LIFE CYCLE ASSESSMENT OF BIOETHANOL PRODUCTION FROM WATER HYACINTH USING PROCESS SIMULATION

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Thesis submitted in partial fulfillment of the requirements for the degree Master of Science in Chemical and Process Engineering

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Sri Lanka

October 2023

Declaration of the candidate and supervisors

Declaration of the candidate

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Abstract

Water Hyacinth (WH) is an undesirable plant in the aquatic vegetation with a proven record of the possibility as a raw material to produce bioethanol. One of the advantages of using water hyacinth as a bioethanol feedstock is that it does not require land use or significant resource consumption for cultivation. The aim of this study was to evaluate the performance of water hyacinth as a bioethanol feedstock by modelling bioethanol production plant for future industrial purposes beyond labs-scale for different bioethanol production methods using the Aspen Plus software. By alternating two feedstock pretreatment methods (alkaline and dilute acid) and two bioethanol dehydration techniques (extractive and azeotropic distillation), four process scenarios were created (WH1, WH2, WH3, and WH4) for mass and energy flow comparison. Results showed that the alkaline pretreatment provided a 254 L/tonne-WH yield which is higher compared with the obtained by yield dilute acid pretreatment method (210 L/tonne-WH). Additionally, the process pathway that used NaOH for pretreatment and extractive distillation for the dehydration (WH1) resulted the least energy usage for the plant (45,310 MJ/FU). Based on these results, a comprehensive LCA was performed for bioethanol production from WH. The total energy consumption for the cradle-to-gate life cycle to produce bioethanol from WH is 56,202 MJ/FU. The study also evaluated energy sustainability indicators resulting 0.54 net ratio and a 1.87 renewability factor. Further, the study conducted a sensitivity analysis to interpret the effects of the key process parameters at two stages within the research project; first, for the bioethanol production process; second, for the life cycle. The prominent finding is that the parameter with the highest impact on the production plant and the life cycle is the solid loading ratio. Moreover, the energy hotspot was identified as the pretreatment stage. Finally, the study discussed feasible methods water hyacinth can be used for commercial production of fuel-grade bioethanol.

Keywords: Bioethanol Production, Feedstock Pretreatment, Life Cycle Assessment, Water Hyacinth, Process Simulation.

Acknowledgement

I would like to extend my sincere gratitude to my two supervisors Dr Mahinsasa Rathnayake and Dr Dilhara Sethunga, for mentoring me throughout my journey in completing this thesis. I thank them for their invaluable guidance, advice, and encouragement throughout the research process.

This research study was supported by the Senate Research Committee Grant with grant No. SRC/LT/2021/18 at the University of Moratuwa, Sri Lanka. Further, the funding for the purchase of the SimaPro LCA software was provided by the EUSL-TESS (Techno-economic Societal Sustainable Development Training in Sri Lanka) project, which is co-funded by the European Union under the auspices of Erasmus+ Capacity Building in Higher Education Programme. I would like to acknowledge the Department of Chemical and Process Engineering, University of Moratuwa, Sri Lanka, for providing the required process simulation software tools and computational facilities.

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Symbols/Abbreviations	**Terms**
2G	Second Generation
BE	Bioethanol
CO_2	Carbon Dioxide
EtOH	Ethanol
EU	European Union
FU	Function Unit
G	Glucose
GHG	Green House Gas
GWP	Global Warming Potential
H_2O	Water
H_2SO_4	Sulphuric Acid
LCA	Life Cycle Assessment
LCB	Lignocellulosic Biomass
NaOH	Sodium Hydroxide
NER	Net Energy Ratio
NEV	Net Energy Value
NRnEV	Net Renewable Energy Value
O_2	Oxygen
pH	Potential of Hydrogen
Rn	Renewability factor
SHCF	Separate Hydrolysis and Co-Fermentation
SSF	Simultaneous Saccharification and Fermentation
WH	Water Hyacinth
Wt%	Weight Percentage
X	Xylose

Chapter 1

Introduction

The utilisation of fossil fuels for energy generation is considered non-renewable because of the fast rates of fuel resource depletion and the environmental impacts, including high greenhouse gas (GHG) emissions [1]. Therefore, renewable energy has become the focus of research, and liquid biofuels have become a leading renewable energy source since they can be used as substitutes for fossil fuels, such as petrol and diesel [2]. For example, studies show that blending bioethanol from crop residues with gasoline can reduce GHG emissions due to fossil fuel-based transportation by 50% [3]. Moreover, the use of liquid biofuels can help to establish energy security while bringing economic benefits to the country, such as foreign exchange savings.

Many countries around the world have established strategies and made commitments to reduce the use of liquid fossil fuels by adapting alternative biofuels, such as bioethanol and biodiesel, as renewable and clean energy sources [4]. For example, the United States of America (USA), Brazil, and The European Union (EU) are widely converting their transportation liquid fuel to gasohol which is a blend of bioethanol and gasoline [5]. The two components (bioethanol and gasoline) can be mixed in different proportions to increase the octane number, which results in reducing emissions from vehicles. Depending on the blended ethanol amount, the fuel is named E10, E85, E100, etc. [6]. Blended bioethanol provides an increasing contribution to the global transportation fuel supply with various new initiatives [7]. Currently, USA and Brazil are the largest bioethanol producers in the world, and Brazil is the biggest exporter [8]. Furthermore, the USA has committed to increasing its total biofuel usage up to 136 billion litres by 2022 [8]. The world market for bioethanol was 110 billion litres in the year 2018 and is predicted to increase the demand up to 140 billion litres by 2022 [9][10]. Figure 1.1 shows the change in liquid biofuel production in the past decade.

According to the global biofuel production data, Figure 1.1 clearly shows that bioethanol has more demand than biodiesel as a liquid biofuel in commercial applications and transportation. In addition, Figure 1.2 shows the trend for bioethanol production increase for the last decade. Thus, the availability of bioethanol feedstocks would be a major concern to cater to the increasing demand in the future.

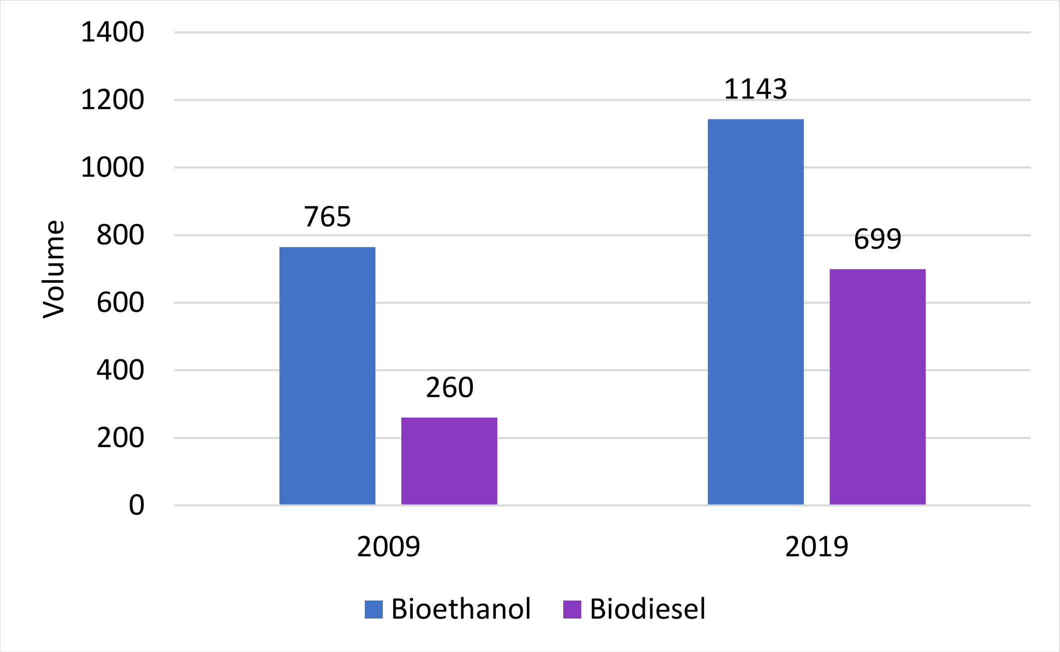


Figure 1.1: Global bioethanol and biodiesel production in 2009 and 2019 [7]

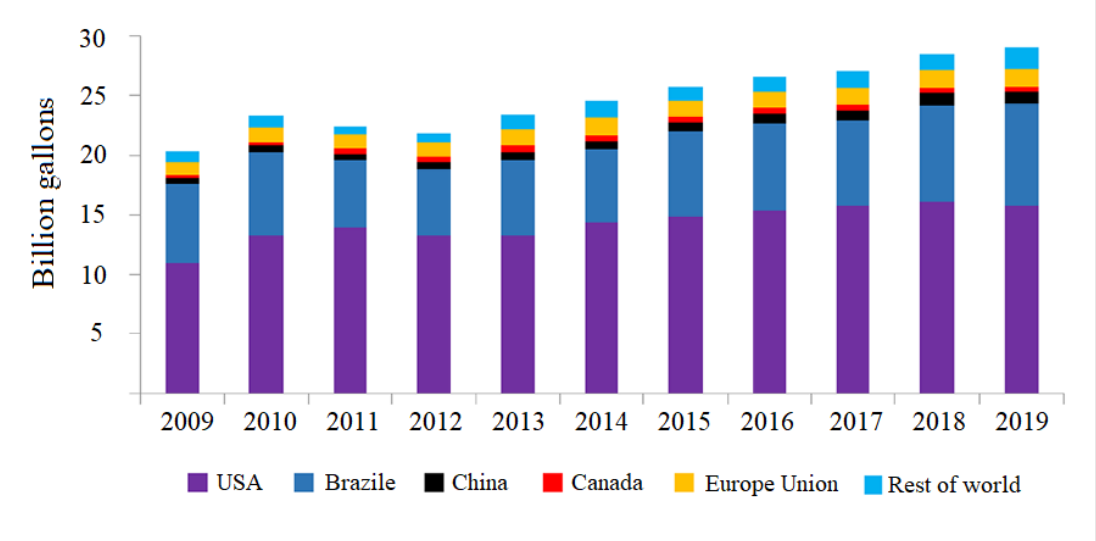


Figure 1.2: Progress in bioethanol production in the last decade [11]

In recent years, various published research studies have been focusing on a variety of potential feedstocks for bioethanol production, such as starches and sugars, lignocellulosic feedstocks, including rice straw, bagasse, wheat straw, etc. [12][13]. The utilisation of starches and sugars (first generation bioethanol feedstocks) would reach saturation of bioethanol production quantities due to the limitations of feedstocks availability and competition for food security. Hence, research studies have focused more on lignocellulosic bioethanol feedstocks, as most of them are either crop residues or biomass admittable to a waste category.

A study delineated that globally about 73.9 million tonnes per annum of lignocellulosic biomass on a dry basis is available from wasted crops which is convertible to 49.1 billion litres of bioethanol. Furthermore, the same study revealed that 491 GL of bioethanol is producible after combining the wasted crop with crop residue, which is ten folds higher than that of the wasted crop-only production [14].

Water Hyacinth (WH), with the scientific name *Eichhornia Crassipes,* invasive aquatic weed that grows rapidly in eutrophicated water bodies with no efficient method of disposal. However, the indication of availability of fermentable sugar with high cellulose and hemicellulose content led scientists to further investigate WH as a potential feedstock for bioethanol [14][15]. Other advantages that have drawn attention to WH include non-competition for land occupation, no significant use as a raw material for other value additions, a high growth of 1,540 kg/ha per week [15], and its utilisation remarks of "waste-to-energy" principles.

Life Cycle Assessment (LCA) is a standard framework for environmental sustainability assessment of products and processes [16]. LCA broaden the perspective beyond the traditional view of processes to provide a holistic view of a product's environmental performance, including relevant upstream and downstream activities that can have contributions to significant environmental impacts [17]. Even though there are studies on different methods of producing bioethanol using WH at a laboratory/pilot scale, the existing literature has no report of a comprehensive LCA for industrial-scale bioethanol production from WH. Moreover, there are still no published studies or reports of an industrial-scale bioethanol production plant using WH as the feedstock. This makes it quite difficult to obtain life cycle inventory data for the bioethanol conversion and purification stages of WH from a real industrial plant via conventional inventory data collection methods of LCA. However, chemical process simulation can be utilised as a technique to model and design scaled-up chemical processes based on process modelling principles and findings from laboratory/pilot scale experiments [18]. Thereby, process simulations can provide the required inventory data of the production process, such as energy inputs/outputs and mass flows of environmental emissions/wastes for LCA. Thus, process simulation-based LCA supports the required analysis of environmental impacts and identification of process sustainability improvement options of a process where no commercial-scale plant is available for conventional inventory data collection. Hence, this MSc research performs process simulations using a standard simulation tool and utilises the calculated inventory data to conduct a comprehensive LCA with the objectives as follows.

Objectives of study

This research aims to conduct a comprehensive LCA for an industrial-scale bioethanol production process from WH. The objectives of this study can be indicated as follows.

1. Simulate a scaled-up bioethanol production plant in a process simulation tool using WH as the feedstock.
2. Evaluate net energy indicators of a scaled-up bioethanol production process from WH for different process-routes.
3. Assess life cycle environmental impacts including GWP and environmental sustainability of WH as a feedstock for the production of fuel-grade bioethanol.

Scope of study

The scope for this study is performing an LCA of bioethanol production from WH. The system boundary of the study starts from the harvesting of WH to bioethanol production at fuel-grade purity (cradle-to-gate). Since there are no published real industrial plant data, laboratory/pilot scale experiments reported in the literature will be used to estimate the input data and process conditions for the scaled-up process simulation. Process simulation results will be used for the required inventory data calculations to carry out a comprehensive LCA. The study performs a cradle-to-gate net energy analysis and evaluates the net energy indicators to determine the energy sustainability of the process. Life cycle environmental impact assessment is also conducted for the selected system boundary. The analysis will be carried out for different scenarios, such as different fuel types for process energy supply, process technology/routes, etc. A sensitivity analysis will also be performed to analyse the effect of the variation of the major process parameters on life cycle environmental impacts.

Chapter 2

Literature review

2.1 The study background

Bioethanol can be produced from an array of crops, and the feedstocks can be segregated into four generations depending on their fermentable sugar availability and molecular structure [10].

The first generation is the conventional feedstocks which are mostly food-grade starch-based crops, such as sugarcane, corn, cassava, and potato [19][13]. These compete with the arable land, and it can create conflicts between its use as food for human consumption and as feed for energy production. Hence, these feedstocks cannot be considered viable in the long-term journey of switching from fossil fuels to biofuels.

The second-generation feedstocks are lignocellulosic biomass, which has gained interest over the recent years because of its abundance and the low cost of the feedstock. Rice straw, wheat straw, sugar cane bagasse, corn stover, wood, and forestry residues can be mentioned as popular examples [20].

Algal biomass is considered the third-generation feedstock for biofuel production. Since the process is non-toxic, eco-friendly, and, most importantly, has a high capacity to capture CO_2 due to the high growth rate, algal biomass has caught momentum in the industry [21]. However, growing and harvesting can be economically challenging, especially with high capital costs and energy requirements for harvesting, and extensive downstream processing when scaling up from laboratory to industry [22].

The fourth-generation bioethanol production is carried out via genetically modified algae. By the modification of algae, the ability to capture CO_2 can be increased along with the rate of production of compounds, such as triacylglycerol [10]. Regardless of the potential, the process requires stringent process controlling and high-tech equipment to avoid contamination of the environment and the ecosystem on an industrial scale. This results in a high capital cost which is the main limitation in further development as of now [22].

Comparatively, out of these four generations, the second-generation (2G) bioethanol by the valorisation of lignocellulosic biomass is a more suitable option considering the industrial maturity and the potential to reduce greenhouse gas emissions and with the capability to offset the CO_2 emissions in the cultivation stage of the biomass.

2.2 Lignocellulosic biomass

Lignocellulosic biomass is a form of biomass with abundant availability which is categorizable as agro-residues, forestry residues, energy crops and cellulosic waste [23]. In the present time, the mostly used 2G feedstock is cereal residues which are agricultural wastes, such as wheat straw, rice straw, corn stover, and sugarcane bagasse [12]. Lignocellulosic materials are made out of three predominant components: cellulose, hemicellulose, and lignin. Other than that, there is moisture, ash and some proteins depending on the biomass [24]. Cellulose are long chains of B-glucose monomers, which are attached to each other by hemicellulose with hydrogen bonds. Hemicellulose molecular weight is lesser compared to cellulose. Thes two types of polymers can be an be converted to hexose (C_6 sugars mannose, glucose and galactose) and pentose (C_5 sugars such as xylose and arabinose). Further, Hemicellulose is linked with lignin by covalent bonds. Lignin provides rigidness to plants and protects against microbial attack [25].

Table 2.1 shows different types of lignocellulosic biomass and their compositions. According to the composition of various lignocellulosic biomass sources in Table 2.1, WH has a comparatively higher total cellulose/hemicellulose content while having lower lignin content, which is favourable for bioethanol production. Low content of lignin would make the feedstock pretreatment operation easier while having reduced energy generation from separated lignin solid residues after the pretreatment process.

Table 2.1: Lignocellulosic Composition of different Biomass [26][27]

LCB type	Cellulose %	Hemicellulose %	Lignin %
WH	24.5	34.1	8.6
Walnut shell	23.3	20.4	53.5
Hazelnut shell	25.2	28.2	42.1
Bamboo leaves	34.14	25.55	35.03
Sugarcane bagasse	35	35.8	16.1
Barley straw	35.4	28.7	13.1
Rice straw	35.8	21.5	24.4
Rice husk	37.1	29.4	24.1
Corn stover	38.4	22.9	20.1
Bamboo plant	41.8	18	29.3
Spruce wood	43	29.4	27.6
Beechwood	44.2	33.5	21.8
Eucalyptus	44.9	28.9	26.2
Corn Stalk	50	20	30

2.3 Significance of WH

WH is an aquatic weed that can be considered a waste material that needs treatment due to its invasive behaviour; because of this invasive nature, WH has been ranked in the world's top 100 worst invasive species according to the global database [28]. This tropical plant which is native to the Amazon River in South America, has now spread across more than 50 countries [29]. Because of the adaptability to extreme weather conditions, WH can infest water streams regardless of the season and water conditions, with a maximum growth rate to 22 tonnes/km^2 per day [15] and a 7-12 doubling time [30]. This scenario destroys not only domestic vegetation but also aquatic ecosystems by depleting dissolved oxygen and other nutrients [31]. Even though there are various methods established to mitigate the growth of this weed, none of them has been successful enough without causing ecologically and economically negative impacts [8]. For instance, a study mentioned introducing WH for constructed wetlands for water treatment coupled with biogas production via anaerobic digestion. However, the authors suggest after an LCA for the project, since the WH growth rate and potential to use for biogas are critical for the GHG effect, further studies are a must [32].

