Synthesis of Sustainable Integrated Biorefinery via Reaction Pathway Synthesis: Economic, Incremental Enviromental Burden and Energy Assessment with Multiobjective Optimization

Viknesh Andiappan, Andy S. Y. Ko, Veronica W. S. Lau, Lik Yin Ng, Rex T. L. Ng, Nishanth G. Chemmangattuvalappil, and Denny K. S. Ng
Dept. of Chemical and Environmental Engineering, Centre of Excellence for Green Technologies, The University of Nottingham Malaysia Campus, Broga Road, 43500 Semenyih, Selangor, Malaysia

DOI 10.1002/aic.14616
Published online September 26, 2014 in Wiley Online Library (wileyonlinelibrary.com)

With the increasing attention toward sustainable development, biomass has been identified as one of the most promising sources of renewable energy. To convert biomass into value-added products and energy, an integrated processing facility, known as an integrated biorefinery is needed. To date, various biomass conversion systems such as gasification, pyrolysis, anaerobic digestion and fermentation are well established. Due to a large number of technologies available, systematic synthesis of a sustainable integrated biorefinery which simultaneously considers economic performance, environmental impact, and energy requirement is a challenging task. To address this issue, multiobjective optimization approaches are used in this work to synthesize a sustainable integrated biorefinery. In addition, a novel approach (incremental environmental burden) to assess the environmental impact for an integrated biorefinery is presented. To illustrate the proposed approach, a palm-based biomass case study is solved. © 2014 American Institute of Chemical Engineers *AIChE J*, 61: 132–146, 2015

Keywords: integrated biorefinery, sustainability, multiobjective optimization, reaction pathway, palm-based biomass

Introduction

Fossil fuel is considered as the focal point of industrialization and has cemented itself as a major precursor or feedstock for commodity, bulk and specialty chemicals production. However, due to the vast consumption of fossil fuels, the levels of carbon dioxide and greenhouse gases in the atmosphere have increased over the years.[1] With the attention shifting to idea of sustainable energy production, many researchers have identified biomass as a cure for the addiction toward fossil fuel.[2,3] A renewable resource such as biomass has high potential to meet chemical and energy demands while minimizing environmental impact as well as increasing sustainability.[4] Recent research works have shown that derivatives from biomass feedstock such as biofuels and biochemicals impose much lower carbon footprint as compared to their fossil fuel derived counterparts.[5]

To provide a sustainable supply of biofuels and biochemicals, the design of an integrated biorefinery plays an important role.[3] An integrated biorefinery is established as a processing facility which integrates multiple biomass conversion processes to produce biofuels, biochemicals, and power.[6] Research works have been conducted to further improve the performance of individual biomass conversions with detailed techno-economic studies and optimization. Some of the areas explored in the previous works include heat and power generation,[7] bioalcohol production,[8] and biodiesel production.[9] In addition, more biomass processing technologies such as gasification, pyrolysis, Fischer–Tropsch synthesis and methanol synthesis are getting mature and implemented in the industry. However, as more processing technologies become established, it would be increasingly complex to design an integrated biorefinery. This is due to the increase in the degree of freedom in feedstock and product selection, the processing technologies, energy consumption as well as environmental impact.

In view of the aforementioned issues, the challenge in the synthesis and design of an integrated biorefinery is to assimilate multiple processing technologies as well as identify potential pathways based on various criteria. To address the aforementioned issues, Kokossis and Yang[10] highlighted the pivotal role of systematic approaches to enhance screening capabilities in synthesizing and designing integrated biorefineries. Later, Kokossis and Yang[11] presented the potential of system tools in providing solutions for complex biorefinery design problems. In this respect, several systematic approaches such as P-graph method,[12] C—H—O ternary diagram approach,[13] thermodynamic feasibility approach[14] and automated targeting[15,16] have been proposed.

Conversely, several systematic approaches proposed have considered chemical reaction pathway synthesis method.[17–19]

Correspondence concerning this article should be addressed to D. K. S. Ng at Denny.Ng@nottingham.edu.my; Viknesh Andiappan at vicksama_viknesh89@hotmail.com; Andy S. Y. Ko at andykosy@hotmail.com; Veronica W. S. Lau at veronlws@yahoo.com; Lik Yin Ng at kebx2nli@nottingham.edu.my; Nishanth C. Chemmangattuvalappil at Nishanth.C@nottingham.edu.my.

As shown in previous works, chemical reaction pathway synthesis is recognized as the most important element in screening potential pathways. Conventionally, the chemical process design cannot proceed without determining the reaction pathway based on a comprehensive comparison of available alternatives.[20] However, such a comparison is difficult to be performed in the synthesis of biorefineries as such systems have unique features, making them more difficult to synthesize. This is mainly due to the complexity of the structure and varying composition of biomass feedstock.[21] Therefore, past contributions in the area of chemical reaction pathway synthesis for conventional process design cannot be applied directly in the synthesis of integrated biorefineries. Viewing such limitations, various works have been presented to address this issue. For example, Ng et al.[21] proposed a hierarchical approach (Evolutionary Technique and Forward-Reverse Synthesis Tree) for synthesis and analysis of reaction pathways in an integrated biorefinery. Later, Bao et al.[22] developed a systematic approach based on a superstructure model to determine the potential technology pathways to synthesize an integrated biorefinery. Conversely, Hechinger et al.[23] developed an integrated approach which combined two methodologies known as the Reaction Network Flux Analysis (RNFA) and Computer-Aided Molecular Design to produce biofuels. Voll and Marquardt[24] also adapted the RNFA method to systematically identify and rank large number of alternative reaction pathways for a biorefinery based on limited data. Later, Pham and El-Halwagi[25] introduced a two-stage approach to synthesize and optimize integrated biorefinery configurations. Ponce-Ortega et al.[26] further extended the previous work[25] to include disjunctive programming for optimization of reaction pathways in a biorefinery. Besides, Kelloway and Daoutidis[27] presented a systematic analysis which uses Monte Carlo sampling to explicitly evaluate and compare different reaction pathways in the synthesis of biorefineries. Meanwhile, Murillo-Alvarado et al.[28] also presented a systematic approach to identify optimal reaction pathways of a biorefinery, taking into account of feedstock and product selection. Recently, Gong and You[29] developed a detailed superstructure of algal biorefinery processes for carbon sequestration and utilization. Based on the superstructure, the optimal design algal biorefinery is determined by minimizing the unit carbon sequestration and utilization costs.

As shown in literature, various criteria or objectives (e.g., economic performance, environmental impact, process safety, etc.) have been considered for the synthesis of an integrated biorefinery. For instance, Sammons et al.[30] developed a flexible framework to optimize the gross profit (GP) of different production pathways for a biorefinery. Later, Sammons et al.[31] developed a framework for optimizing product portfolios and process configurations in an integrated biorefinery. This work was then extended further to determine optimal processing routes based on net present value (NPV) with environmental constraints.[32] Zondervan et al.[33] presented an optimization model that optimizes yield, waste, and fixed cost. Viewing that most works are restricted to steady state conditions, Tay et al.[34] and Tang et al.[35] adapted a robust optimization approach to synthesize an integrated biorefinery which considers uncertainties in supply and demand of biomass feedstock. Morales-Rodriguez et al.[36] also considered uncertainties such as uncertainties in market prices and subsidy policies to evaluate the economic feasibility of a lignocellulosic ethanol biorefinery.

However, it is noted that the aforementioned works are limited to a single optimization objective. To synthesize a sustainable integrated biorefinery, multiobjective optimization should be used to trade off different perspectives simultaneously (e.g., economic performance, environment impact, process safety and health, etc.). Tan et al.[37] adapted fuzzy optimization to determine optimal biofuel system configurations based on different environmental impact categories. Later, Tan et al.[38] further extended the fuzzy optimization approach to determine optimal bioenergy system configuration subject to three footprint metrics, which are land use, water and carbon footprints. Tay et al.[39] also adapted the fuzzy optimization approach to determine an optimum integrated biorefinery, considering economic and environmental objectives simultaneously. Meanwhile, Shabbir et al.[40] presented a hybrid optimization approach to synthesize a gasification-based integrated biorefinery with consideration of economic and environment impact. Gebreslassie et al.[41] developed a comprehensive superstructure of an algal biorefinery for biofuel production. In addition, a multiobjective problem was solved using a heuristic algorithm and a Pareto-optimal curve was obtained. The Pareto-optimal curve indicated the trade-off between NPV and global warming potential (GWP).[41] Similarly, Zhang et al.[42] adapted the ε–constraint method for the synthesis of a hydrocarbon biorefinery based on NPV and GWP objectives. Recently, some works have addressed additional objectives such as investment costs,[27,43] carbon efficiency,[27] and process efficiency[43] for an integrated biorefinery. Conversely, several works have considered aspects such as selection of biomass feedstock,[28,44] processing steps,[28] process internal demands,[45] process safety,[46,47] inherent occupational health,[47] and process life cycle.[48,49]

Despite the usefulness of the aforementioned works, several improvements can be introduced. For example, a number of contributions focused on a biorefinery which produces a single product from a single feedstock.[43,45] Meanwhile, some works gave focus only to the selection of thermochemical pathways such as gasification,[40,49] fast pyrolysis,[41,48] and hydrocracking[48,49] for an integrated biorefinery. Since biochemical pathways such as fermentation and hydrolysis are also available for selection, a wide range of biomass feedstock and products can be considered in the synthesis of an integrated biorefinery.

Note that most of the environmental considerations in previous works adapted the life cycle assessment (LCA) methodology to evaluate the environmental burden of a synthesized integrated biorefinery with feedstock such as corn stover,[49] bagasse,[45] hybrid poplar,[48] sugar cane, wood chips, wheat straw, jatropha, and algae.[28,29,44] Based on the LCA methodology, the potential environmental impacts associated with inputs and outputs of every stage in a given life cycle are determined. For each stage, the inputs and outputs are calculated and aggregated over the life cycle. These inputs and outputs are then converted into their effects on the environment and the sum of these environmental impacts represents the overall environmental effect of the life cycle for a given product or pathway. This means that the applied LCA method does not consider the incremental increase or decrease in environmental impact for a given pathway. For instance, if a chemical reactant of high environmental impact is converted into a product of low environmental impact, it is noted that the LCA method is unable to determine the

Table 1. Environmental Burden Calculation for Pathway 10

Reaction	$2C_4H_{10}$	$5CO_2$	$4CH_3COOH$	$2H_2O$
Tonne mole	2.00	5.00	4.00	2.00
Molecular weight	58.00	44.00	60.00	18.00
Mass (Tonne)	116.00	220.00	240.00	36.00
α (Tonne/Tonne Product)	0.48	0.92	1.00	0.15
PF (kg of CO_2 equivalent)	0.00	1.00	0.00	0.00

In the above table, the chemical species CH_3COOH represents the main product while H_2O, C_4H_{10}, and CO_2 represent the side product and reactants, respectively, for Pathway 10.

changes of environmental impact within a reaction pathway. As such, it is vital to develop an assessment approach to which is able to determine the incremental environmental burden within a reaction pathway. With such assessment, pathways that can potentially turn harmful emissions from other industries (e.g., carbon monoxide [CO], CO_2, etc.) into value-added products can be identified to synthesize a more environmentally friendly integrated biorefinery.

Conversely, the multiobjective optimization models in previous works have only considered economic,[39,44] environmental,[48,49] and process safety[46,47] objectives. According to Executive Order 13514 released by Environmental Protection Agency in 2012, it is important of industrial processes to reduce energy intensity. Therefore, energy consumption within the synthesized integrated biorefinery should also be taken into consideration.

