



# A comprehensive analysis of biphasic reaction system for economical biodiesel production process

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## ARTICLE INFO

### Keywords:

Biofuel  
Biphasic reaction  
Hydrodeoxygenation  
Cyclopentyl methyl ether  
TEA  
LCA

## ABSTRACT

Biofuels are promising sources of renewable energy, however the economically feasible biofuel process has not yet proposed because of the system complexity and a wide range of process variations. This study explores the practical potential of biodiesel production processes through sequential reactions. Proposed sequential reaction started with xylose dehydration reaction producing furfural followed by furfural hydrogenation, condensation, and hydrodeoxygenation for biodiesel production. Rigorous reaction and separation models were constructed by using reaction experiments and thermodynamic data. The optimal biofuel process has been also proposed through flowsheet optimization. Detail technoeconomic analysis and life cycle assessment are provided to assess the impacts of certain parameters on economics and greenhouse gas emission. The results of this study show that the levelized cost of biodiesel production is \$3.66 gal<sup>-1</sup>, and the corresponding global warming potential (GWP) is 57.18 gCO<sub>2</sub>eq MJ<sup>-1</sup> for the base case. The production cost and GWP can reach \$3.26 gal<sup>-1</sup> and 29.39 gCO<sub>2</sub>eq MJ<sup>-1</sup> depending on the xylose concentration and the furfural yield. The feed costs of xylose and hydrogen account for more than 80% of the levelized cost of biodiesel production and the steam utility required for refining products takes the largest portion of GWP, ranging from 33% to 65% of the total. These results ascertain that the economic feasibility of biodiesel production can be achievable by using only the sugar components in biomass, and the economics and GWP depend on the feed condition and the use of efficient separation process.

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## 1. Introduction

The increased use of fossil fuels accelerates global environmental degradation, and unprecedented disasters caused by extreme weather events have increased awareness of the need for sources of renewable energy [1,2]. Of the candidates for such energy, biofuels have attracted significant attention as a way to mitigate environmental issues, and in particular the global warming that results from emissions of carbon dioxide [3]. However, although many attempts have been made to render biofuels economically viable, they are not yet competitive with petroleum due to their low conversion and expensive separation process. To overcome this challenge, policies have been put in place to encourage the use of biofuels, such as providing incentives for fuels blended with

biofuels, but the share of them as an energy source remains insignificant [3,4].

The need to reduce biofuel production costs has led researchers to focus on finding cost-effective reaction pathways and catalysts to improve reaction performance. The development of pretreatment has opened the possibility of commercially available methods of converting biomass feedstock into diluted sugars such as pentoses and hexoses, separated from cellulose, lignins, and humins [5,6]. These sugars are mainly obtained from hemicellulose consisting of 25–30% lignocelluloses. Pentoses can be upgraded into various useful chemicals and fuels via consecutive chemical processes, such as dehydration, hydrogenation, and aldol condensation [7]. It is worth noting that hexoses such as glucose can also be used to produce furfural, but doing so is more technically challenging than using xylose [8]. Production of the

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<https://doi.org/10.1016/j.rser.2022.113122>

Received 1 July 2022; Received in revised form 30 November 2022; Accepted 18 December 2022

Available online 22 December 2022

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Abbreviation			
2-MF	2-methylfuran	HPLC	High-performance liquid chromatography
CAPEX	Annualized capital	IO	Input-output
CC	Climate change impact	LCA	Life cycle assessment
CMPE	Cyclopentyl methyl ether	LHSV	Liquid hourly space velocity
CtG	Cradle to gate	LHV	Low heating value
CW	Cooling water	OPEX	Operating expenditure
FAST	Fourier amplitude sensitivity testing	RI	Refractive index
GC-FID	Gas chromatography with flame-ionization detector	RoW	Non-European (Rest-of-World)
GSA	Global sensitivity analysis	SI	Supporting information
HDO	Hydrodeoxygenation	TEA	Technoeconomic analysis
		WT	Waste treatment
		WWT	Wastewater treatment

undesirable furfural byproduct 5-hydroxymethyl and low furfural yield are common difficulties of hexose conversion into furfural [8,9]. For this reason, we focus on analyzing the biodiesel processes using xylose, which is currently available for producing furfural at an industrial scale [10].

Chemical and biological pretreatment processes are attractive means of producing sugars at industrial levels. Each method has its own merits and drawbacks. For instance, acid pretreatment requires a short residence time and mild temperatures, but neutralization and recycling processes are required for the acid after processing. Biological methods commonly have long pretreatment times but consume less energy [6]. Regarding the biodiesel process overall, the pretreatment process greatly affects the subsequent processes required for biodiesel production because the concentration of refined sugar products varies depending on the production process of the fermentable sugar [11]. 2–10 wt% of xylose in diluted solution is often considered industrially appropriate [12,13], but some studies have argued that xylose products can be more concentrated, depending on the available biomass resources and catalysts [6,8,14,15]. In addition, the concentration of xylose is adjustable using the refinery process. For instance, Kuo et al. found that 45.8 wt% xylose solution could be obtained using an optimized diluted acid pretreatment process [5]. This dependence of the condition of xylose feed on the subsequent upgrading process necessitates quantitative analyses of its impacts on production costs to develop an economically competitive process in relation to the provided feed conditions.

Efforts to improve reaction performance for converting pentoses into useful chemicals have led to the development of reactors with high product yields. One example of this is the technique of adding an organic solvent to a diluted xylose solution to produce furfural, which is a versatile intermediate for producing various renewable chemicals and biofuels [16,17]. This biphasic reaction reportedly achieves 99% furfural yield, depending on the organic solvent used [18]. More reviews on the reaction performances of biphasic reaction to produce furfural can be found in Supplementary Information (SI). Despite the high yield of the biphasic reaction system, the separation cost is an impediment to its practical application, as large amounts of organic solvent needs to supply to overcome low penetration of the furfural from the water to the organic solvent [13,19]. Likewise, the high concentration of xylose in water would reduce the yield of the furfural in biphasic reaction systems [20]. To obtain insight into the future development of biofuel production methods using a biphasic reaction, quantitative analyses to elucidate the influence of the characteristics of the reaction system on the technoeconomic cost and greenhouse gas emissions, which depend on the amount of organic solvent and xylose concentration in water, should be performed. This analysis can only be performed through rigorous simulations of the entire process of producing biofuel from fermentable sugar or biomass feed.

Production of diesel-grade C15 hydrocarbons from xylose-based furans has been attempted [21,22]; this can be performed using a series of

unit processes, including the dehydration of xylose to furfural [23,24], selective hydrogenation of furfural to 2-methylfuran [25], condensation of furans [26–29], and hydrodeoxygenation (HDO) of condensed compounds [30,31]. Although each unit process has been studied independently to achieve optimum results, the feasibility of the unused pentoses as high-quality fuels is not fully understood. An economical and environmental analysis through the integration of the unit processes for the feasible valorization of unused sugars is highly recommended to explore the potential of its practical application in the interrelationship of unit process variables.

