

# Multi-objective optimization methodology for process synthesis and intensification: Gasification-based biomass conversion into transportation fuels

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## ABSTRACT

The transport sector increasing energy demand has encouraged the search for alternative technologies for bio-fuels production with lower manufacturing costs and higher process efficiency and environmental performance. Lignocellulosic biofuels are equivalents to petroleum products and can be adapted to meet the properties requirements of current engines. However, their major disadvantages are the high production costs and the lack of infrastructure. In this work, the focus is on the implementation of a multi-objective optimization methodology for synthesis of novel intensified biomass-to-liquid (BtL) technologies with lower environmental impact and costs, as well as higher process safety and efficiency. A novel optimization methodology is applied to two process configurations that were synthesized in a previous work [1], in which the evaluation of a BtL processing super-structure under different economic constraints and product profiles scenarios was performed. From the configurations, the two case studies with higher production of both gasoline and diesel were selected for this work. For the synthesis of intensified BtL technologies, the optimal separation units' design parameters that meet the combination of economic, safety and environmental indexes, and two green chemistry metrics were selected. By applying the methodology, the optimal intensified process presents a higher return on investment of 22 (%/y) compared to 18 (%/y) for the base case flowsheet.

## 1. Introduction

Given the actual situation of the transport fuels and its major drawbacks in terms of energy consumption, greenhouse gas (GHG)

emissions and production costs, the chemical industry has increased its attention on biorefinery systems due to their capability of processing biobased feedstocks into valuable products in a sustainable and more profitable manner. For the application of biorefinery systems it is

**Abbreviations:** *actualrecovery*, actual recovery flowrate; *ael*, amount of electricity; *as*, amount of steam; *asl*, amount of steel; BC, base case; BC3-GLTUF, initial configuration of gasification and LTFT-fractional upgrading-fractionation; BtL, biomass to liquid; C., column; CA1-GLTHT, initial configuration of gasification and combined LTFT-HTFT-fractional upgrading-fractionation; *CCtot*, total capital cost of the plant; *Cl*, value of impact for category *i*; *COL*, cost of operating labor; *CRM*, raw materials cost; *CWT*, cost of waste treatment and disposal; *DDE*, dynamic data exchange; *DE*, differential evolution; *DETL*, differential evolution with tabu list; *ECtot*, total cost of utilities or energy cost; *EI99*, eco-indicator 99; *Fi*, occurrence frequency of incident *i*; *FT*, Fischer-Tropsch; *G*, Generation; *G+1*, next generation; *GAMS*, general algebraic modeling system; *GGE*, gasoline gallons equivalent; *HTFT*, high-temperature Fischer-Tropsch; *IR*, individual risk; *LC50*, lethal concentration; *LC50*, lethal concentration of the chemical in air that kills 50 % of the test animals; *bioLPG*, bio-based liquified petroleum gas; *LTFT*, low temperature Fischer-Tropsch; *MESH*, material balances, equilibrium relationships, summation equations, and heat balances; *MI*, mass intensity; *MINLP*, mixed integer nonlinear programming; *minrecovery*, minimum recovery flowrate; *PI*, process intensification; *Prod.*, product; *Px,y*, probability of injury or decease caused by the incident *i*; *TCOM*, total cost of manufacturing; *TCOM<sub>GGE</sub>*, total cost of manufacturing per gasoline gallon equivalent; *TL*, tabu list; *TS*, tabu search; *U<sup>-i</sup><sub>G</sub>*, trial vector; *VB*, visual basic; *ω*, weighting factor for damage; *Xi,G*, target vector.

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necessary to focus on the synthesis of new process configurations oriented towards a shift from fossil-derived fuels and conventional biofuels to advanced biofuels in a more sustainable, environmentally, safety and economically feasible way. Biomass plants configurations can vary extensively since the processing tasks can be adapted according to desired product profiles. The application of alternative raw materials and the development of new technologies for the substitution of current technologies in the chemical industry will lead to new products such as biochemicals and biofuels that will replace the existing fossil-derived chemicals and fuels due to improved properties and lower production costs. For this, process systems engineering (PSE) tools such as process synthesis, process modelling and simulation, process intensification and process optimization should be applied to approach feasible processes.

From these tools, process synthesis determines the optimal processing units and their interconnections, as well as the optimal design for the conversion of specific feedstocks into desired products. On the other hand, process intensification (PI) technologies are implemented to chemical production processes by evaluating possible modifications in equipment or different sections of the process that can offer drastic improvements to the total process.

Nowadays, PI strategies have increased their application aiming at improving chemical plants by designing cost-effective, safer, environmentally friendly and compact new infrastructure [2]. In both process and equipment level innovative methodologies are defined and applied to achieve improvements on the process efficiency, product quality, reduction of production costs and equipment size, as well as, minimizing waste streams and energy consumption [3,4]. Improvement of a process can be achieved by the development of innovative equipment and techniques, adjustment of the process variables, enhancement of physical and chemical phenomena in some unit operations, structural changes or replacement of unit operations by more promising process units, and utilization of new energy sources [5,6].

It is important to highlight that the different concepts and principles that can be varied and manipulated will generate partial alternative designs, from which the final intensified equipment and process will be synthesized [7]. However, it can be expected that the synthesis of these partial designs and its combination into the final improved process and equipment will not be straightforward; instead, there must be some conflicts and contradictions, and the identification of the most promising intensified solution will demand a deep analysis and rigorous decision process [7,8].

To simplify the identification of the most promising PI option different technological and process constraints should be considered and various methods to quickly quantify the possible process improvements should be applied. Therefore, in order to select and implement the optimal PI technology, systematic methodologies are required to support the identification of the most suitable option for a given problem and to remove or eliminate the encountered conflicts or contradictions [9]. Among the methods that have been classified to perform PI are heuristic, mathematical optimization, and hybrid methods [4].

As mentioned, knowledge-based heuristic methods (verified through simulation and experimentation) and process optimization methods are the most common methods for PI. The latter concentrates on optimizing operating parameters and adjusting the unit operations and process configuration according to a given objective or objectives. For the implementation of optimization-based methods, the formulation of a superstructure and its definition as a mixed integer nonlinear programming (MINLP) optimization problem is mostly required [4]. Likewise, stochastic optimization methods can be useful to solve problems related to PI considering the variation of process design parameters in order to achieve a multi-objective function [10]. Moreover, since intensified processes show highly non-linear, non-convex models with a large number of continuous, discrete and disjunctive variables, stochastic optimization is a good strategy to be able to find optimal solutions in these circumstances.

Several works have focused on unit operation-based representations

and heuristic methods supported by process simulators for evaluation and identification of new intensified designs considering multi-objectives. For instance, Barnes et al. [11] developed a novel adsorption-based gas separation technology for PI of upstream gas separations and achieved CAPEX savings, as well as, equipment, weight and footprint reductions compared to conventional technologies. Rong [12] formulated a four-step procedure for intensification of distillation systems for multicomponent separations and systematically generated all the possible dividing-wall columns from the simple column sequences aiming at reduce capital and energy costs. Likewise, Torres-Ortega et al. [13] evaluated the possible structural changes of a non-sharp quaternary distillation configuration and different alternatives were generated following the PI principle to reduce the number of equipment units and total annual cost.

On the other hand, other authors have focused on PI strategies capable of synthesizing improved process alternatives for the production of biochemicals and have recently developed and fully set-up as optimization algorithms in automated and computationally efficient ways. These authors have focused their studies in PI methodologies based on building blocks instead of individual unit operations. In the phenomena-based building block (PBB) approach, also called bottom-up approach, to identify potential process options and their interconnections, the problem is defined and analyzed for a defined process improvement. Lutze et al. [14] describes this approach, in which phenomena are connected and screened to form process options considering feasibility and performance constraints. In this stepwise framework, the most promising process options are selected and then replaced by the required unit operations. Here, at unit operation level additional constraints are defined, to analyze its feasibility and performance with respect to an objective function. Demirel et al. [15,16] proposed and implemented a method for simultaneous process design and intensification considering the representation of process units, flowsheets and superstructures using building blocks. Through this method, optimal intensified designs for different case studies were achieved by solving the proposed MINLP model. The PBB superstructure handled various objective functions and generated different intensified flowsheets without knowing these designs beforehand. Babi et al. [17] proposed a computer-aided methodology for PI, in which PBBs were used to represent process flowsheets and then, the most promising structure considering economic, life cycle and sustainability metrics was transformed into unit operations. Likewise, Babi et al. [18] introduced a superstructure-based approach for the synthesis of intensified flowsheets that reduce the carbon footprint, energy costs and number of equipment.

Moreover, other authors have applied hybrid methods, in which first intensified designs are generated with the support of heuristic rules and process simulators such as Aspen Plus and then are optimized by means of a multi-objective algorithm combining stochastic methods like differential evolution (DE) with tabu list (TL). For instance, Alcocer-Garcia et al. [19] evaluated improvements in the purification of levulinic acid by considering the substitution of conventional separation technologies with PI equipment including thermally couplings or single or multiple walls in a column. The resulting intensified designs were then optimized with a hybrid algorithm (Differential Evolution with Tabu List (DETL)) considering the minimization of the total annual cost and the environmental impact.

However, the majority of these studies have only focused on applying one optimization approach for PI and most importantly, have mainly consider improvements emphasizing on evaluating either the technical, economic and/or environmental impact and/or sustainability without considering all these metrics simultaneously.

In this work, several of these intensification approaches have been combined and five metrics have been selected to develop and evaluate a multi-objective optimization methodology for synthesis of novel intensified designs. To achieve this, two gasification-based process routes, which were synthesized in a previous work from the implementation of a MINLP superstructure algorithm [1], are selected as case studies for the

conversion of biomass-to-liquid transportation fuels into gasoline and diesel. Then, the case studies are intensified through the application of a multi-objective optimization methodology. The proposed methodology evaluates the intensification of the case studies considering the variation of process design parameters in order to meet a multi-objective function including the combination of economic, environmental and safety indexes, and two green chemistry metrics, namely resources efficiency and mass intensity, towards environmental sustainability. By synthesizing more sustainable intensified biomass conversion technologies with lower production costs, environmental impact, and safety risks, as well as higher resources efficiency, this approach can lead to an increase in the substitution of fossil-derived raw materials and the production of biofuels and biochemicals. Moreover, since the generation of bio-based products is achieved through the case studies, it is expected that the implementation of the selected indicators will allow to transform the case studies into more sustainable and green solutions by reducing the emissions and wastes and increasing their utilization according to the new principles of circular economy.

