PROCESS SIMULATION-BASED LIFE CYCLE ASSESSMENT FOR FUEL-GRADE BIOETHANOL PRODUCTION FROM PADDY RICE STRAW

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DECLARATION

I declare that this is my own work, and this thesis does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any other University or Institute of higher learning, and to the best of my knowledge and belief, it does not contain any material previously published or written by another person except where the acknowledgment is made in the text. I retain the right to use this content in whole or part in future works (such as articles or books).

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The above candidate has carried out research for the MSc thesis under my supervision. I confirm that the declaration made above by the student is true and correct.

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Signature of the Supervisors: Date: 28.12.2023

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B. Signed by
Dr. G.S.M.D.P. Sethunga

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ABSTRACT

For the life cycle scenario of bioethanol production from unutilized rice straw, the life cycle stage of paddy rice cultivation can be excluded with a zero-inventory allocation rule, i.e., rice straw with no applied valorization in current practice. This study evaluates the life cycle net energy analysis, greenhouse gas (GHG) assessment, and comparative life cycle environmental impact assessment for nine (09) scenarios of scaled-up bioethanol production process routes using unutilized rice straw as the feedstock. Three different feedstock pretreatment technologies and three different bioethanol dehydration technologies are incorporated to develop the process route scenarios for scaled-up processing plant models. The process simulation technique is integrated to model the scaled-up production plants to produce bioethanol at 99.7 vol% purity from unutilized rice straw, and the simulation results are retrieved to calculate inventory data for life cycle assessment (LCA). This research aims to determine the most environmentally benign scenario of the process route to produce fuel-grade bioethanol at an industrial scale from unutilized rice straw. The simulated mass flow and energy flow results are comparable with those of real plants, reported in the published literature, which validates the process simulation results in this study. According to the overall results, fuel-grade bioethanol production using rice straw via adopting dilute acid pretreatment technology for feedstock pretreatment and extractive distillation technology for bioethanol dehydration showcases the most sustainable routine from environmental and energy perspectives. Inclusive of energy generation using the waste flows in the process (i.e., spent wash and solid residues), the life cycle net energy analysis results show a net energy gain of 7,804.0 MJ/m^3 of bioethanol with a net renewable energy gain of 38,230.9 MJ/m^3 of bioethanol that corresponds to a net energy ratio of 1.20 and renewability factor of 5.49 for the base-case scenario developed for Sri Lankan context with dilute acid pretreatment and extractive distillation. The life cycle GHG assessment exhibits a net global warming potential of 584.8 kg CO_2 eq/m^3 of bioethanol. The effect of system boundary expansion up to the end-of-life stage as gasohol (E10), the sensitivity of the key process parameters, and the economic benefit via valorization of unutilized rice straw are further analyzed and discussed.

Keywords: Bioethanol production, Unutilized rice straw, Simulation integrated LCA, Net energy analysis, GHG assessment

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LIST OF ABBREVIATIONS

Abbreviation	**Description**
AD	Anaerobic digestion
CHP	Combined Heat and Power
COD	Chemical Oxygen Demand
DS	Dehydration Scenario
GHG	Greenhouse Gas
GWP	Global Warming Potential
IPCC	Intergovernmental Panel for Climate Change
LCA	Life Cycle Assessment
LCIA	Life Cycle Inventory Analysis
MCF	Methane Correction Factor
NA	Not applicable
NEV	Net Energy Value
NER	Net Energy Ratio
NRnEV	Net Renewable Energy Value
NRTL	Non-Random Two Liquid
PS	Pretreatment Scenario
Rn	Renewability
SSF	Simultaneous Saccharification and Fermentation
UASB	Up-flow Anaerobic Sludge Blanket

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CHAPTER 1

1. INTRODUCTION

Global energy consumption increases along with the rapid growth of technology and population. Thus, the demand for existing energy sources expands. When considering different energy sources, such as liquid fuels, coal, renewable energy, natural gas, nuclear energy, and hydroelectricity, liquid fuels have the highest demand along with the increasing energy consumption (at an average annual rate of 1.4%) in the transportation sector. This demand is currently catered mainly from crude oil derivatives; gasoline and diesel [1]. However, with the rapid rate of consumption, existing crude oil sources can fulfill the energy demand only for the next few decades [2]. Therefore, there is a requirement for renewable liquid biofuels like bioethanol to provide the increasing energy demand and reduce the environmental impacts.

Bioethanol is used as a commercial fuel in various countries, mainly Brazil, the USA, China, Thailand, etc. [3]. Brazil uses bioethanol as its primary transportation fuel where cane molasses and bagasse coming out as byproducts from the cane sugar manufacturing process are the major feedstocks to produce bioethanol [4], [5]. The United States utilizes corn-based feedstocks to produce bioethanol [4]. To reduce environmental impacts in the transportation sector, the United States and the European Union promote biofuels, including bioethanol. European Union has launched tangible action plans to achieve the targeted circular economy in Europe by 2030, by promoting biofuels [6], [7]. Considering the actions taken by the European Union and the USA, the Indian government also has taken steps to promote bioethanol with a mandatory blending level of 20% [8]. Furthermore, the Biomass Nippon Strategy Promotion Council has developed criteria to expand domestic biofuel production with a long-term target of six thousand million liters of bioethanol in Japan, including lignocellulosic feedstocks [9]. Also, Major automobile manufacturers, including Mercedes Benz, Toyota, and General Motors have introduced Flexible Fuel Vehicles (FFV) to promote the utilization of bioethanol as a transportation fuel. Approximately five million FFVs are used currently in the USA and about 70% of new vehicle purchases in Brazil are FFVs. Thus, Bioethanol has become the major renewable transportation energy source in the world [4].

Fuel-grade bioethanol (purity > 99.5 vol%) is blended with gasoline in different fractions to produce gasohol blends (E5, E10, E20, and E85). These gasohol blends ranging from E3 to E85 are readily used in vehicles without further engine modifications. Gasohol blends provide an added advantage of octane number enhancement, which avoids the use of toxic octane boosters in pure gasoline, such as Methyl Tertiary-Butyl Ether (MTBE), Tetra-Ethyl Lead (TEL), and other synthetic oxygenates [10].

Bioethanol is commercially produced from starch-based feedstocks (first-generation bioethanol feedstocks) and lignocellulosic feedstocks (second-generation bioethanol feedstocks). The use of starch-based feedstocks, such as corn, rice, sweet potato, sweet sorghum, etc. for bioethanol production would affect their availability in food supply chains by hindering global food security. When compared with edible feedstocks, non-edible lignocellulosic feedstock materials, especially agricultural residues are renewable and widely available at a lower cost as well [11]–[13]. It is expected that second-generation bioethanol will exceed first-generation biofuel production in about the next ten years [11]. Thus, the use of widely available agricultural residues, such as rice straw, wheat straw, corn stover, and sugarcane bagasse to produce bioethanol can be a better option.

Rice is the staple food for approximately half of the global population, especially Asians. The annual global rice grain production is around 987.93 – 1,481.89 million tonnes whereas rice straw is generated as a residue for about 740.95 – 1,111.42 million tonnes [14]. Countries, such as China, India, and Thailand annually generate approximate amounts of 74.70, 60.08, and 12.15 million tonnes of rice straw, respectively [15]. These countries have already initiated the utilization of rice straw as a feedstock to produce fuel-grade bioethanol. When compared to countries like Thailand, Sri Lanka also generates a significant amount of rice straw annually, i.e., approximately 2.8 million tonnes per year. [16]. However, in the current practice of Sri Lanka, a certain percentage of rice straw out of the total generation is currently utilized as a soil conditioner for the next season of cultivation. The major fraction of rice straw is openly burned within the paddy fields. Thus, rice straw can be considered as an abundantly available lignocellulosic feedstock for future second generation bioethanol production in Sri Lanka. It would be very useful to study the feasibility and assess the energy/environmental aspects of a scaled-up bioethanol production plant in Sri Lanka utilizing this rice straw availability as the feedstock.

Life Cycle Assessment (LCA) is a standard assessment methodology of bioethanol production that can evaluate the sustainability of any process/product in terms of energy /environmental, social, and economic perspectives. In the existing literature, several studies have been conducted in different countries to evaluate the life cycle net energy analysis and environmental impact assessment of bioethanol production using rice straw. An LCA study conducted in Thailand concludes that among the sustainable value-addition approaches using rice straw; 1. Co-generation of heat and electricity, 2. Bio-DME production, 3. Bio-Ethanol Production, and 4. Fertilizer production, the most environmentally-benign approach is bioethanol production [17]. Two studies conducted in Japan and Thailand conclude that heat and electricity co-generated using lignin-containing solid residues and biogas from wastewater treatment are sufficient (with a surplus) to cater the process energy requirement for bioethanol plants [18], [19]. A study in Japan has performed a net energy analysis for bioethanol production using high-yield rice plants and has resulted in Net Energy Ratio values, NER > 1, and Renewability factors, Rn > 1 [18]. Also, for published LCA studies done in Thailand and India, positive Net Energy Values (NEV) and Net Renewable Energy Values (NRnEV) have been reported for bioethanol production from rice straw. Further, NER > 1, and Rn > 1 have been reported for bioethanol production using rice straw in India [20]. Also, these studies have resulted in net GHG emission reductions through bioethanol production using rice straw along with other harmful environmental emissions.

The cradle-to-gate life cycle of fuel-grade bioethanol production from unutilized rice straw can be categorized into five major life cycle stages, namely, 1. Paddy rice straw collection, 2. Rice straw transportation, 3. Rice straw pretreatment 4. Bioethanol conversion, and 5. Bioethanol dehydration. Existing LCA studies show that the hotspots of energy consumption and environmental impacts are oriented in the feedstock pretreatment and dehydration stages along with the technologies of process operations. When considering the process operations conducted in bioethanol production using lignocellulosic feedstocks, such as rice straw, feedstock pretreatment and dehydration of bioethanol operations are significant. The efficiency and effectiveness of rice straw pretreatment methodologies directly contribute to the extracted cellulose and hemicellulose content from the solid phase into the liquid phase. The higher the amounts of cellulose and hemicellulose extracted, the higher the bioethanol yield. However, the extraction of cellulose and hemicellulose and separating lignin is a highly energy-demanding operation. Thus, it is important to determine a more feasible pretreatment technology for rice straw to produce bioethanol. There are several rice straw pretreatment technologies commercially available including dilute acid pretreatment, alkaline pretreatment, steam explosion, ammonia pretreatment, microwave pretreatment, etc. In addition, hydrous bioethanol that can be purified via distillation maximum up to the ethanol-water azeotrope is required to further dehydrate at ethanol purity > 99.5 vol% to obtain fuel-grade anhydrous bioethanol. There are many bioethanol dehydration techniques, such as extractive distillation, azeotropic distillation, pressure swing distillation, molecular sieve adsorption, pervaporation, etc. Therefore, the energy and environmental performance of a bioethanol production process from a lignocellulosic feedstock like rice straw would depend on the feedstock pretreatment technology and the dehydration technology applied.

In the published literature, several studies have compared the process techniques used in bioethanol production using rice straw. A simulation-based study has compared two dehydration technologies; i.e. azeotropic distillation and extractive distillation, for bioethanol production from rice straw [21]. The results show that extractive distillation is more advantageous in economic aspects than that of azeotropic distillation. The total energy consumption in each process with each dehydration technique is 4.67 kWh/kg of rice straw, and 1.10 kWh/kg of rice straw, respectively. Accordingly, Azeotropic distillation consumes approximately a four times higher amount of process energy than extractive distillation [21]. An LCA study conducted in India has reported that the net energy values for dilute acid pretreatment and steam explosion as 14.9 MJ/L and 16.3 MJ/L, respectively. Net Energy Ratios are 2.3 and 2.7 for both scenarios, respectively. GHG reduction percentages for both scenarios are 77% and 89%, respectively [22]. These varied results conclude that the life cycle impacts of the fuel-grade bioethanol production process would depend on the process technologies applied.

However, in the existing literature, there is no published LCA study with net energy analysis and environmental impact analysis comparing the combinative effect of feedstock pretreatment and bioethanol dehydration technologies for the case of any lignocellulosic bioethanol feedstock, including rice straw. Therefore, this study focuses on assessing the life cycle effect of feedstock pretreatment techniques and bioethanol dehydration techniques for the scaled-up bioethanol production process from unutilized rice straw. The three most frequently utilized three pretreatment technologies, i.e., dilute acid pretreatment, alkaline pretreatment, and steam explosion combined with three frequently available dehydration techniques, i.e., azeotropic distillation, extractive distillation, and pressure swing distillation are compared as separate life cycle scenarios considering a cradle-to-gate life cycle scope. Multiple process scenarios can be defined from a base-case scenario to other scenarios, considering the pretreatment and dehydration techniques adopted. There are no bioethanol plants available in the case of Sri Lanka for life cycle data retrieval and multiple process technologies cannot be evaluated with a fair comparison using real plant data. Hence, the process simulation technology is integrated in this study to model the scaled-up bioethanol processes in each scenario, separately. All the process scenarios with different combinations of feedstock pretreatment and bioethanol dehydration techniques are simulated in a process simulator, and the process simulation results are utilized for the inventory data retrieval for the LCA.

Determination of the most environmentally benign and renewable combination of feedstock pretreatment and bioethanol dehydration technologies is important for decision-making in the pre-design of a scaled-up bioethanol production process using rice straw as the feedstock for the case of Sri Lanka as well as any other country in the world where new bioethanol plants are possible to establish with feedstock availability. Thus, the comparative analysis of the effect of the applied pretreatment and dehydration techniques on the life cycle performance of bioethanol production would provide valuable information for the development of commercial-scale biorefineries using rice straw as feedstock in the future.

1.1 Objectives of this study

This research aims to conduct a comprehensive LCA for a set of process scenarios with the possible combinations of feedstock pretreatment and bioethanol dehydration technologies for an industrial-scale bioethanol production process from rice straw. The objectives of this study can be indicated as follows.

- Utilize the process simulation technology to model scaled-up bioethanol production plants using rice straw as the feedstock with multiple scenarios of feedstock pretreatment and bioethanol dehydration technologies and calculate required inventory data for LCA.
- Evaluate the net energy efficiency of the life cycle of the scaled-up bioethanol production process from unutilized rice straw and life cycle GHG assessment for a base case scenario.
- Assess the life cycle environmental impacts and environmental sustainability to produce bioethanol at an industrial scale with the multiple process scenarios and identify the most environmentally benign combination of feedstock pretreatment and bioethanol dehydration technologies.

1.2 Scope of this study

The scope of this study is to perform an LCA of bioethanol production from unutilized rice straw. The system boundary of the study is from the harvesting of paddy rice with rice straw generation to bioethanol production at fuel grade purity (cradle-to-gate). Since there are no published real industrial plant data for the case of Sri Lanka, laboratory/pilot scale experiments and plant data of real plants in other countries reported in the literature will be used to determine the input data and process conditions for the scaled-up process simulations. 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 multiple scenarios, developed for combinations of different feedstock pretreatment and bioethanol dehydration technologies. A sensitivity analysis will also be performed for the initial base case scenario to analyze the effect of the variation of the major process parameters on life cycle environmental impacts.

CHAPTER 2

2. LITERATURE REVIEW

2.1 Rice straw generation

Rice is the staple food of approximately half of the world's population, including most Asians. Table 2.1 represents the top countries that produce rice straw with their annular rice straw generation [15], [16]. The annual global rice straw generation is approximately around 740.95 – 1,111.42 million tonnes [14]. A small fraction of this generated rice straw is subjected to value addition annually. The most conventional practice is the open burning of the remaining rice straw within the paddy fields. Thus, unutilized rice straw can be introduced as an abundantly available lignocellulosic feedstock material for scaled-up fuel-grade bioethanol production.

Table 2.1: Rice straw generation in major rice cultivating countries

Country	Annual rice straw generation (million tonnes)
China	74.70
India	60.08
Indonesia	23.33
Bangladesh	17.13
Vietnam	15.57
Thailand	12.15
Myanmar	9.86
Philippines	5.93
Brazil	4.60
Japan	4.44
Sri Lanka	2.80

2.2 Rice straw composition

The amounts of cellulosic compounds contained in rice straw are significant in bioethanol production. Thus, various rice straw compositions in the published literature are considered to obtain an accurate average value. Table 2.2, Table 2.3, and Table 2.4 represent cellulosic composition, ultimate analysis, and proximate analysis of globally distributed rice straw.

Table 2.2: Composition of rice straw generated in different countries

No	Reference	Country/source	Cellulose (% wt)	Hemicellulose (% wt)	Lignin (% wt)	Ash / other (% wt)
1	[22]	India	35 - 40	17 - 25	10 - 20	-
2	[18]	Japan	43	25	12	20
3	[23]	Thailand	37.1	26.8	15.1	21
4	[19]	Thailand	37.1	26.8	15.1	21
6	[24]	India	33 -47	19-27	5-24	18.3
7	[24]	China	33.35	31.42	4.84	30.39
8	[20]	India	36 - 40	15 - 20	20 - 30	-
9	[25]	-	(36.2 - 47)	(19-24.5)	(9.9-24)	-
10	[26]	Switchgrass	31.98	25.19	18.13	24.7
11	[27]	Taiwan	21–31	30–35	4–19	13.4
12	[28]	Sri Lanka	40	45	15	-
13	[29]	India	40	18	5.5–7.1	-
14	[30]	China	36.5	25.6	12.8	25.1
15	[1]	Colorado	26.45	27.29	28.03	18.23
16	[31]	China	37.5	26.9	11.7	23.9
17	[32]	India	38.1	19.9	14.1	27.9
18	[33]	-	32	36.7	22.3	9.0
19	[34]	-	32-47	19-27	(05-24)	-
20	[35]	-	41	21.5	14.8	22.7
21	[36]	Thailand	32-47	19-27	(05-24)	-
22	[37]	Sri Lanka	38.2	3.9	30	27.9
23	[38]	Taiwan	34.6	24.8	14.8	25.9
25	[13]	-	32-47	19-27	(5-24)	-
26	[39]	Taiwan	36.6	16.1	14.9	32.4
27	[40]	Iran	45.8	11.3	13.8	29.1
28	[41]	-	38.6	19.7	(5-24)	-
29	This study	Average	36.7	23.9	16.0	23.3

Table 2.3: The ultimate analysis composition of rice straw observed in different countries

No.	Reference	Country	Component (wt %)							
			C	H	S	N	O	Cl	Moisture	Ash
1.	[42]	Thailand (Ash-free basis)	38.17	5.02	0.09	0.58	35.28	-	10.0	-
2.	[42]	California (Ash-free basis)	35.20	4.79	0.17	0.80	33.92	-	10.0	-
3.	[43]	China	35.37	4.82	0.14	0.96	39.15	-	9.1	10.46
4.	[24]	India	38.24	5.20	0.18	0.87	36.26	0.58	-	18.67

Table 2.4: The proximate analysis composition of rice straw observed in different countries

No.	Reference	Country	Composition (wt %)			
			Fixed Carbon	Moisture	Volatile matter	Ash
1.	[43]	China	16.75	9.1	63.69	10.46
2.	[24]	India (Dry Basis)	15.86	-	65.47	18.67

2.3 Available process operations in the bioethanol production process using rice straw

Feedstock pretreatment, fermentation of sugar solution and bioethanol conversion, and bioethanol dehydration are the key process operations available in bioethanol production using rice straw. Different types of technologies are used in pre-treatment, fermentation, and dehydration operations. Table 2.5, Table 2.6, and Table 2.7 summarize the major pre-treatment, fermentation, and dehydration technologies available in the literature, respectively.

Table 2.5: Major pre-treatment technologies available in published studies

No.	Reference	Description	Pretreatment techniques			
			Technique	Conditions if available	Efficiency/conversion	
1	[22]	An LCA study to determine the global warming potential and the net energy analysis of second-generation bioethanol production in India. This study compares two different pre-treatment techniques. [i.e., Dilute acid pre-treatment (DA) and Steam explosion (SE)]	1. Dilute sulfuric acid pre-treatment	Temperature: 162 ^{o}C Pressure: 5 bars Acid concentration: 1(wt)% Residence time: 10 min	Glucose recovery Xylose recovery	95% 59%
			2. Steam explosion	Temperature: 190 ^{o}C Acid concentration: 0.5 (wt)% Residence time: 10 min	Glucose recovery Xylose recovery	59% 95%
2	[18]	This study analyses the net energy balance of a bioethanol production system from a high-yield rice plant cultivated in Japan. There are two scenarios, i.e., 01: - Bioethanol is produced only from rice grains and the required energy is cogenerated using rice straw and husks. 02: - Bioethanol is produced from the whole plant (including grains, straw, and husks). The required energy is cogenerated using lignin.	Concentrated acid pre-treatment	-	Efficiency	85%
3	[17]	A comparative LCA study on the utilization of rice straw as an alternative biofuel and fertilizer in Thailand. There are four options for rice straw utilization. 1. Direct combustion for both heat and power. 2. Bio-chemical conversion to bioethanol. 3. Thermochemical conversion to bio–Dimethyl Ether (DME). 4. Incorporation into the soil as an organic fertilizer.	Dilute acid pre-treatment	-	-	-

Table 2.5 continued.

4	[23]	A process simulation-based LCA study analyzes the bioethanol production process using cassava, cane molasses, and rice straw. There are three scenarios considering the bioethanol production process. 1. With total renewable fuels. 2. With non-renewable process energy supply. 3. With waste recovery and toxicity evaluation.	Dilute acid pre-treatment	Temperature: 121 ºC Pressure: 5 atm Residence time: 15 min	Recovery	90 %
5	[19]	A comparative study to compare the life cycle greenhouse gas emission of projected rice straw-based power plants and bioethanol production plants in Thailand.	Dilute acid pre-treatment	-	Cellulose and hemicellulose conversion	90 %
6	[44]	An LCA study was conducted to evaluate the net energy consumption, CO_2 emission, and production costs for bioethanol production using rice straw from two different paddy rice varieties: Koshihikari and Leafstar	Liquid hot water pretreatment and lime pretreatment	solid concentration - 30% (w/w) Liquid hot water conditions: Temperature - 80 °C Residence time - 1 h Lime pretreatments conditions:10 % lime Temperature - 120 °C Residence time - 1 h	-	-
7	[45]	A study to evaluate the best mild alkaline pretreatment condition for rice straw pretreatment to produce bioethanol	Mild alkaline pretreatment	Biomass loading – 20 % NaOH concentration – 1.5 % (w/w) Temperature – 121 ° C Residence time – 20 min	Cellulose conversion efficiency	91 %
8	[46]	A study proposing a cost-effective method to manage rice crop residue via bioethanol production using alkaline pretreatment	Alkaline pretreatment	NaOH concentration – 1 % Straw: NaOH loading rate – 1:10 Temperature – 121 °C, Pressure – 15 psi Residence time – 30 min	Glucan enrichment	63 %

Table 2.6: Major fermentation technologies available in published studies

No	Reference	Description	Fermentation			
			Technique	**Conditions if available**	**Conversion / efficiency (%)**	
1	[22]	An LCA study to determine the global warming potential and the net energy analysis of second-generation bioethanol production in India. This study compares two different pre-treatment techniques. [i.e., Dilute acid pre-treatment (DA) and Steam explosion (SE)]	Enzymatic hydrolysis and fermentation (for both pre-treatment techniques)	**Enzymatic hydrolysis conditions**	**Saccharification yield**	
				Enzyme: cellulase	1. DA	74
				Temperature: 50 ºC		
				WIS/ Total solid loading: 15% - 20%	2. SE	72
				Residence time: 48h		
				Fermentation conditions		
				Organism: *Saccharomyces cerevisiae*	**Glucose to EtOH**	90
				Temperature: 32 ºC	**Xylose to EtOH**	80
				Pressure: 1 bar		
				Residence time: 1 day		
2	[18]	This study analyses the net energy balance of a bioethanol production system from a high-yield rice plant cultivated in Japan. There are two scenarios, i.e., 01: - Bioethanol is produced only from rice grains and the required energy is cogenerated using rice straw and husks. 02: - Bioethanol is produced from the whole plant (including grains, straw, and husks). The required energy is cogenerated using lignin.	-	-	Efficiency	90
3	[17]	A comparative LCA study on the utilization of rice straw as an alternative biofuel and fertilizer in Thailand. There are four options for rice straw utilization. 1. Direct combustion for both heat and power. 2. Bio-chemical conversion to bioethanol. 3. Thermochemical conversion to bio–Dimethyl Ether (DME). 4. Incorporation into the soil as an organic fertilizer.	Enzymatic hydrolysis process & co-fermentation	Enzyme: cellulase	-	-

Table 2.6 continued.

4	[23]	A process simulation-based LCA study analyzes the bioethanol production process using cassava, cane molasses, and rice straw. There are three scenarios considering the bioethanol production process. 1. With total renewable fuels. 2. With non-renewable process energy supply. 3. With waste recovery and toxicity evaluation.	Enzyme hydrolysis and simultaneous saccharification and fermentation (SSF)	Enzyme: cellulase Temperature: 60 ºC Pressure: 1atm Residence time: 2h **SSF** Temperature: 30 ºC Pressure: 1 atm Residence time: 48h	Fermentation efficiency Glucose conversion Xylose conversion Yield from C5/C6 sugars	90 90 68 51
5	[19]	A comparative study to compare the life cycle greenhouse gas emission of projected rice straw-based power plants and bioethanol production plants in Thailand.	Enzyme hydrolysis & saccharification & co-fermentation	Enzyme: Cellulase Fermenting Organism: *Zymomonasmobilis*	Cellulose hydrolysis and recovery efficiency Glucose conversion Xylose conversion Yield from C5 /C6 sugars	90 90 67.5 51

Table 2.7: Major dehydration technologies available in published studies

No	Reference	Description	Dehydration technique	Entertainers/ solvents/ adsorbents used	Process conditions / Efficiency	
1	[22]	An LCA study to determine the global warming potential and the net energy analysis of second-generation bioethanol production in India. This study compares two different pre-treatment techniques. [i.e., Dilute acid pre-treatment (DA) and Steam explosion (SE)]	Pressure swing adsorption via molecular sieves	-	-	
2	[23]	A process simulation-based LCA study to analyze the bioethanol production process using cassava, cane molasses, and rice straw. There are three scenarios considering the bioethanol production process. 1. With total renewable fuels. 2. With non-renewable process energy supply. 3. With waste recovery and toxicity evaluation.	Extractive distillation	Ethylene glycol	Dehydration efficiency	99.9
					Reflux ratio	0.87
3	[47]	A study to determine the most cost-effective and environmentally benign heterogeneous azeotropic distillation technology for ethanol dehydration concerning the entrainer type adopted.	Heterogenic azeotropic distillation	Methyl tert-butyl ether	Number of stages	Reflux ratio
					Column 01: 23	4.05
					Column 02: 30	4.15
				Tert-amyl methyl ether	Column 01: 18	4.05
					Column 02: 18	5.15
				Ethyl tert-butyl ether	Column 01: 60	28
4	[44]	An LCA study was conducted to evaluate the net energy consumption, CO2 emission, and production costs for bioethanol production using rice straw from two different paddy rice varieties: Koshihikari and Leafstar	Vacuum extractive distillation	Glycerol	Energy consumption (MJ/L)	4.2

Table 2.7 continued.

5	[48]	This study reviews different dehydration technologies used in anhydrous bioethanol production from different feedstocks.	Pervaporation	-	Energy consumption (MJ/ kg ethanol)	Initial and final $X_{ethanol}$ (wt. %)
					4.61	8 – 99.5
			Solvent extraction	-	6.28	10 – 98
			Low-pressure distillation	-	11.72	6.4 – 98
			Azeotropic distillation	Benzene	15.49	6.4 – 99.95
				Pentane	10.05	6.4 – 99.95
				Diethyl ether	12.56	6.4 – 99.95
			Extractive distillation	Ethylene glycol	18.84	6.4 – 99.95
				Gasoline	9.21	6.4 – 99.95
			Extractive distillation with salt	Potassium acetate	9.27	7.5 – 60
				Calcium chloride	5.02	7.5 – 99
6	[49]	A study including a comparative analysis of the dehydration of ethanol based on adsorption processes and distillation-based processes	Temperature swing distillation	Wood pulp, Oak sawdust	Particle size (mm)	10 – 40
					Maximum adsorption (g water/kg ads /min)	3.78
			Concentration swing adsorption	Adsorbent: activated carbon	Particle size (mm)	0.4
					Pressure (bar)	3 – 5
				Desorbent: acetone	Temperature (°C)	25
					Maximum adsorption (mol ethanol /kg)	4.7

2.4 Available LCA studies on fuel-grade bioethanol production

There are several published LCA studies on bioethanol production using starch-based and lignocellulosic feedstocks, such as cassava, cane molasses, sweet potato, corn stover, wheat straw, rice straw, etc. Thailand utilizes cassava as a major feedstock to produce bioethanol, and there are many LCA studies conducted to evaluate the environmental impacts of related processes [23] [50] [51]. Net energy analysis and environmental impact assessments for the lifecycle of fuel-grade bioethanol production using sugar cane molasses are also conducted globally [51] [23] [52]. Similarly, there are published LCA studies for bioethanol production from other starch-based feedstocks, such as sweet potato and maize [3]. Table 2.8 showcases summarized LCA results for bioethanol production from starch-based feedstocks.

However, the utilization of edible feedstock to produce fuel-grade bioethanol threatens global food security. Thus, lignocellulosic materials, such as forest residue, rice straw, corn stover, wheat straw, etc. are more favorable feedstock options for bioethanol production. Even though pretreatment of lignocellulosic feedstock consumes higher energy in bioethanol production, the overall production process is sustainable and economically viable according to the published LCA studies. An LCA study conducted in the Netherlands to evaluate the bioethanol production process using corn stover shows that NER>1 and Renewability factor>1[53]. In addition, an LCA study conducted for bioethanol production from wheat straw in the UK shows a GHG emission of 3,359 kgCO_2 eq./m^3 of bioethanol [54]. Apart from them, rice straw is also a major lignocellulosic feedstock, which is widely used for fuel-grade bioethanol production. There are several LCA studies to evaluate the energy sustainability and the environmental impacts of fuel-grade bioethanol production using rice straw as a feedstock. Table 2.8 includes summarized LCA results for bioethanol production from lignocellulosic feedstocks.

An LCA study is performed in Thailand, to compare different value addition procedures for rice straw, i.e., fertilizer manufacturing, DME (Di Methyl Ether) production, bioethanol and biogas production, and direct combustion for electricity from rice straw. The value addition of rice straw avoids the hazardous effects contributed by the in-situ burning of rice straw. The compared LCA results show the production of bioethanol and biogas using rice straw is the most environmentally benign process [17].

A comprehensive LCA study conducted in Thailand compares the bioethanol production processes from cassava, rice straw, and cane molasses considering the following three scenarios, i.e., base case - Renewable process energy supply, scenario 01 – Non-renewable process energy supply, and scenario 02 – for waste recovery and toxicity evaluation. Process simulation is incorporated in this study to obtain unbiased results. The simulated results are contrasted with existing bioethanol plant information, to validate the accuracy of the results obtained. The use of sustainable design techniques, such as renewable process energy and sustainable waste treatment, increases the energy efficiency, renewability, and sustainability of all three feedstocks. The results show the highest sustainability approach to produce bioethanol from cassava in scenario 2. Even though the bioethanol generation from cassava results in the most sustainable approach in this study, bioethanol production from rice straw also shows a positive impact on sustainability with Net Energy Ratio, Renewability, and a reduced greenhouse gas emission of 0.85, 3.92, and 1,488.7 kgCO_2eq./m^3 of bioethanol, respectively [23].

A net energy analysis is conducted in Japan comparing two scenarios. i.e., scenario 1: - paddy rice to produce bioethanol and straw and husk for cogeneration and scenario 2: - paddy rice, rice straw, and husks to produce bioethanol and the by-products (lignin and unreacted cellulose and hemicellulose) for cogeneration. Both scenarios have resulted in positive energy values and energy ratios greater than one, concluding incorporating rice straw to produce bioethanol is a sustainable approach [18].

An LCA study is conducted in India to determine the most sustainable and environmentally benign approach to produce bioethanol from rice straw considering two different pre-treatment techniques, i.e., dilute acid pretreatment and steam explosion. The inventory data is collected from several experiments performed at an operating pilot-scale plant. Results show that both processes are environmentally benign processes and sustainable in energy perspective. This study concludes that the steam explosion life cycle scenario resulted in higher environmental and energy benefits. Net energy values for dilute acid pretreatment and steam explosion are 14.9 MJ/L and 16.3 MJ/L. Net Energy Ratios are 2.3 and 2.7 for both scenarios respectively. GHG reduction percentages for both scenarios are 77% and 89%, respectively [22]. These varied results conclude that the sustainability of the bioethanol production process depends on the technique used.

In addition to feedstock pretreatment, bioethanol dehydration is also an important step, which heavily influences the sustainability of bioethanol production using rice straw as feedstock. Despite there being many published LCA studies on bioethanol production using rice straw, there is no existing published LCA study to compare bioethanol dehydration techniques, combined with the feedstock pretreatment technologies. Hence, this study aims to conduct a comparative LCA to evaluate the process sustainability of scaled-up fuel-grade bioethanol production using unutilized rice straw, from energy and environmental perspectives, respectively.

Table 2.8: Summarized results in available published LCA studies

No	Reference	Country	Feedstock	Ethanol yield (L/tonne of rice straw)	Process energy (MJ/m^3 of bioethanol)	Net Energy Value (MJ/m^3 of bioethanol)	Net Renewable Energy Value (MJ/m^3 of bioethanol)	Net Energy Ratio	Renewability factor	Net GHG emission (kg CO_2 eq. / m^3 of bioethanol)
1	[23]	Thailand	Cassava	166.7	12,986	5,753.00	18,719	1.32	4.96	425
2	[50]	Thailand	Cassava	166.7	20,113	3,720.00	-	0.85	0.87	2,863
3	[51]	Thailand	Cassava	161.0	12,994	-	-	1.19	1.38	1,922
4	[51]	Thailand	Cane molasses	217.7	17,616	-	-	1.11	3.21	654
5	[23]	Thailand	Cane molasses	225.0	18,868	2,744.00	21,640	1.09	3.08	558
6	[52]	Mexico	Cane molasses	83.2	14,487	-	-	-	4.8	780
7	[3]	China	Sweet potato	156.5	10,730	-	-	1.48	1.57	1,474
8	[53]	Netherlands	Corn stover	300.0	9,500	-	-	1.09	2.12	-
9	[54]	UK	Wheat straw	330.5	9,500	-	-	-	-	3,359
10	[23]	Thailand	Rice straw	260.0	23,170	(4,331.00)	18,840.00	0.85	3.82	1,502
11	[17]	Thailand	Rice straw	260.0	28,734	-	-	-	-	1,312
12	[18]	Japan	Rice straw	373.0	22,890	1,648.00	-	1.17	3.46	-
13	[44]	-	Rice straw	250.0	11,560	-	-	-	-	1,145
14	[22]	India	Rice straw	239.0	18,394	6,978.00	14,900.00	1.36	2.30	1,222
15	[55]	Europe	Rice straw	-	-	(1,252.60)	-	0.20	-	-

CHAPTER 3

3. METHODOLOGY

In this study, a comprehensive life cycle assessment is performed to determine the most environmentally benign process routine to produce fuel-grade bioethanol at commercial scale from unutilized rice straw as the feedstock integrating the most environmentally benign feedstock pretreatment technology and bioethanol dehydration technology. Life cycle assessment (LCA) is a systematic methodology to identify the environmental impacts of a product/process throughout its life cycle. LCA of a product/process helps to,

- Identify potential hotspots (Processes where environmental impacts are higher) in the current process and improve the sustainability of the process.
- Make decisions in strategic planning, process development and redesigning, and achieving sustainability goals.
- Select the respective environmental and sustainability indicators.
- Market the process/product as an environmentally benign process/product.

The standard LCA framework is described under ISO 14040/44 standards and includes four main phases, i.e., goal and scope definition, life cycle inventory data analysis, life cycle impact assessment, and interpretation of results. Figure 3.1 interprets the LCA frameworks and the interrelationship among the respective steps.

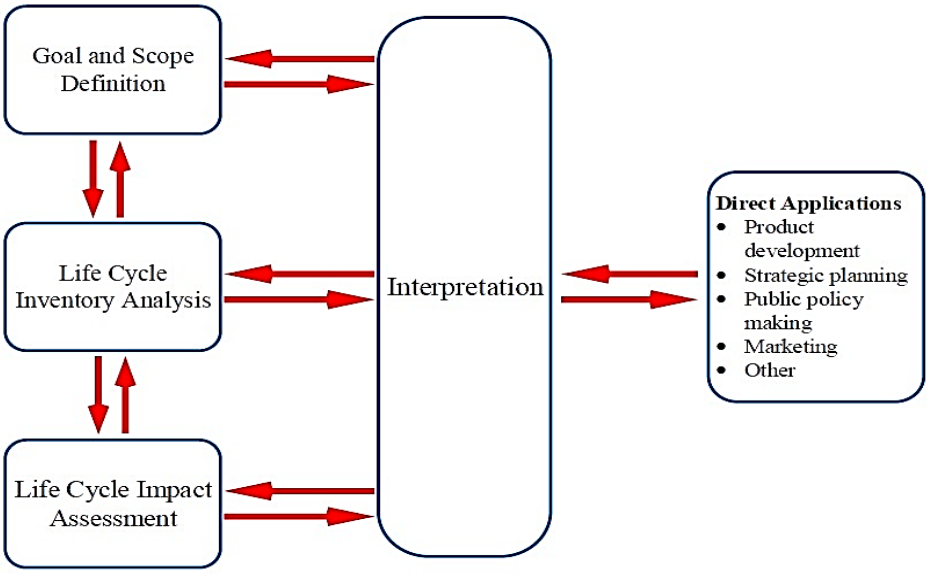


Fig. 3.1: Life Cycle Assessment Framework according to ISO 140040/44 standard

This study adopts the ISO 14040/44 standard methodology to evaluate the life cycles of different process routes for scaled-up fuel-grade bioethanol production plants from unutilized rice straw as feedstock. According to the standard LCA methodology, there are four interdependent phases, such as goal and scope definition, life cycle inventory data collection, life cycle impact assessment, and interpretation of results.

3.1 Goal and scope definition

The goal of this study is to conduct a comprehensive LCA to compare the possible process routes of scaled-up fuel-grade bioethanol production from unutilized rice straw with different feedstock pretreatment and bioethanol dehydration technologies. For a fair comparison of the process routes considered in this study, 1 m^3 of bioethanol with 99.7 vol % purity is selected as the functional unit. The considered life cycle system boundary of the scaled-up bioethanol production processes from unutilized rice straw has the cradle-to-gate life cycle scope starting from the unutilized rice straw collection stage to the bioethanol dehydration stage with final output at 99.7 vol % purity.

Figure 3.2 displays the considered cradle-to-gate system boundary of fuel-grade bioethanol production using unutilized rice straw as the feedstock.