According to the recent advances in biodiesel production, the conversion of biomass into fuels has become more promising [32]; however, economic viability remains out of reach due to the necessary processes of sugar upgrading and energy-intensive separation. In particular, the energy cost required to refine biodiesel is a major part of the total biodiesel production cost. Thus, the design of efficient separation should receive as much attention as that paid to reactions. However, studies of biodiesel production have generally neglected—or incorporate an overly simplified understanding of—the separation processes because it involves many challenges. A comprehensive study that takes into account both the reaction and separation systems requires a rigorous process model that cannot be obtained without the necessary thermodynamic data to precisely describe phase equilibria of the diluted product-solvent system. As presented in this study, thermodynamic characteristics can have a decisive impact not only on separation efficiency but also on economics and carbon emissions. Several studies are worth mentioning as attempts to show the economic impact of the separation process by designing the entire process of biodiesel production using various reaction pathways [33–36]. In particular, Baral et al. [33] reported comprehensive analytical results taking into account the uncertainties in the process, as well as the economic parameters, and concluded that the minimum selling price for the economic viability of bio-jet fuel can reach \$2.75–3.45 gal<sup>-1</sup> using biological production methods (in an ‘optimistic future’ case). Olcay et al. performed a comprehensive analysis for aviation biofuels via phasic reaction [37]. They introduced tetrahydrofuran as the organic solvent to attain the high furfural yield and designed the complete biofuel production process. The resulted minimum selling price of bio-jet fuel varies in the range of \$4.36–6.31 gal<sup>-1</sup> requiring monetary incentives to meet economic viability. Reviews However, we could not identify any published study that has analyzed this process using validated thermodynamic property data of the key components in the feed and product streams. Furthermore, almost no biodiesel production studies that take into account uncertainties in the feed concentration can be found, although the results of this work could significantly change overall efficiency throughout the entirety of the production process.

In this study, we provide evidences showing that the optimized processes that convert diluted xylose into furfural using cyclopentyl methyl ether (CPME) as the organic solvent for the biphasic reaction, from which biodiesel is produced in subsequent reactions can be

considered as economically feasible alternatives to produce energy source, and identify the condition for its industrial application. The main components of the product stream are the C15+ middle distillates, produced by HDO of 5,5-bis(5-methylfuran-2-yl)pentan-2-one (trimer in Fig. S1). The rigorous simulation results of the suggested process elucidate the economic and environmental impacts of biphasic solvents on the desirable thermodynamic properties of catalysts and solvents. The impacts of uncertainties in the process and economic parameters on the economic viability and carbon emissions of the biodiesel production process were also quantitatively investigated. This will help clarify the understanding of how the nonlinear behavior of feed-product-solvent equilibrium systems affects biodiesel production costs and the resulting carbon emissions. The assessment of catalysts and solvents for biodiesel production requires experiments to measure reaction performance as well as simulations of the entire process to estimate the profitability of marketing the biodiesel. Accordingly, the sensitivity analyses of the economic viability of biodiesel production processes using simulation in tandem with experimental results have been conducted.

This paper presents the results in the following order: experimental results, process design strategies, base case simulations, and sensitivity analyses including process and economic parameters. The two system boundaries for techno-economic analysis (TEA) and life-cycle assessment (LCA) are defined (Fig. 1). Note that the pretreatment process is not included in the system boundaries as this study aims at analyzing the sugar upgrading process while precluding the impact of the pretreatment on the TEA and LCA results. Rather, this study provides the condition of pretreatment process to secure the economic feasibility of the biodiesel production by independently optimizing the upgrading process depending on varying xylose feedstock concentration of which condition is determined by pretreatment process. Case 1 considers the case where all of the required utilities are purchased from outside of the system boundary. In Case 2, part of the required steam is supplied from the onsite steam-generation boiler. This paper mainly follows Case 1 because the amount of energy required for separation and the resultant carbon emissions are directly reflected in the TEA and LCA results. The results from Case 2 are provided to show how much production costs and carbon emissions change depending on onsite steam generation using lignin residues, which is generally presented in the SI.

## 2. Experiment

Many attempts have been made to improve furfural selectivity; for example, organic solvents are commonly used in dehydration. The organic solvents are added to the aqueous solution of xylose to form a biphasic system, which in turn prevents further conversion of furfural-producing byproducts [18]. Various solvents are tested to attain high

furfural selectivity by forming two immiscible phases in the xylose dehydration system [38–46]; however, the large amount of energy required to retain the solvents separate from water impedes the development of the economically viable processes. Among the tested organic solvents, CPME is the most efficient for achieving high furfural yield [18, 20]. CPME is often considered as a competitive alternative to the existing ethereal solvents due to its various benefits as an organic solvent such as high stability under both acidic and basic conditions, and low formation of peroxide. In addition, recycling CPME by separating it from the biphasic solution formed with water requires relatively low energy compared with the other solvent because of its low solubility in water (1.1 g per 100 g of water) and low vaporization energy (69.2 kcal kg<sup>-1</sup>). In tandem with the high performance of xylose conversion reaction, these thermodynamic properties make CPME stand out as an economical and environmentally friendly solvent for biodiesel production processes. Furfural can be transformed into biofuels such as biodiesel via a series of reactions of hydrogenation, condensation, and HDO [12,47]. In these reactions, undesired by-products are inevitably produced and thereby lower the quality of the biofuels produced. These by-products should be removed to satisfy biodiesel standards provided by the American Society Testing and Materials or the European Standards for commercialization [2,48]. The refinement of remains is an energy-intensive process that lowers the profitability of biofuel production.

We performed experiments to confirm the data for the series reactions for converting diluted xylose into biodiesel, after which we used the biodiesel to evaluate the cost of practical reactors. Information on the experiments is given in Table S3, and the detailed experimental methods are described in the following subsections. For the separation processes, thermodynamic data were obtained from the previously available experimental results [20].

### 2.1. Dehydration of xylose to furfural

The catalytic dehydration of xylose to furfural was performed in a round-bottomed flask. An aqueous solution of xylose (10 wt%, 25 g) was mixed with Amberlyst-15 (1.5 g). CPME (25 g, Sigma-Aldrich) was added to the mixture, and the prepared biphasic mixture was heated to 150 °C while being agitated at 300 rpm. After 3 h reaction, CPME and aqueous phases were separately collected, and the concentrations of prepared furfural in both phases were measured using an Agilent 7890A with a flame-ignition detector (GC-FID) equipped with an HP-5MS capillary column (60 m × 0.25 mm × 250 μm). The quantity of the furfural was determined using 1-butanol as an internal standard (Fig. S2). The concentration of furfural in the CPME phase, where the sum of the furfural weight in water and CPME phase divided by the initial weight of xylose was 51.0 wt%, and the conversion of xylose was 76.1%, was 34.1 g L<sup>-1</sup>.

