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Sustainable production of lignocellulosic bioethanol towards zero waste biorefinery

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ABSTRACT

This study proposes a novel process design for lignocellulosic biomass to ethanol conversion with zero waste generation. In comparison to traditional bioethanol process, the proposed new process not only produces ethanol, but also converts waste streams into high value-added by-products by undergoing multi-stage refinery steps. The feasibility the proposed process design, especially the additional waste processing, has been carried out. The results showed that co-producing by-products could significantly contribute to the profitability by decreasing the ethanol minimum viable sales price from $2.24/gal to $1.78/gal, comparing with traditionally produced bioethanol. It was also found that ethanol minimum sale price is highly sensitive to the lignin price fluctuation. The water pollution can be avoided in the proposed process due to an additional water recycling step, however, there is a trade-off between reduced water pollution and increased CO_2 emissions when fossil fuel is used as operation energy. The results showed that, to ensure proposed bioethanol plant have environmental advantage with traditional ethanol refinery plant, the CO_2 emission per kWh for all kinds of electricity should not be over 0.11 kg/kWh. Thus, we suggest that the proposed concept of zero-waste bioethanol plants could be established in Countries with access of sufficient renewable electricity supply.

Introduction

The economic growth results in massive energy consumption, which leads to a series of environmental issues worldwide. Governments have been making strict emission standards for environmental protection. A universal environmental goal was set in Paris Agreement that aims to keep the global temperature increase to well below 2 °C, thus ambitious decarbonization goals have been set by most developed countries to be underpinned by implementing powerful law and policies. COP26 reaffirms temperature goal in the Paris Agreement and phased out low-efficiency fossil fuel subsidies [1] The UK parliament passed an amendment for cutting emissions in 2019 in order to achieve the pollution reduction ambitions, which set a net-zero emission precedent [2]. Followed by European Commission published "The European Green Deal" action plan, aiming to achieve clean energy conversion, pollution reduction and net-zero greenhouse gas emissions in 2050 [3]. US government launched a "clean energy revolution" that will invest $2 trillion to achieve 100 % clean electricity by 2035 [4].

Lignocellulosic biomass is one promising renewable resource due to its low price, abundance and efficient conversion technologies (i.e., combined heat and power and pyrolysis). On the one hand, the technologies to convert lignocellulosic biomass into biochemicals, such as biodegradable plastics (Polyhydroxyalkanoates), succinic acid and ethanol, are mature. These chemicals have the potential to replace fossil fuels derived chemicals by providing technological support. Besides, the feedstock supply could be ensured due to the abundance availability globally. According to Langholtz et al. [5], over 1.04 dry million tons (Mt) of biomass will be available for energy consumption in US by 2030. Scarlat et al. [6] and Verkerk et al. [7] estimated that the total availability of crop residues and forest biomass in EU are 483,017 Mt and 551,000 Mt dry matter per year respectively. With the development of conversion technologies and encouragment by governmental policies, biorefineries are gradually flourishing. Biochemicals and bioenergy account for approximately 2 % and 9 % of the present global energy

Abbreviations: RFA, Renewable Fuel Association; CBP, Consolidated Bioprocessing; NREL, National Renewable Energy Laboratory; CHP, Combined Heat and Power; CEPCI, Chemical Engineering Plant Cost Index; PPI, Producer Price Index; MESP, Minimum Ethanol Selling Price; EIA, Energy Information Administration; Mt, Million Ton.

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market, projecting its shares reach to 20 % and 10 % respectively in 2030 [8,9], this promotes sustainable economies in low-carbon fuel demands. Due to the fact that the development of lignocellulosic biomass biorefinery is still in developing phase, a huge technical gap existed in replacing fossil chemicals. Although the purchase price of cellulosic biomass feedstocks is competitive with petroleum on an energy basis, the lack of economic competitiveness in biochemicals is the main challenge for biorefinery [10,11].

Bioethanol has been identified as the most widely used biomass-based biofuel [12]. According to REN 21 report, the ethanol production in 2020 was 2.2 EJ, which provided around 3.5 % of transport energy [13]. It significantly contributes to reducing pollution and alleviating dependence on fossil fuels. The interest in bioethanol usage has been increasing for the past few decades. According to Renewable Fuel Association (RFA), the global bioethanol production is approximately 26 billion gallons in 2020 [14], among which US and Brazil contribute over 80 %.

At the present, the main feedstock of ethanol production is the first-generation biomass, namely food[15]. Due to the first-generation ethanol feedstock edibleness characteristics (conflict with feeding purpose), its development is restricted. While second-generation biomass representing lignocellulosic biomass could fulfil the first-generation gap, which feedstock applied from non-edible agriculture and forestry wastes. Developing lignocellulosic biomass-based ethanol production not only reduces feeding conflict but also pollution.

Various methods have been studied for boosting bioethanol production. Azhar et al. [12] compared key factors affecting ethanol production, such as the efficiency of yeast strain, reaction temperature, PH value, sugar concentration and time. They summarized the optimal fermentation reaction based on various yeast strains. López-Linares et al. [16] investigated the main process variables in acid pre-treatment process, which gain the maximization of enzymatic hydrolysis yield in order to increase sugar content. They found that the enzymatic hydrolysis at 202 °C with 5 min times has the optimal output, in which 87 % of the glucose content was released from rapeseed raw straw. While Nascimento et al. [17] analysed the effect of alkaline pre-treatment on sugarcan bagasse enzymatic hydrolysis. They confirmed the best condition for hydrolysis that the feedstock under 4 % NaOH with 60 min reaction time at 121 °C. Nakanishi et al. [18] attempted to optimize bioethanol refinery process and reaction temperature with alkaline pre-treatment which a 14.6 % of ethanol productivity in L ethanol /ton sugarcane compared with steam explosion as pre-treatment method.