Under the circumstances, using WH as biomass can be considered an opportunity for commercial cultivation to produce bioethanol due to its rapid growth rate and, more specifically, being a waste with no competition with fertile land for food crops. Moreover, the low lignin content and high cellulose and hemicellulose content make WH an attractive substrate for bioethanol production. According to Table 2.1, WH has the lowest lignin content (only 8.6%), and its hemicellulose content is only lesser than that of the sugarcane bagasse out of the mentioned feedstocks. Another reason for WH to become more attractive among other lignocellulosic feedstocks is due to its special properties of cellulose, i.e., the low crystalline index compared to feedstocks such as metasequoia, miscanthus and water peanuts and faster hydrolysis rate with a low by-product yield [33][34]. Table 2.2 summarises the chemical composition of WH reported in different literature. Based on the maturity of the plant and the environment, the composition might vary.

Table 2.2: Chemical composition of WH

	Composition (wt%)					
Reference	[8]	[35]	[36]	[37]	[38]	[39]
Country	India	India	China	Vietnam	Malaysia	India
Cellulose	22	25	25	29	18	19
Hemicellulose	34	32	35	25	48	40
Lignin	07	03	10	08	04	05
Protein	14			17	13	
Mineral ash	12		20	06		36
Nitrogen			03			
Other				15		

2.4 The conversion process of WH to bioethanol

Once WH is harvested, it needs washing to get soil and mud out before solar drying as preparation. Then the sun-dried biomass will undergo crushing or milling. Milling not only increases the surface area by reducing the size, which encourages enzymatic hydrolysis but also reduces the cellulose crystallinity and reduces the extent of cellulose polymerisation.

There are two technologies that can be used to convert lignocellulosic biomass into bioethanol; biochemical and thermochemical conversion [10]. Since thermochemical conversion technology uses high temperatures and pressures as compared to biochemical conversion technology, energy consumption is high, resulting in detrimental effects on the environment and higher operating costs for the plant [40]. Therefore, scaling up to industrial production biochemical methods is more suitable.

The biochemical method entails four main steps [41].

1. Pretreatment (physical and chemical) to degrade and remove lignin
2. Hydrolysis
3. Fermentation
4. Distillation and dehydration

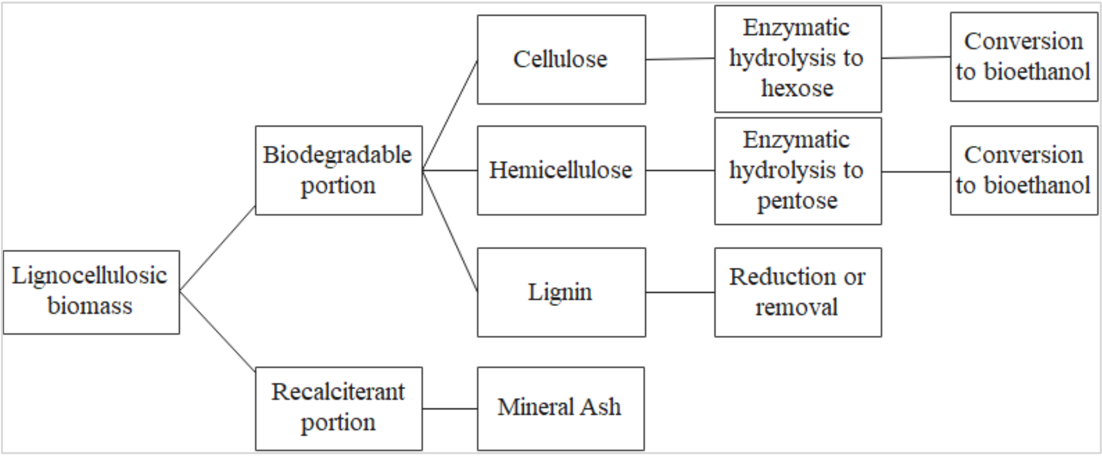


Figure 2.1: Lignocellulosic biomass to bioethanol [23]

Even though WH is an attractive option to produce bioethanol, because of lignin, cellulose, and hemicellulose are not accessible for hydrolysation. Therefore, the most important step can be mentioned as the pretreatment to break down and remove lignin to expose cellulose to hydrolyse. The pretreatment step can be considered a preparation step with the goal of increasing the accessibility of cellulose and hemicellulose for saccharification by disrupting the lignin structure. Furthermore, this step can contribute more than 40% of the entire operation cost and be the most energy-consuming stage [12]. Figure 2.2 shows a schematic structure of lignocellulosic biomass before and after pretreatment.

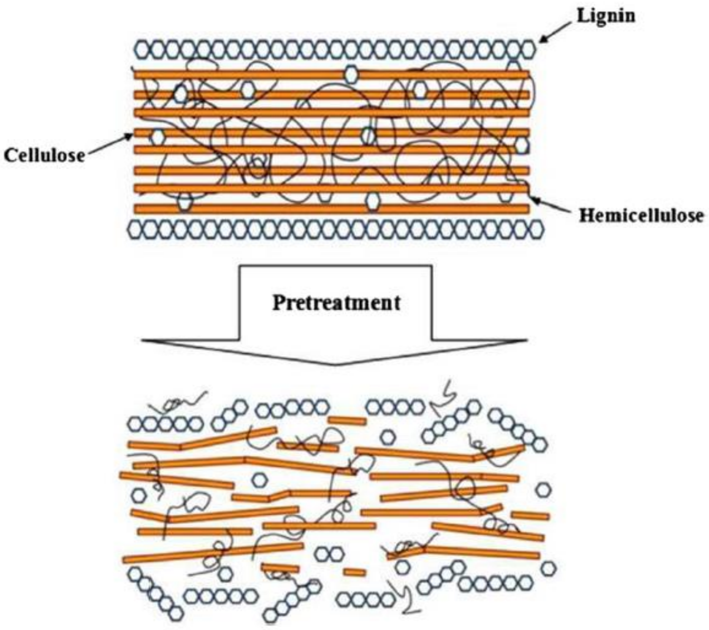


Figure 2.2: Schematic structure of lignocellulose before and after pretreatment [27]

There are multiple aspects to consider in the most suitable pretreatment method. First and foremost, the method should be able to expose cellulose and hemicellulose, encouraging the conversion to reduce sugars. In other words, the method should be able to give a high product yield. Other than that, the technology should be eco-friendly, time effective, simple and easily adaptable to a larger scale, and cost-effective [12][42]. The ideal pretreatment method will consume less energy and create less harmful, toxic inhibitor compounds. In addition, it is more desirable if the chosen method can pre-treat different types of feeds without much alteration to the native lignin structure while reducing the crystallinity index of cellulose and preserving high amounts of sugars [26].

Pretreatment methods for biomass can be broadly categorized into five distinct categories: physical, chemical, physiochemical, thermochemical, and biological pretreatment. Physical pretreatment techniques focus on enhancing accessibility to reducing sugars by reducing particle size and breaking down crystalline structures, typically achieved through methods like milling, grinding, or crushing [1]. On the other hand, biological pretreatment harnesses the power of microorganisms, particularly fungal cellulases, to degrade complex polymers such as lignin and hemicellulose. While it offers cost advantages, it does suffer from the drawback of requiring extended retention times due to its relatively slow hydrolysis rate, making it less suitable for rapid industrial applications [1].

Chemical pretreatments, carried out in either acidic or alkaline mediums, have gained prominence in the industry for their competitive results. Alkaline pretreatment induces structural alterations in lignin, swelling and decrystallisation of cellulose, and partial solvation of hemicellulose through the degradation of ester and glycosidic side chains [5][6]. Acid pretreatment, on the other hand, has the notable advantage of sometimes eliminating the need for subsequent enzymatic hydrolysis steps. Additionally, physiochemical pretreatment methods, such as the steam explosion technique, utilize high pressure and temperature (190 °C – 270 °C) in a brief period, followed by rapid depressurization, to disrupt the biomass's structural integrity. This method has proven effective even with larger particle sizes, streamlining feedstock preparation. Another example for thermochemical pretreatment is Liquid Hot Water (LHW) technique. Within the realm of thermochemical pretreatment, techniques such as gasification, and pyrolysis offer versatile options for the production of various fuels, surpassing the capabilities of chemical pretreatments and expanding the horizons of biomass conversion [2][3][4].

Table 2.3 is a summary of some pretreatment methods and their advantages and disadvantages according to the literature.

Table 2.3: Comparison of pretreatment methods for lignocellulosic feedstocks

Pretreatment method	**Advantages**	**Disadvantages**
Dilute acid (H_2SO_4)	• High glucose yield • Hemicellulose solubilisation • Scenario-based enzyme hydrolysis may not require because the acid itself can hydrolyse the sugars	• Release of toxic compounds (furfural, hydroxy-methyl furfural, acetic acid, formic acid, levulinic acid • Loss of sugar in the form of gypsum • Leave most of the cellulose intact without hydrolysing • Because corrosivity damages equipment • High cost of reactors
Alkali treatment (NaOH)	• Hydrolyse both cellulose and hemicellulose • Efficient lignin removal • Reduces inhibitor production • Causes less sugar degradation compared to acid pretreatment	• Partial degradation of hemicellulose • Potential to generate inhibitors
Steam explosion (high-pressure steam)	• Simple process • High yield of glucose • Low capital investment	• High energy consumption • Partial degradation of hemicellulose • Less effective on softwoods
Liquid hot water	• It can interfere with hydrolysis since it only removes soluble lignin	• High water consumption • High energy consumption
Ammonia fibre explosion	• Does not produce inhibitors • High efficiency • Selectivity for reaction with lignin	• Does not work on feedstock with high lignin content • Uses high pressure
Oxidation	• Lower production of by-products	• High cost
Microbial (fungi)	• Lower energy consumption • Eco-friendly	• A very slow rate of hydrolysis

Source [8][12][43]

Table 2.4: Process conditions for different pretreatment methods for lignocellulosic feedstocks [23]

Feedstock	**Acid Treatment**			**Alkali Treatment**			**Steam explosion**		
	Process conditions	**Reducing sugars**	**BE yield g/l**	**Process conditions**	**Reducing sugars**	**BE yield**	**Process condition**	**Reducing Sugars %**	**BE yield**
Rice straw	100 °C; 2 h	14 g/l	40.6	50-90 °C	Glucose 81%	0.032 g/g			
				1%; 50 °C; 72 h	94 g/l	13.8 g/l			
Corn stover	0.75%; 200 °C	-	Approx. 100	0.1%	230g/l	10.7 v/v	200 °C; 10 min	84.7	78.30%
Wheat straw	2%; 180 °C; 10 min	43 g/l	0.44				151 °C; 16 min	G 59.3; X 55.7	55 g/l
Sugarcane bagasse				15%; 175 °C; 1.5 h	5.29 g/l	8.8 g/l			
Switchgrass				0.5%; 60 °C; 20 min	269.30 g/kg	17.26 g/l			
							200 °C; 10 min	G 50.9; X 27.9	88.30%

2.4.1 Dilute acid pretreatment process conditions

Dilute acid pretreatment is widely studied for industrial use because of the simplicity and the capability to disruption of the lignocellulosic matrix compared to other methods. It is suggested because of the loose matrix of lignocellulosic structure in WH, using a dilute acid solution is suitable to increase the enzymatic hydrolysis of cellulose and hemicellulose by using it as a catalyst [44]. Table 2.5 shows process conditions noted in previous studies conducted on a lab scale using H_2SO_4 to delignify WH.

Table 2.3: Dilute acid pretreatment process conditions for WH

Pretreatment agent	**Pretreatment operating conditions**	**Reducing sugar yield**	**Reference**
H_2SO_4	1% (w/v) Solid loading 3.33% 121 °C; 30 min	0.2 g/g dry WH	[45]
H_2SO_4	0.5% (w/v) Solid loading 8% RT; 24 H	0.21 g/g dry WH	[46]
H_2SO_4	2 % (w/v) Solid loading 10% 121 °C; 40 min	0.52 g/g dry WH	[39]
H_2SO_4	2 % (v/v) Solid loading 10% 121 °C; 60 min	0.15 g/g dry WH	[35]

Moreover, studies have proven the possibility of increasing the yield of reducing sugars by introducing enzymatic hydrolysis to the process, followed by dilute acid pretreatment. As per [45], by adding 0.05 g of cellulase and maintaining for 96 h at 45 °C it is possible to recover a total of 402.93 mg of reducing sugars from 1 g of WH, whereas in [35] by adding a cellulase load of 30 FPU/g at 50 °C for 24 h it was

425.6 mg/g dry WH. However, enzymatic hydrolysis can increase the cost of the process not just only because of the additional operational unit but also because of the price point of cellulase and xylanase in the industry. Also, since recycling enzymes are difficult due to the adsorption of cellulase to residual plant material, it is advisable to optimise the pretreatment instead of relying on enzymatic hydrolysis to increase sugar recovery.

Nevertheless, it is also mentioned in the literature that high concentrations of the acid can destroy polysaccharides resulting in a lower yield, and also there is the disadvantage of hemicellulose degrading to furfural and hydroxy-methyl furfural [39] (44). Ultimately, the effectiveness of the pretreatment depends on the physical structure and the chemical composition of the lignocellulosic material [30]. Therefore, even though using H_2SO_4 is the well-known method for pretreatment for other lignocellulosic biomass, because of the formation of inhibitors and considering the effectiveness for WH, this study will predominantly focus on alkaline pretreatment.

2.4.2 Alkali pretreatment process conditions

Using alkali pretreatment is considered a reliable method because of the simplicity, and the selective removal of lignin without losing reducing sugars and carbohydrates leads to better hydrolysis. Sulphite, sodium hydroxide, ammonium hydroxide and lime can be used for alkali treatment; however, according to the literature, sodium hydroxide (NaOH) is the most desirable due to its effectiveness. [23]

Table 2.5 shows the alkaline pretreatment process conditions for WH using NaOH as the pretreatment agent and yeast strains for simultaneous saccharification and fermentation SSF. As compared to the maximum bioethanol yield that can be obtained from each alkaline pretreatment condition, the yeast co-culture containing *Saccharomyces cerevisiae*, *Scheffersomyces stipites* and singular culture *Kluveromyces marxianus* KP231175 has resulted in the best ethanol yield.

Table 2.4 Alkaline pretreatment process conditions for WH and yeast strains for SSF

Pretreatment agent	**Pretreatment operating conditions**	**Yeast strain for SSF**	**Ethanol Yield g/l**	**Reference**
NaOH	0.5% (w/v) Solid loading 8% RT; 24 H	*Kluveromyces marxianus* KP231175 (42 °C)	8.09	[47]
NaOH	0.5% (w/v) Solid loading 8% 121 °C; 30 min	*Kluveromyces marxianus* KP231175 (42 °C)	8.40	
NaOH	0.5% (w/v) Solid loading 8% RT; 24 H	*Saccharomyces cerevisiae* (30 °C)	5.83	
NaOH	0.5% (w/v) Solid loading 8% 121 °C; 30 min	*Saccharomyces cerevisiae* (30 °C)	6.81	
NaOH	2.75% (w/v) Solid loading 10% 121 °C; 60 min	*Saccharomyces cerevisiae*	4.3	[39]
NaOH	2.75% (w/v) Solid loading 10% 121 °C; 60 min	*Scheffersomyces stipitis*	6.2	
NaOH	2.75% (w/v) Solid loading 10% 121 °C; 60 min	*Saccharomyces cerevisiae* + *Scheffersomyces stipitis*	9.8	
NaOH /H_2O_2 pre-treated	1.5% (v/v)/ 3% (w/v) Solid loading 5% 25 °C; 24 h	*Kluveromyces marxianus* K213 (42 °C)	7.34	[48]
NaOH /H_2O_2 pre-treated	1.5% (v/v)/ 3% (w/v) Solid loading 5% 25 °C; 24 h	*Saccharomyces* angel (30 °C)	4.45	

2.4.3 Simultaneous Saccharification and Fermentation (SSF)

Recent studies suggest that SSF is better than separate hydrolysis and fermentation because of its efficiency and comparatively higher ethanol yield due to the fermentation of produced sugar during hydrolysis into ethanol immediately in the same reactor. This reduces inhibitors getting generated, thus increasing the ethanol yield. Furthermore, the capital cost is lower due to the lesser required number of reactors since both hydrolysis and fermentation operations happen in the same reactor [49]. However, the difference in the process conditions in saccharification and fermentation is a factor to be mindful of when designing the process. To enhance the effectiveness, a pre-hydrolysis step is proposed [49].

Research conducted by Chen *et al.* using corn stover concluded that with 20% solid loading, *Saccharomyces cerevisiae* IPE005 18 IU compared with *Saccharomyces cerevisiae* IPE003 gave the highest reducing sugar yield after 48 h. Also, it showed more tolerance to inhibitor furfural [49].

2.4.4 Dehydration

For fuel-grade ethanol (EtOH), the concentration of ethanol should be larger than 99.5% (v/v). Since ethanol-water mixture forms a minimum boiling azeotrope with 89.4 mol% EtOH at 78.2 °C, further separation of ethanol from water cannot be done via a conventional distillation [5]. Hence, a special process is required to remove the remaining amount of water. There are a variety of advanced distillation technologies that can be used to further purify the mixtures having azeotropes, such as azeotropic distillation, molecule sieve adsorption, pressure-swing distillation, and extractive distillation.

Regardless of recent developments in pervaporation and adsorption with molecular sieves, for commercial production of anhydrous bioethanol, extractive distillation is still dominant as the separation technology [50]. The most commonly used solvent for extractive distillation is ethylene glycol, glycerol and n-pentane [51]. Furthermore, it is important to note, to improve efficiency, different solvents such as glycerol, hyperbranched polymers and ionic liquids are currently being explored [52]. Nevertheless, ethylene glycol is still widely used in commercial production. Another study mentioned that separation through azeotropic distillation using benzene is an effective method. However, the authors stated the addition of the entrainer directly affects energy consumption, increasing the operation cost, which could negatively affect an industrial-scale plant [11]. Moreover, the same study suggests liquid-liquid extraction as an alternative method and pervaporation for a smaller-scale plant because of the fouling issue in the pervaporation technology, which causes instability of membrane leading to additional costs limiting industrial-scale application.

When choosing the most suitable technology for the dehydration of bioethanol to obtain fuel-grade purity (i.e., > 99.5%), the energy consumption for 1 kg of anhydrous ethanol is the main parameter to consider. For industrial-scale plants, the cost is also another prominent factor [53]. A study has reported, under similar conditions in a two-column sequence, extractive distillation had a total duty of 2,008 kW while azeotropic distillation had 6,943 kW [51]. Furthermore, in between azeotropic distillation (USD 3 million), molecular sieve adsorption (USD 2.3 million), and extractive distillation technologies, extractive distillation gave the lowest capital cost, which was USD 2 million [53].

Considering all the facts, such as energy consumption, cost, safety, availability, and process complexity, extractive distillation with conventional ethylene glycol or other appropriate solvents can be used as the dehydration technology for scaled-up bioethanol production from WH. Ethylene glycol changes the relative volatility of bioethanol to achieve the required separation and is practically more feasible in use at large-scale plants [54]. Thus, in consideration of various factors based on the published literature, extractive distillation with ethylene glycol can be utilised as the dehydration technique for the industrial-scale process simulation.