To address the aforementioned issues, a systematic multiobjective optimization approach is required to synthesize an integrated biorefinery which considers economic, environmental, and energy performances simultaneously. As mentioned previously, chemical reaction pathway synthesis is identified as the most important element in screening pathways for a biorefinery. Therefore, this work presents a systematic approach that will enable decision makers to evaluate different reaction pathways in biorefinery to maximize economic performance while minimizing environmental impact and energy consumption. The proposed approach also accounts for different types of available biomass feedstock with varying composition of lignin, cellulose, and hemicellulose. Besides, a novel approach referred as Incremental Environmental Burden Assessment (IEBA) is introduced to quantify environmental impact of a given reaction pathway in an integrated biorefinery. This new approach allows computation and identification of reaction pathways that reduce or increase total environmental impact for an integrated biorefinery. Lastly, potential reaction pathways differ in their heat of reaction due to different reaction yields as well as various combinations of reactants. As such, heat of reaction is used to analyze the energy consumption for a given reaction pathway. This method of analysis becomes important especially when the reaction pathways compared do not start from the same biomass feedstock or do not form the same product.

Incremental IEBA

In the synthesis of an integrated biorefinery, it is possible to produce a product via various reaction pathways. Within these reaction pathways, the reactants and products involved would potentially impose an environmental impact. To examine and compare the environmental impact among reaction pathways, environmental impact scores are assigned to each pathway. In cases where the environmental impact may be approximately the same, the incremental environmental impact can vary considerably depending on the pathways chosen. For instance, ethanoic acid can be produced via Monsanto Process by reaction of methanol and CO. The environmental impact score and incremental environmental burden calculated for this pathway is $+1.40$ tonne CO_2 equivalent and -1.40 tonne CO_2 equivalent per tonne of ethanoic acid, respectively. An alternative pathway involving oxidation of butane imposes an environmental impact score of $+0.92$ tonne CO_2 equivalent and incremental impact score of -0.92 tonne CO_2 equivalent per tonne of ethanoic acid. The conversion rates for the aforementioned pathways are 99% and 82%, respectively. From here, it can be said that the pathway with the least environmental impact score would be the oxidation of butane. However, when both pathways are compared on the basis of incremental environmental burden, the Monsanto Process takes precedence due to its higher incremental decrease in environmental impact. Moreover, the higher conversion rate in the Monsanto Process indicates that most of the reactant with high environmental impact (e.g., CO) is consumed to produce a product with low environmental impact. Therefore, it is necessary to identify not only if a given pathway has a low environmental impact but also which would be most desirable in terms of its incremental environmental burden.

IEBA is an approach introduced to assess the incremental environmental burden by quantifying reactants and products associated with each reaction pathway. Analogous to the approach presented by Seider et al.[50] (which estimates the economic potential of a particular reaction via cost factors), IEBA uses environmental potency factors[51] to calculate incremental environmental burden scores for each pathway based on per tonne of product formed. With this approach, pathways that help reduce environmental impact can be identified to synthesize an integrated biorefinery. This becomes important especially when reaction pathways involve converting chemical reactants of high environmental impact into products of low environmental impact. To illustrate the concept of this novel approach, the following equations are used to determine the incremental environmental burden score for a particular pathway j;

Given that

$$\text{Potency Factor (tonne of } CO_2 \text{ equivalent)} = \text{PF}$$

$$\text{Component to Product Ratio} \left(\frac{\text{tonne of Component}}{\text{tonne of Product}}\right) = \alpha$$

The incremental environmental burden score for Pathway j' is calculated using Eq. 1

$$E_{ijk}\left(\frac{\text{tonne of } CO_2 \text{ equivalent}}{\text{tonne of Product}}\right) = \sum \alpha^{\text{Product}} \text{PF}^{\text{Product}} - \sum \alpha^{\text{Reactant}} \text{PF}^{\text{Reactant}} \quad (1)$$

Note that a negative incremental environmental burden score represents a pathway that reduces environmental impact, while a positive value indicates its contribution in the impact on the environment. Note also that the boundary for this approach is within each respective reaction pathway. A quantitative representation of this approach is shown in Table 1.

Problem Statement

With various reaction pathways available, the design of an integrated biorefinery can be a highly complex problem. The synthesis problem addressed is stated as follows: Biomass feedstock $i \in I$ with the flow rate of R_{ij}^{I} and its composition of lignin,

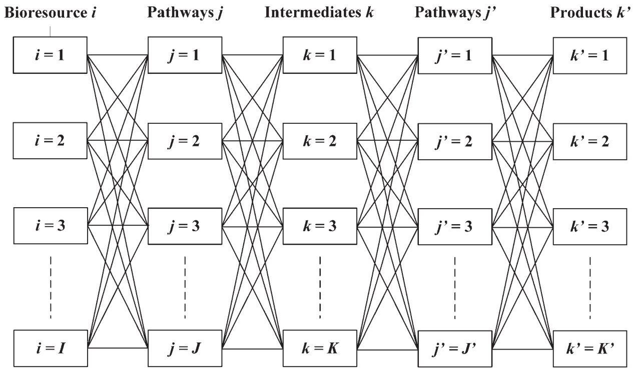

Figure 1. Superstructure for an integrated biorefinery.

cellulose, and hemicellulose (x^{Lignin}, $x^{\mathrm{Cellulose}}$, $x^{\mathrm{Hemicellulose}}$), can be converted to intermediates $k \in K$ through pathways $j \in J$ at a given conversion rate V^{I}_{ijk}. Intermediates k with flow rate $R^{\mathrm{II}}_{kj'}$ can be further converted to products $k' \in K'$ via pathways $j' \in J'$ at a given conversion rate $V^{\mathrm{II}}_{kj'k'}$. The total production rates of intermediates k and products k' are represented by T^{Inter}_{k} and $T^{\mathrm{Prod}}_{k'}$, respectively. In this work, three objective functions (economic, environmental, and energy performance) are taken into consideration in synthesizing an integrated biorefinery. The economic performance is determined by gross profit (GP^{Total}) of an integrated biorefinery. Besides, the environmental impact of an integrated biorefinery is evaluated by the total environmental burden (EB^{Total}). Meanwhile, the energy consumption of the integrated biorefinery is determined using the summation of reaction heat (H^{Total}). The key problem lies within the three objective functions as they are often conflicting in nature. Due to such confliction, it is necessary to develop a systematic approach to synthesize a sustainable integrated biorefinery with maximum economic performance, minimum environmental impact, and energy consumption simultaneously. In this work, bilevel optimization and fuzzy optimization are alternative approaches adapted to optimize the three aforementioned objective functions simultaneously. A detailed description of the developed model is presented in the following sections.

Optimization Model

Figure 1 illustrates a general superstructure of an integrated biorefinery with biomass feedstock B^{Bio}_{i} processed through pathways j to form intermediates k, and by additional conversion to intermediates k' via pathway j'. The flow rates of biomass (R^{I}_{ij}), intermediates ($R^{\mathrm{II}}_{kj'}$), and products ($T^{\mathrm{Prod}}_{k'}$) are also included in the optimization model. Equation 2 below represents the splitting of biomass feedstock to all potential pathways in the j level

$$B^{\mathrm{Bio}}_{i} = \sum_{j} R^{\mathrm{I}}_{ij} \quad \forall i \tag{2}$$

After being processed in pathways j, biomass feedstock B^{Bio}_{i} is converted to intermediate k at a given conversion rate of V^{I}_{ijk} to give a total production rate of T^{Inter}_{k}. The equation for total production of intermediates k is given by

$$T^{\mathrm{Inter}}_{k} = \sum_{j} \sum_{i} \left(R^{\mathrm{I}}_{ij} V^{\mathrm{I}}_{ijk} \right) \quad \forall k \tag{3}$$

Consequently, intermediates k are spread to potential pathways at level j' for further conversion to products k'. The constraints for splitting are given in Eq. 4 while the total production of product k' ($T^{\mathrm{Prod}}_{k'}$) at a given conversion rate $V^{\mathrm{II}}_{kj'k'}$ is given by Eq. 5

$$T^{\mathrm{Inter}}_{k} = \sum_{j'} R^{\mathrm{II}}_{kj'} \quad \forall k \tag{4}$$

$$T^{\mathrm{Prod}}_{k'} = \sum_{j'} \sum_{k} \left(R^{\mathrm{II}}_{kj'} V^{\mathrm{II}}_{kj'k'} \right) \quad \forall k' \tag{5}$$

In this work, the objective is to synthesize an integrated biorefinery with maximum economic performance, minimum environmental burden, and energy consumption. To determine the economic performance, GP is utilized and determined via Eq. 6

$$GP^{\mathrm{Total}} = \sum_{k'} T^{\mathrm{Prod}}_{k'} C^{\mathrm{Prod}}_{k'} - \sum_{i} B^{\mathrm{Bio}}_{i} C^{\mathrm{Bio}}_{i} \tag{6}$$

$C^{\mathrm{Prod}}_{k'}$ is the cost of the end product while C^{Bio}_{i} is the cost of biomass feedstock.

Conversely, the environmental burden is one of the critical parameters to be considered when designing an integrated biorefinery. As shown previously, to determine the environmental burden posed by pathways j and j', standardized incremental environmental burden scores E_{ijk} and $E_{kj'k'}$ are assigned, respectively. With these scores calculated from Eq. 1, the total environmental burden, (EB^{Total}) for an integrated biorefinery can be determined via Eq. 7. Note that a negative EB^{Total} represents an environmentally friendly biorefinery, while a positive value indicates its contribution toward the impact on the environment

$$EB^{\mathrm{Total}} = \sum_{k} \sum_{j} \sum_{i} \left(R^{\mathrm{I}}_{ij} V^{\mathrm{I}}_{ijk} E_{ijk} \right) + \sum_{k'} \sum_{j'} \sum_{k} \left(R^{\mathrm{II}}_{kj'} V^{\mathrm{II}}_{kj'k'} E_{kj'k'} \right) \tag{7}$$

According to literature, there are different assessment methods that can be adapted to measure environmental burden scores such as IEBA and Waste Reduction algorithm. Therefore, Eq. 7 can be modified based on the chosen method of measurement.

Apart from that, it is important for an integrated biorefinery to operate at minimal energy consumption. Since the focus of this work is on the reaction pathways of an integrated biorefinery, the heat of reaction would be taken as the analysis for energy consumption of a given pathway. To determine the total production of reaction heat for pathways j and j', Eq. 8 is included in the model

$$H^{\mathrm{Total}} = \sum_{k} \sum_{j} \sum_{i} \left(R^{\mathrm{I}}_{ij} V^{\mathrm{I}}_{ijk} H_{ijk} \right) + \sum_{k'} \sum_{j'} \sum_{k} \left(R^{\mathrm{II}}_{kj'} V^{\mathrm{II}}_{kj'k'} H_{kj'k'} \right) \tag{8}$$

H_{ijk} and $H_{kj'k'}$ are heats of reaction for pathways j and j', respectively. It is also noted that Eq. 8 can be modified according to chosen measurement of energy consumption for a given pathway.

As mentioned previously, the objective of this work is to synthesize a sustainable integrated biorefinery with maximum economic performance, minimum environmental impact, and energy consumption simultaneously. To achieve this, it is necessary to formulate the reaction pathway synthesis problem as a multiobjective problem. In this respect, this work presents two alternative approaches to address the multiobjective problem which include bilevel optimization and fuzzy optimization.