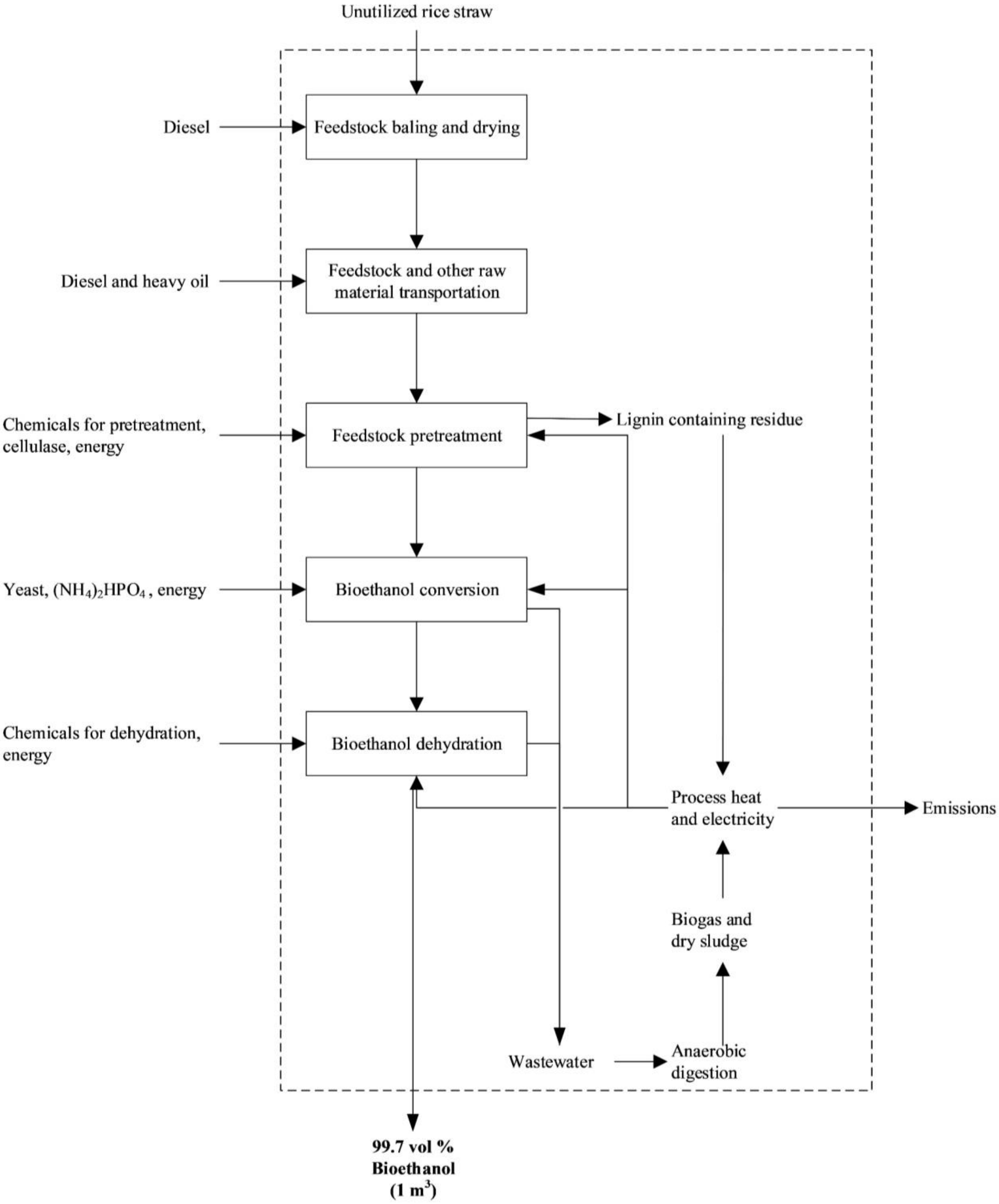


Fig. 3.2: System boundary for the life cycle of fuel-grade bioethanol production with 99.7 vol % purity using unutilized rice straw as the feedstock

3.2 Life cycle scenario description

Life cycle scenarios for the comparative LCA study are developed according to the different process routes considered in scaled-up bioethanol production from unutilized rice straw. Three feedstock pretreatment scenarios (dilute acid pretreatment, alkaline pretreatment, and steam explosion) and three bioethanol dehydration scenarios (extractive distillation, azeotropic distillation, and pressure swing distillation) are adopted to develop nine different process routes for scaled-up fuel-grade bioethanol production from unutilized rice straw.

In this study, the process simulation technology is used to model scaled-up fuel-grade bioethanol production plants from unutilized rice straw as the feedstock. Process simulation-based inventory calculations along with the relevant literature-based inventory data are analyzed based on the ISO 14040/44 standard LCA methodology.

3.2.1 Base-case scenario

The base-case life cycle scenario for fuel-grade bioethanol production from unutilized rice straw is defined by adopting dilute acid pretreatment as feedstock pretreatment technology and extractive distillation as the dehydration technology.

Initially, the base-case scenario is developed considering the Sri Lankan context to evaluate the life cycle net energy analysis and life cycle GHG emission analysis. The life cycle scope and considerations for the base-case scenario of this study adopting the Sri Lankan context are described as follows.

(a) **Life cycle scope and process description for the base-case scenario**

Figure 3.3 illustrates the cradle-to-gate system boundary for the fuel-grade bioethanol production life cycle for the base-case scenario. Since unutilized rice straw is the considered feedstock for this study, there is no inventory allocation from the paddy rice cultivation stage. Thus, the paddy rice cultivation stage can be excluded from the system boundary, and inventory data are evaluated starting from unutilized rice straw collection after paddy rice harvesting. Then the collected rice straw is dried, baled, and transported to the bioethanol processing plant.

Cellulose and hemicellulose are the main compounds in rice straw which are convertible into sugars via fermentation. However, the presence of lignin in rice straw hinders cellulose and hemicellulose recovery. Therefore, a pretreatment operation is required for rice straw to separate lignin and recover cellulose and hemicellulose. In this study, the dilute acid pre-treatment technique with diluted sulfuric acid (1 w/v%) is considered as the feedstock pre-treatment method. The aqueous phase containing cellulose and hemicellulose is then subjected to enzymatic hydrolysis to convert into glucose, xylose, and C_6/C_5 sugars. Thereafter, the solid phase containing lignin, ash, and other unconvertible residue is separated using a filter press. This solid residue is used as a fuel source to cogenerate process heat and power requirements. The remaining acidic sugar solution is then neutralized using $Ca(OH)_2$.

The neutralized sugar solution undergoes simultaneous saccharification and fermentation (SSF) in the presence of yeast (Saccharomyces cerevisiae) and $(NH_4)_2HPO_4$. After fermentation, a dilute ethanol solution (approximately 4.5 wt % of ethanol) is obtained and further purified using conventional distillation methods. To produce fuel-grade bioethanol, anhydrous bioethanol (> 99.5 vol % purity of ethanol) is required. Therefore, the ethanol solution that is purified using initial distillation is further dehydrated using extractive distillation to obtain fuel-grade bioethanol in the base-case scenario. Finally, the spent wash obtained from the distillation columns (in both initial distillation and dehydration units) is anaerobically digested (AD) to produce biogas. This biogas is used as a fuel to cogenerate process heat and power for the same production process.

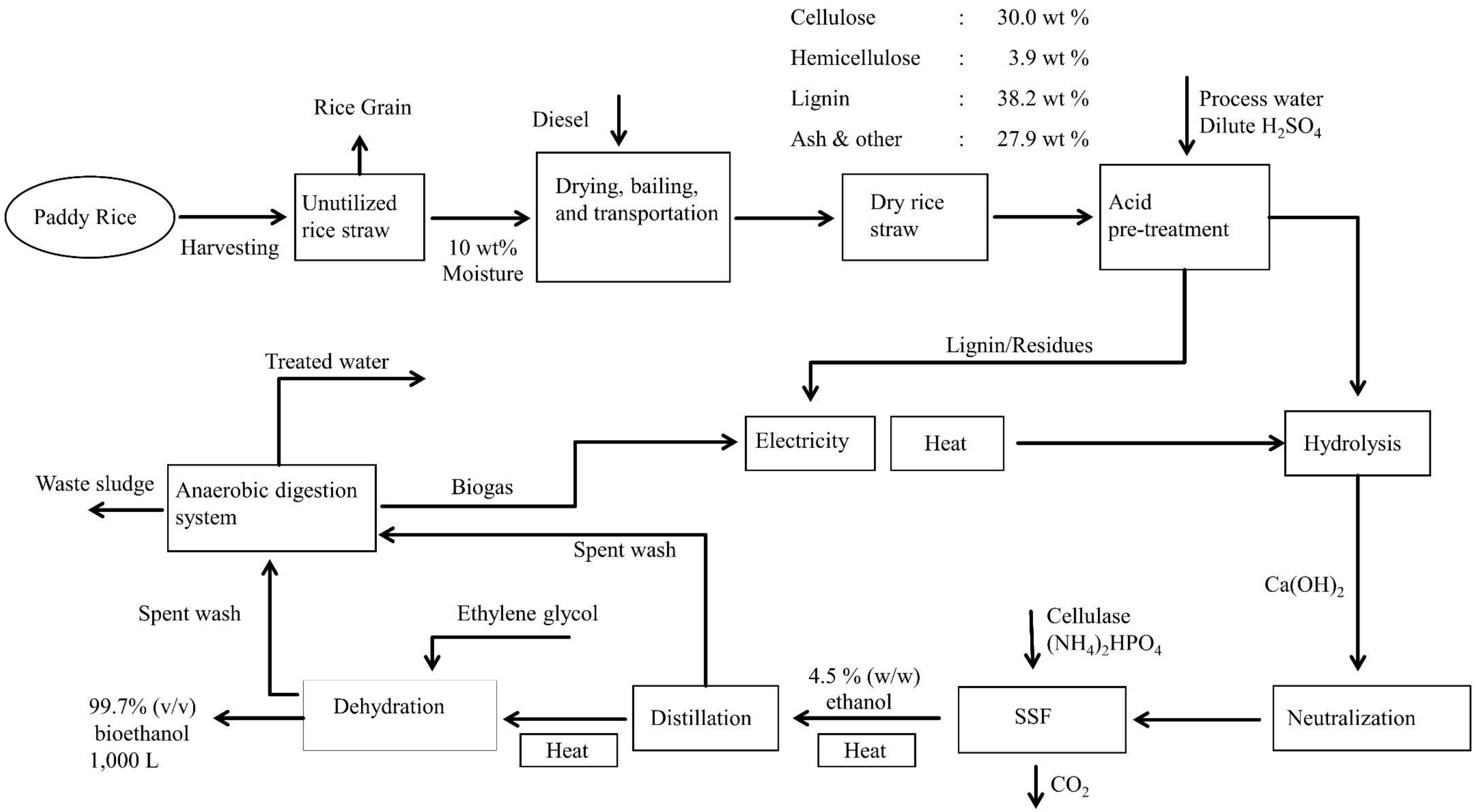


Fig. 3.3: System boundary for the base-case scenario

(b) Life cycle considerations for the base-case scenario

Energy consumption and generation in the modeled cradle-to-gate bioethanol production process for the base-case scenario are considered for the process net energy analysis and GHG assessment. Process simulations and inventory calculations are conducted for the process based on literature-based considerations.

- The life cycle considerations in this study are reached by taking Sri Lanka as the location
- Unutilized rice straw in Sri Lanka is used as the feedstock material for the base-case scenario to produce fuel-grade bioethanol
- The average moisture content in rice straw is approximately 10 wt%
- Dry rice straw in Sri Lanka has an average dry basis composition of cellulose: 30 wt %, hemicellulose: 3.9 wt %, lignin: 38 wt%, and others, including ash: 27.9 wt% [56]
- Energy inputs for transportation and raw materials/chemicals manufacturing processes are derived from fossil energy sources
- The effects of infrastructure processes are negligible at the considered scale of this study [23]
- Spent wash from bioethanol-producing stages is digested by Upflow Anaerobic Sludge Blanket (UASB) reactors to produce biogas (65% methane) [57]
- Biogas production rate from anaerobic digestion is calculated using equation 01

$$Generated\ Methane\ Amount(kg) = wastewater\ volume\ \times COD \times B_0 \times MCF \qquad (01)$$

Where, B_0 is the maximum possible methane-producing capacity (i.e., 0.25 kg-CH_4/kg-COD) and MCF is the Methane Conversion Factor (i.e., 0.8) [58].

- Recovered solid residues (after pre-treatment operation) and generated biogas are used to generate combined heat and power [19]
- The creditable surplus power generation is assigned to the grid-mix power in Sri Lanka.
- Gypsum coming out from neutralization and solid sludge generated from AD are used as fertilizers back in the paddy fields [23]
- The opportunity loss of rice straw utilization for the most possible valorization option, i.e., application as manure, is compensated through:
  - Utilizing dried AD sludge and gypsum as fertilizers [59]
  - Leaving an uncut straw height of about 15 cm above the ground [22]
  - The environmental credit by avoiding the open-field burning of rice straw [23]

Similarly, nine life cycle scenarios for fuel-grade bioethanol production from unutilized rice straw are developed considering the global average rice straw composition. Life cycle scenarios under global average rice straw composition are developed by adopting different feedstock pretreatment technologies and bioethanol dehydration technologies. In addition to net energy analysis, environmental life cycle impact assessments are evaluated for all life cycle scenarios corresponding to the global average rice straw composition.

3.2.2 Life cycle scenarios of feedstock pretreatment technologies

In addition to dilute acid pretreatment, alkaline pretreatment, and steam explosion technologies are two common technologies used to extract the convertible cellulose content in rice straw. Thus, this study adopts dilute acid pretreatment, alkaline pretreatment, and steam explosion technologies to create different life cycle scenarios for fuel-grade bioethanol production from unutilized rice straw, based on the type of feedstock pretreatment technology. Life cycle scenarios of feedstock pretreatment technologies, i.e., pretreatment scenarios (PS) are defined as follows.

- PS 01 – Dilute acid pretreatment scenario
- PS 02 – Alkaline pretreatment scenario
- PS 03 – Steam explosion pretreatment scenario

3.2.3 Life cycle scenarios of bioethanol dehydration technologies

Extractive distillation, azeotropic distillation, and pressure swing distillation are three different technologies used to dehydrate bioethanol. Different life cycle scenarios are created considering the dehydration method adopted in the process of fuel-grade bioethanol production from unutilized rice straw. Life cycle scenarios of feedstock pretreatment technologies, i.e., dehydration scenarios (DS) are defined as follows.

- DS 01 – Extractive distillation dehydration scenario
- DS 02 – Azeotropic distillation dehydration scenario
- DS 03 – Pressure swing distillation dehydration scenario

Figures 3.4 and 3.5 display the respective process block diagrams for fuel-grade bioethanol production with different pretreatment scenarios and dehydration scenarios, respectively. Combination of these pretreatment scenarios and bioethanol dehydration scenarios, nine life cycle scenarios are created for fuel-grade bioethanol production from unutilized rice straw as feedstock.

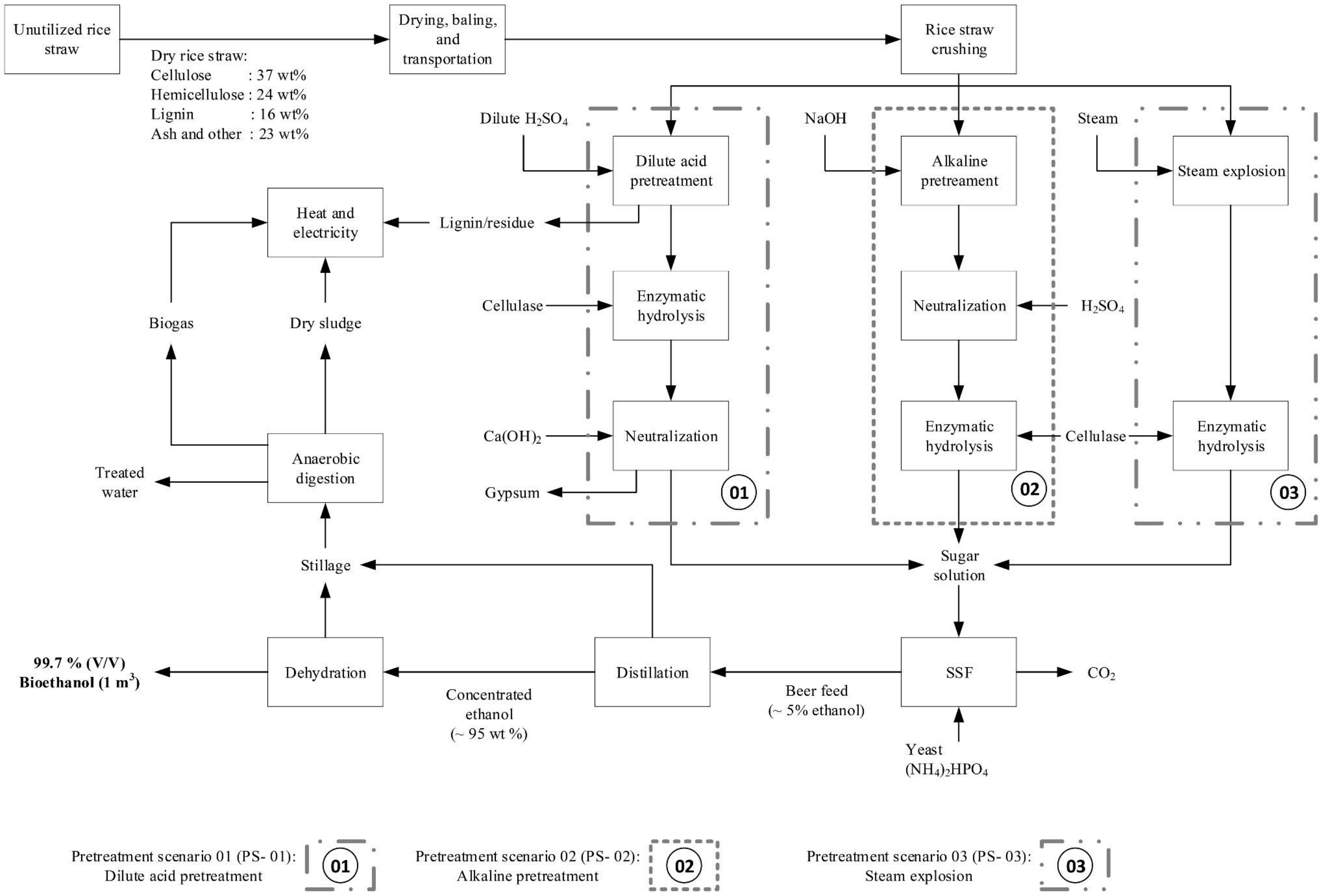


Fig. 3.4: Process flow diagram of fuel-grade bioethanol production using unutilized rice straw for different feedstock pretreatment scenarios

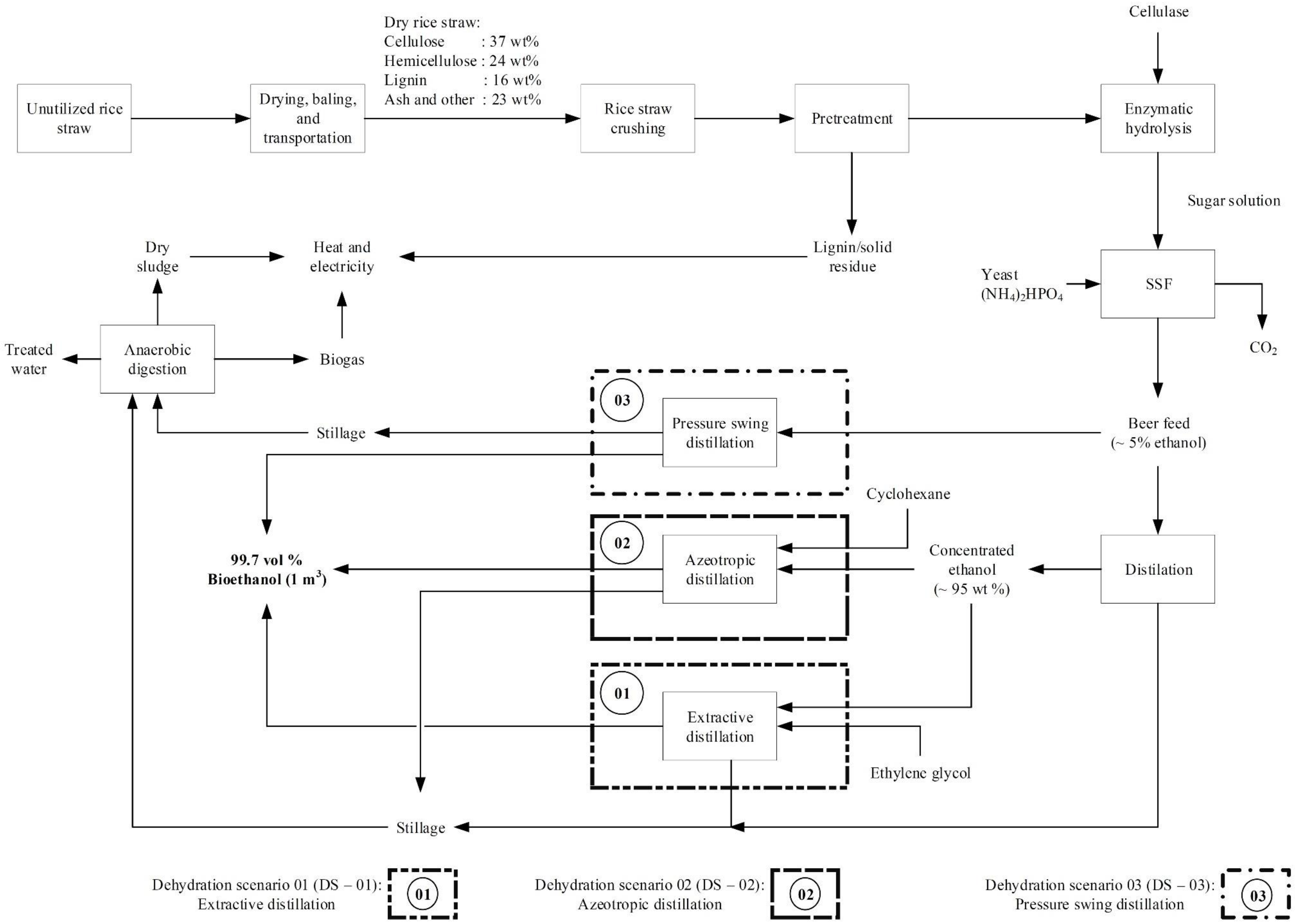


Fig. 3.5: Process flow diagram of fuel-grade bioethanol production using unutilized rice straw for different bioethanol dehydration scenarios

Table 3.1 lists the nine lifecycle scenarios with their corresponding feedstock pretreatment scenario and the bioethanol dehydration scenario.

Table 3.1: Feedstock pretreatment technologies and bioethanol dehydration technologies adopted in each lifecycle scenario

Life cycle scenario	Pretreatment technology	Dehydration technology
Scenario (a)	PS -01: Dilute acid pretreatment	DS 01: Extractive distillation
Scenario (b)		DS 02: Azeotropic distillation
Scenario (c)		DS 03: Pressure swing distillation
Scenario (d)	PS – 02: Alkaline pretreatment	DS 01: Extractive distillation
Scenario (e)		DS 02: Azeotropic distillation
Scenario (f)		DS 03: Pressure swing distillation
Scenario (g)	PS- 03: Steam explosion	DS 01: Extractive distillation
Scenario (h)		DS 02: Azeotropic distillation
Scenario (i)		DS 03: Pressure swing distillation

Energy flow inventory analysis, mass flow inventory analysis, and emission flow inventory analysis are performed for the nine life cycle scenarios along with the life cycle stages considered. Inventory data collection and calculations are performed for each scenario based on the considerations adopted in the base-case scenario. However, the global average rice straw composition is considered to develop the process simulation models. Additional considerations adopted are listed as follows,

- Dry rice straw has an average dry basis composition of cellulose: 37 wt %, hemicellulose: 24 wt %, lignin: 16 wt%, and others, including ash: 23 wt%.
- Recovered solid residues (after the pre-treatment operation and anaerobic digestion) and generated biogas are used to cogenerate process heat and power [19].
- Excess heat and power requirements are fulfilled by using renewable fuels, such as wood chips and rice husk.

3.3 Life Cycle Impact Assessment

In LCIA, the inventory data collected are transformed into net energy and environmental impact indicators. This study includes a life cycle net energy analysis and an environmental impact assessment.

3.3.1 Methodology for Net Energy Analysis

This study considers four net energy indicators given in equations 04, 05, 06, and 07 for the net energy analysis of the nine life cycle scenarios. Net energy inputs and net energy outputs for life cycle stages are calculated to evaluate the net energy indicators for each life cycle scenario.

$$Net\ Energy\ Value\ (NEV) = Total\ net\ energy\ outputs - Total\ net\ energy\ inputs \qquad 06$$

$$Net\ Energy\ Ratio\ (NER) = \frac{Total\ net\ energy\ inputs}{Total\ net\ energy\ outputs} \qquad 07$$

$$Net\ Renewable\ Energy\ Value\ (NRnEV) = Total\ net\ bioenergy\ outputs - Total\ net\ fossil\ energy\ input \quad 08$$

$$Renewability\ (Rn) = \frac{Total\ net\ bioenergy\ inputs}{Total\ net\ fossil\ energy\ outputs} \qquad 09$$

3.3.2 Methodology for Global Warming Potential (GWP) for the base-case scenario

The GWP is a measurement of the total GHG emissions from an activity, both directly and indirectly, or accumulated over the considered life cycle. The overall GWP value is calculated using equation 8 considering individual GHG emission amounts and their characterization factors for the global warming potential.

$$GWP = \sum GWP_i \times m_i \qquad (8)$$

GWP_i = Global Warming Potential value of substance i, m_i = amount of substance i

Initially, the global warming potential from the base case scenario is evaluated using manual calculations with the aid of Microsoft Excel software. The GWP_i values for individual GHGs, such as CO_2, CH_4, and N_2O applied in the Greenhouse gas protocol method are given in Table 3.2 [68].

Table 3.2: Global warming potential values for CO_2, CH_4, N_2O [9]

Emission	GWP value for 100-year time zone (IPCC fourth assessment report)
CO_2	1
CH_4	25
N_2O	298

GWP- Global Warming Potential
IPCC - Intergovernmental Panel on Climate Change

3.3.3 Methodology for environmental impact assessment

Attributional life cycle environmental impact assessment is evaluated according to ISO 14040/44 standards using SimaPro 9.1.1 software with the ReCiPe 2016 Midpoint (H) V1.03 characterization method. Impact assessment categories; global warming, stratospheric ozone depletion, ozone formation, human health, fine particulate matter formation, ozone formation, terrestrial ecosystems, terrestrial acidification, freshwater eutrophication, marine eutrophication, terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, human carcinogenic toxicity, and human non-carcinogenic toxicity are evaluated for the production of 1 m^3 of fuel-grade bioethanol at 99.7 vol % purity using unutilized rice straw as the feedstock.

CHAPTER 4

4. LIFE CYCLE INVENTORY ANALYSIS

4.1 Inventory data for upstream life cycle stages

The cradle-to-gate life cycle of the fuel-grade bioethanol production process using unutilized rice straw is further categorized into five life cycle stages, i.e., feedstock baling and drying stage, feedstock, raw materials, and renewable fuel transportation stage, feedstock pretreatment stage, bioethanol conversion stage, and bioethanol dehydration stage. 1,000 L (1 m^3) of fuel-grade bioethanol production at 99.7 vol % purity is selected as the functional unit for this study Energy, mass, and emission inventory data per 1 m^3 of bioethanol at 99.7 vol % purity, are collected considering life cycle stages for each life cycle scenario. Inventory data for the feedstock baling and drying stage, feedstock, raw materials, and renewable fuel transportation stage, raw material manufacturing procedures, and fuel combustion are collected from published literature sources.

4.1.1 Chemicals and raw materials manufacturing for bioethanol processing stages

Table 4.1 summarizes the average energy consumption for required chemicals and raw materials manufacturing. The energy content of direct steam used in the pre-treatment unit is calculated using steam properties. Emissions associated with the manufacturing phase of each chemical and raw material are adopted from the Eco-invent database.

Table 4.1: Average energy consumption for raw material manufacturing

Raw material name	Average energy consumption for manufacturing (MJ/kg)	Reference
H_2SO_4	5.8	[63]
NaOH	16.0	[22]
Enzymes	5.8	[64]
$Ca(OH)_2$	4.8	[65]
Yeast	5.8	[64]
$(NH_4)_2HPO_4$	25.6	[63]
Ethylene glycol	14.0	[63]
Cyclohexane	39.8	[66]

4.1.2 Feedstock baling and drying stage

The inventory data collection starts with the life cycle stage of feedstock baling and drying stage. This study uses unutilized waste rice straw as feedstock. Therefore, the inventory allocation for the rice cultivation stage is zero. Hence, the initial process step is to collect rice straw from the paddy fields into rice straw bales. Unutilized rice straw at the paddy rice cultivation fields is separated and collected into bales using a baling machine. The average bale size considered in this study is 0.2 m^3 and the average diesel consumed to bale 1 tonne of unutilized dry rice straw is 1.2 L [60].

According to process simulation results observed in the base-case scenario, 5.84 tonnes of dry rice straw are required to produce 1 m^3 of 99.7 vol% bioethanol. Thus, the baling and drying machine consumes 7.0 L of diesel/ m^3 of bioethanol (5.88 kg of diesel/ m^3 of bioethanol) in the base-case scenario. Similarly, diesel requirements for baling and drying machines in the alternative life cycle scenarios are calculated.

Table 4.2 displays the emission factors related to fuel combustion in farming machinery and transportation media. Respective emissions in diesel combustion in the feedstock baling and drying stage for all life cycle scenarios are obtained using the displayed emission factors.

Table 4.2: Emission factors related to fuel combustion in farming machinery and transportation media

Emission	Emission factors for diesel combustion			Emission factors for heavy oil combustion in shipping (mg/tkm)
	Farming machinery (mg/kg diesel)	10–tonne trucks (mg/tkm)	15–tonne trucks (mg/tkm)	
CO_2	2,640,000.00	74,000.00	70,000.00	6,200.00
CO	4,100.00	280.00	260.00	24.00
CH_4	93.00	1.00	1.00	0.20
NO_x	25,000.00	600.00	560.00	130.00
N_2O	21.00	1.60	1.50	0.20
NH_3	8.80	0.20	0.20	0.02
SO_2	-	-	-	57.00
NMVOC	2,300.00	1.30	0.21	-
Particulates	1,300.00	11.00	11.00	-

4.1.3 Feedstock, raw material, and renewable fuel transportation stage

The feedstock, raw material, and fuel transportation stage considers feedstock transportation from paddy fields, raw material/chemicals transportation from foreign countries to the process plant, and renewable fuel (wood chips and rice husk) transportation from local suppliers to the process plant. A 10-tonne truck with a fuel economy of 4.5 km/L is used for feedstock transportation, renewable fuel transportation, and inland transportation of raw materials. Average round trip transportation distances for feedstock transportation from paddy fields, inland transportation of raw materials/chemicals from the local port to the process plant, and woodchips and rice husks transportation from local suppliers are 100 km, 400 km, and 100 km, respectively. The diesel volumes consumed for feedstock transportation from paddy fields, inland transportation of raw materials/chemicals from the local port to the process plant, and woodchips and rice husks transportation from local suppliers for each scenario are calculated using equation 01 [60].

$$Diesel\ volume\ (L) = \frac{distance\ (km) \times material\ amount\ (km)}{truck\ fuel\ economy\ \left(\frac{km}{L}\right) \times trcuck\ capacity\ (tonne)} \qquad 01$$

The average nautical distance to transport raw materials/chemicals from foreign countries to the local port is considered 6,000 km. Energy consumption in nautical transportation is calculated using equation 02 [60].

$$E_{nautical} = 0.08\ \left(\frac{MJ}{tonne.km}\right) \times nautical\ distance\ (km) \times material\ amount\ (tonne) \qquad 02$$

The average energy required to transport one tonne of material amount for one km nautical distance is taken as 0.08 MJ/tonne.km.

The volume of diesel required for feedstock transportation from paddy fields to the bioethanol plant is 12.97 L/ m^3 of bioethanol for the base-case scenario under the Sri Lankan context. Table 4.3 summarizes the total energy consumption for transportation of each chemical used in the process for the same life cycle scenario.

Table 4.3: Energy consumption in transportation of raw materials

Raw Material	Consumption (kg / m^3 of bioethanol)	$E_{nautical}$ (MJ / m^3 of bioethanol)	$E_{inland\ transport}$ (MJ / m^3 of bioethanol)	E_{total} (MJ / m^3 of bioethanol)	Reference
H_2SO_4	636.02	305.29	256.12	561.41	[22]
$Ca(OH)_2$ [a]	480.47	230.63	193.48	424.11	-
$(NH_4)_2HPO_4$	15.41	7.40	6.21	13.61	[22]
Enzyme	26.70	12.82	10.75	23.57	[23]
Yeast	8.23	3.95	3.32	7.27	[23]
Ethylene Glycol [a]	0.28	0.13	0.11	0.25	-

[a] Calculated values from process simulations

Thus, corresponding energy consumption in feedstock, raw material, and renewable fuel transportation stage for nine life cycle scenarios is calculated similarly.

Table 4.2 lists emission factors for diesel and heavy oil combustion in feedstock, raw materials, and renewable fuel transportation stage for each life cycle scenario.

The bioethanol processing life cycle stages to produce 1 m^3 of fuel-grade bioethanol with 99.7 vol% from unutilized rice straw for nine life cycle scenarios are simulated using Aspen Plus simulation software. The material and energy consumption/generation results from process simulation models are used to develop the energy, mass, and emission inventories for bioethanol processing stages.

4.2 Process simulation for bioethanol conversion processing life cycle stages

After the feedstock transportation stage, the feedstock is transformed for bioethanol processing stages to produce fuel-grade bioethanol. Bioethanol processing life cycle stages, including the feedstock pretreatment stage, bioethanol conversion stage, and bioethanol dehydration stage are simulated using Aspen Plus process simulation software. In this study, nine process simulation models are developed for the nine life cycle scenarios considered under the global average rice straw composition. The required inventory data for material, energy, and emission flow for bioethanol processing life cycle stages are calculated using process simulation results.

The R-Stoic reactor model and the RadFrac rigorous distillation model in the Aspen plus model library environment are used to simulate reactors and distillation columns, respectively. The Non-Random Two Liquid (NRTL) activity coefficient model is used as the thermodynamic property method to simulate the feedstock pretreatment stage and bioethanol conversion stage. The thermodynamic property method used to simulate the bioethanol dehydration stage is the Universal Quasichemical - Redlich Kwong (UNIQ-RK) activity coefficient model.

The process simulation results are used to evaluate the energy requirements for the bioethanol production process for each life cycle scenario. The lignin-containing solid residue from the feedstock pretreatment stage and biogas and dried sludge obtained after wastewater treatment are used as fuel to cogenerate process energy. Additional power and heat requirements are compensated by the combustion of renewable fuels, such as wood chips and rice husk. summarizes the CHP efficiencies adopted for each fuel utilized in the fuel-grade bioethanol production process.

Table 4.4: Fuels, heating values, and efficiencies for the calculation of process energy cogeneration

Fuel type	**LHV*** **(MJ/kg)**	**Combined Heat and Power unit efficiencies**			**Reference**
		η_B	η_E	η_{CHP}	
Biogas	22.40	0.90	0.35	0.80	[23]
Lignin\ solid residue	19.00	0.90	0.32	0.82	[61]
Woodchips\rice husks	14.00	0.90	0.32	0.82	[61]

[*] LHV- Lower Heating Values

The wastewater volume generated in the base-case scenario is 18.25 $m^3/\ m^3$ of bioethanol. The corresponding COD value is calculated considering the composition of wastewater. Table 4.5 represents the wastewater composition resulting from the base-case scenario.

Table 4.5: Concentration of organic components in generated wastewater in base-case scenario (Calculated values using process simulation results)

Component	**Concentration (g/L)**
Glucose	9.60
Xylose	4.08
Ethanol	5.29
Ethylene Glycol	3.18×10^{-5}

The calculated COD value of wastewater for the base-case scenario context is 14.41 kg/m^3. Thus, the corresponding amount of CH_4 generation is 73.64 $m^3/\ m^3$ of bioethanol, and the generated biogas (65 % CH_4) amount is 113.29 $m^3/\ m^3$ of bioethanol.

In addition, cogenerated heat and power amounts for the same scenario are summarized in Table 4.6. Since excess heat and power are cogenerated, other renewable fuels are not utilized in the base-case scenario.

Table 4.6: Process energy cogeneration for the base-case scenario

Fuel type	**Energy generation (MJ/ m^3 of bioethanol)**	
	Heat	**Power**
Biogas	1,141.9	888.2
Solid residue	43,922.3	10,017.4

As such, calculations for process energy supply are performed for the alternative life cycle scenarios. For the life cycle scenarios demanding excess energy, wood chips and rice husk are used as fuel to cogenerate excess energy demand.

Further, the emissions resulting from bioethanol production processes are calculated according to the type of energy consumed, energy source, and their respective emission factors. The emission factors for each fuel utilized in bioethanol production processes for all bioethanol production life cycle scenarios are listed in Table 4.7 [23].

Table 4.7: Literature-based emission factors for combustion of fuel

Emissions	Energy source			
	Biogas (mg/MJ)	**Wood chips/Rice husks (mg/MJ)**	**Lignin and other solid residues (mg/MJ)**	**Sri Lankan energy grid-mix (kg/kWh)**
CO_2	-	-	-	0.549
CO	310.00	90.00	90.00	0.000288
CH_4	440.00	3.10	3.10	-
NO	-	-	-	0.00139
NO_x	200.00	81.00	81.00	-
N_2O	1.60	0.80	0.80	-
SO_2	-	1.90	1.90	0.00172
NMVOC	10.00	5.10	5.10	-
Particulates	-	61.00	61.00	-

4.2.1 Feedstock pretreatment stage

In this life cycle stage, transported unutilized rice straw is first crushed, pretreated, and subjected to enzymatic hydrolysis to obtain a sugar solution according to the pretreatment scenario (i.e., PS – 01, PS – 02, and PS – 03) adopted in each life cycle scenario.

Initially, unutilized rice straw is crushed (< 10 mm particle size) using a knife mill having a handling capacity of 200 kg/hr with an average power-consuming rate of 5 kWh [60]. Then, the crushed rice straw is pretreated and hydrolyzed according to the pretreatment scenario adopted.

(a) PS 01 – Dilute acid pretreatment

In pretreatment, scenario 01 (PS – 01), dilute sulfuric acid is used to pretreat rice straw to extract the sugar convertible cellulose and hemicellulose content to a slurry-liquid phase. Initially, rice straw is mixed with dilute sulfuric acid, water, and high-pressure steam at 121 °C for five hours. Next, solid residue containing lignin, unconverted cellulose/hemicellulose, and other solid components are separated using a filter press. The liquid phase containing sugar-convertible cellulose and hemicellulose is then hydrolyzed at 55 °C for 24 hours using cellulase as the enzyme. The acidic sugar solution is neutralized using $Ca(OH)_2$. The neutralization process produces gypsum as a byproduct which is reused as a fertilizer in paddy rice cultivation fields.

(b) PS 02 – Alkaline pretreatment

Dilute NaOH is used as the alkaline medium to pretreat rice straw in PS – 02. Initially, crushed rice straw is soaked in dilute NaOH solution for five hours and then pretreated at 121 °C for 20 minutes [45]. After the pretreatment, the alkaline slurry with black liquor is neutralized using dilute sulfuric acid. Then the liquid solution containing recovered cellulose and hemicellulose is separated from the black liquor slurry and transferred for enzymatic hydrolysis. The sugar solution resulting from enzymatic hydrolysis is sent to the SSF unit for bioethanol conversion.

(c) PS 03 – Steam Explosion

In the steam explosion of rice straw, high-pressure steam at 10-bar is injected three times into the straw digester. The operating temperature for the explosion is 200 °C and the reaction is carried out for 10 minutes per steam injection. Next, the recovered cellulose and hemicellulose mixture is separated using a filter press. The cellulose-rich solution is then subjected to enzymatic hydrolysis with cellulase for 48 hours.

Table 4.8 lists the process conditions, related chemical reactions, conversions, and efficiencies for pretreatment scenarios adopted in this study.

The lignin-containing residue separated after the pretreatment of rice straw in every scenario is used as a fuel to cogenerate process energy and heat. Finally, the sugar solution resulting in each pretreatment scenario is sent to the fermentation and bioethanol conversion processing stages.