2.5 Life Cycle Assessment

Life Cycle Assessment is the technique used to assess resource and energy utilisation in a process and the environmental impact caused by the process to evaluate environmental sustainability. The LCA technique helps to decide on the most suitable method of conversion to minimise negative environmental impacts and identify the hotspot stages affecting the sustainability and the environmentally-benign aspects of the process [16][18].

For the past decade, many researchers have conducted LCAs for bioethanol production from lignocellulosic biomass feedstocks. Table 2.7 shows the summary of the potential GHG reduction when using bioethanol from different feedstocks.

Table 2.5: GHG reduction for gasohol from different biomass [10]

Biomass	**GHG reduction potential (%)**
Poplar	30 – 70
Willow	19 – 20
Miscanthus	90 – 130
Switchgrass	88 – 100
Corn cob	100

Davis *et al.* compared E15 and E85 gasohol derived from wheat straw. The study suggested that higher blending of ethanol with gasoline resulted in better reduction of GHG emissions. To illustrate, E85 and E15 reduced GHG by 73% and 13%, respectively, as compared to conventional gasoline. Furthermore, E85 made from corn stover is capable of reducing GHG by 86 – 223% [55].

In addition, there is a comparison of two pretreatment methods utilising SimaPro 7.3.3 with the simulation done by Aspen Plus process simulations on poplar for E10, E85, and E100 via dilute acid and liquid hot water followed by Separate Hydrolysis and Co-Fermentation (SHCF) using *Zymomanas mobilis* which concluded dilute acid pretreatment has better environmental advantages [56]. These mentioned feedstocks, especially switch grass and corn cob, which are similar to WH have better potential in reducing GHG emissions. However, there are no available LCA studies for comparison and assessment of the GHG reduction potential of WH as a bioethanol feedstock.

Similarly, industrial process plant data are still unavailable for bioethanol production from WH to carry out a comprehensive LCA using conventional inventory data collection methods. Therefore, inventory data for a scaled-up plant will have to be developed based on the laboratory scale data to choose which method is the most viable for mass production of bioethanol via WH in an industrial scale plant [8] [39]. As a solution for this problem, process simulators like Aspen Plus software can be used. By modelling the process, mass and energy requirements can be estimated with lesser time and resource utilisation than real industrial scale plant construction to obtain process data. In addition, this gives the flexibility to analyse alternative scenarios of the production pathways [57]. Moreover, results show that simulation-based cleaner process designs can improve the energy efficiency, renewability, and environmentally sensitive aspects of a bioethanol feedstock for future scaled-up applications. By using the parameters from process simulations, a comprehensive life cycle assessment with sensitivity analysis can be effectively carried out as well [18].

Chapter 3

Methodology

3.1 Standard LCA Methodology and Framework

Life Cycle Assessment (LCA) in this study adopts the standard ISO 14040/44 framework as the LCA methodology. Figure 3.1 illustrates the standard LCA methodology, which consists of four phases, Goal and Scope Definition (ISO 14040), Inventory Analysis (ISO 140041), Impact Assessment (ISO 14042), and Interpretation (ISO 14043), along with LCA Requirements and Guidelines (ISO 14044).

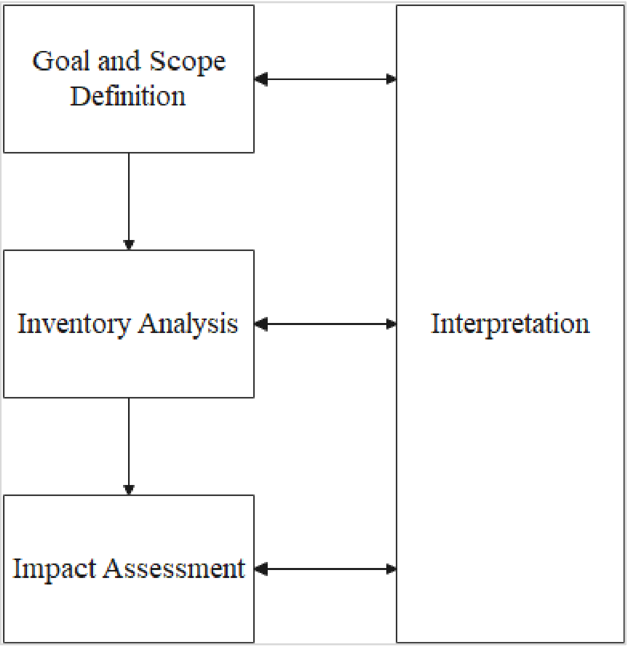


Figure 3.1: Standard LCA Framework according to ISO14040/44

3.2 Goal and scope definition

As per the framework, the first step develops the goal and scope definition where the objectives/purpose and life cycle scope/system boundary of the study are defined. The main objective and purpose of this research are to evaluate the life cycle environmental impacts and environmental sustainability of WH as a feedstock to produce bioethanol at an industrial scale.

In this analysis, the function unit for inventory calculations was chosen as 1,000 L (1 m^3) of bioethanol at 99.7% (v/v) purity [58]. The harvesting yield, feedstock input and inventory considerations for transportation, and key parameters for feedstock preparation will be selected from the literature. Then, to obtain inventory data for LCA, literature-based calculations will be performed for the feedstock harvesting and preparation stage, and process simulation-based calculations will be carried out for the bioethanol conversion stage and bioethanol purification stage. Figure 3.2 summarises the research methodology specific to this study based on the LCA methodology and framework.

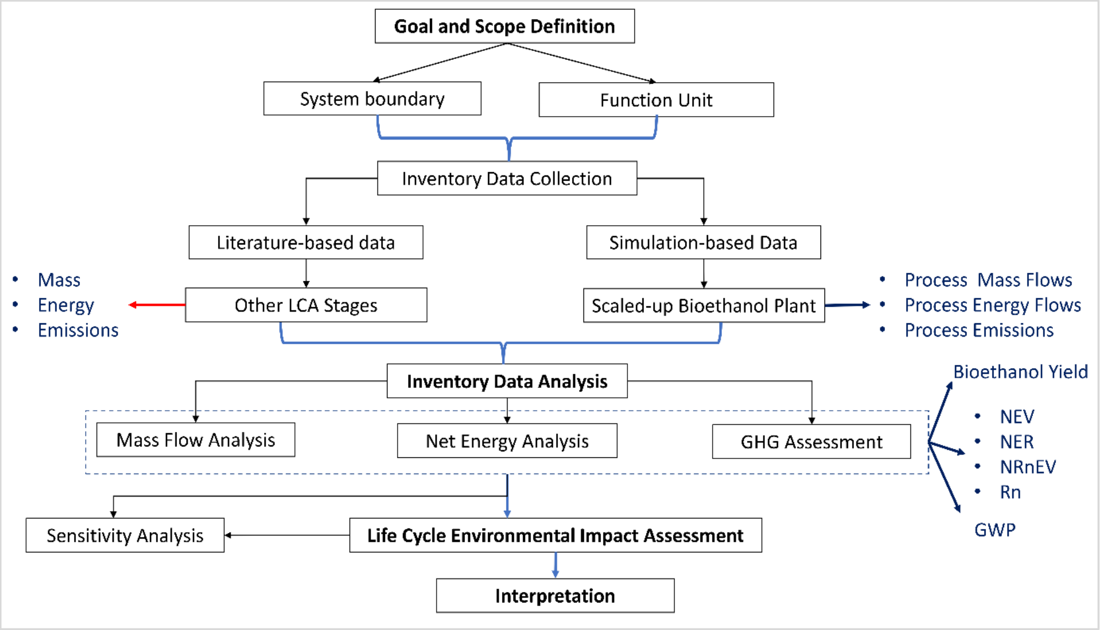


Figure 3.2: Overall research methodology

Figure 3.3 shows the cradle-to-gate life cycle scope developed for this study. The life cycle scope of the bioethanol production process can be divided into five main stages as follows.

1. Raw material transportation
2. Feedstock harvesting
3. Feedstock preparation
4. Process stage 1
5. Process stage 2
6. Process stage 3

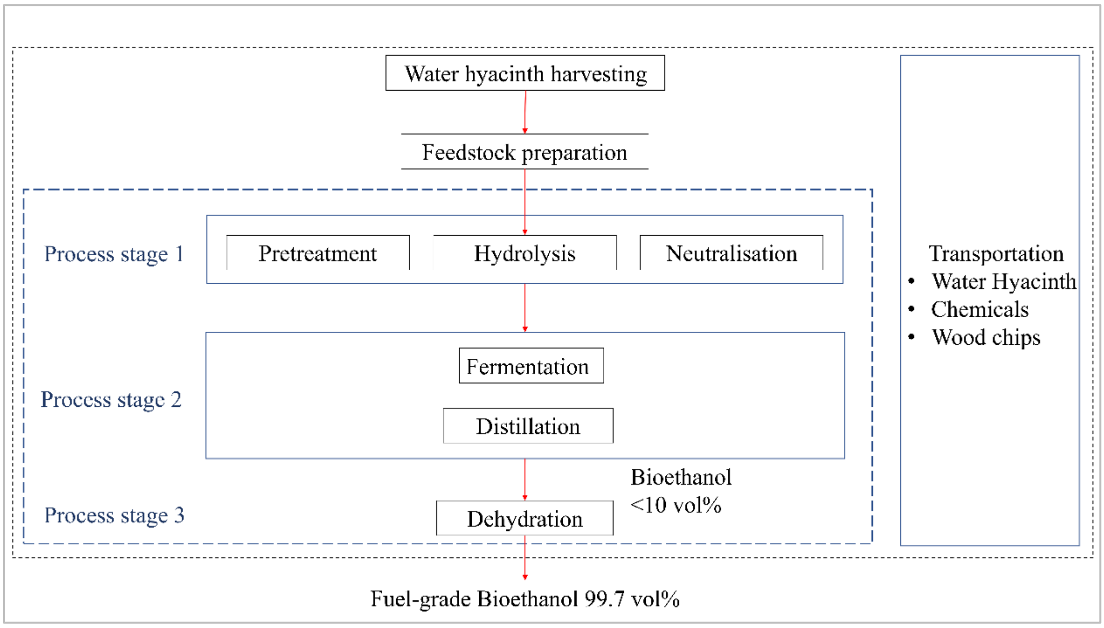


Figure 3.3: Life cycle scope for bioethanol production from WH.

For the process simulation of the bioethanol conversion and purification stages, along with the recycle portion will use the Aspen Plus process simulation software. Since there is no published information on an industrial-scale plant that uses WH as the feedstock, process input data needed for the process simulation will be based on published experimental studies at a laboratory/pilot scale.

Figure 3.4 shows the cradle-to-gate system boundary with details on inputs/outputs for the bioethanol production process from WH.

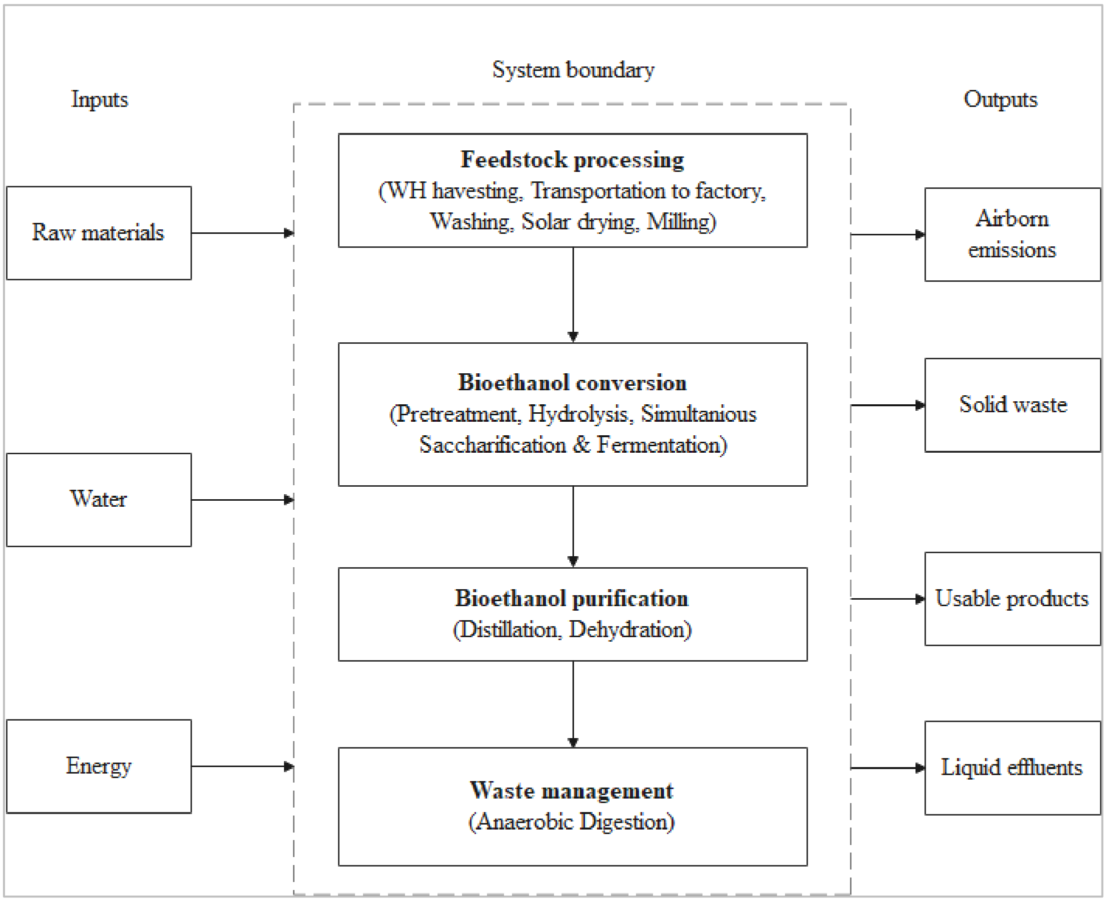


Figure 3.4: System boundary diagram for the LCA

3.3 Inventory analysis

3.3.1 Literature-based inventory data calculations

Literature-based data for the feedstock harvesting and preparation stage will be converted to functional unit basis and necessary calculations for the inventory analysis by using Excel software.

The following considerations were made for this study

1. WH loss during harvesting, loading to the truck and transportation is 10%
2. Harvesting machinery and transportation trucks use diesel as fuel
3. Since WH is an aquatic weed that grows freely, fertilisers, herbicides or pesticides were not used, and the cultivation stage is excluded from the system boundary as there is no planned cultivation process.
4. WH loss during the washing, drying and crushing process is 10%.
5. Dried WH is crushed using a diesel crusher
6. Any conveyor belt used in the plant use electricity
7. Production of chemicals used for the process uses fossil energy

Calculations for energy consumption for the harvesting process are carried out using equation 3.1.

$$Fuel\ consumed\ for\ Harvesting\ \left(\frac{L}{tonne}\right) = \frac{Equipment\ fuel\ economy\ \left(\frac{L}{ha}\right)}{Harvesting\ yield\ \left(\frac{tonnes}{ha}\right)} \quad (3.1)$$

For harvesting larger quantities of WH, an amphibious excavator or a weed harvester is required. The fuel economy of the harvester is 12 km/L with a 2.5 m harvesting width. The growth density of WH is 8 kg/m^2 on average [59].

Calculations for energy consumption for the feedstock crushing process are carried out using equation 3.2.

$$Electricity\ for\ crushing\ \left(\frac{MJ}{tonne}\right) = \frac{Power\ rating\ of\ Crusher\ (kWh)\ \times 3.6}{Crushing\ capacity\ (tonnes)} \quad (3.2)$$

First, harvested WH is washed to remove mud and soil near the harvesting lake and left to partially dry (40% moisture content) before transporting to the bioethanol production facility. Once the feedstock is in the factory, to avoid inhibitors and further remove impurities and minerals or any toxins that can potentially interfere with the process, it is spray washed from the recycled water from the process. Then, as suggested in the published literature, WH is left to sundry until it reaches 35% moisture level to remove further any absorbed eutrophic water from the plant [60].

There are two transport mediums used for raw material transportation. All the necessary imported chemicals use nautical transportation, and from the port to the factory, a transportation truck. For inland transportation, trucks with 4.5 fuel economy and 10 tonnes capacity are selected. The distance between the WH harvesting location and the factory, the distance from the port to the factory, and the distance of transportation for wood chips are considered as 50 km, 200 km and 20 km.

Calculations for diesel consumption in nautical transportation will be calculated using equation 3.3.

$$E_{nautical}\ (MJ) =\ 6000\ (km)\ \times 0.08\ \left(\frac{MJ}{tonne.km}\right) \times material\ ammount\ (tonn \quad (3.3)$$

Calculations for diesel consumption in transportation will be calculated using equation 3.4.

$$Diesel\ volume\ (L) = \frac{Distance\ (km) \times Material\ amount\ (tonne)}{Truck\ fuel\ economy\ \left(\frac{km}{L}\right) \times Truck\ capacity\ (tonne)} \tag{3.4}$$

3.3.2 Process simulation-based inventory data calculations

This study uses Aspen Plus process simulation software: 1. To obtain ethanol distillation and dehydration properties, 2. To simulate the bioethanol production process. The Aspen plus property database is used to obtain the ethanol-water binary properties in the distillation unit process and ethanol-water-ethylene glycol ternary properties in the dehydration unit process. In the Aspen Plus simulation tool, Non-Random Two Liquid (NRTL), an activity coefficient model is used as the thermodynamic property method to model the chemical thermodynamics of the ethanol/water mixture in the liquid phase. The RadFrac Rigorous distillation column model can be used for distillation column modelling in the Aspen Plus software tool, and the R-Stoic reactor model can be used for conversion reactors. Other process equipment in the scaled-up bioethanol production process can be simulated using the relevant equipment models available in the Aspen Equipment model library. The energy consumption of each unit process and mass flow data in the bioethanol production process are determined from the results obtained from process simulations.

Further, ethanol-water binary properties, ethanol-water-ethylene glycol and ethanol-water-cyclohexane ternary properties in the distillation and dehydration unit processes, respectively, were obtained from the Aspen Plus database. For the dehydration of bioethanol, the thermal property method UNIQ-RK was used as the thermal property method. This part of the simulation was simulated separately based on the data obtained from the conversion stage.

3.4 Scenario description

Based on the data obtained from previous studies, process conditions were selected, and four process routes with combinations of two feedstock pretreatment methods (i.e., alkali pretreatment and diluted acid pretreatment) and two bioethanol dehydration techniques (i.e., azeotropic distillation and extractive distillation) are studied, separately, and compared each other to assess the most energy efficient process route to apply for the life cycle and further studies. For clear identification, the four scenarios of the bioethanol production process from WH are abbreviated as WH1, WH2, WH3, and WH4 as follows.