However, biofuel production might lead to serious environmental consequence [19], for instance, producing ethanol from lignocellulose often apply external strong corrosive solvent (such as sulfuric acid and slaked lime) to enhance hydrolysis reaction efficiency, which improperly treated wastewater might cause potential of secondary pollution. Thus, zero waste emission and low production cost related to high by-products valuation have been commenced as new trends for lignocellulosic biomass refinery against environmental pollution and fossil fuel competition in the future. Research efforts have already been made to optimize the biorefinery process in order to reduce pollution towards minimise waste by enhancing by-products utilisation efficiency. Humbird et al. [20] designed ethanol conversion process using corn stalk as the feedstock, in which waste by-products were burnt to provide heat and energy to support the operation of the whole system. While wastewater undergo simple treatment and discharged into environment, pollutants cannot be fully recycle (49.5 % soluble solids in wastewater). The large amount of wastewater pollutants might cause environmental hazard. Bbosa et al. [21] attempted to increase high-value added by-products in bioethanol production by applying hydrothermal liquefaction. Others attempts were to apply microorganisms known as consolidated bioprocessing (CBP) in lignocellulose pre-treatment, by replacing polluted catalysts in the first stage of lignocellulosic refinery. Carrillo-Nieves et al. [22] applied white-rot fungus to decompose lignin in order to enhance lignocellulosic feedstocks fermentation, which potentially avoids pollutants to achieve zero waste. In spite of CBP having great potential for accomplishing zero waste, low technology readiness levels and poor economic performance restricted its commercial scale possibility at present.

Therefore, using relatively mature technologies to optimise biorefinery processes has become a practical method for minimising negative impacts on the environment and increasing profits of refinery plants. In order to improve the efficiency of biorefinery products and reduce pollution, this research attempts to propose a zero-waste sustainable bioethanol refinery process for large commercial biorefinery by adopting mature fractionation technology to extract value-added by-products (mainly lignin and furfural) from ethanol distillation waste.

A traditional commercial-scale biomass to ethanol biorefinery plant includes the following nine main process steps: (1) feed handling; (2) feedstock pre-treatment; (3) enzyme production; (4) hydrolysis and fermentation; (5) distillation; (6) combined heat and power generation; (7) waste water treatment; (8) storage and (9) utilities management (water system and power system), as presented by Renewable Energy Laboratory (NREL) [20] as an example shown in Fig. 1. Firstly, feedstock is loaded and shredded for downsizing in the ***feed handing process***, followed by the feedstock ***pre-treatment processing*** to decompose lignocellulosic biomass into its components (cellulose, hemicellulose and lignin) at 158 °C for 5 min duration time. for high efficiency hydrolysis. The sulfuric acid, as a proven competitive low cost and high efficiency pre-treatment solution, has been wildly applied in feedstock pre-treatment. Then, the pre-treated feedstock mixes with enzyme that is produced in the ***enzyme production process*** (commonly use a *T.reesei*-like fungus as ***enzyme production*** feedstock) for ***hydrolysis and fermentation*** under a suitable reaction condition. Finally, the glucose and pentoses that hydrolysed from cellulose and hemicellulose, catalysed by enzyme converting to ethanol. The ***ethanol distillation process*** will separate ethanol, lignin and stillage. The ethanol and stillage will be further processed for the ***storage*** and the ***wastewater processing*** (the grey flow chart in Fig. 1) respectively. The ***storage*** plays a crucial role for elemental sources (i.e., sulfuric acid, protein, ammonia and other inorganic soluble solids) supplying to bioethanol plant. Eutrophic stillage undergoing anaerobic digestion (under ***wastewater treatment processing***) produces treated water and biogas, which as feed transfer to ***feedstocks pre-treatment processing*** and ***combined heat and power (CHP)*** for process water recycling and operation. While the waste water brine discharged into environment. Extracted lignin (from ***ethanol distillation***) and biogas (from ***wastewater treatment***) will be combusted in a ***CHP*** system to produce energy (i.e., heat, power and steam) for biorefinery plant operation and electricity grid in order to increase plant profitability. The ash will be disposed to landfill. The ***utilities*** include on-site recirculation of cooling water and external electricity from grid to support biorefinery plant operation.

From the above description of traditional commercial-scale bioethanol production process, it is clear that various waste streams (such as CO_2, wastewater and eutrophic content) are discarded to the environment, causing secondary pollutants while simultaneously reducing the benefits to sustainable development, although its original intention was to reuse agricultural waste and protect the environment. For instance, in traditional ethanol refinery process, stillage from ***ethanol distillation*** contains abundant organics (such as furfural, glucose and sugars), which high value contents convert to low value biogas for combustion. Lignin is a huge potential raw material for chemistry industry [23]. While most of lignin in traditional bioethanol refinery will be burnt for power generation, which not only causes source waste but also environmental impact. There is no doubt that the lignocellulose-based bioethanol production cost is much higher than ethanol market value [24]. Thus, optimising processing design and increasing by-products value is key to reducing production costs currently.

In comparison to the traditional process, this work aims to maximise the value-added by-products and achieve zero waste emission, and proposed a by-products processing path that extracts value-added lignin,