Table 4.8: Process conditions for feedstock pretreatment technologies

Equipment	**Parameter**	**Pretreatment scenario**		
		PS – 01	**PS – 02**	**PS – 03**
Pretreatment unit	Operating conditions	5 bar, 121 °C for 15 minutes	5 bar, 121 °C for 20 minutes	10 bar, 200 °C, 10 minutes
	Pretreatment agent	Dilute H_2SO_4	Dilute NaOH (2 M)	Steam at 10 bar 200 °C
	Reactions involved	-	-	-
Neutralization unit	Operating conditions	60 °C, 1 atm	50 °C, 1 atm	-
	Neutralizing agent	$Ca(OH)_2$	H_2SO_4	-
	Reactions involved	$H_2SO_4(aq) + Ca(OH)_2(aq) \rightarrow CaSO_4(s) + H_2O(l)$	$NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O(l)$	-
Enzymatic hydrolysis unit	Operating conditions	Solid loading rate = 3:1 At 162 °C, 5 bar For 24 hr $X_{cellulose} = 90\%$ $X_{hemicellulose} = 90\%$	Solid loading rate = 4:1 At 50 °C, 5 bar For 48 hr $X_{cellulose} = 90.3\%$ $X_{hemicellulose} = 92.4\%$	Solid loading rate = 6:1 At 55 °C, 1 bar for 72 hr $X_{cellulose} = 86\%$ $X_{hemicellulose} = 86\%$
	Enzymes used	Cellulase		
	Reactions involved	$C_6H_{10}O_5(aq) + H_2O(aq) \xrightarrow{Enzyme} C_6H_{12}O_6(aq)$ $C_5H_8O_4(aq) + H_2O(aq) \xrightarrow{Enzyme} C_5H_{10}O_5\ (aq)$		
Reference		[23], [60]	[45]	[62]

4.2.2 Bioethanol conversion stage

The sugar solution obtained from the pretreatment scenario is fermented in an SSF (Simultaneous Saccharification and Fermentation) unit using yeast (Saccharomyces cerevisiae). After fermentation, a dilute ethanol solution is obtained with an ethanol concentration of around 5 – 7 wt %. This dilute ethanol solution is then concentrated using conventional distillation technologies. Table 4.9 displays the process conditions, related reactions, conversions, and efficiencies adopted for unit operations in the bioethanol conversion stage.

4.2.3 Bioethanol dehydration stage

In this life cycle stage, the ethanol produced at the bioethanol conversion stage is further dehydrated to obtain fuel-grade bioethanol. Due to the azeotrope formed between ethanol and water at 95.0 wt%, advanced distillation technologies are used to dehydrate bioethanol produced at the bioethanol conversion stage. This study considers three bioethanol dehydration scenarios to dehydrate bioethanol to produce 1 m^3 of fuel-grade bioethanol with a purity of 99.7 vol%. Table 4.10 shows the process operation conditions of each dehydration scenario adopted in this study.

(a) DS – 01: Extractive distillation

In extractive distillation, ethylene glycol is used as the solvent to extract ethanol from an ethanol-water solution. Two distillation columns are used in extractive distillation; the major column to dehydrate bioethanol and the second column to recover ethylene glycol.

(b) DS – 02: Azeotropic distillation

Cyclohexane is used as the entrainer in azeotropic distillation to dehydrate concentrated bioethanol produced at the bioethanol conversion stage. There are two columns in operation in azeotropic distillation as in extractive distillation; the first column is to dehydrate bioethanol and the second column is to recover cyclohexane.

(c) DS – 03: Pressure swing distillation

The beer feed resulting after SSF in the bioethanol conversion stage (before distillation) is directly transferred for dehydration in pressure swing distillation. In pressure swing distillation, two distillation columns are adopted; one column operates at a lower pressure (0.1 bar) and the secondary column operates at a higher pressure (20 bar). The variation of pressure in columns changes the azeotropic concentration to higher ethanol concentrations, reducing the water content in the azeotrope.

Table 4.9: Process conditions for bioethanol conversion processing stages

Unit	**Chemicals used**	**Operating conditions**			**Reactions involved**
		PS – 01	**PS – 02**	**PS – 03**	
SSF	Yeast $(NH_4)_2HPO_4$	30°C at 1 atm for 48 h $X_{glucose} = 90.0\ \%$ $X_{xylose} = 68.0\ \%$ $\eta_{yield} = 51\ \%$	30°C at 1 atm for 48 h $X_{glucose} = 100.0\ \%$ $X_{xylose} = 50.0\ \%$ $\eta_{yield} = 51\ \%$	30°C at 1 atm for 48 h $X_{glucose} = 93.1\ \%$ $X_{xylose} = 71.9\ \%$ $\eta_{yield} = 51\ \%$	$C_6H_{12}O_6(aq) \rightarrow 2\ C_2H_5OH(aq) + 2\ CO_2(g)$ $3C_5H_{10}O_5(aq) \rightarrow 5\ C_2H_5OH(aq) + 5\ CO_2(g)$
Distillation	-	Pressure: 1 atm Number of stages: 30 Reflux ratio: 7.70	Pressure: 1 atm Number of stages: 30 Reflux ratio: 3.02	Pressure: 1 atm Number of stages: 30 Reflux ratio: 6.16	-
References		[23], [60]	[45]	[62]	

Table 4.10: Process conditions for bioethanol dehydration technologies

Parameter	**DS – 01**		**DS – 02**		**DS – 03**	
	Column 01	**Column 02**	**Column 01**	**Column 02**	**Column 01**	**Column 02**
Operating pressure (atm)	0.81	0.26	1.00	1.00	0.10	20.00
Chemicals/solvents used	Ethylene glycol	-	Cyclohexane	-	-	-
Number of stages	20.00	12.00	30.00	20.00	20.00	50.00

4.3 Creditable environmental emissions

The bioethanol production itself utilizes green energy throughout the process and there is a surplus power within the plant. This surplus power is credited to the Sri Lankan national power grid mix. Accordingly, the corresponding emissions can be credited. Table 4.11 represents the emission factors for the Sri Lankan electricity grid mix [67].

Table 4.11: Emission factors for Sri Lankan electricity grid-mix [67]

Emission type	**Emission factors (kg/kWh)**
CO_2	5.49×10^{-1}
SO_2	1.72×10^{-3}
NO	1.39×10^{-3}
CO	2.88×10^{-4}

CHAPTER 5

5. RESULTS AND DISCUSSION FOR THE BASE-CASE SCENARIO

5.1 Process simulation results

Figure 5.1 displays the process simulation flowsheet, including detailed material and energy flow for the base-case scenario of fuel-grade bioethanol production from unutilized rice straw in Sri Lanka. According to simulation results, the bioethanol yield with 99.7 vol % purity from unutilized rice straw in the scaled-up process is 171.34 L /tonne of rice straw (dry basis). The scaled-up bioethanol plant for the base-case scenario was simulated in the Aspen Plus process simulation software to obtain 1m^3 of bioethanol at 99.7 vol % purity. According to the simulation results, 5.84 tonnes of unutilized rice straw (dry basis) is required to produce 1 m^3 of bioethanol at 99.7 vol % purity.

Table 5.1 lists the process simulation-based results for process energy consumption in each plant equipment in the scaled-up plant for the base-case scenario, including the rice straw crusher for pre-processing. The total process energy consumption by all plant equipment is 24,314.8 MJ/ m^3 of bioethanol where the total steam consumption is 16,378.4 MJ/ m^3 of bioethanol and the total power consumption is 7,936.3 MJ/ m^3 of bioethanol.

Table 5.2 shows bioethanol yield and total process energy input, reported in other published studies in comparison to the same parameters in the base-case scenario. Accordingly, the process energy input resulting from the simulation model in this study is comparable with that of bioethanol production plants, as reported in the already published literature. However, the bioethanol yield in the base-case scenario is lower compared to other studies. The plausible reason is the lower cellulose and hemicellulose content in the Sri Lankan rice straw that was considered in this case study. Therefore, process simulations performed for the base-case scenario can be validated for the retrieval of life cycle inventory data.

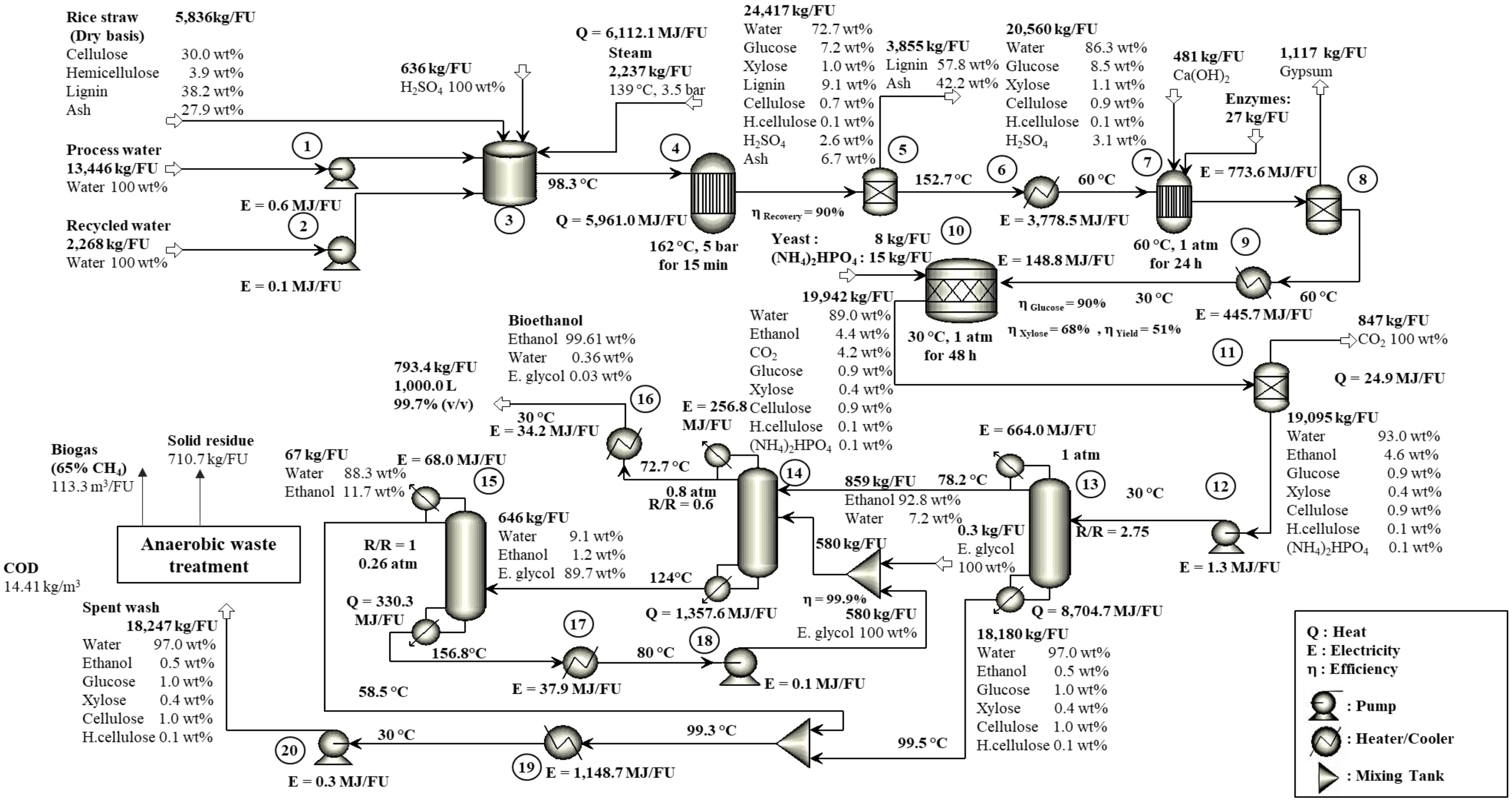


Fig. 5.1: Process simulation flowsheet for scaled-up bioethanol production plant from unutilized rice straw. Where, 1: Pump no.1, 2: Pump no. 2, 3: Mixing tank, 4: Pre-treatment unit, 5: Filter no. 1, 6: Cooler no. 1, 7: Neutralizing unit, 8: Filter no. 2, 9: Cooler no. 2, 10; SSF unit, 11: Scrubber, 12: Pump no. 2, 13: Concentration column, 14: Dehydration column 1, 15: Dehydration column 2, 16: Cooler no. 3, 17: Cooler no. 4, 18: Pump no. 3, 19: Spent wash cooler, 20: Spent wash pump

Table 5.1: Energy consumption results for individual plant equipment in base-case scenario (basis: 1 m^3 of bioethanol at 99.7 vol% purity)

No	**Equipment**	**Energy consumption (MJ/m^3 of bioethanol)**		
		Heat	**Power**	**Total**
1	Crusher	-	577.8	577.8
2	Pump no. 1	-	0.6	0.6
3	Pump no. 2	-	0.1	0.1
4	Mixing tank	-	0.05	0.05
5	Pretreatment unit	5,961.0	-	5,961.0
6	Filter no. 1	-	0.03	0.03
7	Cooler no. 1	-	3,778.5	3,778.5
8	Neutralizing unit	-	773.6	773.6
9	Filter no. 2	-	0.02	0.02
10	Cooler no. 2	-	445.7	445.7
11	SSF	-	148.8	148.8
12	Scrubber	24.9	-	24.9
13	Pump no. 3	-	1.4	1.4
14	Concentration column	8,704.7	664.0	9,368.6
15	Dehydration column 1	1,357.6	256.8	1,614.4
16	Dehydration column 2	330.3	67.9	398.3
17	Cooler no. 3	-	34.2	34.2
18	Cooler no. 4	-	37.9	37.9
19	Pump no. 4	-	0.1	0.1
20	Spent wash cooler	-	1,148.7	1,148.7
21	Spent wash pump	-	0.3	0.3
22	Total	16,378.4	7,936.4	24,314.8

Table 5.2: Literature-based comparison of process parameters

Country	**Process ethanol yield (L/tonne of rice straw)**	**Process energy consumption (MJ/ m^3 of bioethanol)**			**References**
		Heat	**Power**	**Total**	
Thailand	260.0	17,467.0	5,703.0	23,170.0	[23]
India	239.0	16,345.5	2,048.5	18,394.0	[22]
Japan	250.0	-	-	11,560.0	[44]
Japan	373.0	-	-	22,890.0	[18]
Thailand	260.0	-	-	28,734.0	[17]
Sri Lanka	171.3	16,378.4	7,936.4	24,314.8	[60]

Energy inputs for each life cycle stage in the considered system boundary are calculated considering the process energy consumption and energy uptake for manufacturing and transportation of raw materials/chemicals for the base-case scenario. The total heat consumption, total power consumption, and percentage energy consumption for each life cycle stage are summarized in Table 5.3.

Table 5.3: Energy consumption results for process stages for base-case scenario (basis: 1 m^3 of bioethanol at 99.7 vol% purity)

Stage	**Energy consumption (MJ/ m^3 of bioethanol)**			
	Fossil	**Heat**	**Power**	**Total per stage**
Feedstock baling and drying	317.28	-	-	317.28
Feedstock and raw material transportation	1,617.76	-	-	1,617.76
Feedstock Pretreatment				23,780.06
1. Chemicals / raw materials	6,130.67	-	-	
2. Direct steam	-	6,112.11	-	
3. Process	-	5,960.95	5,576.33	
Bioethanol conversion				9,986.04
1. Chemicals / raw materials	442.36	-	-	
2. Process	-	8,729.54	814.13	
Bioethanol dehydration				3,237.72
1. Chemicals / raw materials	3.90	-	-	
2. Process energy	-	1,687.95	1,545.87	
Total	8,511.97	22,490.55	7,936.33	38,938.85

Figure 5.2 indicates the graphical representation of stage-wise energy consumption for the base-case scenario. The feedstock pre-treatment stage is responsible for 61.1 % of the total cradle-to-gate energy input, which is the highest energy uptake stage. The bioethanol conversion stage corresponds to the second highest energy consumption (25.7 % of the total).

The bioethanol dehydration stage utilizes only about 8.3 % of the total energy requirement, which implies that converting hydrous bioethanol to fuel-grade anhydrous bioethanol is not highly energy-intensive compared to other upstream bioethanol conversion operations. Thus, upgrading an existing bioethanol plant to obtain fuel-grade bioethanol via extractive distillation is feasible without incurring high energy demand for the upgraded section of the bioethanol plant.

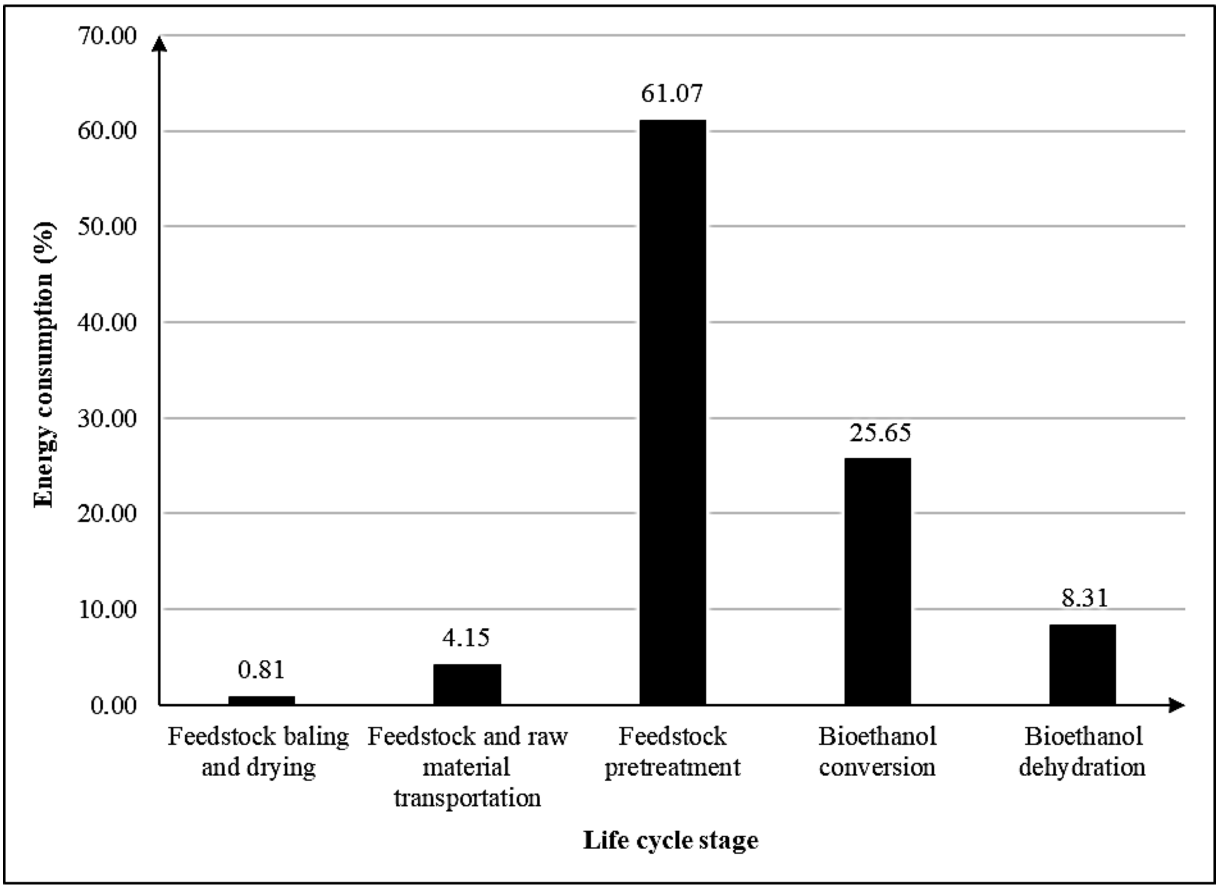


Fig. 5.2: Life cycle stage-wise energy consumption in cradle-to-gate system boundary of base-case scenario

5.2 Life cycle net energy analysis for the base-case scenario

Table 5.4 lists the life cycle net energy balance, including the calculated net energy indicators for the cradle-to-gate bioethanol production from unutilized rice straw in Sri Lanka. The total net energy input is 38,938.9 MJ/ m^3 of bioethanol, which contains the total net fossil fuel energy input of 8,512.0 MJ/ m^3 of bioethanol. The total net energy output is 46,742.8 MJ/ m^3 of bioethanol, which is entirely a bioenergy output (surplus process energy + energy content in bioethanol). Calculation results for NEV and NRnEV are positive values (7,804.0 MJ/ m^3 of bioethanol m^3 of bioethanol and 38,230.9 MJ/ m^3 of bioethanol, respectively) as well as NER and Rn for the process, are greater than 1 (1.20 and 5.49, respectively).

Table 5.4: Net energy balance for cradle-to-gate bioethanol process from unutilized rice straw for the base case scenario (basis: 1 m^3 of bioethanol at 99.7 vol% purity)

Description	**Energy input/output (MJ/ m^3 of bioethanol)**		
	Heat	**Power**	**Fossil**
Feedstock baling and drying stage	-	-	317.3
Feedstock, raw materials, and renewable fuel transportation stage			
Feedstock transportation	-	-	587.6
Raw Materials/Chemicals transportation			1,030.2
Feedstock pretreatment stage			
Raw material manufacturing	6,112.1		6,130.7
Direct steam	-	-	-
Energy consumption	5,961.0	5,576.3	-
Bioethanol Conversion stage			
Raw material manufacturing	-	-	442.4
Energy consumption	8,729.5	814.1	-
Bioethanol Dehydration stage			
Raw material manufacturing	-	-	3.9
Energy consumption	1,687.9	1,545.9	-
Total energy consumption	22,490.6	7,936.4	8,512.0
Energy generation (Lignin residue + Biogas)	45,064.2	10,905.5	-
Surplus energy	22,573.6	2,969.2	-
Energy content in 1,000 L of bioethanol at 99.7 vol % purity		21,200.0	
Total net energy inputs		38,938.9	
Total net fossil energy inputs		8,512.0	
Total net energy outputs		46,742.8	
Total net bioenergy outputs		46,742.8	
Net Energy Value (NEV)		7,804.0	
Net Renewable Energy Value (NRnEV)		38,230.9	
Net Energy Ratio (NER)*		1.20	
Renewability (Rn) *		5.49	

* Dimensionless parameters

Figure 5.3 illustrates the resulting net energy indicators for the base-case scenario in graphical form. A net bioenergy surplus is observed in the process when comparing the process energy consumption with generation. Thus, NEV and NRnEV for the considered life cycle of bioethanol production using rice straw in the base-case scenario are positive values, where the total net energy output is greater than the total net energy input, including fossil energy inputs. This implies that the considered cradle-to-gate bioethanol production process in the base-case scenario is self-sufficient in terms of energy.

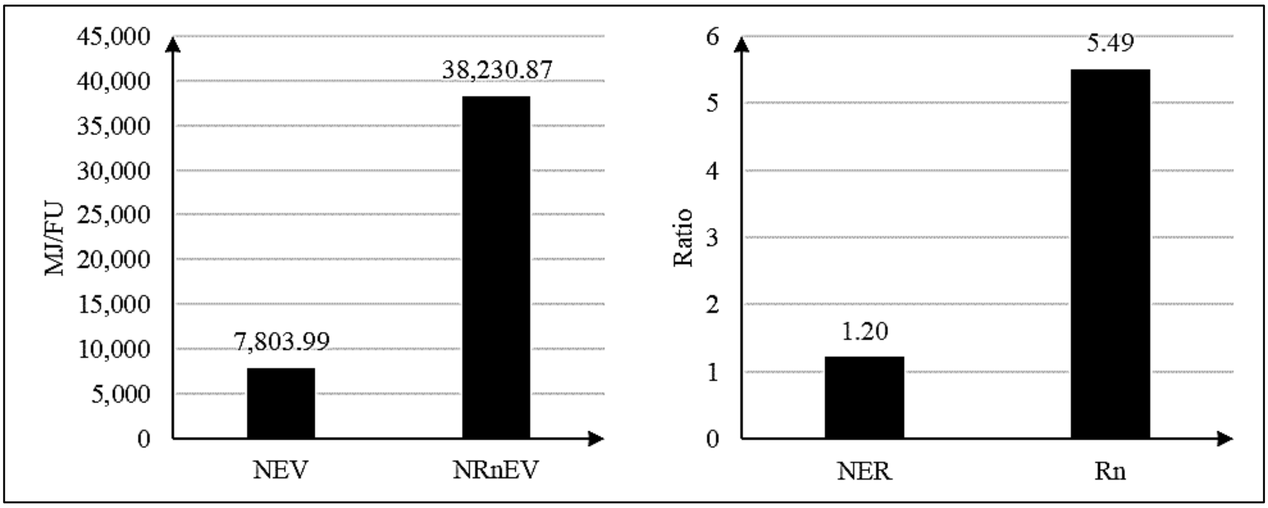


Fig. 5.3:Net energy indicator results

Table 5.5 lists the net energy indicators and GWP values of relevant published LCA studies on bioethanol production using rice straw, comparable to this study. According to Table 5.5, some of the published LCA studies for bioethanol production using rice straw that included inventory allocation from the rice cultivation stage have reported negative values for NEV and NRnEV indicators as well as NER and Rn values lesser than 1. Even though positive values have been reported, the net energy indicator values in other published studies are lower compared to that of the base-case scenario in this study. Hence, the introduced life cycle consideration for unutilized rice straw in this study (zero inventory allocation from the cultivation stage) has affected the life cycle of bioethanol production from rice straw more sustainable and renewable. Therefore, the net energy analysis results in the base-case scenario indicate that the life cycle consideration of zero inventory allocation for the rice cultivation stage is a determinant factor in future LCA studies for the cases/scenarios of unutilized rice straw valorization through bioethanol production.

Table 5.5: Results comparison of published LCA studies in existing literature

Country	NEV [a] (MJ/ m^3 of bioethanol)	NRnEV [b] (MJ/ m^3 of bioethanol)	NER [c]	Rn [d]	GHG [e] emissions (kg CO_2 eq./ m^3 of bioethanol)	Reference
Thailand	(4,331.0)	18,840.0	0.85	3.92	1,502.00	[23]
Europe	(1,252.6)	-	0.20	-	-	[55]
Japan	1,648.00	-	1.17	-	-	[18]
Japan	-	-	-	-	1,145.00	[44]
India	6,978.0	14,900.0	1.36	2.30	1,222.00	[22]
Sri Lanka	7,804.0	38,230.9	1.20	5.94	584.76	[60]

[a] NEV: Net Energy Value

[b] NRnEV: Net Renewable Energy Value

[c] NER: Net Energy Ratio

[d] Rn: Renewability

[e] GHG: Greenhouse Gas

5.3 Life cycle GHG assessment for base-case scenario

Table 5.6 presents the GHG emissions in respective life cycle stages and the creditable GHG amounts for the base-case scenario. According to the calculation results shown in Table 4.6, the net GWP value for 1 m^3 of bioethanol at 99.7 vol % purity is 584.76 kg CO_2 eq./ m^3 of bioethanol. This GWP value is significantly lower compared to various published LCA studies on bioethanol production from rice straw. The major reason for this reduction of GWP value is the cancellation of GHG emissions from the rice cultivation stage implied by the life cycle consideration for unutilized rice straw. In addition, the scaled-up bioethanol production plant which was simulated with improved energy efficiency and waste recovery methods, also contributes to a lower total GWP value, compared to that of other bioethanol plants reported in the literature. Thus, the result findings and the methodologies in this study contribute to designing new scaled-up process plants for more environmentally benign bioethanol production using unutilized rice straw as the feedstock.

Table 5.6: Life cycle stage-wise GHG emission results for the base-case scenario (basis: 1 m^3 of bioethanol at 99.7 vol% purity)

Life cycle stage	**GHG emissions (kg CO_2 eq./ m^3 of bioethanol)**				
	CO_2	**CH_4**	**N_2O**	**Total GHG [a]**	**Grand total**
01. Feedstock bailing and drying stage	15.53	0.01	0.04	15.58	15.58
02. Feedstock, raw materials, and renewable fuel transportation stage					121.92
Feedstock transportation	43.19	0.01	0.28	43.48	
Nautical transportation of raw materials	43.42	0.04	0.42	43.87	
Inland transportation of raw materials	34.55	0.001	0.02	34.57	
03. Feedstock Pretreatment					803.17
Biogas combustion	-	6.66	0.29	6.95	
Lignin combustion	-	0.85	2.61	3.45	
Direct steam	-	2.17	1.49	3.66	
Chemicals / raw materials	789.11	-	-	789.11	
04. Bioethanol conversion stage					75.73
Biogas combustion	-	3.16	0.14	3.30	
Lignin combustion	-	0.72	2.21	2.92	
Chemicals / raw materials	69.51	-	-	69.51	
05. Bioethanol dehydration					3.91
Biogas combustion	-	1.86	0.08	1.94	
Lignin combustion	-	0.24	0.73	0.97	
Chemicals / raw materials	1.00	-	-	1.00	
06. Credits					
Surplus energy	(452.71)	10.87	6.28	(435.56)	(435.56)
Total GHG emissions					584.76

[a] GHG: Greenhouse Gas

Figure 5.4 depicts the graphical interpretation of GHG emissions in each life cycle stage in the base-case scenario. The highest amount of GHG emitted in the feedstock pre-treatment stage corresponds to 803.17 kg CO_2 eq. / m^3 of bioethanol. The bioethanol dehydration stage has the least significant GHG emissions (3.91 kg CO_2 eq./ m^3 of bioethanol) which interprets its very low influence on environmental impacts compared to that of other life cycle stages in the bioethanol production life cycle.

However, there can be policy-wise reluctance and social barriers in developing countries like Sri Lanka assuming that a high energy intake and increased GHG emissions would be there for fuel-grade bioethanol production. This dilemma would restrain the valorization of unutilized rice straw via bioethanol production and upgrade existing bioethanol production plants up to fuel-grade bioethanol purity. Nevertheless, this study provides useful findings to promote policy decision-making for upgrading any existing plant and establishment of new plants for fuel-grade (anhydrous) bioethanol production from unutilized rice straw as the feedstock, with more environmental sustainability.

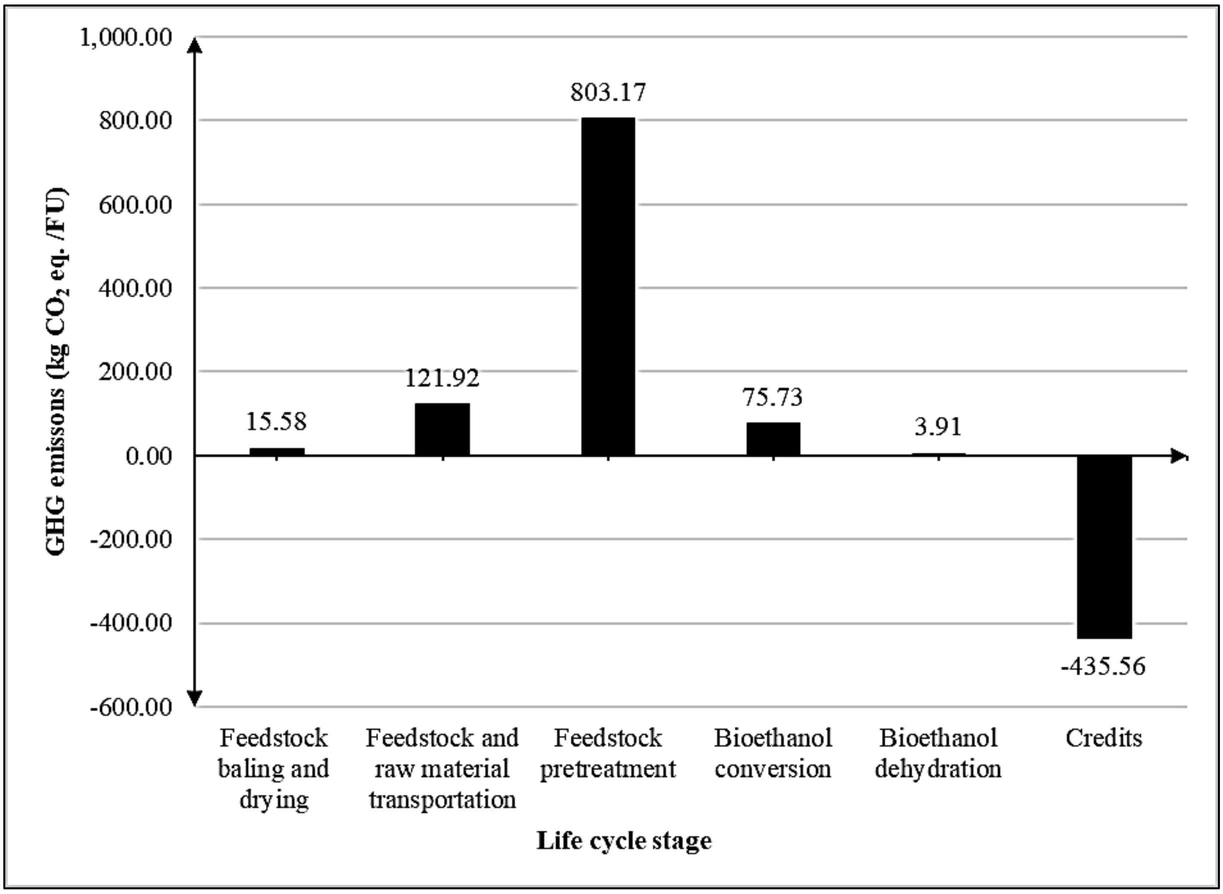


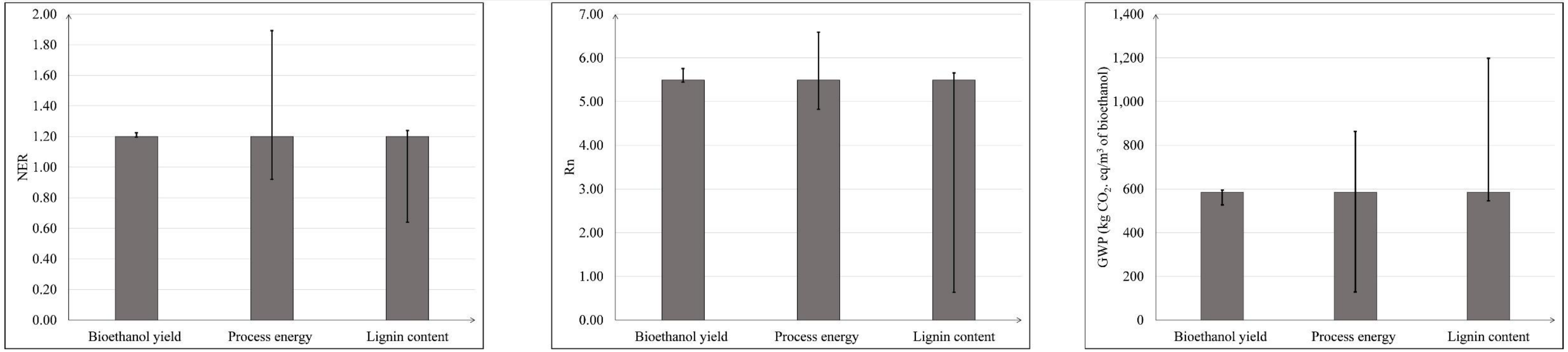
Fig. 5.4: Life cycle stage-wise GWP for bioethanol production from unutilized rice straw

5.4 Sensitivity analysis

In an LCA study, possible variations of the key parameters affect the final results and may alter the interpretations of the findings. Hence, the sensitivity of net energy and GWP indicators due to the key parameter variations is analyzed for the base-case scenario in this study. For the sensitivity analysis, three key parameters, i.e., bioethanol yield (L/tonne of rice straw), process energy consumption (MJ/ m^3 of bioethanol), and lignin composition in rice straw (wt%) are considered with their possible variation ranges globally, according to the already published studies as listed in Table 5.5. The sensitivity of the impact indicators, such as NER, Rn, and GWP is observed concerning the three key parameter variations. Figure 5.5 illustrates the results of the sensitivity analysis.

Description	**Sensitivity parameter**		
	Bioethanol yield (L/tonne of rice straw)	**Process energy (MJ/m^3 of bioethanol)**	**Lignin content (wt %)**
Parameter value in this study	171.34	24,314.77	38
Decreased / increased range	160 - 280	15,000 – 30,000	10 – 40
Net Energy Ratio (NER)	1.20 – 1.22	1.89 – 0.92	0.64 – 1.24
Renewability (Rn)	5.45 – 5.76	6.59 – 4.82	2.92 – 5.66
Global Warming Potential (GWP)	595.19 – 527.56	128.68 – 863.12	1,197.95 – 545.64

(a)



(b) (c) (d)

Fig. 5.5: Sensitivity analysis of net energy and GWP indicators due to key parameter variations in base-case scenarios; (a) Sensitivity analysis results (b) Net Energy Ratio (NER) (c) Renewability (Rn) (d) Global Warming Potential (GWP)

The results from sensitivity analysis provide meaningful interpretations of the possible deviations of net energy and GWP indicators. The yield parameter of bioethanol production processes from rice straw has reported a global variation of 160 – 280 L/tonne of rice straw. Within this range of variation, the bioethanol yield parameter shows the lowest sensitivity for the NER, Rn, and GWP indicator results, compared to the other two key parameters: process energy consumption and lignin content in rice straw. At the base values of process energy consumption and lignin content in this study, variation of bioethanol yield has an inconsiderable effect on the impact indicators. However, the process energy consumption parameter holds a significantly higher sensitivity for all three impact indicators. The process energy consumption could vary due to various reasons, such as the technology of bioethanol production process operations, the age of the plant, the efficiency of equipment, etc. The base value of process energy consumption to produce $1m^3$ of bioethanol for the base-case scenario in this study is 24,314.8 MJ which could vary from 15,000 MJ to 30,000 MJ, globally. As per the sensitivity results, the NER reaches the value of 1.00 at approximately 28,200 MJ of process energy consumption. Further increase of process energy consumption results NER <1 implies the process is not viable in terms of energy sustainability. Nevertheless, an increase in process energy consumption does not alter the renewability, Rn < 1.00. Among the impact indicators, GWP has the highest sensitivity towards the variation of process energy consumption. A decrease in process energy consumption from 24,314.77 MJ/ m^3 of bioethanol to 15,000 MJ/ m^3 of bioethanol could reduce GWP from 584.76 kg CO_2 eq./ m^3 of bioethanol to 128.68 kg CO_2 eq. / m^3 of bioethanol, which interprets the strong correlation between energy consumption and GHG emissions.

Sri Lankan rice straw with a higher lignin content of 38.0 wt % as the base value was considered for the base-case scenario. However, the lignin content of rice straw could globally vary from 10 wt % to 40 wt % according to published studies [15], [27], [33], [39], [40]. When the lignin content lowers, cellulose and hemicellulose contents in rice straw could increase by making an improved bioethanol yield. Even though improved bioethanol yield due to higher cellulose and hemicellulose contents may slightly increase NER and Rn while reducing GWP, reduced lignin content strongly affects the self-sufficiency of process energy generation within the system, i.e., lower lignin content in rice straw reduces the process energy generation. Thus, there is a threshold of lignin content in any lignocellulosic feedstock to retain the energy renewability and sustainability of a bioethanol production process [69]. Hence, the sensitivity analysis in this study is extended for the variation of the lignin content in rice straw to find the threshold that makes the bioethanol production process import heat and power from other energy sources. According to the sensitivity analysis results, 15.8 wt % of lignin content in rice straw is found as the threshold, in resulting zero surplus energy generation within the system with NER = 1 and Rn = 1. Further, GWP exceeds 1,000 kg of CO_2 eq./m^3 of ethanol with this decrease of lignin content in rice straw. Therefore, the sensitivity analysis in this study elaborates the factors behind the favorable impact indicator results in the considered case in this study, relevant to bioethanol production from unutilized rice straw with high lignin content.

5.5 Economic estimation and GHG credits for system boundary expansion

Fuel-grade bioethanol can be blended with gasoline at different proportions that produce various gasohol types (E3, E10, E20, E85, E87, E100, etc.). Gasohol from E3 to E85 can be used in vehicles without any engine modification. Hence, a system boundary expansion of E10 gasohol production and its end use is considered in this study in terms of economic estimation and GHG credits. If E10 gasohol is produced, 10% of gasoline imported to Sri Lanka can be substituted from fuel-grade bioethanol, produced locally using unutilized rice straw which corresponds to 22,400 m^3 of bioethanol per year.