- WH1 - Alkaline pretreatment with NaOH + extractive dehydration
- WH2 - Alkaline pretreatment with NaOH + azeotropic dehydration
- WH3 - Acid pretreatment with H_2SO_4 + extractive dehydration
- WH4 - Acid pretreatment with H_2SO_4 + azeotropic dehydration

To minimise variables for mass flow and energy comparisons, literature-based process conditions for alkaline pretreatment and dilute acid pretreatment similar process conditions are selected. Figure 3.5 depicts the fuel-grade bioethanol production process from WH. Table 3.1 shows the conditions used for process simulations for bioethanol production from WH.

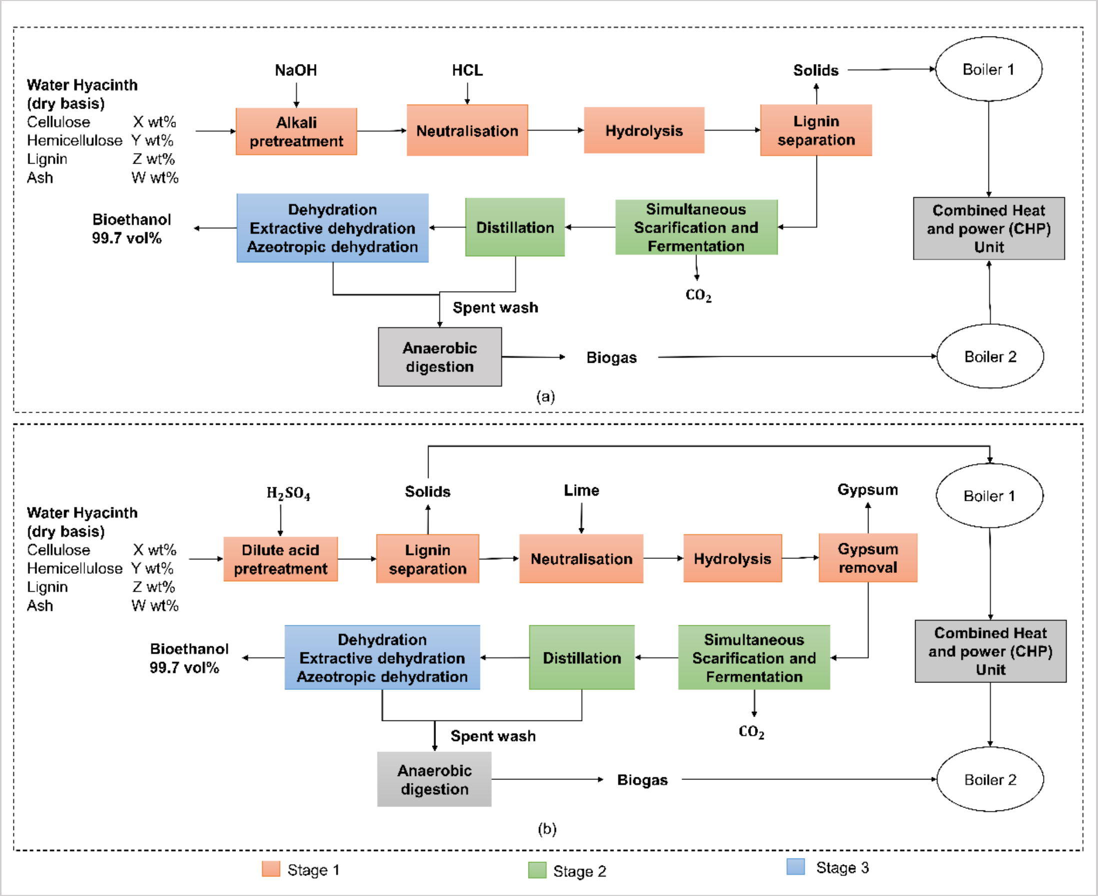


Figure 3.5: Diagram of process system boundary: (a). Bioethanol conversion from WH via alkali pretreatment, (b). Bioethanol conversion from WH via dilute acid pretreatment

At the bioethanol conversion stage, WH feedstock in scenarios WH1 and WH2 pre-treated with the alkaline pretreatment method. The mixing tank is loaded with WH having a solid loading of 10% (w/v) and 2% (w/v) sodium hydroxide (NaOH) as the alkaline agent at 121 °C for 40 mins to delignify before enzymatic hydrolysis to optimise cellulose and hemicellulose recovery [39]. To maintain the suggested temperature, steam at 200 °C and 5 bar was given to the pretreatment reactor. For scenarios, WH3 and WH4, WH is pre-treated with diluted H_2SO_4 under the same conditions [39]. Once the substrate is treated, the broth is cooled down and hydrolysed with cellulase and xylanase after regulating pH to 4.8. Next, the process was replicated for acid pretreatment [45][35].

During enzymatic hydrolysis at 50 °C for 72 h, cellulose and hemicellulose obtained from two pretreatment methods are converted into reducing sugars. Based on the published studies, 1 kg of cellulose gives 1.1 kg of glucose [61]. It was also found that a total reducing sugar content of 13.5 g/l can be gained by *A.niger* after 72 h of incubation [39]. During the process, 42.64% of hemicellulose was able to recover, resulting in a total of 40.50 kg of xylose and glucose.

The alkali pretreatment process gives access to cellulose and hemicellulose to hydrolyse after delignification. The mass flow analysis shows 99% of cellulose and 43% of hemicellulose recovery during the alkali treatment process. On the other hand, the dilute acid pretreatment hydrolyses (acid hydrolysis) cellulose and hemicellulose while delignifying exposing more cellulose and hemicellulose for enzymatic hydrolysis, giving a total recovery of 97% cellulose and 44% hemicellulose.

Gained reducing sugars were then converted to ethanol by SSF using a coculture of *S.cerevisiae* and *S.stipites* to 1:1 ratio at 28 °C for better fermentation and fewer inhibitor products.

Table 3.1: Process conditions for pretreatment and conversion stages

Process operation	Chemicals Used	Process conditions	Reactions	Reference
Pretreatment				
Alkaline pretreatment	NaOH	Solid loading 10% (w/v) 121 ºC; 40 min		[39]
Neutralisation	HCl		$NaOH + HCl \rightarrow NaCl + H_2O$	
Dilute acid pretreatment	H_2SO_4	Solid loading 10% (w/v) 121 ºC; 40 min		[35]
Neutralisation	$Ca(OH)_2$		$H_2SO_4(aq) + Ca(OH)_2(aq) \rightarrow CaSO_4 \cdot 2H_2O(s)$	
Enzymatic hydrolysis	Cellulase and Xylanase	50 ºC, 4.8 pH; 72 h	$C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6$ $C_5H_8O_4 + H_2O \rightarrow C_5H_{10}O_5$	
Bioethanol conversion				
Simultaneous saccharification and fermentation (SSF)	Yeast and nutrients	28 ºC, 1 atm for 36 h	$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$ $3C_5H_{10}O_5 \rightarrow 5C_2H_5OH + 5CO_2$	[62]

In the bioethanol purification stage, the fermented bioethanol solution from SSF is purified using distillation up to 91 wt%. The distillate was finally dehydrated using extractive or azeotropic dehydration techniques, depending on the scenario, to achieve the required purity of 99.7 vol%. Table 3.2: Distillation column design specifications for the four scenarios. Table 3.2 expresses design specs for distillation columns for the four scenarios.

Table 3.2: Distillation column design specifications for the four scenarios

Scenario	Dehydration column	Recovery column
WH1	Number of stages: 15 Reflux ratio: 0.5	Number of stages: 1 Reflux ratio: 0.5
WH2	Number of stages: 30 Reflux ratio: 1	Number of stages: 20 Reflux ratio: 0.9
WH3	Number of stages: 15 Reflux ratio: 0.6	Number of stages: 12 Reflux ratio: 0.5
WH4	Number of stages: 30 Reflux ratio: 1	Number of stages: 20 Reflux ratio: 0.9

3.3.1 Energy supply for bioethanol plant

The energy requirement for the simulated plant is considered to be supplied by a combination of heat generated in the in-situ heat and power (CHP) unit and electricity from the national grid. The entirety of electricity generated in the CHP unit is credited to the national power grid. Fuel for the CHP unit is fulfilled biogas from anaerobic digestion, lignin-rich dried solid residue and wood chips. Biogas and solid fuels are considered to be burned in two separate boilers.

The amount of biogas produced during four scenarios is calculated using equation 3.5, where wastewater volume is obtained from simulation results while COD (Chemical Oxygen demand) is calculated based on the composition of the effluent of the bioethanol purification unit. B_0, the maximum CH_4 production capacity and MCF, methane conversion factor was taken from literature, based on industrial standards suitable for a bioethanol plant [63].

$$Methane\ amount\ (m^3) = Waste\ water\ volume \times COD \times B_0 \times MCF \tag{3.5}$$

$$CH_4 = \text{wastewater volume} \times \mathrm{COD} \times 0.25 \times 0.8$$

Wastewater is treated by up-flow anaerobic sludge blanket (UASB) reactors. It is one of the core methods identified in the industry as an advanced technology for wastewater treatment for environmental protection. It has the potential to leave less sludge and less CO_2 release while giving more methane [64]. Furthermore, in terms of suitability, UASB is recommended for incidences where the wastewater has more than 1,500 mg/L of COD. Since the plant wastewater outlet surpasses the minimum COD stranded with the richness of cellulose, hemicellulose, and unrecovered bioethanol from the purification, for better output UASB is suitable for wastewater treatment. Moreover, it requires a low energy demand and simple technology to adapt, occupying less reactor volume and releasing high-grade energy as biogas [64].

When the in-situ fuel sources are insufficient to supply the required process heat energy in each process scenario, biomass (wood chips, wood residues, etc.) from external resources is utilised as additional fuel for heat energy generation.

The efficiencies of the two boilers (solid burner and gas burner) are mentioned in Table 3.3

Table 3.3: average heating values of fuel and efficiencies of the CHP unit [18]

Fuel Type	**Average heating value**	**Combined Heat and Power (CHP) efficiencies**		
		Boiler	**Electricity generation**	**Overall CHP**
Biogas (65% CH4)	22.4	0.9	0.35	0.8
Lignin	19	0.8	0.13	0.7
Wood chips	14	0.8	0.13	0.7

3.5 Scenario-based mass and energy flow analysis

Mass and energy flows of the bioethanol production process scenarios are evaluated based on the obtained process simulation results, and mass flow analysis and energy flow analysis are performed. The study further evaluates the process net energy ratio and the renewability factor of the process to understand the sustainability of the selected process scenarios.

A sensitivity analysis for the bioethanol yield and the total process energy consumption is performed in this study by varying five sensitivity parameters, i.e., lignin content in WH, cellulose content in WH, the ratio for solid loading, pretreatment efficiency (cellulose/hemicellulose recovery efficiency), and fermentation efficiency. For this sensitivity analysis, the set system boundary is the production stage which consists of pre-treatment, bioethanol conversion, distillation, and dehydration. The variation ranges of the sensitivity parameters are determined based on lab-scale data for bioethanol synthesis from WH, reported in the published literature. Table 3.4 indicates the five sensitivity parameters and their variation ranges considered in the study.

Table 3.4: Key parameter variations range for process sensitivity analysis

Sensitivity parameter	Initial value used in this study	Variation range	Reference
Lignin percentage in WH (wt%)	4.8%	3 – 14%	[35][65]
Cellulose percentage in WH (wt%)	19.2%	18 – 55%	[65][38]
Solid loading (biomass: water)	1:10	1:3 – 1:15	[66]
Pretreatment process efficiency (%)	Cellulose: 99 Hemicellulose: 57	Cellulose: ±5% Hemicellulose: ±5%	[67]
Fermentation efficiency (%)	Glucose: 90 Xylose: 80	Glucose: ±5% Xylose: ±5%	[67]

3.6 Life Cycle Impact Assessment

3.6.1 Net Energy Analysis

The energy flow balance and net energy analysis are carried out by analysing the energy input and output flows evaluated in inventory data analysis. The key energy performance indicators, such as Net Energy Value (NEV), Net Renewable Energy Value (NRnEV), Net Energy Ratio (NER), and Renewability (Rn), are calculated as the results of net energy analysis [58]. Equations 3.4 to 3.7 list the equations to calculate the net energy indicators, respectively.

$$NEV = \text{total net energy outputs} - \text{total net energy inputs} \tag{3.6}$$

$$NRnEV = \text{total net energy outputs} - \text{total fossil energy inputs} \tag{3.7}$$

$$NER = \text{net energy outputs}/\text{net energy inputs} \tag{3.8}$$

$$Renewability = \text{net bioenergy outputs}/\text{net fossil energy inputs} \tag{3.9}$$

3.6.2 Global Warming Potential (GWP)

GWP indicates the total GHG emissions of a process accumulated over the course of the life cycle. The GWP is calculated using equation 3.10, where GWP_i is the GWP of substance I and m_i is the emitted amount of substance i.

The greenhouse gas protocol method with climate change factors from IPCC 2021 sixth assessment report (AR6) for a 100-year time horizon is adopted to calculate the GWP for the bioethanol process to produce 1 m^3 of fuel-grade bioethanol from WH. The CO_2 equivalent characterisation is done by multiplying with their characterisation factors for the GWP of 29.8 for CH_4 (fossil-based), 27 for CH_4 (non-fossil based) and 273 for N_2O. The same climate change factors are used is the Global Recipe Midpoint (H) method.

$$GWP = \sum GWP_i \times m_i \tag{3.10}$$

3.6.3 Life Cycle Environmental Impact Assessment

The life cycle environmental impacts, such as global warming, acidification, ecotoxicity, eutrophication, resource depletion, etc., are evaluated for the analysed bioethanol production process life cycle. As the initial step, impact categories are separately calculated for the life cycle inventory which is called impact characterisation [68]. The impact can be calculated either as mid-point or end-point characterisation. For lower uncertainty of the LCA results, mid-point characterisation is performed for the life cycle environmental impact assessment in this study. The impact characterisation is performed using the ReCiPe midpoint (H) V1.12 impact assessment method in the SimaPro version 9.5 LCA software. To carry out a comprehensive environmental impact, there are eighteen midpoint indicators (Particular matter, Ozon formation (human health), ionising radiation, Ozon depletion, human toxicity (carcinogenic), human toxicity (non-carcinogenic), global warming, water use, freshwater ecotoxicity, freshwater eutrophication, Ozon formation (terrestrial ecosystem), terrestrial ecotoxicity, terrestrial acidification, land use/transformation, marine ecotoxicity, marine eutrophication, mineral resources, fossil resources). Based on the output from SimaPro software, the impact categories with the most significant impact values are selected for interpretation of the results.

3.7 Interpretation of LCA Results

3.7.1 Sensitivity analysis

In this study, sensitivity analysis was carried out for two boundaries, 1) considering only the bioethanol production process and 2) the cradle-to-gate life cycle. The first sensitivity analysis was conducted as part of the mass and energy analysis of the process and discussed in section 4.1.2.

LCA conducted based on process simulation can give an unbiased sensitivity analysis regardless of the number of scenarios and process methods. When considering multiple scenarios, the inventory data variations can be complex. However, process simulation allows these bottlenecks to be bypassed, giving results in an efficient, timely manner and giving the platform to crosscheck accuracy. This study performs a life cycle sensitivity analysis for the base case by varying three key parameters; process energy consumption (MJ/FU), bioethanol yield (kg/tonne-WH), and solid loading (dry biomass (kg): water (L). The parameters and their sensitivity range are determined based on previous studies [69][66]. The effects of these parameters on prominent indicators, net energy ratio, renewability factor, GWP, Human non-carcinogenic toxicity, marine ecotoxicity, and freshwater ecotoxicity are discussed. Table 3.5 indicates the three sensitivity parameters and their variation range considered in this study.

Table 3.5: Key parameter variations for life cycle sensitivity analysis

Sensitivity parameter	**Base case value**	**Variation range**
Process energy consumption (MJ/FU)	45,310	±20%
bioethanol yield (dry basis) (kg/tonne-WH)	202	184-355
Solid loading	1:10	1:3-1:10

Chapter 4

Results and discussion

4.1 Process Simulation Results and Analysis

4.1.1 Process mass flow analysis

Figures 4.1 – 4.4 show the simulated process flow diagrams that embody a scaled-up bioethanol plant to have an output of 1 m^3 of at 99.7 vol% purity. Flowsheets include overall process schematics and mass flow results from the process simulations conducted in Aspen Plus, simulation software for scenarios WH1, WH2, WH3, and WH4, respectively. According to simulation results, the bioethanol yield for scenarios WH1 and WH2 is 254.45 L/tonne-WH (dry basis). For scenarios WH3 and WH4, the yield is 209.65 L/tonne-WH (dry basis), which suggests a requirement of 3.96 and 4.82 tonnes of dry WH to produce 1 m^3 of bioethanol at 99.7 vol%. Based on the obtained yield, it is evident an additional amount of 863 kg of dry WH is required to produce 1 m^3 of fuel-grade bioethanol in a biorefinery that valorises WH via dilute acid pretreatment. This shows that the bioethanol yield depends on the pretreatment method. Results also show that alkaline pretreatment suits better for WH for the delignification. In terms of the suitability of WH as a viable feedstock for bioethanol production, the simulation-based mass flow results are comparable with other aquatic plants and lignocellulosic feedstocks.

Furthermore, the obtained yield falls within the range of results of other studies that have concluded bioethanol yield on a lab scale using WH as the source of cellulose. Bioethanol yields from previous studies are summarised in Table 4.1 for comparison purposes. Table 4.2 summarises process mass flow results, including all the additional chemicals required to produce 1 m^3 of bioethanol.