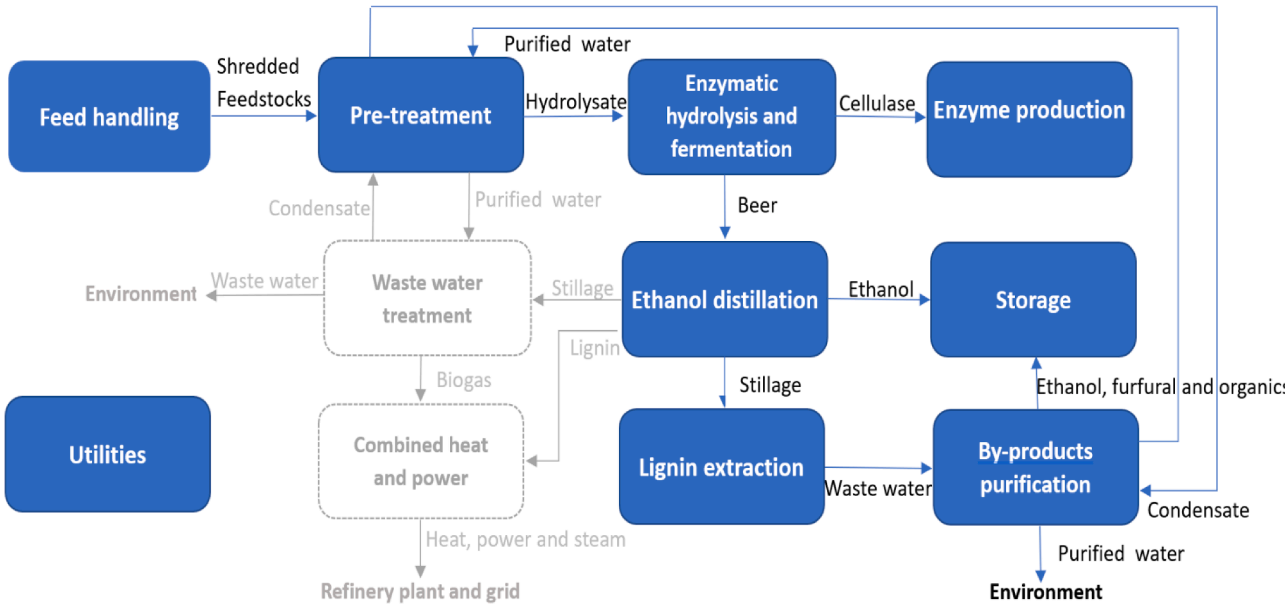

Fig. 1. Simplified flowsheet of zero waste and traditional (grey, [20]) ethanol biorefinery process.

furfural and other organics. To realise this, wet stillage (produced from ***ethanol distillation***) will be filtered and dried to separate lignin and wastewater in ***lignin extraction process*** (Fig. 1). In this process, the insoluble organics (such as lignin and ash), small amounts of water and soluble organics will be removed from stillage. The eutrophic wastewater will be further extracted to generate furfural, ethanol and other organics powder by multistage fractionation in ***by-products purification processing*** and storing in ***storage*** as presented in Fig. 1. As same with traditional bioethanol production process, purified water will pump to ***feedstock pre-treatment processing*** for water recycling. Except for essential usage, the rest purified water will discharge into environment. The organic powder will be returned to soil as fertilizer for soil organic matter protection. Due to no power and heat produced from the refinery process, the plant operation related power and heat need to be provided from industry electricity grid. The major process updates are summarised as below:

- Multistage wastewater fractionation to extract high value-added materials;
- Lignin extraction replaces CHP production;
- Using latest available Chemical Engineering Plant Cost Index (CEPCI) and Producer Price Index (PPI) for data analysis;
- Recycling water from ***by-products purification processing*** to ***feedstocks pre-treatment processing*** to reduce utilities costs;
- energy is supplied from external renewable sources.

This work aims to improve financial feasibility by maximising the yield of value-added by-products extracted from waste residues, meanwhile reducing carbon dioxide emissions and other pollutants in bioethanol refinery. Finally, the proposed zero-waste bioethanol refinery is to be compared with traditional bioethanol refinery in terms of financial contribution and pollutant emissions.

Materials and methods

To achieve the innovation of bioethanol production process, the design of zero-waste process was standing on the excellent previous traditional ethanol production. Therefore, the ***by-products purification process*** and ***lignin extraction process*** towards zero emission were developed in this research. While, the other areas (i.e., feed loading, pretreatment, enzyme production, hydrolysis and fermentation, distillation, utility, and storage process) are similar to the NREL's process. The process design of ***by-products purification process*** and ***lignin extraction process*** will be illustrated in the following section. The feedstock of ethanol biorefinery is corn stalk, which the feedstock characteristic will illustrate in section 2.4.

Lignin extraction process design

The stillage which includes insoluble content and wastewater is extracted from ***ethanol distillation process***, venting in the tank and filtered wet lignin and waste water in filter (see Fig. 2). The wet lignin is then washed in washing tank in order to remove soluble content. After further percolation, the washed water mixes with waste water transferred for further purification in ***by-products purification***. Coordinating with compressor heater, wet lignin will be dried by hot nitrogen flow, dried lignin and insoluble content will be subsequently collected and stored. The moisture from wet lignin will chill and mix with waste water stream transfer to ***by-products purification.*** The detailed Aspen simulation model is illustrated in S.1 of Supplementary.

By-product purification process design

Due to the fact that different compounds in waste water have different boiling points, (i.e., 161.7 °C for furfural [25], 78.4 °C for ethanol [26], and 100 °C for water [27]) high value-added by-products can be extracted from waste water. Firstly, the waste water from ***lignin extraction process*** and condensate from ***feedstock pre-treatment process*** will vent and pump to heat exchanger, then transfer to flash tank in order to separate soluble organics (mainly glucose and xylose represented high-boiling components) and other soluble components (see Fig. 3). This is followed by the most of water will be extracted after two dehydration processes, which will be stored in ***utilities*** for ***feedstock pre-treatment process*** water recycling and discharged into environment respectively. A small part of the rest waste water, which contains water, ethanol and furfural, will remain in ethanol fractionating column for ethanol distillation, ethanol can be separated at a reaction temperature of 80 °C in fractionating column. The waste water will further be dehydrated in tertiary dehydration column, which ensures high concentration furfural could easily extract from mix aqueous solutions in furfural rectification column. In the end, this process will extract high value-added by-products which includes lignin in ***lignin extraction***;

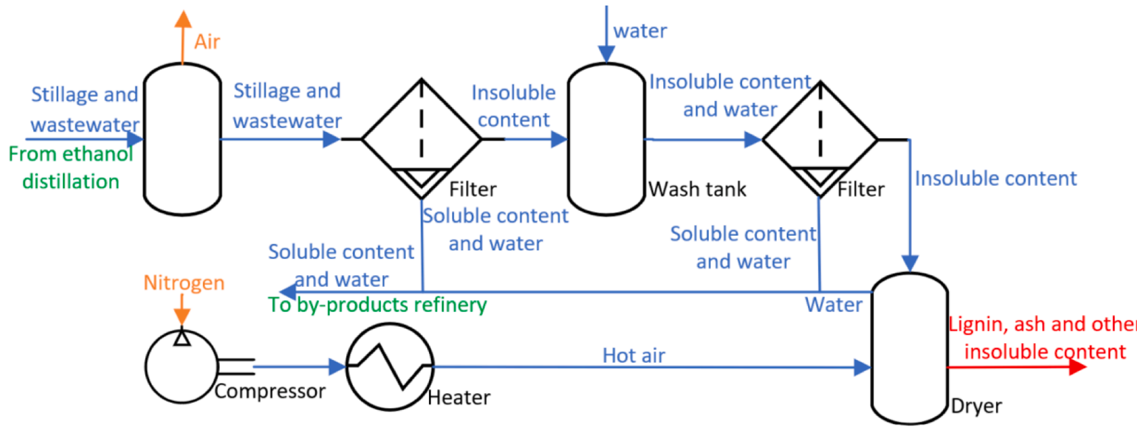

Fig. 2. Lignin extraction flowsheet in concept process diagram.