Table 5.8 summarizes the economic estimation and GHG assessment results for the system boundary expansion for the base-case scenario. According to economic estimation results, an annual net import cost of about USD 13.62 million can be saved by producing E10 gasohol within the country. GHG assessment results considering the system boundary expansion (Utilization of E10 gasohol by substituting 10% of gasoline combusted in vehicles) show a GHG credit of more than 40,837 tonnes of CO_2 eq. per year. In addition, this system boundary expansion accounts for further GHG credits considering the avoidance of field burning of unutilized rice straw without compensating it for the opportunity loss of rice straw as manure. Avoidance of field burning of rice straw credits a GHG amount of 92 kg of CO_2 eq. per tonne of rice straw that corresponds to 12,027 kg of CO_2 eq, per year. Thus, the net GHG credit from both E10 gasohol substitution and avoidance of field burning of rice straw is approximately 39,766 tonnes of CO_2 eq. per year. Therefore, the system boundary expansion from cradle-to-gate to cradle-to-grave makes the bioethanol production life cycle using unutilized rice straw entirely carbon-negative, which is an attractive opportunity for policy decision-making in developing countries like Sri Lanka.

Table 5.7: Economic estimation results for E10 gasohol from rice straw bioethanol

Description	Unit	Value	Reference
Gasoline (Octane 95) imports*	m^3/year	224,000	[70]
Gasoline importation cost per year	USD/m^3	607.21	[70]
Gasoline substitution from E10 gasohol per year	m^3/year	22,400	
Net Import Cost Saving	Millions USD/year	13.62	
GHG credit for substituting gasoline	kg of CO_2 eq./ m^3 of bioethanol	1,823.08	[22]
GHG credit by substituting from E10 gasohol	tonnes of CO_2 eq./year	40,836.92	
GHG credit for avoiding field burning of rice straw	kg of CO_2 eq./tonnes of rice straw	92	[22]
GHG credit by substituting from E10 gasohol + avoiding field burning of rice straw	tonnes of CO_2 eq./year	52,864.27	
Total GHG emission for bioethanol production	tonnes of CO_2 eq./year	13,098.56	
Net GHG credit	tonnes of CO_2 eq./year	39,765.71	

*Available recent data as per the year 2017

CHAPTER 6

6 RESULTS AND DISCUSSION FOR THE LCA OF ALTERNATIVE LIFE CYCLE SCENARIOS

6.1 Process simulation results for the alternative life cycle scenarios

The scaled-up fuel-grade bioethanol process plant models for alternative life cycle scenarios are simulated in the Aspen Plus process simulation software to obtain 1 m^3 of bioethanol at 99.7 vol % purity. Appendix B includes the detailed process simulation models for each scenario including detailed material and energy flows. The simulation results are used to develop detailed material and energy inventories for the respective life cycle scenario.

Table 6.1 elaborates on the detailed life cycle material inventory, including bioethanol yield resulting from the nine alternative life cycle scenarios. The highest bioethanol yield (315.35 L per tonne of rice straw) is observed in life cycle scenarios (b) and (h) and the lowest bioethanol yield (283. 60 L per tonne of rice straw) is observed in life cycle scenario (f). Inclusive of all life cycle scenarios corresponding to PS – 01 and PS – 02 generate higher bioethanol yields of approximately 315.0 L per tonne of rice straw. Dilute acid pretreatment technology adopted in life cycle scenarios of PS – 02 accounts for higher cellulose and hemicellulose conversions into glucose and xylose (i.e., 90%), respectively, compared to steam explosion pretreatment technology adopted in life cycle scenarios of PS – 03 (i.e., 86 %). In contrast, the net sugar conversion fractions in life cycle scenarios of PS – 01 ($X_{glucose} = 90\%, X_{xylose} = 68\%$) are comparatively lower concerning the life cycle scenarios of PS – 03 $\left(X_{glucose} = 93.1\ \%, X_{xylose} = 71.9\ \%\right)$. Thus, approximately similar bioethanol yields are observed in the life cycle scenarios of PS – 01 and PS – 02. Further, life cycle scenarios related to PS – 02 where alkaline pretreatment technology is used as the feedstock pretreatment method, display the least bioethanol yields, approximately in a range between 283.0 and 310 L per tonne of rice straw. Even though higher cellulose and hemicellulose conversion fractions (i.e., $X_{cellulose} = 90.3\%$ and $X_{hemicellulose} = 92.4\ \%$) are followed in alkaline pretreatment of rice straw, life cycle scenarios corresponding to PS – 02 account for lower conversions of xylose in SSF. Thus, life cycle scenarios of PS – 02 result in lower bioethanol yields. In addition to feedstock pretreatment scenarios, dehydration scenarios also display variations in bioethanol yields. Considering the dehydration scenarios, the highest bioethanol yields are observed in life cycle scenarios corresponding to DS – 02, where azeotropic distillation is adopted as the bioethanol dehydration technology. The lowest bioethanol yield is observed from the life cycle scenarios corresponding to DS – 03, where pressure swing distillation is adopted as the bioethanol dehydration technology. Corresponding with the bioethanol yield, the operating hours, feedstock requirement, raw material consumption, and process energy demand to produce 1 m^3 of fuel-grade bioethanol at 99.7 vol% purity are varied.

The operating hours of the modeled bioethanol process plants to obtain 1 m^3 of fuel-grade bioethanol at 99.7 vol% purity have an indirectly proportional relationship with the bioethanol yield. Thus, bioethanol process plants with lower bioethanol yields display higher operating hours and inversely. The average operating hours for the modeled bioethanol process plant with an average bioethanol yield of around 315 L per tonne of rice straw is approximately 3.17 hours. However, the life cycle scenario (f), corresponding to the lowest bioethanol yield i.e., 2.83 L/tonne of rice straw, displays the highest operating hours, i.e., 3.53 hours, leading to higher feedstock, raw materials, and process energy demands to produce 1 m^3 of fuel-grade bioethanol at 99.7 % vol purity from unutilized rice straw.

In addition to the operating hours, the feedstock, i.e., unutilized rice straw requirement to produce 1 m^3 of fuel-grade bioethanol at 99.7 vol% purity for each life cycle scenario is also varied with the respective bioethanol yield. The unutilized rice straw requirement for most of the scenarios is approximately 3,171 kg/m^3 of bioethanol. Life cycle scenarios corresponding to PS – 02 display the highest rice straw requirements (> 3,235 kg/m^3 of bioethanol) while the life cycle scenario (f) corresponds to the highest rice straw requirement of 3,526.14 kg/m^3 of bioethanol. In correspondence to the processed rice straw quantities in respective bioethanol plants, variations in fossil fuel consumption, raw materials and chemicals consumption, and process water consumption are observed. Thus, life cycle scenario (f) where alkaline pretreatment technology is adopted as the feedstock pretreatment technology and pressure swing distillation technology as the bioethanol dehydration technology corresponds to higher raw materials and chemicals consumption, fossil fuel (diesel and heavy oil) consumption, and process energy consumption.

Further, Table 6.1 summarizes the generated spent-wash amounts, corresponding COD values, generated biogas amounts, and the lignin-containing solid residue contents resulting from process simulation models of each life cycle scenario. Anaerobic digestion of spent wash collected from each life cycle scenario generates biogas which is utilized as a renewable fuel source to cater to the process energy demand. Life cycle scenario (d) generates the highest biogas amount, 240.07 m^3/m^3 of bioethanol and life cycle scenario (h) corresponds to the least biogas generation, i.e., 74.54 m^3/m^3 of bioethanol. According to equation (01), biogas generation depends on the amount of spent wash collected and the COD value of the spent wash. Process simulation results show that the spent-wash quantities generated in life cycle scenarios under PS – 02 have the highest organic component concentrations leading to wastewaters with high COD values. Thus, life cycle scenarios corresponding to PS – 02 generate higher biogas quantities compared to other life cycle scenarios. Life cycle scenarios under PS – 03 display the least organic component concentrations in wastewater. Hence, the life cycle scenarios of PS–03 display the least biogas generations. In addition to biogas, solid reside containing lignin and other unconverted cellulosic compounds is used as a solid fuel source to cater to the process energy demand. However, net heat and power cogenerated from both biogas and solid residue are insufficient for all the alternative life cycle scenarios. Thus, wood chips and rice husks are used as additional renewable energy sources to cater to the excess energy demand.

Life cycle scenarios from (a) to (e), account for surplus power generation and require wood chips and rice husk only to cater the excess heat demand. However, higher excess heat demands observed in life cycle scenarios (d) and (e) require more renewable fuel compared to life cycle scenarios (a), (b), and (c). Further, life cycle scenarios from (f) to (i) demand both excess heat and power. Therefore, comparatively higher wood chips and rice husk requirements are observed in life cycle scenarios (f), (g), (h), and (i).

Table 6.1: Life cycle inventory for the production of fuel-grade bioethanol at 99.7 vol% purity from unutilised rice straw as the feedstock

Parameter	**Unit**	**Life cycle scenario**								
		(a)	**(b)**	**(c)**	**(d)**	**(e)**	**(f)**	**(g)**	**(h)**	**(i)**
Bioethanol yield	L/tonne	315.08	315.35	315.29	308.76	309.04	283.60	315.09	315.35	308.88
Operating hours	hr	3.17	3.17	3.17	3.24	3.24	3.53	3.17	3.17	3.24
Feedstock baling and drying stage										
Diesel	L	3.81	3.81	3.81	3.89	3.88	4.23	3.81	3.81	3.89
Feedstock, raw materials, and renewable fuel transportation stage										
Diesel for inland transportation										
Feedstock	L	7.93	7.93	7.93	8.10	8.09	8.82	7.93	7.93	8.09
Chemicals/ raw materials	L	1.93	1.94	1.92	6.17	6.21	6.71	0.40	0.41	0.41
Woodchips/ rice husk	L	0.54	1.28	0.81	5.21	7.61	9.40	5.24	11.47	9.69
Nautical transportation										
Heavy oil	L	2.25	2.27	2.25	7.23	7.27	7.86	0.47	0.48	0.48
Feedstock pretreatment stage										
Rice straw	kg	3,173.81	3,171.11	3,171.70	3,238.78	3,235.83	3,526.14	3,173.71	3,171.11	3,237.53
Process water	L	7,991.64	7,984.86	7,986.33	12,955.10	12,943.32	14,104.55	15,868.57	15,855.56	16,187.65
H_2SO_4	kg	85.89	85.81	85.83	316.79	316.79	345.21	-	-	-
NaOH	kg	-	-	-	259.10	258.87	282.09	-	-	-
Steam	kg	1,529.77	1,528.48	1,528.76	-	-	-	3,491.09	3,488.22	3,561.28
Enzyme	kg	27.58	27.55	27.56	27.14	27.11	29.55	26.35	26.33	26.88
$Ca(OH)_2$	kg	65.06	65.01	65.02	-	-	-	-	-	-

Table 6.1 continued

Bioethanol conversion stage										
Yeast	kg	7.85	7.84	7.84	7.59	7.59	8.27	7.82	7.81	7.98
$(NH_4)_2HPO_4$	kg	5.73	5.72	5.72	5.54	5.54	6.04	5.71	5.70	5.82
Bioethanol dehydration stage										
Ethylene glycol	kg	0.49	-	-	0.83	-	-	0.36	-	-
Cyclohexane	kg	-	2.36	-	-	4.94	-	-	0.95	-
Spent-wash characteristics										
Volume	L	9,666.54	9,642.34	9,677.03	13,273.05	14,037.13	14,537.75	52,179.75	48,416.61	49,453.77
COD	kg /m^3	24.59	22.86	24.33	41.99	39.40	22.24	3.56	3.57	4.20
Fuel for process energy supply										
Biogas	m^3	102.41	94.95	101.44	240.07	238.26	140.54	80.09	74.54	89.48
Lignin/solid residue	kg	1,560.68	1,550.80	1,558.59	1,805.30	1,801.81	1,825.22	1,611.71	1,604.02	1,653.15
Wood chips and rice husks	kg	214.62	511.52	324.06	2,083.64	3,042.75	3,759.07	2,095.72	4,587.98	3,875.96
Process byproducts										
Electricity	kWh	1,001.83	897.60	699.85	1,090.80	443.89	-	-	-	-
Gypsum	kg	150.77	150.64	150.67	-	-	-	-	-	-
CO_2	kg	770.33	769.68	769.82	760.12	759.43	827.57	767.07	766.45	782.50

Along with the life cycle material consumption, energy consumption in each equipment in simulated bioethanol process models is obtained from process simulation results. Process energy consumption values in bioethanol processing stages are calculated for nine scenarios using the process simulation results. Appendix B lists the equipment-wise energy consumption results for all the alternative life cycle scenarios considered in this study. Figure 5.1 and Table 30 display the process energy consumption in each life cycle scenario including process heat and power consumption. The lowest process energy consumption is observed in life scenario (a), i.e., 20,880.12 MJ/m^3 of bioethanol, while the highest process energy consumption is observed in scenario (f), i.e., 78,751.30 MJ/m^3 of bioethanol. Considering the pretreatment scenarios, the lowest process energy consumption is observed in life cycle scenarios corresponding to PS – 01, where dilute acid pretreatment technology is used as the feedstock pretreatment technology. The higher amounts of energy consumed to heat the process water in alkaline pretreatment in PS – 02 have resulted in increased heat consumption in respective life cycle scenarios. Life cycle scenarios corresponding to PS – 03, include larger process water quantities due to the higher solid-to-liquid ratios adopted. Thus, processing larger water volumes throughout the bioethanol production process increases the total energy consumption in life cycle scenarios corresponding to PS – 03. Considering the dehydration scenarios, DS – 01; extractive distillation consumes comparatively lower energy to produce 1 m^3 of fuel grade bioethanol at 99.7 vol% purity, while DS – 02; azeotropic distillation consumes the highest energy to produce 1 m^3 of fuel grade bioethanol at 99.7 vol% purity.

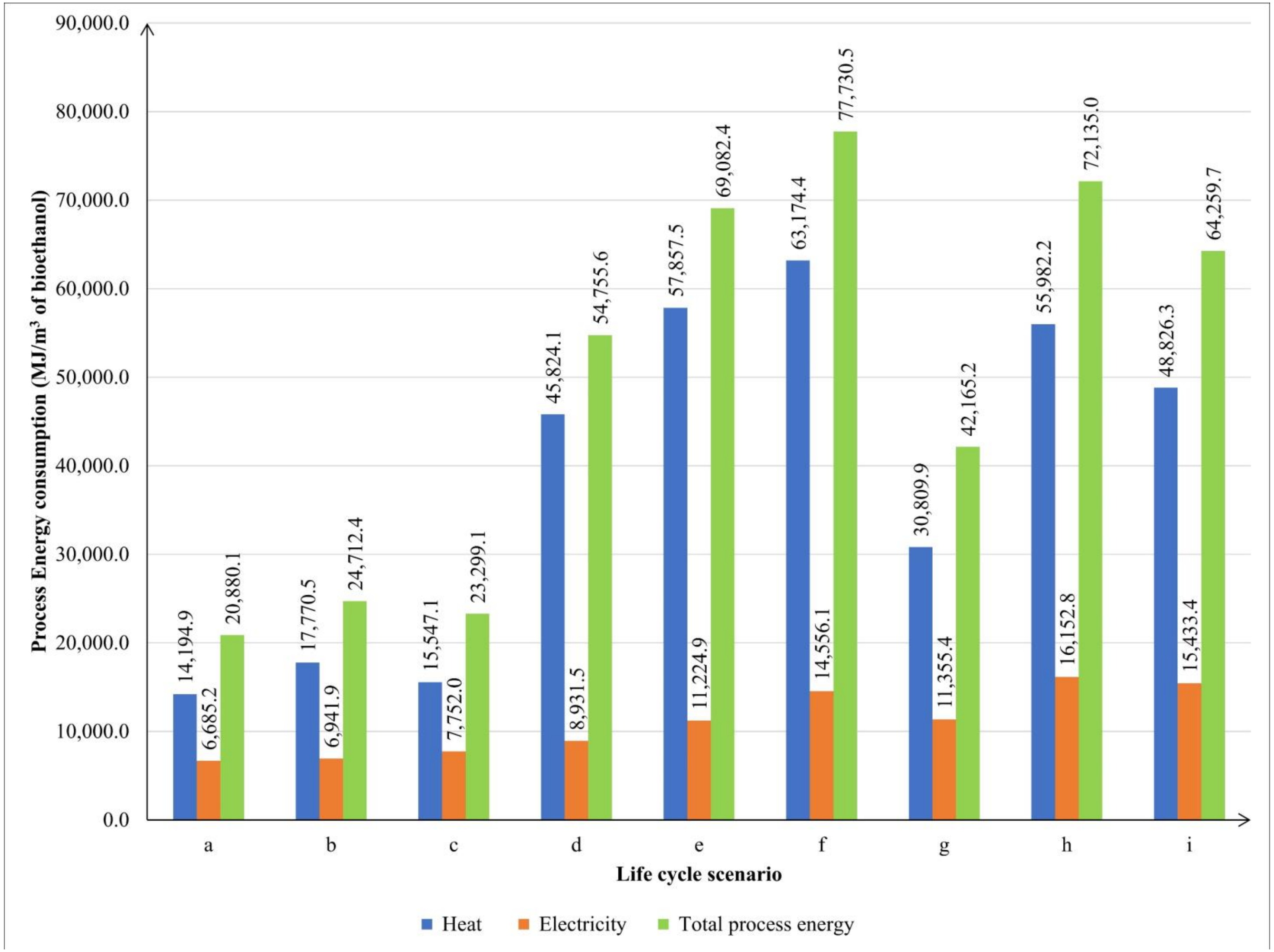


Fig. 6.1: Process energy consumption for life cycle scenarios of fuel-grade bioethanol production from unutilized rice straw: 1 m3 of bioethanol at 99.7 vol% purity

Table 6.2: Process energy consumption in alternative life cycle scenarios

Life cycle scenario	**Heat (MJ/m^3 of bioethanol)**	**Power (MJ/m^3 of bioethanol)**	**Total process energy (MJ/m^3 of bioethanol)**
(a)	14,194.88	6,685.24	20,880.12
(b)	17,770.46	6,941.94	24,712.40
(c)	15,547.09	7,752.04	23,299.13
(d)	46,909.64	8,975.93	54,755.61
(e)	57,857.48	11,224.94	69,082.42
(f)	63,174.37	14,556.13	77,730.50
(g)	30,809.89	11,355.35	42,165.24
(h)	55,982.22	16,152.80	72,135.02
(i)	48,826.28	15,433.39	64,259.67

Further, net energy consumptions for each life cycle stage for all the alternative life cycle scenarios are calculated considering the process energy consumption and fossil energy uptake for feedstock baling and drying, raw material/s chemicals manufacturing, and transportation of feedstock, raw materials/chemicals, and renewable fuels. Figure 5.2 indicates the graphical representation of stage-wise energy consumption percentages for each life cycle scenario. When compared with the bioethanol processing stages feedstock baling and drying stage and feedstock, raw material, and fuel transportation stage consume a negligible amount of energy. Among the five life cycle stages, the feedstock pretreatment stage consumes the highest energy percentile except for scenarios (c), (h), and (i). Life cycle scenarios under PS – 02 show the highest percentile of energy consumption for the feedstock pretreatment stage, claiming energy-intensive pretreatment technology for fuel-grade bioethanol production from unutilized rice straw. Further, life cycle scenarios under DS – 03 also showcase higher energy uptake percentiles for the bioethanol dehydration stage. Life cycle scenarios under DS – 01 display the least energy uptake percentile, (< 8.3 %) claiming the least energy-intensive bioethanol dehydration technology to produce fuel-grade bioethanol from unutilized rice straw.

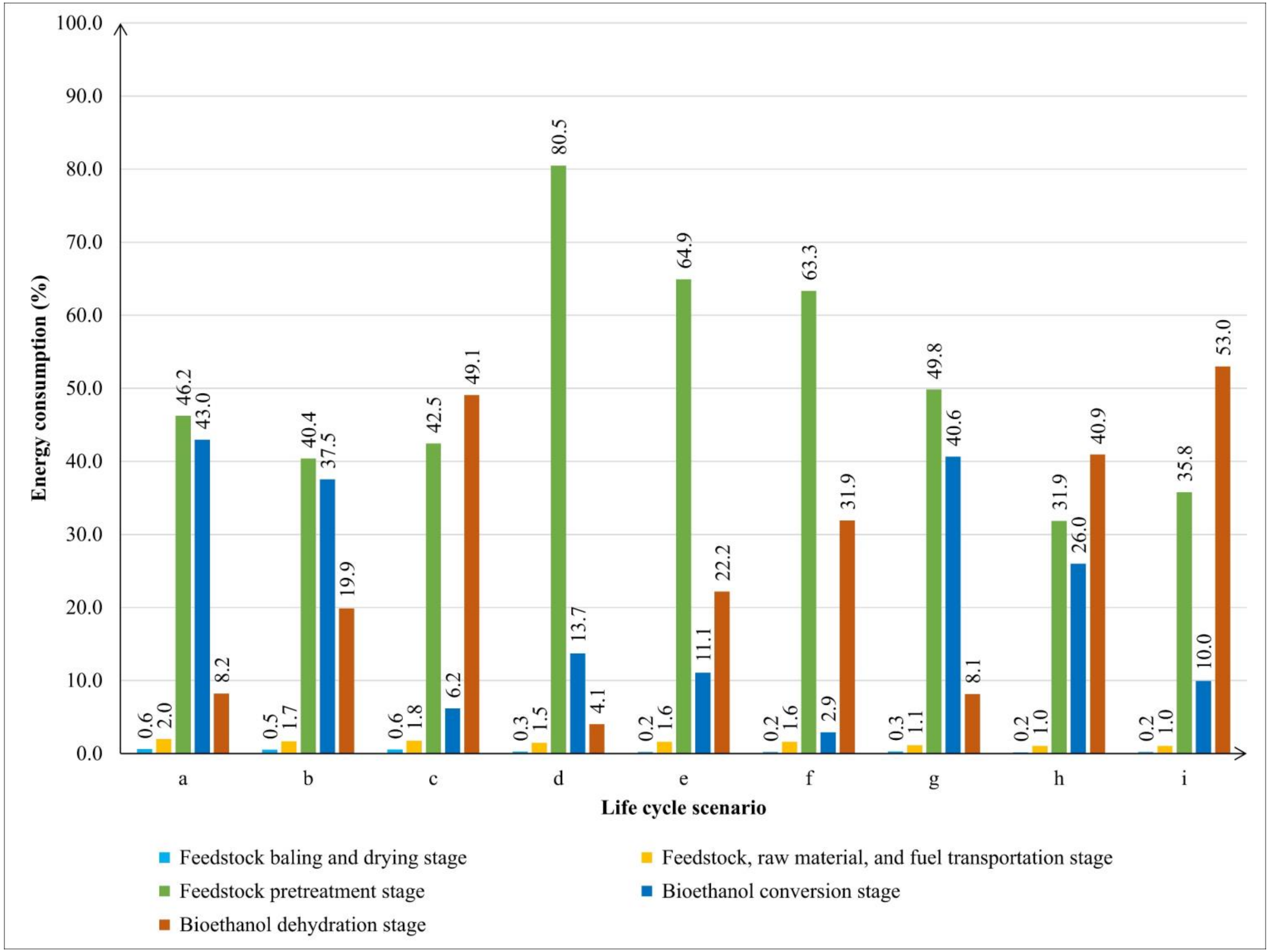


Fig. 6.2: Stage-wise energy consumption for life cycle scenarios of fuel-grade bioethanol production from unutilized rice straw: basis - 1 m3 of bioethanol at 99.7 vol % purity

6.2 Net energy analysis for the alternative life cycle scenarios

Tables 6.3, 6.4, and 6.5 display the life cycle net energy balance, including the calculated net energy indicators for the cradle-to-gate bioethanol production life cycles from unutilized rice straw. The total net energy consumption, total net fossil energy consumption, total net energy outputs, and total net bioenergy outputs are calculated using the energy flow results obtained for each life cycle scenario. Further, the net energy indicators are calculated and Figures 6.3, 6.4, 6.5, and 6.6 display the graphical interpretation of each net energy indicator value for respective life cycle scenarios.

Table 6.3: Net energy balance for life cycle scenarios corresponding to pretreatment scenario 01

Description	Energy input/output (MJ/m^3 of bioethanol at 99.7 vol% purity)								
	Scenario (a)			Scenario (b)			Scenario (c)		
	Heat	Power	Fossil	Heat	Power	Fossil	Heat	Power	Fossil
Feedstock baling and drying stage									
Baling and drying	-	-	163.16	-	-	163.02			163.05
Feedstock, raw material, and fuel transportation stage									
Feedstock	-	-	339.91	-	-	339.63			339.69
Raw Materials/Chemicals	-	-	174.95	-	-	176.49			174.39
Wood chips and rice husk	-	-	22.99	-	-	4.06			2.57
Feedstock pretreatment stage									
Raw Materials/Chemicals	-	-	967.77	-	-	966.95	-	-	967.13
Direct steam	4,368.12	-	-	4,364.41	-	-	4,365.21	-	-
Process energy consumption	2,785.72	4,412.99	-	2,782.51	4,409.25	-	2,783.20	4,410.06	-
Bioethanol conversion stage									
Raw Materials/Chemicals	-	-	192.11	-	-	191.95			191.99
Process energy consumption	10,007.80	1,449.70	-	9,999.30	1,448.47	-	1,474.53	151.20	-
Bioethanol dehydration stage									
Raw Materials/Chemicals	-	-	6.91			93.76	-	-	-
Process energy consumption	1,401.37	822.56	-	4,988.65	1,084.23	-	11,289.36	3,190.78	-

Table 6.3 continued.

Total energy consumption	18,563.00	6,685.24	1,867.80	22,134.87	6,941.94	1,935.85	19,912.31	7,752.04	1,838.81
Energy generation									
Biogas	1,032.29	802.89	-	957.12	744.43	-	1,022.48	795.26	-
Lignin/solid residue	14,826.46	9,488.94	-	14,732.61	9,428.87	-	14,806.63	9,476.24	-
Wood chips/rice husks	2,704.25	-	-	6,445.14	-	-	4,083.19	-	-
Surplus energy	-	3,606.58	-	-	3,231.36	-	-	2,519.47	-
Energy content in 1 m3 of bioethanol at 99.7 vol% purity		21,200.00			21,200.00			21,200.00	
Total net energy inputs		27,116.05			30,949.65			29,503.15	
Total net fossil energy inputs		1,867.80			1,935.85			1,838.81	
Total net energy outputs		24,806.58			24,494.38			23,719.47	
Total net bioenergy outputs		24,806.58			24,494.38			23,719.47	
NEV		(2,309.46)			(6,455.27)			(5,783.68)	
NRnEV		22,938.78			22,558.52			21,880.66	
NER*		0.91			0.79			0.80	
Rn*		13.28			12.65			12.90	

* - Dimensionless parameters

Table 6.4: Net energy balance for life cycle scenarios corresponding to pretreatment scenario - 02

Description	**Energy input/output (MJ/m^3 of bioethanol at 99.7 vol% purity)**								
	Scenario (e)			**Scenario (f)**			**Scenario (g)**		
	Heat	**Power**	**Fossil**	**Heat**	**Power**	**Fossil**	**Heat**	**Power**	**Fossil**
<u>Feedstock baling and drying stage</u>									
Baling and drying	-	-	166.50	-	-	166.35	-	-	181.27
<u>Feedstock, raw material, and fuel transportation stage</u>									
Feedstock	-	-	346.87	-	-	346.56	-	-	377.65
Raw Materials/Chemicals	-	-	560.75	-	-	563.97	-	-	609.68
Wood chips and rice husk	-	-	17.57	-	-	396.06	-	-	360.79
<u>Feedstock pretreatment stage</u>									
Raw Materials/Chemicals	-	-	6,113.87	-	-	6,108.31	-	-	6,656.33
Direct steam	-	-	-	-	-	-	-	-	-
Process energy consumption	36,786.02	7,123.35	-	36,751.61	7,116.87	-	40,150.20	7,755.37	-
<u>Bioethanol conversion stage</u>									
Raw Materials/Chemicals	-	-	185.95	-	-	185.78	-	-	202.45
Process energy consumption	8,626.91	843.28	-	15,790.89	2,210.46	-	2,168.66	150.67	-
<u>Bioethanol dehydration stage</u>									
Raw Materials/Chemicals	-	-	11.66	-	-	196.58	-	-	-
Process energy consumption	1,496.71	1,009.31	-	13,571.33	3,310.14	-	17,266.57	5,586.14	-

Table 6.4 continued.

Total energy consumption	46,909.64	8,975.93	7,403.18	66,113.84	12,637.46	7,963.60	59,585.43	13,492.19	8,388.16
Energy generation									
Biogas	2,419.90	1,882.15	-	2,401.65	1,867.95	-	1,416.63	1,101.83	-
Lignin/solid residue	17,150.33	10,976.21	-	17,117.17	10,954.99	-	17,339.63	11,097.36	-
Wood chips/rice husks	27,339.40	-	-	46,595.02	-	-	40,829.17	1,293.00	-
Surplus energy	-	3,882.43	-	-	185.48	-	-	-	-
Energy content in 1 m3 of bioethanol at 99.7 vol% purity		21,200.00			21,200.00			21,200.00	
Total net energy inputs		63,288.75			86,714.90			81,465.78	
Total net fossil energy inputs		7,403.18			7,963.60			8,388.16	
Total net energy outputs		25,082.43			21,385.48			21,200.00	
Total net bioenergy outputs		25,082.43			21,385.48			21,200.00	
NEV		(38,206.32)			(65,329.42)			(60,265.78)	
NRnEV		17,679.25			13,421.87			12,811.84	
NER *		0.40			0.25			0.26	
Rn *		3.39			2.69			2.53	

* - Dimensionless parameters

Table 6.5: Net energy balance for life cycle scenarios corresponding to pretreatment scenario - 03

	Energy input/output (MJ/m^3 of bioethanol at 99.7 vol% purity)								
Description	**Scenario (g)**			**Scenario (h)**			**Scenario (i)**		
	Heat	**Power**	**Fossil**	**Heat**	**Power**	**Fossil**	**Heat**	**Power**	**Fossil**
Feedstock baling and drying stage									
Baling and drying	-	-	163.15	-	-	163.02	-	-	166.43
Feedstock, raw material, and fuel transportation stage									
Feedstock	-	-	339.90	-	-	339.63	-	-	346.74
Raw Materials/Chemicals	-	-	36.55	-	-	37.06	-	-	36.95
Wood chips and rice husk	-	-	224.45	-	-	491.37	-	-	415.12
Feedstock pretreatment stage									
Raw Materials/Chemicals	-	-	152.83	-	-	152.71	-	-	155.91
Direct steam	10,554.54	-	-	10,545.88	-	-	10,766.77	-	-
Process energy consumption	8,824.35	7,286.55	-	8,816.30	7,280.58	-	9,022.24	7,372.21	-
Bioethanol conversion stage									
Raw Materials/Chemicals	-	-	191.48	-	-	191.32	-	-	195.33
Process energy consumption	20,460.58	1,220.56	-	20,443.81	1,219.56		7,248.56	157.13	-
Bioethanol dehydration stage									
Raw Materials/Chemicals	-	-	5.05			37.97	-	-	-
Process energy consumption	1,524.96	2,848.24	-	26,722.12	7,652.66		32,555.48	7,904.05	-

Table 6.5 continued.

Total energy consumption	41,364.43	11,355.35	1,113.42	66,528.11	16,152.80	1,413.07	59,593.05	15,433.39	1,316.48
Energy generation									
Biogas	807.34	627.93	-	751.35	584.38		901.96	701.52	-
Lignin/solid residue	15,311.26	9,799.20	-	15,238.18	9,752.44		15,704.88	10,051.12	-
Wood chips/rice husks	25,245.83	928.22	-	50,538.58	5,815.98		42,986.21	4,680.75	-
Surplus energy	-	-	-	-	-	-	-	-	-
Energy content in 1 m3 of bioethanol at 99.7 vol% purity	21,200.00			21,200.00			21,200.00		
Total net energy inputs	53,833.20			84,093.98			76,342.91		
Total net fossil energy inputs	1,113.42			1,413.07			1,316.48		
Total net energy outputs	21,200.00			21,200.00			21,200.00		
Total net bioenergy outputs	21,200.00			21,200.00			21,200.00		
NEV	(32,633.20)			(62,893.98)			(55,142.91)		
NRnEV	20,086.58			19,786.93			19,883.52		
NER *	0.39			0.25			0.28		
Rn *	19.04			15.00			16.10		

* - Dimensionless parameters

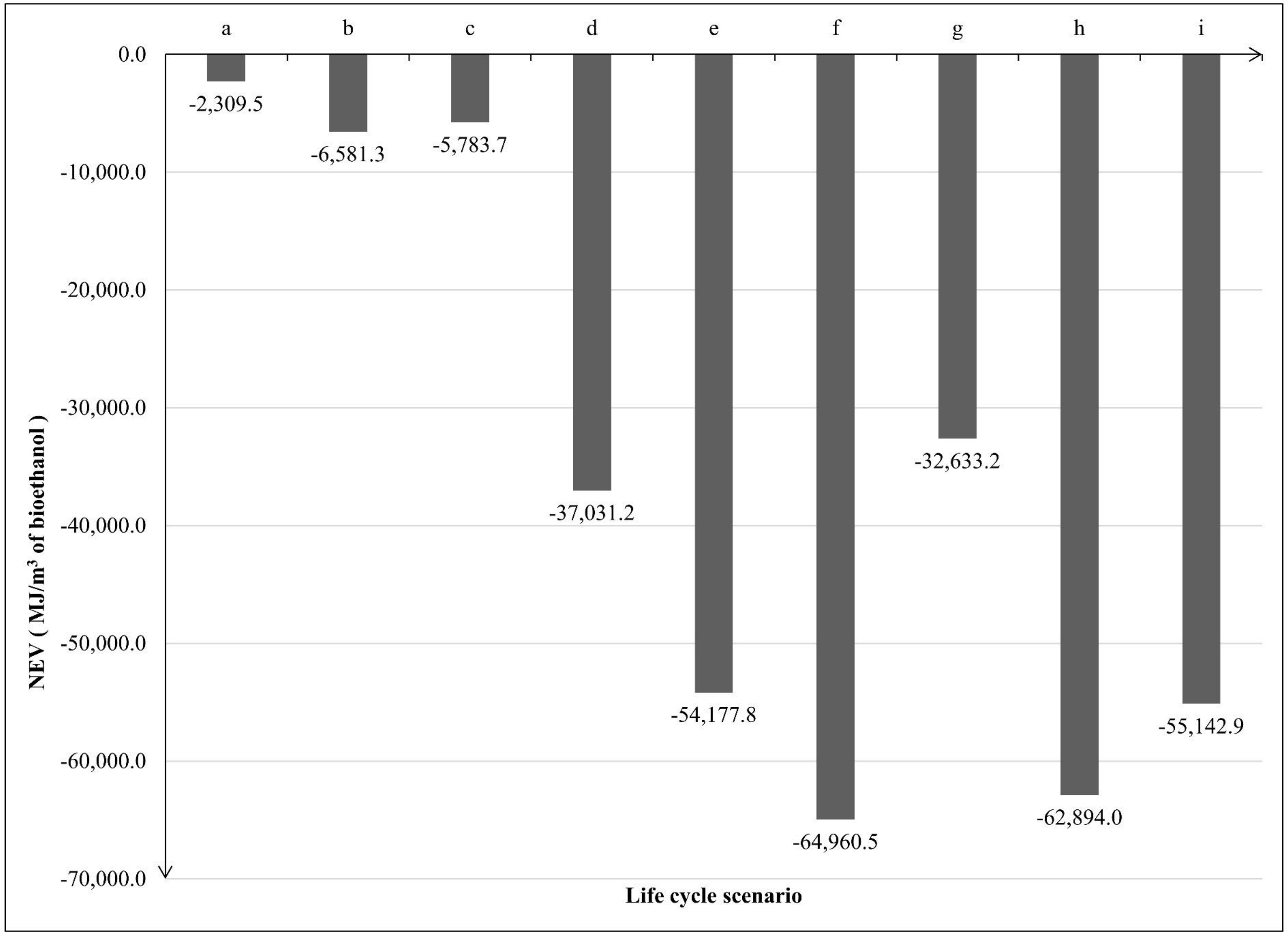


Fig. 6.3: Net energy values for life cycle scenarios of fuel-grade bioethanol production from unutilized rice straw: basis – 1 m^3 of bioethanol at 99.7 vol% purity

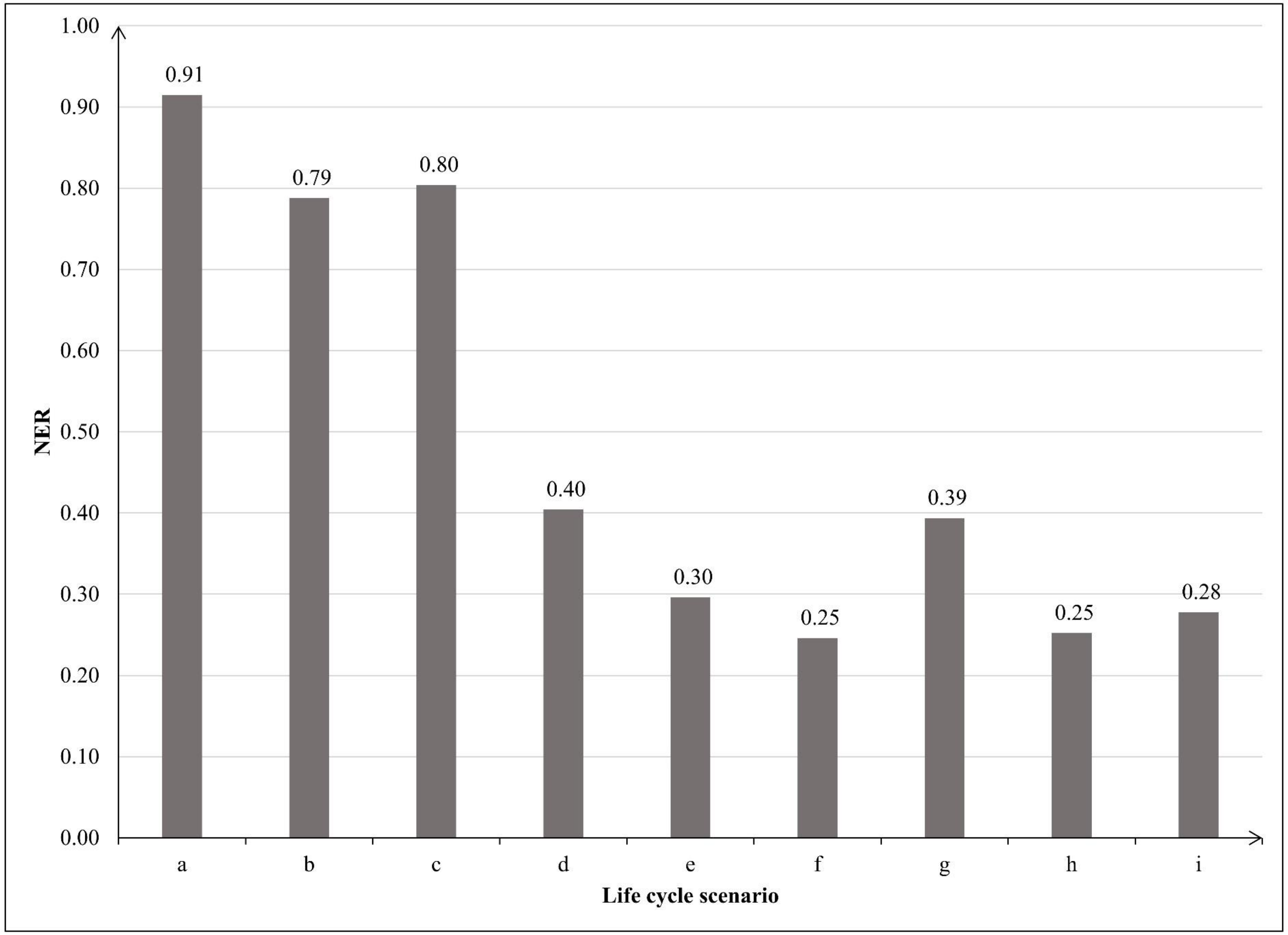


Fig. 6.4: Net energy ratios of life cycle scenarios for fuel-grade bioethanol production from unutilized rice straw: basis - 1 m3 of fuel grade bioethanol at 99.7 vol% purity

Figures 6.3 and 6.4 display the graphical interpretation of corresponding NEVs and NERs resulting in alternative life cycle scenarios to produce 1 m^3 of fuel-grade bioethanol at 99.7 vol% purity. Higher net energy inputs compared to net energy outputs resulted in negative net energy values ($NEV<0$) and $NER < 1$ for all the life cycle scenarios claiming a net energy loss. Even though higher bioethanol yields are observed compared to bioethanol production under the base-case scenario, the average lignin content considered in other life cycles is lower. Hence, cogenerated process surplus energy quantities are insufficient to surpass the total net energy inputs in the considered life cycle scenarios. However, scenario (a) where dilute acid pretreatment and extractive distillation technologies are adopted for feedstock pretreatment technology and bioethanol dehydration technology, respectively, showcases the least negative NEV, i.e., - 2,309.46 MJ/m^3 of bioethanol and highest NER, i.e., 0.91. The highest negative NEV, i.e., - 64,960.47 MJ/m^3 of bioethanol and the least NER, i.e., 0.25 are observed in scenario (f), where alkaline pretreatment and pressure swing distillation technologies are used as the corresponding feedstock pretreatment technology and bioethanol dehydration technology.