Table 4.1: Bioethanol yield from other lignocellulosic biomasses

Feedstock	Yield (L/ tonne biomass)	Reference
Rice Straw	239	[70]
Corn stover	300	[71]
Wheat straw	330	[72]
Switchgrass	318	[73]
Softwood forest residues	248	[74]
Hardwood chips	250	[75]
WH (WH1, WH2)	254	This study
WH (WH3, WH4)	209	This study
WH	0.12-0.35 kg/kg-WH	[39][76][60][77]
WH	0.201 kg/kg-WH	This study
Duck weed	0.218 kg/kg-WH	[78]
Common reed	0.165 kg/kg-WH	[79]
Water lettuce	0.215 kg/kg-WH	[80]

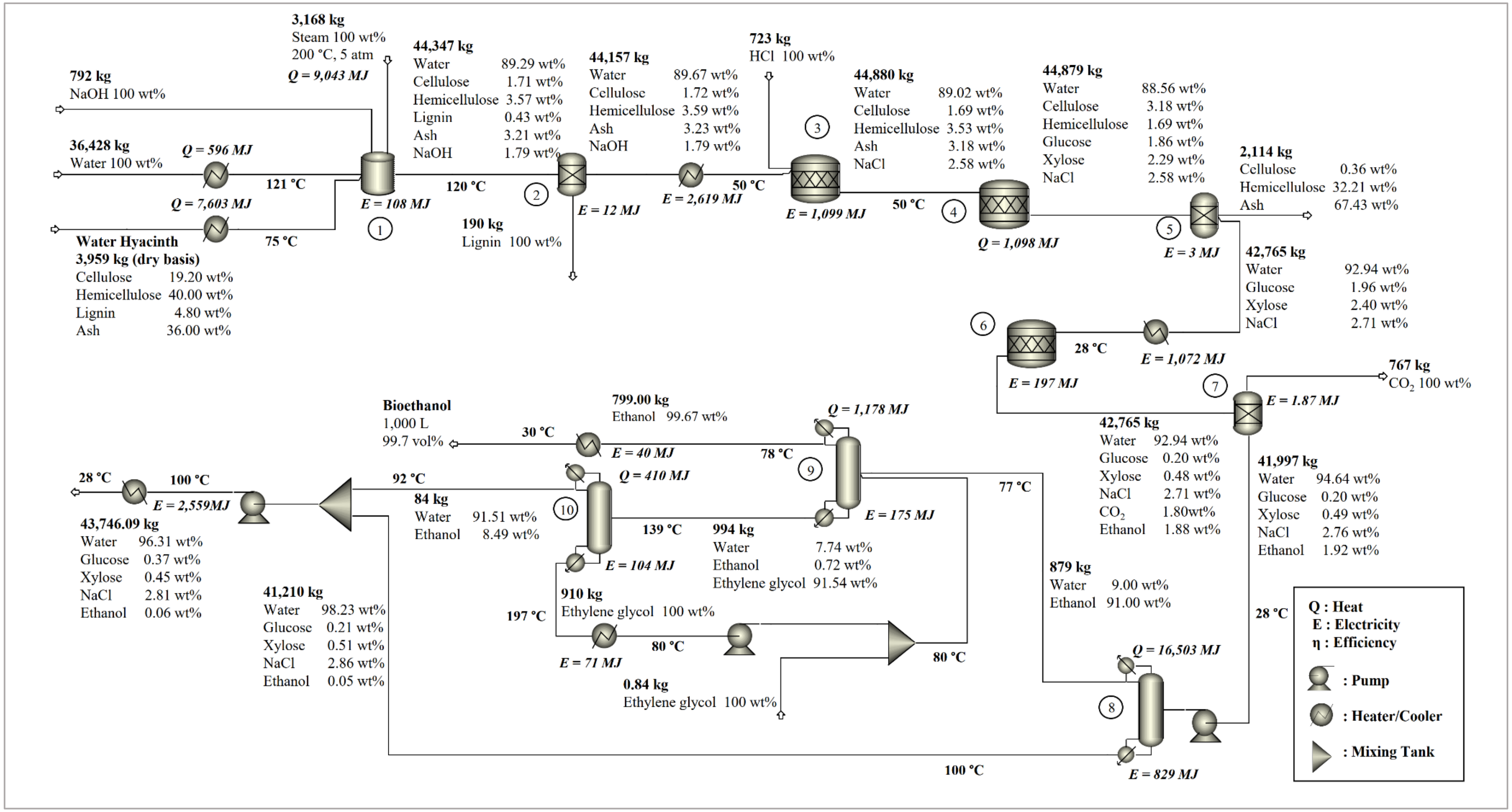


Figure 4.1: Simulated process diagram – Scenario WH1. Where, **1**: Mixing tank, **2**: Nutsche filter, **3**: Neutralising tank, **4:** Hydrolysing unit, **5:** Filter press, **6:** SSF, **7:** Scrubber, **8:** Distillation column, **9:** Dehydration column, **10:** Recovery column

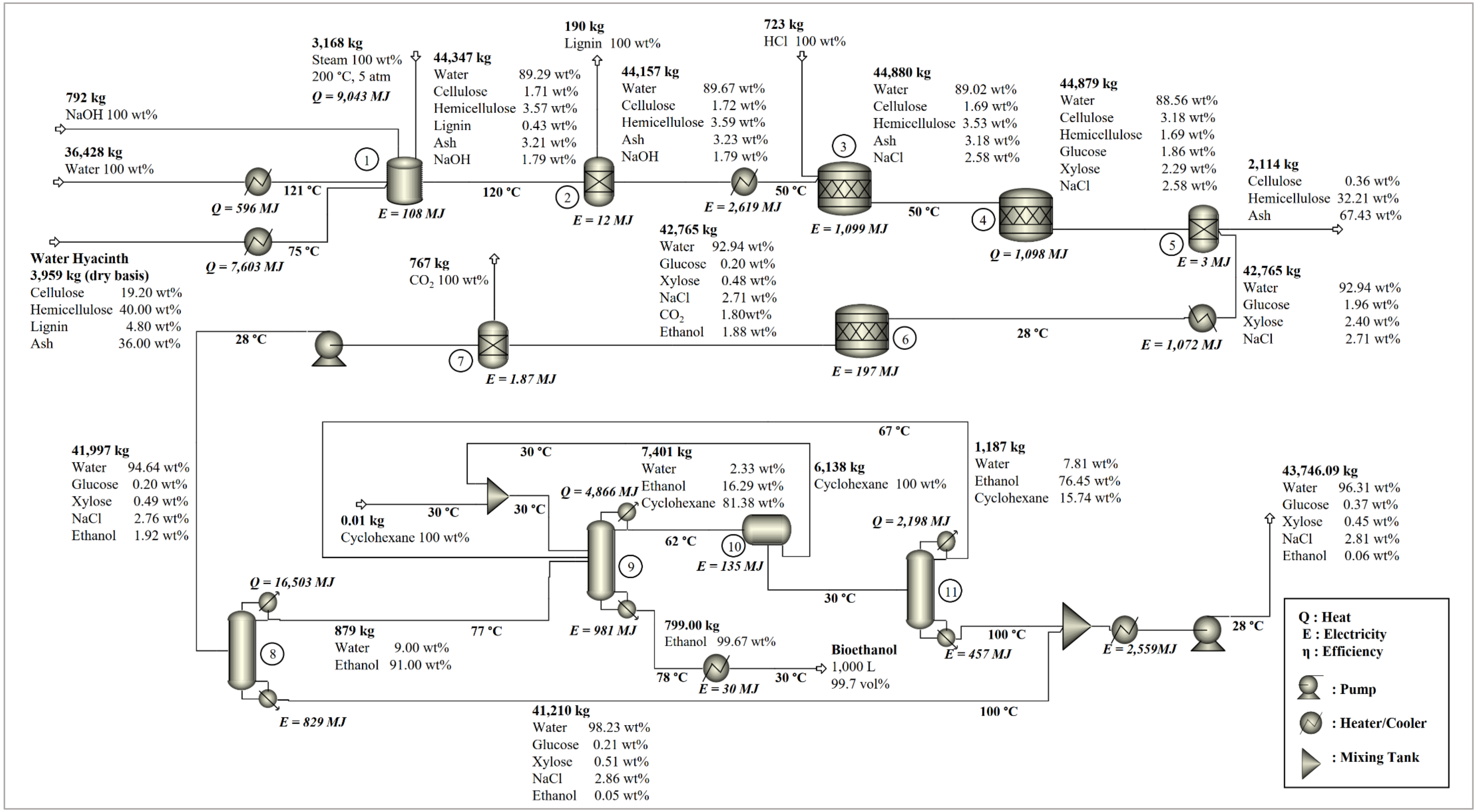


Figure 4.2: Simulated process diagram – Scenario WH2. Where, **1**: Mixing tank, **2**: Nutsche filter, **3**: Neutralising tank, **4:** Hydrolysing unit, **5:** Filter press, **6:** SSF, **7:** Scrubber, **8:** Distillation column, **9:** Dehydration column, **10:** Decanter **11:** Recovery column

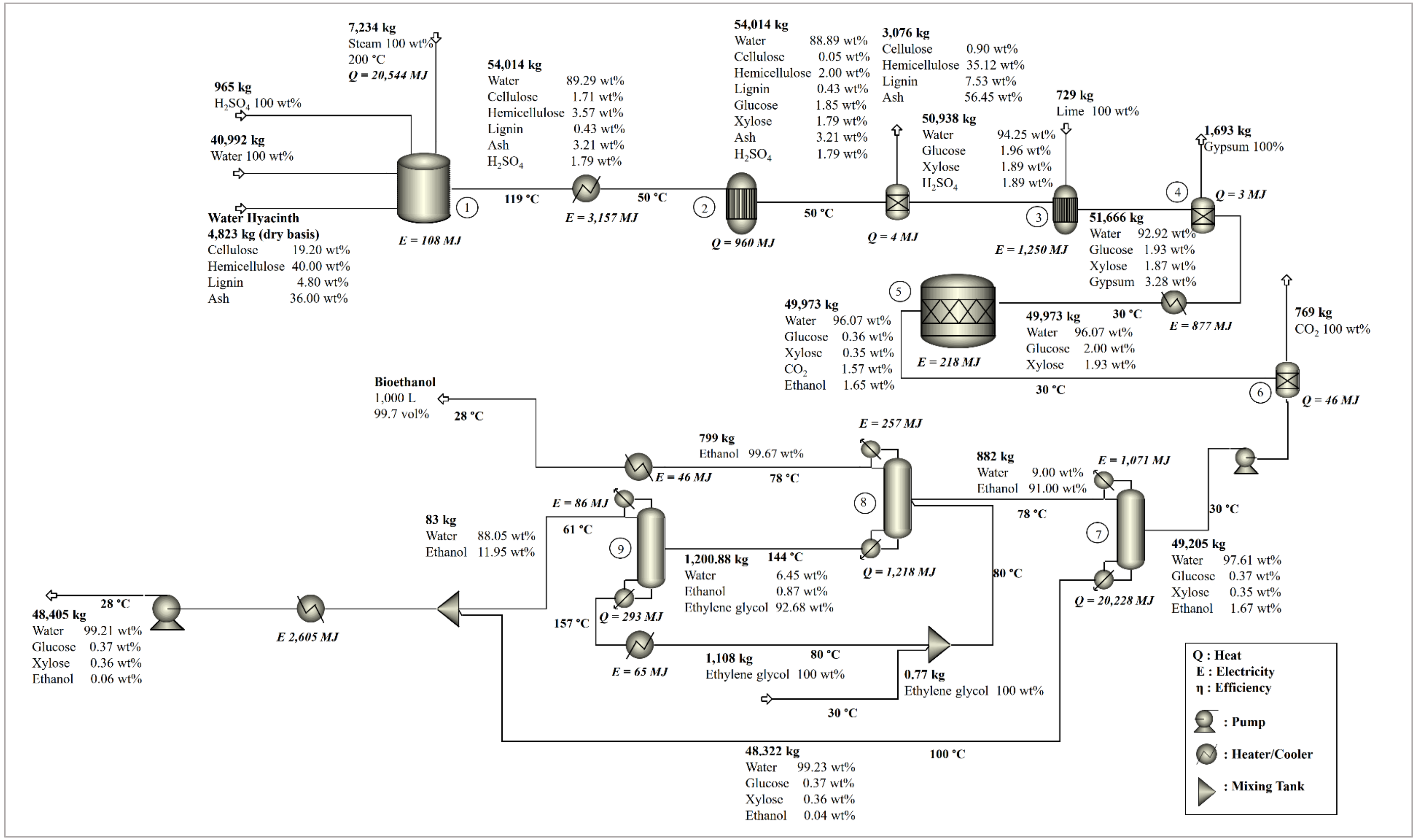


Figure 4.3: Simulated process diagram – Scenario WH3. Where, **1**: Mixing tank, **2**: Hydrolysing unit, **3**: Neutralising tank, **4:** Gypsum removing unit **5:** SSF, **6:** Scrubber, **7:** Distillation column,**8:** Dehydration column, **9:** Recovery column

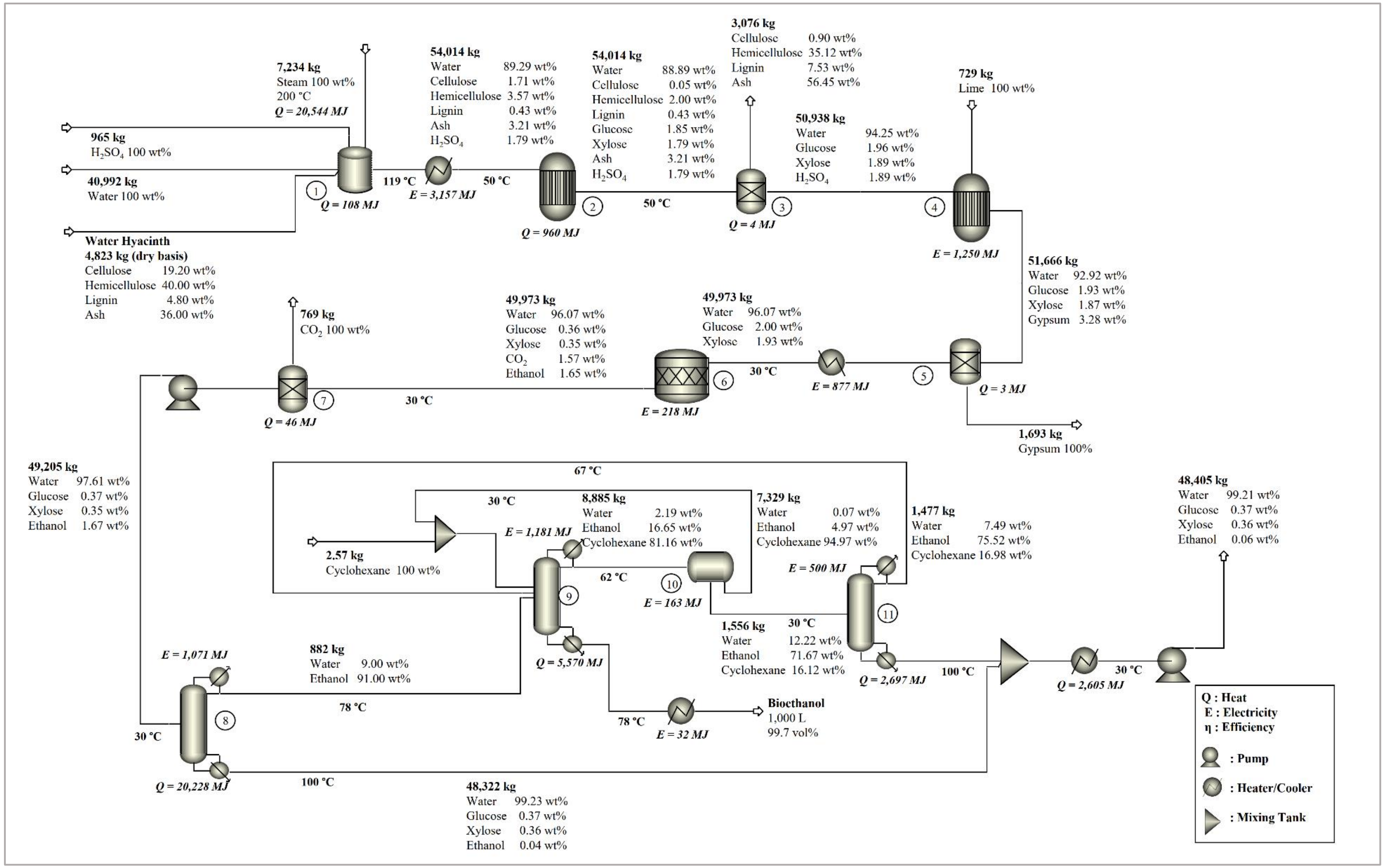


Figure 4.4: Simulated process diagram – Scenario WH4. Where, **1**: Mixing tank, **2**: Hydrolysing unit, **3**: Filter press, **4:** Neutralising tank,**5:** Gypsum removing unit, **6:** SSF, **7:** Scrubber, **8:** Distillation column, **9:** Dehydration column, **10:** Decanter **11:** Recovery column

Table 4.2: Raw material consumption for WH1 – WH4 scenarios

Inventory	Mass flow (kg/FU)			
	WH1	**WH2**	**WH3**	**WH4**
Feedstock preparation				
Harvested WH	59,541.93	59,541.93	72,520.86	72,520.86
Bioethanol conversion				
WH (dry basis)	3,959.54	3,959.54	4,822.64	4,822.64
Water	39,595.39	39,595.39	48,226.37	48,226.37
NaOH	791.91	791.91		
H_2SO_4		-	964.53	964.53
Enzyme	23.17		23.17	-
HCl	722.66	722.66		
Lime		-	728.65	728.65
Yeast	9.75	9.75	9.75	9.75
$(NH_4)_2HPO_4$	9.48	9.40	10	9.88
$CaCl_2$	210.26	210.26	242.12	239.16
Bioethanol purification				
Cyclohexane		2.55		2.57
Ethylene Glycol	0.84		0.77	

Once the process was simulated as per the efficiencies based on previous studies, results show that the process utilises 791.9 kg/FU of NaOH to alkaline the medium for the expected bioethanol output. NaOH reacts with ester links in WH solubilising lignin, creating black liquor [81]. Delignification of WH opens the possibility of obtaining convertible sugars approximately at 0.470 kg/kg-WH. In contrast, sulfuric acid consumption for dilute acid pretreatment is observed as 964.53 kg/FU giving a reduced sugar yield of 0.407 kg/kg-WH. Therefore, comparatively, an alkaline substrate gives 21.8% more recovery of cellulose and hemicellulose compared with a substrate with H_2SO_4. In both pretreatment methods, cellulose recovery was higher compared with hemicellulose recovery. During these two pretreatment methods, while NaOH converts into NaCl, H_2SO_4 converts into gypsum. This gypsum is a usable byproduct that can be utilised as a fertiliser or in construction applications.

The recoverable gypsum mass as a by-product of bioethanol production is 1,693 kg/FU.

By the end of fermentation, the beer feed entering the distillation column has 1.92 wt% for WH1 and WH2 and 1.64 wt% for WH3 and WH4 of ethanol. Fermented ethanol is purified to 91% mass purity with 99% recovery using distillation columns. Subsequently, the aqueous ethanol mixture is dehydrated using either extractive distillation or azeotropic distillation methods to achieve anhydrous bioethanol at > 99.5 vol% purity for commercial fuel purposes. The volume purity of the final product is 99.7%. In the use of both of the dehydration techniques, the efficiency of recovery of columns is considered as 99% in this study. Since the recovery is considered as 99% with given specifications, dehydration can be ruled out as an influencing factor for the bioethanol yield. Hence, as per the mass flow results, bioethanol yield solely depends on stage 1 of the process. Spent wash generation was observed as 41,200 L/FU, where this carbon-enriched effluent stream is directed to anaerobic digestion tanks.

