrolysis of eucalyptus globulus wood. Bioresource Technology, 109, 77–85. https://doi.org/10.1016/j.biortech.2012.01.018

Haigh, K. F., Petersen, A. M., Gottumukkala, L., Mandegari, M., Naleli, K., & Görgens, J. F. (2018). Simulation and comparison of processes for biobutanol production from lignocellulose via Abe Fermentation. Biofuels, Bioproducts and Biorefining, 12(6), 1023–1036. https://doi.org/10.1002/bbb.1917

Hao, N., Bezerra, T. L., Wu, Q., Ben, H., Sun, Q., Adhikari, S., & Ragauskas, A. J. (2017). Effect of autohydrolysis pretreatment on biomass structure and the resulting bio-oil from a pyrolysis process. Fuel, 206, 494–503. https://doi.org/10.1016/j.fuel.2017.06.013

Harmsen, P., Huijgen, W., Bermudez, L., & Bakker, R. (2010). Literature review of physical and chemical pretreatment processes for lignocellulosic biomass. Biosynergy. https://edepot.wur.nl/150289

Hendriks, A. T. W. M., & Zeeman, G. (2009). Pretreatments to enhance the digestibility of lignocellulosic biomass. Bioresource Technology, 100(1), 10–18. https://doi.org/10.1016/j.biortech.2008.05.027

Hideno, A., Inoue, H., Tsukahara, K., Fujimoto, S., Minowa, T., Inoue, S., Endo, T., & Sawayama, S. (2009). Wet disk milling pretreatment without sulfuric acid for enzymatic hydrolysis of rice straw. Bioresource Technology, 100(10), 2706–2711. https://doi.org/10.1016/j.biortech.2008.12.057

Hoekman, S. K. (2009). Biofuels in the U.S. – challenges and opportunities. Renewable Energy, 34(1), 14–22. https://doi.org/10.1016/j.renene.2008.04.030

Huang, H., Khanna, M., Önal, H., & Chen, X. (2013). Stacking low carbon policies on the Renewable Fuels Standard: Economic and Greenhouse Gas Implications. Energy Policy, 56, 5–15. https://doi.org/10.1016/j.enpol.2012.06.002

Iea. (n.d.). Global energy crisis – topics. IEA. https://www.iea.org/topics/global-energy-crisis

Indriani, D. W., Susilo, B., & Mashur. (2021). The effect of microwave power on lignocellulose content, physical and chemical characteristics of biomass: A Review. IOP Conference Series: Earth and Environmental Science, 924(1), 012069. https://doi.org/10.1088/1755-1315/924/1/012069

Inyang, V., Laseinde, O. T., & Kanakana, G. M. (2022). Techniques and applications of lignocellulose biomass sources as transport fuels and other bioproducts. International Journal of Low-Carbon Technologies, 17, 900–909. https://doi.org/10.1093/ijlct/ctac068

Ishola, M. M., Brandberg, T., & Taherzadeh, M. J. (2015). Simultaneous glucose and xylose utilization for improved ethanol production from lignocellulosic biomass through SSFF with encapsulated yeast. Biomass and Bioenergy, 77, 192–199. https://doi.org/10.1016/j.biombioe.2015.03.021

Jang, S.-K., Jung, C.-D., Yu, J.-H., & Kim, H. (2020). Environmentally friendly approach for the production of glucose and high-purity xylooligosaccharides from edible biomass byproducts. Applied Sciences, 10(22), 8119. https://doi.org/10.3390/app10228119

Jiang, W., Wen, Z., Wu, M., Li, H., Yang, J., Lin, J., Lin, Y., Yang, L., & Cen, P. (2014). The effect of ph control on acetone–butanol–ethanol fermentation by clostridium acetobutylicum ATCC 824 with xylose and D-glucose and D-xylose mixture. Chinese Journal of Chemical Engineering, 22(8), 937–942. https://doi.org/10.1016/j.cjche.2014.06.003

Jönsson, L. J., & Martín, C. (2016). Pretreatment of lignocellulose: Formation of inhibitory by-products and strategies for minimizing their effects. Bioresource Technology, 199, 103–112. https://doi.org/10.1016/j.biortech.2015.10.009