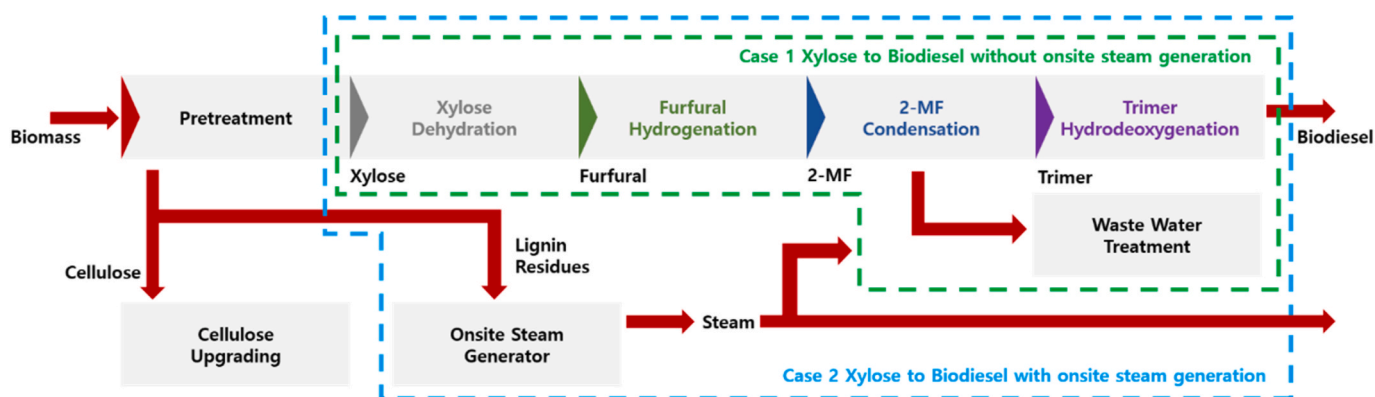


Fig. 1. System boundaries for TEA and LCA in this study. Case 1 considers the biodiesel production process starting from xylose without the onsite steam generator. Case 2 includes onsite steam generation. Both of the cases incorporate the entire biodiesel production process, except for the pretreatment and the cellulose upgrading process in their system boundaries. Note that the wastewater treatment unit processes the wastewater streams from the entire process.

## 2.2. Selective hydrogenation of furfural to 2-methylfuran

For the HDO of furfural in CPME, mesoporous Cu–Al<sub>2</sub>O<sub>3</sub> (20 wt% CuO), synthesized by the solvent-precipitation method reported by Park et al. [49], was promoted by 2 wt% sodium. This catalyst was reduced in a stainless-steel reactor by 99.99% H<sub>2</sub> (80 mL min<sup>-1</sup>) at 300 °C for 1 h under atmospheric pressure [49]. After cooling to the reaction temperature of 250 °C and tuning the H<sub>2</sub> flowrate to 13 mL min<sup>-1</sup>, 5 vol% furfural in CPME was fed by a high-performance liquid chromatography (HPLC) pump at 0.064 mL min<sup>-1</sup>. The experiment was conducted at a weight hourly space velocity of furfural of 0.223 gFur<sup>-1</sup> gcat<sup>-1</sup> h<sup>-1</sup> and a molar ratio H<sub>2</sub>/furfural of 15.1 over 48 h. The product was continuously condensed and collected for analysis using a gas chromatograph equipped with a flame ionization detector and HP-INNOWAX column (50 m × 0.2 mm × 0.4 μm). The furfural was nearly completely converted in the reaction, and the measured weight balance ranged from 95% to 100%. The average product yield of 2-methylfuran (2-MF) was estimated to be ca. 78.7 mol% with by-products such as 2-pentanone (5.2 mol%), 2-pentanol (2.2%), and γ-valerolactone (1.7%) (Fig. S3).

## 2.3. Condensation of furfural and 2-methylfuran to trimer

2-MF and furfural were condensed using a continuous flow fixed-bed reactor (1 cm I.D., 4.5 cm long, made of stainless steel) [12]. The catalyst powder (3 mL) of silica-supported phosphotungstic acid (15 wt%) was prepared based on our previous study [12] and placed in the reactor. The catalyst bed was heated to 90 °C, and the reactant flow (1.5 mL h<sup>-1</sup>) was added at 0.5 h<sup>-1</sup> liquid hourly space velocity (LHSV). A mixture of reactants was composed of 2-MF (75 mol%) and furfural (25 mol%). The prepared products were quantified using a YL HPLC equipped with a YL9170 refractive index (RI) detector and an Agilent Eclipse XDB-C18 column (5 μm, 4.6 × 150 mm<sup>2</sup>). The catalysis results were calculated using the HPLC results (Fig. S4). During the reaction, two 2-MF

molecules and one furfural molecule condensed to form trimer 1, C<sub>15</sub>H<sub>14</sub>O<sub>3</sub>, and three 2-MF molecules condensed to form trimer 2, C<sub>15</sub>H<sub>14</sub>O<sub>3</sub>. The observed trimer yield was 80–96% (Fig. S4), which can be obtained from Eqn. (1).

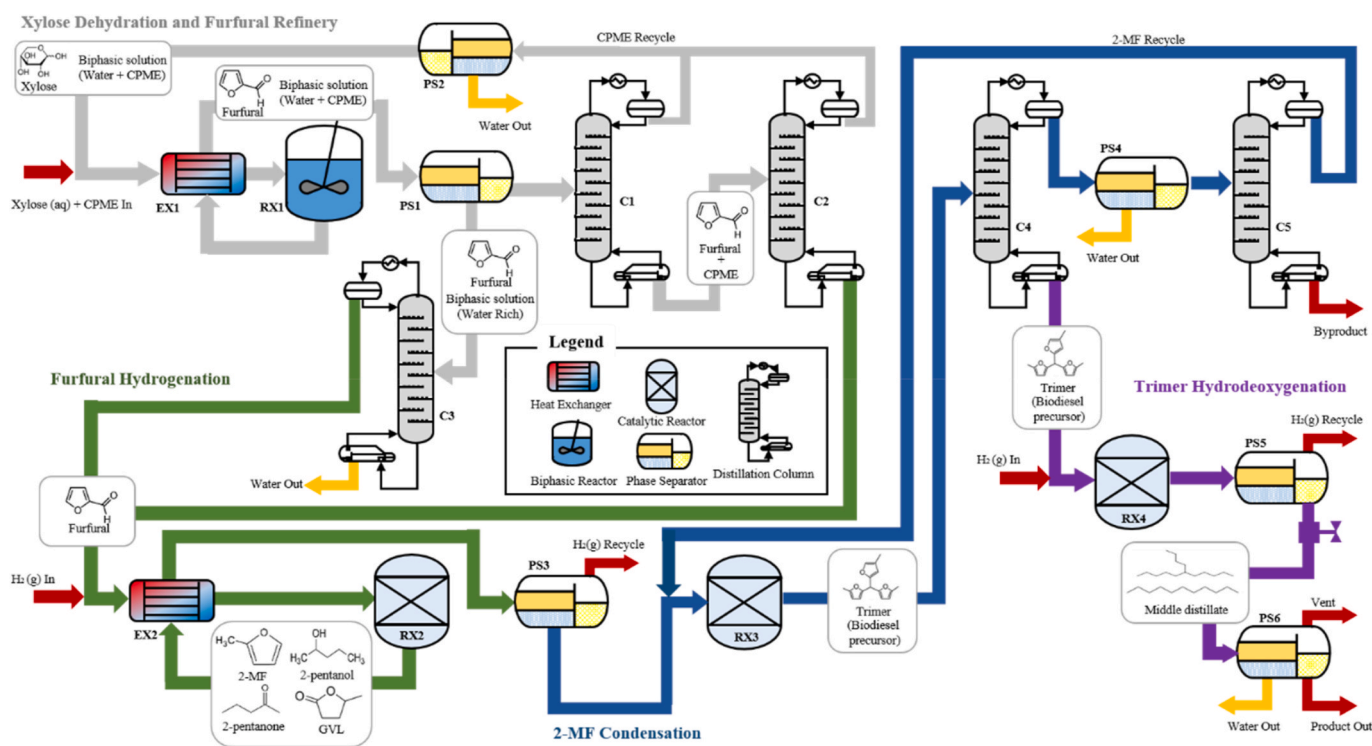
$$(\text{yield of trimer}) = \frac{3 \times (\text{mol of trimers 1 and 2 in the product})}{(\text{mol of 2-MF reactant entering the reactor})} \% \quad (1)$$

## 2.4. Hydrodeoxygenation of trimer

The prepared trimer was hydrodeoxygenated using a two-step continuous flow fixed-bed reactor system [30,50]. In the first step, commercially available Pd/C powder was placed at the upper parts of the reactor, and in the second, tungstate-zirconia-supported Ru (Ru/WZr) catalyst was placed at the lower part of the reactor, along the downward flow stream. Prior to the reaction, the catalysts in the reactors were reduced under a H<sub>2</sub> flow (200 mL min<sup>-1</sup>, 1 bar) at 350 °C for 2 h. The HDO was performed under a continuous H<sub>2</sub> flow (600 mL min<sup>-1</sup>), with the reaction pressure maintained at 100 bar using a back pressure regulator (BPR). The upper and lower parts of the reactor were heated to 200 °C and 350 °C, respectively. The trimer reactant was pumped into the reactor at a flow rate of 0.1 g min<sup>-1</sup>. The product was cooled with a chiller and collected for characterization.