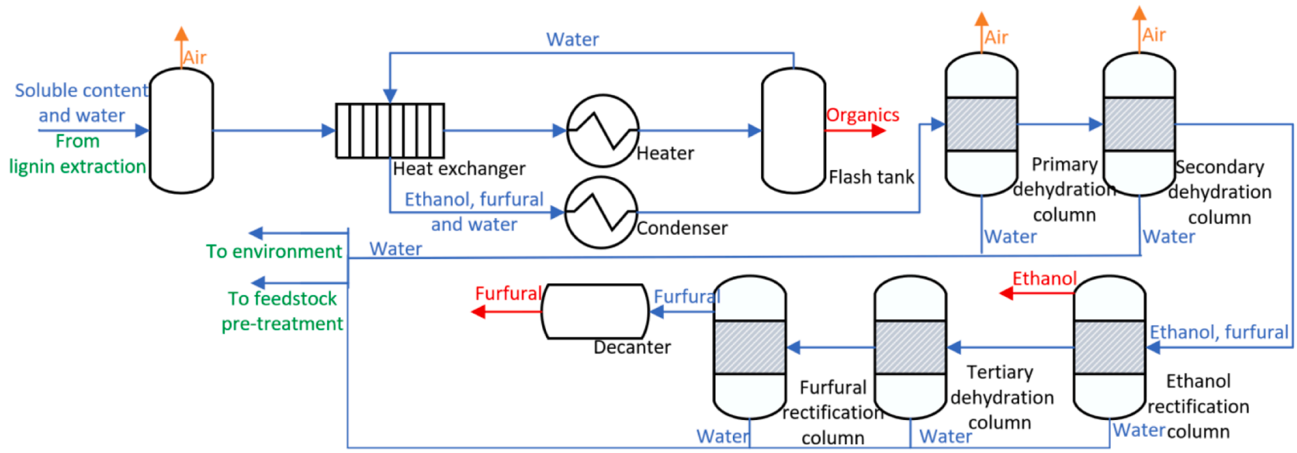

Fig. 3. Wastewater multistage purification process in concept process diagram.

ethanol, furfural, purified water and soluble organics powder in ***By-product purification***. The purified water can be reused in ***feedstock pre-treatment*** for operation cost reduction, while dried soluble organics can be returned to soil as fertilizer for environmentally sustainable purposes. The detailed ***by-products purification*** Aspen simulation model is illustrated in S.2 of Supplementary.

The detailed instructions for critical main units used during the process simulations, including washing tank, drying and dehydrating, are listed in Table 1.

Evaluation criteria

In order to comprehensively evaluate and compare the traditional and the zero-waste ethanol biorefinery, financial analysis and environmental impact analysis, in the form of CO_2 emissions, are carried out. The financial analysis is based on year values U.S. dollars in 2020 exchange currency, while the economic assumptions and parameters are similar to the NREL reports [20]. The equipment sizing and related operating and capital costs were determined by the simulation results from Aspen Plus. The operating costs include: (1) variable operating costs associated with feedstocks, raw materials, waste handling, and by-product credits; and (2) fixed operating costs consisting of employees' salaries, labour burden, maintenance, and property insurance. The variable operating costs are calculated based on the Aspen Plus simulation results. The fixed operating costs are estimated following the assumptions of the NREL report [20].

In the aspect of CO_2 emission, zero waste biorefinery was calculated based on electricity consumption related CO_2 emission intensity (g CO_2/kWh) and its energy consumption which was estimated based on results of the energy balance generated by the Aspen Plus simulation, including the thermal energy required in the heat exchangers, re-boilers, as well as the electric energy needs of the pumps, compressors, mills and other equipment.

Table 1
Description of the unit operation block in Aspen plus simulation.

	Units	Functions	ASPEN blocks
Lignin extraction	Insoluble organics filter	Separate liquid and insoluble components	Filter
	Solid washing	Solid washing	SWash
	Dryer	Solid drying	Flash 2
	Air compressor	nitrogen pressure from 1 bar to 1.2 bar	Compr
By-products purification	Heater	Waste water heating	HeatX
	Flash tank	high-boiling components separation	Flash 2
	Dehydration column	Waste water Dehydration	RadFrac
	Dehydration column	Waste water Dehydration	RadFrac
	Ethanol Separation column	Ethanol extraction	RadFrac
	Dehydration column	Waste water Dehydration	RadFrac
	Furfural Separation column	Furfural extraction	RadFrac
	Decanter	Furfural refinery	Decanter

Feedstock composition

The design of biorefinery process is significant impact by the type and composition of biomass feedstocks. The type of feedstock can affect the important components design and process network design. Such as pre-treatment technologies selection, reactors design and flow rate control. The composition of feedstocks significant influences sugar conversion, which further affects ethanol production. Therefore, a large amount, stable supply and quality steady feedstock are desired. Corn stalk is one of the sustainable potential agricultural residues.

The composition of corn stalk may vary depending on the local weather conditions, soil conditions and the type of harvesting and storage. This research evaluated various research papers [8,20,28,29] and averaged composition, as shown in Table 2.

Process design technique parameters

The process network design was proposed based on NREL research. Therefore, the capacity of designed ethanol refinery plant was 2000 metric tonnes corn stalks per day with 8410 operation hours, which the feedstock inlet flow was 104167 kg/h. Depending on conversion efficiency (detailed process conversions rate were shown in [20]), the ethanol yield of refinery plant was 21808 kg/h (99.38 % purity). As by-products of ethanol production, the stillage and waste water 403607 kg/h, which will be extracted and purified to high value-added by-products and clean water. For ethanol biorefinery sustainable development and zero waste emission, wastes will move to proposed zero waste process (***lignin extraction process*** and ***by-products purification process***). The detailed simulation model technique configuration and equipment distribution will be listed in Table S.1 of Supplementary.