Comparatively, the least negative NEVs and higher NERs are observed in life cycle scenarios under PS – 01, where dilute acid pretreatment is used as the feedstock pretreatment technology. Similarly, the life cycle scenarios under DS – 01 where extractive distillation technology is adopted as the bioethanol dehydration technology display the least negative NEVs and higher NERs compared to other life cycle scenarios with different bioethanol dehydration technologies.

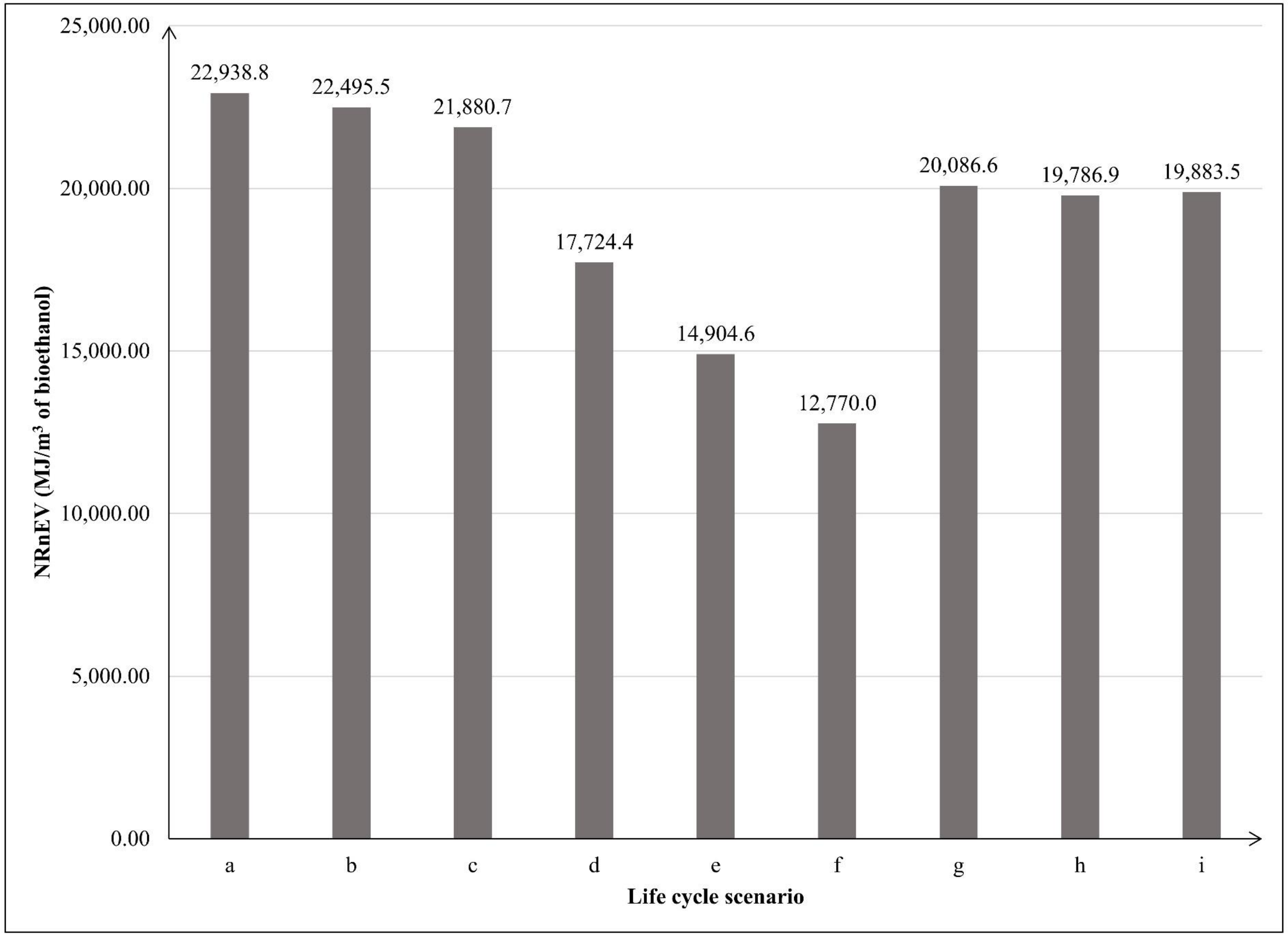


Fig. 6.5: Net Renewable Energy Values of life cycle scenarios for fuel-grade bioethanol production from unutilized rice straw: basis – 1 m^3 of bioethanol at 99.7 vol% purity

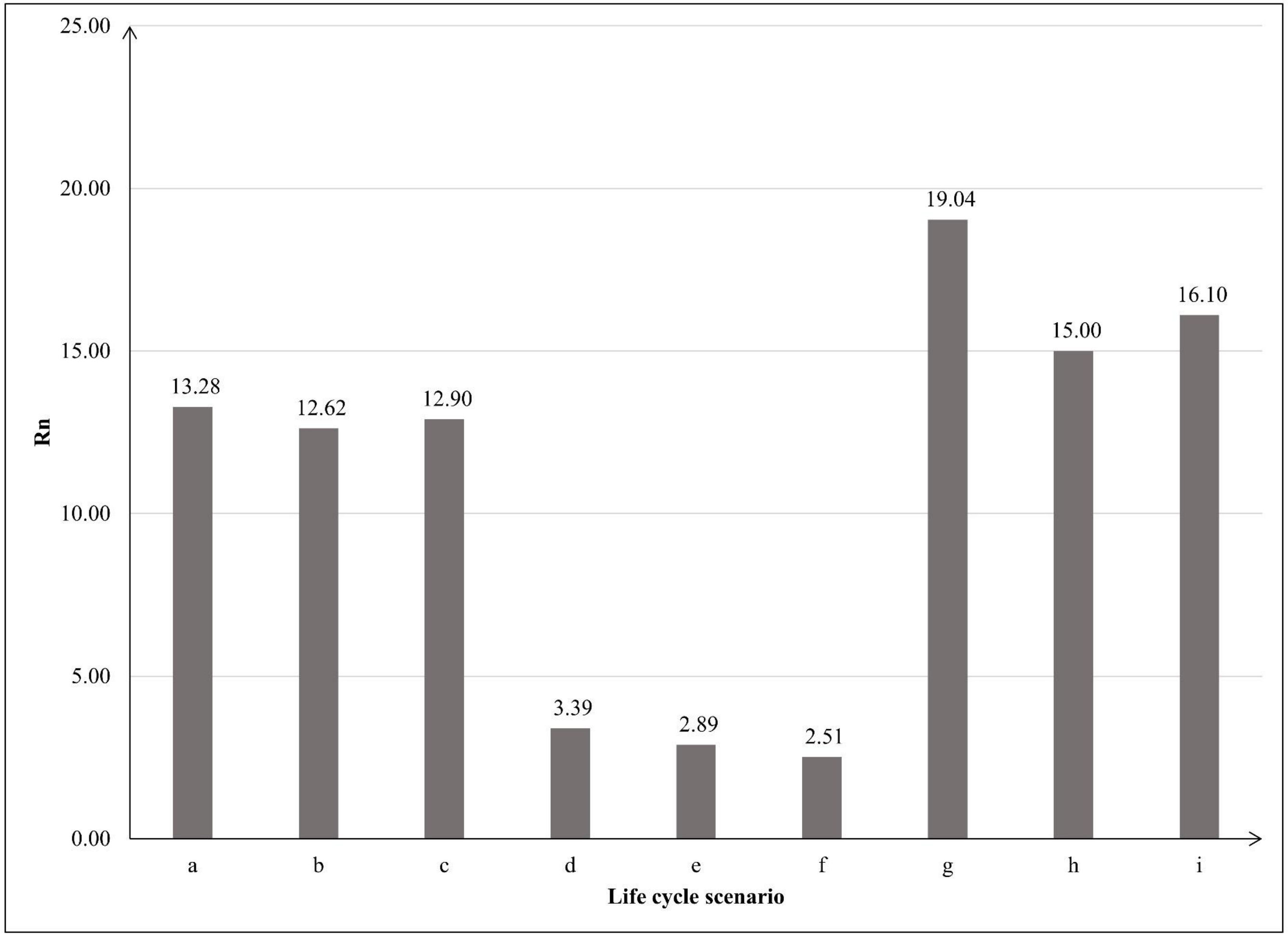


Fig. 6.6: Renewability factors of life cycle scenarios for fuel-grade bioethanol production from unutilized rice straw

Figures 5.5 and 5.6 show the NRnEV values and renewability factors resulting from the alternative life cycle scenarios considered in this study. All the alternative life cycle scenarios display net renewable energy gain with positive NRnEV values and Rn > 1 to produce 1 m^3 of fuel-grade bioethanol at 99.7 vol % purity from unutilized rice straw as the feedstock. The highest NRnEV, i.e., 22,938.78 MJ/m^3 of bioethanol and renewability factor is resulted, i.e., 19.04 for life cycle scenario (g) where steam explosion and extractive distillation technologies are adopted as the feedstock pretreatment technology and bioethanol dehydration technology, respectively. Even though with lowest net bioenergy outputs are observed, the life cycle scenarios of PS – 03, display higher NRnEV and renewability factors. Steam explosion technology does not consume chemicals, such as sulfuric acid, neutralizing agents in feedstock pretreatment. Hence, the life cycle scenarios under PS – 03 consume a comparatively lower amount of fossil energy to produce 1 m^3 of fuel-grade bioethanol using rice straw. Thus, net renewable energy gains and renewability factors for life cycle scenarios under PS – 03 are higher compared to other life cycle scenarios.

Further, the fossil energy consumption in life cycle scenarios under PS – 02 is approximately 7 times higher than that of in life cycle scenarios under PS – 03. Higher fossil energy consumptions and comparatively lower net bio-energy outputs per 1 m^3 of fuel-grade bioethanol at 99.7 vol % purity, cause life cycle scenarios under PS – 02 to result in lower net renewable gains.

In addition, life cycle scenarios under DS – 01(extractive distillation) follow higher renewable energy gains considering the other life cycle scenarios with different bioethanol dehydration technologies. Life cycle scenarios under DS – 02 (azeotropic distillation) show the least renewable energy gains due to the higher energy consumption for bioethanol dehydration. The lowest NRnEV, i.e., 12,770.02 MJ/m^3 of bioethanol renewability factor, i.e., 2.51 are observed in life cycle scenario (f), where alkaline pretreatment and pressure swing distillation technologies are adopted as the feedstock pretreatment technology and the bioethanol dehydration technology, respectively. The lower bioethanol yield resulting from life cycle scenario (f) contributes to a higher fossil energy consumption to produce 1 m3 of fuel-grade bioethanol at 99.7 vol% purity from unutilized rice straw. Thus, the lowest bioenergy gain and lowest renewability factor are observed for the life cycle scenario (f).

6.3 Life Cycle Impact Assessment

Table 6.6 lists the scenario-based environmental impacts that resulted in producing 1 m^3 of fuel-grade bioethanol at 99.7 vol % purity from unutilized rice straw. The results conclude that the life cycle scenarios under PS – 01, where dilute acid pretreatment technology is adopted as the feedstock pretreatment technology, contribute to low environmental impacts. Starting with the global warming potential (GWP), life cycle scenarios under PS – 01 (scenario (a), scenario (b), scenario (c)), result in negative values (- 170.52 kg CO_2 eq./m^3 of bioethanol, - 107.51 kg CO_2 eq./m^3 of bioethanol, - 5.14 kg CO_2 eq./m^3 of bioethanol), claiming a net carbon credit in the production of 1 m^3 of fuel-grade bioethanol at 99.7 vol % purity from unutilized rice straw. The main cause for creditable GHG emission for life cycle scenarios under PS – 01 is the availability of surplus bioenergy (electricity) to be credited to the national electricity grid mix. Even though scenarios (d) and (e) credit surplus bioenergy (electricity), higher fossil energy consumption in alkaline pretreatment (PS – 02) and higher energy consumption in azeotropic distillation dehydration technology (DS – 02) effect to result in a positive GWP value. The least GWP is observed in the life cycle scenario (a), where dilute acid pretreatment and extractive distillation are adopted as the feedstock pretreatment technology and bioethanol dehydration technology, respectively. The highest GWP value, 839.45 kg CO_2 eq./m^3 of bioethanol is observed in the life cycle scenario (f). Considering the dehydration scenarios, life cycle scenarios under DS – 01 where extractive distillation technology is used for bioethanol dehydration, contribute to lower GWP values, compared to other life scenarios under DS – 02 and DS – 03.

Table 6.6: Scenario-based environmental impacts (basis: 1 m^3 of fuel-grade bioethanol at 99.7 vol % purity)

Impact category	**Unit**	**Life cycle scenario**								
		(a)	**(b)**	**(c)**	**(d)**	**(e)**	**(f)**	**(g)**	**(h)**	**(i)**
Global warming	kg CO$_2$ eq.	(170.52)	(107.51)	(5.14)	196.48	543.66	839.45	310.92	341.07	340.42
Stratospheric ozone depletion	kg CFC11 eq.	4.90E-04	5.23E-04	5.04E-04	8.36E-04	6.73E-04	1.02E-03	6.89E-04	9.98E-04	9.25E-04
Ozone formation, Human health	kg NOx eq.	2.05	2.59	2.82	6.57	6.45	10.71	6.18	9.16	8.45
Fine particulate matter formation	kg PM2.5 eq.	2.38	2.74	2.70	7.34	6.67	10.09	4.81	7.28	6.65
Ozone formation, Terrestrial ecosystems	kg NOx eq.	2.09	2.63	2.85	6.62	6.49	10.77	6.23	9.22	8.51
Terrestrial acidification	kg SO$_2$ eq.	0.59	0.98	1.38	6.68	7.74	10.62	3.20	4.33	4.08
Freshwater eutrophication	kg P eq.	0.13	0.13	0.13	0.89	0.89	0.97	0.11	0.11	0.11
Marine eutrophication	kg N eq.	0.25	0.25	0.25	0.28	0.28	0.30	0.24	0.24	0.24
Terrestrial ecotoxicity	kg 1,4-DCB	406.90	406.46	406.61	400.41	399.97	435.97	388.76	388.47	396.58
Freshwater ecotoxicity	kg 1,4-DCB	8.13	8.15	8.09	39.87	39.90	43.34	7.71	7.71	7.84
Marine ecotoxicity	kg 1,4-DCB	12.14	12.17	12.08	56.61	56.67	61.55	11.52	11.51	11.72
Human carcinogenic toxicity	kg 1,4-DCB	0.46	0.47	0.46	1.81	1.82	1.97	0.45	0.46	0.46
Human non-carcinogenic toxicity	kg 1,4-DCB	485.42	486.44	484.10	1,617.53	1,619.55	1,759.17	461.97	461.94	470.54

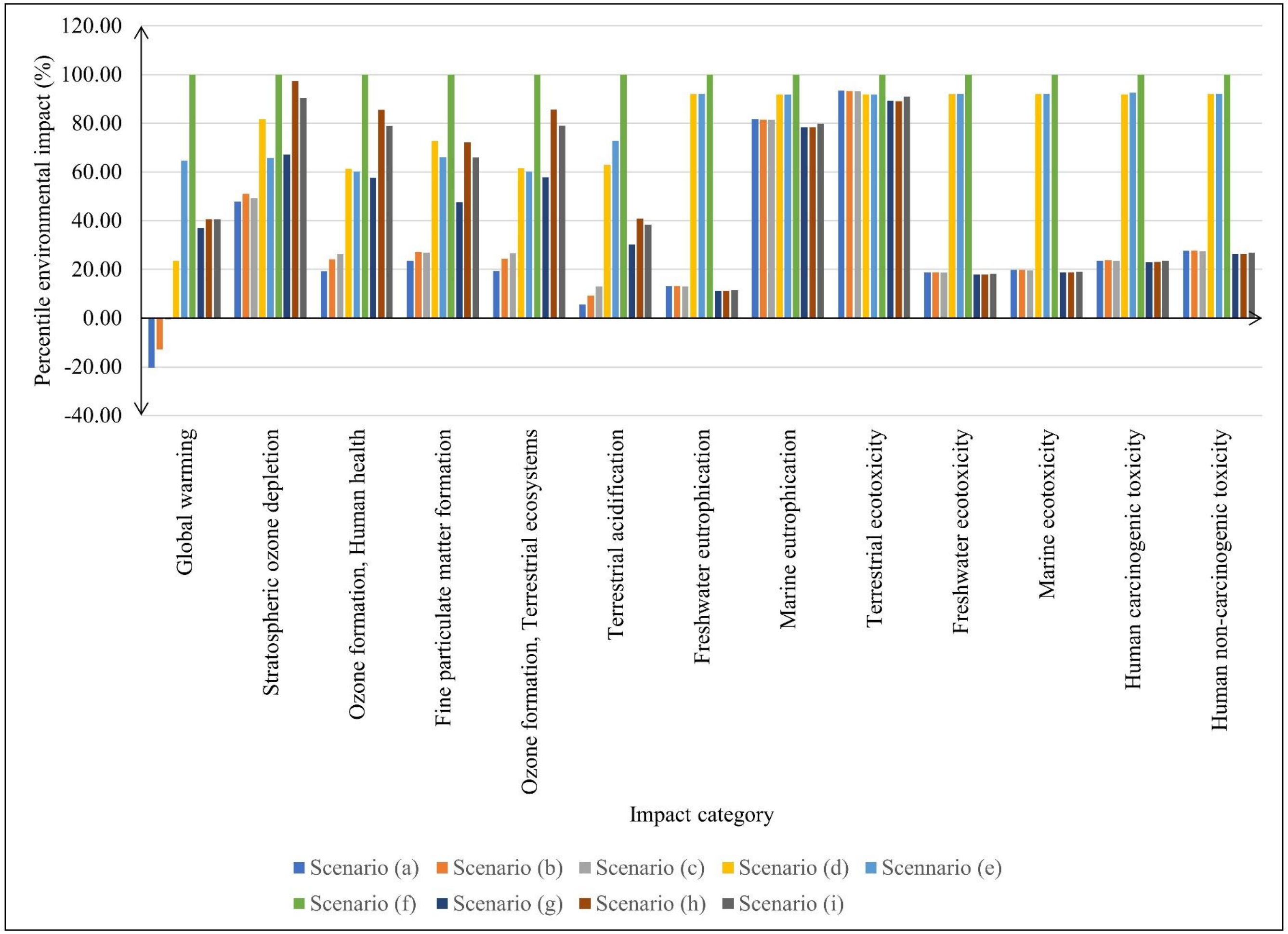


Fig. 6.7: Life cycle impact assessment results of life cycle scenarios for fuel grade bioethanol production from unutilized rice straw

In addition to global warming, the highest contribution to the impact of stratospheric ozone depletion is observed from life cycle scenario (f), i.e., 1.02 $\times 10^{-3}$ kg CFC11eq./ m^3 of bioethanol and the least contribution is observed from scenario (a), i.e., 4.90 $\times 10^{-4}$ kg CFC11eq./ m^3 of bioethanol. The life cycle scenarios under PS – 01 result in distinctive low contributions to stratospheric ozone depletion, and comparatively higher energy-consuming life cycle scenarios result in a high contribution for the considered impact. Similar to global warming impact, life cycle scenarios of DS – 01, claims a lower stratospheric ozone depletion compared to life cycle scenarios corresponding to DS – 02 and DS – 03. A similar contribution pattern is observed in considered life cycle scenarios, for the environmental impacts, ozone formation – human health and ozone formation – terrestrial ecosystems.

Considering the environmental impacts, such as fine particulate matter formation and terrestrial acidification, scenario (a) contributed to the least impact and scenario (f) contributed to the highest impact. However, for the toxicity impacts including freshwater ecotoxicity, marine ecotoxicity, human carcinogenic toxicity, and human non-carcinogenic toxicity all the life cycle scenarios display similar behavior. Life cycle scenarios under PS – 02 show the highest impact for the ecotoxicity and toxicity impact while other life cycle scenarios display an approximately similar impact.

Figure 5.7 displays the relative environmental impact of the life cycle scenarios. The relative environmental impact for a life cycle scenario is obtained by calculating the percentile fraction of the impact to the maximum environmental impact value of the nine life cycle scenarios. Life cycle scenario (f) displays 100% relative impact for all the environmental impacts considered in this study. Consequently, life cycle scenario (a) shows a relative impact lower than 20% for all the environmental impacts. Considering the life cycle environmental impacts, life cycle scenario (a) implies the most environmentally benign process routine to produce fuel-grade bioethanol from unutilized rice straw claiming a net CO_2 credit to the environment.

6.4 Sensitivity analysis

LCA assists in the sensitivity analysis for alternative life cycle scenarios with different process routes. In this study, sensitivity analysis is conducted for the best environmentally performing scenarios, i.e., scenarios under PS – 01 (scenario (a), scenario (b), and scenario (c)) by varying three critical uncertainty parameters, i.e., bioethanol yield (L/tonne), process energy consumption (MJ/m^3 of bioethanol), and lignin composition (% wt). The variation range for the uncertainty parameter bioethanol yield; 255.24 – 346.89 L/tonne of rice straw is determined considering ±10% variation from the highest and the lowest bioethanol yields observed from the nine life cycle scenarios in this study. The variation ranges for the remaining uncertainty parameters are determined considering the reported literature data as in the sensitivity analysis conducted for the base-case scenario.

Table 6.8 shows the sensitivity results of NER, Rn, and environmental impacts, for the parameter variations in the considered life cycle scenarios. The highest uncertainty is observed for process energy consumption followed by lignin composition. The corresponding variation in process energy consumption results in wide impact result variation ranges for all three life cycle scenarios. For instance, NER for scenario (c) ranges from 1.32 – 0.59 for the variation of process energy consumption from 15,000 MJ/m^3 of bioethanol to 30,000 MJ/m^3 of bioethanol. Corresponding sensitivity ranges of scenario (c) for bioethanol yield variation and lignin composition variation are 0.66 – 0.88 and 0.76 – 1.07, respectively. As such, the uncertainty of the process energy consumption causes the highest sensitivity for the majority of the environmental impact indicators. Further, the sensitivity results of scenario (b) for global warming ranges between 122.71 kg CO_2 eq. / m^3 of bioethanol – (528.02) kg CO_2 eq. / m^3 of bioethanol for the uncertainty of process energy consumption. Thus, high sensitivity to process energy consumption implies the lower the process energy consumption, the more creditable surplus energy resulting in replacing the Sri Lankan energy grid mix. However, the higher process energy consumption demands higher wood chips and risk husk consumption resulting in more diesel consumption in transportation stages. Thus, causing higher environmental emissions and fossil energy consumption per production of 1 m^3 of fuel-grade bioethanol using rice straw.

Further, the second most sensitive variation is observed for the uncertainty of lignin composition in rice straw. Low lignin composition in rice straw, generates a lower quantity of energy due to the reduced lignin solid residue amount. Therefore, to cater the excess process energy demand extra wood chips and rice husk is required causing additional transportation operations. Further, lower lignin composition relatively indicates higher cellulose and hemicellulose composition resulting higher bioethanol yields. However the sensitivity of energy and environmental indicators is negligible for relatively higher bioethanol yields. Thus, lower lignin compositions in rice straw reduces the sustainable energy and environmental performance in the considered fuel-grade bioethanol production life cycle. On the contrary, higher lignin compositions in rice straw increase the energy cogeneration causing surplus energy in the system. Crediting the surplus electricity to the national energy grid-mix to replace fossil generated electricity, results in significantly reduced environmental impacts and higher renewable energy gains.

However, the sensitivity results of the environmental impacts, such as freshwater eutrophication, marine eutrophication, terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, human carcinogenic toxicity, and human non-carcinogenic toxicity are zero for the uncertainty of both indicators, i.e., process energy consumption and lignin composition. According to the process contribution results observed for each environmental impact listed under Appendix D, the key environmental emissions for the environmental impacts with zero sensitivity for process energy consumption and lignin composition, are contributed from the chemical and other raw materials consumed in the bioethanol production process. Thus, the uncertainty of the process parameters; process energy consumption and lignin composition do not vary the amounts of chemicals and raw material consumed to produce 1 m^3 of bioethanol from rice straw. In addition, the uncertainty of bioethanol yield results in the lowest sensitivity for energy indicators and all the environmental impact indicators. The lower bioethanol yields consume higher energy amounts and higher raw materials, creating high environmental emissions per 1 m^3 of bioethanol produced from rice straw. Inversely, higher bioethanol yields provide 1 m^3 of bioethanol with minimum energy and raw material consumption resulting in favorable energy indicators and low environmental impact indicators.

Considering the sensitivity analysis results, it is recommended to improve the energy efficiency of the system with lower process energy consumption (clean process designs and energy recovery systems) and select rice straw feedstocks with a fair lignin composition to increase the renewability of the process with lower environmental impact.

Table 6.7:Sensitivity analysis for life cycle scenarios under PS – 01. (basis: 1 m^3 bioethanol at 99.7 vol%).

Impact category	**Unit**	**Varied by bioethanol yield (L / tonne of rice straw)**			**Varied by process energy consumption (MJ / m^3 of bioethanol)**			**Varied by lignin composition (wt %)**		
		(a)	**(b)**	**(c)**	**(a)**	**(b)**	**(c)**	**(a)**	**(b)**	**(c)**
Parameter values in the study		315.08	315.35	315.29	20,880.12	24,712.40	23,299.13	16.04	16.04	16.04
Decreases increased range		255.24 – 346.89			15,000.00 – 30,000.00			10.00 – 40.00		
NER	-	0.76 – 1.00	0.65 – 0.86	0.66 – 0.88	1.32 – 0.60	1.30 – 0.63	1.32 – 0.59	0.87 – 1.25	0.75 – 0.96	0.76 – 1.07
Rn	-	11.11 – 14.43	10.53 – 13.72	10.70 – 14.06	15.17 – 11.40	14.34 – 11.84	15.21 – 11.67	12.55 – 18.40	12.01 – 15.44	12.26 – 17.14
Global warming	kg CO_2 eq.	(155.00) – (210.36)	(97.78) – (132.58)	(4.74) – (6.13)	280.73 – (462.05)	122.71 – (528.02)	339.21 – (432.12)	(878.04) – 7.58	(814.15) – 70.51	(712.03) – 172.92
Stratospheric ozone depletion	×10^{-4} kg CFC11 eq.	4.45 – 6.08	4.75 – 6.49	4.57 – 6.24	5.52 – 4.51	5.61 – 4.71	5.48 – 4.50	5.49 – 4.76	5.79 – 5.09	5.62 – 4.90
Ozone formation, Human health	kg NOx eq.	1.86 – 2.56	2.35 – 3.23	2.55 – 3.51	4.37 – 0.57	3.84 – 0.47	4.56 – 0.66	(0.15) – 2.62	0.36 – 3.16	0.61 – 3.38
Fine particulate matter formation	kg PM2.5 eq.	2.15 – 2.95	2.48 – 3.40	2.45 – 3.36	3.46 – 1.69	3.34 – 1.75	3.51 – 1.72	1.93 – 2.50	2.25 – 2.86	2.24 – 2.82
Ozone formation, Terrestrial ecosystems	kg NOx eq.	1.89 – 2.60	2.38 – 3.27	2.58 – 3.55	4.41 – 0.60	3.87 – 0.50	4.60 – 0.69	(0.11) – 2.65	0.40 – 3.19	0.64 – 3.41
Terrestrial acidification	kg SO_2 eq.	0.53 – 0.73	0.88 – 1.22	1.25 – 1.72	2.83 – (0.86)	2.14 – (1.10)	3.08 – (0.72)	(2.41) – 1.34	(2.03) – 1.73	(1.61) – 2.14
Freshwater eutrophication	kg P eq.	0.12 – 0.16	0.12 – 0.16	0.11 – 0.16	-	-	-	-	-	-
Marine eutrophication	kg N eq.	0.23 – 0.31	0.23 – 0.31	0.23 – 0.31	-	-	-	-	-	-
Terrestrial ecotoxicity	kg 1,4-DCB	369.58 – 502.21	369.58 – 502.21	369.58 – 502.21	-	-	-	-	-	-
Freshwater ecotoxicity	kg 1,4-DCB	7.39 – 10.04	7.41 – 10.07	7.35 – 9.99	-	-	-	-	-	-

Table 6.7 continued.

Marine ecotoxicity	kg 1,4-DCB	11.03 – 14.99	11.07 – 15.04	10.98 – 14.92	-	-	-	-	-	-
Human carcinogenic toxicity	kg 1,4-DCB	0.42 – 0.57	0.43 – 0.58	0.42 – 0.57	-	-	-	-	-	-
Human non-carcinogenic toxicity	kg 1,4-DCB	440.93 – 599.14	442.30 – 601.01	440.00 – 597.89	-	-	-	-	-	-

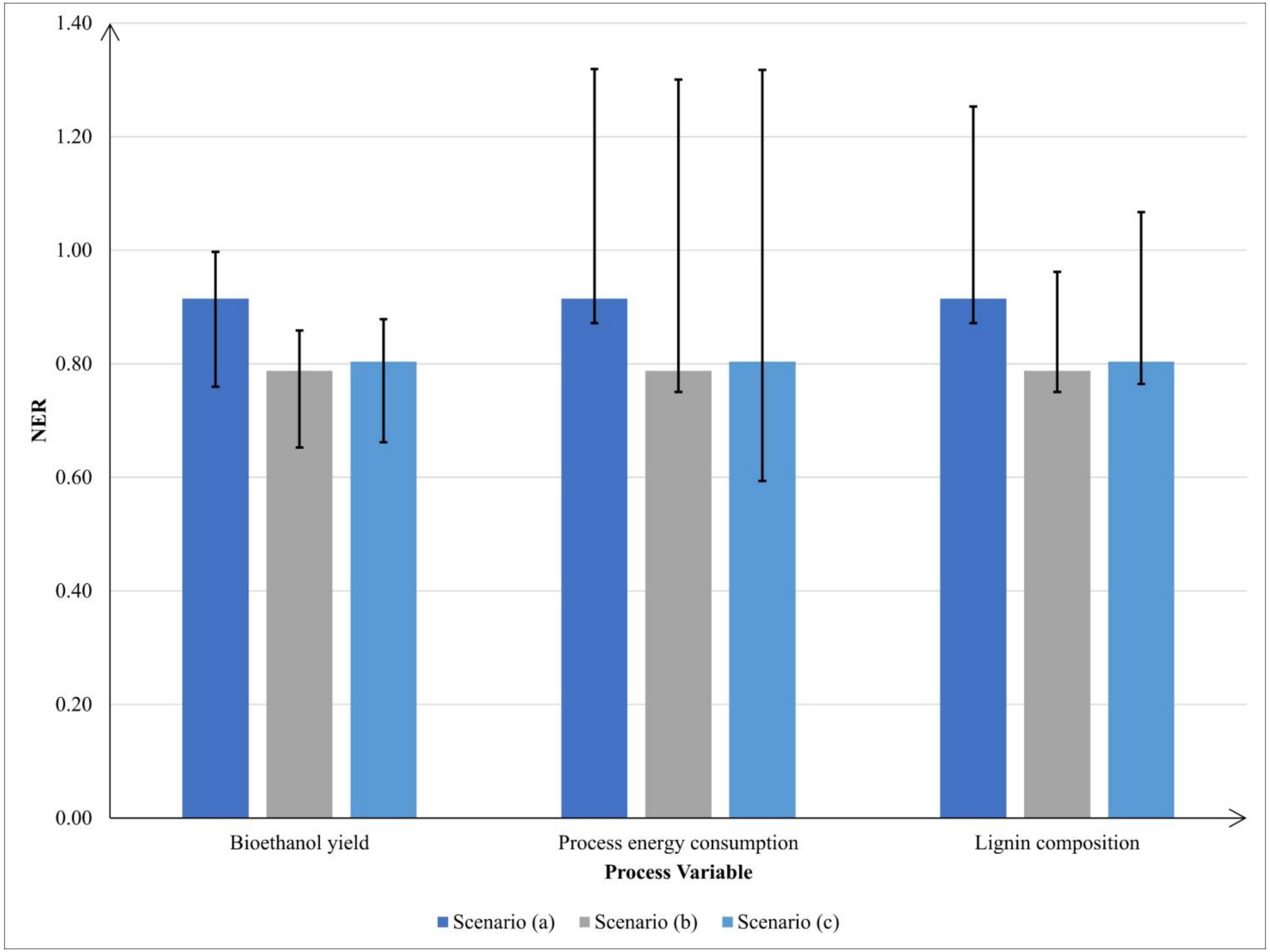


Fig. 6.8: Sensitivity of net energy indicator: NER

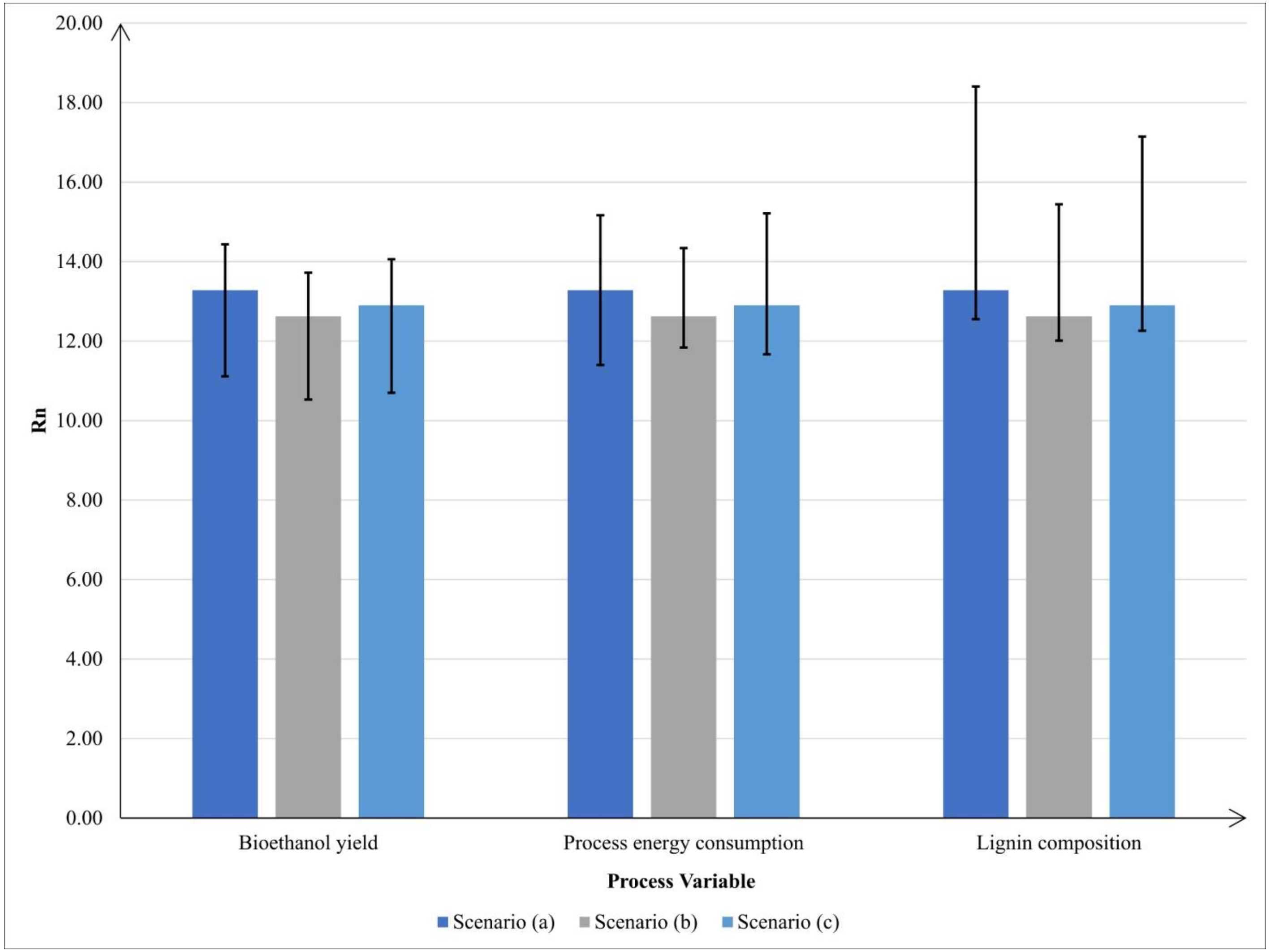


Fig. 6.9: Sensitivity of net energy indicator: Rn

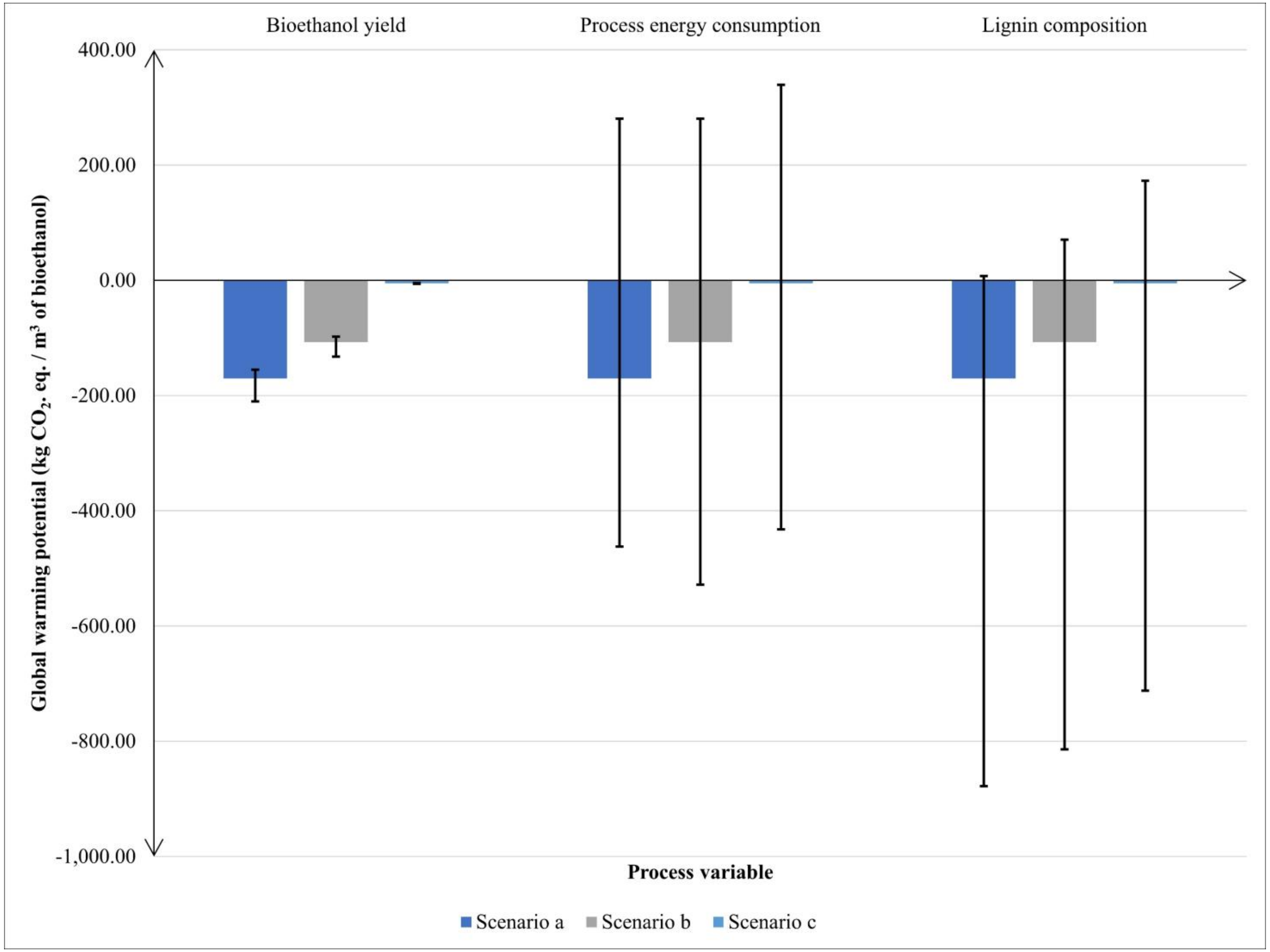


Fig. 6.10: Sensitivity of environmental impact indicators: Global warming

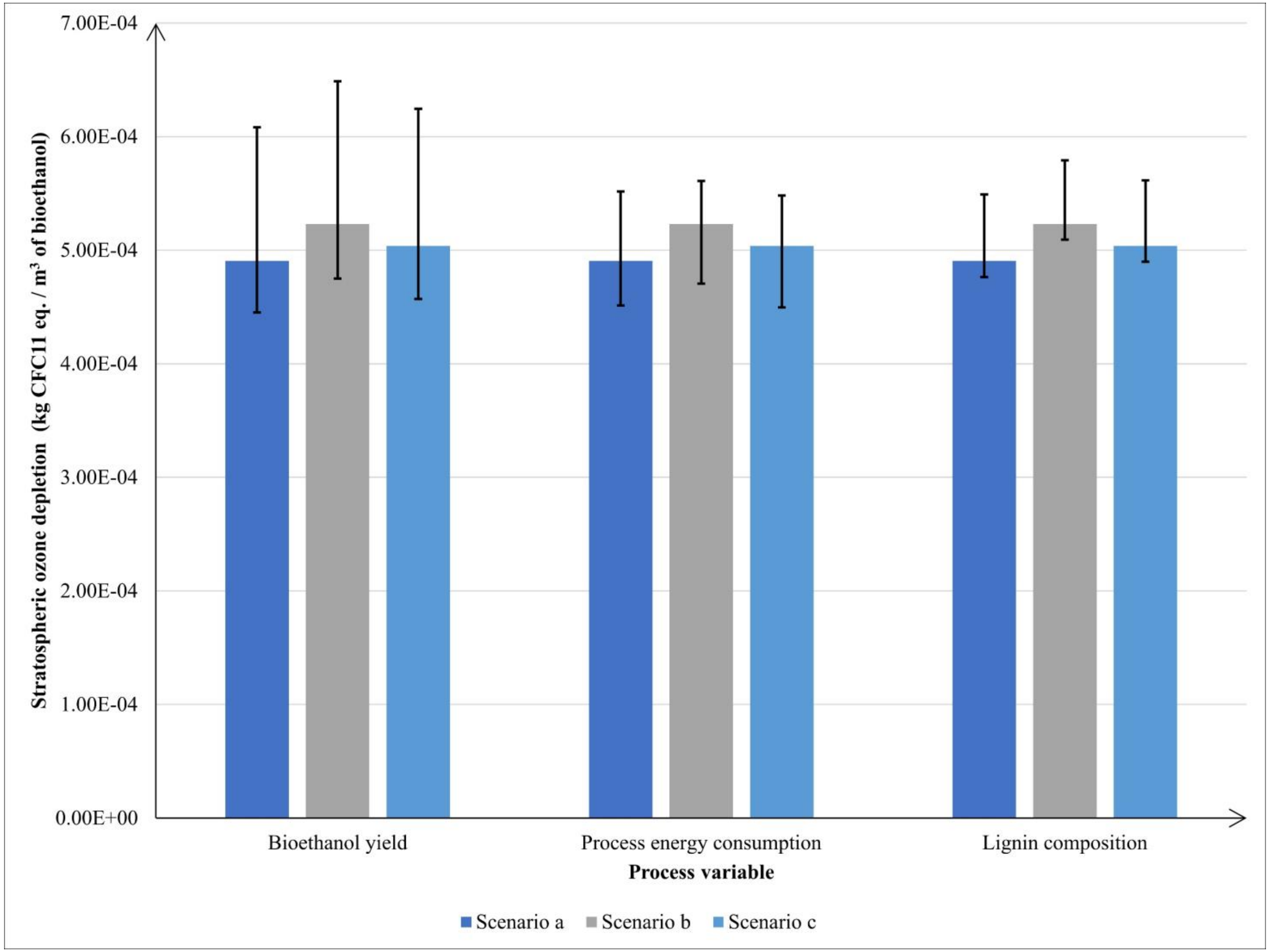


Fig. 6.11: Sensitivity of environmental impact indicators: Stratospheric ozone depletion