### 1.1. Problem statement

In a previous work, a BtL building block superstructure was defined as a MINLP problem in the General Algebraic Modeling System (GAMS), which set the objective to minimize the total cost of manufacturing (TCOM) of BtL fuels under different constraint scenarios and product profiles [1]. From its implementation, different processing blocks interconnections were found and optimal process flowsheets' configurations were generated, which demonstrated the power and usefulness of the mathematical approach. However, even though the economic aspects are indeed a critical issue, the feasibility of the BtL processes not only relies on the lowest production costs but also in the lowest environmental impact, individual risks, and in the generation of sustainable process configurations.

Based on this, in the present work a methodology for intensification of the most promising flowsheets' configurations is presented. First, the process simulator Aspen Plus is used to perform the rigorous simulation of two process flowsheets, selected as case studies. Then, the optimization methodology for process synthesis-intensification through a stochastic algorithm DETL in a hybrid platform is implemented to the case studies. The hybrid platform involves the linking between the process simulator Aspen Plus and the multi-objective optimization algorithm programmed in Excel through a Visual Basic macro. Finally, for its

implementation, an objective function combining the return on investment (ROI), the eco-indicator 99 (EI99) and Individual risk (IR) as economic, environmental and safety indicators, respectively, is defined. Likewise, the sustainability of the BtL processes is quantified with two green metrics: resources efficiency (E-factor) and mass intensity (MI). By applying the methodology, the main purpose is to demonstrate the role of the variation of the unit operations' design parameters in the intensification of a process and their correlation with the five objective functions.

Besides the case studies, the proposed methodology for PI through multi-objective optimization approaches can be considered as a tool for different chemical processes to find economically and sustainable attractive designs with low environmental impacts and safety risks.

## 2. Methodology

The methodology of multi-objective optimization for PI is focused on the application of two optimization techniques, first, at *process flowsheet level* to find the optimal process configuration by interconnection of processing blocks through a superstructure-based algorithm [1], and second, at *unit operation level* for improvement of processing tasks by the variation of design parameters through a DETL algorithm, which main objective is to achieve a multi-objective function. The methodology of optimization for process synthesis-intensification is illustrated in Fig. 1.

At the process flowsheet level, the process information including the required process units and equipment for the manufacturing process, as well as the input and output flowrates, and operating conditions are investigated and collected. From the selection of the processing steps and collected data, a superstructure-based optimization algorithm was set-up by Ibarra-Gonzalez et al. [1] As result of the superstructure implementation, novel flowsheet designs were synthesized under specific product profile scenarios and aiming to reduce the TCOM of the BtL fuels production processes [1].

Then, at the unit operation level, which is the focus of this work, since most of these chemical processes have a multi-objective nature and usually there are several objectives in conflict between them, a multi-objective optimization method is implemented for PI. For its implementation, first, the selection of case studies is performed by analyzing and comparing the novel flowsheets configurations synthesized from the superstructure approach and by selecting the two process flowsheets that meet specific criteria. Then, the rigorous simulation of the case studies is performed in Aspen Plus considering a lignocellulosic biomass

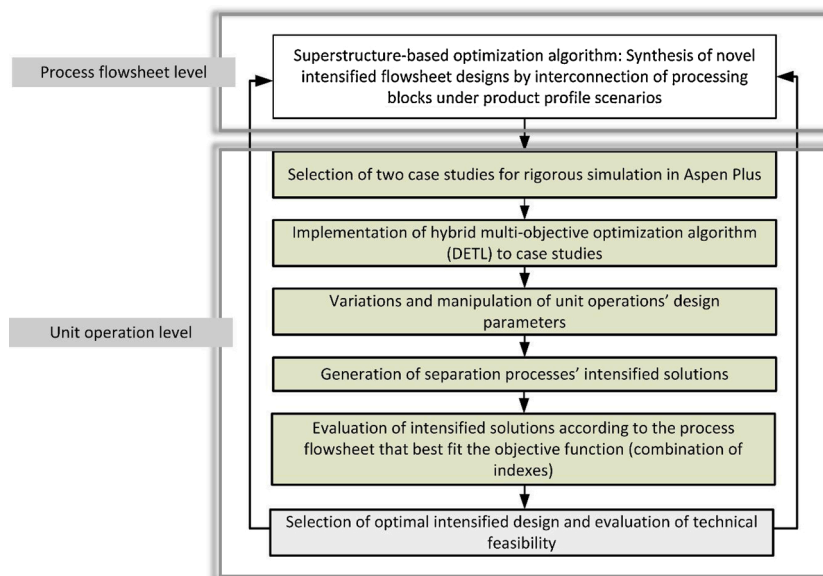


Fig. 1. Multi-objective optimization methodology for process synthesis-intensification.

feedstock capacity of 50,000 kg/h. The capacity of the plant has been selected according to the availability of the forestry biomass, mainly wood residues, in the Nordic countries where forests cover a considerable part of the whole land area. For instance, in Finland and Sweden the percentage of forest area is 86 % and 51 %, respectively [20,21]. In Denmark only 11 % of land area is covered by forest and in Norway 20 % [22].

The process simulations provide the real plant separation technologies' configurations and needs for the optimal process routes. Moreover, these simulation flowsheets are the starting point for the multi-objective optimization of the optimal process routes in terms of equipment design variables.

The next step is the implementation of a DETL method for process optimization, which is carried out in a hybrid platform. The hybrid platform involves the linking between the process simulator Aspen Plus and a multi-objective optimization algorithm programmed in Excel through a Visual Basic macro. This method can evaluate the possible improvements of the selected processes based on technical, economic, environmental and safety indicators, as well as green chemistry metrics.

After the set-up of the algorithm, the specification of design parameters and their corresponding search ranges in a feasible region is performed, which allows finding the optimal operating design parameters and re-designing equipment towards the objective function. From the variation and manipulation of the unit operations design parameters, not only one intensified solution is obtained but several intensified solutions. The intensified solutions are evaluated and the process flowsheet with the design parameters that best fit the objective function (combination of performance indexes) is selected. Moreover, when a new intensified equipment or process is designed for the substitution of an existing one, it is necessary to evaluate and compare the initial process design with the final intensified design using the same platform to keep the consistency of the comparison and to further determine if its implementation is practical, feasible and suitable for the industrial sector. Finally, after identifying the most promising PI option, the intensified unit operations can be integrated in the total process flowsheet to evaluate its technical feasibility.

All the steps presented by this methodology approach can be iterated and applied to different flowsheet configurations or chemical processes.

In the following sections, the explanation and implementation of the proposed methodology is described in detail.

### 3. Selection of case studies

In the previous work by Ibarra-Gonzalez et al. [1] novel process flowsheets were generated for the conversion of softwood biomass into liquid biofuels. Among the novel process flowsheets, five are gasification-based technologies for the production of gasoline and diesel. BtL conversion via gasification followed by Fischer-Tropsch (FT) synthesis and syncrude upgrading reactions produces high-quality fuels compatible with conventional fossil fuels. Moreover, depending on the FT scheme (low temperature or high temperature) different product profiles can be achieved.

In this work, the methodology proposed in Fig. 1 is applied to the previously synthesized gasification-based process flowsheets. For this, as starting point, two of the novel flowsheet designs by Ibarra-Gonzalez et al. [1] were selected as case studies. The selection of the two process flowsheets for the multi-objective optimization was performed based on the following criteria and supported by the information reported in Table 1. The criteria defined for the selection of the case studies is listed in order of importance.

#### Criteria for selection of case studies:

- Higher production of both gasoline and diesel fuels
- Lower total cost of manufacturing per gasoline gallon equivalent (TCOM<sub>GGE</sub>)
- Lower total cost of manufacturing (TCOM)

**Table 1**

Comparison of the novel processes synthesized from the superstructure-based [1,23].

|                                               | BC3-GLTUF  | CA1-GLTHT  | CA2-GLTHT  | CA3-GLTHT  |
|-----------------------------------------------|------------|------------|------------|------------|
| Upgraded prod. [kg/h]                         | 700        | 1,022      | 1,069      | 1,030      |
| Total fuel prod. wt. %                        | 87         | 90         | 97         | 45         |
| Gasoline wt. %                                | 38         | 69         | 80         | 10         |
| Diesel wt. %                                  | 49         | 21         | 17         | 35         |
| CC <sub>tot</sub> (\$/year)                   | 82,834     | 88,412     | 88,652     | 95,115     |
| C <sub>OL</sub> (\$/year)                     | 1,621,120  | 1,621,120  | 1,621,120  | 1,621,120  |
| C <sub>RM</sub> (\$/year)                     | 4,680,232  | 6,934,368  | 7,313,331  | 3,955,324  |
| EC <sub>tot</sub> (\$/year)                   | 152,704    | 235,434    | 229,412    | 122,105    |
| C <sub>WT</sub> (\$/year)                     | 4,289,046  | 4,484,208  | 4,371,508  | 4,456,510  |
| TCOM (\$/year)                                | 15,668,889 | 18,784,844 | 19,105,008 | 14,949,035 |
| TCOM w/energy integration (\$/year)           | 15,341,811 | 18,274,260 | 18,766,123 | 14,680,510 |
| Productivity (GGE/year)                       | 1,903,308  | 2,416,304  | 3,586,161  | 1,800,690  |
| TCOM <sub>GGE</sub> (\$/GGE) at 500 kg/h feed | 8.1        | 7.5        | 5.2        | 8.1        |

Therefore, the process configurations that present the higher production of both fuels and promote the simultaneous production of gasoline and diesel, and that were found as the optimal technological routes in terms of TCOM for the production of both synthetic fuels were selected. These case studies are gasification-based process routes followed by syngas upgrading to hydrocarbons via high temperature (HT) and/or low temperature (LT) FT reactions and subsequent fractional hydrocarbon upgrading to transportation fuels, and final separation of desired fuels and by-products. More specifically;

- 1 BC3-GLTUF = Gasification followed by low temperature Fischer-Tropsch (FT) and FT fractional upgrading units (bio-based liquefied petroleum gas (bioLPG) oligomerization, naphtha isomerization and catalytic reforming, and wax hydrocracking) and final upgraded product fractionation, as presented in Fig. 2.
- 2 CA1-GLTHT = Gasification followed by simultaneous high and low temperature FT reactions and FT fractional upgrading blocks (distillate hydrotreating, wax hydrocracking, naphtha isomerization and reforming, and tail gas alkylation) and final upgraded product fractionation, as presented in Fig. 3.