Equipment cost estimation

In this work, costs related to equipment, installation, staff salary and energy are referred in 2020 and adjusted by Chemical Engineering Plant Cost Index (CEPCI), Producer Price Index (PPI), Labour Index and EIA Average Wholesale price of the year 2020.

For the equipment selection, capacity of equipment is determined based on the flow rate simulated by Aspen model. At meanwhile, To make sure validity of zero waste model, equipment install factor and scaling factor of each individual equipment were applied from [20].

Results and discussion

This research presents the thermodynamic model of zero waste bioethanol production network design, which converts wastes to high value-added by-products. The estimated results in this research are presented from the aspect of model material balance, energy consumption, economic and environmental analysis. An overview picture of ethanol biorefinery process stream flow was illustrated in Fig. 4 that the vented gas and material from utilities are not shown in this figure.

Material balance

Aspen Plus process model simulated the process that stillage discharge from ***ethanol distillation process*** undergoing ***Lignin extraction*** and ***By-product purification***. The obtained high-value added by-products and its purity by ***Lignin extraction*** and ***By-product purification process*** are presented in Table 3.

In ***lignin extraction process***, the insoluble contents such as lignin, cellulose and ash were extracted with 12 % moisture, which accounts 6.4 % of total inlet stillage (26024.1 kg/h). According to the simulation results, lignin shares approximate 47.0 % of extracted insoluble solid that is worth between 300 and 450 US dollars per metric ton based on market value in 2020 [30,31] ($375/t, assumed for the calculations in this work). While the soluble content and waste water mix aqueous solutions (375283 kg/h) will move to ***By-product purification*** for high value content refinery.

In ***by-products purification***, 25080.7 kg of solid soluble organics are extracted per hour which accounts for approximately 7 % of mixed aqueous solutions. 90.1 % purity of ethanol (202 kg/h) and 98.7 % purity furfural (528.3 kg/h) could contribute $250 [32,33] and $1600/t [34] for biorefinery plant cash flow respectively. 349440 kg/h of purified water with 99.5 % purity was generated in ***By-product purification***, out of which 136508 kg/h replace utility water for water recycling in ***pre-treatment process***. The rest of 212932 kg of purified water will be discharged into environment per hour. The recycled purified water could save 0.23 million dollars for refinery plant a year. The detailed flowrate of each stream is presented in Table S.2 of Supplementary.

The Aspen simulation result showed that 21808 kg/h ethanol extract after the ***Ethanol distillation*** process and the ethanol from By-product purification is 202 kg/h. Given the total feed rate of raw material of 104167 kg/h, it can except an overall ethanol conversion rate of 21.1 % from the raw materials. This result is in a good agreement with the experimental data reported by [39] with an overall ethanol production of 24.1 kg/ton corn stalk and the overall conversion ratio of 24.1 %. the discrepancy between simulated modelling results and the reported experimental data might be caused by simplified modelling assumption.

Energy consumption

In the aspect of energy consumption, according to Aspen Plus simulation results, the total energy consumption of ***lignin extraction*** and ***by-products purification*** is 399.08 MW (1436677.55 MJ/h) shown in Table 4. Among that ***by-products purification*** shares the largest energy consumption, which account for 397.65 MW.

In the lignin extraction process, the stillage and lignin mixed solution come through the filter, and the wet lignin and stillage were separated. To produce value-added by-products, lignin needs further heating to remove moisture. Therefore, the most of energy consumption for lignin extraction was in the heater and condenser (account for 88.8 % of total energy consumption). The extracted stillage will be further undergone By-product purification process.

In the By-product purification process, 375283 kg of stillage needs to purify each hour. Among that most of content is water, accounting for 92.8 % of total stillage. Therefore, it needs massive energy for purification. First of all, stillage was heated to 78.4 °C for ethanol extraction, then followed to 100 °C for water removal. In the end, enhance to 161.7 °C for furfural extraction. In this process, massive energy is needed in order to separate water from other materials, which results in 236.26 MW in heater and condenser. The following dehydration of By-product purification process was 142.65 MW, which accounts for 35.9 %. It should be noticed that a 119.34 MW consumption in ethanol purification, that because of vapourised water content in ethanol.

Table 5 summarised the energy consumption distribution during in ethanol production and energy content of ethanol and by-products. It was shown that the total energy consumption for ethanol production was 566.87 MW. While the produced ethanol only contained 162.70 MW, which accounts for approximate 28.7 % of energy consumption. One of the major reasons is the energy content of high value-added by-products cannot take account in total energy content. From energy point

Table 2
Summary of corn stalk composition.

Corn stalk (dry wt %)			
Glucan	35.05	Extractives	14.65
Xylan	19.53	Arabinan	2.38
Lignin	15.76	Galactan	1.43
Ash	4.93	Mannan	0.60
Acetate	1.81	Sucrose	0.77
Protein	3.10	Moisture (wt %)	20 %