Jönsson, L. J., Alriksson, B., & Nilvebrant, N.-O. (2013). Bioconversion of lignocellulose: Inhibitors and detoxification. Biotechnology for Biofuels, 6(1). https://doi.org/10.1186/1754-6834-6-16

Jung, Y. H., & Kim, K. H. (2017). Evaluation of the main inhibitors from lignocellulose pretreatment for enzymatic hydrolysis and yeast fermentation. BioResources, 12(4), 9348–9356. https://doi.org/10.15376/biores.12.4.9348-9356

Kang, Q., Appels, L., Tan, T., & Dewil, R. (2014). Bioethanol from lignocellulosic biomass: Current findings determine research priorities. The Scientific World Journal, 2014, 1–13. https://doi.org/10.1155/2014/298153

Karimi, K., Khoshnevisan, B., & Denayer, J. F. M. (2024). Critical impacts of energy targeting on the sustainability of advanced biobutanol separation. Biofuel Research Journal, 11(01), 1999–2012. https://doi.org/10.18331/brj2024.11.1.2

Karthick, C., & Kasianantham, N. (2023). Experimental assessment of biobutanol degradation exposed to automotive components: A material compatibility approach. Process Safety and Environmental Protection, 170, 215–228. https://doi.org/10.1016/j.psep.2022.12.009

Kasani, A. A., Esmaeili, A., & Golzary, A. (2022). Software tools for microalgae biorefineries: Cultivation, separation, conversion process integration, modeling, and Optimization. Algal Research, 61, 102597. https://doi.org/10.1016/j.algal.2021.102597

Kellner, M. I., Madachy, R. J., & Raffo, D. M. (1999). Software process simulation modeling: Why? what? how? Journal of Systems and Software, 46(2–3), 91–105. https://doi.org/10.1016/s0164-1212(99)00003-5

Khan, S., Das, P., Abdul Quadir, M., Thaher, M. I., Mahata, C., Sayadi, S., & Al-Jabri, H. (2023). Microalgal feedstock for biofuel production: Recent advances, challenges, and future perspective. Fermentation, 9(3), 281. https://doi.org/10.3390/fermentation9030281

Kiran, B., Kumar, R., & Deshmukh, D. (2014). Perspectives of Microalgal Biofuels as a renewable source of energy. Energy Conversion and Management, 88, 1228–1244. https://doi.org/10.1016/j.enconman.2014.06.022

Kujawska, A., Kujawski, J., Bryjak, M., & Kujawski, W. (2015). Abe fermentation products recovery methods—a review. Renewable and Sustainable Energy Reviews, 48, 648–661. https://doi.org/10.1016/j.rser.2015.04.028

Kukharonak, H., Ivashko, V., Pukalskas, S., Rimkus, A., & Matijošius, J. (2017). Operation of a spark-ignition engine on mixtures of petrol and n-Butanol. Procedia Engineering, 187, 588–598. https://doi.org/10.1016/j.proeng.2017.04.418

Kumar, A. K., & Sharma, S. (2017). Recent updates on different methods of pretreatment of Lignocellulosic Feedstocks: A Review. Bioresources and Bioprocessing, 4(1). https://doi.org/10.1186/s40643-017-0137-9

Kumar, P., Barrett, D. M., Delwiche, M. J., & Stroeve, P. (2009). Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. Industrial & Engineering Chemistry Research, 48(8), 3713–3729. https://doi.org/10.1021/ie801542g

Lassmann, T., Kravanja, P., & Friedl, A. (2014). Simulation of the downstream processing in the ethanol production from lignocellulosic biomass with Aspen Plus® and IPSEpro. Energy, Sustainability and Society, 4(1). https://doi.org/10.1186/s13705-014-0027-3

Lee, J. M., Jameel, H., & Venditti, R. A. (2010). A comparison of the autohydrolysis and ammonia fiber explosion (AFEX) pretreatments on the subsequent enzymatic hydrolysis of coastal Bermuda grass. Bioresource Technology, 101(14), 5449–5458. https://doi.org/10.1016/j.biortech.2010.02.055

Lee, S. Y., Park, J. H., Jang, S. H., Nielsen, L. K., Kim, J., & Jung, K. S. (2008). Fermentative butanol production by Clostridia. Biotechnology and Bioengineering, 101(2), 209–228. https://doi.org/10.1002/bit.22003