Bilevel optimization

Bilevel optimization was introduced based on a static Stackelberg game with leader-follower strategy.[52] In a leader-follower scenario, the leader's optimization task is modelled at the upper level, constrained by the follower's optimization task at the lower level.[53] Bilevel optimization problems often appear as leader-follower problems and the basic principle is to have the main optimization problem optimized while recognizing that the second level problems are independently optimised.[54] This means that the second level problem is required to be an optimal solution to solve the main optimisation.[55] The applications of this approach can be found in a number of research areas such as design of reliable process networks,[56] supply chains,[57,58] production planning,[59,60] and water network synthesis.[54]

Bilevel optimization approach is incorporated in this work to synthesize an integrated biorefinery with maximum achievable economic performance while keeping to environmental burden and heat of reaction constraints. For this work, the second optimization problems (followers) would be Eqs. 9 and 10

$$\begin{aligned}\text{maximize } EB^{\text{Total}} &= \sum_{k}\sum_{j}\sum_{i}\left(R^{\text{I}}_{ij}V^{\text{I}}_{ijk}E_{ijk}\right)\\ &+\sum_{k'}\sum_{j'}\sum_{k}\left(R^{\text{II}}_{kj'}V^{\text{II}}_{kj'k'}E_{kj'k'}\right)\end{aligned} \tag{9}$$

$$\begin{aligned}\text{maximize } H^{\text{Total}} &= \sum_{k}\sum_{j}\sum_{i}\left(R^{\text{I}}_{ij}V^{\text{I}}_{ijk}H_{ijk}\right)\\ &+\sum_{k'}\sum_{j'}\sum_{k}\left(R^{\text{II}}_{kj'}V^{\text{II}}_{kj'k'}H_{kj'k'}\right)\end{aligned} \tag{10}$$

The optimal solutions attained would serve as equations for the main optimization problem (leader), which is taken from Eq. 6 and is maximized as shown in Eq. 11

$$\text{maximize } GP^{\text{Total}} = \sum_{k'}T^{\text{Prod}}_{k'}C^{\text{Prod}}_{k'} - \sum_{i}B^{\text{Bio}}_{i}C^{\text{Bio}}_{i} \tag{11}$$

However, incorporating these two equations alone would not aid in solving the main optimization problem in Eq. 11 as it may stretch the optimization to infeasible regions of EB^{Total} and H^{Total} (discussed in the section on Range of Feasibility). Therefore, a weighting factor W is introduced to the secondary optimization problems to help ease the primary optimization problem in Eq. 11. As a result, the formulation is shown in the following

$$\text{maximize } GP^{\text{Total}} = \sum_{k'}T^{\text{Prod}}_{k'}C^{\text{Prod}}_{k'} - \sum_{i}B^{\text{Bio}}_{i}C^{\text{Bio}}_{i}$$

$$\text{subject to } \left\{W^{\text{EB}} \times \text{minimize } EB^{\text{Total}} = \sum_{k}\sum_{j}\sum_{i}\left(R^{\text{I}}_{ij}V^{\text{I}}_{ijk}E_{ijk}\right) + \sum_{k'}\sum_{j'}\sum_{k}\left(R^{\text{II}}_{kj'}V^{\text{II}}_{kj'k'}E_{kj'k'}\right)\right\} \text{ and}$$

$$\left\{W^{\text{H}} \times \text{minimize } H^{\text{Total}} = \sum_{j}\sum_{i}\left(R^{\text{I}}_{ij}V^{\text{I}}_{ijk}H_{ijk}\right) + \sum_{j'}\sum_{k}\left(R^{\text{II}}_{kj'}V^{\text{II}}_{kj'k'}H_{kj'k'}\right)\right\}$$

The weighting factors reflect the preference structure of the designer or decision maker and offer an advantage in terms of simplicity.[61]

Fuzzy optimization

The application of the fuzzy set theory in optimal decision-making was introduced by Bellman and Zadeh.[62] Zimmermann[63] then extended this application by integrating it into mathematical programming containing multiple objectives. In this approach, a trade-off between multiple objectives is made possible by introducing a continuous interdependence variable λ which is known as the degree of satisfaction. Every objective will be satisfied partially at least to λ, hence, integrating the multiple objectives into a single parameter within the model.

The fuzzy optimization approach has been evidently used in the synthesis of integrated biorefineries. For example, Tan et al.[38] employed the fuzzy approach to synthesize an optimal bioenergy supply system in terms of biomass production and environmental footprints. Later, Tay et al.[39] applied this approach to synthesize an integrated biorefinery considering economic and environmental performances for a kraft pulp and paper industry. Kasivisvanathan et al.[64] also adapted the fuzzy approach in retrofitting an integrated biorefinery to an existing palm oil mill which fulfils economic and environmental objectives. Ng et al.[47,65] developed multiobjective optimization models which considered economic, environmental, inherent safety, and inherent health objectives for a palm oil processing complex. The fuzzy optimization approach has also been adapted in other areas such as water network synthesis[54] as well as carbon capture and storage planning.[66]

In this work, fuzzy optimization is adapted by introducing a degree of satisfaction λ for economic performance, environmental burden, and heat of reaction objectives. It is assumed that the specified fuzzy goals in this model possess a linear membership function between upper and lower limits.[39] To satisfy the aforesaid goals simultaneously, the optimization objective is to maximize λ (as shown in Eq. 12) subject to preset upper and lower boundaries as shown in Eqs. 13–15

$$\text{maximize } \lambda \tag{12}$$

whereby

$$\frac{GP^{\text{Total}} - GP^{\text{Total,L}}}{GP^{\text{Total, U}} - GP^{\text{Total,L}}} \geq \lambda \tag{13}$$

$$\frac{EB^{\text{Total,U}} - EB^{\text{Total}}}{EB^{\text{Total,U}} - EB^{\text{Total,L}}} \geq \lambda \tag{14}$$

$$\frac{H^{\text{Total,U}} - H^{\text{Total}}}{H^{\text{Total,U}} - H^{\text{Total,L}}} \geq \lambda \tag{15}$$

Since λ is a continuous variable ranged between 0 to 1 Eq. 16 is also included in the optimization model

Table 2. Lignocellulosic Compositions of EFB[75]

Components	Composition (% of Dry Matter)
Lignin	39.00
Cellulose	22.00
Hemicellulose	29.00

$$0 \leq \lambda \leq 1 \tag{16}$$

Based on the equations above, λ reaches 1 when the synthesized biorefinery achieves a GP^{Total} higher or equal to its upper limit, $GP^{\text{Total, U}}$. In addition, λ reaches 1 when both EB^{Total} and H^{Total} approach minimum values, $EB^{\text{Total, L}}$ and $H^{\text{Total, L}}$, respectively. With λ representing the interaction between the three objectives, the highest λ indicates highest satisfaction of each objective in fuzzy optimization. This means that GP^{Total} will approach its upper limit, while EB^{Total} and H^{Total} would tend to their lower limits by maximizing the degree of satisfaction (λ close to 1). Based on the max–min aggregation rule, the maximum of all objectives will be determined. Note that the targets will most likely signify only partial satisfaction of the goals. Hence, the result corresponds to a compromised solution.[67]

To illustrate the proposed approach, a palm-based biomass case study is solved with constraints from Eqs. 1–10 via bilevel and fuzzy optimization. Following this, the results are then evaluated via sensitivity analysis.

Case Study

To date, Malaysia is responsible for 39% of world palm oil production and 44% of world exports.[68] Being one of the biggest producers and exporters of palm oil and palm oil products, Malaysia in fact can contribute by substantially harnessing a sustainable resource management, in the form of a biorefinery with palm-based biomass as its feedstock.[69] This case study focuses on palm-based biomass feedstock known as empty fruit bunches (EFB), with lignocellulosic composition as shown in Table 2 and feed of 50,000 tonnes per year. For this case study, a simple superstructure is developed (shown in Figure 2) based on the reactions listed in Table 3. The pathways consist of reactions from biochemical and thermochemical platforms. The end products chosen for this work are alcohols, acids, and alkanes as they are common homologous groups produced for various applications such as transportation fuels and edible oils.[70–72] It is noted that the developed superstructure can be revised to incorporate more comprehensive network structures to synthesize an integrated biorefinery. The objective of this case study is to select reaction pathways which maximize economic performance while minimizing environmental burden and heat of reaction.

As mentioned previously, economic, environmental, and energy performances are determined via Eqs. 8, 9, and 10, respectively. The market price of products and biomass feedstock is shown in Table 4. Note that, these prices can be revised according to current market prices for each product to produce an up to date economic analysis. To determine the environmental and energy performance, Table 5 contains environmental and energy performance measures for each pathway. Note also that the measure energy consumption is based on heat of reaction. All pathways release heat (exothermic) or require heat (endothermic) for reaction. The reaction heat for a particular pathway, (H_{ijk}) can be determined by obtaining the difference between the heat of formation of products ($H_{ijk}^{\text{Product},f}$) and reactants ($H_{ijk}^{\text{Reactant},f}$) as shown in Equation 17. It is noted that v_i and v_k are stoichiometric coefficients of each reactant and product respectively. Note also that the Equation 17 determines the raw total of reaction heat for each pathway j. Similarly, Equation 17 can be revised to determine the raw total of reaction heat for each pathway $j'(H_{kjk}{}')$

$$H_{ijk} = v_k H_{ijk}^{\text{Product},f} - v_i H_{ijk}^{\text{Reactant},f} \qquad \forall_i \forall_j \forall_k \tag{17}$$

However, data on the heat of formation for biomass feedstock is not available due to the different compositions of cellulose, hemicellulose, and lignin. Despite this, the heat of formation for a particular biomass feedstock can be

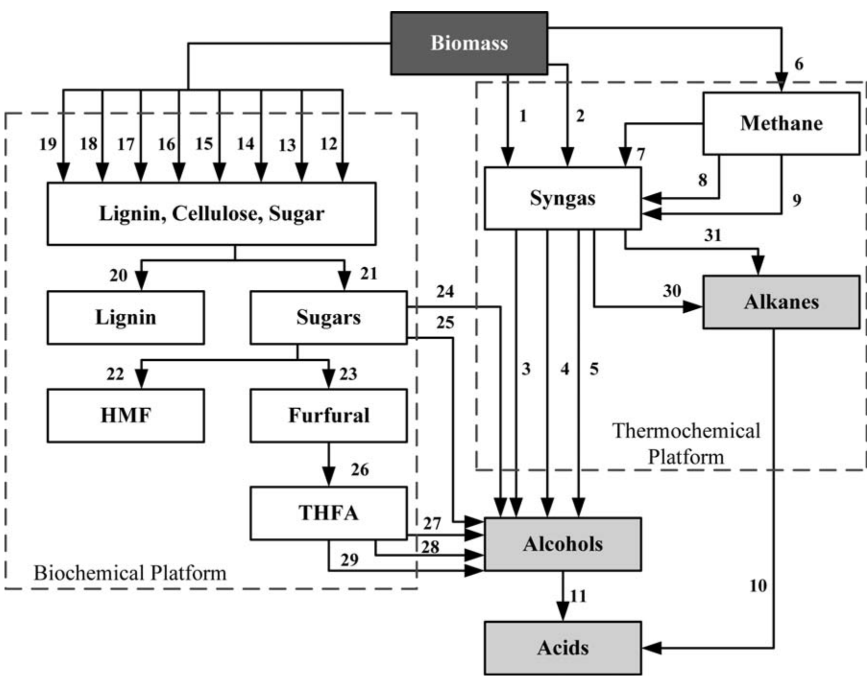

Figure 2. Production of alcohols, acids, and alkanes from lignocellulosic biomass.