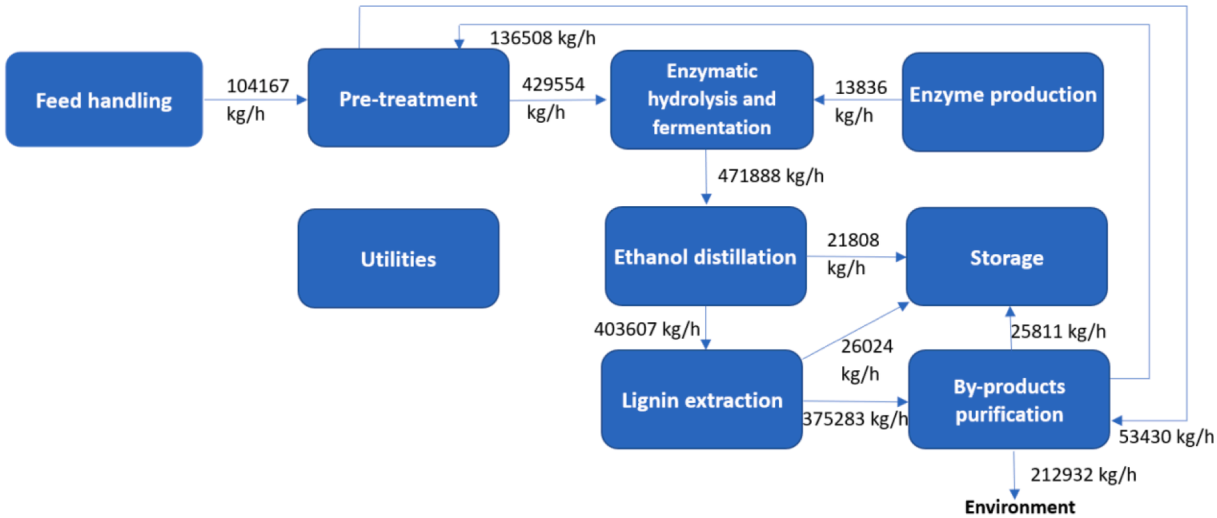

Fig. 4. The stream flow of zero waste ethanol biorefinery process.

Table 3
By-products yield from the zero waste biorefinery process simulated by Aspen Plus.

	Yield (kg/h)	Purity (%)
Raw lignin	26024.1	47.0
Organics	25080.7	–
Raw ethanol	202.0	90.1
Furfural	528.3	98.7
Purified water	349,440	99.5

of review, this ethanol refinery production process is not profitable. The main purpose of research is high value-added products rather than energy balance. In the aspect of sustainable development, the benefits of material is much more valuable than that in the aspect of energy.

Financial analysis

In this work, costs related to equipment, installation, staff salary and energy are referred in 2020 and adjusted by Chemical Engineering Plant Cost Index (CEPCI), Producer Price Index (PPI), Labour Index and EIA Average Wholesale price of the year 2020. The capital cost and operation cost breakdown by process areas and cost components are shown in Fig. 5 and Fig. 6. The total capital cost of proposed zero waste refinery plant is 145 million dollars, while the most expensive area is in ***pre-treatment process***, which requires multiple stages to condition pretreated slurry by over liming. Biorefinery plant operation cost is divided into fixed operation cost and variable cost which include by-products; energy consumption and capital depreciation. Compared to traditional bioethanol process, the energy source of zero waste bioethanol process is from external electrical grid. There is no doubt that energy consumption occupied the largest operation cost (76.46 M $/year). On the other hand, by-products are refined to high value-added commodities contributing to increased plant revenues (89.39 M$/year). The detailed equipment cost and capacity of ***Lignin extraction*** and ***By-product purification*** are presented in Table S.3 of Supplementary.

Table 6 compares the minimum ethanol selling price (MESP) between the proposed zero waste and the traditional biorefinery plant. MESP is a parameter indicating the lowest ethanol price that could cover cost and generate 10 % internal rate of return (IRR) for the ethanol refinery plant. MESP of zero waste biorefinery plant is 20.5 % lower than that of the traditional biorefinery plant ($1.78/gal against $2.24/gal). While that average ethanol market price was $2.04/gal on April of 2021 [35], indicating a considerable profit space in proposed ethanol process.

Table 4
Energy consumption in zero waste emission biorefinery simulated by Aspen Plus.

Process	Unit name	Function	Energy consumption (MW)
Lignin extraction	Compressor	Compress air	0.13
	Heater	Heating air	0.45
	condenser	Colling steam	0.82
	Pump	Stillage transfer	0.02
	Pump	Wastewater transfer	0.01
	Primary Filter	Solid filtering	0.00
	Washing water Filter	Solid filtering	0.00
	Total Sum		**1.43**
By-product purification	Heat exchanger	Organics extraction	18.74
	Heater	Organics extraction	15.59
	Wastewater condenser	Wastewater colling	220.67
	Furfural condenser	Furfural steam cooling	0.87
	Wastewater pump	Wastewater pumping	0.06
	1st dehydration pump	Wastewater pumping	0.04
	2nd dehydration pump	Wastewater pumping	0.01
	Ethanol pump	Wastewater pumping	0.00
	3rd dehydration pump	Wastewater pumping	0.00
	1st dehydration column	Water extraction	15.88
	2nd dehydration column	Water extraction	3.66
	Ethanol column	Ethanol extraction	119.34
	3rd dehydration column	Water extraction	1.99
	Furfural column	Furfural extraction	0.80
	Total Sum		**397.65**

Waste water recycles into refinery plant operation, which results in the raw material cost drop from 14.1 to 13.6 cents/gal ethanol. In traditional ethanol refinery plant, higher capital cost leads to higher capital depreciation and average return on investment, while the limited by-products restrict its profitability, which rise up potential cost

Table 5
Energy consumption and production for ethanol refinery.

	Energy (MW)	Market price ($/ton)
Energy consumption for ethanol production	167.79	–
Energy consumption for value-added production	399.08	–
Produced ethanol	162.70	1650.95
Raw lignin	–	375
Organics	–	0
Furfural	–	1600

(minimum ethanol selling price). Thus, zero waste biorefinery plant has a great advantage in MESP. On the other hand, large amount of electricity consumes during ethanol production results in a significant utility cost increase (the utility cost from 1.5 cents/gal raise to 125.3 cents/gal).