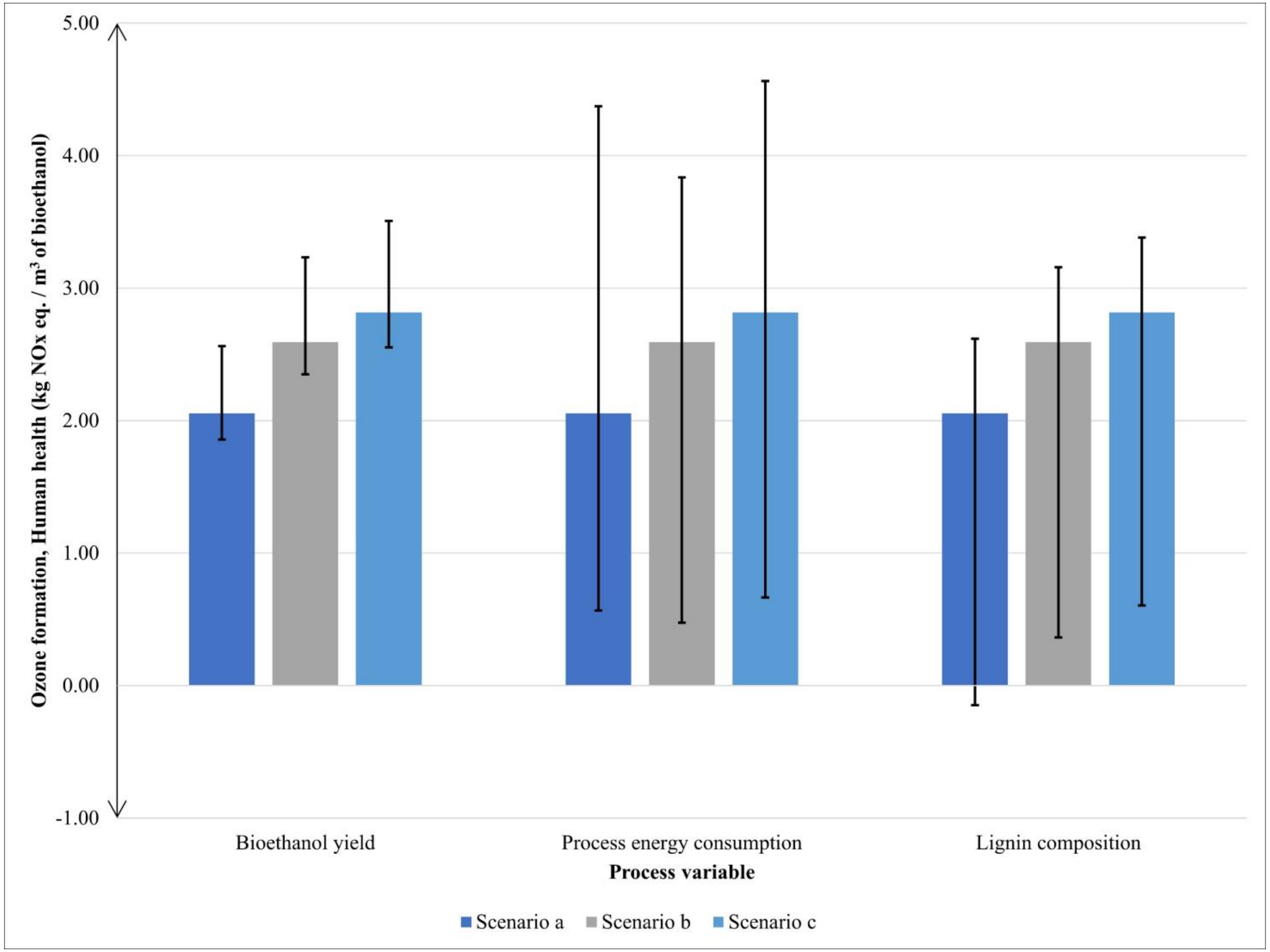


Fig. 6.12: Sensitivity of environmental impact indicators: Ozone formation, Human health

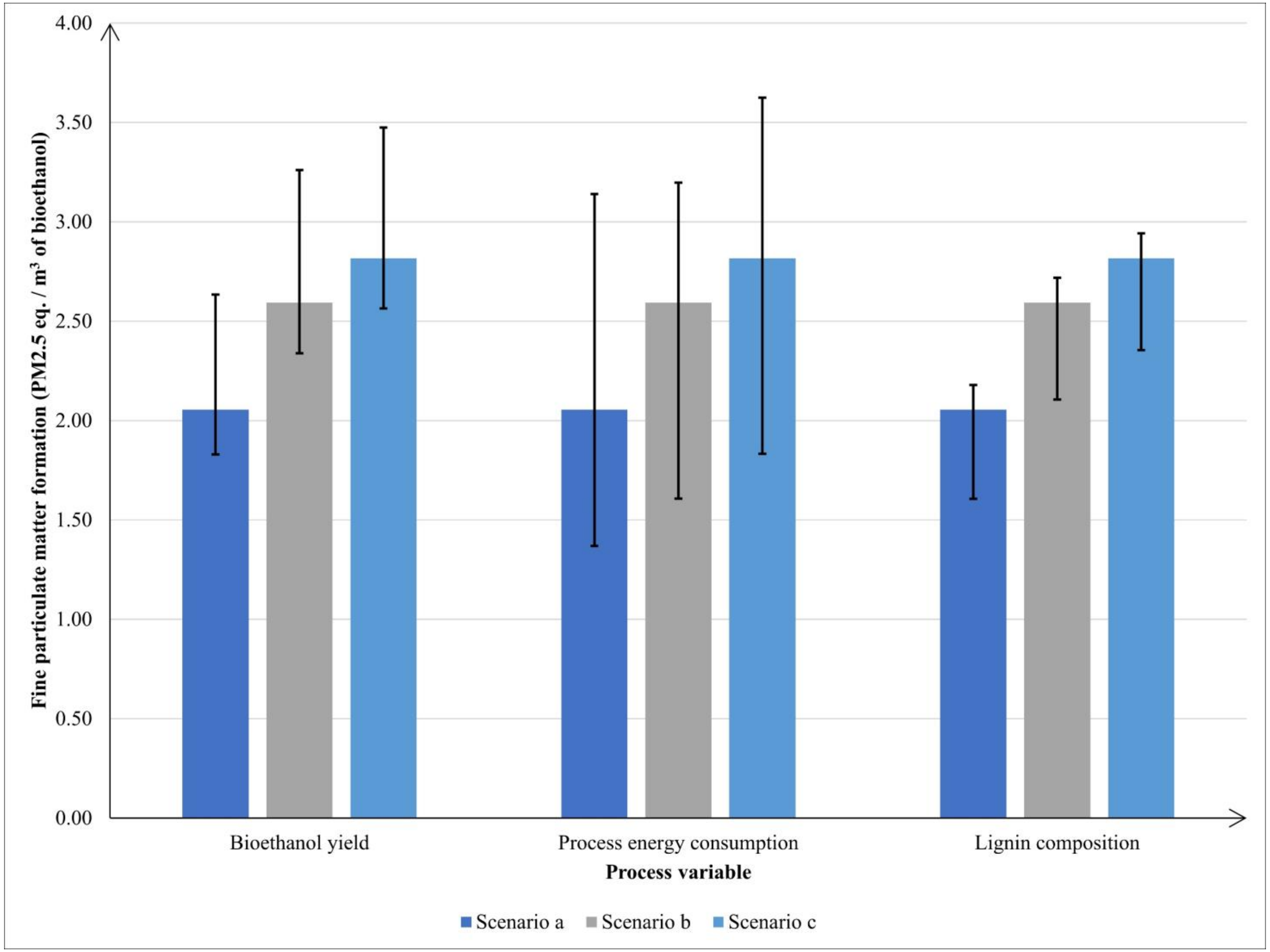


Fig. 6.13: Sensitivity of environmental impact indicators: Fine particulate matter formation

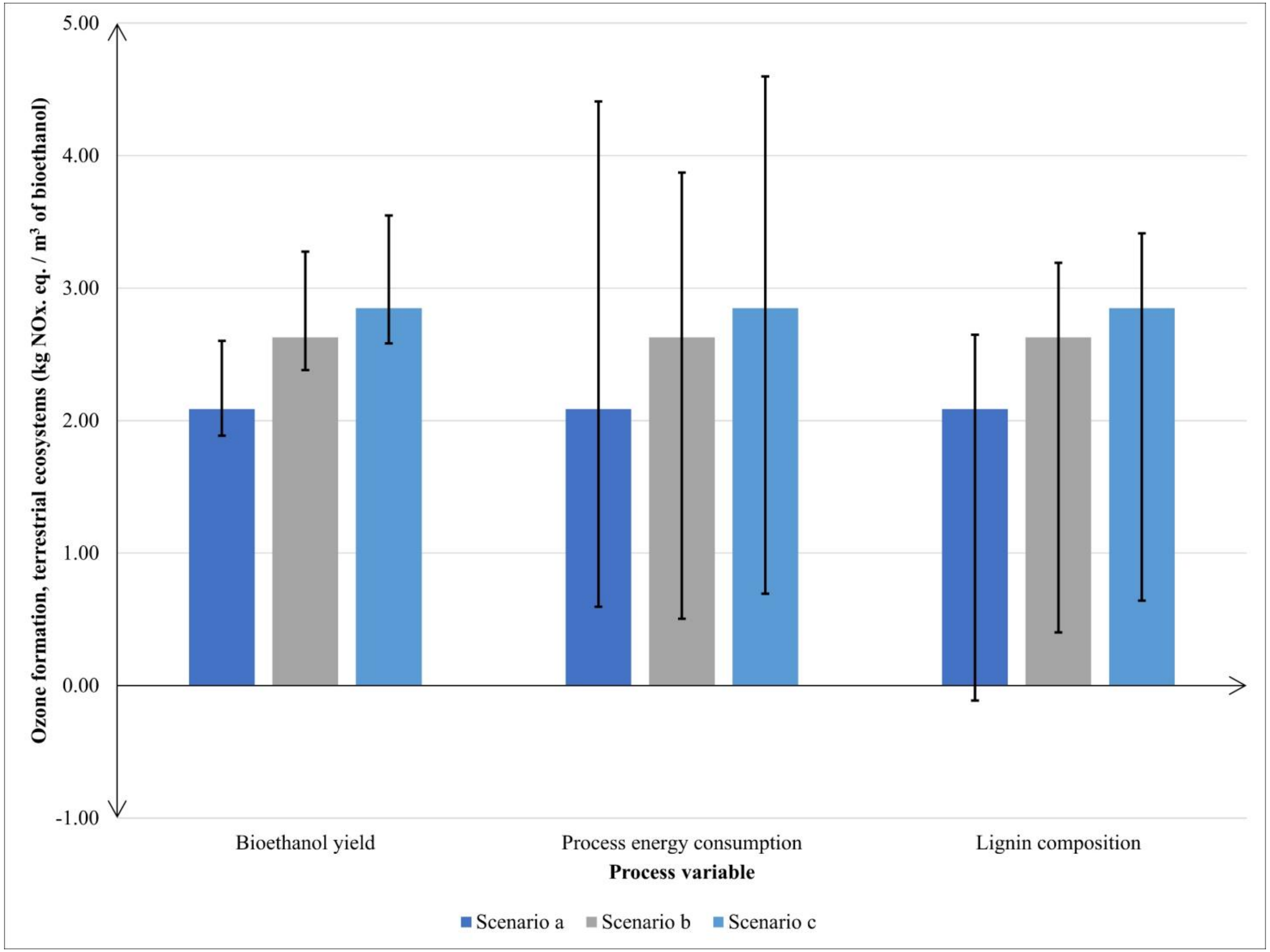


Fig. 6.14: Sensitivity of environmental impact indicators: Ozone formation, terrestrial ecosystems

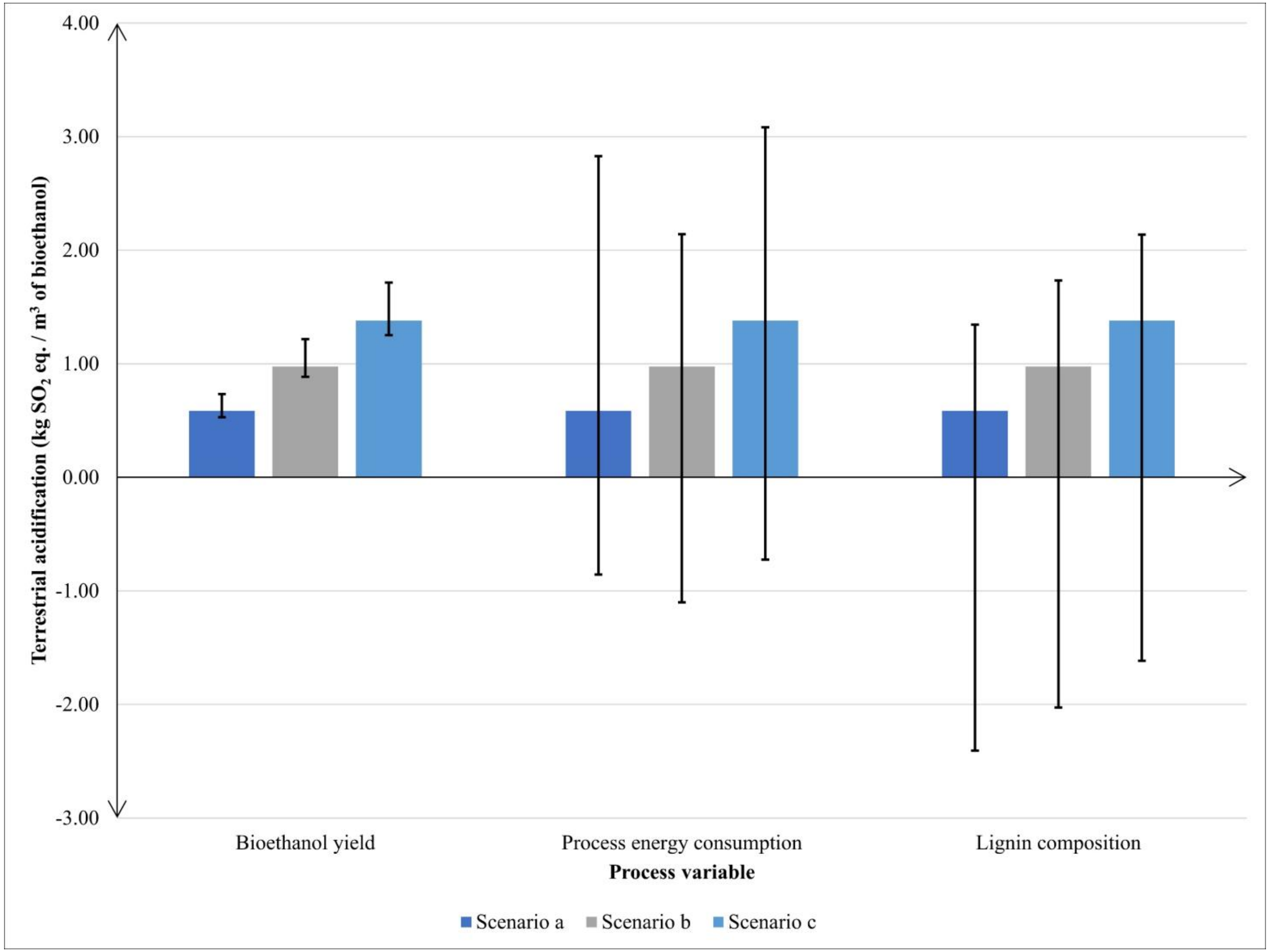


Fig. 6.15: Sensitivity of environmental impact indicators: Terrestrial acidification

CHAPTER 7

CONCLUSION

This study successfully claims its key objective of determining the most environmentally and energy benign process route to produce fuel-grade bioethanol from unutilized rice straw via a systematic and comparative LCA evaluation. Initially a base-case scenario is developed considering the Sri Lankan context with a net energy analysis and life cycle GHG assessment. Along with the key objectives, this study uses process simulation technique to model different process route scenarios for fuel-grade bioethanol production from unutilized rice straw.

This study concludes initially that valorization of unutilized rice straw in Sri Lanka to produce fuel-grade bioethanol reaches higher net energy gain and renewability along with a lower GWP, compared to reported real plants in the published literature. Hence, consideration of zero inventory allocation from the paddy rice cultivation stage for unutilized rice straw as a bioethanol feedstock will be a determinant factor for future studies and the establishment of new bioethanol plants. Fuel-grade (anhydrous) bioethanol production from unutilized rice straw contributes to replacing gasoline imports and consumption for a country like Sri Lanka with an agricultural economy that cultivates paddy rice as a major crop. The associated economic benefits with foreign currency savings are significant as revealed in this study. Further, the use of unutilized rice straw while avoiding field burning along with gasohol blending provides a net GHG credit. In addition, the life cycle stage-wise net energy analysis and GHG assessment reveal that the bioethanol dehydration stage consumes a low energy amount and is responsible for low GHG emissions, compared to that of other life cycle stages. Thus, the findings from this study with a simulated process plant would support the decision-making for upgrading existing bioethanol plants and the establishment of new fuel-grade bioethanol plants through the valorization of unutilized rice straw at a commercial scale in the future.

Further, this study models nine (09) alternative process route scenarios for bioethanol production from rice straw with an unbiased LCA comparison. The LCA evaluation reveals useful findings for environmentally benign routes for bioethanol production from rice straw indulging different feedstock technologies (i.e., dilute acid pretreatment, alkaline pretreatment, and steam explosion) and bioethanol dehydration technologies (i.e., extractive distillation, azeotropic distillation, and pressure swing distillation). From the fair comparison, dilute acid pretreatment is the most energy-efficient, renewable, and environmentally benign feedstock pretreatment technology followed by steam explosion, and finally, alkaline pretreatment. Comparatively low amounts of steam/hot water consumption and high conversions observed in dilute acid pretreatment causes the technology to be more environmentally benign. The most environmentally benign, energy efficient, and renewable bioethanol dehydration technology is extractive distillation followed by, azeotropic distillation and then steam explosion. Reduced process complexity, low energy, and solvent consumption in extractive distillation results in the most energy-efficient and, thus, the most environmentally benign approach for bioethanol dehydration. Hence, the most sustainable process route in terms of environmental and energy perspectives, to produce bioethanol from rice straw is obtained via the combination of dilute acid pretreatment as the feedstock pretreatment technology and extractive distillation as the bioethanol dehydration technology. However, the energy and environmental sustainability of remaining bioethanol process plant models can be improved via integrating more sustainable approaches. Adaptation of more energy recovery systems, clean production technologies, and efficient transportation media, are recommended to motivate the renewability and sustainability of the bioethanol production process from rice straw via all the different technological approaches considered in this study. Further, due to the absence of real-life process plant models to produce bioethanol from unutilized rice straw via different process routes, the results are validated for the real-life bioethanol processing plants with other feedstock materials. To mitigate this limitation, it is recommended to compare the process plant simulation models with real life process plants with same feedstock utilization in future studies. Along with the results obtained via this research, there is a possibility to evaluate the social and economic sustainability of the bioethanol production from unutilized rice straw with a comprehensive techno-economic assessment. Thus, it is recommended to conduct a comparative techno-economic assessment to evaluate the most profitable and socially viable procedure to produce fuel-grade bioethanol production from unutilized rice straw.

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A. APPENDIX A

Process block diagrams for the life cycle scenarios of the cradle-to-gate bioethanol production using rice straw as the feedstock

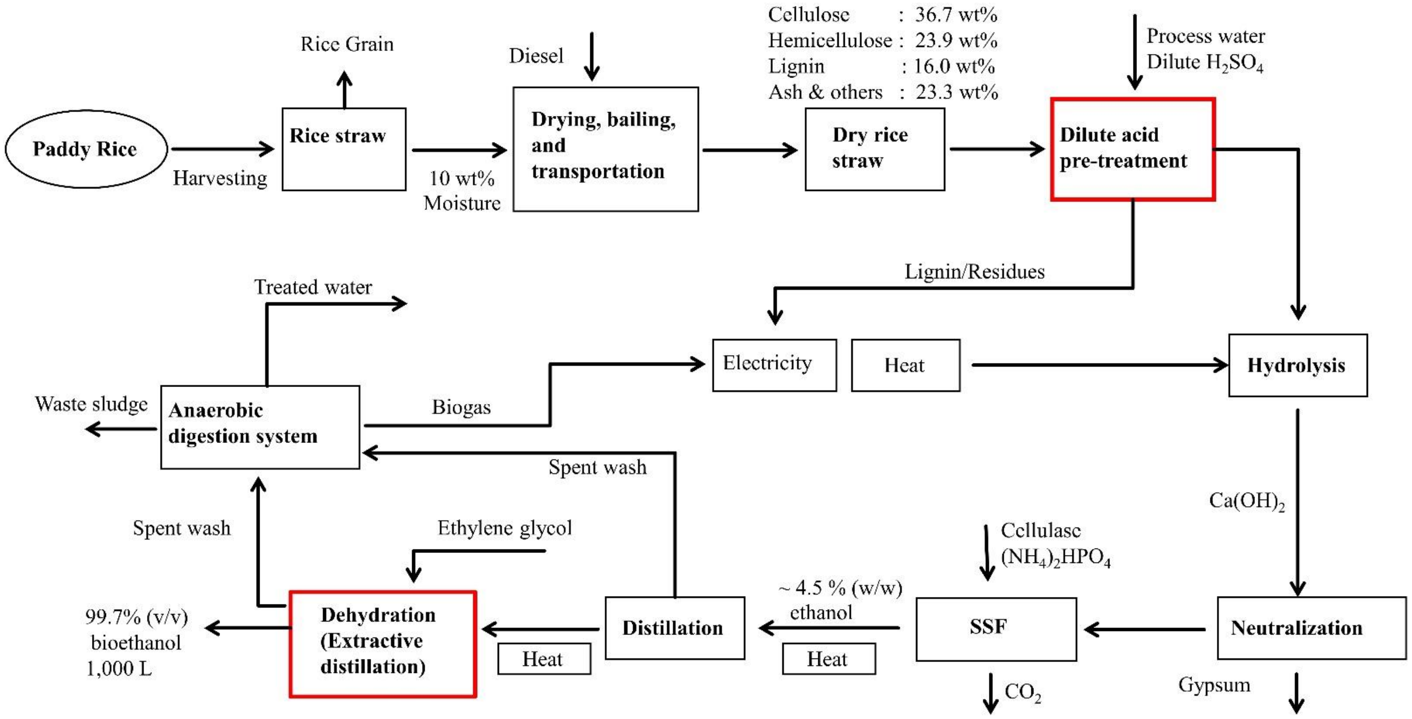

Fig. A.1: Process block diagram for life a scenario (a)

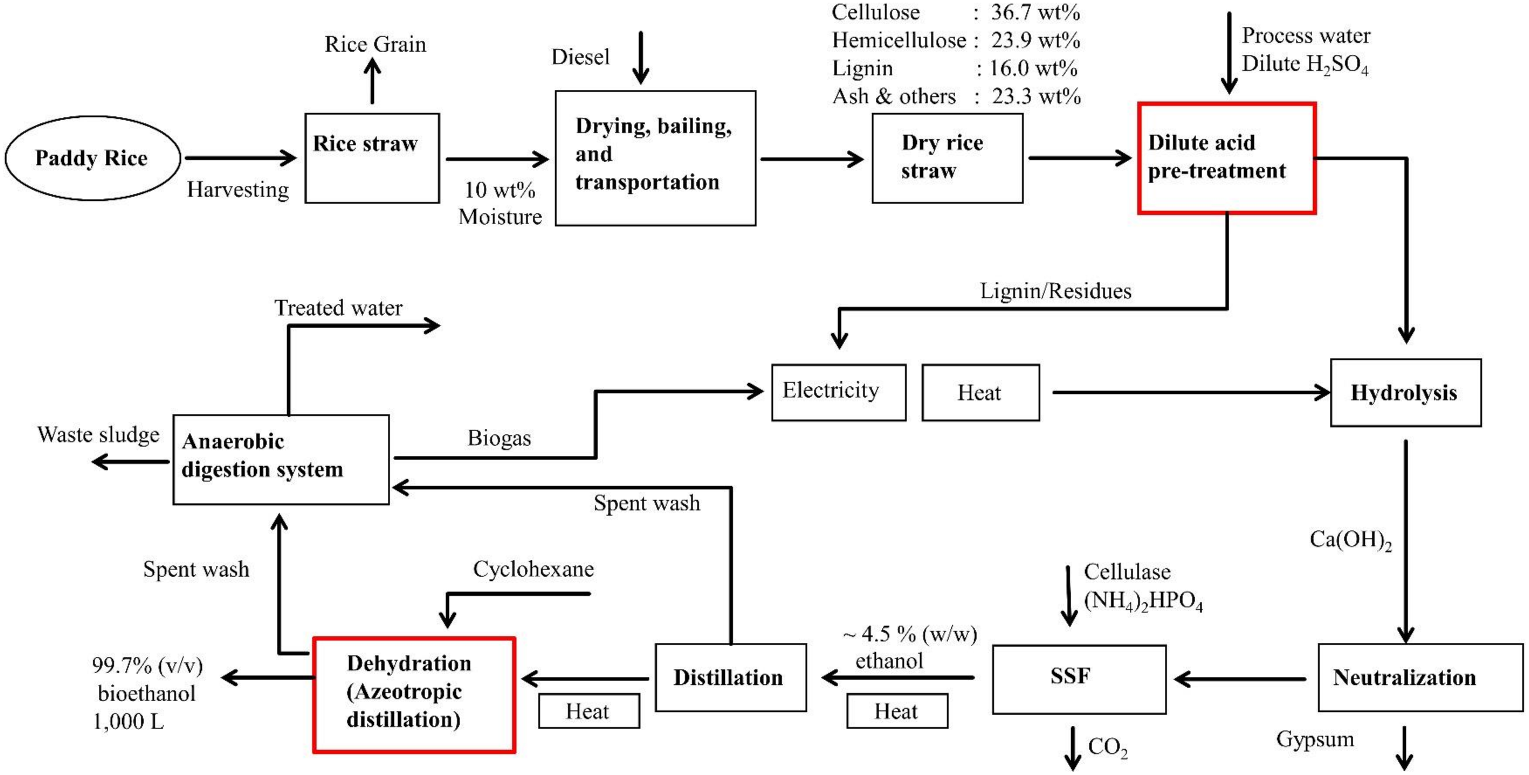

Fig. A.2: Process block diagram for life cycle scenario (b)

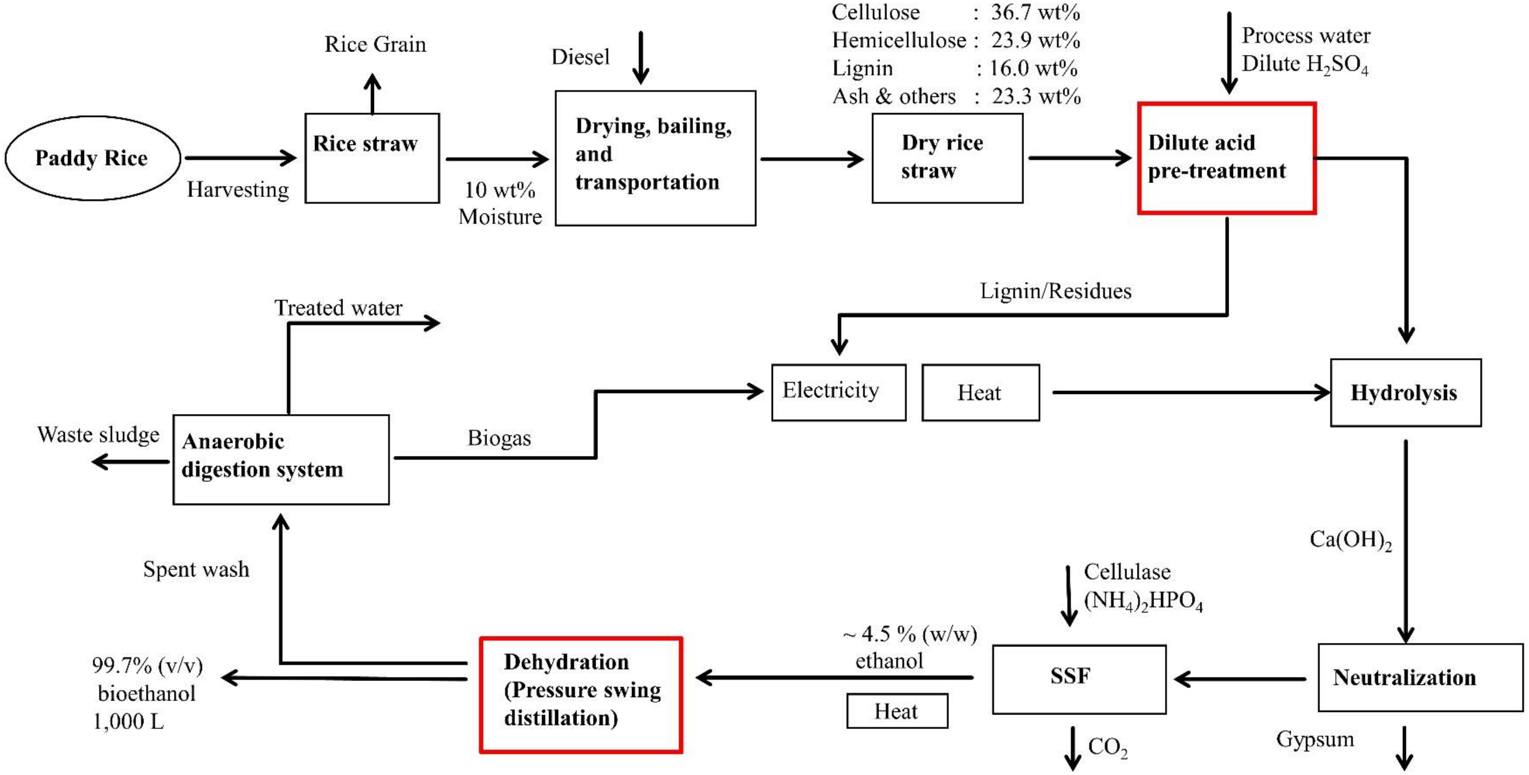

Fig. A.3: Process block diagram for life cycle scenario (c)

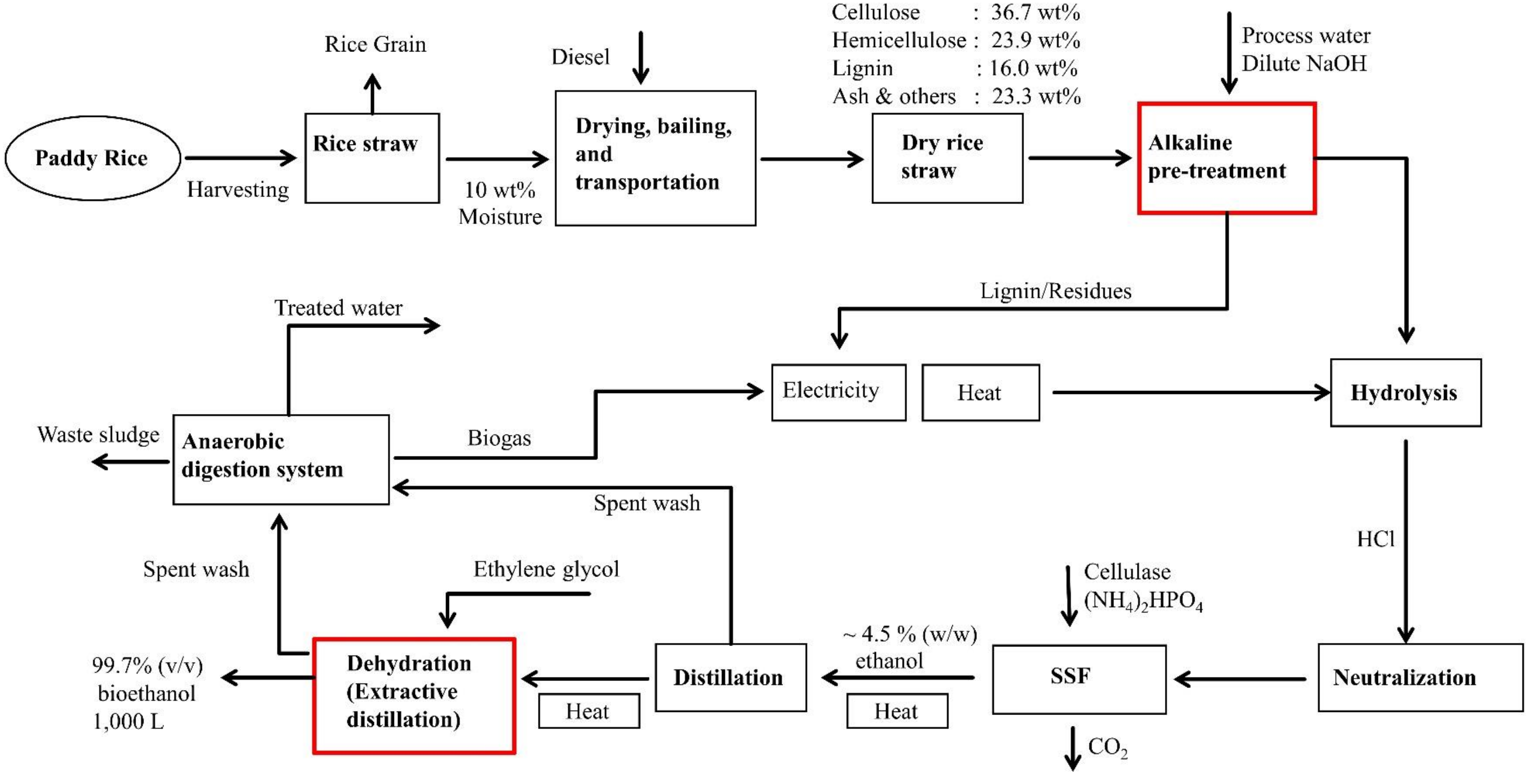

Fig. A.4: Process block diagram for life cycle scenario (d)