As can be observed in Figs. 2 and 3, the separation columns (C) presented in each process flowsheet configuration were numbered as C.n (C.1, C.2, C.3...C.n), which is done to facilitate the identification, analysis and further optimization set up.

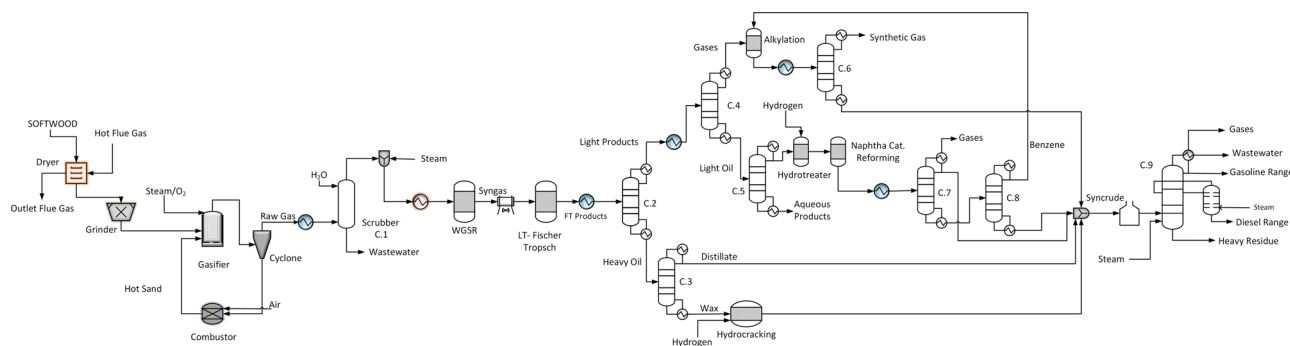
The multi-objective optimization methodology considering the variation of the unit operations' design parameters will be applied only for the intensification of the separation units C.n. of the selected case studies to find the optimal operating conditions that meet an objective function that combines economic, environmental and safety indexes, as well as the evaluation of two green chemistry metrics (resources efficiency and mass intensity).

To implement the optimization methodology for intensification, first, it is required to perform the rigorous simulation of the case studies' process flowsheets. These process flowsheets are the initial process designs to be intensified by the optimization algorithm through the hybrid platform. The rigorous simulation will be described in the following section and the implementation of the hybrid platform for the multi-objective optimization of the case studies is presented in Section 5.

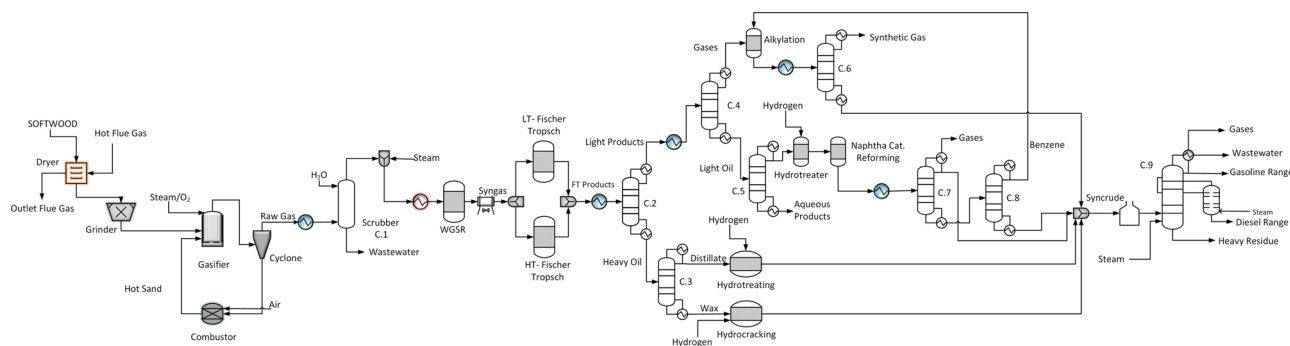
### 4. Case studies flowsheet set-up and rigorous simulations on Aspen Plus

After the selection of the case studies, the next step is to perform their





**Fig. 2.** Case Study 1: Process flowsheet for BC3-GLTUF from superstructured-based approach.



**Fig. 3. Case Study 2: Process flowsheet for CA1-GLTHT from superstructured-based approach.**

rigorous simulation to generate the initial process designs to be intensified. For the modeling and simulation of BtL industrial processes, including reaction and separation technologies, the definition of a substitute mixture is required. Defining the real intermediate stream mixtures for the case studies allow finding the most suitable separation processes to be intensified through the multi-objective optimization algorithm. Therefore, model compounds are used to represent the complex mixtures, namely syngas, FT hydrocarbon product, upgraded fractions and final advanced transportation fuels. The selection of the model compounds will depend on the experimental information available on the literature for each of the product streams. For instance, the model compounds selected for the representation of the low temperature Fischer-Tropsch (LTFT) product mixture are presented in [Table 2](#), which were selected using as reference the generic composition of Fe-LTFT syncrude reported by de Klerk [24] and literature data [25,26]. The biomass gasification was carried out in a fluidized bed reactor using as gasifying agents steam and air at 800–1000 °C, residence times of 3–4 s, and atmospheric pressures [27,28]. The operating conditions of the LTFT reaction are 200–250 °C, 2–2.5 MPa with an inlet H<sub>2</sub>:CO ratio of syngas of 2:1 [28,29].

After the mixtures' definition, process flowsheet set-up and rigorous simulations are performed in Aspen Plus V8.8. For the simulation set-up, the thermodynamic package Soave-Redlich-Kwong equation of state with Kabadi-Danner mixing rules was selected due to its recommended application for mixtures containing water and hydrocarbons [30]. It provides high accuracy in water-hydrocarbon systems over a wide range of temperatures and predicts the instability of the liquid phase [31]. In addition, the electrolyte and non-electrolyte NRTL model with Redlich-Kwong equation of state were employed for the separation units. To model the unit operations, the Aspen Plus Yield reactor, RYield, was used to model the gasification and hydrotreating reactions. The stoichiometric reactor (RStoic) was used to model the combustor and the upgrading of the FT hydrocarbons. The separation units were model using the RadFrac block and the final fractionating column was model with a PetroFrac. All modules in the flowsheets of the selected case

studies were solved in Aspen by means of solving the entire set of MESH (material balances, equilibrium relationships, summation equations, and heat (enthalpy) balances). Moreover, an input plant capacity of 50,000 kg/h (forest residues) considering the availability of the feedstock in the Nordic countries was selected to resemble a real plant capacity more closely.

The resulting process flowsheets are the initial process designs to be intensified in terms of the separation processes' design parameters. The intensification will be achieved through the implementation of an optimization algorithm in a hybrid platform, as described in the following section.

## 5. Implementation of hybrid multi-objective optimization algorithm to case studies

The next step after the synthesis and rigorous simulation of the selected novel flowsheet designs is to implement a multi-objective optimization method in a hybrid platform to find the process routes' optimal operating conditions that meet the objective function conformed by the combination of economic, environmental and safety indexes, as well as green chemistry metrics. The simultaneous evaluation of sustainable, economic, environmental and safety aspects at the design stage represents an important improvement in selecting the optimal intensified BtL process route.

More specifically, the multi-objective optimization of the two BTL case studies is performed using a multi-objective optimization technique known as Differential Evolution with Tabu List (DETL). For the optimization, as objective function, the combination of five different and contrasting indexes representing the economic factor (return on investment), environmental impact (eco-indicator 99), and the process safety (individual risk) as well as two green metrics (resources efficiency and mass intensity) has been defined. The implementation of the DETL method is carried out in a hybrid platform, which involves the linking between the process simulator Aspen Plus and a DETL optimization algorithm programmed in Excel through a Visual Basic (VB) macro, as

**Table 2**

LTFT product mixture from woody biomass.

| Product Fraction | Carbon Range                     | Component            | Mass % |
|------------------|----------------------------------|----------------------|--------|
| Tail Gas         | C <sub>1</sub> -C <sub>2</sub>   | Methane              | 4,3    |
|                  |                                  | Ethylene             | 1      |
|                  |                                  | Ethane               | 1      |
| LPG              | C <sub>3</sub> -C <sub>4</sub>   | Propene              | 2,94   |
|                  |                                  | Propane              | 0,74   |
|                  |                                  | Butene               | 3,06   |
|                  |                                  | Butane               | 1,06   |
|                  |                                  | 1-pentene            | 1,45   |
| Naphtha          | C <sub>5</sub> -C <sub>10</sub>  | N-pentane            | 0,53   |
|                  |                                  | Hexene               | 1,44   |
|                  |                                  | N-hexane             | 0,53   |
|                  |                                  | Heptene              | 1,3    |
|                  |                                  | Heptane              | 0,61   |
|                  |                                  | Octene               | 1,23   |
|                  |                                  | Octane               | 0,58   |
|                  |                                  | Nonene               | 1,15   |
|                  |                                  | Nonane               | 0,54   |
|                  |                                  | Decene               | 1,13   |
|                  |                                  | Decane               | 0,51   |
|                  |                                  | 1-pentanol           | 0,42   |
|                  |                                  | 1-hexanol            | 0,53   |
|                  |                                  | 1-heptanol           | 0,35   |
| Distillate       | C <sub>11</sub> -C <sub>22</sub> | Undecene             | 0,84   |
|                  |                                  | Undecane             | 2,14   |
|                  |                                  | Dodecene             | 0,76   |
|                  |                                  | Dodecane             | 1,94   |
|                  |                                  | Tridecene            | 0,68   |
|                  |                                  | Tridecane            | 1,73   |
|                  |                                  | Tetradecene          | 0,6    |
|                  |                                  | Tetradecane          | 1,54   |
|                  |                                  | Pentadecene          | 0,54   |
|                  |                                  | Pentadecane          | 1,37   |
|                  |                                  | Hexadecene           | 0,48   |
|                  |                                  | Hexadecane           | 1,21   |
|                  |                                  | Heptadecene          | 0,42   |
|                  |                                  | Heptadecane          | 1,07   |
|                  |                                  | Octadecene           | 0,37   |
|                  |                                  | Octadecane           | 0,95   |
|                  |                                  | Nonadecene           | 0,32   |
|                  |                                  | Nonadecane           | 0,82   |
|                  | C <sub>11</sub> -C <sub>22</sub> | Eicosene             | 0,28   |
|                  |                                  | Eicosane             | 0,72   |
|                  |                                  | Uneicosene           | 0,41   |
|                  |                                  | Uneicosane           | 0,01   |
|                  |                                  | 1-undecanol          | 0,12   |
|                  |                                  | 1-dodecanol          | 0,11   |
|                  |                                  | 1-tridecanol         | 0,07   |
| Wax              | C <sub>22</sub> +                | C <sub>22</sub> -ane | 0,87   |
|                  |                                  | C <sub>22</sub> -ene | 0,28   |
|                  |                                  | C <sub>23</sub> -ane | 0,87   |
|                  |                                  | C <sub>23</sub> -ene | 0,16   |
|                  |                                  | C <sub>24</sub> -ane | 0,87   |
|                  |                                  | C <sub>24</sub> -ene | 0,11   |
|                  |                                  | C <sub>25</sub> -ane | 0,87   |
|                  |                                  | C <sub>25</sub> -ene | 0,08   |
|                  |                                  | C <sub>26</sub> -ane | 0,87   |
|                  |                                  | C <sub>26</sub> -ene | 0,05   |
|                  |                                  | C <sub>27</sub> -ane | 0,87   |
|                  |                                  | C <sub>27</sub> -ene | 0,02   |
|                  |                                  | C <sub>28</sub> -ane | 0,86   |
|                  |                                  | C <sub>29</sub> -ane | 0,86   |
|                  |                                  | C <sub>30</sub> -ane | 42,26  |
| Aqueous products | C <sub>1</sub> -C <sub>5</sub>   | Methanol             | 0,45   |
|                  |                                  | Propanol             | 1,03   |
|                  |                                  | Butanol              | 2,41   |
|                  |                                  | Acetic Acid          | 0,3    |