## 3. Process design and analysis

Here, we designed a process to produce and refine 100,000 tons of biodiesel per year, as shown in Fig. 2, as constrained by this specific xylose flowrate. The proposed biodiesel production can be divided into four parts: xylose dehydration and furfural refinery, furfural hydrogenation, 2-MF condensation, and trimer hydrodeoxygenation. The water streams separated from the process contain small quantities of acid or organic substances, therefore proper wastewater treatment (WWT) is required. The process simulated in this study did not include a WWT



**Fig. 2.** Schematic representation of biofuel production using a biphasic reaction. The stream lines are colour coded according to the unit process. (1) Gray lines: xylose dehydration and furfural refinery, (2) green lines: furfural hydrogenation, (3) blue lines: 2-MF condensation, (4) purple lines: furan trimer hydrodeoxygenation, (5) yellow lines: water stream out from process, and (6) red lines: input and output stream except for water stream. The pre-conditioning heaters, pumps, and compressors are omitted, and a detailed process flow diagram can be found in the SI.



unit, but the cost and the resultant carbon emission are considered in the TEA and LCA study, with reference to previous studies [33]. More details of process design are presented in SI.

### 3.1. Process optimization

In tandem with the efficient arrangement of process units, optimizing the operating variables can further improve production profit. In this study, the objective function for optimization is the annualized total biodiesel production cost, which consists of the annualized capital (CAPEX) and operating expenditure (OPEX). The CAPEX is evaluated via

equipment sizing, following Sandler et al. [51], and the equipment installation cost is calculated using the bare module cost, as per the Guthrie method [52]. Detailed information on TEA, including economic parameters and unit sizing, is provided in the SI.

The total cost of biodiesel production is a function of various variables, which can be classified into three groups: (1) operating conditions, including column pressure, reflux ratio, and heat duties in heat exchangers; (2) external process parameters, such as the amount of CPME in the process input stream and furfural conversion; and (3) economic parameters such as CPME and diesel prices. Because only the operating conditions are adjustable by the operators, they are the target

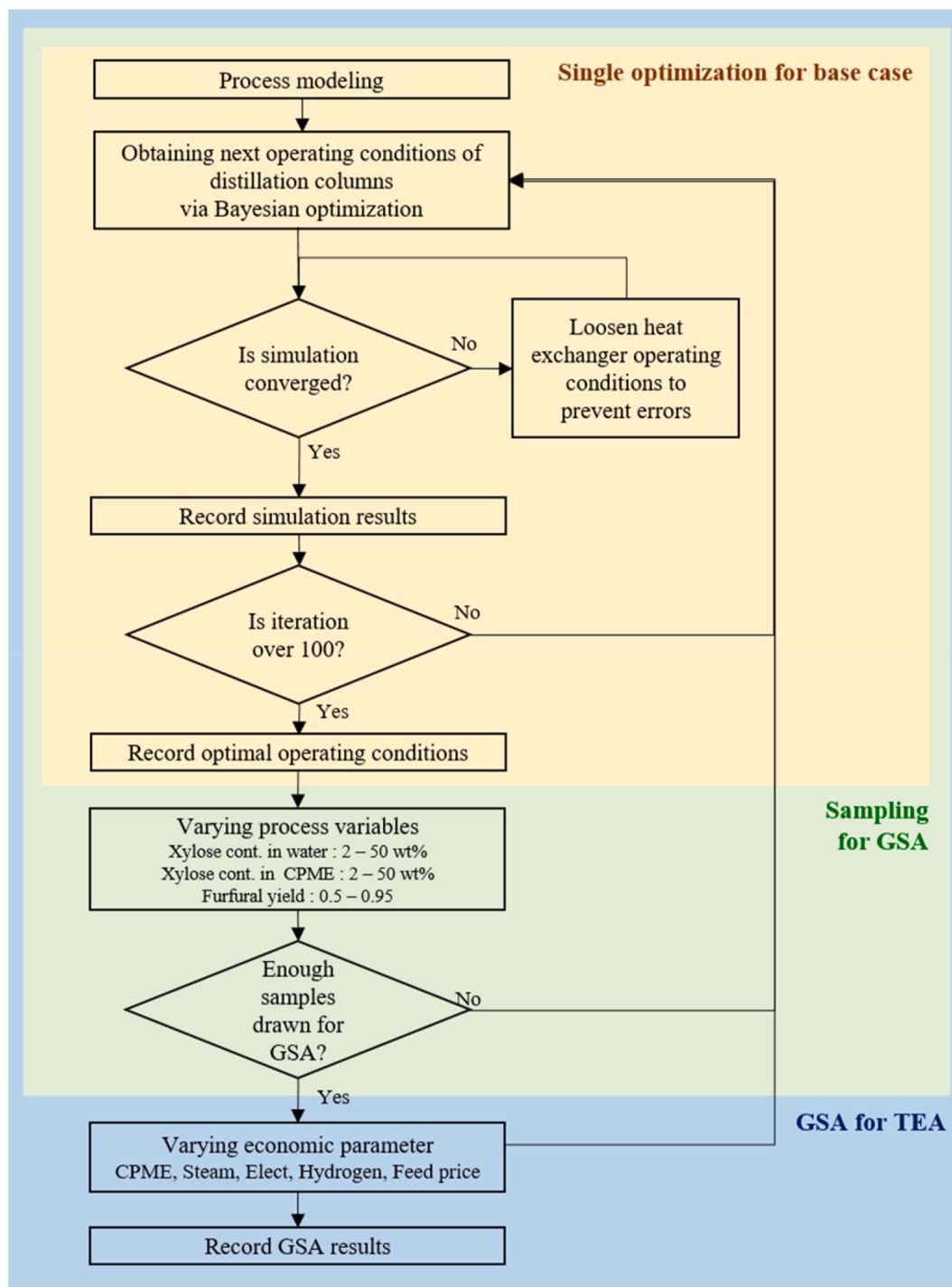


Fig. 3. Overall procedure of process optimization and global sensitivity analysis.

of optimization. Among the various operating conditions that affect the cost, we use the reflux and boilup ratio for each distillation column, and the other conditions are assumed to be appropriately determined based on the column variables. A Bayesian optimization with an acquisition function that exploits expected improvement is used to efficiently find the optimal operating condition [53]. The use of Bayesian optimization facilitates the sensitivity analyses indicated in the following section, and these require repeated optimization of a highly nonlinear process model by rapidly searching through near-optimum operating conditions. Fig. 3 shows the overall optimization procedure. The data required for TEA are collected from the Aspen Plus simulation, and the objective function value is calculated in Matlab 2019b.