Li, C., Knierim, B., Manisseri, C., Arora, R., Scheller, H. V., Auer, M., Vogel, K. P., Simmons, B. A., & Singh, S. (2010). Comparison of Dilute Acid and Ionic liquid pretreatment of switchgrass: Biomass recalcitrance, delignification and enzymatic saccharification. Bioresource Technology, 101(13), 4900–4906. https://doi.org/10.1016/j.biortech.2009.10.066

Li, M., Guo, C., Luo, B., Chen, C., Wang, S., & Min, D. (2019). Comparing impacts of physicochemical properties and hydrolytic inhibitors on enzymatic hydrolysis of sugarcane bagasse. Bioprocess and Biosystems Engineering, 43(1), 111–122. https://doi.org/10.1007/s00449-019-02209-3

Liakakou, E. T., Vreugdenhil, B. J., Cerone, N., Zimbardi, F., Pinto, F., André, R., Marques, P., Mata, R., & Girio, F. (2019). Gasification of lignin-rich residues for the production of biofuels via syngas fermentation: Comparison of Gasification Technologies. Fuel, 251, 580–592. https://doi.org/10.1016/j.fuel.2019.04.081

Lima, M. A., Lavorente, G. B., da Silva, H. K., Bragatto, J., Rezende, C. A., Bernardinelli, O. D., deAzevedo, E. R., Gomez, L. D., McQueen-Mason, S. J., Labate, C. A., & Polikarpov, I. (2013). Effects of pretreatment on morphology, chemical composition and enzymatic digestibility of eucalyptus bark: A potentially valuable source of fermentable sugars for biofuel production – part 1. Biotechnology for Biofuels, 6(1). https://doi.org/10.1186/1754-6834-6-75

Lin, Z., Cong, W., & Zhang, J. (2023). Biobutanol production from acetone–butanol–ethanol fermentation: Developments and prospects. Fermentation, 9(9), 847. https://doi.org/10.3390/fermentation9090847

Liu, J., Wu, M., & Wang, M. (2009). Simulation of the process for producing butanol from corn fermentation. Industrial & Engineering Chemistry Research, 48(11), 5551–5557. https://doi.org/10.1021/ie900274z

Liu, W.-J., & Yu, H.-Q. (2021). Thermochemical conversion of lignocellulosic biomass into mass-producible fuels: Emerging technology progress and environmental sustainability evaluation. ACS Environmental Au, 2(2), 98–114. https://doi.org/10.1021/acsenvironau.1c00025

Liu, Y., Geng, Y., Zhou, Q., & Yuan, W. (2017). The effect of furfural and 5-hydroxymethyl furfural on butyric acid fermentation by clostridium tyrobutyricum. Journal of Chemical Technology & Biotechnology, 93(3), 849–854. https://doi.org/10.1002/jctb.5439

Liu, Y., Yuan, Y., Ramya, G., Mohan Singh, S., Thuy Lan Chi, N., Pugazhendhi, A., Xia, C., & Mathimani, T. (2022). A review on the promising fuel of the future – biobutanol; the hindrances and future perspectives. Fuel, 327, 125166. https://doi.org/10.1016/j.fuel.2022.125166

Liu, Z. L., Slininger, P. J., Dien, B. S., Berhow, M. A., Kurtzman, C. P., & Gorsich, S. W. (2004). Adaptive response of yeasts to furfural and 5-hydroxymethylfurfural and New Chemical Evidence for HMF conversion to 2,5-bis-hydroxymethylfuran. Journal of Industrial Microbiology & Biotechnology, 31(8), 345–352. https://doi.org/10.1007/s10295-004-0148-3

Lloyd, T. A., & Wyman, C. E. (2005). Combined sugar yields for dilute sulfuric acid pretreatment of corn stover followed by enzymatic hydrolysis of the remaining solids. Bioresource Technology, 96(18), 1967–1977. https://doi.org/10.1016/j.biortech.2005.01.011

Loow, Y.-L., Wu, T. Y., Md. Jahim, J., Mohammad, A. W., & Teoh, W. H. (2016). Typical conversion of lignocellulosic biomass into reducing sugars using dilute acid hydrolysis and alkaline pretreatment. Cellulose, 23(3), 1491–1520. https://doi.org/10.1007/s10570-016-0936-8