Table 3. List of Pathways and Yield

Pathway	Process	Product	Yield or Conversion (%)
1	Pyrolysis	Syngas	94.00
2	Gasification	Syngas	90.00
3	Conversion of Syngas to Alcohols	Methanol, Ethanol	16.10
4	Conversion of Syngas to Alcohols	Methanol, Ethanol	14.80
5	Hydrogenation of CO	Methanol, Ethanol, Propanol, Butanol	19.00
6	Anaerobic Digestion	Methane	40.00
7	Water Gas Shift Reaction	Syngas	100.00
8	Reaction of Methane with CO_2	Syngas	100.00
9	Oxidation of Methane	Syngas	100.00
10	Oxidation of Butane	Methanoic Acid, Ethanoic Acid	82.00
11	Monsanto Process	Ethanoic Acid	99.00
12	Ammonia Explosion	Sugars, Lignin	98.00
13	Alkaline Hydrolysis	Sugars, Lignin	90.00
14	CO_2 Explosion	Sugars, Lignin	75.00
15	SO_2 added Steam Explosion	Sugars, Lignin	95.00
16	Acid Hydrolysis with Suphuric Acid	Sugars, Lignin	10.70
17	Acid Hydrolysis with Toluenesulphonic Acid	Sugars, Lignin	9.20
18	Acid Hydrolysis with Phosphoric Acid	Sugars, Lignin	16.80
19	Steam Explosion	Sugars, Lignin	49.20
20	Organosolv Separation	Lignin	79.00[a]
21	Organosolv Separation	Sugars	97.00[a]
22	Autohydrolysis	HMF	90.90
23	Dehydration of Sugars	Furfural	40.90
24	Yeast Fermentation	Ethanol	61.90
25	Bacterial Fermentation	Ethanol	41.00
26	Hydrogenation of Furfural	THFA	98.20
27	Hydrogenation of THFA	1,2-PeD, 1,5-PeD, PeOH	94.10
28	Hydrogenation of THFA	1,2-PeD, 1,5-PeD, PeOH	39.30
29	Hydrogenation of THFA	1,2-PeD, 1,5-PeD, PeOH	30.60
30	Hydrogenation of CO	Butane	18.00
31	Fischer–Tropsch	Butane	80.00

[a]Separation Efficiency.

estimated using heat of combustion of cellulose, hemicellulose, and lignin, respectively. Based on the heating values given by Wooley and Putsche,[73] the following demonstrates how the heat of formation is calculated for the lignin component of biomass

$$C_{7.3}H_{13.9}O_{1.3} + 10.125O_2 \rightarrow 6.95H_2O + 7.2\ CO_2$$

$$\Delta H_c^0 = 3265.48\ \text{kJ/mol}$$

$$\left(6.95H^{H_2O,f} + 7.3H^{CO_2,f}\right) - \left(10.125H^{O_2,f} + H^{\text{Lignin},f}\right)$$

$$= 3265.48\ \text{kJ/mol}$$

$$H^{\text{Lignin},f} = -8120.87\ \text{kJ/mol}$$

It is noted that the same procedure is repeated for cellulose and hemicellulose components based on their respective heating values. With the heats of formation for each component estimated, the thermodynamic mixing rule shown in Eq. 18 enables the heat of formation for biomass to be determined. As a result, the formulated model can now cater for varying compositions of biomass feedstock

$$\begin{aligned} H^{\text{Bio},f} \;=\; & x^{\text{Lignin}} H^{\text{Lignin},f} + x^{\text{Cellulose}} H^{\text{Cellulose},f} \\ & + x^{\text{Hemi-Cellulose}} H^{\text{Hemi-cellulose},f} \end{aligned} \tag{18}$$

In this case study, the following five scenarios are considered in synthesizing an integrated biorefinery;

1. Design for maximum economic potential
2. Design for minimum environmental burden
3. Design for minimum heat of reaction
4. Design considering the three conflicting objectives via bilevel optimization
5. Design considering the three conflicting objectives via fuzzy optimization

The first three scenarios are shown to determine the upper and lower limits of each objective function. Using these limits, the last two scenarios are performed to trade off the three conflicting objective functions. In this case study, a linear programming model is formulated for all five scenarios. All scenarios are solved using the commercial optimization software LINGO version 13, in Dell Vostro 3400 with Intel Core i5 (2.40GHz) and 4GB DDR3 RAM in an average time of 0.1 s of Central Processing Unit (CPU) time.

Table 4. Price of Products and Raw Material

Final Product	Revenue from Final Product (U.S.$) per tonne
Methanol	450.00
Ethanol	1200.00
Butanol	2094.40
Pentanol	2700.00
Pentanediol	9700.00
Methanoic acid	800.00
Ethanoic acid	620.00
Methane	160.00
Ethane	423.50
Butane	2340.00
Raw material	Cost of Raw Material (U.S.$) per tonne
Biomass (EFB)	170.00

Table 5. Summary of Environmental Burden Scores and Heat of Reactions

Pathway	Emissions (Tonne of CO_2 Equivalent/Tonne of Product)	Heat of Reaction (MJ/Tonne of Product)
1	64.00	calculated based on biomass composition
2	232.00	calculated based on biomass composition
3	−24.07	−5847.28
4	−24.07	−8418.47
5	−25.57	−5566.52
6	21.00	calculated based on biomass composition
7	−42.00	103095.00
8	−53.00	123675.00
9	−79.50	−17765.00
10	−0.92	−3318.17
11	−1.40	−2866.17
12	2.56	calculated based on biomass composition
13	0.00	calculated based on biomass composition
14	11.00	calculated based on biomass composition
15	0.00	calculated based on biomass composition
16	0.24	calculated based on biomass composition
17	0.00	calculated based on biomass composition
18	0.00	calculated based on biomass composition
19	0.00	calculated based on biomass composition
20	0.00	calculated based on biomass composition
21	0.00	calculated based on biomass composition
22	0.00	−3505.43
23	0.00	11438.38
24	0.00	225.65
25	0.00	225.65
26	1.96	−2183.23
27	0.00	−1500.74
28	0.00	−1500.74
29	0.00	254.01
30	−25.57	−4414.83
31	15.75	−3555.00

Scenario 1: Design for maximum economic potential

In this scenario, an integrated biorefinery was synthesized by solving the presented optimization model constraints (Eqs. 1–10) using the optimization objective in Eq. 19 and parameters listed in Tables 2–5. The model formulated in this scenario consists of 72 continuous variables and 83 constraints.

$$\text{maximize } GP^{\text{Total}} \tag{19}$$

Based on results obtained, the maximum GP^{Total} is found to be U.S. \$92.42 million (per annum). This indicates the pathways that spawn the highest profit. Besides that, the total environmental burden, EB^{Total} and total heat of reaction H^{Total} were found to be $+1.09$ million tonne of CO_2 equivalent (per annum) and -1.22×10^{10} MJ (per annum), respectively. The pathways selected in this scenario are from the biochemical platform. These pathways are Pathway 12 (Biomass Pretreatment), 20 and 21 simultaneously (Organosolv Separation), 23 (Dehydration of Sugars), 26 (Furfural Hydrogenation), and 27 (Hydrogenation of Tetrahydrofurfuryl Alcohol (THFA)). Figure 3 illustrates the synthesized configuration and it can be seen that products such as pentanediol and pentanol were produced.

Scenario 2: Design for minimum environmental burden

In this scenario, the pathway with the minimum environmental burden is determined. Identical constraints in Scenario 1 are used for this optimization, to solve Eq. 20

$$\text{minimize } EB^{\text{Total}} \tag{20}$$

The optimization result obtained for minimum EB^{Total} is -4.46 million tonne of CO_2 equivalent/y while the corresponding GP^{Total} and H^{Total} is determined as U.S. \$-4.13 million/y and -2.94×10^{10} MJ/y, respectively. This deficit proves that additional expenditure is required to produce a highly environmental process. The pathways selected consist of thermochemical pathways, which are Pathway 6 (Anaerobic Digestion), 9 (Oxidation of Methane), 5 (Hydrogenation of CO), and 11 (Monsanto Process). Figure 4 shows the synthesized biorefinery configuration for the targeted result achieved in this scenario and it is noted that ethanoic acid is the product produced.

Scenario 3: Design for minimum heat of reaction

For this scenario, the pathway with the minimum heat of reaction is determined (Eq. 21). Identical constraints in Scenarios 1 and 2 are used for this optimization

$$\text{minimize } H^{\text{Total}} \tag{21}$$

The optimization result obtained for minimum H^{Total} is -4.61×10^{11} MJ/y while the corresponding GP^{Total} and EB^{Total} is determined as U.S. \$10.29 million/y and $+12.60$ million tonne of CO_2 equivalent/y, respectively. The reactions pathways selected here are Pathway 1 (Pyrolysis), 31 (Fischer–Tropsch), and 10 (Oxidation of Butane), which represent the thermochemical platform. Figure 5 shows the

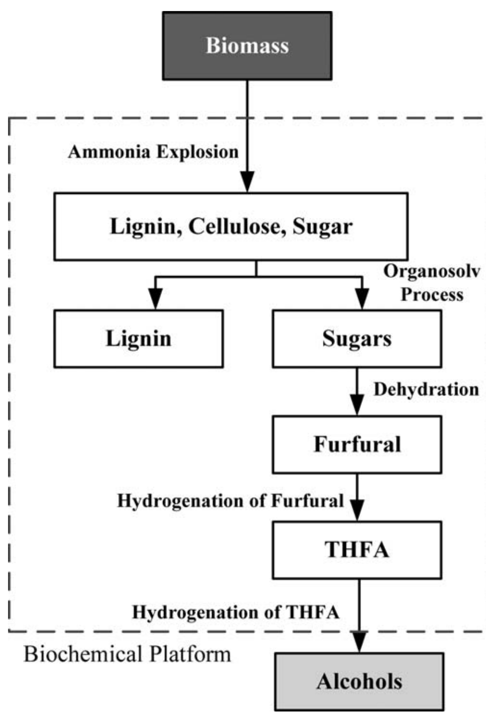

Figure 3. General flow diagram of synthesized integrated biorefinery (Scenario 1).

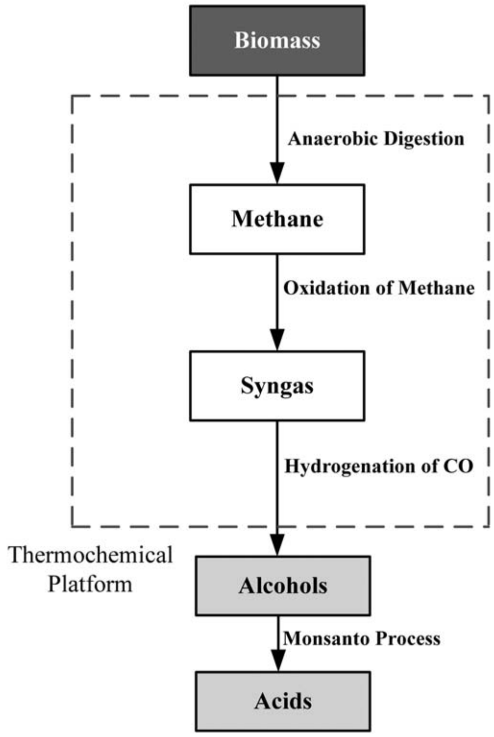

Figure 4. General flow diagram of synthesized integrated biorefinery (Scenario 2).

synthesized biorefinery configuration for the targeted result achieved in this scenario which yields ethanoic acid and methanoic acid.