The external variables and economic parameters are determined by the developed catalysts and the economic environment, so they are not adjustable during the process. The impact of the nonadjustable variables on the profitability of the proposed biodiesel process was assessed using sensitivity analyses, and the results are given in the results section.

### 3.2. Life cycle assessment on climate change

LCA is an analytical technique used to address various environmental aspects and the potential impacts of a product throughout its life cycle, from raw material extraction to final disposal or recycling. The LCA methodology used in this study follows the ISO 14040 and 14044 series, consisting of four distinct phases: goal and scope definition, inventory analyses, impact assessment, and interpretation [54]. The method of impact assessment and impact category indicator are drawn from IPCC 2013 and climate change CC 100a [55]. This assessment method directly follows IPCC's fifth assessment report (AR5) without including climate carbon feedbacks of non-reference gases that may impose additional uncertainties [56].

The information on the mass and energy balances of the optimized process is retrieved from the Aspen Plus simulation. The background data for upstream and downstream is sourced from Ecoinvent database version 3.71, as listed in Table S10 [57]. The geographical coverage of non-European (RoW) data are selected and global data are selected secondarily when the RoW data are not available [57]. In cases where the technical routes are not specified, averaged data are applied to the LCA to achieve technical representativeness. The functional unit of CCclimate change impact (CC) is defined as 1 MJ of biodiesel in LHV, as in the reference flow of the system presented in Table S9. The system boundary is cradle to gate (CtG), from xylose dehydration to hydrodeoxygenation, excluding biomass pretreatment to extract xylose, as shown in Fig. 1. The pretreatment method of feedstock biomass for the system is not defined because the CC of xylose is greatly dependent on the raw biomass (Table S9) and the specifics of the pretreatment method. Prasad et al. [56] analyzed CO<sub>2</sub> emissions from the four pretreatment methods and showed that the amount of greenhouse gas (GHG) emissions produced can deviate 400 times, from 0.94 to 385 kgCO<sub>2</sub>eq kg<sup>-1</sup> fermentable sugar, depending on the method chosen.

The input-output (IO) information required for LCA, such as raw material, ancillary input, energy/utility, resource, product, waste, and emission can be found in the SI. The CC of the steam produced from the onsite generator is calculated using the process design data acquired from a technical report published by the National Renewable Energy Laboratory (NREL) and partially modified for Case 2 [58].

### 3.3. Sensitivity analysis

To obtain a high furfural conversion, the amount of CPME should be similar to the amount of water. In addition, the price of the organic solution necessary for implementing the two phases of xylose dehydration may strongly affect the economic viability of the biodiesel process. Accordingly, we assess how varying the xylose concentration, the amount of CPME, and the conversion of xylose affect the economics of the proposed process, using a global sensitivity analysis (GSA) based on

the levelized cost of biodiesel. The GSA was repeated for economic parameters (prices of CPME, steam, electricity, hydrogen gas, and xylose feed) to determine how these affect the levelized cost of the biodiesel produced. Fourier amplitude sensitivity testing (FAST) was used to perform variance-based GSA by calculating sensitivity indices [59,60]. Xylose conversion varied from 0.5 to 0.95 to cover the experimental results [18], and the xylose concentration in water and CPME both varied from 4 wt% to 50 wt%. Note that the xylose concentration is defined in this study to indicate the relative amount of xylose to water and CPME in the stream as it enters the xylose dehydration reactor RX1. For instance, the xylose concentration in CPME is calculated by (weight of xylose)/(weight of xylose + weight of CPME)%. Thus, a high concentration of xylose in CPME implies a small amount of CPME in the solution. The ranges of the varying economic parameters are determined in reference to the literature. When data from the literature is not available, the uncertain parameters are set to values from the ones in the base set to the twice values of those. Table 1 summarizes the uncertainties of the parameters, and Fig. 3 presents the schematic flow diagram of the GSA procedure, including the optimization procedure.

## 4. Results and discussion

### 4.1. Base case analysis

Before the sensitivity analyses, base case analyses were performed, setting the parameters as in Table 1. In Case 1, which does not utilize the onsite steam generator, the levelized cost of biodiesel calculated is \$3.66 gal<sup>-1</sup>, and the CC of the base case is estimated to be 57.18 gCO<sub>2</sub>eq MJ<sup>-1</sup>. Taking into account the historic price of diesel, lying in the range \$1.5–5 gal<sup>-1</sup>, economic viability is conditionally achievable, primarily owing to the dominant impact of the cost of xylose feed on the levelized biodiesel cost. Considering the fact that the base case process utilizes pentoses, which is only a part of biomass, the biodiesel production process can become more attractive in terms of profitability if all other parts such as cellulose and lignin residues, are used [34]. Comparing the CC of conventional diesel production (99 gCO<sub>2</sub>eq MJ<sup>-1</sup>) [64], the suggested process can abate carbon emissions, even without the onsite steam generation. Including the analyses of Case 2 and detailed breakdown of the levelized cost, further analyses results are discussed, together with the sensitivity results.

**Table 1**  
Ranges of process and economic parameters.

Parameter	Base set	Lower bound	Upper bound	Reference
<b>Process parameters</b>				
Xylose concentration in water (wt%)	10	4	50	[61]
Xylose concentration in CPME (wt%)	10	4	50	[18]
Furfural yield	0.9	0.5	0.95	This work and [18]
<b>Economic parameters</b>				
Xylose price (\$ kg <sup>-1</sup> )	0.3	0.3	0.6	[5]
CPME price (\$ kg <sup>-1</sup> )	0.05	0.05	5	-
Steam, 450 psig price (\$ kg <sup>-1</sup> )	0.014	0.014	0.028	[62]
Steam, 150 psig price (\$ kg <sup>-1</sup> )	0.0105	0.0105	0.021	
Steam, 50 psig price (\$ kg <sup>-1</sup> )	0.0066	0.0066	0.0132	
Electricity price (\$ kWh <sup>-1</sup> )	0.06	0.06	0.12	
Cooling water price (\$ m <sup>-3</sup> )	0.02	0.02	0.04	
Hydrogen price (\$ kg <sup>-1</sup> )	1.3	1.3	3	[63]
WWT price (\$ MT <sup>-1</sup> )	56	56	112	[36]

#### 4.2. Sensitivity analysis results on varying process parameters

Fig. 4a presents the distribution of the leveled cost of biodiesel production and the sensitivity indices of the parameters for Case 1. The data points are determined by FAST and the economic parameters are fixed at the values for the base set (Table 1) in this section. The decrease in furfural yield most effectively increases the leveled cost by reducing the amount of biodiesel produced. Although the degree of the impact of xylose concentrations on the cost is less than that of the furfural yield, their impact is not negligible, according to the sensitivity indices. The xylose concentration in water and CPME have similar impacts on the leveled cost, as can be seen in Fig. 4a.