Luo, H., Liu, Z., Xie, F., Bilal, M., & Peng, F. (2021). Lignocellulosic biomass to biobutanol: Toxic effects and response mechanism of the combined stress of lignin-derived phenolic acids and phenolic aldehydes to clostridium acetobutylicum. Industrial Crops and Products, 170, 113722. https://doi.org/10.1016/j.indcrop.2021.113722

Luyben, W. L. (2008). Control of the heterogeneous azeotropic n-butanol/water distillation system. Energy & Fuels, 22(6), 4249–4258. https://doi.org/10.1021/ef8004064

Ma, H., Liu, W.-W., Chen, X., Wu, Y.-J., & Yu, Z.-L. (2009). Enhanced enzymatic saccharification of Rice Straw by microwave pretreatment. Bioresource Technology, 100(3), 1279–1284. https://doi.org/10.1016/j.biortech.2008.08.045

Martinez, A., Rodriguez, M. E., York, S. W., Preston, J. F., & Ingram, L. O. (2000). Effects of ca(oh)2 treatments (“overliming”) on the composition and toxicity of bagasse hemicellulose hydrolysates. Biotechnology and Bioengineering, 69(5), 526–536. https://doi.org/10.1002/1097-0290(20000905)69:5<526::aid-bit7>3.0.co;2-e

Meramo-Hurtado, S. I., González-Delgado, Á., Rehmann, L., Quinones-Bolanos, E., & Mehvar, M. (2021). Comparative analysis of biorefinery designs based on acetone-butanol-ethanol fermentation under exergetic, techno-economic, and sensitivity analyses towards a sustainability perspective. Journal of Cleaner Production, 298, 126761. https://doi.org/10.1016/j.jclepro.2021.126761

Millati, R., Niklasson, C., & Taherzadeh, M. J. (2002). Effect of ph, time and temperature of overliming on detoxification of dilute-acid hydrolyzates for fermentation by saccharomyces cerevisiae. Process Biochemistry, 38(4), 515–522. https://doi.org/10.1016/s0032-9592(02)00176-0

Mohd Azhar, S. H., Abdulla, R., Jambo, S. A., Marbawi, H., Gansau, J. A., Mohd Faik, A. A., & Rodrigues, K. F. (2017). Yeasts in sustainable bioethanol production: A Review. Biochemistry and Biophysics Reports, 10, 52–61. https://doi.org/10.1016/j.bbrep.2017.03.003

Moon, H. G., Jang, Y.-S., Cho, C., Lee, J., Binkley, R., & Lee, S. Y. (2016). One hundred years of clostridial butanol fermentation. FEMS Microbiology Letters. https://doi.org/10.1093/femsle/fnw001

Mosier, N., Ladisch, M., Holtzapple, M., Lee, Y. Y., Elander, R., Dale, B., & Wyman, C. (2005). Features of promising technologies for pretreatment of Lignocellulosic Biomass. Bioresource Technology, 96(6), 673–686. https://doi.org/10.1016/j.biortech.2004.06.025

Nandhini, R., Rameshwar, S. S., Sivaprakash, B., Rajamohan, N., & Monisha, R. S. (2023). Carbon neutrality in biobutanol production through microbial fermentation technique from lignocellulosic materials – a biorefinery approach. Journal of Cleaner Production, 413, 137470. https://doi.org/10.1016/j.jclepro.2023.137470

Nashiruddin, N. I., Manas, N. H., Rahman, R. A., Azelee, N. I., Dailin, D. J., & Shaarani, S. M. (2020). Pretreatment and enzymatic hydrolysis of lignocellulosic biomass for reducing sugar production. Applied Environmental Science and Engineering for a Sustainable Future, 1–27. https://doi.org/10.1007/978-3-030-39208-6_1

Nauman Aftab, M., Iqbal, I., Riaz, F., Karadag, A., & Tabatabaei, M. (2019). Different pretreatment methods of lignocellulosic biomass for use in biofuel production. Biomass for Bioenergy - Recent Trends and Future Challenges. https://doi.org/10.5772/intechopen.84995