4.1.2 Process energy analysis

Table 4.3 shows the process simulation-based energy consumption results for scenarios WH1 – WH4 indicating segregated steam and electricity requirements to function in the scaled-up model process plant. Total energy consumption values for the four scenarios are 45,310.93 MJ, 51,99.82 MJ, 53,530.92.75 MJ, and 60,211.49 MJ per 1 m^3 of fuel-grade bioethanol, respectively. Upon process simulation results analysis, it is evident that the conversion stage consumes most of the energy regardless of the pretreatment method in the plant. Figure 4.5 shows the breakdown of energy consumption for the defined scenarios with the respective energy, including the percentage distribution. As per the simulation results, the alkaline pretreatment process consumes 23,440.69 MJ/FU compared with 27,161.76 MJ/FU, the energy consumed for the dilute acid pretreatment process. The percentage difference between alkaline pretreatment and dilute acid is 16% against alkaline pretreatment. The energy consumptions for the pretreatment stage reflect 51.73% of the total energy consumption for scenario WH1, WH2 - 45.08%, WH3 - 51.21%, and WH4 - 44.37%. The reason for WH2 and WH4 to have a relatively low distribution for pretreatment is that the azeotropic dehydration technique consumes more energy compared with extractive distillation for the FU. The energy difference between the two analysed dehydration techniques is 148% on average. Moreover, these results reflect previous comparative studies for dehydration methods in terms of energy usage [53]. Hence, based on the achieved data, extractive distillation is a better dehydration technique in terms of energy consumption.

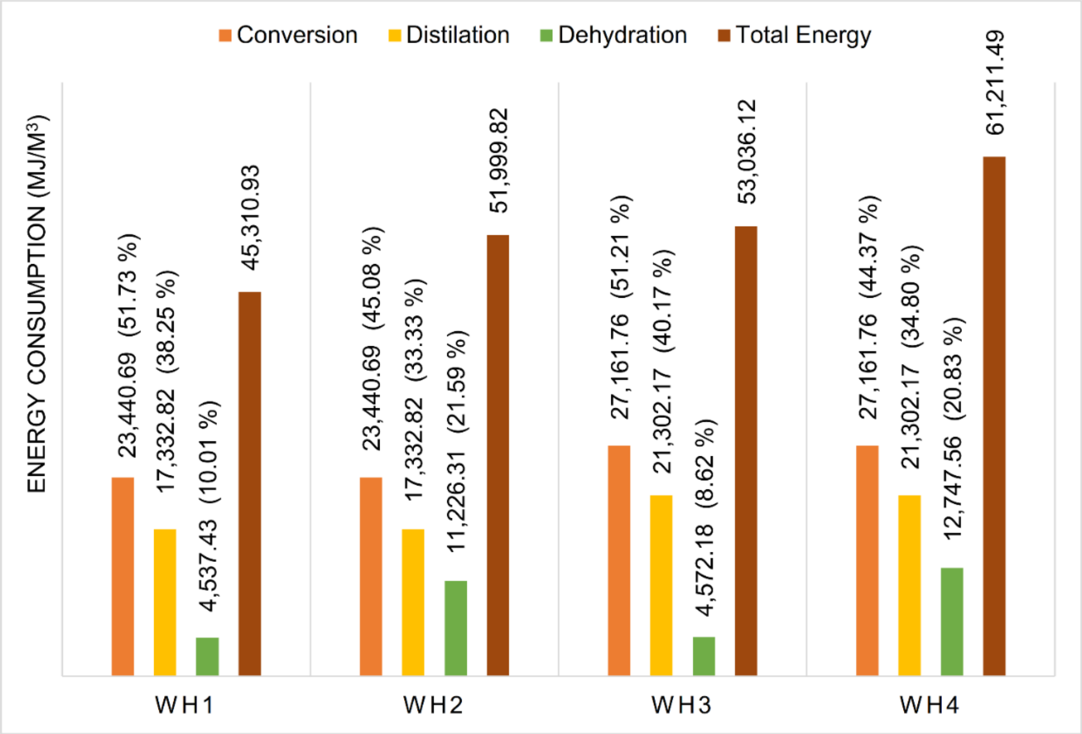


Figure 4.5: Stagewise energy consumption for WH1 – WH4 scenarios

Despite the scenario, the designed bioethanol plant consumes steam the most and percentage-wise, the steam demand remains at 81 ± 1% of the total energy requirement.

Table 4.3: Energy consumption results for individual plant equipment for WH1 – WH4 scenarios (MJ/FU)

Unit	**WH1**		**WH2**		**WH3**		**WH4**	
	Steam	**Electricity**	**Steam**	**Electricity**	**Steam**	**Electricity**	**Steam**	**Electricity**
Pretreatment reactor	17,242.10	108.00	17,242.10	108.00	20,544.22	108.00	20,652.22	
Nutch filter		12.00		12.00				
Neutralising tank		1,098.53		1,098.95		1,250.45		1,250.45
Hydrolysis rector	1,098.53		1,098.53		960.19		960.19	
Residual solids removal		3.00		3.00		4.00		4.00
Gypsum removal						3.00		3.00
SSF		197.20		197.20		218.38		218.38
CO_2 scrubber		1.87		1.87		45.00		45.00
Distillation column	16,503.16	828.63	16,503.16	828.63	20,227.88	1,070.69	20,227.88	1,070.69
Dehydration column	1,178.04	174.62	4,865.56	981.39	1,218.34	257.27	5,570.15	1,180.57
Recovery column	410.01	103.86	2,198.73	456.82	292.73	86.47	2,696.96	499.66
Decanter				135.04				162.86
Other Utilities		6,351.38		6,268.82	5.00	6,744.49	5.00	6,664.49
Total	36,431.85	8,879.09	41,908.09	10,091.73	43,248.36	9,787.76	50,112.39	11,099.10
Total Energy	**45,310.93**		**51,999.82**		**53,036.12**		**61,211.49**	

Figure 4.6 shows the change in the process net energy ratio and the renewability factor amongst the four scenarios. To be a viable alternative for non-renewable energy sources, biofuel would have to provide a net energy gain. Results show the process energy ratio less than 1 for all four scenarios. However, the renewability factor is promising and remains more than 5 for all cases.

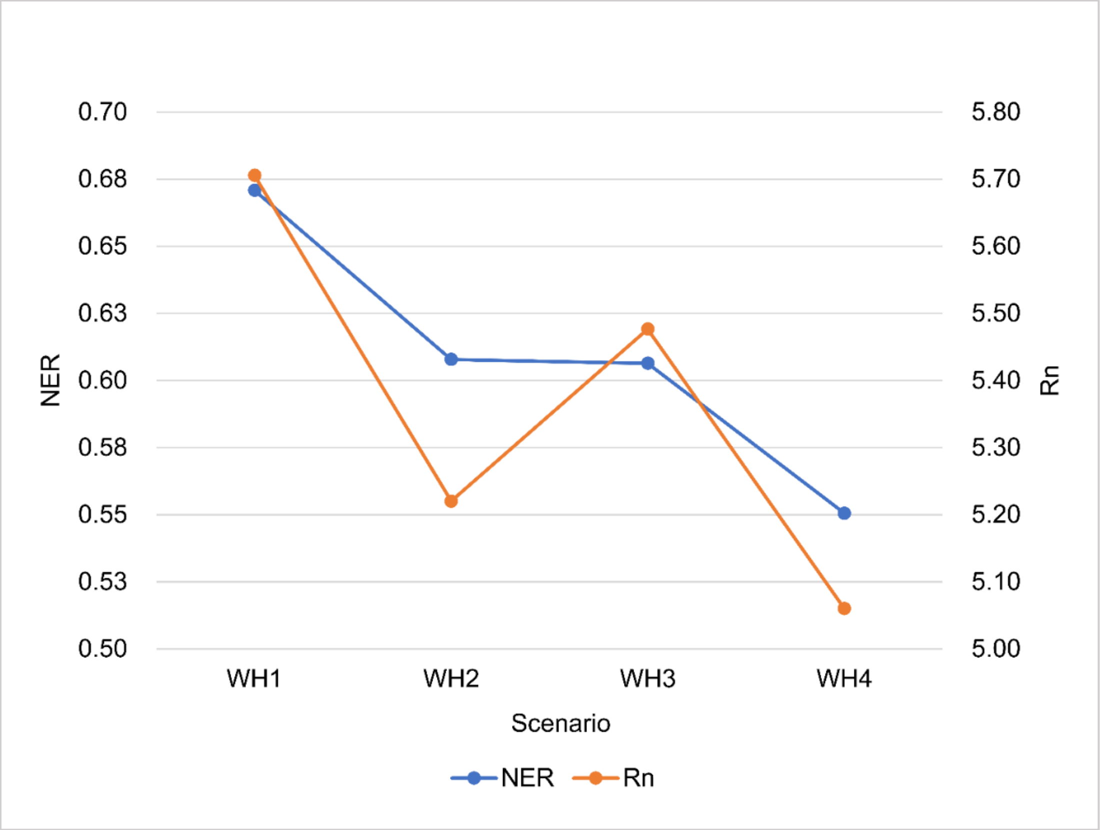


Figure 4.6: Results for process NER and Rn indicator for WH1 – WH4 scenarios

Based on these results, for further investigations and to perform the LCA scenario, WH1 is chosen. Figure 4.7 shows the steam and heat flow diagram within the process for scenario WH1. As seen in figure 4.7, the percentage for stage 1 within the plant, which is pretreatment utilises 52% of the energy uptake. The lowest energy consumption is observed during the dehydration to achieve the required purity for fuel-grade bioethanol. The designed bioethanol plant mostly consumes steam. The rest is only 20% which is direct electricity. As shown in the chart, 36,432 MJ/FU of steam input gets distributed among the three stages as 40%, 36%, and 4%. The 8,879 MJ of electricity gets distributed as 11%, 2%, and 7%.

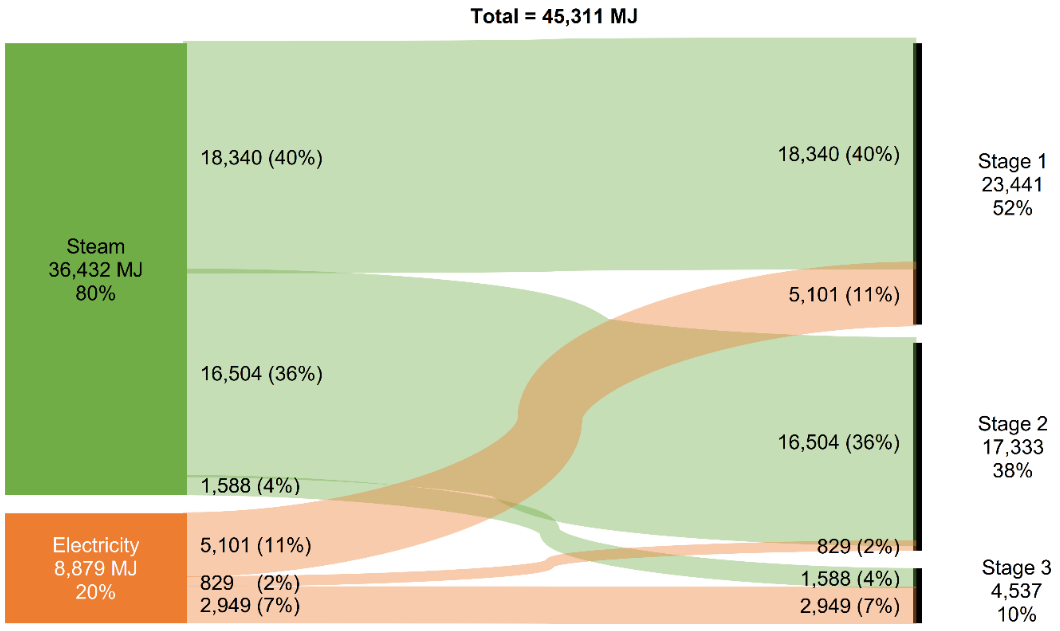


Figure 4.7: Energy flow for WH1 scenario

The supply of steam is fully supplied by the in-situ CHP unit. Fuel requirement for the CHP unit is predominantly fulfilled by lignin-rich solid residues and biogas from the wastewater treatment tank. Lignin-rich solid residue contributes more to the energy requirement by providing 30,644.99 MJ/FU, whilst 3,587.67 MJ/FU is gained by burning biogas. Since the energy supply via waste is not sufficient, wood chips are used as an additional source of fuel to accommodate the steam deficit. After factoring in the efficiencies of the boilers and CHP unit, the energy flows for steam and electricity generation are shown in Table 4.4.

The total process energy consumption by WH as a bioethanol feedstock is higher than most of the other lignocellulosic feedstocks in the reviewed publications. In summary of existing studies, 25,520 MJ/FU for wood [65], 25,500 MJ/FU for switchgrass [65], 22,050 MJ/FU for tall fescue [20] and 29,800 MJ/FU for rice straw [66] for a bioethanol production facility can be mentioned. However, a study conducted on corn stover concluded an energy consumption of 41,280 MJ/FU, which is comparable to the WH of this study.

Table 4.4: Energy flow analysis results

	WH1		**WH2**		**WH3**		**WH4**	
	Steam	**Electricity**	**Steam**	**Electricity**	**Steam**	**Electricity**	**Steam**	**Electricity**
CHP unit output								
Biogas	1,614.45	1,255.68	1,545.61	1,202.14	1,996.22	1,552.61	1,941.65	1,510.17
Lignin and solid residues	24,953.78	5,691.21	24,953.78	5,691.21	33,309.67	7,596.94	33,309.67	7,596.94
Wood chips	9,863.68	2,249.61	15,408.58	3,514.24	7,942.33	1,811.41	14,861.23	3,389.40
Total generated energy	36,431.91	9,196.51	41,907.97	10,407.59	43,248.22	10,960.97	50,112.55	12,496.52
Electricity contributed to the grid		9,196.51		10,407.59		10,960.97		12,496.52
Electricity is taken from the grid		8,879.09		10,091.73		9,787.76		11,099.10
Fossil energy input (60% of electricity)		5,327.45		6,055.04		5,872.66		6,659.46
Process net energy input	45,310.93		51,999.82		53,036.12		61,211.49	
Process net energy output	30,396.51		31,607.59		32,160.97		33,696.52	
Net energy ratio	0.67		0.61		0.61		0.55	
Renewability	5.71		5.22		5.48		5.06	

After assessing the results and compared with the results with previous literature data and actual plant data, it is evident that there is room for improvement in terms of energy efficiency when establishing in the industry. Carrying a sensitivity analysis can provide information about hot spots with the most potential for improvement and how it will affect the interpretation of results. Further, it is also possible to locate reasons for the energy difference in many other lignocellulosic feedstocks by a sensitivity analysis.

The composition of WH can change globally depending on the maturity of the plant and the climate [8], resulting in different lignin and cellulose percentages. As shown in Figure 4.8 lignin percentage has a low sensitivity towards the yield and the rest of the indicators, whilst cellulose percentage variation has a bigger impact within the possible variation range. Since the plant utilises lignin as a fuel source to generate steam, low lignin content affects the energy supply. Results of this study revealed that when the lignin percentage is 14 NER is 0.63 and Rn is 5.74. Even though it can be anticipated that when the lignin amount rises, NER and Rn simultaneously increase because, as a percentage that affects the percentage of the rest of the components (cellulose and hemicellulose), the sugar supply reduces for the fermentation.

The effectiveness of the pretreatment can vary due to the structure of the process plant, as well as the part of the plant used, such as roots, stems or/and leaves. A 5% decrease in pretreatment efficiency reduces the yield by 10.21 kg/tonne-WH, and an increase of 5% make the yield reduced by 14.79 kg/tonne-WH. On the other hand, fermentation efficiencies also can change the output because it can change based on the yeast strain used for the fermentation and the presence of inhibitors. The ±5% fermentation efficiency affected the yield by +12.21 kg/tonne-WH and -11.79 kg/tonne-WH difference. At this point, it is noteworthy the correlation between the yield and the process energy uptake per FU is the better the bioethanol yield, the lesser the process energy consumption. Moreover, the changes of pretreatment and fermentation changes alone are not sufficient for the process NER to be >1.

Table 4.5: Process sensitivity analysis results

	99.7 Yield (kg/tonne)	**Energy (MJ)**	**NER**	**Rn**
Base case (WH1)	201.79	45,310.93	0.67	5.71
Lignin percentage in WH (wt%)	205.00 - 184.00	44,907.07 - 49,021.02	0.67 - 0.63	5.06 - 5.74
Cellulose percentage in WH (wt%)	197.00 - 355.00	46,476.61 - 27,206.56	0.66 - 0.99	5.60 - 8.33
Solid loading (biomass: water)	201.79 - 201.79	20,428.79 - 63,761.79	1.84 - 0.54	11.82 - 5.00
Pretreatment process efficiency (%)	187.00 - 212	48,990.95 - 43,371.24	0.63 - 0.69	5.39 - 5.89
Fermentation efficiency (%)	190.00 - 214.00	47,984.19 - 42,919.64	0.65 - 0.69	5.52 - 5.86

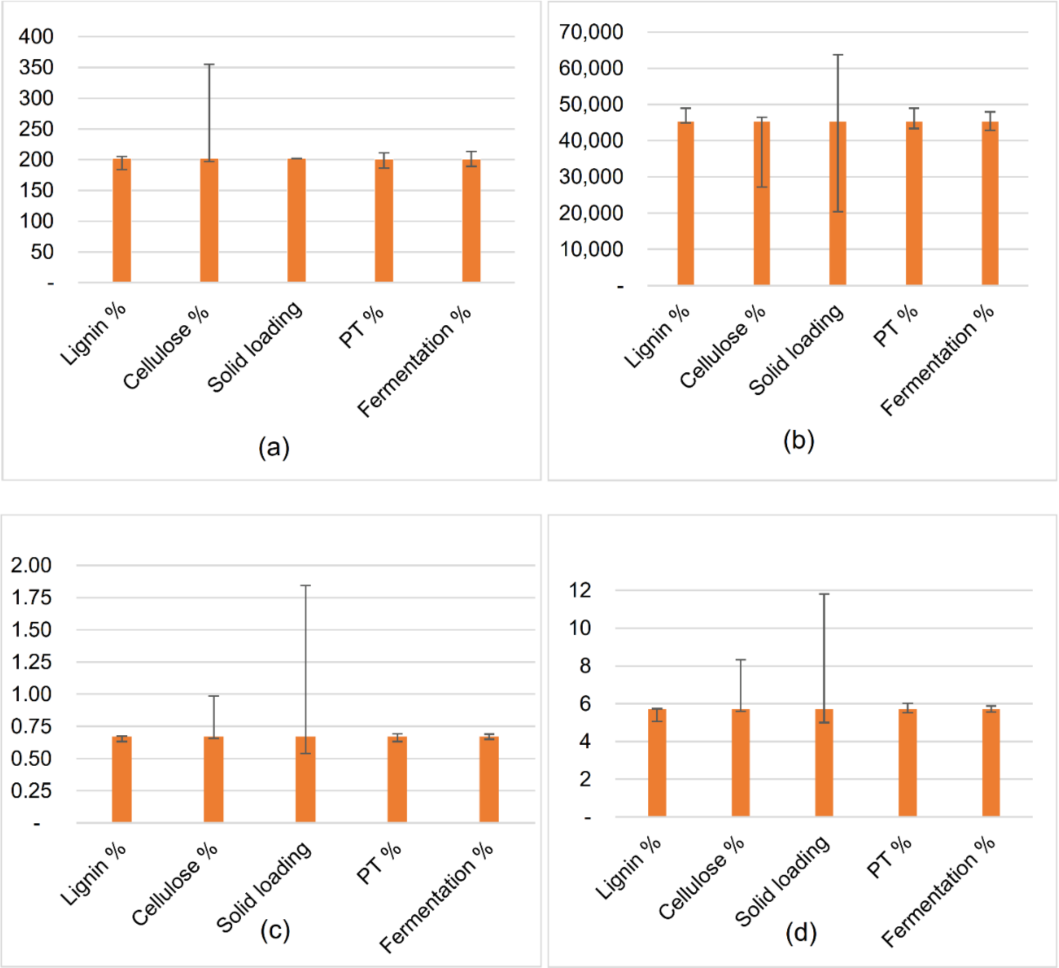


Figure 4.8: Sensitivity analysis results indicating; **a** Yield, **b** Process energy consumption, **c** Net energy ratio, **d** Renewability indicator

Well-mixing is needed within the reactor to achieve optimum output. Therein, appropriate reactor design and minimum limitations with stirring are crucial to have satisfactory mixing [82]. However, for industrial applications, high solid loading is desirable for energy efficiency. The majority of industrial and pilot-scale published studies with competitive results are with high solid loading representing more than 20% (w/w). Results give a better understanding of industrial implications and how the important factors, such as yield, energy consumption and environmental impacts, change along with the liquid volume in a biorefinery. Sensitivity results clearly confirm solid loading parameter has the highest impact on key indicators. However, solid loading has no sensitivity towards the bioethanol yield since WH to water ration does not affect cellulose and hemicellulose percentage nor the recovery, but it has a significant sensitivity toward the energy consumption.