depicted in Fig. 4.

Process simulators, such as Aspen Plus enable the modeling and detailed economic evaluation of current and novel process flowsheets. However, in a process simulator, the optimization of the process structure is not possible without varying the parameters by hand. Moreover, if economical and other target functions are chosen, the parameter

optimization becomes a tedious and difficult task. Thus, the most efficient strategy is to combine a rigorous simulation model with a robust multi-objective optimization algorithm.

The coupling between Aspen Plus and Microsoft Excel was performed by defining in VB macros the optimization method and the different data that is being exchanged between the platforms. For instance, as can be observed in Fig. 4, the data from Aspen Plus to Microsoft Excel includes mass flowrates, mass fractions and mole fractions, heat duties, unit operations' temperatures, liquid and vapor densities in the column stages and so on. On the other hand, the data from Microsoft Excel to Aspen Plus includes the definition of the search ranges (in the feasible region) that the design parameters can take until finding the optimal operation conditions of the system. These decision variables include the columns' number of stages, feed stage, reflux ratio, bottom rate, column diameter and so on. Furthermore, objective functions, constraint vectors of purity and mass flowrate of components, equations and literature information for the calculation of economic, environmental and security factors and green chemistry metrics were also defined in Microsoft Excel.

It is important to clarify that in this work, for the calculation of economic, environmental, security indexes and green chemistry metrics, all unit operations including separation and reaction units are considered. However, the effect of the variation of the design parameters on the performance indexes can be only evaluated for the separation units because the reactions units were defined based on stoichiometric reactions and conversions.

### 5.1. Multi-objective optimization method

The stochastic methods have been proven as capable of solving complex optimization problems, highly non-linear and potentially non-convex [32,33]. DETL has its basis in natural selection theory. Initially, Differential Evolution (DE) was proposed considering a single objective function [34]. Further, the method was adapted by Madavan and Field [35] to solve multi-objective problems. DE is a parallel direct search method which utilizes NP D-dimensional parameter vectors  $X_{i,G}$ , in which  $i$  can take values of 1, 2, ..., NP. The DE algorithm is summarized in four steps: initialization, mutation, crossover, evaluation, and selection.

In the initialization step, the algorithm searches in a D-dimensional space  $\mathbb{R}^D$ , which starts randomly as:

$$X_{i,G}^{\rightarrow} = [X_{1,i,G}, X_{2,i,G}, X_{3,i,G}, \dots, X_{D,i,G}] \quad (1)$$

Regarding the mutation step, it has indeed a pretty similar biological meaning, which can be described as a change or disturbance with a random element. Starting from a parent vector (named target vector)  $X_{i,G}, i = 1, 2, 3, \dots, NP$ , this parent vector is further muted to generate a donor vector. Finally, the trial vector is obtained recombining both the donor and target vector. The process can be depicted as follows:

$$V_{i,G}^{\rightarrow} = X_{i,G}^{\rightarrow} + F \cdot (X_{r_{2,G}}^{\rightarrow} - X_{r_{3,G}}^{\rightarrow}) \quad (2)$$

with random integer indexes  $r_1, r_2, r_3 \in \{1, 2, \dots, NP\}$  mutually different and with  $F > 0$ .  $F$  is a real and constant factor  $\in [0, 2]$ , which controls the amplification of the differential variation  $X_{r_{2,G}}^{\rightarrow} - X_{r_{3,G}}^{\rightarrow}$ .

Following with the crossover step, the target vector exchanges its components with the target vector under this operation to form the trial vector  $U_{i,G}^{\rightarrow} = [u_{1,i,G}, u_{2,i,G}, u_{3,i,G}, \dots, u_{D,i,G}]$ . So, the trial vector is obtained as:

$$u_{j,i,G} = v_{j,i,G} \quad \text{for } j = \langle n \rangle_D, \langle n+1 \rangle_D, \dots, \langle n+L-1 \rangle_D \\ x_{j,i,G} \text{ for all other } j \in [1, D] \quad (3)$$

To keep the population size as a constant number, the selection step determines if the target or the trial vector survives from the generation (G) to the next generation (G + 1). The selection operation is described as follows:

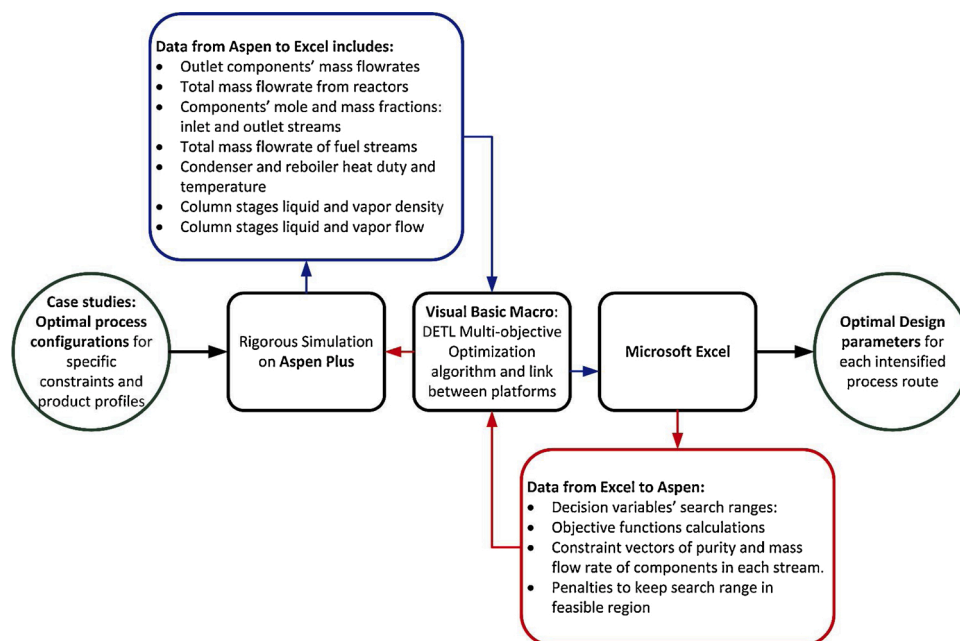


Fig. 4. Hybrid multi-objective optimization algorithm implementation.

$$\begin{aligned} \vec{X}_{i,G+1} &= \vec{U}_{i,G} & \text{if } f(\vec{U}_{i,G}) \leq f(\vec{X}_{i,G}) \\ \vec{X}_{i,G+1} &= \vec{X}_{i,G} & \text{if } f(\vec{U}_{i,G}) > f(\vec{X}_{i,G}) \end{aligned} \quad (4)$$

Regarding Tabu concepts, Both the Tabu list concept (TL) and Tabu Search (TS) previously proposed by Glover [36] allow avoiding revisiting the search space by keeping a record of the visited points. TL is randomly initialized at an initial population and continuously updated with the newly generated trial individuals. This tabu check is carried out in the generation step to the trial vector, and the new trial individual is generated repeatedly until it is not near to any individual in the TL. The total trial individuals (NP) are generated by the repetition of the above steps. The newly generated NP trial vectors are combined with the parent population to form a combined population with total 2NP individuals.

## 5.2. Hybrid platform: link between Microsoft Excel-aspen plus

The global optimization process is performed in a hybrid platform linking Aspen Plus and Microsoft Excel. This method was previously implemented by Zhang and Rangaiah [37]. In Microsoft Excel, the DETL algorithm is written by means of a visual basic macro and the model of the process configurations are solved in Aspen Plus. Initially, the vector of decision variables is sent from Microsoft Excel to Aspen Plus by means of dynamic data exchange (DDE). Those values are assigned to process variables in Aspen Plus modeler. After simulation, Aspen Plus returns the output data to Microsoft Excel as resulting vector containing output data (flow streams, mass and mole fractions, reboiler heat duty, condenser and reboiler temperatures, etc.). Finally, Microsoft Excel analyzes the objective function values and proposes new values of decision variables according to DETL methodology. The parameters used for the DETL optimization process were: 120 individuals, 800 maximum number of generations, a tabu list size of 60 individuals (50 % of the total number of individuals), a tabu radius of  $1 \times 10^{-6}$ , a mutation probability of 0.3 and crossover probability of 0.8. These parameters were obtained from preliminary calculations performed by Srinivas and Rangaiah [38,39].

## 5.3. Objective function: performance indexes

The case studies BC3-GLTUF and CA1-GLTHT were designed and intensified having as objective function the combination of five indexes including the return on investment (ROI), individual risk (IR) as quantification of the potential risk of the process, the Eco-indicator 99 (EI99) that quantifies the environmental impact and two green chemistry metrics (resources efficiency and mass intensity). The performance indexes are described below.