Nayak, P., Dalve, P., Sai, R. A., Jain, R., Moudgalya, K. M., Naren, P. R., Fritzson, P., & Wagner, D. (2019). Chemical process simulation using OpenModelica. Industrial & Engineering Chemistry Research, 58(26), 11164–11174. https://doi.org/10.1021/acs.iecr.9b00104

Ndaba, B., Chiyanzu, I., & Marx, S. (2015). N-butanol derived from biochemical and Chemical Routes: A Review. Biotechnology Reports, 8, 1–9. https://doi.org/10.1016/j.btre.2015.08.001

Ng, L. Y., Andiappan, V., Chemmangattuvalappil, N. G., & Ng, D. K. S. (2015). A systematic methodology for optimal mixture design in an integrated biorefinery. 12th International Symposium on Process Systems Engineering and 25th European Symposium on Computer Aided Process Engineering, 1205–1210. https://doi.org/10.1016/b978-0-444-63577-8.50046-2

Nitsos, C. K., Choli-Papadopoulou, T., Matis, K. A., & Triantafyllidis, K. S. (2016). Optimization of hydrothermal pretreatment of hardwood and softwood lignocellulosic residues for selective hemicellulose recovery and improved cellulose enzymatic hydrolysis. ACS Sustainable Chemistry & Engineering, 4(9), 4529–4544. https://doi.org/10.1021/acssuschemeng.6b00535

Oh, H. W., Lee, S. C., Woo, H. C., & Han Kim, Y. (2021). Energy-efficient biobutanol recovery process using 1-heptanol extraction. Chemical Engineering & Technology, 44(12), 2316–2326. https://doi.org/10.1002/ceat.202100154

Pandey, J. K., & Kumar, G. N. (2023). Study of combustion and emission of a SI engine at various CR fuelled with different ratios of biobutanol/hydrogen fuel. International Journal of Hydrogen Energy, 48(72), 28222–28234. https://doi.org/10.1016/j.ijhydene.2023.04.031

Patakova, P., Linhova, M., Rychtera, M., Paulova, L., & Melzoch, K. (2013). Novel and neglected issues of acetone–butanol–ethanol (ABE) fermentation by Clostridia: Clostridium metabolic diversity, tools for process mapping and continuous fermentation systems. Biotechnology Advances, 31(1), 58–67. https://doi.org/10.1016/j.biotechadv.2012.01.010

Paul, S. K., & Chakraborty, S. (2019). Mixing effects on the kinetics of enzymatic hydrolysis of lignocellulosic sunn hemp fibres for Bioethanol Production. Chemical Engineering Journal, 377, 120103. https://doi.org/10.1016/j.cej.2018.10.040

Pelkmans, L. (Ed.). (2021). (rep.). Implementation of bioenergy in Canada – 2021 update. Retrieved January 8, 2024, from https://www.ieabioenergy.com/wp-content/uploads/2021/11/CountryReport2021_Canada_final.pdf.

Pendse, D. S., Deshmukh, M., & Pande, A. (2023). Different pre-treatments and kinetic models for bioethanol production from Lignocellulosic Biomass: A Review. Heliyon, 9(6). https://doi.org/10.1016/j.heliyon.2023.e16604

PETTERSEN, R. O. G. E. R. C. (1984). The chemical composition of Wood. Advances in Chemistry, 57–126. https://doi.org/10.1021/ba-1984-0207.ch002

Pu, Y., Treasure, T., Gonzalez, R., Venditti, R., & Jameel, H. (2011). Autohydrolysis pretreatment of mixed hardwoods to extract value prior to combustion. BioResources, 6(4), 4840–4855. https://doi.org/10.15376/biores.6.4.4856-4870

Qi, G.-X., Xiong, L., Huang, C., Chen, X.-F., Lin, X.-Q., & Chen, X.-D. (2015). Solvents production from a mixture of glucose and xylose by mixed fermentation of clostridium acetobutylicum and saccharomyces cerevisiae. Applied Biochemistry and Biotechnology, 177(4), 996–1002. https://doi.org/10.1007/s12010-015-1790-0

Quintero, J. A., & Cardona, C. A. (2011). Process simulation of fuel ethanol production from Lignocellulosics using Aspen Plus. Industrial & Engineering Chemistry Research, 50(10), 6205–6212. https://doi.org/10.1021/ie101767x