The heat exchanger EX1 requires the highest expenditure. This is mainly because EX1 is located at the initial stages of the process, leading to the necessity of a large heat-exchanging area to process the large amount of streams. After the xylose dehydration, the flowrates of the streams became reduced due to separation and recycling, diminishing the sizes of the corresponding units. The wide range of uncertainty in the cost of installing EX1 can be explained in the same way, given that the amount of streams that EX1 has to process largely depends on xylose concentration. The capital costs for the column C1 and C3, which are responsible for recycling CPME and removing water from the produced furfural stream, respectively, take the largest portion of the total CAPEX, except for the heat exchanger EX1. Similar to the reason for the high cost of EX1, the high costs of the columns C1 and C3 are related to the high flowrates of the streams entering into them. This implies that the amount of energy required for separating and recycling water and CPME

at the reboilers of C1 and C3 should be large. This can be checked in Fig. 4c, which shows that the operating costs of the separation columns C1 and C3 are relatively high relative to those of the other units.

In addition to the cost of supplying the hydrogen gas, steam utility costs take up the largest portion of the operating cost, as can be seen in Fig. 4c. Considering that hydrogen gas cannot be reduced further to meet the target amount of biodiesel production (the narrow distribution of purged hydrogen), regardless of the burden of separating the water-furfural-CPME system, the steam utility cost is the main contributor to the leveled cost. The cost for supplying the acid catalyst is small, relative to the cost of supplying steam and the hydrogen feed, but it is distributed across a wide range of the operating cost. This is because the acid catalyst can only be recycled with difficulty, so the make-up cost varies in response to the acidic concentration in the biphasic solution. Adding an acid recovery unit to the currently suggested process would worsen economic viability.

Although the size of the equipment and the number of utilities must be greater to separate the larger amounts of solution, the separation cannot perfectly recycle the CPME solvent, and larger amounts of solution entail larger amounts that must be purged. This is the reason for the distribution of the CPME make-up cost shown in Fig. 4c.

The trends in operating costs are directly reflected in the CC results, as seen in Fig. 4d. Just as in the operating costs, steam accounts for the major portion of the CC. A noticeable difference is seen between the distributions of the operating costs, and the CC gives the reverse of the impact of CPME and other factors. The CC caused by the make-up of the

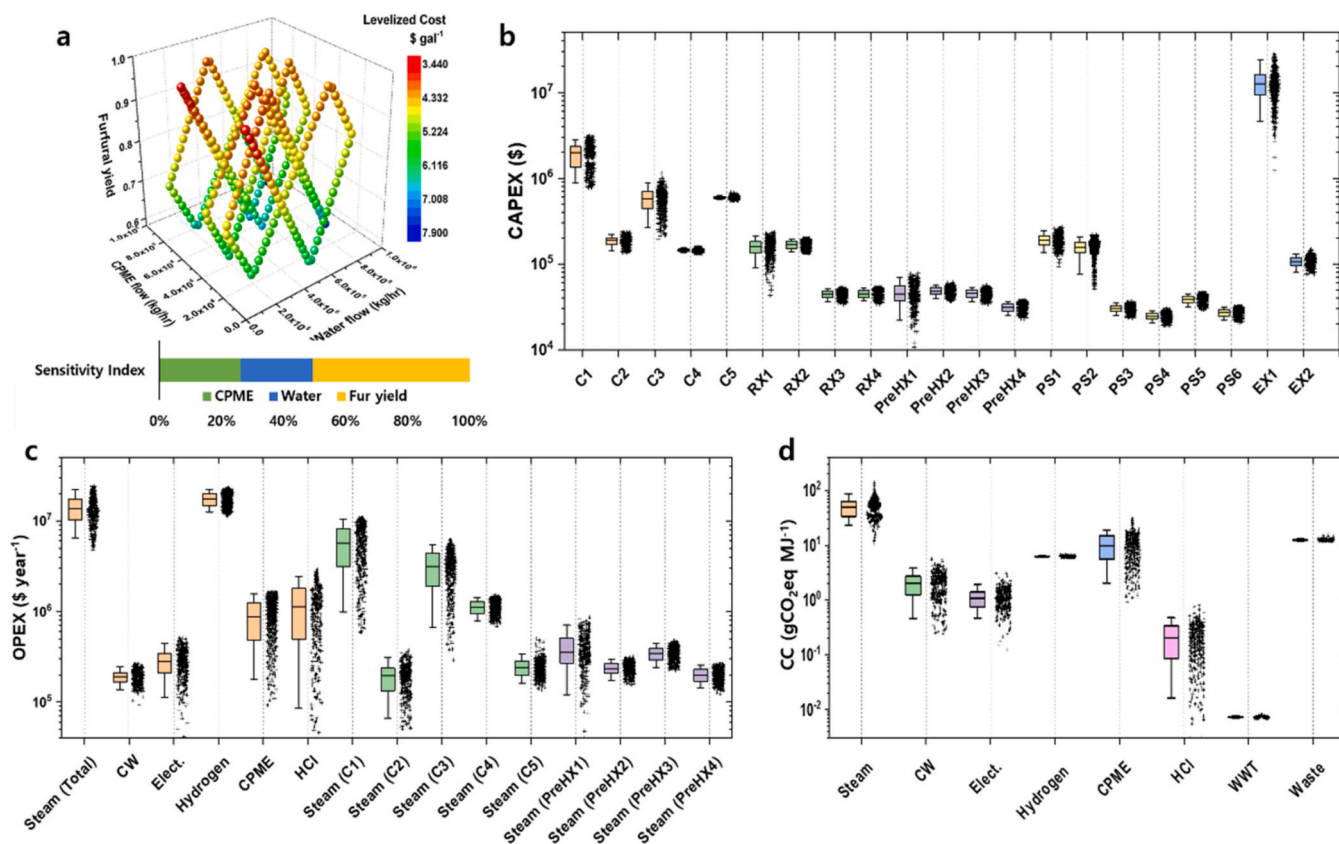


Fig. 4. TEA results for Case 1 with varying process parameters. (a) Distribution of the leveled cost of biodiesel produced by the suggested process, (b) installation cost, and (c) annual utility cost and annual make-up feed cost. (d) CC distribution by carbon emission causes. CW and WWT indicate the cooling water and waste water treatment. Waste in (d) indicates the solid waste disposal system for treating the wastes produced from the reactors. PreHX1, PreHX2, and PreHX3 indicate the pre-conditioning heaters to set the temperature of RX1, RX2, and RX3. Steams (C1)-(C5) indicate the steam costs required for the corresponding units.

CPME is higher than that caused by the hydrogen supply and the acid catalyst make-up. Owing to the high per-unit CC of CPME [65], a small amount of unrecycled CPME causes a large amount of CC.

The use of purchased steam utility and CPME make-up together are the most important in terms of economics and CC, and both are closely related to the separation and recycling of the organic solvent. Detailed information on the production cost of the biodiesel and the corresponding CC is available in the SI.