### 5.3.1. Return on investment (ROI)

The return on investment (ROI) is the annual interest rate made by the profits on the original investment, it provides a snapshot view of the profitability of the plant. The ROI calculation is based on the annual revenue, the annual production costs and the total capital investment, as depicted in Eq. (5) [40]. The ROI is generally stated as a percentage per year.

$$ROI = \frac{\text{annual revenue} - \text{annual production cost}}{\text{total capital investment}} \times 100 \quad (5)$$

### 5.3.2. Environmental impact: eco-indicator 99 (EI99)

The environmental impact is quantified with the Eco-indicator 99 (EI99), which evaluates the sustainability of the processes and quantifies the environmental impact due to the multiple activities performed in the process [41]. The method is based in the evaluation of three major damage categories: human health, ecosystem quality and resources depletion. The impact categories include values of EI99 for respiratory effects, carcinogenic, land occupation and others reported by Geodkoop and Spriensma in their methodology report [42]. In the case of distillation columns, the factors that have the strongest influence on EI99 are the steam used to supply the heat duty, electricity utilized for pumping of cooling water, and the steel necessary to build the equipment [32,43]. The EI99 can be represented mathematically according to Eq. (6).

$$EI99 = \sum_i \omega_{ci} as + \sum_i \omega_{ci} sl + \sum_i \omega_{ci} el \quad (6)$$

Where  $\omega$  is a weighting factor for damage,  $c_i$  is the value of impact for category  $i$ , "as" is the amount of steam utilized by the process, "sl" is the amount of steel used to build the equipment, and "el" is the electricity

required by the process. The values for the impact categories  $c_i$  have been reported in literature [42].

### 5.3.3. Security impact: individual risks (IR)

The security impact will quantify the individual risks (IR) and identify the process route that may cause less damage with less frequency. The IR can be defined as the risk of injury or decease to a person in the vicinity of a hazard. The main objective of this index is the estimation of likelihood affectation caused by the specific incident that occurs with a certain frequency. The mathematical expression for calculating the individual risk in reactors and separation units is presented in Eq. (7) [44].

$$IR = \sum f_i P_{x,y} \quad (7)$$

Where  $f_i$  is the occurrence frequency of incident  $i$ , whereas  $P_{x,y}$  is the probability of injury or decease caused by the incident  $i$ . The frequency  $f_i$  values for each incident were taken according to those reported by American Institute of Chemical Engineers [44].

For the calculation, the information of approximately 120 components at the inlet and outlet of unit operations was given including heat of combustion, lethal concentration (LC50) (Concentration of the chemical in air that kills 50 % of the test animals during the observation period), lower and upper flammability limit, vapor density and molecular weight.

### 5.3.4. Resources efficiency (E-factor)

The E-factor is defined as the mass ratio of waste to product, as depicted in Eq. (8) [45]. The E-factor is the actual amount of waste produced in the process, defined as everything but the desired product. It includes reagents and solvent losses, all process aids and byproducts, and so on. However, water is generally excluded from the calculation [46]. In most cases, inclusion of water used in the process can lead to an exceptionally high E-factor, which makes the environmental impact appear much worse than it actually is and indicate that a process is not particularly efficient when it actually is [47]. It is important to clarify that when an aqueous waste stream is considered in the process, only the inorganic salts and organic compounds contained in the water are counted.

$$E_{\text{factor}} = \frac{\text{mass of all wastes}}{\text{mass of product}} \quad (8)$$

The ideal value of the E-factor is zero. Nevertheless, different industry sectors present different E-factors depending on the degree of the technical development of the industry, the competitiveness of particular products, the cost of waste as a part of the products selling price and other factors. Common E-factor's values in the chemical industry sectors have are reported in Table 3. Moreover, this metric is a useful measure of the potential environmental acceptability of a chemical process. For instance, a higher E-factor means more waste and, thus, greater negative environmental impact [46].

### 5.3.5. Mass intensity (MI)

Mass Intensity (MI) measures the amount of material needed to synthesize a desired product or products, as depicted in Eq. (9). It takes into account yields, stoichiometry, solvents, and reagents used in a

reaction mixture. More precisely, MI considers everything that is put into a reaction vessel including reactants, reagents, solvents, catalysts and so on. It also includes all mass used in acid, base, salt and organic solvent washes, and organic solvents used for extractions, crystallizations, or for solvent switching [45,48]. MI is expressed on a weight/weight basis and in the ideal situation it should present a value of 1.

$$MI = \frac{\text{total mass used in a process or process step}}{\text{mass of product}} \quad (9)$$

As can be observed from Eq. (9), the calculation of MI includes everything that is used in a process or process step, but water is excluded from the calculation. Water is not included because is generally not integral to the chemical reaction and is mainly used during work-up operations such as phase separations (e.g. scrubbing and fractionation).

### 5.3.6. Multi-objective function for intensification

In this work, as described previously, the simultaneous evaluation of economics, environmental impact, inherent safety and sustainability is performed at the design stage, which represents an important improvement in selecting the optimal intensified process route that meets these indicators. More specifically, the multi-objective optimization problem considers the maximization of the return on investment and the minimization of the environmental impact, individual risks and process wastes towards the synthesis of the most promising design for the BtL conversion through gasification-based technologies.

Thus, once the economic, environmental, safety and sustainability (green metrics) indexes and the decision variables have been defined, the mathematical optimization problem considering all performance indexes, variables and constraints can be expressed according to Eq. (10).

$$\min \left[ \frac{1}{ROI}, EI_{99}, IR, E_{\text{factor}}, MI \right] = f(Nt_i, F_{S_i}, R_i, F_{D/B_i}, VF, LF, D_i, Q_{Reb_i}, F_{c_{j,i}}) \quad (10)$$

where  $Nt_i$  represents the total number of stages of column  $i$ ,  $F_{S_i}$  is the feed stage of column  $i$ ,  $R_i$  is the reflux ratio of column  $i$ ,  $F_{D/B_i}$  is the distillate or bottom flowrate,  $VF$  is the interconnection vapor flow,  $LF$  is the interconnection liquid flow,  $D_i$  is the diameter of column  $i$ ,  $Q_{Reb_i}$  is the reboiler duty of column  $i$ , and  $F_{c_{j,i}}$  is the flowrate of component  $j$  in column  $i$ .

## 6. Variations and manipulation of unit operations' design parameters

In BtL processes, separations are essential components for the removal of impurities and for the recovery of product fractions that need to be upgraded into transportation fuels, as can be observed from Figs. 2 and 3. However, they are highly energy-intensive and thus, account for a high proportion of the plant costs. PI can be adopted to reduce the energy consumption and to improve the separation units' efficiency by manipulation of their design parameters and generating intensified solutions.

For these reasons, in this work, the multi-objective optimization of each case study considered the intensification of 10 separation units (C.1-C.9 and a stripper) through the manipulation of 47 continuous and discrete variables and the solution of the MESH equations. The optimization algorithm considers the variation of these decision variables and the evaluation of the objective function formed by the combination of the five performance indexes. Table 4 shows the type of unit operation and the corresponding decision variables used in the optimization. Likewise, in Table 4, as example the search range used in the optimization for intensification of BC3-GLTUF is presented.

Initially, the search ranges were wider but after some optimization trials it was found that the range could be narrowed to reduce the convergence time and to focus on the feasible region. The search range is

**Table 3**  
E-factors in the chemical industry.

| Type of industry sector | E-Factor* |
|-------------------------|-----------|
| Oil refining            | <0.1      |
| Bulk Chemicals          | <1–5      |
| Fine Chemicals          | 5–50      |
| Pharmaceuticals         | 25–100    |

\* kg waste/kg product.



**Table 4**

Type of unit operation and decision variables used in the multi-objective optimization.

| Type of unit operation                             | Type of variable               | Category   | Search range         |
|----------------------------------------------------|--------------------------------|------------|----------------------|
| Absorber (C.1)                                     | Number of stages               | Discrete   | 5–15                 |
|                                                    | Feed stages                    | Discrete   | 5–15                 |
|                                                    | Diameter                       | Continuous | 1–6 (m)              |
|                                                    | Water inlet flowrate           | Continuous | 23150–23600 (kmol/h) |
|                                                    | Number of stages               | Discrete   | 10–25                |
| Distillation column (C.2-C.8); e.g. ranges for C.3 | Feed stage                     | Discrete   | 7–16                 |
|                                                    | Reflux ratio                   | Continuous | 4.5–8                |
|                                                    | Bottom flowrate                | Continuous | 31900–32000 (kg/h)   |
|                                                    | Diameter                       | Continuous | 1–3 (m)              |
|                                                    | Number of stages               | Discrete   | 10–16                |
|                                                    | Feed stage                     | Discrete   | 9–16                 |
|                                                    | Bottom flowrate                | Continuous | 6700–6850 (kg/h)     |
| Fractionation column (C.9) Stripper                | Diameter                       | Continuous | 1–7.5 (m)            |
|                                                    | Steam inlet flowrate           | Continuous | 11000–14000 (kg/h)   |
|                                                    | Main column connecting stages: |            |                      |
|                                                    | Liquid Draw                    | Discrete   | 10–12                |
|                                                    | Overhead return                | Discrete   | 7–9                  |
|                                                    | Number of stages               | Discrete   | 3–6                  |

given to iteratively adjust the decision variables of each unit operation until achieving the optimal solution to the specified objectives.

Furthermore, for the optimization problem of the selected process flowsheets' configurations, the product streams flowrates were manipulated and the recoveries of the light key components or heavy key components in each distillate and/or bottom stream were included as constraints, as depicted as follows.

$$\text{If } (\min_{\text{recovery}} - \text{actual}_{\text{recovery}}) \leq 0, \text{ then the penalty is equal to } 0, \\ \text{else penalty} = ((\min_{\text{recovery}} - \text{actual}_{\text{recovery}}) * 1000) \quad (11)$$

This means that if the actual component flowrate is higher or equal to the minimum recovery requirement, then the constraint is satisfied, and no penalty is given to the objective function. On the other hand, if the actual flowrate is lower than the minimum recovery then a big number equal to  $((\min_{\text{recovery}} - \text{actual}_{\text{recovery}}) * 1000)$  is given as penalty. Thus, the optimization problem is restricted to satisfy the constraint vector of mass flowrate for the interest components in the stream mixture. The same restrictions were applied for the constraint vector of purity.