Rajan, K., & Carrier, D. J. (2014). Effect of dilute acid pretreatment conditions and washing on the production of inhibitors and on recovery of sugars during wheat straw enzymatic hydrolysis. Biomass and Bioenergy, 62, 222–227. https://doi.org/10.1016/j.biombioe.2014.01.013

Rajinipriya, M., Nagalakshmaiah, M., Robert, M., & Elkoun, S. (2018). Importance of agricultural and industrial waste in the field of nanocellulose and recent industrial developments of wood based nanocellulose: A Review. ACS Sustainable Chemistry & Engineering, 6(3), 2807–2828. https://doi.org/10.1021/acssuschemeng.7b03437

Ranjan, A., Khanna, S., & Moholkar, V. S. (2013). Feasibility of rice straw as alternate substrate for biobutanol production. Applied Energy, 103, 32–38. https://doi.org/10.1016/j.apenergy.2012.10.035

Restiawaty, E., Harimawan, A., Rizki, N., & Irfan Rafi, F. (2021). Modelling and simulation of biobutanol fermentation by clostridium saccharoperbutylacetonicum N1-4. IOP Conference Series: Materials Science and Engineering, 1143(1), 012018. https://doi.org/10.1088/1757-899x/1143/1/012018

Rigual, V., Santos, T. M., Domínguez, J. C., Alonso, M. V., Oliet, M., & Rodriguez, F. (2018). Evaluation of hardwood and softwood fractionation using autohydrolysis and Ionic Liquid Microwave Pretreatment. Biomass and Bioenergy, 117, 190–197. https://doi.org/10.1016/j.biombioe.2018.07.014

Rios-González, L. J., Morales-Martínez, T. K., Rodríguez-Flores, M. F., Rodríguez-De la Garza, J. A., Castillo-Quiroz, D., Castro-Montoya, A. J., & Martinez, A. (2017). Autohydrolysis pretreatment assessment in ethanol production from agave bagasse. Bioresource Technology, 242, 184–190. https://doi.org/10.1016/j.biortech.2017.03.039

Ruiz, E., Cara, C., Manzanares, P., Ballesteros, M., & Castro, E. (2008). Evaluation of steam explosion pre-treatment for enzymatic hydrolysis of sunflower stalks. Enzyme and Microbial Technology, 42(2), 160–166. https://doi.org/10.1016/j.enzmictec.2007.09.002

Sabaruddin, F. A., Megashah, L. N., Shazleen, S. S., & Ariffin, H. (2023). Emerging trends in the appliance of Ultrasonic Technology for valorization of agricultural residue into versatile products. Ultrasonics Sonochemistry, 99, 106572. https://doi.org/10.1016/j.ultsonch.2023.106572

Sanchez-Ramirez E., Quiroz-Ramirez J.J., Segovia-Hernandez J.G., Errico M. (2018). Biobutanol purification by liquid- liquid extraction assisted divided wall columns. Chemical Engineering Transactions, 69, 217-222. https://doi.org/10.3303/CET1869037

Sandesh, K., & Ujwal, P. (2021). Trends and perspectives of liquid biofuel – process and industrial viability. Energy Conversion and Management: X, 10, 100075. https://doi.org/10.1016/j.ecmx.2020.100075

Sarangi, P. K., & Nanda, S. (2018). Recent developments and challenges of acetone-butanol-ethanol fermentation. Recent Advancements in Biofuels and Bioenergy Utilization, 111–123. https://doi.org/10.1007/978-981-13-1307-3_5

Sassner, P., Galbe, M., & Zacchi, G. (2008). Techno-economic evaluation of bioethanol production from three different lignocellulosic materials. Biomass and Bioenergy, 32(5), 422–430. https://doi.org/10.1016/j.biombioe.2007.10.014

Shuba, E. S., & Kifle, D. (2018). Microalgae to biofuels: ‘promising’ alternative and renewable energy, review. Renewable and Sustainable Energy Reviews, 81, 743–755. https://doi.org/10.1016/j.rser.2017.08.042

Stephens, C. H., Whitmore, P. M., Morris, H. R., & Bier, M. E. (2008). Hydrolysis of the amorphous cellulose in cotton-based paper. Biomacromolecules, 9(4), 1093–1099. https://doi.org/10.1021/bm800049w