Model validation

There are limited data available to perform validation of the proposed zero-waste biorefinery concept since it is quite novel. Lynd et al. [36] optimized the NERL process with three types of models in 2017. In one of process models, the authors proposed a process that extracts lignin only, while the waste water undergoes anaerobic treatment discharged into environment with external energy from electricity. The total capital cost of Lee et al. was $250 million against $281 million of our proposed process. If remove inflation impact to the year 2017, our proposed process capital cost will adjust to 269 million. The capital cost contributes by direct investment (equipment expenditure) and indirect

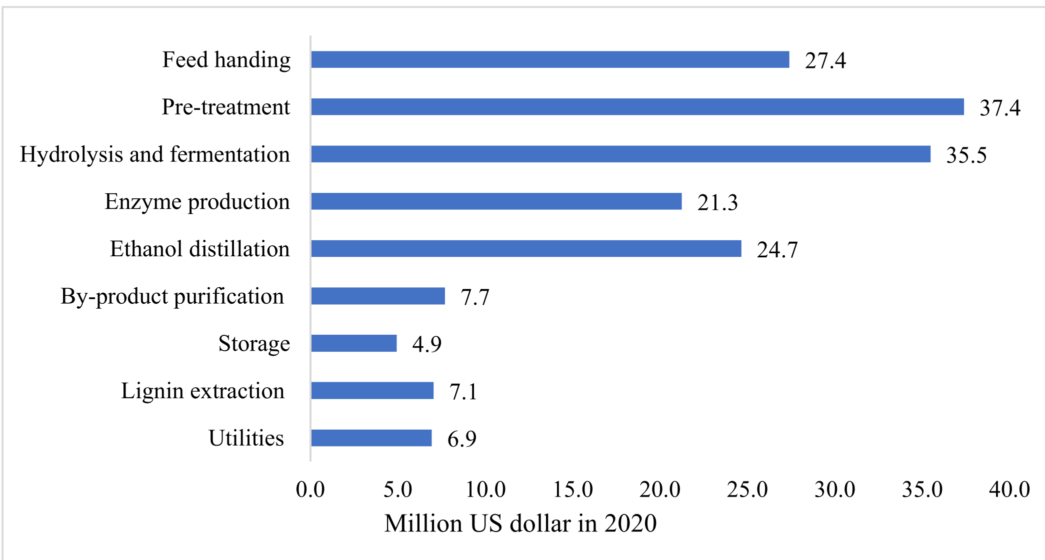

Fig. 5. Zero waste biorefinery plant capital cost breakdown by sub-processes.

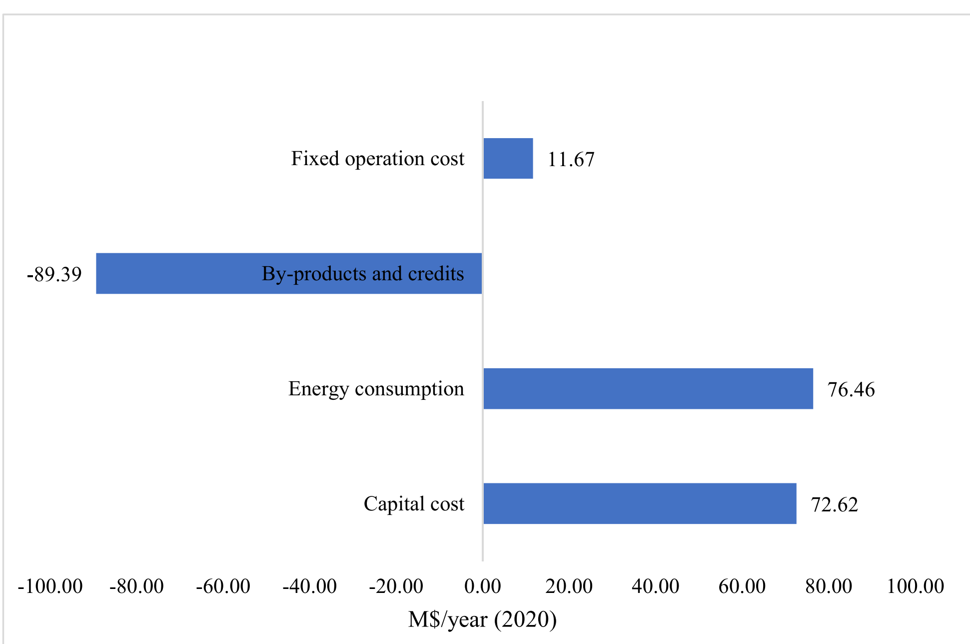

Fig. 6. Zero waste biorefinery plant operation cost distribution.

Table 6
Minimum Ethanol Selling Price distribution in zero waste and traditional biorefinery plant (cents/gal ethanol).

Name	Zero waste biorefinery plant	NREL (traditional) biorefinery plant
Feedstock and Handling	74.1	
Sulfuric Acid	2.7	
Ammonia	7.2	
Glucose (enzyme production)	21.4	
Other Raw Materials	13.6	14.1
Utility cost	125.3	1.5
By-product income	−146.5	−10.8
Fixed Costs	19.1	20.1
Capital Depreciation	14.6	22.3
Average Income Tax	8.2	12.7
Average Return on Investment	38.5	59.2
Minimum Ethanol Selling Price	$1.78/gal	$2.24/gal

investment (fixed rate of direct investment). When splitting direct investment contribution, it can be found that the equipment cost for lignin extraction is 10 M$ against our proposed 7.1 M$. One hypotheses is equipment cost reduction with technologies improvement. Thus, we think the assumed data is reliable and acceptable. The difference is because of increased expenditure on multistage refinery processes in the proposed zero-waste concept ***by-products purification***.

CO_2 emission

In terms of environmental impact, CO_2 emission is a critical criterion for biorefinery environmental assessment. Table 7 summarises CO_2 emissions in both zero waste and NREL biorefinery plants, which includes CO_2 produced from reactions in processes and electricity consumption. The CO_2 emission of electricity is calculated based on the data from Energy Information Administration (EIA) in 2020 in US (0.01 kg of CO_2/kWh for average renewable electricity) [37]. The total CO_2 emission of zero waste emission plant accounts for approximate 27.6 % of that in the traditional bioethanol plant. To extract high concentration by-products from mixed aqueous solutions, high volume of water needs to distillate which results in significant electricity consumption in ***By-product purification***. In terms of NREL refinery plant, extracted lignin from stillage convert to heat and power for whole refinery plant operation, leading to high CO_2 emission in ***CHP process***.

To achieve zero waste refinery plant competitiveness in CO_2 emission, 0.11 kg CO_2 emissions per kWh of all kinds of electricity (including renewable and fossil energy) is the maximum requirement. Reducing unit electricity CO_2 emission and developing cleaning energy such as wind power, hydropower and nuclear power are critical for reducing zero waste biorefinery plant CO_2 emissions. Thus, the suggestion is that the zero waste biorefinery plant should be operated in low carbon emissions European countries such as Sweden, Norway and Lithuania with 0.008, 0.019 and 0.022 kg/kWh respectively in 2019 [38], if the CO_2 emissions need to be lower than the traditional refinery plant.