## 7. Generation and evaluation of separation processes' intensified solutions

After the optimization of the case studies BC3-GLTUF and CA1-GLTHT, the optimal set of results for the separation processes' decision variables and the corresponding economic, safety, environmental and green chemistry metrics indexes values were collected. The optimizations were carried out on two computers, one with Intel® Core™ i7-4770 @3.40 GHz and 8 GB of RAM, and the other with Intel® Core™ i5-2320 @3.00 GHz and 12 GB of RAM. To generate the intensified solutions 10 separation units and 47 variables were considered for each case study including continuous and discrete variables. For the generation of the optimal intensified solutions, a computing time of approximately 2 months was necessary due to the complexity of the process designs.

From all the intensified solutions generated by the optimization

algorithm, pareto fronts are calculated. Pareto fronts are usually calculated by turning the multi-objective optimization problem into a sequence of single-objective optimization problems or by exploiting evolutionary methods in which a set of candidate optimal solutions are trace along the Pareto front [49]. Thus, to reduce and identify the intensified alternatives that better meet the objective function, pareto fronts between the indexes are generated. Then, the optimal vector is identified by analyzing all the trends between the five different and contrasting indexes representing the economic factor (return on investment), environmental impact (eco-indicator 99), and the process safety (individual risk) as well as the incorporation of green metrics (resources efficiency and mass intensity). This optimal vector represents the intensified solution that meets the objective function without compromising one index more than the other. From the selected optimal vector, the corresponding design parameters for each intensified case study are found and collected. By applying this approach, the most promising intensified process route among all the process routes can be identified.

From the results collected for the performance indexes, pareto front charts were generated as depicted in Figs. 5–8. All Pareto fronts were obtained after 96,000 evaluations, as afterwards, the vector of decision variables did not produce any meaningful improvement. Thus, it was assumed that the DETL algorithm achieved the convergence at the tested numerical terms. The results reported here correspond to the best solutions obtained. Each vector in the plots represents a different design for the case studies under analysis.

In Figs. 5 and 6, the pareto fronts (for BC3-GLTUF and CA1-GLTHT, respectively) comparing the individual risk (IR) vs the Eco-indicator 99 (EI99) are presented. From the pareto fronts, the optimal vector, which corresponds to the process design that minimizes both the individual risks and environmental impact was selected. According to this, in Figs. 5 and 6, the vector highlighted in red is the one selected as the best structure that has been identified in the subspace of alternatives not only considering these two indexes, but by considering the five indexes simultaneously.

In Fig. 7, the pareto front for CA1-GLTHT comparing the return on investment (ROI) vs the individual risks (IR) is presented. As can be observed from Fig. 7, the trend of the pareto front shows that if the return on investment increases the individual risks of the plant are also increased. When selecting the optimal vector, it is necessary to analyze all the intensified solutions and select the one that achieves the desired objective without compromising the indexes. This analogy is necessary to find the most suitable values for the design parameters that will increase the feasibility of the plant. In this optimization approach the objective is to find the optimal vector that presents the maximum ROI and the minimum IR simultaneously. This vector has been highlighted in red as depicted in Fig. 7. For representation purposes, only the pareto front for CA1-GLTHT is presented since the same trend was observed for BC3-GLTUF.

In Fig. 8, the Pareto front for the mass intensity (MI) vs the resources efficiency (E-factor) is presented for the case study BC3-GLTUF. From Fig. 8, it can be observed that the vectors in the pareto front present a linear trend, which means that the amount of material needed to synthesize a desired product (MI) is a direct function of the mass ratio of waste to product (E-Factor). The relationship shown in Fig. 8 between MI and the E-factor meets Eq. (12) [50]. The same trend was observed in the pareto front for case study CA1-GLTHT.

$$\text{Mass intensity} = E \text{ Factor} + 1 \quad (12)$$

From the pareto fronts calculated and the charts presented, the design parameters (number of stages, feed stage, reflux ratio, bottom flowrate, diameter, condenser and reboiler duty and so on) for the optimal vectors were collected. The performance indexes' optimal vectors correspond to the same set of design parameters for each of the case studies. In the following section, a detailed discussion regarding the relationship between the performance indexes and the design

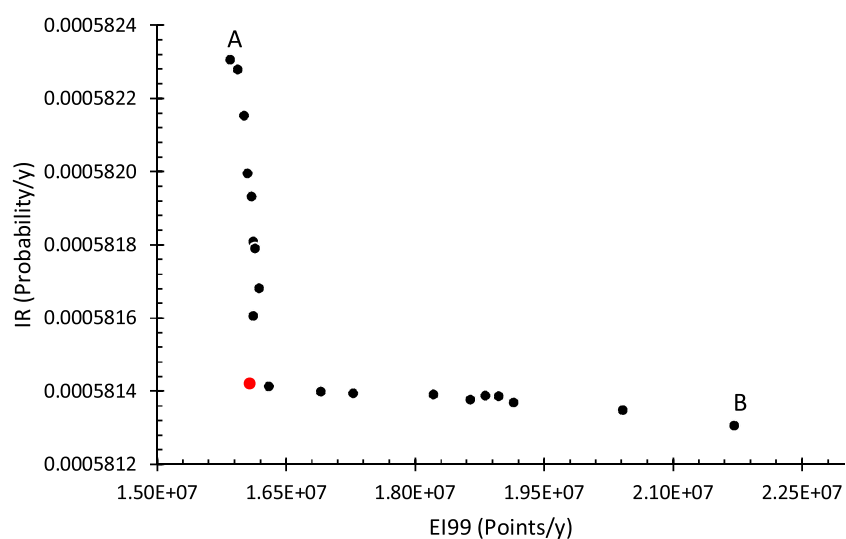


Fig. 5. Pareto front between IR and EI99 for BC3-GLTUF.

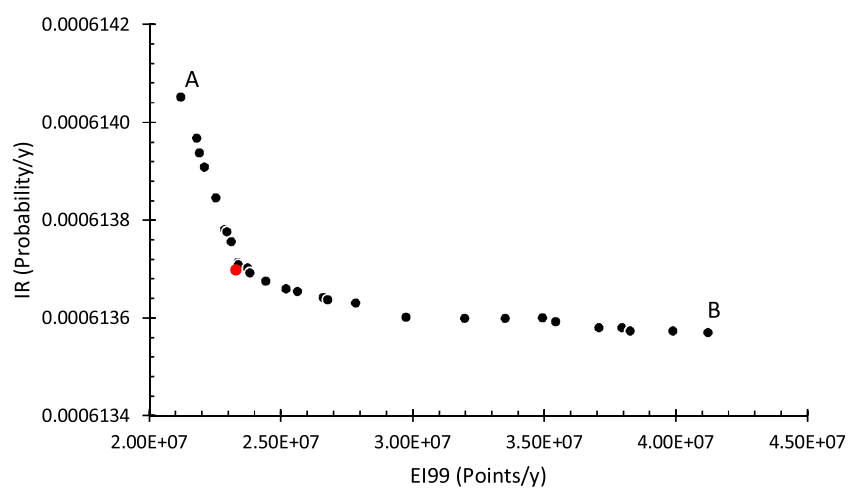


Fig. 6. Pareto front between IR and EI99 for CAI-GLTHT.

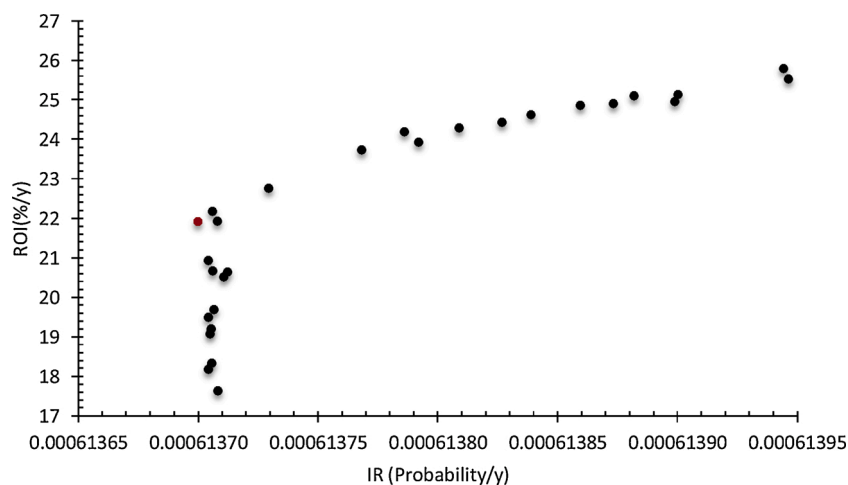


Fig. 7. Pareto front between ROI and IR for CAI-GLTHT.

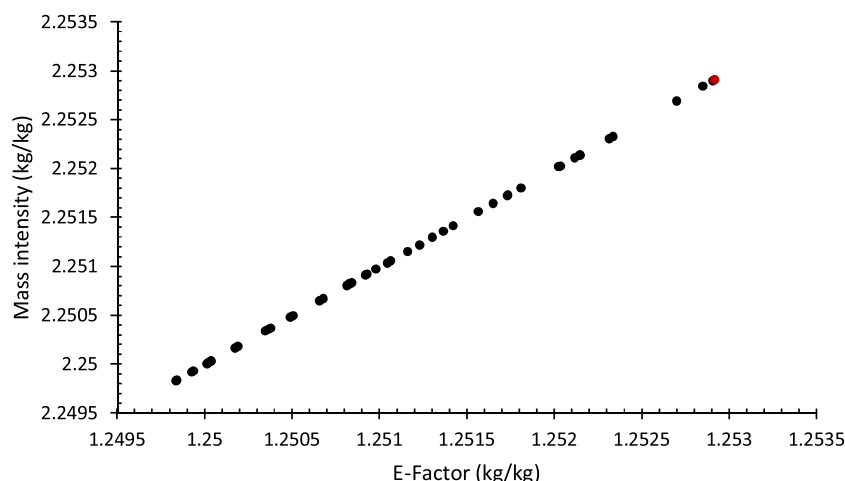


Fig. 8. Pareto front between MI and E-Factor for BC3-GLTUF.

parameters is given.

## 8. Results and discussion: Selection of optimal intensified designs

From the vectors presented in Figs. 5–8, the corresponding design parameters values for each of the separation units involved in each intensified case study were collected, as presented in Tables 5–8. The results allowed to compare the design parameters and performance indexes of the initial configurations with their corresponding intensified configurations. Likewise, it was possible to evaluate the impact of the design parameters on the performance indexes.