Sun, Q., Foston, M., Meng, X., Sawada, D., Pingali, S. V., O’Neill, H. M., Li, H., Wyman, C. E., Langan, P., Ragauskas, A. J., & Kumar, R. (2014). Effect of lignin content on changes occurring in poplar cellulose ultrastructure during dilute acid pretreatment. Biotechnology for Biofuels, 7(1). https://doi.org/10.1186/s13068-014-0150-6

Tangsriwong, K., Lapchit, P., Kittijungjit, T., Klamrassamee, T., Sukjai, Y., & Laoonual, Y. (2020a). Modeling of chemical processes using commercial and open-source software: A comparison between Aspen Plus and DWSIM. IOP Conference Series: Earth and Environmental Science, 463(1), 012057. https://doi.org/10.1088/1755-1315/463/1/012057

Tekin, N., Karatay, S. E., & Dönmez, G. (2023). Optimization studies about efficient biobutanol production from industrial tea waste by clostridium beijerinckii. Fuel, 331, 125763. https://doi.org/10.1016/j.fuel.2022.125763

Tigunova, O. O., Kamenskyh, D. S., Tkachenko, T. V., Yevdokymenko, V. A., Kashkovskiy, V. I., Rakhmetov, D. B., Blume, Y. B., & Shulga, S. M. (2020). Biobutanol production from plant biomass. The Open Agriculture Journal, 14(1), 187–197. https://doi.org/10.2174/1874331502014010187

Trirahayu, D. A., Abidin, A. Z., Putra, R. P., Hidayat, A. S., Safitri, E., & Perdana, M. I. (2022). Process simulation and design considerations for biodiesel production from rubber seed oil. Fuels, 3(4), 563–579. https://doi.org/10.3390/fuels3040034

Tsai, T.-Y., Lo, Y.-C., Dong, C.-D., Nagarajan, D., Chang, J.-S., & Lee, D.-J. (2020). Biobutanol production from lignocellulosic biomass using immobilized clostridium acetobutylicum. Applied Energy, 277, 115531. https://doi.org/10.1016/j.apenergy.2020.115531

U.S. Energy Information Administration - EIA - independent statistics and analysis. Biofuels explained - U.S. Energy Information Administration (EIA). (n.d.). https://www.eia.gov/energyexplained/biofuels/

Ureta, M. M., & Salvadori, V. O. (2022). A review of commercial process simulators applied to food processing. Journal of Food Process Engineering, 46(2). https://doi.org/10.1111/jfpe.14225

Veza, I., Muhamad Said, M. F., & Latiff, Z. A. (2021). Recent advances in butanol production by acetone-butanol-ethanol (ABE) fermentation. Biomass and Bioenergy, 144, 105919. https://doi.org/10.1016/j.biombioe.2020.105919

Wang, F., Shi, D., Han, J., Zhang, G., Jiang, X., Yang, M., Wu, Z., Fu, C., Li, Z., Xian, M., & Zhang, H. (2020). Comparative study on pretreatment processes for different utilization purposes of switchgrass. ACS Omega, 5(35), 21999–22007. https://doi.org/10.1021/acsomega.0c01047

Wang, J., Rajan, K., Annamraju, A., Chmely, S. C., Pingali, S. V., Carrier, D. J., & Labbé, N. (2021). A sequential Autohydrolysis-Ionic liquid fractionation process for high quality lignin production. Energy &amp; Fuels, 35(3), 2293–2302. https://doi.org/10.1021/acs.energyfuels.0c03849

Wang, P., Chen, Y. M., Wang, Y., Lee, Y. Y., Zong, W., Taylor, S., McDonald, T., & Wang, Y. (2019). Towards comprehensive lignocellulosic biomass utilization for bioenergy production: Efficient biobutanol production from acetic acid pretreated switchgrass with Clostridium saccharoperbutylacetonicum N1-4. Applied Energy, 236, 551–559. https://doi.org/10.1016/j.apenergy.2018.12.011

Wang, S., Zhao, W., Lee, T. S., Singer, S. W., Simmons, B. A., Singh, S., Yuan, Q., & Cheng, G. (2018). Dimethyl sulfoxide assisted Ionic liquid pretreatment of switchgrass for Isoprenol Production. ACS