Scenario 4: Design considering the three conflicting objectives via bilevel optimization

Ideally, the lower bound (most negative) values $EB^{\mathrm{Total,L}}$ and $H^{\mathrm{Total,L}}$ are desired on maximizing GP^{Total}. However, this is not possible as results from Scenarios 1–3 indicate that the objectives considered are clearly contradictory to each other. Due to such confliction, bilevel optimization is implemented in this scenario to trade off these objectives by introducing weighting factors for $EB^{\mathrm{Total,L}}$ and $H^{\mathrm{Total,L}}$, respectively. In other words, fractions of the aforementioned lower bounds are targeted in the optimization. With that, optimal solutions are required to use Eqs. 9, 10, and 11. The minimum $EB^{\mathrm{Total,L}}$ (-4.46 million tonne of CO_2 equivalent/y) found from Scenario 2 and the minimum $H^{\mathrm{Total,L}}$ (-4.61×10^{11} MJ/y) from Scenario 3 are taken as the optimal solutions for the secondary optimization problems. For illustration of the bilevel optimization, a value of 20% is taken for both W^{EB} and W^{H} weighting factors as shown in Eqs. 23 and 24. It is also noted that values of W^{EB} and W^{H} are determined based on the priority given by the decision maker

$$\text{maximize } GP^{\mathrm{Total}} \tag{22}$$

$$EB^{\mathrm{Total}} \leq 0.2 \times EB^{\mathrm{Total,L}} \tag{23}$$

$$H^{\mathrm{Total}} \leq 0.2 \times H^{\mathrm{Total,L}} \tag{24}$$

Parameters in Tables 2–5 are reused to solve constraints found in Eqs. 1 to 10 and the objective function in Eq. 22. The model formulated in this scenario consists of 72 continuous variables and 85 constraints. The optimization produced an GP^{Total} of U.S. \$19.11 million/y, EB^{Total} of -0.89 million tonne of CO_2 equivalent/y and H^{Total} of -9.22×10^{10} MJ/y. Figure 6 indicates optimal pathways which maximize economic performance while satisfying the targeted EB^{Total} and H^{Total}. The biochemical pathways selected in this scenario are Pathway 15 (Biomass Pretreatment), 20 and 21 simultaneously (Organosolv Separation), 23 (Dehydration of Sugars), 26 (Furfural Hydrogenation), and 27 (Hydrogenation of THFA). The thermochemical pathways selected are Pathway 1 (Pyrolysis), 6 (Anaerobic Digestion), 9 (Oxidation of Methane), 5 (Hydrogenation of CO), and 11 (Monsanto Process). The products formed for this case would be ethanol, methanol, butanol, pentanol, pentanediol, and ethanoic acid.

Scenario 5: Design considering the three conflicting objectives via fuzzy optimization

Similar to Scenario 4, upper and lower limits required for fuzzy optimization are taken from Scenarios 1–3 and are summarized in Table 6. The model formulated for this scenario consists of 73 continuous variables and 86 constraints. It is noted that economic performance is a predominant element in decision making. As such, a stricter acceptable fuzzy range between the maximum $GP^{\mathrm{Total,U}}$ and an acceptable minimum $GP^{\mathrm{Total,L}}$ is specified. In this scenario, the minimum acceptable $GP^{\mathrm{Total,L}}$ is assumed as 0. Note also that the range of acceptance for the fuzzy goals is dependent on the decision maker and is subject to change on a case by case basis. Equation 12 is maximized subject to constraints in Eqs. 1 to 10 and 13 to 16. The optimization yields a maximum λ of value 0.22 whereby, GP^{Total} is U.S. \$20.33 million/y, EB^{Total} of -0.13 million tonne of CO_2 equivalent/y and H^{Total} of -1.11×10^{11} MJ/y. Figure 7 shows the optimal pathways complying with the degree of satisfaction achieved between the three

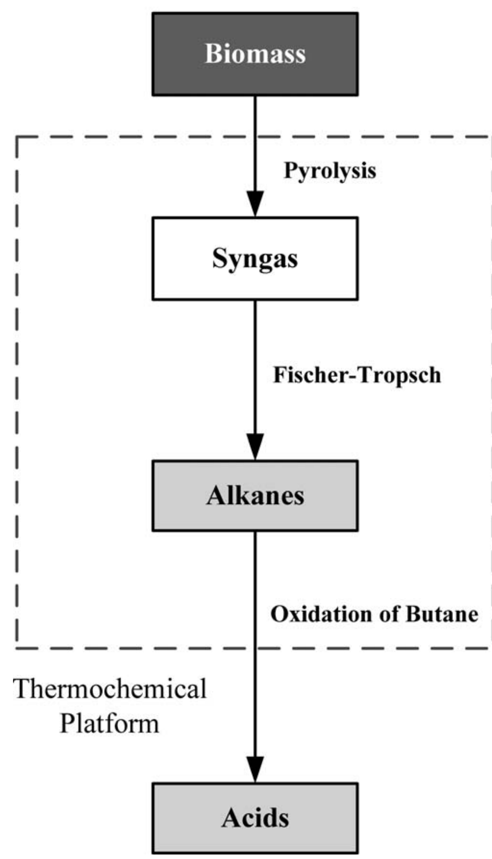

Figure 5. General flow diagram of synthesized integrated biorefinery (Scenario 3).

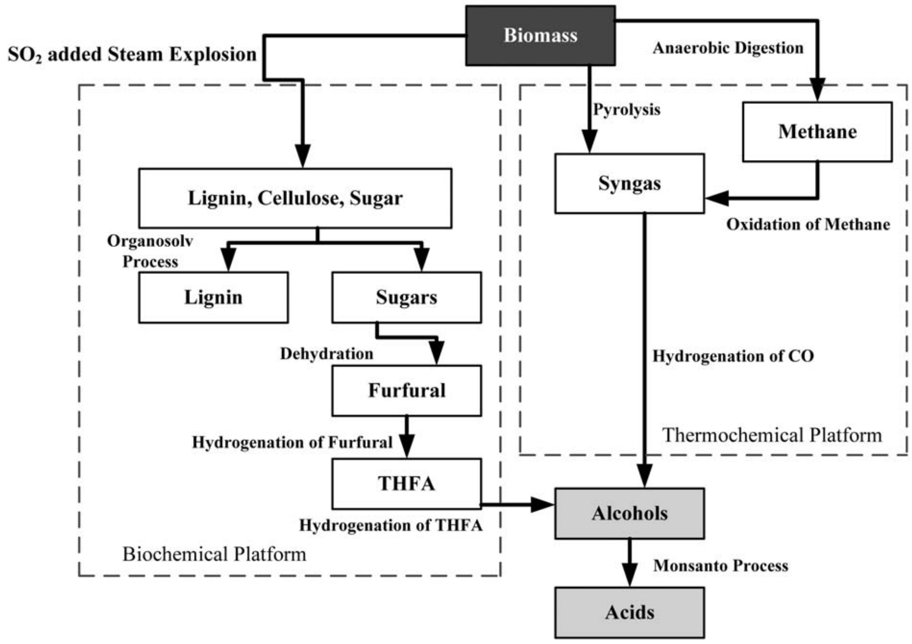

Figure 6. General flow diagram of synthesized integrated biorefinery (Scenario 4).

objectives. The products formed for this case would be the same as the previous scenario, only with different flow rates.

Results Analysis

Table 7 shows a summary of results obtained from Scenarios 1–5. It is found that despite producing high profit and low heat of reaction, Scenario 1 has a positive EB^{Total} value. This indicates that the chosen pathway for this case is clearly not environmental friendly. In Scenario 2, the chosen pathway offers the lowest environmental burden, producing both alcohols and acids. However, a deficit was observed in the economic potential which proves that additional expenditure is required to produce a highly environmental process. In Scenario 3, the pathway selected offers the lowest heat of reaction, producing alkanes and acids. Similar to Scenario 1, the chosen pathways are not environmental friendly despite its promising economic potential. As for Scenario 4 and 5, the EB^{Total} and H^{Total} were found to have negative values while GP^{Total} was found to be positive. This indicates the integrated biorefinery pathways are sustainable as they reduce environmental burden, operate at low heat of reaction, and generate substantial amount of profits by producing alcohols as well as acids. It can be seen in Figures 6 and 7 that the pathways chosen are from both biochemical as well as thermochemical platforms. Pathways which represent the biochemical route are selected to maximize GP^{Total} since alcohols are generally listed in Table 3 as most profitable products in terms of selling price. To minimize EB^{Total} and H^{Total}, the thermochemical pathways were selected due to their environmental friendly process and capability of producing high reaction heat. Despite the similarities between the two scenarios, Scenario 5 yields a higher profit compared to Scenario 4 due to the higher production rates. This, however, leads to more emissions to form more products.

The solutions from Scenarios 4 and 5 are further analyzed in a Pareto analysis, to ensure the generated results are located on Pareto Optimality. Incremental values for each of the three objective functions are introduced while minimizing or maximizing the other to generate the Pareto Front as shown in Figure 8. Each point in the figure represents the economic, environmental and energy performances for each configuration selected. Point 1 corresponds to Scenario 1, where only economic potential is considered. Scenarios 2 (environmental burden only) and 3 (heat of reaction only) are represented by Points 2 and 3, respectively. It is noted that solutions for both Scenarios 4 and 5 (given by Points 4 and 5) are found to be within the optimality region, representing a trade-off between all individually considered cases from Scenarios 1 to 3. Since bilevel and fuzzy optimization can generate solutions that match results in the Pareto analysis methodology, both approaches can serve as alternatives to address the multiobjective reaction pathway synthesis problem. In addition, it is noted that these approaches are more efficient as compared to a Pareto analysis. This is because in Pareto analysis, indefinite number of (Pareto) solution points needs to be generated to determine the optimal solution.

Conversely, it is noted that the weighting factors W^{EB} and W^{H} assigned in bilevel optimization have high influence on the optimal solution. It is also noted that the range of values in which W^{EB} and W^{H} can be assigned is restricted by a feasibility region. In this respect, a sensitivity analysis is presented to establish the level of influence W^{EB} and W^{H} values have on the optimal solution. In addition, the range of feasibility is investigated to determine the operable range in which W^{EB} and W^{H} values can be taken when implementing the bilevel optimization.