In fact, amongst all of the parameter changes, the only parameter showed potential to vary the process energy consumption enough to achieve an energy gain is the solid loading parameter. The highest energy ratio results gave is 1.84 with an energy consumption of 20,428.79 MJ/FU at a solid loading ratio of 1:3. This high solid loading value also gives a high renewability with a 11.82 factor while low solid loading only gave a renewability of 5. Results of the sensitivity analysis suggest maintaining a process energy gain with NER > 1 the threshold the water inflow has to be maintained is 5.2 kg or less per 1 kg of dry biomass in a plant that uses WH as the lignocellulose source to produce fuel-grade bioethanol.

4.2 Life cycle mass flow analysis

Mass flow analysis through the cradle-to-gate life cycle is the primary and utmost needed step to carry out an LCA. Based on the results obtained from the simulation, to produce 1 m^3 of fuel-grade bioethanol, 3,960 kg of dry WH is required, which means after factoring in losses during harvesting and transportation, the moisture content of harvested WH (93%), the mass of 69,640 kg (70 tonnes) of WH is needed to produce 1 m^3 of bioethanol from WH. This gives a bioethanol yield of 14.36 L/tonne-WH (wet).

Due to WH being a water body, the harvesting and transporting process can be challenging due to the additional water and mud that traps in WH clusters and roots. To avoid inhibitor generation, this mud and soil need to be washed thoroughly. Also, to fit in an adequate usable load of WH in the transportation truck, it is recommended to drain and partially dry (reduced to 40% moisture) the harvest near the harvesting site (potentially the riverbank). This reduces the transporting mass of WH to 8,125 kg. During this stage, including the size reduction of the feedstock, the mass loss was considered to be 20%.

In addition, other than the chemicals and material required for the conversion and dehydration of WH to bioethanol, 16.5 L of diesel and 747.75 MJ worth of heavy oil are needed for harvesting and transportation. A noteworthy aspect is considering WH cluster density of 8 kg/m^2, a water body surface area of less than a hectare is needed to produce 1 m^3 of bioethanol [60]

4.3 Life cycle net energy analysis

Produce bioethanol would have to provide a net energy gain during production to be a viable alternative to a non-renewable energy source. Despite the attractiveness of biomass to produce bioethanol, the process cannot be considered sustainable or economically feasible unless there is a net energy gain.

Table 4.7 summarises the energy input throughout the defined life cycle. The life cycle steps are identified as harvesting of WH, production of chemicals and other raw materials, transportation of raw materials to the factory, feedstock preparation, and conversion and purification. The energy intake as steam is biogenic and provided from the CHP unit within the plant. The electricity component (9,196 MJ/FU) generated in the CHP unit is credited as biogenic energy to the national power grid. Direct fossil energy is used for transportation and other machinery for harvesting and feedstock preparation. The electricity generated in Sri Lanka is 60% fuelled by fossil fuels. Therefore, the total fossil-based energy consumption is 16,218 MJ/FU.

Calculated net energy indicators for the life cycle of bioethanol are mentioned in table 4.7. As per results, NEV indicates a -25,805 MJ/FU value based on the base case WH1 scenario adapted for the cradle-to-gate life cycle, which results in 1>NER. Nevertheless, by optimising the conversion and dehydration stage based on the conducted sensitivity analysis of these indicators, there is a possibility to achieve more desirable results. The resulting NRnEV (39,983) and Rn (1.87), however, are desirable.

Table 4.6: Life cycle energy consumption

Description	**Energy input/output (MJ/FU)**		
	Steam	**Electricity**	**Fossil**
Harvesting			
Diesel for WH harvester			12.91
Transportation			
Diesel for WH transportation (Inland)			401.72
Diesel for chemicals transportation (Inland + nautical)			1,055.85
Diesel for wood chips transportation (inland)			24.45
Other raw material			
Chemicals production			8,602.17
Woodchipper			324
Feedstock preparation			
Crusher 1.3 L/tonne			470.01
Conversion and purification			
From Aspen (Plant)	36,431.85	8,879.09	
Total input	**36,431.85**	**8,879.09**	**10,891.10**
Output			
Bioethanol (MJ/FU)		21,200.00	
Electricity		9,196.51	
Total energy inputs		56,202.04	
Total energy outputs		30,396.51	
Total net bioenergy outputs		30,396.51	
Total fossil energy input		16,218.55	
Net energy value (NEV)		**(25,805.53)**	
Net energy ratio (NER)		**0.54**	
Renewability (Rn)		**1.87**	
Net renewable energy value (NRnEV)		**39,983.48**	

4.4 Life cycle environmental impact assessment

Table 4.7 lists the inventory results of the top ten emissions to air per FU. According to the results, CO_2 is the largest emission, with 3,280 kg. Further analysis revealed that 77% of the CO_2 emission is from the pretreatment stage (process stage 1). This high emission is because most of the chemicals and enzymes are added in this stage. Also, stage 1 consumes most of the energy, contributing more CO_2. Sulphur dioxide is the second-largest emission with an amount of 13.20 kg, followed by atmospheric nitrogen with an amount of 9.82 kg, and nitrogen oxides (NO_x) with an amount of 9.11 kg.

Table 4.7: Top ten emissions to air

Emissions	Emission amount (kg/FU)
Carbon dioxide	3,280.00
Sulphur dioxide	13.20
Nitrogen, atmospheric	9.82
Nitrogen oxides	9.11
Particulates, < 2.5 um	5.72
Methane, fossil	4.15
Particulates, > 10 um	3.32
Sulphate	3.21
Carbon monoxide, fossil	2.40
Ammonia	1.44

Table 4.8: Top ten emissions to water

Emission	**Emission amount (kg/FU)**
Sulphate	209.66
Calcium	121.56
Silicon	33.55
Sodium	20.72
Iron	9.01
Phosphate	7.79
Aluminium	7.51
Suspended solids, unspecified	7.38
Nitrate	5.54
Magnesium	3.06

Table 4.8 summarises the top 10 emissions to water during the production of bioethanol from WH. As per LCA results, sulphate is the top emission listed in the table, with an amount of 209.66 kg, calcium and silicon holding second and third place with amounts of 121.56 kg and 33.55 kg.

Table 4.9 presents the environmental impact categories and corresponding units associated with each impact category. The impacts are broken down into individual stages to identify hot spots in the process. The results indicate that the most significant environmental impact is in the category of fossil resource scarcity, with a total impact of 733,024.55 kg of oil equivalent, contributing the most from transportation. The second most impactful category is global warming, with a total impact of 1,501.90 kg of CO_2 equivalent, mainly associated with process stage 1.

Figure 4.9 gives a visual representation and the impact distribution among the stages of the life cycle. It is clear that process stage 1 has a significant effect on all of the impact categories except on fossil resource scarcity. This observation reflects conclusions from previous studies. A review paper found that the largest contributors to environmental impacts in the life cycle of bioethanol production from lignocellulosic biomass were typically energy consumption during the pretreatment due to high energy demand [83].

Other impact categories include ozone formation, human health and terrestrial ecosystems, fine particulate matter formation, terrestrial acidification, freshwater and marine ecotoxicity, and human toxicity, which are all important aspects to consider when evaluating the overall environmental performance of bioethanol production.

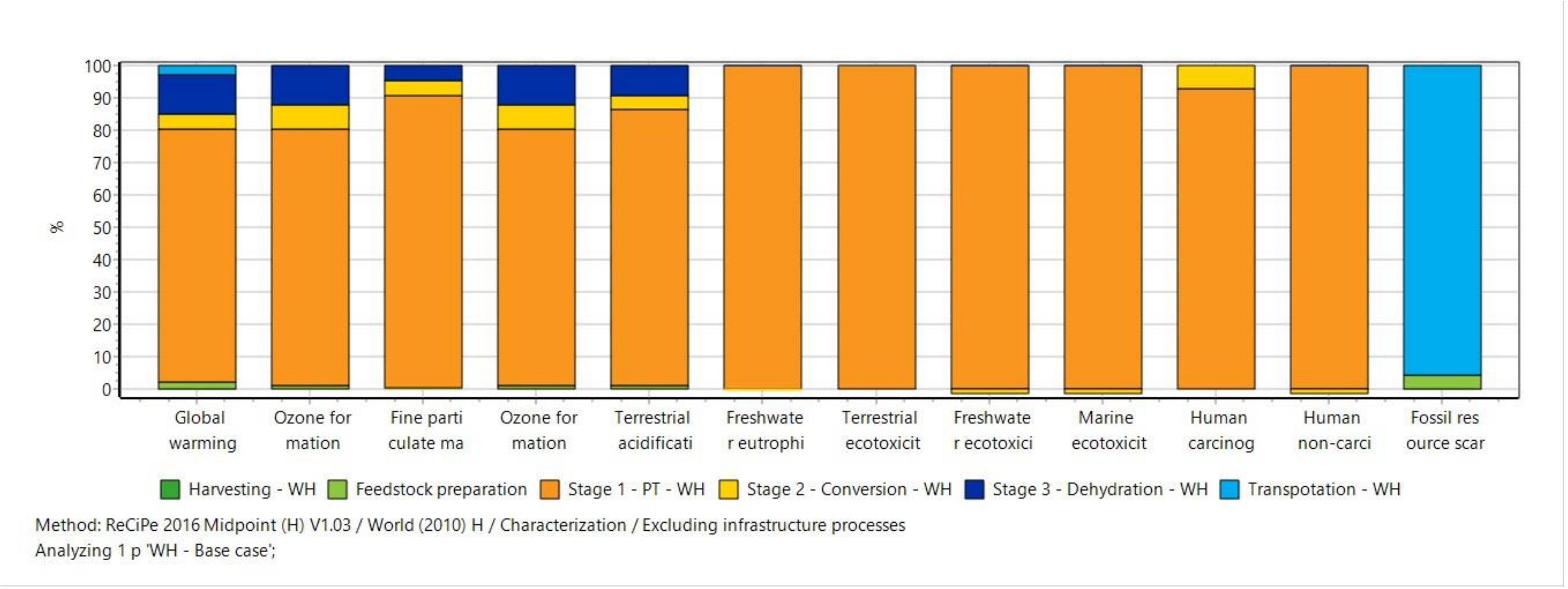
In this study, an important aspect to highlight is the influence of transportation. The chosen transportation distance in this research is arbitrary and specific to the Sri Lankan context, focusing on a lagoon area near a wetland with substantial WH growth. This factor significantly impacts the findings, particularly in the category of fossil resource scarcity.

Furthermore, the defined boundary, specifically concerning diesel and heavy oil for shipping chemicals and its associated emissions during the initial stages of production (the cradle), has a direct effect on the characterization output. For instance, when emissions at the oil rig and refinery are excluded from the system boundary, it results in a minimal impact from heavy oil and diesel. It is worth considering additional studies to precisely determine the extent of these effects. In Figure 4.10 shows the characterization results where the emissions at the production of diesel and heavy oil have been omitted from the system boundary.

Another important aspect of the impact assessment and the interpretation is normalisation of results. Normalisation allows the environmental impacts to be compared to a common baseline. This helps to interpret the extent of an impact of a category compared with other categories. There could be instances where, because of the unit used in a particular category as a numerical value, the impact gets marked as high; however, by normalising, this difference can be bypassed. Once results are normalised in this study, fossil resource scarcity (748) is visibly the category with the highest impact, followed by marine ecotoxicity (204) and freshwater ecotoxicity (123). Figure 4.11 shows the results after normalisation.

Table 4.9: Base case impact assessment

Impact category	Unit	Harvesting	Feedstock preparation	Stage 1	Stage 2	Stage 3	Transportation	Total
Global warming	kg CO_2 eq	0.77	77.35	2,910.37	164.35	445.88	112.38	3,711.10
Ozone formation, Human health	kg NO_x eq	-	0.13	7.34	0.71	1.13	-	9.30
Fine particulate matter formation	kg PM2.5 eq	-	0.06	9.89	0.49	0.52	-	10.96
Ozone formation, Terrestrial ecosystems	kg NO_x eq	-	0.13	7.37	0.72	1.13	-	9.34
Terrestrial acidification	kg SO_2 eq	-	0.20	16.69	0.79	1.82	-	19.50
Freshwater eutrophication	kg P eq	-	-	2.56	-0.01	0.00	-	2.56
Terrestrial ecotoxicity	kg 1,4-DCB	-	-	341.75	0.13	0.00	-	341.88
Freshwater ecotoxicity	kg 1,4-DCB	-	-	153.39	-1.99	0.06	-	151.46
Marine ecotoxicity	kg 1,4-DCB	-	-	212.86	-2.73	0.08	-	210.21
Human carcinogenic toxicity	kg 1,4-DCB	-	-	4.32	0.32	-	-	4.65
Human non-carcinogenic toxicity	kg 1,4-DCB	-	-	5,200.24	-63.55	1.73	-	5,138.42
Fossil resource scarcity	kg oil eq	849.99	30,951.36	-	-	-	701,223.20	733,024.55



Method: ReCiPe 2016 Midpoint (H) V1.03 / World (2010) H / Characterization / Excluding infrastructure processes
Analyzing 1 p 'WH - Base case';

Figure 4.9: Impact assessment of base case (WH1)

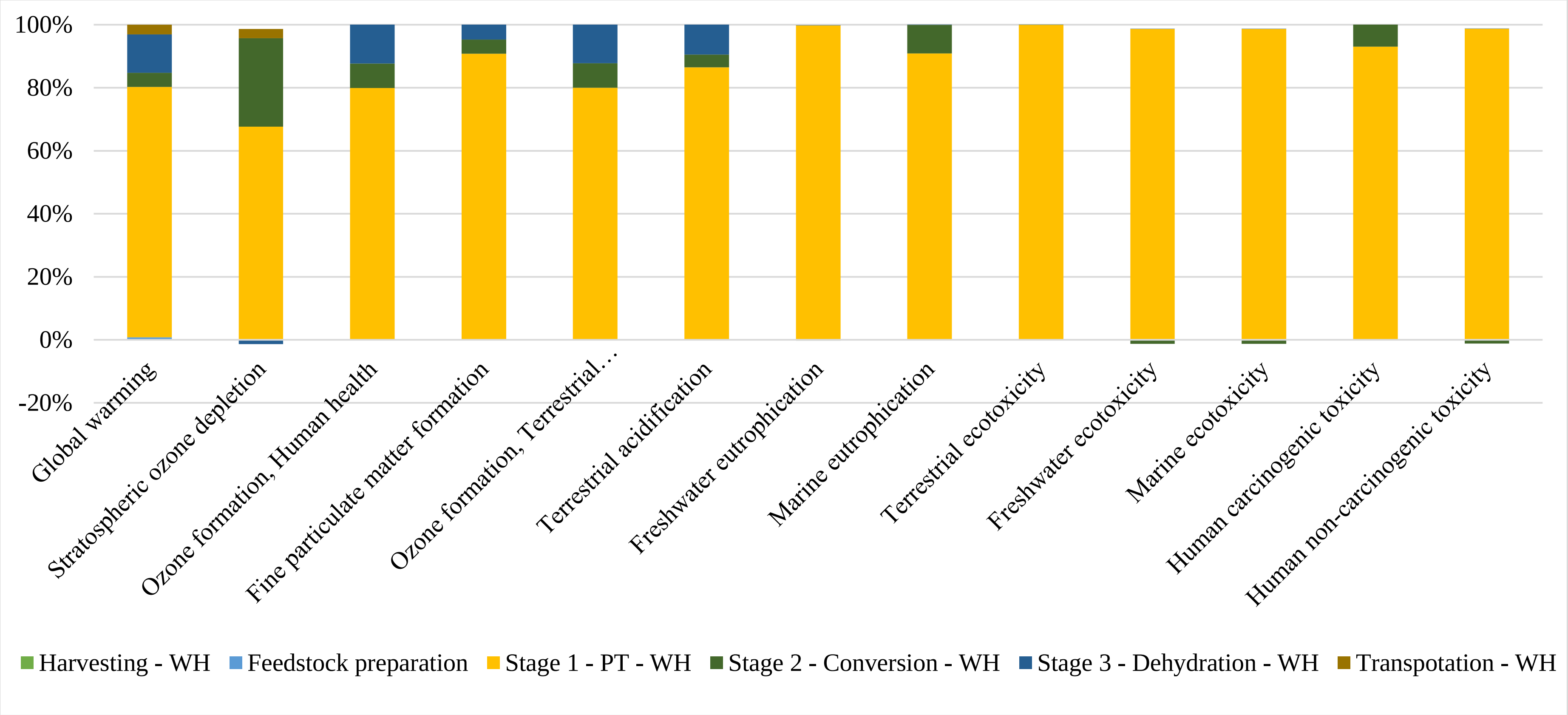
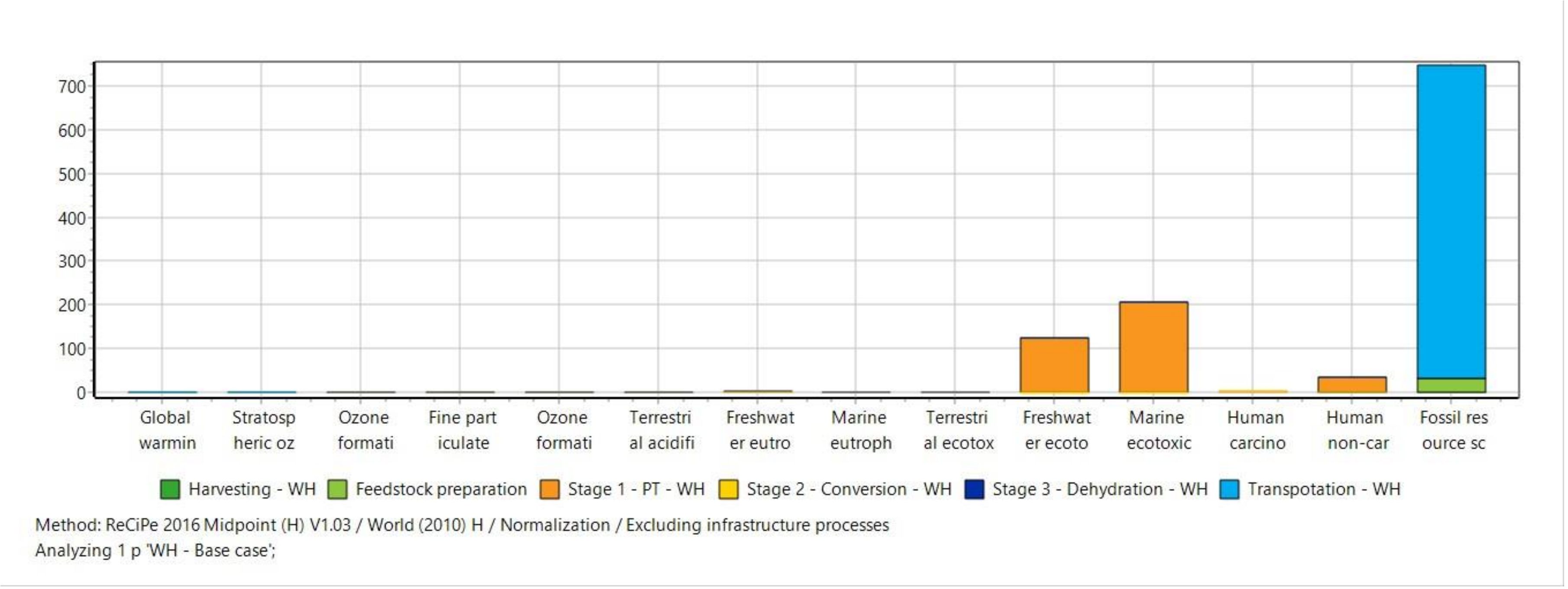


Figure 4.10: Impact assessment of base case excluding crude oil production



Method: ReCiPe 2016 Midpoint (H) V1.03 / World (2010) H / Normalization / Excluding infrastructure processes
Analyzing 1 p 'WH - Base case';

Figure 4.11: Base case normalisation

4.4.1 Life cycle sensitivity analysis

The sensitivity analysis reveals the robustness and susceptibility of the process and to understand the fluctuation of impacts. Table 4.10 indicates the sensitivity results of the life cycle when process energy, bioethanol yield and solid loading are set as the variables.