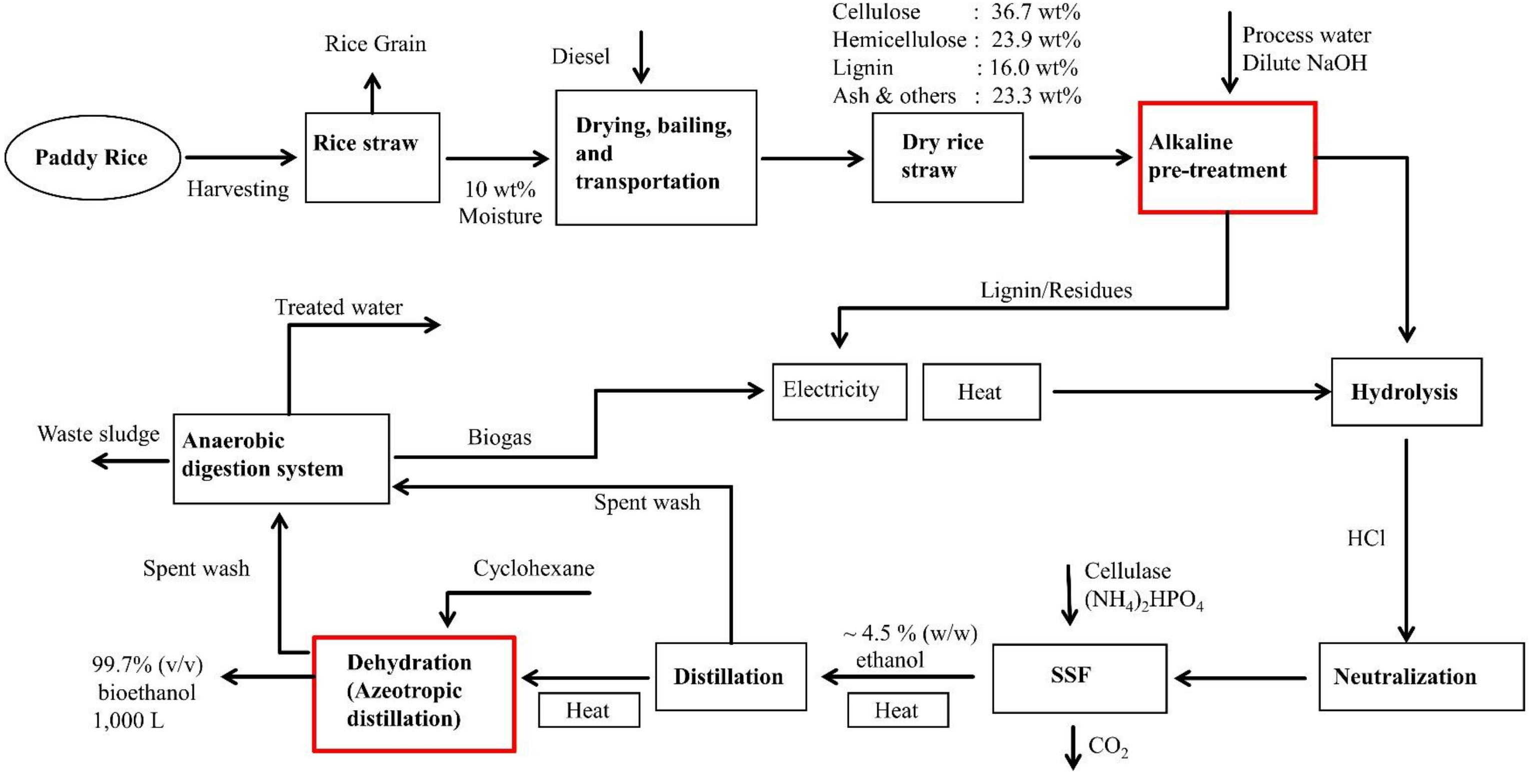

Fig. A.5: Process block diagram for life cycle scenario (e)

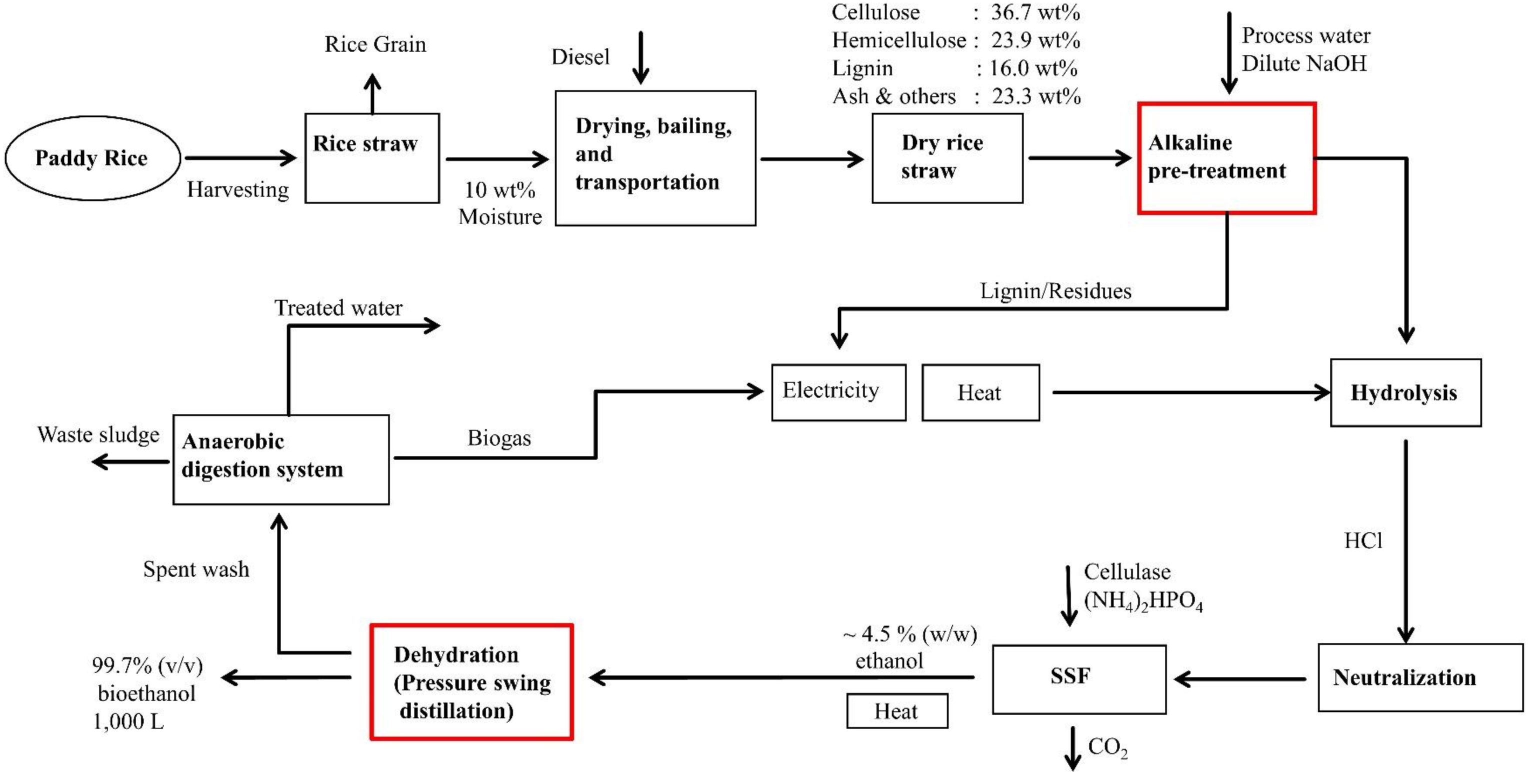

Fig. A.6: Process block diagram for scenario (f)

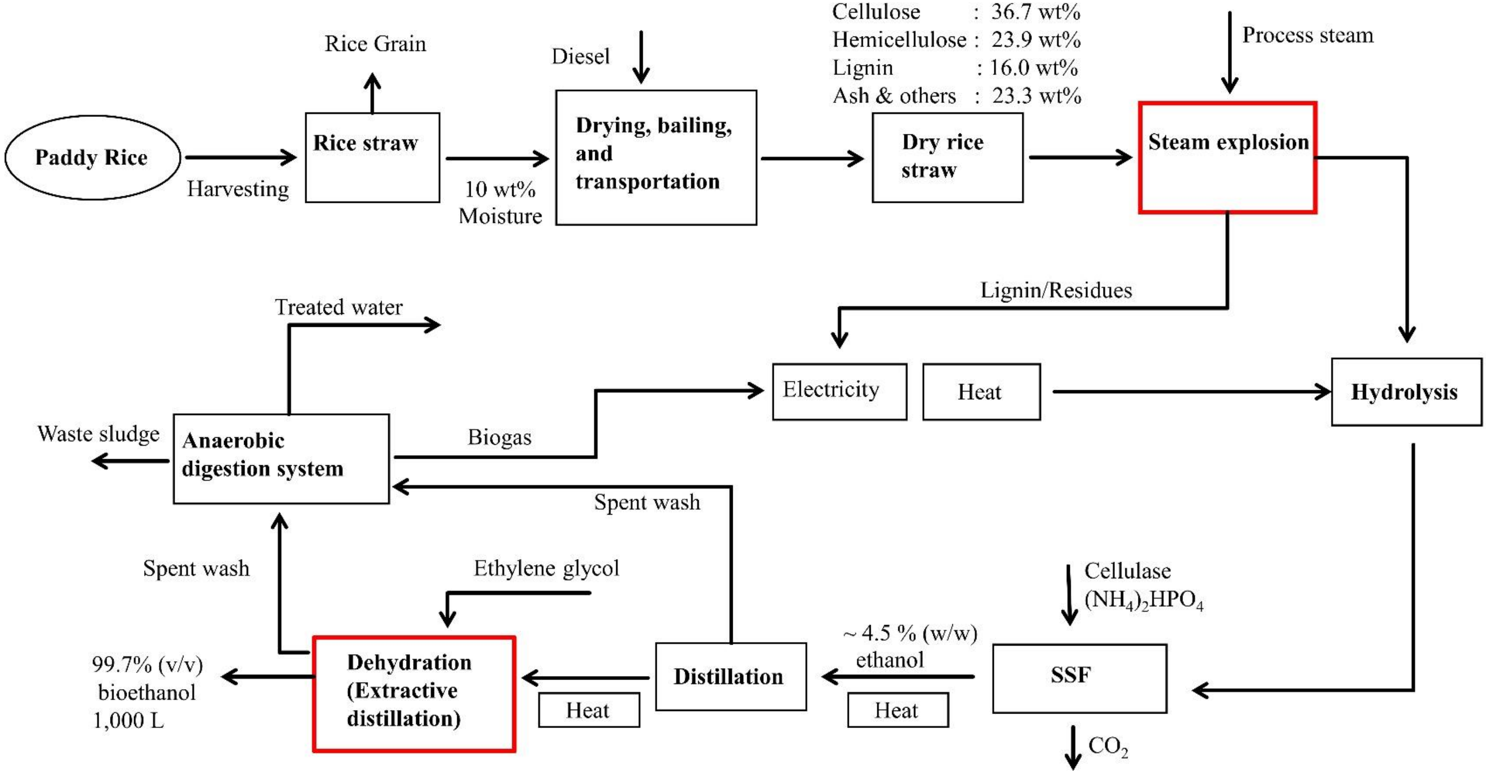

Fig. A.7: Process block diagram for life cycle scenario (g)

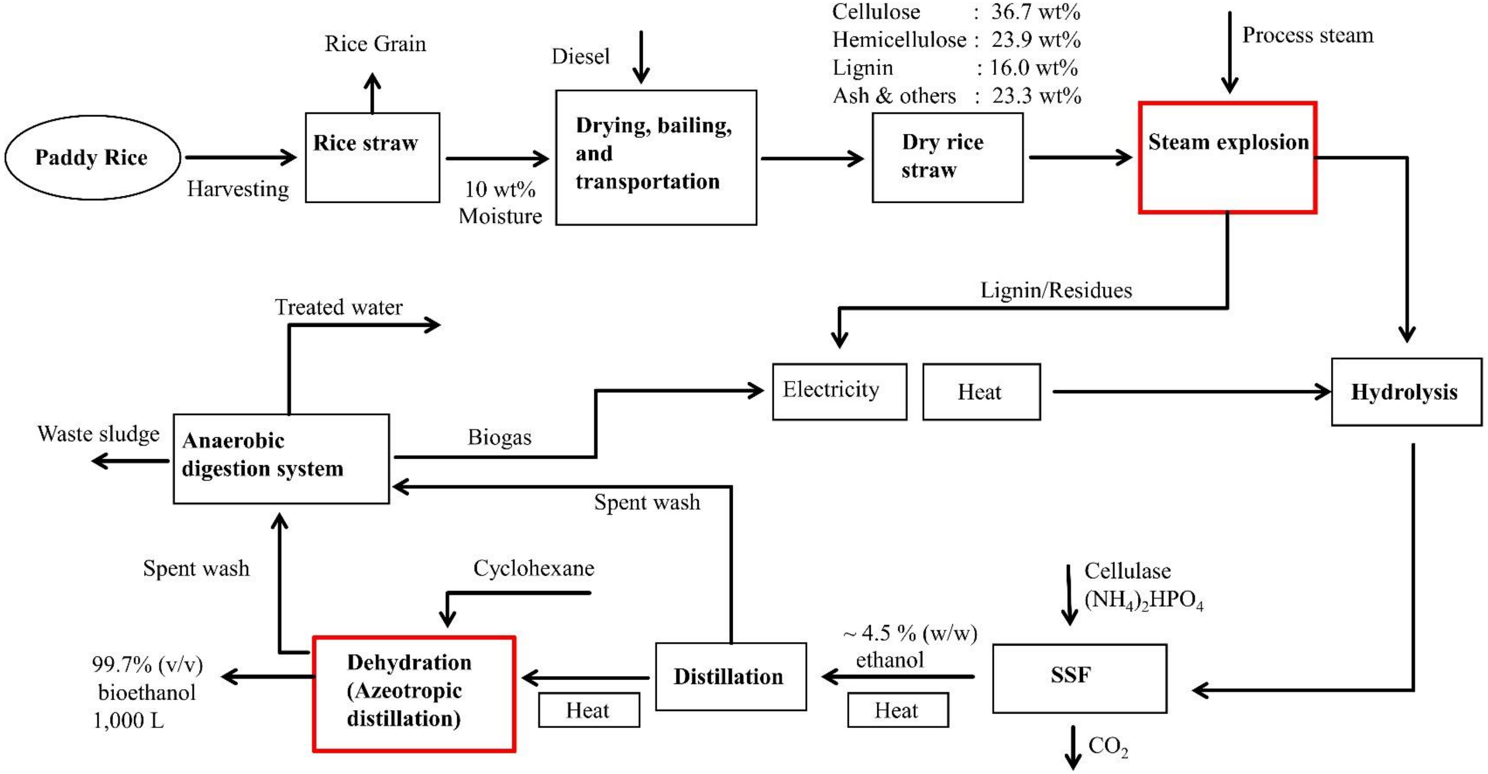

Fig. A.8: Process block diagram for scenario (h)

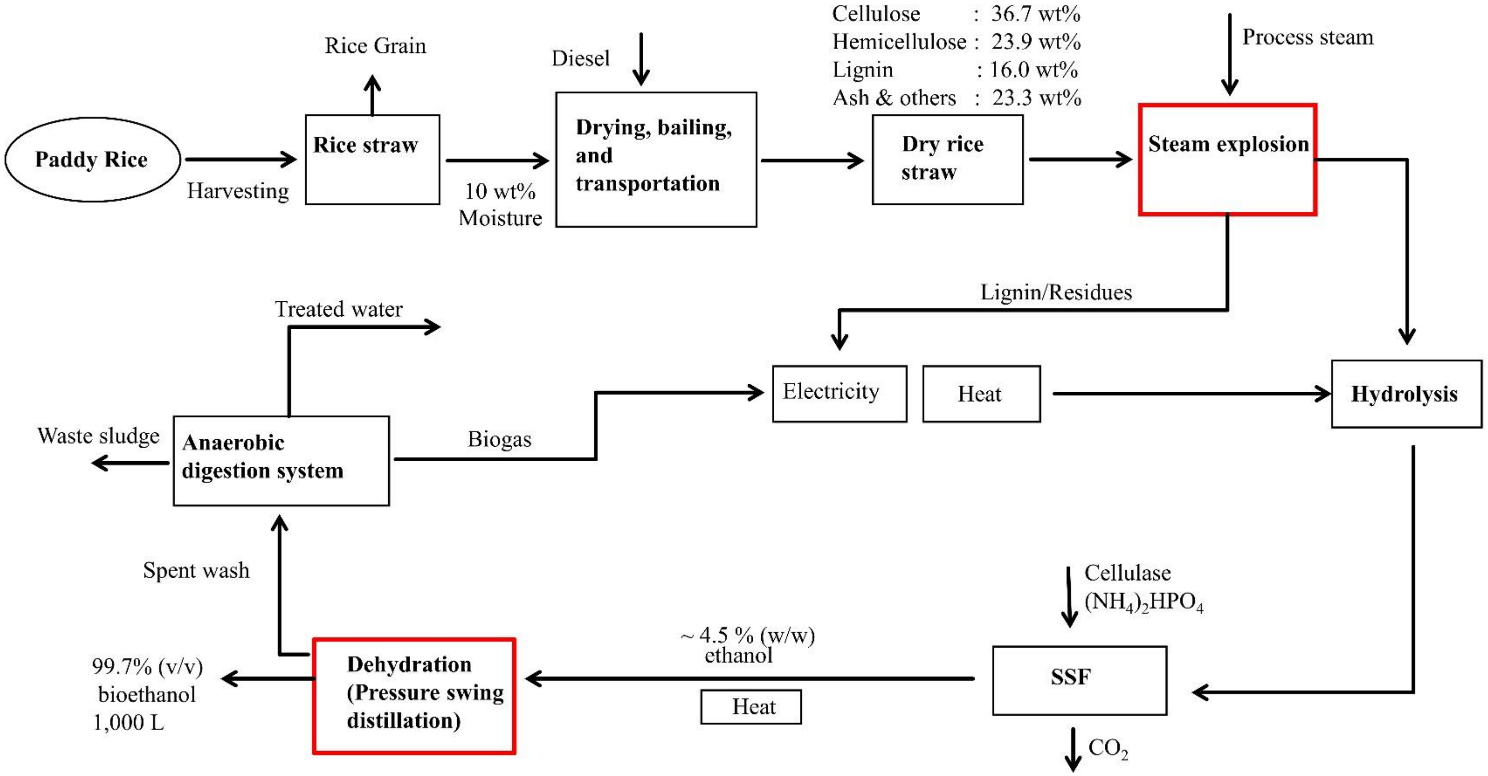

Fig. A.9: Process block diagram for scenario (i)

B. APPENDIX B

Process simulation flow diagrams of life cycle scenarios to produce 1 m^3 of fuel-grade bioethanol at 99.7 vol% from unutilized rice straw

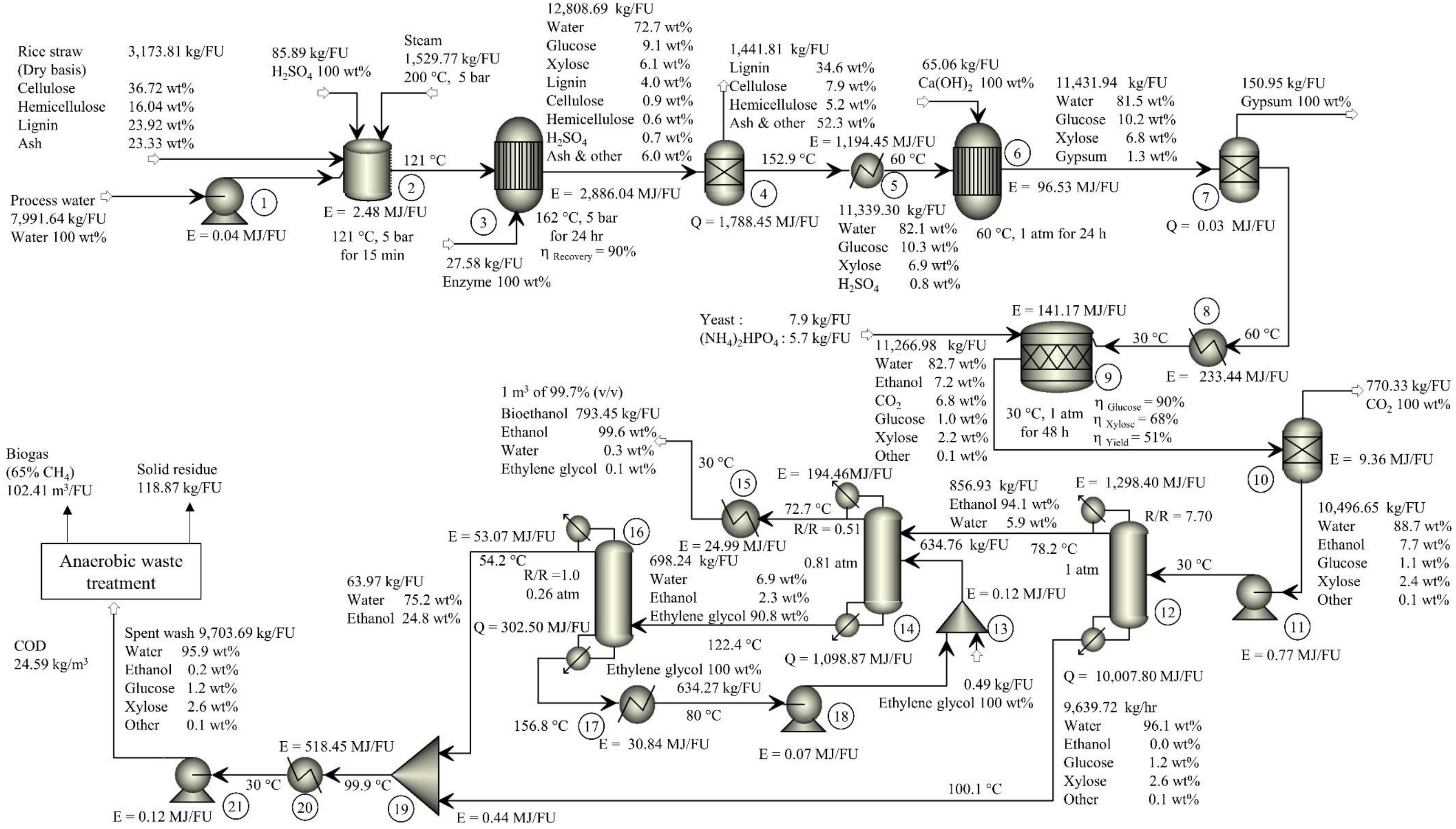

Fig. B.1:Process simulation flow diagram for the life cycle scenario (a). Where, 1: Pump 01, 2: Mixer 01, 3: Pretreatment unit, 4: Filter 01, 5: Cooler 01, 6: Neutralizer, 7: Filter 02, 8: Cooler 02, 9: SSF, 10: Scrubber, 11: Pump 02, 12: Concentration column, 13: Mixer 02, 14: Dehydration column 01, 15: Cooler 03, 16: Dehydration column 02, 17: Cooler 04, 18: Pump 04, 19:Spent-wash mixer, 20:Spent-wash cooler, 21:Spent-wash pump

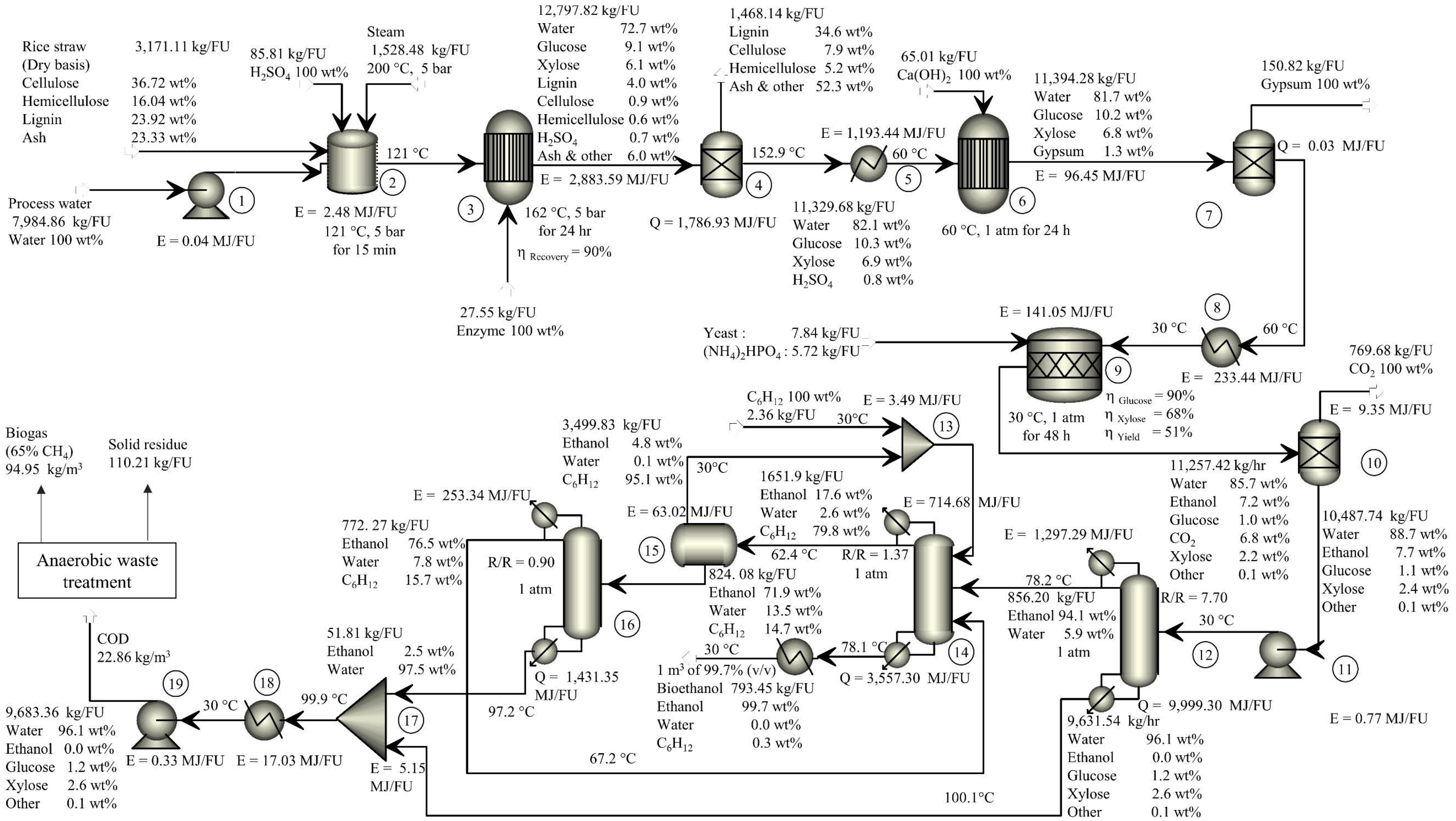

Fig. B.2: Process simulation flow diagram for the life cycle scenario (b). Where, 1: Pump 01, 2: Mixer 01, 3: Pretreatment unit, 4: Filter 01, 5: Cooler 01, 6: Neutralizer, 7: Filter 02, 8: Cooler 02, 9: SSF, 10: Scrubber, 11: Pump 02, 12: Concentration column, 13: Mixer 02, 14: Dehydration column 01, 15: Decanter, 16: Dehydration column 02, 17: Spent-wash mixer, 18: Spent-wash cooler, 19: Spent-wash pump

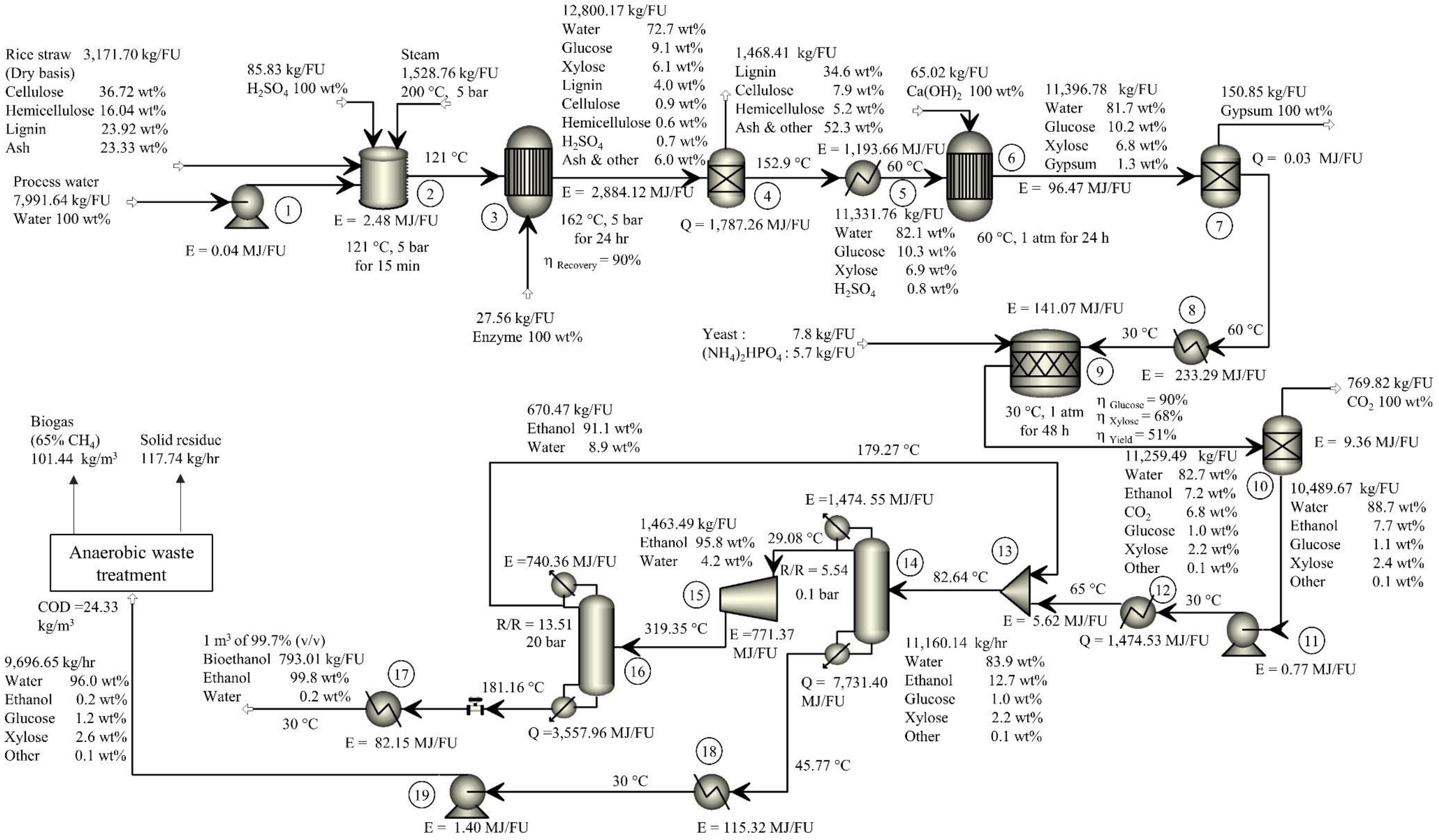

Fig. B.3: Process simulation block diagram for the life cycle scenario (c): Where 1: Pump 01, 2: Mixer 01, 3: Pretreatment unit, 4: Filter 01, 5: Cooler 01, 6: Neutralizer, 7: Filter 02, 8: Cooler 02, 9: SSF, 10: Scrubber, 11: Pump 02, 12: Heater, 13: Mixer 02, 14: Dehydration column 01, 15: Compressor, 16: Dehydration column 02, 17: Cooler 04, 18: Spent-wash cooler, 19: Spent-wash pump

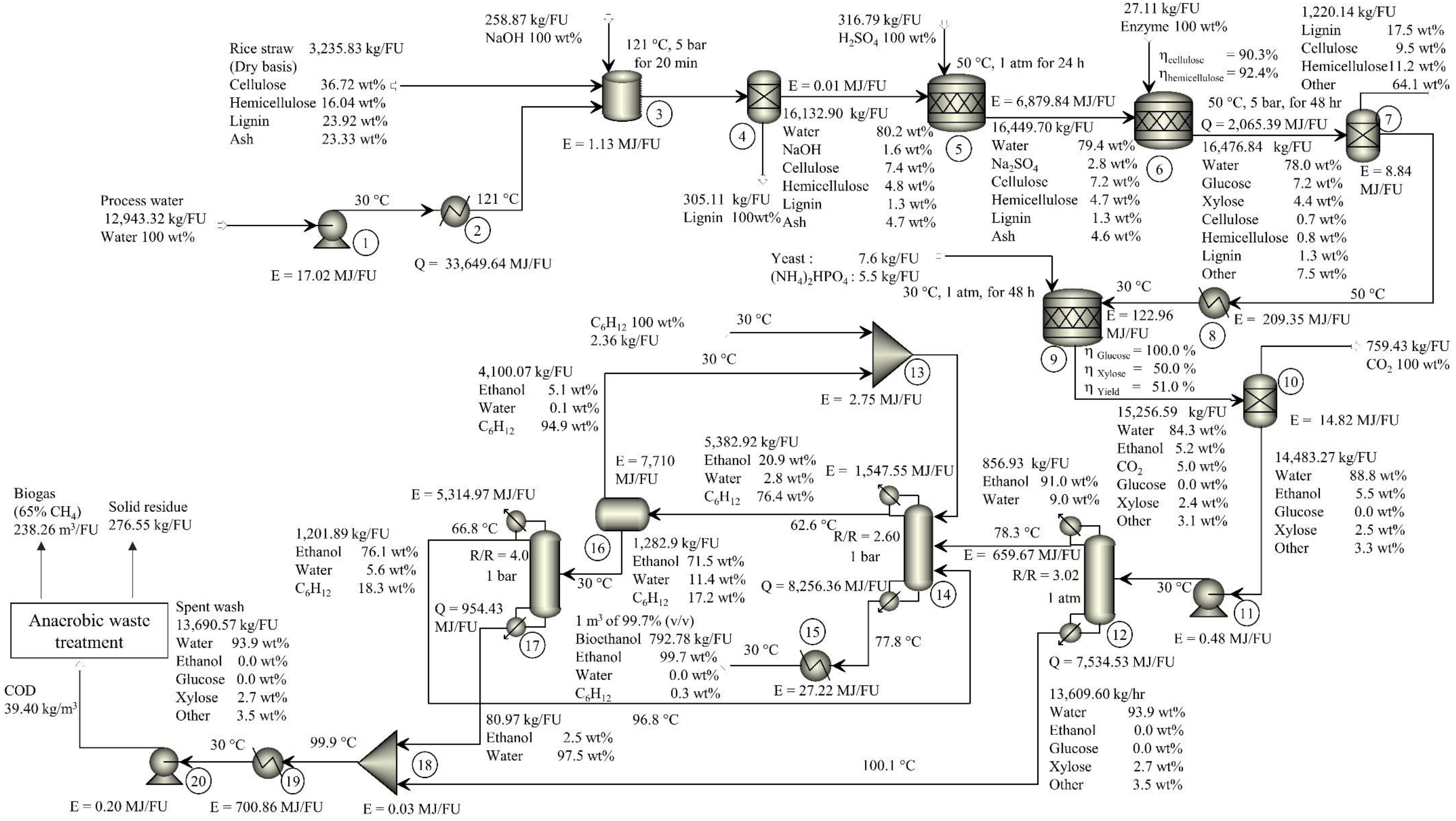

Fig. B.4: Process simulation flow diagram for the life cycle scenario (d), where, 1: Pump 01, 2: Preheater 01, 3: Mixer 01, 4: Filter 01, 5: Neutralizer, 6: Hydrolysis unit, 7: Filter 02, 8: Cooler 01, 9: SSF, 10: Scrubber, 11: Pump 02, 12: Concentration column, 13: Mixer 02, 14: Dehydration column 01, 15: Cooler 02, 16: Dehydration column 02, 17: Cooler 03, 18: Pump 03, 19: Spent-wash mixer, 20: Spent-wash cooler, 21: Spent-wash pump 05

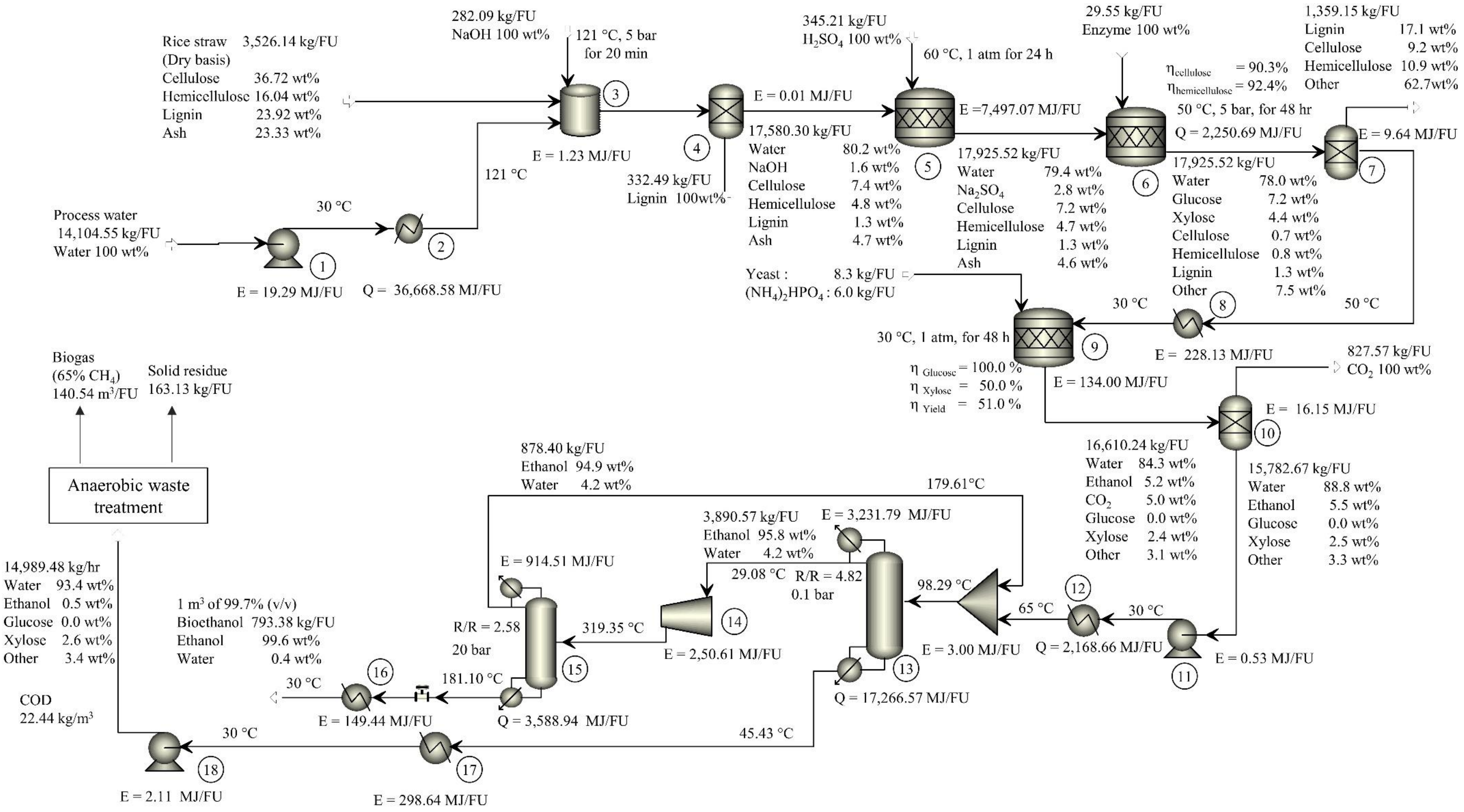

Fig. B.5: Process simulation flow diagram for the life cycle scenario (e), where, 1:Pump 01, 2: Preheater 01, 3: Mixer 01, 4: Filter 01, 5: Neutralizer, 6: Hydrolysis unit, 7: Filter 02, 8: Cooler 01, 9: SSF, 10: Scrubber, 11: Pump 02, 12: Concentration column, 13: Mixer 02, 14: Dehydration column 01, 15: Cooler 02, 16: Decanter, 17: Dehydration column 02, 18: Spent-wash mixer, 19: Spent-wash cooler, 20: Spent-wash pump 05