Table 6. Fuzzy Goals for Economic, Environmental and Energy Performance

Fuzzy Target	Limiting Values	
	Lower	Upper
GP^{Total}	$GP^{\text{Total,L}} = 0.00$	$GP^{\text{Total,U}} = 92.42 \times 10^6$
EB^{Total}	$EB^{\text{Total,L}} = -4.46 \times 10^6$	$EB^{\text{Total,U}} = +1.09 \times 10^6$
H^{Total}	$H^{\text{Total,L}} = -4.61 \times 10^{11}$	$H^{\text{Total,U}} = -1.22 \times 10^{10}$

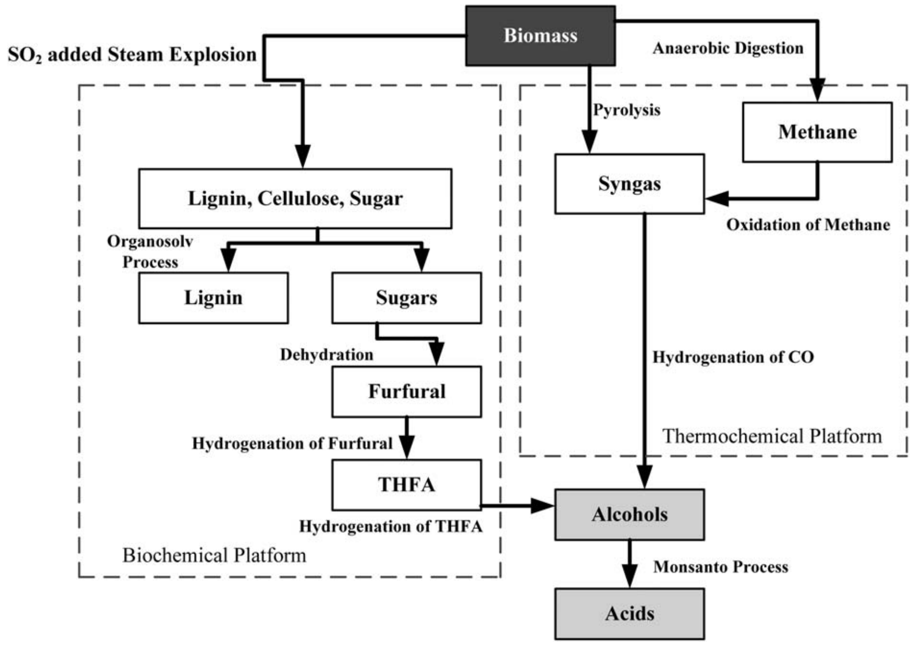

Figure 7. General flow diagram of synthesized integrated biorefinery with degree of satisfaction, λ of 0.22 (Scenario 5).

Sensitivity analysis

According to El-Halwagi,[74] dual prices represent sensitivity coefficients for the optimization. Consider an objective function

$$\text{maximize } f(x)$$

such that

$$h_l(x)=b_l \qquad l=1,\ 2,\ 3, \ldots,\ n$$

As b_l varies, the optimal solution also changes. It can be shown that at the optimum solution and for a small perturbation of Δb_l in the right hand side of the constraint $h_l(x)$ is given by

$$\frac{\Delta f}{\Delta b_l} \approx \text{Dual Price of Constraint } l$$

The marginal value of the objective function for a change in the value of the lth constraint is given by the dual price of the lth constraint. Table 8 shows the dual prices of W^{EB} and W^{H} in Scenario 4, respectively. Based on Table 8, for an objective value of U.S \$ 19.11 million/y, the dual prices for W^{EB} and W^{H} are -0.81×10^8 and -0.30×10^9, respectively. If the constraint W^{EB} is increased by 0.01 ($W^{EB}=0.21$), a change of $(0.01 \times -0.81 \times 10^8)$ would be expected in the objective value. Therefore, results illustrated in Table 9 confirm this hypothesis as the newly obtained objective value is now U.S \$ 18.30 million/y. This further strengthens the claim that W^{EB} and W^{H} values have high level of influence on the objective value, and caution should be taken when assigning them.

Range of feasibility

As mentioned previously, the secondary optimization problems in Eqs. 9 and 10 in bilevel optimization are restricted within a feasibility range. When W^{H} is fixed at 0.1, the range feasibility is shown in Table 10. Based on Table 10, the allowable increase or decrease shows how much to which current values (given by "Current Value") can be increased or decreased. Therefore, the range in which EB^{Total} and H^{Total} are feasible is given in the following

$$-3.84\times 10^6 \leq EB^{Total} \leq 0.94\times 10^6 \tag{25}$$

$$-1.25\times 10^{11} \leq H^{Total} \leq -1.56\times 10^{10} \tag{26}$$

The ranges shown above can then serve to analyze the range in which W^{EB} and W^{H} can be taken at.

When W^{H} was taken at 0.2, Table 11 shows allowable range to which the current values can be increased or decreased. Based on Table 11, the range in which EB^{Total} and H^{Total} are feasible is given by Eqs. 27 and 28

$$-2.13\times 10^6 \leq EB^{Total} \leq 2.12\times 10^6 \tag{27}$$

Table 7. Optimal Results for Case Study

Model Output	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5
GP^{Total} (U.S \$/y)	92.42×10^6	-4.13×10^6	10.29×10^6	19.11×10^6	20.33×10^6
EB^{Total} (tonnes of CO_2 equivalent/y)	$+1.09 \times 10^6$	-4.46×10^6	$+12.60 \times 10^6$	-0.89×10^6	-0.13×10^6
H^{Total} (MJ/y)	-1.22×10^{10}	-2.94×10^{10}	-4.61×10^{11}	-9.22×10^{10}	-1.11×10^{11}
Alkane production rate (t/y)	0.00	0.00	37600.00	0.00	0.00
Alcohol production rate (t/y)	10939.00	3800.00	0.00	6221.00	6519.00
Acid production rate (t/y)	0.00	3762.00	3083.00	3652.00	3838.00

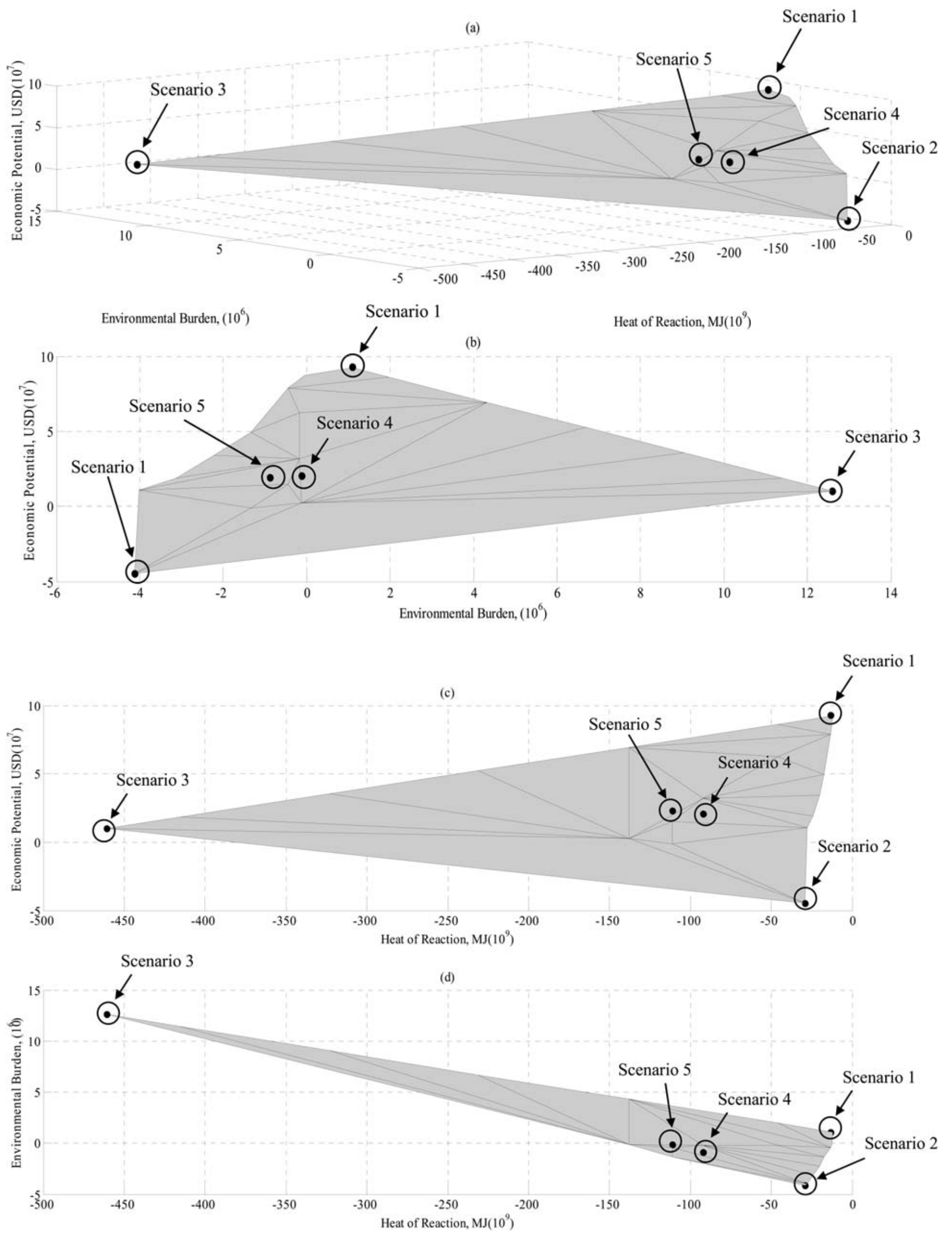

Figure 8. (a) Three-dimensional view of Pareto Front; (b) 2-D view of Pareto Front (GP^{Total} vs. EB^{Total}); (c) 2-D view of Pareto Front (GP^{Total} vs. H^{Total}); (d) 2-D view of Pareto Front (EB^{Total} vs. H^{Total}).

$$-1.25\times10^{11} \le H^{\mathrm{Total}} \le -1.56\times10^{10} \tag{28}$$

Note that when W^{H} was taken at 0.3 the corresponding H^{Total} was observed to have exceeded the lower limit given by Eqs. 26 and 28 hence, resulting in an infeasible solution. Thus, 0.3 is the infeasibility point for W^{H} for which any weighting factors taken greater than 0.2 would give an infeasible result. The same can be said for when W^{EB} is taken at 0.9, as the corresponding EB^{Total} exceeds the lower limit given in Eq. 27. A graphical representation is also provided in Figure 9 to illustrate the feasible regions for the weighting factors to be best taken at. According to Figure 9, region R1 includes W^{EB} values from 0 to 0.8 when W^{H} is fixed at 0.1. As for region R2, it includes W^{EB} values from 0 to 0.4 with W^{H} going up to 0.2. Due to the common values for W^{EB} when W^{H} is 0.1 and 0.2, the upper limit is set at 0.4. Therefore, based on the sensitivity study conducted the bilevel problem is reformulated as the following

Table 8. Dual Prices of W^{EB} and W^{H} in Scenario 4, Respectively

Weighting Factor	Dual Price
W^{EB}	-0.81×10^8
W^{H}	-0.30×10^9

Table 9. Results when $W^{\mathrm{EB}} = 0.21$

Variable	Value
GP^{Total} (U.S $/y)	18.30×10^6
EB^{Total} (tonnes of CO_2 Equivalent/y)	-93.65×10^6
H^{Total} (MJ/y)	-9.22×10^{10}
W^{EB}	-0.81×10^8
W^{H}	-0.30×10^9

Table 10. Feasibility Output when $W^{H} = 0.1$

Variable	Current Value	Allowable Increase	Allowable Decrease
EB^{Total} (tonnes of CO_2 equivalent/y)	-0.89×10^{6}	1.83×10^{6}	2.95×10^{6}
H^{Total} (MJ/y)	-4.61×10^{10}	3.04×10^{10}	7.94×10^{10}