#### 4.3. Contour analysis

For a comprehensive view of the technoeconomics and CC of biphasic biodiesel production, the simulation results are given with contour graphs, as seen in Fig. 5. Note that Fig. 5 presents the results of the Case 1 simulation with the economic parameters fixed at the base set value (Table 1). The line with square marks indicates where the biphasic solution has the xylose concentration in water and CPME in the ratio of 1.6. The line with circle marks indicates 10 wt% of xylose concentration in water. The xylose concentrations indicate the one of the solution in the stream entering the reactor RX1. Fig. 5a and c shows the contours for the levelized cost of biodiesel when the furfural yields are fixed at 0.95 and 0.75. A reduction in furfural yield increases the levelized cost of biodiesel by \$0.5–1 gal<sup>-1</sup> across the entire xylose concentration. This is due to the reduction in the amount of biodiesel produced. Because the suggested process is designed to recover most of the biodiesel produced regardless of the amount of the solution, the degree of increase in the levelized cost caused by the decrease in furfural yield is weakly relevant to the xylose concentration. Thus, the overall trends in the levelized cost are similar in Fig. 5a and c. A similar explanation can be applied to the CC trends, depending on the xylose concentration. The reduction in

furfural yield leads to a decrease in the total amount of the energy produced by biodiesel. As a result, the CC per 1 MJ of biodiesel increases in Fig. 5d (furfural yield = 0.75) compared to Fig. 5b (furfural yield = 0.95). The total amount of biphasic solution has a decisive impact on both economics and CC, so both the levelized cost and CC increase as the data points on the contour graphs move from the upper right corner to the lower left corner. In Fig. 5a and c, the solid lines with marked with squares indicate where the biphasic solution has a xylose concentration in water and CPME in the ratio of 1.6. According to this line, it can be seen that the impact of the increase in xylose concentration in the CPME concentration loses significance on the right side of the contours. On the left side, changes in the amount of water weakly affect the cost, due to the conflicting effects of increasing amounts of solution. For example, when the concentration point moves from Point 1 to Point 3 (Fig. 5a), the separation efficiency of water and CPME is reduced in phase separator PS1. The corresponding data points are marked in Fig. S11 using the mass fraction triangular diagram to check the changing separation efficiency. However, the amount of CPME should be separated from the solution decreases at the same time, leading to a reduced burden of separating CPME. The same principle can be applied to the left side of the solid line with square marks. This analysis results suggest that the ratio of CPME and water is as important as the amount of the solution in increasing profitability by improving the efficiency of separation processes. More discussions on the unit operating cost and CC are presented in SI.

#### 4.4. Sensitivity analysis results on varying economic parameters

The economic parameters may have different impacts depending on the concentrations of the biphasic solutions. Thus, we performed GSA

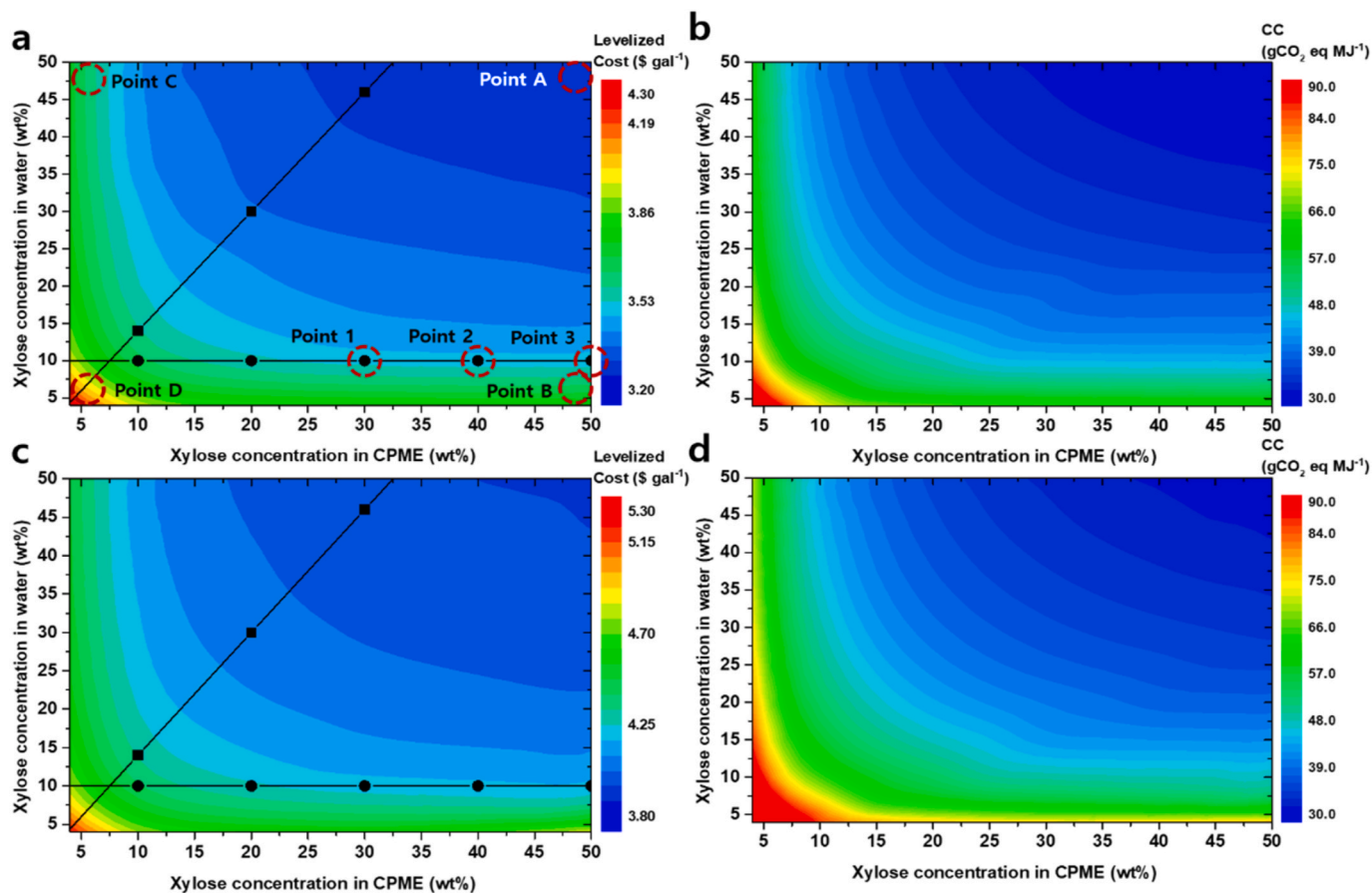


Fig. 5. Global sensitivity analysis results and contour results. (a) Levelized cost with 0.95 furfural yield, (b) CC with 0.95 furfural yield, (c) Levelized cost with 0.75 furfural yield, (d) CC with 0.75 furfural yield.



for the four different concentrations marked in Fig. 5a (the xylose concentration [in CPME, in water]; Point A [50 wt%, 50 wt%], Point B [50 wt%, 5 wt%], Point C [5 wt%, 50 wt%], and Point D [5 wt%, 5 wt%]). The box and whisker plot shows the distribution of the levelized cost, and the vertical bar graph indicates the sensitivity index of each economic parameter in Fig. 6a. When the xylose concentrations are at their highest value at Point A, the energetic burden of separation is minimized, so the corresponding levelized costs are distributed along low values. Due to the small energy required for separation, the cost is affected almost entirely by the price of feed. In particular, the cost of xylose production cost has a dominant impact on the economic viability of biodiesel. In fact, xylose price is the key reason that biodiesel production cost cannot be reduced to less than \$3 gal<sup>-1</sup>. This can be checked again with the results using Point C. At Point C, the amount of the CPME is larger than that of Point A, resulting in a slightly increased economic impact of steam.

At Points B and D, the xylose concentration in water is low, and the increased amount of water raises the cost of water separation. As indicated in Fig. 5, water is closely related to CPME recycling and the economic impacts of CPME make-up are increased at these two points. Because the uncertainty of the price of CPME is large (its upper bound is 100 times larger than the base set value), the economic impact of CPME make-up may be exaggerated in Fig. 6a. Nevertheless, it teaches the valuable lesson; the more expansive CPME is, the more important is the use of concentrated xylose.