In Tables 5 and 6, the optimal results considering the design parameters and performance indexes for BC3-GLTUF/I (where *I* refers to the intensified version) are presented and compared with the initial BC3-GLTUF configuration. Likewise, in Tables 7 and 8, the design parameters and performance indexes for the process configuration CA1-GLTHT and the corresponding intensified configuration (CA1-GLTHT/I) are presented. The initial design parameters for each column *C.n* is presented and compared with the intensified version of each column *C.n/I*, where *n* is the column number.

From the pareto fronts, the trends between the performance indexes can be observed. For instance, from Figs. 5 and 6, it is possible to observe that for the process design vector that causes less damage with less frequency, the value for the Eco-indicator 99 is the highest, which means that the safer it is process, the greater the environmental impact will be. Contrary, to obtain a process with lower environmental impact, the probability of individual accidents will increase, including instantaneous and continuous releases. For instance, as can be observed in both Figs. 5 and 6, the process design with the lowest environmental impact, depicted in the pareto fronts charts as vector **A**, is the one with the highest IR of the process. And vice versa, the process design (Vector **B**) that presents the lowest IR is also the one that presents the highest environmental impact. Thus, the selection of the optimal vector is not based on the one with the lowest environmental impact or the lowest individual probability risk from all the alternatives but the one that presents a balanced behavior among the performance indexes and thus, achieves the objective function considering all the indexes simultaneously.

More specifically, for the case studies, the optimal vector is the one with the separation units' design parameters that achieve the objective considering the combination of the indexes presented in Figs. 5–8. Meaning that the individual risk is minimized, smaller equipment sizes and lower condenser and reboiler duties are achieved and thus, a lower value of the Eco-indicator 99 is observed. Likewise, the intensified design presents lower values for the E-Factor and MI metrics, which

indicates that the amount of wastes is being reduced and the process efficiency is being increased, as presented in Fig. 8 for the relationship between these indexes. Last but not less important, the profitability of the plant is increased by achieving higher values of the return on investment.

Concerning the relationship between the design parameters and the performance indexes, from the plots and the data for the case studies' initial configurations, the initial designs (depicted in Tables 5 and 7 as *C.n*) present higher environmental impacts due to separation units with greater number of stages, larger diameters and thus, more steel necessary to build the equipment. Moreover, higher reflux ratios and reboiler and condenser duties are observed, which reflects on higher energy consumption. This is because a higher condenser and reboiler duty mean higher steam and electricity consumption. Likewise, an increase of the reflux ratio will consequently increase the reboiler duty and the corresponding EI99 of the column.

In addition, if the column diameter is not sized properly, the column will not perform correctly, and operational problems will occur leading to an increase on the occurrence frequency of incidents like leaking or total loss of matter. This analogy explains why the separation units' initial configurations (*C.n*) present higher individual risks (IR).

From the data reported in Tables 5 and 7, it is possible to observe in detail these trends. For instance, for BC3-GLTUF/I (Table 5), the majority of the intensified column designs (*C.1/I*, *C.2/I*, *C.4/I*, *C.5/I* and *C.6/I*) present higher number of stages than the initial designs but present smaller diameters and lower reflux ratios, leading to lower condenser and reboiler duties and lower environmental impact. These behaviors were also observed in the intensified separation units *C.1/I*, *C.2/I*, *C.4/I* and *C.5/I* for CA1-GLTHT/I and lower environmental impact (EI99) was achieved, as depicted in Table 7. The calculated values for the eco-indicator EI99 were of 23,102,926.8 and 27,125,724.5 (points/year) for the initial designs of BC3-GLTUF and CA1-GLTHT, respectively, compared to the EI99 values of the intensified versions, which were 16,067,458.6 (points/year) for BC3-GLTUF/I and 23,265,289.5 (points/year) for CA1-GLTHT/I. Likewise, since the columns' diameters of the initial designs were not sized properly, these designs presented higher values of IR compared to the intensified designs. For instance, the IR values of the initial designs BC3-GLTUF and CA1-GLTHT were of  $5.82 \times 10^{-4}$  (Probability/year) and  $6.18 \times 10^{-4}$  (Probability/year), respectively, compared to the ones of the intensified designs that were  $5.81 \times 10^{-4}$  (Probability/year) for BC3-GLTUF/I and  $6.137 \times 10^{-4}$  (Probability/year) for CA1-GLTHT/I. This also is reflected on the economic metrics. For instance, since the intensified separation units for BC3-GLTUF present smaller equipment sizes and lower energy consumption, a lower TCOM per gasoline gallon equivalent of \$6.76/gge was achieved compared to \$6.79/gge for the

**Table 5**  
Design parameters and performance indexes for BC3-GLTUF and BC3-GLTUF/I (Intensified configuration).

[illegible]

Table 6

Additional design parameters considered for the fractionation column and coupled stripper (C.9) for BC3-GLTUF.

| Design parameters           | C.9   | C.9/I |
|-----------------------------|-------|-------|
| Steam inlet flowrate (kg/h) | 12000 | 12065 |
| Liquid Draw                 | 10    | 12    |
| Overhead return             | 8     | 8     |
| Stripper-Number of stages   | 4     | 5     |

initial designs. Likewise, a higher return on investment of 21(%/y) was achieved compared to the 18(%/y) calculated for the initial design.

For the intensified design CA1-GLTHT/I lower TCOM<sub>GGE</sub> and higher ROI values were calculated. For instance, the TCOM<sub>GGE</sub> was reduced from \$5.59/gge to \$5.55/gge and the ROI increased from 19(%/y) to 22(%/y).

Moreover, concerning the green chemistry metrics, the optimal design of the process allows to improve the recovery and conversion of the product streams without the use of excess reactants and therefore, a reduction of wastes is achieved. The less amount of wastes produced lead to an increase of the process efficiency and thus, a reduction on the E-Factor and MI. For BC3-GLTUF, the E-Factor and MI values were of  $1.259 \left( \frac{\text{kg}}{\text{kg}} \right)$  and  $2.259 \left( \frac{\text{kg}}{\text{kg}} \right)$  compared to  $1.253 \left( \frac{\text{kg}}{\text{kg}} \right)$  and  $2.253 \left( \frac{\text{kg}}{\text{kg}} \right)$  calculated for the intensified configuration BC3-GLTUF/I. The same was observed for CA1-GLTHT, which E-Factor and MI values were  $1.094 \left( \frac{\text{kg}}{\text{kg}} \right)$  and  $2.094 \left( \frac{\text{kg}}{\text{kg}} \right)$ , respectively, compared to the intensified design that presented E-Factor values of  $1.092 \left( \frac{\text{kg}}{\text{kg}} \right)$  and MI values of  $2.092 \left( \frac{\text{kg}}{\text{kg}} \right)$ .

Furthermore, regarding the comparison between both intensified processes, BC3-GLTUF/I presents lower EI99 and IR compared to CA1-GLTHT/I. The main reason why CA1-GLTHT/I presents higher IR is because it presents higher production of transportation fuels and thus, since the calculation of the IR considers instantaneous and continuous chemical releases, it is obvious that if the inlet flow of the unit operations increase then the IR will increase. Therefore, in the case of an event, greater affectation and duration of the incidents will be incurred due to more source of toxic releases, fires, and explosions.

Regarding the EI99, the condenser and reboiler duties reported in [Table 7](#) for CA1-GLTHT/I for most of the columns are higher compared to the ones reported in [Table 5](#) for BC3-GLTUF/I. This is observed because an increase on the energy consumption is presented due to steam and electricity consumption to recover the higher product flow-rates produced by CA1-GLTHT/I. Likewise, in CA1-GLTHT/I most of the columns (C.2, C.3, C.5 and C.8) present greater number of stages compared to BC3-GLTUF/I and thus, more steel to build the equipment is required and an increase on the EI99 is presented.

On the other hand, BC3-GLTUF/I presents higher E-Factor and MI, which translates to less process efficiency due to higher production of wastes. The process efficiency can be reflected in the total biofuels production since BC3-GLTUF/I presents a diesel production of 23,191.9 kg/h and a gasoline production of 27,509.5 kg/h, which in total is lower compared to the total production of CA1-GLTHT/I (diesel production of 14,399.9 kg/h and a gasoline production of 39,177.2 kg/h). The higher productivity achieved in CA1-GLTHT/I is also reflected on the TCOM<sub>GGE</sub> of \$5.55/gge and the higher ROI of 22 (%/y), as reported in [Table 7](#). Therefore, due to the process efficiency and economic metrics the CA1-GLTHT/I is the optimal process route for the maximization of the production of biofuels and ROI, and for the minimization of the wastes and the TCOM<sub>GGE</sub>. The detailed stream table for CA1-GLTHT/I is presented in Table S1, and the corresponding process flowsheet set-up in Aspen Plus is depicted in Fig. S1.