Table 11. Feasibility Output when $W^{H} = 0.2$

Variable	Current Value	Allowable Increase	Allowable Decrease
EB^{Total} (tonnes of CO_2 equivalent/y)	-0.89×10^{6}	3.01×10^{6}	1.24×10^{6}
H^{Total} (MJ/y)	-9.22×10^{10}	7.66×10^{10}	3.33×10^{10}

$$\text{maximize } GP^{\text{Total}} = \sum_{k'} T_{k'}^{\text{Prod}} C_{k'}^{\text{Prod}} - \sum_{i} B_i^{\text{Bio}} C_i^{\text{Bio}}$$

$$\text{subject to} \left\{ W^{\text{EB}} \times \text{minimize } EB^{\text{Total}} = \sum_k \sum_j \sum_i (R_{ij}^{\text{I}} V_{ijk}^{\text{I}} E_{ijk}) + \sum_{k'} \sum_{j'} \sum_k (R_{kj'}^{\text{II}} V_{kj'k'}^{\text{II}} E_{kj'k'}) \right\} \text{ and}$$

$$\left\{ W^{\text{H}} \times \text{minimize } H^{\text{Total}} = \sum_j \sum_i (R_{ij}^{\text{I}} V_{ijk}^{\text{I}} H_{ijk}) + \sum_{j'} \sum_k (R_{kj'}^{\text{II}} V_{kj'k'}^{\text{II}} H_{kj'k'}) \right\}$$

$$\text{whereby } 0 \leq W^{\text{H}} \leq 0.2$$

$$\text{and } 0 \leq W^{\text{EB}} \leq 0.4$$

Though values of W are restricted as shown above, it is still possible to assign values that exceed the given range only if one of the criterions is not given priority at all. This means that the minimum values of either EB^{Total} or H^{Total} is not considered when applying the bilevel optimization demonstrated in Scenario 4. If decisions makers are only focused on achieving maximizing economic potential while keeping minimal environmental burden, Scenario 3 would not be conducted. If the aim is to maximize profits while minimizing heat of reaction, then Scenario 2 is neglected. Moreover, if decision makers decide to neither reduce or increase the environmental burden, W^{EB} can be set to zero and the optimization can result in an economic potential of U.S. $ 87.96 million/y and heat of reaction of -1.22×10^{10} MJ/y.

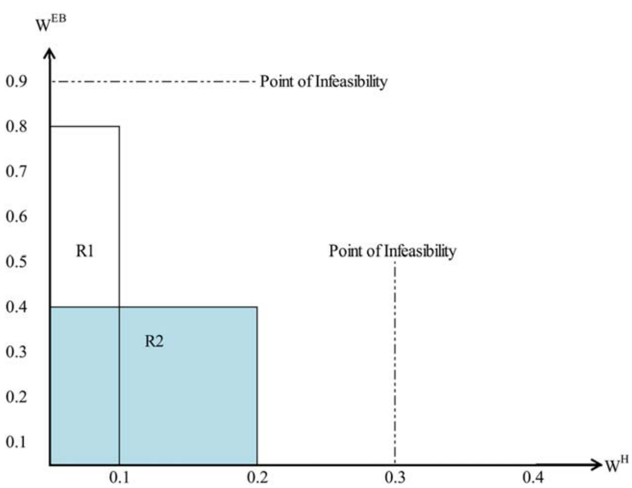

Figure 9. Graphical representation of operable region for weighting factors.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Conclusions

In this work, a systematic multiobjective optimization approach for the synthesis of a sustainable integrated biorefinery is presented. With the proposed approach, decision makers are able to evaluate different reaction pathways based on economic performance, environmental impact and energy consumption simultaneously. Moreover, decision makers are able to consider different types of biomass feedstock based on their compositions of lignin, cellulose, and hemicellulose. Besides that, this work introduced a new assessment known as IEBA, to quantify environmental impact of a given reaction pathway in an integrated biorefinery. IEBA allows computation and identification of reaction pathways that reduce or increase total environmental impact for an integrated biorefinery. This will allow decision makers to identify pathways which can potentially turn harmful emissions (from other industries) into value-added products to synthesize a more environmentally friendly integrated biorefinery. Conversely, the proposed approach determines the energy consumption of each reaction pathway based on the raw total heat of reaction. Apart from that, a sensitivity analysis was performed to evaluate the influence of the weighting factors in the bilevel optimization. It was also found that the secondary problems in the bilevel optimization are restricted within a feasibility range and the weighting factors which correspond to this range were established. In future research work, a systematic approach on establishing appropriate weighting factors corresponding to this range will be included prior to the bilevel optimization to synthesize an integrated biorefinery. Future work will also be directed toward extending the analysis of total raw reaction heat by considering various uses (e.g., generating power, process heating, drying, cooling, etc.) based on their respective qualities (e.g., pressure, temperature, etc.).

Acknowledgments

This work was supported by the Ministry of Science, Technology and Innovation (MOSTI) Malaysia under the Grant No. 06-02-12-SF0224. The Faculty of Engineering at the University of Nottingham Malaysia Campus is also acknowledged for its support toward this project.

Nomenclature

Sets

i = index for biomass feedstock
j = index for pathways
j' = index for pathways
k = index for intermediates
k' = index for final products
l = index for constraints

Variables

$f(x)$ = function of
$h_l(x)$ = equality constraint function of x
b_l = constraint

v_i = stoichiometric coefficient of reactant i
v_k = stoichiometric coefficient of product k
B_i^{Bio} = flow rate of biomass feedstock i in t/y
R_{ij}^{I} = flow rate of bioresource i to pathway j in t/y
$R_{kj'}^{\mathrm{II}}$ = flow rate of intermediate k to pathway j' in t/y
T_k^{Inter} = total production rate of intermediate k in t/y
$T_{k'}^{\mathrm{Prod}}$ = total production rate of product k' in t/y
GP^{Total} = total gross profit in U.S \$/y
EB^{Total} = total environmental burden score in tonne CO_2 equivalent/y
H^{Total} = total heat of reaction in MJ/y
V_{ijk}^{I} = conversion of bioresource i to intermediate k
$V_{kj'k'}^{\mathrm{II}}$ = conversion of intermediate k to product k'
E_{ijk} = environmental burden score for pathway j in kg CO_2 equivalent/t
$E_{kj'k'}$ = environmental burden score for pathway j' in kg CO_2 equivalent/t
$H^{\mathrm{Bio},f}$ = heat of formation of biomass feedstock i in MJ/t
$H^{\mathrm{Lignin},f}$ = heat of formation of lignin in MJ/t
$H^{\mathrm{Cellulose},f}$ = heat of formation of cellulose in MJ/t
$H^{\mathrm{Hemicellulose},f}$ = heat of formation of hemicellulose in MJ/t
H_{ijk} = heat of reaction for pathway j in MJ/t
$H_{kj'k'}$ = heat of reaction for pathway j' in MJ/t

Parameters

C_i^{Bio} = cost of biomass feedstock i in U.S \$/t
$C_{k'}^{\mathrm{Prod}}$ = revenue from product k' in U.S \$/t
W^{EB} = weighting factor for environmental burden
W^{H} = weighting factor for heat of reaction
PF = potency factor
α = component to product ratio

Literature Cited

1. Murphy T. Declining Fossil Fuel Supplies and the Energy Trap. 2011. Available at: http://oilprice.com/Energy/Energy-General/Declining-Fossil-Fuel-Supplies-and-the-Energy-Trap.html.
2. Greenwise. Biofuels 101: Biofuels from Generation to Generation. 2011. Available at: http://livinggreenandsavingenergy.com/biofuels-101-biofuels-from-generation-to-generation.html, accessed on November 19, 2012.
3. Naik SN, Goud VV, Rout PK, Dalai AK. Production of first and second generation biofuels: a comprehensive review. *Renewable Sustainable Energy Rev*. 2010;14(2):578–597.
4. Bridgwater AV. Renewable fuels and chemicals by thermal processing of biomass. *Chem Eng J*. 2003;91(2–3):87–102.
5. Hill J, Nelson E, Tilman D, Polasky S, Tiffany D. Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels. *Proc Natl Acad Sci USA*. 2006;103:11206–11210.
6. Fernando S, Adhikari S, Chandrapal C, Murali N. Biorefineries: current status, challenges, and future direction. *Energy Fuels*. 2006; 20(4):1727–1737.
7. Mohan T, El-Halwagi MM. An algebraic targeting approach for effective utilization of biomass in combined heat and power systems through process integration. *Clean Technol Environ Policy*. 2006; 9(1):13–25.
8. Gnansounou E, Dauriat A. Techno-economic analysis of lignocellulosic ethanol: a review. *Bioresour Technol*. 2010;101(13):4980–4991.
9. Pokoo-Aikins G, Nadim A, El-Halwagi MM, Mahalec V. Design and analysis of biodiesel production from algae grown through carbon sequestration. *Clean Technol Environ Policy*. 2010;12(3):239–254.
10. Kokossis AC, Yang A. A future system challenges in design of renewable bio-energy system and the synthesis of sustainable biorefineries. In: *Proceeding of Seventh International Conference on Foundations of Computer-Aided Process Design*, Colorado, 2009:107–123.
11. Kokossis AC, Yang A. On the use of systems technologies and a systematic approach for the synthesis and the design of future biorefineries. *Comput Chem Eng*. 2010;34(9):1397–1405.
12. Halasz L, Povoden G, Narodoslawsky M. Sustainable processes synthesis for renewable resources. *Resour Conserv Recycling*. 2005; 44(3):293–307.
13. Tay DHS, Kheireddine H, Ng DKS, El-Halwagi MM. Synthesis of an integrated biorefinery via the C–H–O ternary diagram. *Clean Technol Environ Policy*. 2011;13(4):567–579.
14. Tay DHS, Kheireddine H, Ng DKS, El-Halwagi MM, Tan RR. Conceptual synthesis of gasification-based biorefineries using thermodynamic equilibrium optimization models. *Ind Eng Chem Res*. 2011; 50(18):10681–10695.
15. Ng DKS. Automated targeting for the synthesis of an integrated biorefinery. *Chem Eng J*. 2010;162(1):67–74.
16. Tay DHS, Ng DKS. Multiple-cascade automated targeting for synthesis of a gasification-based integrated biorefinery. *J Cleaner Prod*. 2012;34:38–48.
17. Crabtree E, El-Halwagi MM. Synthesis of environmentally acceptable reactions. In: AIChE Symposium, *Volume on Pollution Prevention via Process and Product Modifications*, New York, United States of America, 1994:117–127.
18. Li M, Hu S, Li Y, Shen J. A hierarchical optimization method for reaction path synthesis. *Ind Eng Chem Res*. 2000;39(11):4315–4319.
19. Hu S, Li M, Li Y, Shen J, Liu Z. Reaction path synthesis methodology for waste minimization. *Sci China Ser B Chem*. 2004;47(3):206–213.
20. Douglas JM. *Conceptual Design of Chemical Processes*. New York: McGraw-Hill, ed, 1988. Available at: http://www.scribd.com/doc/134740085/Conceptual-Design-of-Chemical-Processes-by-James-M-Douglas, accessed on May 22, 2014.
21. Ng D, Pham V, El-Halwagi M, Jiménez-Gutiérrez A, Spriggs HD. A hierarchical approach to the synthesis and analysis of integrated biorefineries. In: *Proceeding of Seventh International Conference on Foundations of Computer-Aided Process Design*. Colorado: CRC Press, 2009:425–432. Available at: http://dx.doi.org/10.1201/9781439809136-c38.
22. Bao B, Tay DHS, El-Halwagi MM, Ng DKS, Jiménez-Gutiérrez A. A shortcut method for the preliminary synthesis of process-technology pathways: an optimization approach and application for the conceptual design of integrated biorefineries. *Comput Chem Eng*. 2011;35(8):1374–1383.
23. Hechinger M, Voll A, Marquardt W. Towards an integrated design of biofuels and their production pathways. *Comput Chem Eng* 2010; 34(12):1909–1918.
24. Voll A, Marquardt W. Reaction network flux analysis: optimization-based evaluation of reaction pathways for biorenewables processing. *AIChE J*. 2012;58(6):1788–1801.
25. Pham V, El-halwagi M. Process synthesis and optimization of biorefinery configurations. *AIChE J*. 2012;58(4):1212–1221.
26. Ponce-Ortega JM, Pham V, El-Halwagi MM, El-Baz AA. A disjunctive programming formulation for the optimal design of biorefinery configurations. *Ind Eng Chem Res*. 2012;51(8):3381–3400.
27. Kelloway A, Daoutidis P. Process synthesis of biorefineries: optimization of biomass conversion to fuels and chemicals. *Ind Eng Chem Res*. 2014;53(13):5261–5273.
28. Murillo-Alvarado PE, Ponce-Ortega JM, Serna-González M, Castro-Montoya AJ, El-Halwagi MM. Optimization of pathways for biorefineries involving the selection of feedstocks, products, and processing steps. *Ind Eng Chem Res* 2013;52(14):5177–5190.
29. Gong J, You F. Optimal design and synthesis of algal biorefinery processes for biological carbon sequestration and utilization with zero direct greenhouse gas emissions: MINLP model and global optimization algorithm. *Ind Eng Chem Res*. 2014;53(4):1563–1579.
30. Sammons N, Eden M, Yuan W, Cullinan H, Aksoy B. A flexible framework for optimal biorefinery product allocation. *Environ Prog*. 2007;26(4):349–354.
31. Sammons NE, Yuan W, Eden MR, Aksoy B, Cullinan HT. Optimal biorefinery product allocation by combining process and economic modeling. *Chem Eng Res Des*. 2008;86(7):800–808.
32. Sammons N, Yuan W, Bommareddy S, Eden M, Aksoy B, Cullinan H. A systematic approach to determine economic potential and environmental impact of biorefineries. In: Jeżowski J, Thullie J, editors. *Computer Aided Chemical Engineering*, Vol 26. Elsevier, Amsterdam, Netherlands, 2009:1135–1140.
33. Zondervan E, Nawaz M, de Haan AB, Woodley JM, Gani R. Optimal design of a multi-product biorefinery system. *Comput Chem Eng*. 2011;35(9):1752–1766.
34. Tay DHS, Ng DKS, Tan RR. Robust optimization approach for synthesis of integrated biorefineries with supply and demand uncertainties. *Environ Prog Sustainable Energy*. 2013;32(2):384–389.
35. Tang MC, Chin MWS, Lim KM, Mun YS, Ng RTL, Tay DHS, Ng DKS. Systematic approach for conceptual design of an integrated