Note: The total process stream between zero waste and traditional ethanol biorefinery plant are vary due to process reaction conditions are differ.

Sensitivity analysis

A conventional approach to understanding the importance of individual inputs is to perform single-point sensitivity analysis whereby a metric (e.g., MESP) is evaluated at the lower (-25 %) and higher (+25 %) bounds of each input parameter. Zero waste biorefinery sensitivity analysis has been performed on the impact of the most critical parameters affecting financial feasibility, such as capital cost, by-products income (furfural price, lignin price) and operational expenditure (feedstock price and enzyme price) on MESP (Table 8).

Fig. 7 illustrates MESP performance under single parameter fluctuation, which shows none of parameters plays a domestic role in MESP oscillation (over 25 % deviation). It is clear that MESP is highly sensitive to the lignin price, due to the high value and large amount of this particular by-product. When the lignin price increased from $375.0/ton (base case scenario) to $468.8/ton, the MESP value dropped by 18.5 %. In the meanwhile, electricity price is also a key parameter that affects MESP value with a positive relationship (higher electricity price, higher MESP value). Thus, decreasing electricity prices could increase bioethanol competitiveness in the market, and anyone interested in the zero-waste concept should be focusing on low electricity prices to improve the financial performance of the plant. MESP has a relatively high sensitivity to feedstock price and capital cost, although not as high as in the case of lignin and electricity price. In general, enzyme cost is seen as a bottleneck in bioethanol refineries refinery [39]. However, in this study, its impact on MESP is less sensitive compared to other investigated factors.

Table 8
The effect of individual input on MESP value.

	By-products sale price		
	+25 %	Default value	−25 %
Lignin ($/t)	468.75	375.0	281.25
Furfural ($/t)	2000.0	1600.0	1200.0
Electricity ($/kWh)	0.05	0.04	0.03
Feedstock ($/t)	73.13	58.5	43.88
Capital cost (M$)	351.40	281.12	210.84
Enzyme ($/t)	562.50	450.0	337.50

Table 7
CO_2 emission in zero waste and traditional biorefinery plant.

	Zero waste biorefinery plant			Traditional NREL biorefinery plant		
	Total CO_2 emissions (t/h)	Stream amount (t/h)	Unit CO_2 emission	Total CO_2 emissions (t/h)	Stream amount (t/h)	Unit CO_2 emission
Feed handing	0.01	104.17	0.00	0.00	104.17	0.00
Pre-treatment	0.06	482.98	0.00	0.00	482.98	0.00
Hydrolysis and fermentation	0.02	471.89	0.00	0.00	471.89	0.00
Enzyme production	2.42	47.22	0.05	2.38	47.22	0.05
Ethanol distillation	20.74	510.83	0.04	20.73	510.83	0.04
By-product purification or waste water pre-treatment	7.59	375.28	0.02	4.00	558.17	0.01
Storage	0.00	78.16	0.00	0.00	26.33	0.00
Lignin extraction or CHP	0.01	457.26	0.00	87.67	768.26	0.11
Utilities	0.06	136.51	0.00	0.00	82.22	0.00
Total	30.9			114.7		

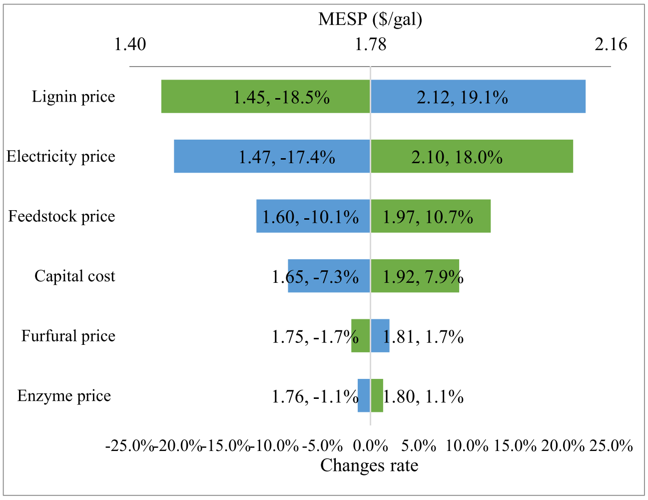

Fig. 7. The impact of parameters on MESP sensitivity.

Conclusions

This study proposed bioethanol refinery process design towards zero-waste emissions, with its technical feasibility has been verified and proven by the Aspen plus simulation. zero waste emission process appears to be more competitive than traditional biorefinery plant in terms of profitability in ethanol market, especially if low electricity prices can be achieved. The results show that feedstock ***pre-treatment process*** and ***fermentation process*** are critical areas in capital cost distribution. High value-added by-products income improves the bioethanol plant's profitability. MESP is an important parameter that evaluates bioethanol plant profitability, which has been employed to evaluate bioethanol plant profitability. Compared to traditional bioethanol plant, zero waste biorefinery plant has a great advantage in controlling capital costs and by-products income creation. However, a potential drawback of the proposed biorefinery plant is electricity resource related CO_2 emission. If the plant operates in high CO_2 intensity of electricity generation. With increasing strict emission standards, zero waste emission biorefinery plant needs to seek upgrading, and ideally to be supplied by green electricity. There is a trade-off identified, in the form of higher electricity consumption, while on the other hand more biomass is transformed into useful products and less waste is generated. High value-added by-products play a crucial role in the proposed bioethanol plant profitability, which leads to MESP sensitivity. The results shown that the by-product (such as lignin) with the higher unit price and productivity results in higher MESP fluctuation. Lignin is main by-product of ethanol refinery which has a higher unit price ($1600/ton), when lignin peddles price increases by 25 %, MESP will reduce by 18.5 %, followed by electricity price and feedstock price. In order to increase zero waste emission ethanol competitiveness, optimizing operation cost will be the primary task, while improving bargaining power and reducing costs (such as feedstock cost and enzyme cost) is an efficient way.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seta.2022.102627.

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