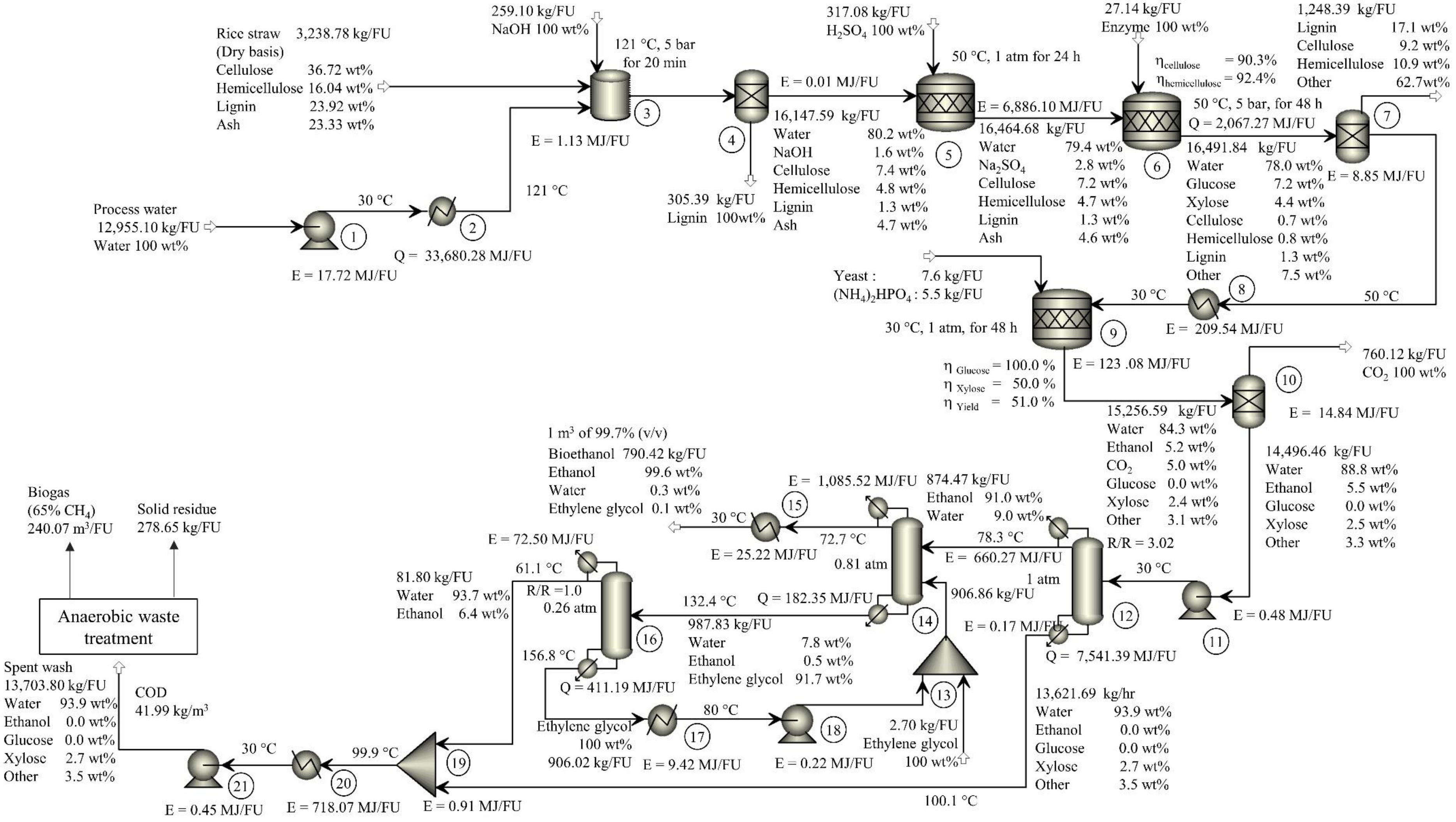

Fig. B.6: Process simulation flow diagram for the life cycle scenario (f), where, 1: Pump 01, 2: Preheater 01, 3: Mixer 01, 4: Filter 01, 5: Neutralizer, 6: Hydrolysis unit, 7: Filter 02, 8: Cooler 01, 9: SSF, 10: Scrubber, 11: Pump 02, 12: Preheater 02, 14: Mixer 02, 15: Dehydration column 01, 14: Compressor, 15: Dehydration column 02, 16: Cooler 03, 17: Spent-wash cooler, 18: Spent-wash pump 05

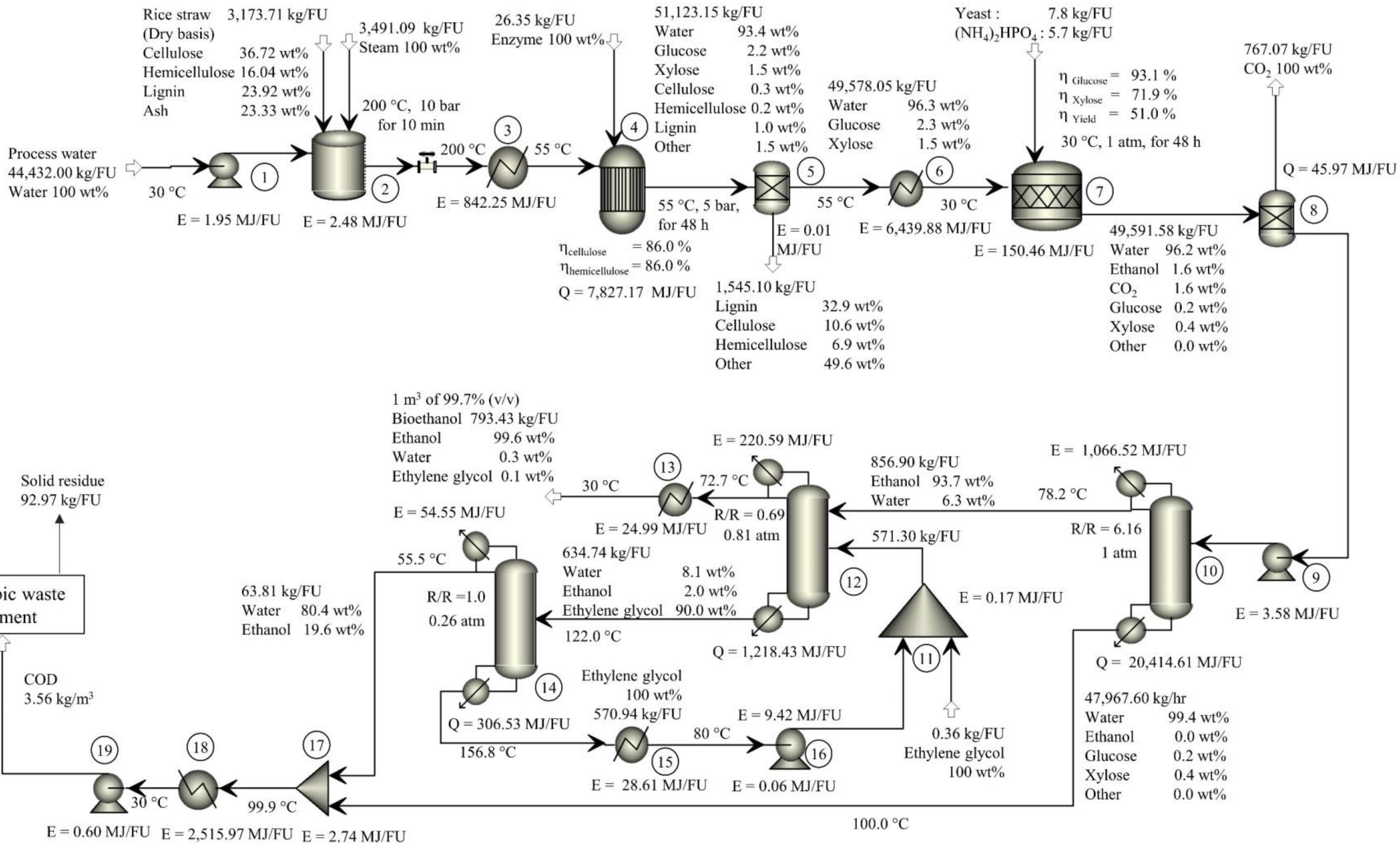

Fig. B.7: Process simulation flow sheet for the life cycle scenario (g), where, 1: Pump 01, 2: Mixer 01, 3: Cooler 01, 4: Pretreatment unit, 5: Filter 01, 6: Cooler 01, 7: SSF, 8: Scrubber, 9: Pump 02, 10: Concentration column, 11: Mixer 02, 12: Dehydration column 01, 13: Cooler 02, 14: Dehydration column 02, 15: Cooler 03, 16: Pump 03, 17: Spent-wash mixer, 18: Spent-wash cooler, 19: Spent-wash pump 05

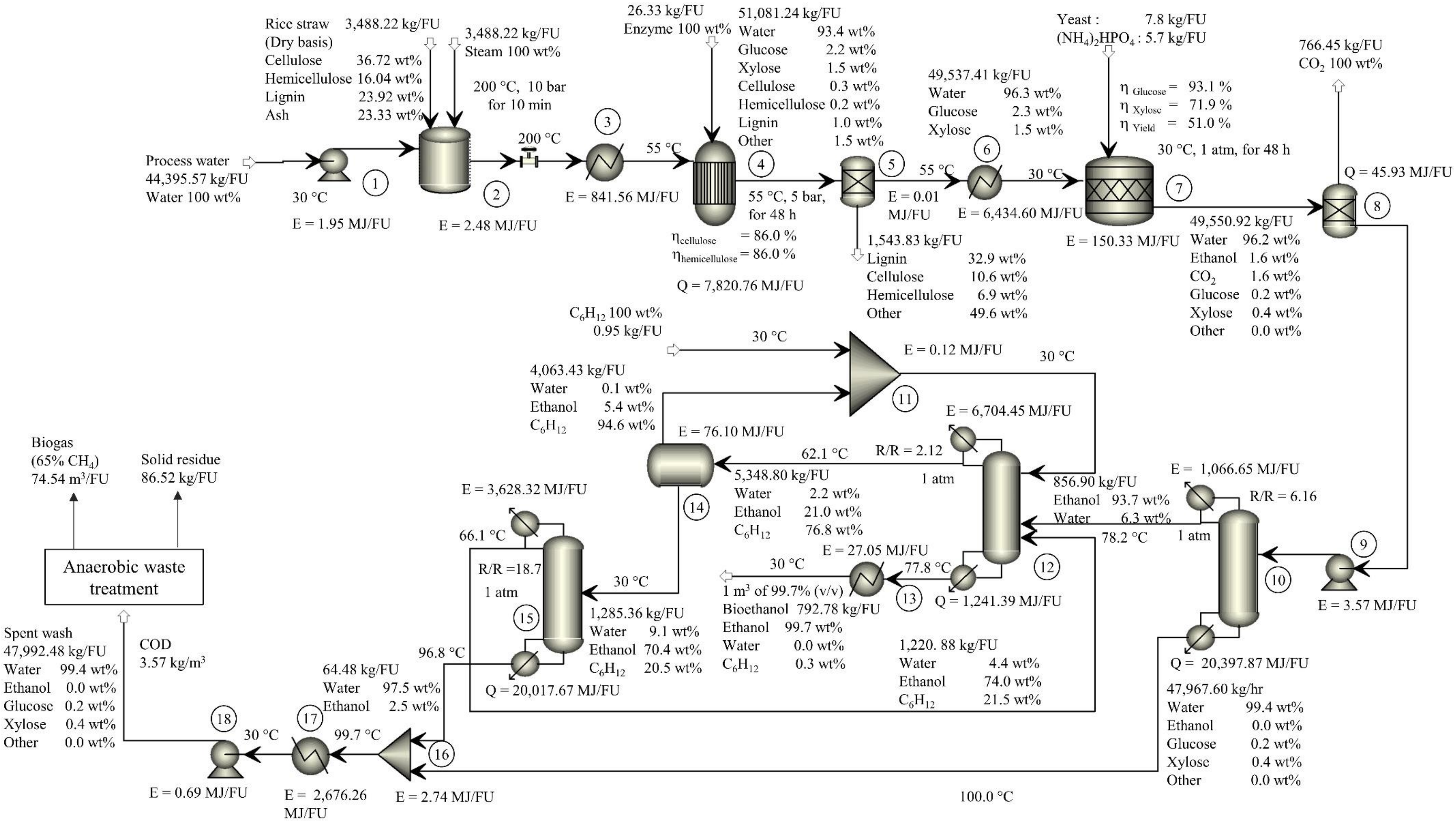

Fig. B.8: Process simulation flow sheet for the life cycle scenario (h), where, 1: Pump 01, 2: Mixer 01, 3: Cooler 01, 4: Pretreatment unit, 5: Filter 01, 6: Cooler 01, 7: SSF, 8: Scrubber, 9: Pump 02, 10: Concentration column, 11: Mixer 02, 12: Dehydration column 01, 13: Cooler 02, 14: Decanter, 15: Dehydration column 02, 16: Spent-wash mixer, 17: Spent-wash cooler, 18: Spent-wash pump 05

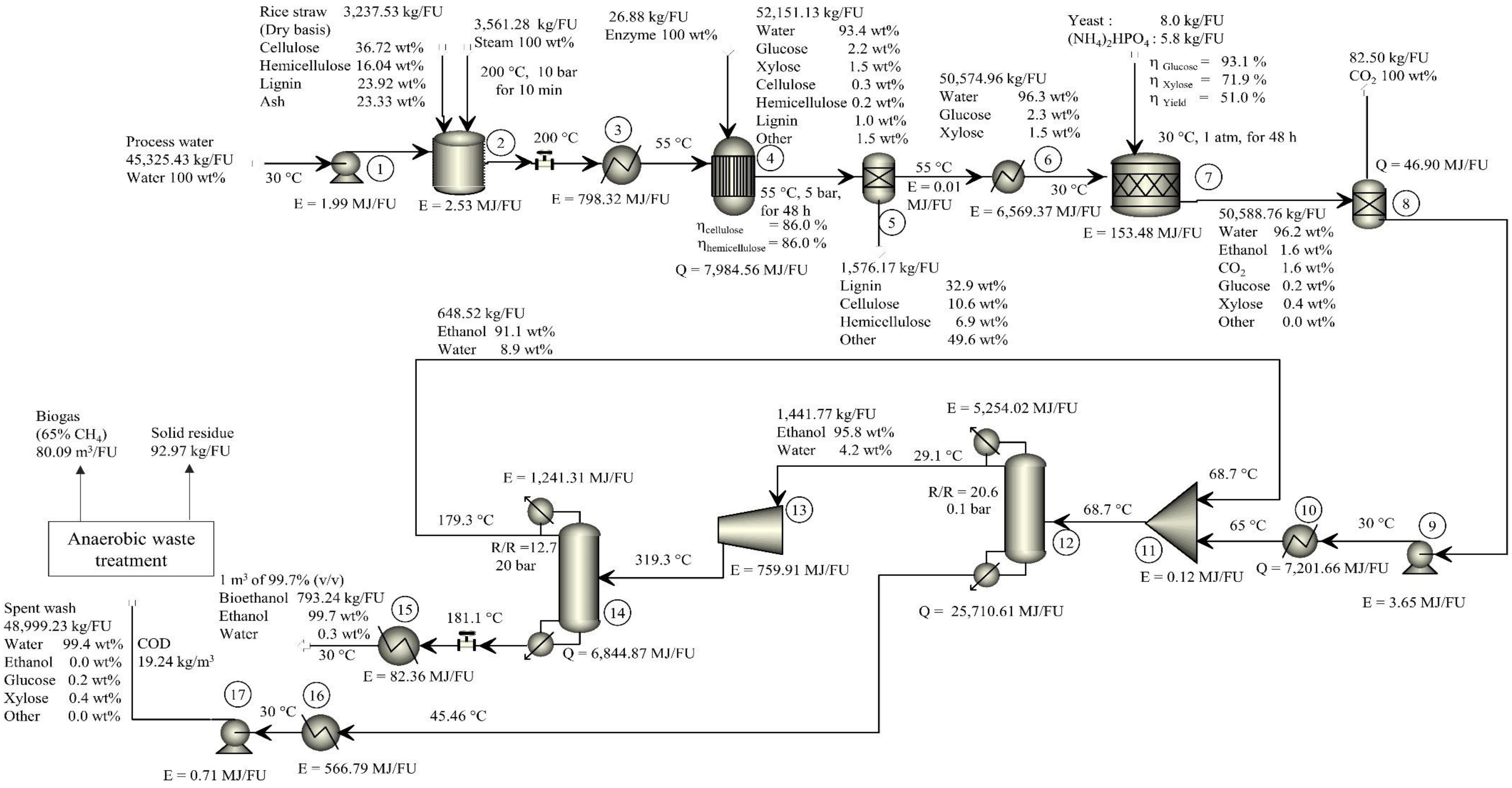

Fig. B.9: Process simulation flow diagram for the life cycle scenario (i), where, 1: Pump 01, 2: Mixer 01, 3: Cooler 01, 4: Pretreatment unit, 5: Filter 01, 6: Cooler 01, 7: SSF, 8: Scrubber, 9: Pump 02, 10: Preheater 02, 11: Mixer 02, 12: Dehydration column 01, 13: Compressor, 14: Dehydration column 02, 15: Cooler 03, 16: Spent-wash cooler, 17: Spent-wash pump 05

C. APPENDIX C

Energy consumption results for individual plant equipment in life cycle scenarios to produce 1 m^3 of fuel-grade bioethanol at 99.7 vol% from unutilized rice straw

Table C.1: Energy consumption results for individual plant equipment in life cycle scenarios corresponding to pretreatment scenario – 01 to produce 1 m^3 of fuel-grade bioethanol at 99.7 vol% from unutilized rice straw

No	Equipment	Energy consumption (MJ/m^3 of bioethanol)					
		Scenario (a)		Scenario (b)		Scenario (c)	
		Heat	Power	Heat	Power	Heat	Power
1	Crusher	997.23	-	995.54	-	995.91	-
2	Pump 01	-	0.04	-	0.04	-	0.04
3	Mixer 01	-	2.48	-	2.48	-	2.48
4	Pretreatment unit	-	2,886.04	-	2,883.59	-	2,884.12
5	Filter 01	1,788.45	-	1,786.93	-	1,787.26	-
6	Cooler 01	-	1,194.45	-	1,193.44	-	1,193.66
7	Neutralizer	-	96.53	-	96.45	-	96.47
8	Filter 02	0.03	-	0.03	-	0.03	-
9	Cooler 02	-	233.44	-	233.25	-	233.29
10	SSF	-	141.17	-	141.05	-	141.07
11	Scrubber	-	9.36	-	9.35	-	9.36
12	Pump 02	-	0.77	-	0.77	-	0.77
13	Heater	NA	NA	NA	NA	1,474.53	-
14	Concentration column	10,007.80	1,298.40	9,999.30	1,297.29	NA	NA
15	Mixer 02	-	0.12	-	3.49	-	5.62
16	Dehydration column 01	1,098.87	194.46	3,557.30	714.68	7,731.40	1,474.55
17	Cooler 03	-	24.99	-	27.19	NA	NA
18	Decanter	NA	NA			NA	NA
19	Compressor	NA	NA	NA	NA	-	771.37
20	Dehydration column 02	302.50	53.07	1,431.35	253.34	3,557.96	740.36

Table C.2 continued.

21	Cooler 04	-	30.84	-	-	-	82.15
22	Pump 04	-	0.07	NA	NA	NA	NA
23	Spent-wash mixer	-	0.44	-	5.15	NA	NA
24	Spent-wash cooler	-	518.45	-	17.03	-	115.32
25	Spent-wash pump	-	0.12	-	0.33	-	1.40
26	Total	14,194.88	6,685.24	17,770.46	6,941.94	15,547.09	7,752.04

Table C.2: Energy consumption results for individual plant equipment in life cycle scenarios corresponding to pretreatment scenario – 02 to produce 1 m^3 of fuel-grade bioethanol at 99.7 vol% from unutilized rice straw

No	**Equipment**	**Energy consumption (MJ/m^3 of bioethanol)**					
		Scenario (d)		**Scenario (e)**		**Scenario (f)**	
		Heat	**Power**	**Heat**	**Power**	**Heat**	**Power**
1	Crusher	1,038.48	-	1,036.59	-	1,230.93	-
2	Pump 01	-	17.72	-	17.70	-	19.29
3	Preheater 01	33,680.28	-	33,649.64	-	36,668.58	-
4	Mixer 01	-	1.13	-	1.13	-	1.23
5	Filter 01	-	0.01	-	0.00	-	0.00
6	Neutralizer	-	6,886.10	-	6,879.84	-	7,497.07
7	Hydrolysis unit	2,067.27	-	2,065.39	-	2,250.69	-
8	Filter 02	-	8.85	-	8.84	-	9.64
9	Cooler 01	-	209.54	-	209.35	-	228.13
10	SSF	-	123.08	-	122.96	-	134.00
11	Scrubber	-	14.84	-	14.82	-	16.15
12	Pump 02	-	0.48	-	0.48	-	0.53
13	Preheater 02	NA	NA	NA	NA	2,168.66	-
14	Concentration column	7,541.39	660.27	7,534.53	659.67	NA	NA
15	Mixer 02	-	0.17	-	2.75	-	3.00
16	Dehydration column 01	1,085.52	182.35	8,256.36	1,547.55	17,266.57	3,231.79
17	Cooler 02	-	25.22	-	27.22	NA	NA
18	Decanter	NA	NA	-	77.10	NA	NA
19	Compressor	NA	NA	NA	NA	-	2,050.61
20	Dehydration column 02	411.19	72.50	5,314.97	954.43	3,588.94	914.51
21	Cooler 03	-	9.42	NA	NA	-	149.44
22	Pump 03	-	0.22	NA	NA	NA	NA
23	Spent-wash mixer	-	0.91	-	0.03	NA	NA
24	Spent-wash cooler	-	718.07	-	700.86	-	298.64
25	Spent-wash pump 05	-	0.45	-	0.20	-	2.11
	Total	45,824.12	8,931.32	57,857.48	11,224.94	63,174.37	14,556.13

Table C.3: Energy consumption results for individual plant equipment in life cycle scenarios corresponding to pretreatment scenario – 03 to produce 1 m^3 of fuel-grade bioethanol at 99.7 vol% from unutilized rice straw

No	**Equipment**	**Energy consumption (MJ/m^3 of bioethanol)**					
		Scenario (g)		**Scenario (h)**		**Scenario (i)**	
		Heat	**Power**	**Heat**	**Power**	**Heat**	**Power**
1	Crusher	997.17	-	995.54	-	1,037.68	-
2	Pump 01	-	1.95	-	1.95	-	1.99
3	Mixer 01	-	2.48	-	2.48	-	2.53
4	Cooler 01		842.25	-	841.56	-	798.32
5	Pretreatment unit	7,827.17	-	7,820.76	-	7,984.56	-
6	Filter 01	-	0.00	-	0.00	-	0.00
7	Cooler 01	-	6,439.88	-	6,434.60	-	6,569.37
8	SSF	-	150.46	-	150.33	-	153.48
9	Scrubber	45.97	-	45.93	-	46.90	-
10	Pump 02	-	3.58	-	3.57	-	3.65
11	Preheater 02	NA	NA	NA	NA	7,201.66	-
12	Concentration column	20,414.61	1,066.52	20,397.87	1,065.65	NA	NA
13	Mixer 02	-	0.12	-	0.12	-	0.12
14	Dehydration column 01	1,218.43	220.59	6,704.45	1,241.39	25,710.61	5,254.02
15	Cooler 02	-	24.99	-	27.05	NA	NA
16	Decanter	NA	NA	-	76.10	NA	NA
17	Compressor	NA	NA	NA	NA	-	759.91
18	Dehydration column 02	306.53	54.55	20,017.67	3,628.32	6,844.87	1,241.31
1	Cooler 03	-	28.61	NA	NA	-	82.36
20	Pump 03	-	0.06	NA	NA	NA	NA
21	Spent-wash mixer	-	2.74	-	2.74	NA	NA
22	Spent-wash cooler	-	2,515.97	-	2,676.26	-	565.63
23	Spent-wash pump 05	-	0.60	-	0.69	-	0.71
	Total	30,809.89	11,355.35	55,982.22	16,152.80	48,826.28	15,433.39

D. APPENDIX D

Process contribution results for environmental impact indicators with a 0.01% cut-off.

Table D.1: Process contribution for global warming (kg CO_2 eq. / m^3 of bioethanol)

Process	Scenario (a)	Scenario (b)	Scenario (c)	Scenario (d)	Scenario (e)	Scenario (f)	Scenario (g)	Scenario (h)	Scenario (i)
NaOH	-	-	-	364.05	363.73	396.35	-	-	-
Enzyme - cellulase	223.46	223.21	223.29	219.89	219.65	239.42	213.49	213.33	217.78
Biogas combustion	35.49	32.83	35.08	83.01	62.75	48.60	27.70	25.77	30.94
Diesel combustion in 10-tonne truck	30.99	33.23	31.77	58.06	65.29	74.29	40.46	59.03	54.22
Heavy oil combustion in shipping	7.24	7.31	7.22	23.21	23.34	25.23	1.51	1.53	1.53
Yeast	18.78	18.76	18.76	18.16	18.16	19.79	18.71	18.69	19.10
H_2SO_4	4.57	4.57	4.57	16.89	16.87	18.39	-	-	-
Lignin combustion	10.19	10.13	10.18	11.79	8.65	11.92	10.53	10.48	10.80
Wood chips and rice husk combustion	1.03	2.46	1.56	10.03	7.66	18.09	10.09	22.08	18.66
Diesel combustion in baling and drying machine	8.48	8.48	8.48	8.64	8.64	9.41	8.48	8.48	8.64
Ethylene glycol	1.07	-	-	1.82	-	-	0.79	-	-
$(NH_4)_2HPO_4$	(20.91)	(20.87)	(20.87)	(20.21)	(20.21)	(22.04)	(20.83)	(20.80)	(21.23)
Sri Lankan energy grid mix	(550.00)	(492.78)	(384.22)	(598.85)	(243.70)	-	-	-	-

Table D.2: Process contribution for stratospheric ozone depletion (kg CFC11 eq./m^3 of bioethanol)

Process	Scenario (a)	Scenario (b)	Scenario (c)	Scenario (d)	Scenario (e)	Scenario (f)	Scenario (g)	Scenario (h)	Scenario (i)
Enzyme - cellulase	7.89E-04	7.88E-04	7.88E-04	7.76E-04	7.75E-04	8.45E-04	7.54E-04	7.53E-04	7.69E-04
Lignin combustion	2.61E-04	2.59E-04	2.61E-04	3.02E-04	2.21E-04	3.05E-04	2.69E-04	2.68E-04	2.76E-04
Wood chips and rice husk combustion	2.64E-05	6.30E-05	3.99E-05	2.57E-04	1.96E-04	4.63E-04	2.58E-04	5.65E-04	4.78E-04
Yeast	1.45E-04	1.45E-04	1.45E-04	1.40E-04	1.40E-04	1.53E-04	1.45E-04	1.44E-04	1.47E-04
Biogas combustion	4.05E-05	3.74E-05	4.00E-05	9.46E-05	7.15E-05	5.54E-05	3.16E-05	2.94E-05	3.53E-05
Diesel combustion in 10-tonne truck	7.32E-06	7.85E-06	7.50E-06	1.37E-05	1.54E-05	1.75E-05	9.56E-06	1.39E-05	1.28E-05
Heavy oil combustion in shipping	2.54E-06	2.56E-06	2.53E-06	8.15E-06	8.20E-06	8.86E-06	5.31E-07	5.39E-07	5.37E-07
Diesel combustion in Baling and drying machine	7.39E-07	7.39E-07	7.39E-07	7.53E-07	7.53E-07	8.20E-07	7.39E-07	7.39E-07	7.53E-07
$(NH_4)_2HPO_4$	(7.82) E-04	(7.81) E-04	(7.81) E-04	(7.56) E-04	(7.56) E-04	(8.24) E-04	(7.79) E-04	(7.78) E-04	(7.94) E-04

Table D.3: Process contribution for ozone formation, human health (kg NO_X eq. / m^3 of bioethanol)

Process	Scenario (a)	Scenario (b)	Scenario (c)	Scenario (d)	Scenario (e)	Scenario (f)	Scenario (g)	Scenario (h)	Scenario (i)
Lignin combustion	2.43	2.41	2.43	2.81	2.06	2.84	2.51	2.50	2.57
Wood chips and rice husk combustion	0.25	0.59	0.37	2.39	1.83	4.31	2.40	5.26	4.45
Biogas combustion	0.46	0.43	0.46	1.09	0.82	0.64	0.36	0.34	0.40
NaOH	-	-	-	0.93	0.93	1.01	-	-	-
Heavy oil combustion in shipping	0.15	0.15	0.15	0.48	0.48	0.52	0.03	0.03	0.03
Enzyme - cellulase	0.48	0.48	0.48	0.48	0.48	0.52	0.46	0.46	0.47
Diesel combustion in 10-tonne truck	0.25	0.27	0.26	0.47	0.53	0.60	0.33	0.48	0.44
H_2SO_4	0.04	0.04	0.04	0.16	0.16	0.17	-	-	-
Diesel combustion in baling and drying machine	0.08	0.08	0.08	0.08	0.08	0.09	0.08	0.08	0.08
Yeast	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Ethylene glycol	0.002	-	-	0.003	-	-	0.001	-	-
$(NH_4)_2HPO_4$	(0.03)	(0.03)	(0.03)	(0.03)	(0.03)	(0.03)	(0.03)	(0.03)	(0.03)
Sri Lankan energy grid mix	(2.13)	(1.91)	(1.49)	(2.32)	(0.94)	-	-	-	-

Table D.4: Process contribution for fine particulate matter formation (kg PM2.5 eq. / m^3 of bioethanol)

Process	**Scenario (a)**	**Scenario (b)**	**Scenario (c)**	**Scenario (d)**	**Scenario (e)**	**Scenario (f)**	**Scenario (g)**	**Scenario (h)**	**Scenario (i)**
Lignin combustion	2.09	2.08	2.09	2.42	1.77	2.44	2.16	2.15	2.21
NaOH	-	-	-	2.27	2.27	2.47	-	-	-
Wood chips and rice husk combustion	0.21	0.50	0.32	2.06	1.57	3.71	2.07	4.53	3.82
H_2SO_4	0.15	0.15	0.15	0.56	0.56	0.61	-	-	-
Enzyme - cellulase	0.47	0.47	0.47	0.46	0.46	0.51	0.45	0.45	0.46
Heavy oil combustion in shipping	0.05	0.05	0.05	0.15	0.15	0.16	0.01	0.01	0.01
Biogas combustion	0.05	0.05	0.05	0.12	0.09	0.07	0.04	0.04	0.04
Diesel combustion in 10-tonne truck	0.03	0.03	0.03	0.06	0.07	0.08	0.04	0.06	0.06
Yeast	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Diesel combustion in baling and drying machine	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ethylene glycol	0.00	-	-	0.00	-	-	0.00	-	-
$(NH_4)_2HPO_4$	(0.001)	(0.001)	(0.001)	(0.001)	(0.001)	(0.002)	(0.001)	(0.001)	(0.001)
Sri Lankan energy grid mix	(0.74)	(0.66)	(0.51)	(0.80)	(0.33)	-	-	-	-

Table D.5: Process contribution for ozone formation, terrestrial ecosystems (kg NO_X eq. / m^3 of bioethanol)

Process	**Scenario (a)**	**Scenario (b)**	**Scenario (c)**	**Scenario (d)**	**Scenario (e)**	**Scenario (f)**	**Scenario (g)**	**Scenario (h)**	**Scenario (i)**
Lignin combustion	2.45	2.43	2.44	2.83	2.08	2.86	2.53	2.51	2.59
Wood chips and rice husk combustion	0.25	0.59	0.37	2.41	1.84	4.34	2.42	5.30	4.48
Biogas combustion	0.47	0.43	0.46	1.09	0.82	0.64	0.36	0.34	0.41
NaOH	-	-	-	0.93	0.93	1.01	-	-	-
Enzyme - cellulase	0.49	0.49	0.49	0.49	0.48	0.53	0.47	0.47	0.48
Heavy oil combustion in shipping	0.15	0.15	0.15	0.48	0.48	0.52	0.03	0.03	0.03
Diesel combustion in 10-tonne truck	0.25	0.27	0.26	0.47	0.53	0.60	0.33	0.48	0.44
H_2SO_4	0.04	0.04	0.04	0.16	0.16	0.17	-	-	-
Diesel combustion in baling and drying machine	0.08	0.08	0.08	0.08	0.08	0.09	0.08	0.08	0.08
Yeast	0.03	0.03	0.03	0.03	0.03	0.04	0.03	0.03	0.03
Ethylene glycol	0.002	-	-	0.004	-	-	0.002	-	-
$(NH_4)_2HPO_4$	(0.03)	(0.03)	(0.03)	(0.03)	(0.03)	(0.03)	(0.03)	(0.03)	(0.03)
Sri Lankan energy grid mix	(2.13)	(1.91)	(1.49)	(2.32)	(0.94)	-	-	-	-

Table D.6: Process contribution for terrestrial acidification (kg SO_2 eq. / m^3 of bioethanol)

Process	**Scenario (a)**	**Scenario (b)**	**Scenario (c)**	**Scenario (d)**	**Scenario (e)**	**Scenario (f)**	**Scenario (g)**	**Scenario (h)**	**Scenario (i)**
NaOH	-	-	-	3.45	3.45	3.75	-	-	-
H_2SO_4	0.52	0.52	0.52	1.93	1.93	2.10	-	-	-
Lignin combustion	0.92	0.92	0.92	1.07	0.78	1.08	0.95	0.95	0.98
Enzyme - cellulase	1.02	1.02	1.02	1.00	1.00	1.09	0.98	0.97	1.00
Wood chips and rice husk combustion	0.09	0.22	0.14	0.91	0.69	1.63	0.91	2.00	1.69
Biogas combustion	0.17	0.15	0.16	0.39	0.29	0.23	0.13	0.12	0.14
Heavy oil combustion in shipping	0.12	0.12	0.12	0.38	0.39	0.42	0.03	0.03	0.03
Diesel combustion in 10-tonne truck	0.09	0.10	0.09	0.17	0.19	0.22	0.12	0.17	0.16
Yeast	0.11	0.11	0.11	0.11	0.11	0.12	0.11	0.11	0.12
Diesel combustion in baling and drying machine	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Ethylene glycol	0.002	-	-	0.004	-	-	0.002	-	-
$(NH_4)_2HPO_4$	(0.05)	(0.05)	(0.05)	(0.05)	(0.05)	(0.05)	(0.05)	(0.05)	(0.05)
Sri Lankan energy grid mix	(2.49)	(2.23)	(1.74)	(2.71)	(1.10)	-	-	-	-

Table D.7: Process contribution for freshwater eutrophication (kg P eq. / m^3 of bioethanol)

Process	**Scenario (a)**	**Scenario (b)**	**Scenario (c)**	**Scenario (d)**	**Scenario (e)**	**Scenario (f)**	**Scenario (g)**	**Scenario (h)**	**Scenario (i)**
NaOH	-	-	-	0.74	0.74	0.81	-	-	-
Enzyme - cellulase	0.12	0.12	0.12	0.11	0.11	0.12	0.11	0.11	0.11
H_2SO_4	0.01	0.01	0.01	0.04	0.04	0.04	-	-	-
Yeast	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
Ethylene glycol	0.0005	-	-	0.001	-	-	0.0004	-	-
$(NH_4)_2HPO_4$	(0.01)	(0.01)	(0.01)	(0.01)	(0.01)	(0.01)	(0.01)	(0.01)	(0.01)

Table D.8: Process contribution for marine eutrophication (kg N eq. / m^3 of bioethanol)

Process	Scenario (a)	Scenario (b)	Scenario (c)	Scenario (d)	Scenario (e)	Scenario (f)	Scenario (g)	Scenario (h)	Scenario (i)
Enzyme - cellulase	0.22	0.22	0.22	0.22	0.22	0.24	0.21	0.21	0.22
NaOH	-	-	-	0.04	0.04	0.04	-	-	-
Yeast	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Ethylene glycol	2.70E-05	-	-	4.57E-05	-	-	1.98E-05	-	-

Table D.9: Process contribution for terrestrial ecotoxicity (kg 1,4 – DCB eq. / m^3 of bioethanol)

Process	Scenario (a)	Scenario (b)	Scenario (c)	Scenario (d)	Scenario (e)	Scenario (f)	Scenario (g)	Scenario (h)	Scenario (i)
Enzyme - cellulase	406.80	406.36	406.51	400.31	399.87	435.86	388.66	388.36	396.48
Yeast	0.10	0.10	0.10	0.10	0.10	0.11	0.10	0.10	0.11

Table D.10: Process contribution for freshwater ecotoxicity (kg 1,4 – DCB eq. / m^3 of bioethanol)

Process	Scenario (a)	Scenario (b)	Scenario (c)	Scenario (d)	Scenario (e)	Scenario (f)	Scenario (g)	Scenario (h)	Scenario (i)
NaOH	-	-	-	31.82	31.79	34.64	-	-	-
Enzyme - cellulase	9.30	9.29	9.29	9.15	9.14	9.96	8.88	8.87	9.06
Ethylene glycol	0.04	-	-	0.06	-	-	0.03	-	-
$(NH_4)_2HPO_4$	(1.20)	(1.20)	(1.20)	(1.16)	(1.16)	(1.27)	(1.20)	(1.19)	(1.22)

Table D.11: Process contribution for marine ecotoxicity (kg 1,4 – DCB eq. / m^3 of bioethanol)

Process	**Scenario (a)**	**Scenario (b)**	**Scenario (c)**	**Scenario (d)**	**Scenario (e)**	**Scenario (f)**	**Scenario (g)**	**Scenario (h)**	**Scenario (i)**
NaOH	-	-	-	44.60	44.57	48.56	-	-	-
Enzyme - cellulase	13.74	13.73	13.73	13.52	13.51	14.73	13.13	13.12	13.40
Ethylene glycol	0.05	-	-	0.08	-	-	0.04	-	-
$(NH_4)_2HPO_4$	(1.65)	(1.65)	(1.65)	(1.60)	(1.60)	(1.74)	(1.65)	(1.64)	(1.68)

Table D.12: Process contribution for human carcinogenic toxicity (kg 1,4 – DCB eq. / m^3 of bioethanol)

Process	**Scenario (a)**	**Scenario (b)**	**Scenario (c)**	**Scenario (d)**	**Scenario (e)**	**Scenario (f)**	**Scenario (g)**	**Scenario (h)**	**Scenario (i)**
NaOH	-	-	-	1.36	1.36	1.48	-	-	-
Yeast	0.26	0.26	0.26	0.25	0.25	0.28	0.26	0.26	0.27
Enzyme - cellulase	0.20	0.20	0.20	0.20	0.20	0.22	0.19	0.19	0.20

Table D.13: process contribution for human non-carcinogenic toxicity (kg 1,4 – DCB eq. / m^3 of bioethanol)

Process	**Scenario (a)**	**Scenario (b)**	**Scenario (c)**	**Scenario (d)**	**Scenario (e)**	**Scenario (f)**	**Scenario (g)**	**Scenario (h)**	**Scenario (i)**
NaOH	-	-	-	1,138.48	1,137.47	1,239.50	-	-	-
Enzyme - cellulase	522.80	522.23	522.42	514.46	513.89	560.14	499.48	499.10	509.53
Ethylene glycol	1.01	-	-	1.71	-	-	0.74	-	-
$(NH_4)_2HPO_4$	(38.48)	(38.42)	(38.42)	(37.21)	(37.21)	(40.57)	(38.35)	(38.28)	(39.09)