biorefinery with uncertainties. *Clean Technol. Environ. Policy*. 2013; 15(5):783–799.
36. Morales-Rodriguez R, Meyer AS, Gernaey KV, Sin G. A framework for model-based optimization of bioprocesses under uncertainty: lignocellulosic ethanol production case. *Comput Chem Eng*. 2012;42:115–129.
37. Tan RR, Culaba AB, Aviso KB. A fuzzy linear programming extension of the general matrix-based life cycle model. *J Cleaner Prod*. 2008;16(13):1358–1367.
38. Tan RR, Ballacillo J-AB, Aviso KB, Culaba AB. A fuzzy multiple-objective approach to the optimization of bioenergy system footprints. *Chem Eng Res Des*. 2009;87(9):1162–1170.
39. Tay DHS, Ng DKS, Sammons NE, Eden MR. Fuzzy optimization approach for the synthesis of a sustainable integrated biorefinery. *Ind Eng Chem Res*. 2011;50(3):1652–1665.
40. Shabbir Z, Tay DHS, Ng DKS. A hybrid optimisation model for the synthesis of sustainable gasification-based integrated biorefinery. *Chem Eng Res Des*. 2012;90(10):1568–1581.
41. Gebreslassie BH, Waymire R, You F. Sustainable design and synthesis of algae-based biorefinery for simultaneous hydrocarbon biofuel production and carbon sequestration. *Am Inst Chem Eng*. 2013;59(5): 1599–1621.
42. Zhang Q, Gong J, Skwarczek M, Yue D, You F. Sustainable process design and synthesis of hydrocarbon biorefinery through fast pyrolysis and hydroprocessing. *Am Inst Chem Eng*. 2014;60(3):980–994.
43. Peduzzi E, Tock L, Boissonnet G, Maréchal F. Thermo-economic evaluation and optimization of the thermo-chemical conversion of biomass into methanol. *Energy*. 2013;58:9–16.
44. Santibañez-Aguilar JE, González-Campos JB, Ponce-Ortega JM, Serna-González M, El-Halwagi MM. Optimal planning of a biomass conversion system considering economic and environmental aspects. *Ind Eng Chem Res*. 2011;50(14):8558–8570.
45. Furlan FF, Costa CBB, de Castro Fonseca G, de Pelegrini Soares R, Secchi AR, da Cruz AJG, de Campos Giordano R. Assessing the production of first and second generation bioethanol from sugarcane through the integration of global optimization and process detailed modeling. *Comput. Chem. Eng*. 2012;43:1–9.
46. El-Halwagi AM, Rosas C, Ponce-Ortega JM, Jiménez-Gutiérrez A, Mannan MS, El-Halwagi MM. Multiobjective optimization of biorefineries with economic and safety objectives. *AIChE J*. 2013;59(7): 2427–2434.
47. Ng RTL, Hassim MH, Ng DKS. Process synthesis and optimization of a sustainable integrated biorefinery via fuzzy optimization. *AIChE J*. 2013;59(11):4212–4227.
48. Gebreslassie BH, Slivinsky M, Wang B, You F. Life cycle optimization for sustainable design and operations of hydrocarbon biorefinery via fast pyrolysis, hydrotreating and hydrocracking. *Comput Chem Eng*. 2013;50:71–91.
49. Wang B, Gebreslassie BH, You F. Sustainable design and synthesis of hydrocarbon biorefinery via gasification pathway: integrated life cycle assessment and technoeconomic analysis with multiobjective superstructure optimization. *Comput Chem Eng*. 2013;52:55–76.
50. Seider WD, Seader J, Lewin DR. *Product and Process Design Principles: Synthesis, Analysis, and Evaluation*, 2nd ed. New York: Wiley, 2004.
51. Institute of Chemical Engineers (IChemE). The Sustainibility Metrics. 2010. Available at: https://www.icheme.org/communities/special-interest-groups/sustainability/~/media/Documents/SubjectGroups/Sustainability/Newsletters/SustainabilityMetrics.ashx.
52. Stackelberg HV. *The Theory of the Market Economy*. London: Oxford University Press, 1952.
53. Sinha A, Malo P, Frantsev A, Deb K. Finding optimal strategies in a multi-period multi-leader–follower Stackelberg game using an evolutionary algorithm. *Comput Oper Res*. 2014;41:374–385.
54. Aviso KB, Tan RR, Culaba AB, Cruz JB Jr. Bi-level fuzzy optimization approach for water exchange in eco-industrial parks. *Process Saf Environ Prot*. 2010;88(1):31–40.
55. Calvete HI, Galé C. The bilevel linear/linear fractional programming problem. *Eur J Oper Res*. 1999;114(1):188–197.
56. Takama N, Umeda T. Multi-level, multi-objective optimization in process engineering. *Chem Eng Sci*. 1981;36(1):129–136.
57. Ryu J. A multi-level programming optimization approach to enterprise-wide supply chain planning. In: Puigjaner L, Espuña A, editors. *European Symposium on Computer-Aided Process Engineering-15, 38th European Symposium of the Working Party on Computer Aided Process Engineering*, Vol. 20. Elsevier, Amsterdam, Netherlands, 2005:571–576. Available at: http://www.sciencedirect.com/science/article/pii/S1570794605802172.
58. Roghanian E, Sadjadi SJ, Aryanezhad MB. A probabilistic bi-level linear multi-objective programming problem to supply chain planning. *Appl Math Comput*. 2007;188(1):786–800.
59. Chu Y, You F. Integrated scheduling and dynamic optimization by stackelberg game: bilevel model formulation and efficient solution algorithm. *Ind Eng Chem Res*. 2014;53:5564–5581.
60. Cao D, Chen M. Capacitated plant selection in a decentralized manufacturing environment: a bilevel optimization approach. *Eur J Oper Res*. 2006;169(1):97–110.
61. Goel T, Stander N. Multi-Objective Optimization Using LS-OPT. 2007.
62. Bellman RE, Zadeh LA. Decision-making in a fuzzy environment. *Manage Sci*. 1970;17(4):141–164. Available at: http://pubsonline.informs.org/doi/abs/10.1287/mnsc.17.4.B141.
63. Zimmermann H-J. Fuzzy programming and linear programming with several objective functions. *Fuzzy Sets Syst*. 1978;1(1):45–55.
64. Kasivisvanathan H, Ng RTL, Tay DHS, Ng DKS. Fuzzy optimisation for retrofitting a palm oil mill into a sustainable palm oil-based integrated biorefinery. *Chem Eng J*. 2012;200–202:694–709.
65. Ng RTL, Ng DKS. Systematic approach for synthesis of integrated palm oil processing complex. Part 1: single owner. *Ind Eng Chem Res*. 2013;52(30):10206–10220.
66. Tan RR, Ng DKS, Foo DCY, Aviso KB. Crisp and fuzzy integer programming models for optimal carbon sequestration retrofit in the power sector. *Chem Eng Res Des*. 2010;88(12):1580–1588.
67. Ubando AT, Culaba AB, Aviso KB, Tan RR. Simultaneous carbon footprint allocation and design of trigeneration plants using fuzzy fractional programming. *Clean Technol Environ Policy*. 2013;15(5): 823–832.
68. Malaysian Palm Oil Council. Malaysian Palm Oil Industry. 2012. Available at: http://www.mpoc.org.my/Malaysian_Palm_Oil_Industry.aspx, accessed on April 1, 2013.
69. Chew TL, Bhatia S. Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery. *Bioresour Technol*. 2008;99(17):7911–7922.
70. Biofuels. Biofuels: What are they? 2010. Available at: http://biofuel.org.uk/, accessed on July 10, 2013.
71. Nexant I. PERP Program - Green Acetyls. 2010. Available at: http://www.chemsystems.com/about/cs/news/items/PERP 0809S7_Green Acetyls.cfm, accessed on July 10, 2013.
72. Oilgae. Biogasoline - Definition, Glossary, Details - Oilgae. 2013. Available at: http://www.oilgae.com/ref/glos/biogasoline.html, accessed July 10, 2013.
73. Wooley RJ, Putsche V. Development of an ASPEN PLUS physical property database for biofuels components. *Victoria*. 1996;1–38.
74. El-Halwagi MM. *Sustainable Design Thorugh Process Integration*. Oxford: Elsevier, 2012.
75. Sukiran MA. Pyrolysis of Empty Oil Palm Fruit Bunches Using the Quartz Fluidised-Fixed Reactor. 2008.

Manuscript received June 10, 2014, and revision received Aug. 26, 2014.