#### 4.5. CC contribution analysis by causes

Fig. 6b shows the breakdown of the CC contribution for the biodiesel production process using the biphasic mass fraction equal to Point A through Point D. For all of the mass fraction points, steam accounts for the largest portion of CC. The CPME portions of CC vary from 1% to 22% depending on the feed condition, and the CCs caused by the CPME make-up have high values when water is abundant in the biphasic solution for the same reason that its economic impact is high at these points (Points B and D). Waste disposal, which is mostly from the xylose dehydration reactor, RX1, is a main contributor to CC. The high CC caused by the waste treatment is found because we assumed that waste should be treated as hazardous waste to calculate CC conservatively. Recall that GHG emissions from all sources are considered without assuming the proportion of bio carbon content. The amount of waste disposal here varies in a narrow range because the waste from RX1 is xylose coke, and the xylose feed flowrate is taken as fixed in this study. As the amounts of CC caused by other contributors vary, the contribution ratio of the waste treatment changes accordingly.

## 5. Conclusion

We designed a process and optimized it for biodiesel production using a biphasic reaction to determine the necessary conditions to attain economic viability. The wide range of immiscibility of CPME and water makes CPME an attractive organic solvent for furfural refining because it reduces the energy burden involved in recycling the organic solvent. However, the thermodynamic properties of the CPME-water-furfural system reduce separation efficiency when the amount of water in the system is relatively large, leading to an increase in the cost required for the water-separation system. When the parameters are given as the base set, the levelized cost is calculated as \$3.66 gal<sup>-1</sup>, and the corresponding CC is 57.18 gCO<sub>2</sub>eq MJ<sup>-1</sup>. The production cost and CC can be reduced to \$3.26 gal<sup>-1</sup> and 29.39 gCO<sub>2</sub>eq MJ<sup>-1</sup>, depending on the xylose concentration and the furfural yield, conditionally meeting economic viability even without the onsite steam generation or utilization of cellulose. The xylose price is responsible for more than 80% of the levelized cost and the use of steam for CPME recycling is the most responsible for CC. Care must be taken in interpreting the levelized cost and the CC suggested in this study as the results reflect only the indirect impact of the pre-treatment process such as xylose price and concentration. In order to obtain the actual values of the biodiesel levelized cost and CC, an integrated process converting biomass to biodiesel should be designed and analyzed.

The organic solvent should be immiscible with water over a wide range of water concentrations and should maintain a high yield of furfural in the biphasic reaction, even with little water in the diluted xylose to reduce the energy burden of the water removal. Finding a more suitable solvent may reduce the amount of make-up necessary, but a small amount is unavoidable. This leads to a conclusion that the processes with biphasic reactions are bound to a general type of separation process, which consist of a phase separator and two separation processes for a water-rich phase and a solvent-rich phase to recover furfural. Considering that distillation columns are the most reliable operating units for the industrial level of separation, the proposed design may provide a generic example of the furfural refinery process [19,66]. In addition, the costs of a separation system for furfural isolation dominate the total biodiesel production costs, excepting the feed costs, meaning that the cost reduction for the furfural refinery is vital for designing biodiesel processes. In this context, CPME shows the appropriate properties for serving as an organic solvent for biodiesel production because it lowers the required energy for furfural separation by forming a wide range of immiscible liquid-liquid phase equilibria with water. This thermodynamic property of CPME facilitates high-purity, low-energy CPME recycling, lowering the impact of CPME on the economic

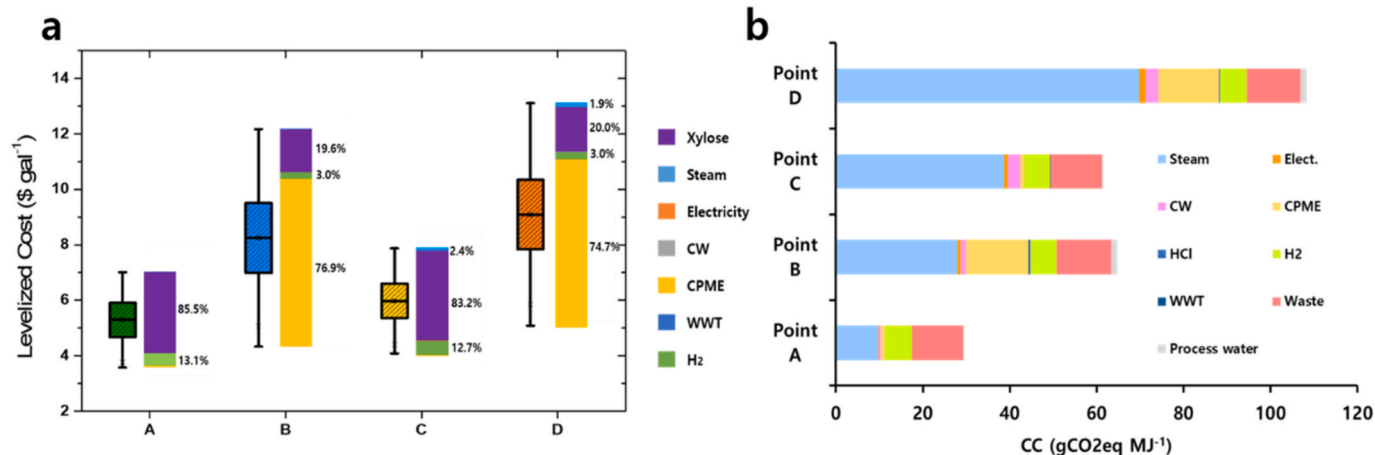


Fig. 6. Economic and CC analysis results. (a) GSA results of economic parameters. (b) CC contribution breakdown. WT, CW, and WWT are indicating waste treatment, cooling water, and waste water treatment.

feasibility of the proposed process. When CPME is mixed with water in a single phase, the separation of CPME requires intensive energy because the boiling points of water and CPME are similar, reflecting their low relative volatility. As a result, the remaining water content in the CPME-rich stream from the outlet of PS1 greatly affects the profitability of the process overall. As this process uses diluted xylose as its source of produce biodiesel, this dependence on water can be critical to the profit. Thus, to ensure the economic viability of the biodiesel production process using biphasic reactions, a solvent with the proper thermodynamic properties (similar to those of CPME and that can be easily separated from water) should be developed. Otherwise, an efficient way of reducing the amount of water obtained from diluted xylose should be developed while maintaining a high furfural yield. In tandem with the amount of the biphasic solution, the sensitivity analyses suggest that the mixing ratio of it has critical impact on the practical potential of the process because they affect both of the separation efficiency and the reaction performances [18]. Thus, care must be taken in adjusting the amount of the organic solvent depending on the xylose concentration in water to increase the profitability of the production process.

### Credit author statement

Kyeongsu Kim: Methodology, Software, Validation, Conceptualization, Writing – original draft, Visualization. Young-Woong Suh: Data curation, Validation. Jeong-Myeong Ha: Resources, Funding acquisition. Jinjoo An: Writing-Reviewing and Editing. Ung Lee: Conceptualization, Writing-Reviewing and Editing.

### 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

Data will be made available on request.

### Acknowledgement

This research was supported by the Technology Development Program to Solve Climate Change of the National Research Foundation (NRF) funded by the Ministry of Science and ICT (NRF-2020M1A2A2079798, NRF-2020M3H7A1098271) and KIST institutional project.

### Appendix B. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rser.2022.113122>.

### Appendix A. Supplementary information

Supplementary information to this article is available.

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