Figures 4.12 – 4.15 depicts the sensitivity results of the analysis. Figure 4.12 shows how NER and Rn change compared with the base case value 0.54 and 1.84, respectively. According to the results, solid loading contributes to the largest fluctuation of NER and Rn. An important noteworthy point is that by reducing the solid-liquid ratio, there is potential to achieve a NER>1. On the flip side, the minimal changes due to process energy variation and yield change those results are not big enough to make NER>1.

Results further indicate that changes in the bioethanol yield have a relatively small effect on GWP, whilst yield change does not affect human toxicity, marine ecotoxicity and freshwater ecotoxicity impact categories at all. Moreover, variations in process energy consumption have a visible impact on GWP within the possible range of variation with negligible effect on other categories. Overall, the most prominent outcome of the sensitivity analysis is that solid loading plays a key role in environmental impacts. By reducing the water volume added to the primary reactor at the pretreatment stage, can improve the process from an environmental perspective.

Table 4.10: Life cycle sensitivity analysis results

	NER	**Rn**	**GWP (kg-CO_2 eq)**	**Human toxicity (kg-1,4-DCB)**	**Marine ecotoxicity (kg-1,4-DCB)**	**Freshwater ecotoxicity (kg-1,4-DCB)**
Base case	0.54	1.84	3,711	5,138	210	151
Process energy consumption	0.48 – 0.61	1.80 – 1.88	3,401 – 4,018	N/A	N/A	N/A
Bioethanol yield	Negligible	1.83 – 1.88	3,685 – 3,714	N/A	N/A	N/A
Solid loading	0.43 – 1.53	1.48 – 5.08	1,743 – 5,118	1,808 – 7,520	69 – 311	50 – 224

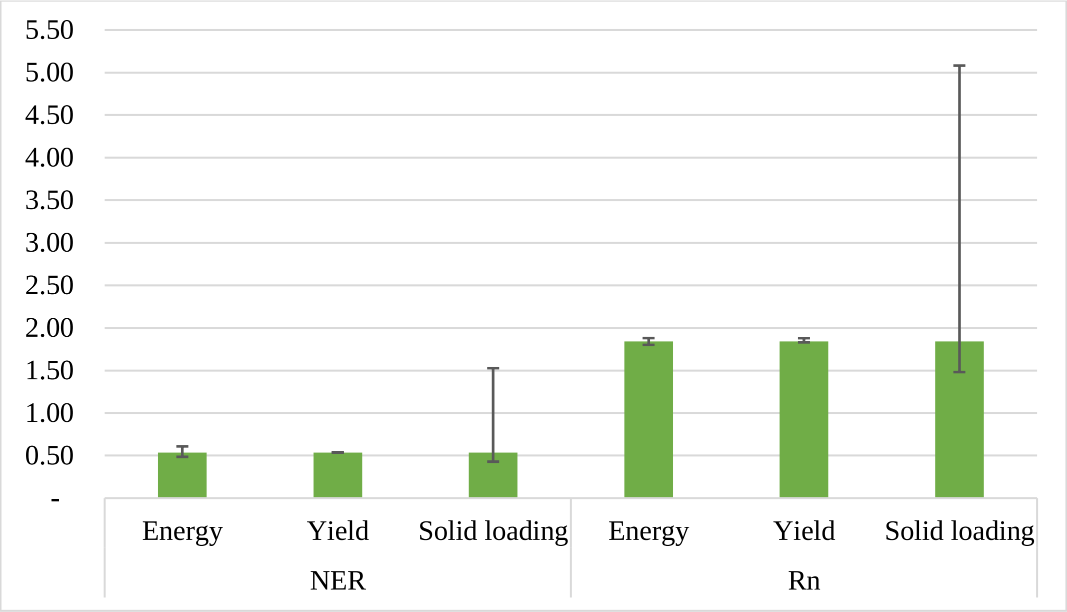


Figure 4.12: Life cycle sensitivity analysis results for NER and Rn

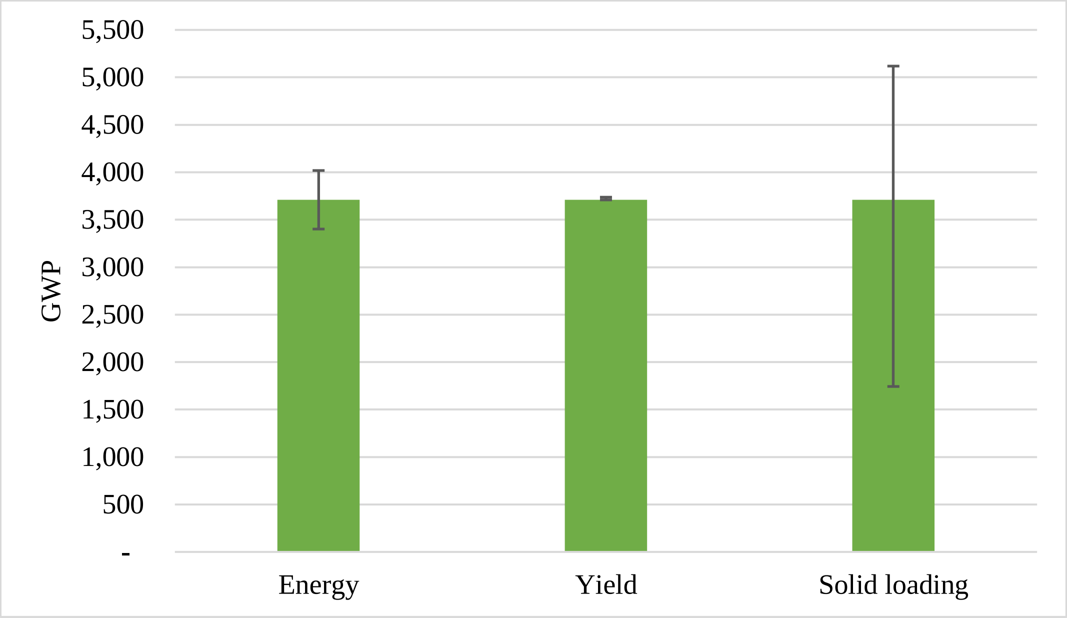


Figure 4.13: Life cycle sensitivity analysis results for GWP

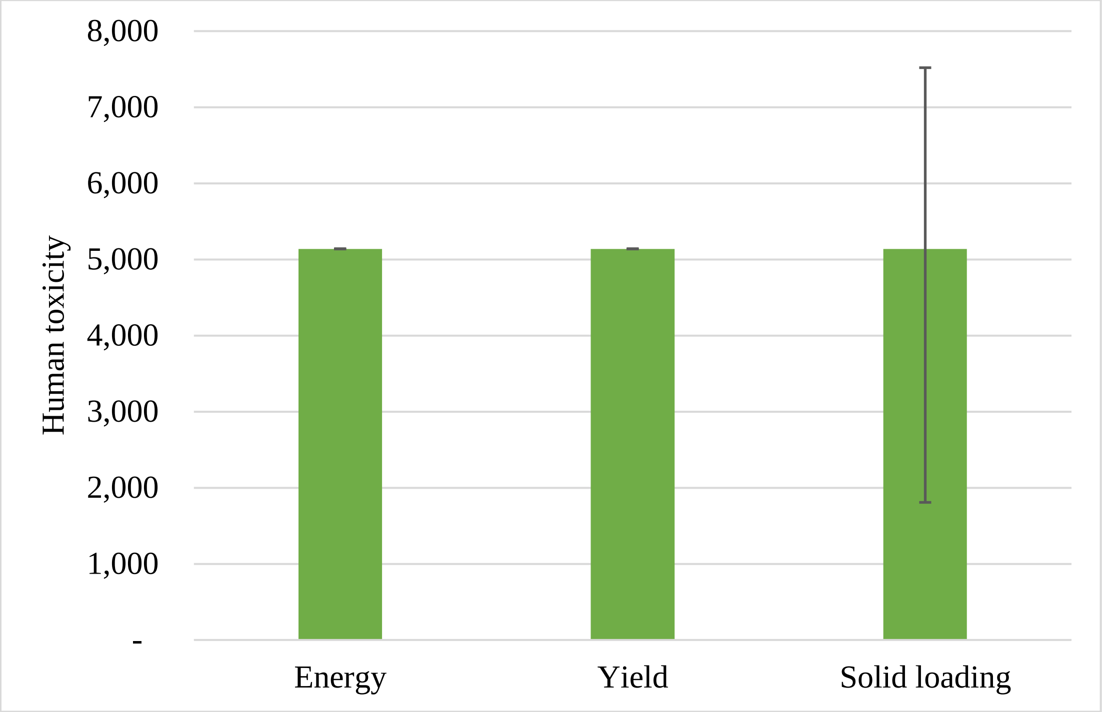


Figure 4.14: Life cycle sensitivity analysis results for human toxicity

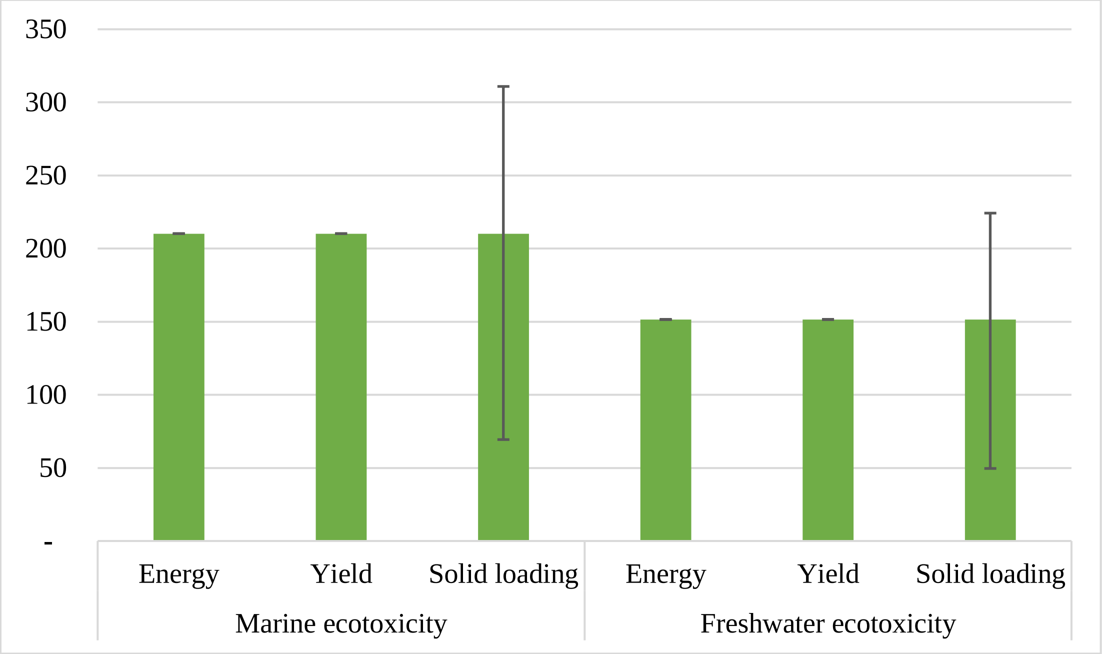


Figure 4.15: Life cycle sensitivity analysis results for marine ecotoxicity and freshwater ecotoxicity

4.4.2 GHG comparison for different gasohol blends

GHG mitigation is one of the most important initiatives spoken globally [84]. And There are international policies in the transport sector that recognise GHG emission reduction by substituting gasoline with bioethanol. The US Renewable Fuel Standard (RFS), US Environment Protection Agency (EPA), and the EU Renewable Energy Directive (RED) can be mentioned as a few. EPA has identified that compared to gasoline, biofuels have the potential to reduce GHG emissions by more than 60% [70]. As per the given distinct identification number by the EPA and the GHG reduction potential, it is required for lignocellulosic bioethanol to not only reduce GHG emissions by more than 60% but also the produced bioethanol must show the minimum GHG reduction as on the legislation [70]. This is another reason why it is important to carry out an LCA for the biofuel production process since the framework allows to assess environmental impacts throughout the life cycle.

The cradle-to-grave life cycle GHG emission of E100 for scenario WH1 is 3,711 kg-CO_2 eq/FU. As per the base case scenario, due to the high energy uptake as a result of the low solid loading ratio, E100 does not give a GHG reduction. However, when results are in-depth analysed in the life cycle sensitivity analysis, it shows that bioethanol made from WH has the potential for a GHG reduction. Compared with previous studies, switched grass has proven to result in a 65-70% reduction. This allows for +4% reduction for E5 blend and a 17-19% reduction for E20 blend. However, not every previous study supports the positive impacts of a GWP reduction there are studies that show results that have closer to double the amount of E0 GWP for E100 [83][85].

4.5 Limitations of this study and future works

Process simulations in this study were conducted using the existing models in the Aspen Plus process simulator. Results obtained by using these models can be different and deviate from a realistic representation of an actual plant. Moreover, there is no accessible real plant that converts WH into bioethanol as of now to practically pursue a trial run.

The notion that bioenergy and bioproducts have the capacity to reduce unfavourable environmental impacts is based on the theory that the carbon contained in bio-based products is biogenic carbon which is considered carbon neutral. However, the production of these products uses chemicals and other resources that are not carbon-free.

As emissions of transportation trucks depend on the travel distance, the location of the plant plays an important role in the outcome of the study. Trucks are diesel fuelled and hence have a significant environmental impact. Therefore, a change in distance has the potential to alter the result of the study drastically. Since the system under analysis is not established in practice yet, the distance between the harvesting body and the plant, so as the distance from the port to the factory included in calculations, are assumptions made bade on considerations instead of actual distances. Further, distance is not the only factor that determines the emissions. It also depends on the speed, traffic situation during transportation and the efficiency of the truck engine, which can change with the age of the truck and maintenance.

LCA studies require a large amount of data, which may vary significantly depending on the specific circumstances of the production process. This can make it difficult to compare the environmental impact of different bioethanol production processes, as well as to make accurate predictions about the potential impact of changes to the process.

In industry, energy analysis is commonly used to make decisions about resource utilization and process design with the goal of reducing energy consumption. However, relying solely on theoretical mass and energy analysis may not accurately reflect real-world commercial applications. To gain a better understanding of the environmental and financial implications of a process, it is recommended to use other sustainability assessment tools in conjunction with energy analysis, such as Life Cycle Assessment, techno-economic analysis, and/or exergy analysis [86]. Exergy analysis is particularly useful as it not only considers the quantity of material and energy flows, but also the quality of process streams. By identifying thermodynamic losses and environmental impacts, exergy analysis can help decision-makers pinpoint cost losses [87]. Therefore, to more accurately assess the suitability of using waste heat as a feedstock for producing bioethanol, future research should consider expanding the scope of sustainability assessment tools beyond energy analysis based on the results of this study.

Conclusion and Recommendations

The study analysed and compared four different ways to produce bioethanol on a larger scale using WH as the feedstock. These four routes combine two different techniques for pretreatment and dehydration. Based on these finding most energy efficient option was applied to the cradle-to-gate life cycle of bioethanol production from WH to understand the sustainability aspects of the process. The process simulation-based analysis provided important findings on the key mass and energy flow indicators of scaled-up bioethanol production from WH as the feedstock. The findings reveal that there is a significant improvement in bioethanol yield when WH is processed via alkaline pretreatment compared with dilute acid pretreatment under the same conditions. Approximately 0.86 tonnes of an additional dry WH quantity are required to produce 1 m^3 of bioethanol when dilute acid pretreatment is adopted as the pretreatment method. Further, the process route with the combination of alkaline pretreatment along with extractive dehydration indicated less energy consumption in comparison to other studied process routes. All considered process route scenarios did not show positive energy gains under the selected process conditions. Nevertheless, the findings from sensitivity analysis when the process was considered as the system boundary, the results pointed out that the solid loading ratio (dry biomass: water) plays a key role in the process performance of fuel-grade bioethanol production using WH, where it is advisable to maintain a ratio of 5.2 kg of water threshold per 1 kg of dry WH for positive energy gain from the overall bioethanol production process.

The life cycle assessment reviled, that global warming, human toxicity, marine ecotoxicity and freshwater ecotoxicity as the category with biggest impact. Process stage 1 is identified as the hot spot of the life cycle. The results from this study show the feasible ways of utilising WH as a fuel-grade bioethanol feedstock for industrial-scale production, and the findings support future LCA and implementations of new bioethanol production plants using WH as a feedstock.

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