Sustainable Chemistry & Engineering, 6(3), 4354–4361. https://doi.org/10.1021/acssuschemeng.7b04908

Wang, Z., Winestrand, S., Gillgren, T., & Jönsson, L. J. (2018). Chemical and structural factors influencing enzymatic saccharification of wood from Aspen, birch and spruce. Biomass and Bioenergy, 109, 125–134. https://doi.org/10.1016/j.biombioe.2017.12.020

Wi, S. G., Cho, E. J., Lee, D.-S., Lee, S. J., Lee, Y. J., & Bae, H.-J. (2015). Lignocellulose conversion for biofuel: A new pretreatment greatly improves downstream biocatalytic hydrolysis of various lignocellulosic materials. Biotechnology for Biofuels, 8(1). https://doi.org/10.1186/s13068-015-0419-4

Williams, C. L., Westover, T. L., Emerson, R. M., Tumuluru, J. S., & Li, C. (2015). Sources of biomass feedstock variability and the potential impact on biofuels production. BioEnergy Research, 9(1), 1–14. https://doi.org/10.1007/s12155-015-9694-y

World energy trilemma index: 2022. World Energy Council. (n.d.). https://www.worldenergy.org/publications/entry/world-energy-trilemma-index-2022

Xu, Z., & Huang, F. (2014). Pretreatment methods for Bioethanol Production. Applied Biochemistry and Biotechnology, 174(1), 43–62. https://doi.org/10.1007/s12010-014-1015-y

Yan, P., Liu, X., Xu, Z., & Zhang, Z. C. (2021). Markedly different decomposition temperature and products of biomass pyrolysis at low temperature—differentiation of acids in their effects on pretreatment. Sustainable Chemistry, 2(1), 8–23. https://doi.org/10.3390/suschem2010002

Yang, Q., Chen, Y., Yu, S., Hou, Q., Wu, M., Jiang, T., Wang, K., & Liu, W. (2022). Changes of lignin structure of Poplar Wood Chips in autohydrolysis pretreatment and bleachability of Chemi-Thermomechanical Pulp. Industrial Crops and Products, 176, 114420. https://doi.org/10.1016/j.indcrop.2021.114420

Zalazar-Garcia, D., Fernandez, A., Rodriguez-Ortiz, L., Rodriguez, R., & Mazza, G. (2022). Sustainable slow-pyrolysis simulation of 12 Lignocellulosic Bio-wastes: Co2 emission, energy, and water consumption. IOP Conference Series: Earth and Environmental Science, 952(1), 012008. https://doi.org/10.1088/1755-1315/952/1/012008

Zeynali, R., Khojastehpour, M., & Ebrahimi-Nik, M. (2017). Effect of ultrasonic pre-treatment on biogas yield and specific energy in anaerobic digestion of fruit and vegetable wholesale market wastes. Sustainable Environment Research, 27(6), 259–264. https://doi.org/10.1016/j.serj.2017.07.001

Zhang, R., Lu, X., Sun, Y., Wang, X., & Zhang, S. (2010). Modeling and optimization of dilute nitric acid hydrolysis on corn stover. Journal of Chemical Technology & Biotechnology, 86(2), 306–314. https://doi.org/10.1002/jctb.2529

Zhang, Y., Xia, C., Lu, M., & Tu, M. (2018). Effect of overliming and activated carbon detoxification on inhibitors removal and butanol fermentation of Poplar prehydrolysates. Biotechnology for Biofuels, 11(1). https://doi.org/10.1186/s13068-018-1182-0

Zheng, B., Yu, S., Chen, Z., & Huo, Y.-X. (2022). A Consolidated Review of commercial-scale high-value products from lignocellulosic biomass. Frontiers in Microbiology, 13. https://doi.org/10.3389/fmicb.2022.933882

Zhou, N., Thilakarathna, W. P., He, Q. S., & Rupasinghe, H. P. (2022). A review: Depolymerization of lignin to generate high-value bio-products: Opportunities, challenges, and prospects. Frontiers in Energy Research, 9. https://doi.org/10.3389/fenrg.2021.758744

Zoghlami, A., & Paës, G. (2019). Lignocellulosic biomass: Understanding recalcitrance and predicting hydrolysis. Frontiers in Chemistry, 7. https://doi.org/10.3389/fchem.2019.00874