**Table 7**  
Design parameters and performance indexes for CA1-GLTHT and CA1-GLTHT/I (Intensified configuration).

| Design parameters             |              |                                       |       |         |       |       |       |                   |       |         |              |         |       |                                       |       |        |       |  |  |
|-------------------------------|--------------|---------------------------------------|-------|---------|-------|-------|-------|-------------------|-------|---------|--------------|---------|-------|---------------------------------------|-------|--------|-------|--|--|
| C.1                           | C.1/I        | C.2                                   | C.2/I | C.3     | C.3/I | C.4   | C.4/I | C.5               | C.5/I | C.6     | C.6/I        | C.7     | C.7/I | C.8                                   | C.8/I | C.9    | C.9/I |  |  |
| Number of stages              | 5            | 6                                     | 20    | 24      | 20    | 20    | 13    | 16                | 12    | 16      | 10           | 9       | 60    | 52                                    | 27    | 39     | 15    |  |  |
| Feed stage                    | 5            | 6                                     | 9     | 14      | 12    | 9     | 5     | 9                 | 10    | 10      | 3            | 4       | 36    | 39                                    | 15    | 22     | 15    |  |  |
| Reflux ratio                  | —            | —                                     | 2     | 1.1     | 6     | 5.2   | 3     | 2.9               | 1     | 0.82    | 5            | 5       | 3     | 2.7                                   | 6     | 4.6    | —     |  |  |
| Bottom flowrate (kg/h)        | —            | —                                     | 25245 | 25225.4 | 16898 | 16896 | 45110 | 45110.7           | 30350 | 30302.6 | 24210        | 24216.1 | 9017  | 9035.7                                | 5256  | 5243.8 | 3550  |  |  |
| Diameter (m)                  | 5.7          | 2.6                                   | 11.2  | 4.2     | 3.5   | 1.5   | 3.2   | 3.3               | 1.7   | 2.1     | 2.3          | 2.1     | 1.6   | 1.6                                   | 1.7   | 1.4    | 7.1   |  |  |
| Condenser duty (kW)           | —            | —                                     | 56703 | 32325   | 6057  | 5303  | 11670 | 11361             | 3225  | 2962    | 7684         | 7615    | 3699  | 3372                                  | 2949  | 2355   | 37163 |  |  |
| Reboiler duty (kW)            | —            | —                                     | 67608 | 43202   | 7243  | 6466  | 17736 | 17437             | 2416  | 2151    | 10207        | 10228   | 3813  | 3493                                  | 3075  | 2479   | —     |  |  |
| Water inlet flowrate (kmol/h) | 23151.9      | 23465.4                               |       |         |       |       |       |                   |       |         |              |         |       |                                       |       |        |       |  |  |
| Performance indexes           |              |                                       |       |         |       |       |       |                   |       |         |              |         |       |                                       |       |        |       |  |  |
| CA1-GLTHT                     |              |                                       |       |         |       |       |       |                   |       |         |              |         |       |                                       |       |        |       |  |  |
| CA1-GLTHT/I                   |              |                                       |       |         |       |       |       |                   |       |         |              |         |       |                                       |       |        |       |  |  |
| EI99 (Points/y)               | 27,125,724.5 | E-factor (kg/kg)                      |       |         | 1.094 |       |       | EI99 (Points/y)   |       |         | 23,265,289.5 |         |       | E-factor (kg/kg)                      |       |        | 1.092 |  |  |
| IR (Probability /y)           | 0.000618     | MI (kg/kg)                            |       |         | 2.094 |       |       | IR Probability/y) |       |         | 0.0006137    |         |       | MI (kg/kg)                            |       |        | 2.092 |  |  |
| ROI (%/y)                     | 19           | TCOM <sub>GGE</sub> (50000 kg/h feed) |       |         | 5.59  |       |       | ROI (%/y)         |       |         | 22           |         |       | TCOM <sub>GGE</sub> (50000 kg/h feed) |       |        | 5.55  |  |  |

## Declaration of Competing Interest

The authors report no declarations of interest.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.cep.2021.108327>.

## References

- [1] P. Ibarra González, B.-G. Rong, Integrated methodology for optimal synthesis of lignocellulosic biomass-to-liquid fuels production processes: 2. Superstructure MINLP modeling and evaluation for optimal biofuels process synthesis and integration, *Ind. Eng. Chem. Res.* 59 (2020) 14898–14913, <https://doi.org/10.1021/acs.iecr.0c02903>.
- [2] J.P.M. Sanders, J.H. Clark, G.J. Harmsen, H.J. Heeres, J.J. Heijnen, S.R.A. Kersten, W.P.M. van Swaaij, J.A. Moulijn, Process intensification in the future production of base chemicals from biomass, *Chem. Eng. Process. Process Intensif.* 51 (2012) 117–136, <https://doi.org/10.1016/j.cep.2011.08.007>.
- [3] D.F. Rivas, E. Castro-Hernández, A.L. Villanueva Perales, W. van der Meer, Evaluation method for process intensification alternatives, *Chem. Eng. Process. Process Intensif.* 123 (2018) 221–232, <https://doi.org/10.1016/j.cep.2017.08.013>.
- [4] S. Sitter, Q. Chen, I.E. Grossmann, An overview of process intensification methods, *Curr. Opin. Chem. Eng.* 25 (2019) 87–94, <https://doi.org/10.1016/j.coche.2018.12.006>.
- [5] A. Stankiewicz, J.A. Moulijn, Process intensification: transforming chemical engineering, *Chem. Eng. Prog.* 96 (2000) 22–33.
- [6] T. Van Gerven, A. Stankiewicz, Structure, energy, synergy, time—the fundamentals of process intensification, *Ind. Eng. Chem. Res.* 48 (2009) 2465–2474, <https://doi.org/10.1021/ie801501y>.
- [7] B.G. Rong, E. Kolehmainen, I. Turunen, Methodology of conceptual process synthesis for process intensification, *Comput. Aided Chem. Eng.* 25 (2008) 283–288, [https://doi.org/10.1016/S1570-7946\(08\)80052-1](https://doi.org/10.1016/S1570-7946(08)80052-1).
- [8] D.A. Reay, C. Ramshaw, A. Harvey, Process Intensification: Engineering for Efficiency, Sustainability and Flexibility, 2nd ed., Elsevier, 2013 <https://doi.org/10.1016/C2012-0-00253-0>.
- [9] M.H. Barecka, M. Stankiewicz, A. Górak, A novel approach for process retrofitting through process intensification: ethylene oxide case study, *Chem. Eng. Res. Des.* 123 (2017) 295–316, <https://doi.org/10.1016/j.cherd.2017.05.014>.
- [10] C. Gutiérrez-Antonio, A. Bonilla-Petriciolet, Stochastic optimization for process intensification, in: J.G. Segovia-Hernández, A. Bonilla-Petriciolet (Eds.), *Process Intensif. Chem. Eng.*, 1st ed., Springer International Publishing, 2016, pp. 261–277, [https://doi.org/10.1007/978-3-319-28392-0\\_9](https://doi.org/10.1007/978-3-319-28392-0_9).
- [11] W. Barnes, C.-C. Chen, T. Fowler, P. McMahon, A.K. Nagavarapu, D. Shatto, Novel adsorption-based gas treating technology platform for upstream gas separations, *Offshore Technol. Conf., Offshore Technology Conference* (2018), <https://doi.org/10.4043/29001-MS>.
- [12] B.-G. Rong, Synthesis of dividing-wall columns (DWC) for multicomponent distillations—A systematic approach, *Chem. Eng. Res. Des.* 89 (2011) 1281–1294, <https://doi.org/10.1016/j.cherd.2011.03.014>.
- [13] C.E. Torres-Ortega, M. Errico, B.G. Rong, Design and optimization of modified non-sharp column configurations for quaternary distillations, *Comput. Chem. Eng.* 74 (2015) 15–27, <https://doi.org/10.1016/j.compchemeng.2014.12.006>.
- [14] P. Lutze, D.K. Babi, J.M. Woodley, R. Gani, Phenomena based methodology for process synthesis incorporating process intensification, *Ind. Eng. Chem. Res.* 52 (2013) 7127–7144, <https://doi.org/10.1021/ie302513y>.
- [15] S.E. Demirel, J. Li, M.M.F. Hasan, A general framework for process synthesis, integration, and intensification, *Ind. Eng. Chem. Res.* 58 (2019) 5950–5967, <https://doi.org/10.1021/acs.iecr.8b05961>.
- [16] S.E. Demirel, J. Li, M.M.F. Hasan, Systematic process intensification using building blocks, *Comput. Chem. Eng.* 105 (2017) 2–38, <https://doi.org/10.1016/j.compchemeng.2017.01.044>.
- [17] D.K. Babi, P. Lutze, J.M. Woodley, R. Gani, A process synthesis-intensification framework for the development of sustainable membrane-based operations, *Chem. Eng. Process. Process Intensif.* 86 (2014) 173–195, <https://doi.org/10.1016/j.cep.2014.07.001>.
- [18] D.K. Babi, J. Holtbrügge, P. Lutze, A. Gorak, J.M. Woodley, R. Gani, Sustainable process synthesis-intensification, *Comput. Chem. Eng.* 81 (2015) 218–244, <https://doi.org/10.1016/j.compchemeng.2015.04.030>.
- [19] H. Alcocer-García, J.G. Segovia-Hernández, O.A. Prado-Rubio, E. Sánchez-Ramírez, J.J. Quiroz-Ramírez, Multi-objective optimization of intensified processes for the purification of levulinic acid involving economic and environmental objectives, *Chem. Eng. Process. - Process Intensif.* 136 (2019) 123–137, <https://doi.org/10.1016/j.cep.2019.01.008>.
- [20] A. Peltola (Ed.), Finnish Statistical Yearbook of Forestry, 44th ed., 2014.
- [21] J.-O. Loman (Ed.), Swedish Statistical Yearbook of Forestry 2008, 7th ed., Swedish Forest Agency, Jönköping, 2008.
- [22] T. Johansson, Mixed stands in Nordic countries—A challenge for the future, *Biomass Bioenergy* 24 (2003) 365–372, [https://doi.org/10.1016/S0961-9534\(02\)00165-4](https://doi.org/10.1016/S0961-9534(02)00165-4).
- [23] P. Ibarra-Gonzalez, B.-G. Rong, 10. Lignocellulosic biofuels process synthesis and intensification: superstructure-based methodology, *Process Intensif.*, De Gruyter, 2019, pp. 277–325, <https://doi.org/10.1515/9783110596120-010>.
- [24] A. de Klerk, Fischer–Tropsch fuels refinery design, *Energy Environ. Sci.* 4 (2011) 1177, <https://doi.org/10.1039/c0ee00692k>.
- [25] U.S. Betchel, Department of Energy, Aspen Process Flowsheet Simulation Model of a Battelle Biomass-Based Gasification, Fischer–Tropsch Liquefaction and Combined-Cycle Power Plant, 1998.
- [26] Z. Sa, T. Rahardjo, C. Valkenburg, L.J. Snowden-Swan, S.B. Jones, M.A. Machinal, Techno-economic Analysis for the Thermochemical Conversion of Biomass to Liquid Fuels, 2011.
- [27] P. Mponzi, Production of Biofuels by Fischer Tropsch Synthesis, 2011 (Accessed 7 December 2020), <https://lutpub.lut.fi/handle/10024/71973>.
- [28] M. Binder, M. Kraussler, M. Kuba, M. Luisser, Hydrogen from biomass gasification, *IEA Bioenergy*, 2018.
- [29] P.M. Maitlis, A. de Klerk, Greener Fischer–Tropsch Processes for Fuels and Feedstocks, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2013, <https://doi.org/10.1002/9783527656837>.
- [30] Aspen Physical Property System: Physical Property Methods and Models 11.1, 2001.
- [31] V.N. Kabadi, R.P. Danner, A modified Soave-Redlich-Kwong equation of state for water-hydrocarbon phase equilibria, *Ind. Eng. Chem. Process Des. Dev.* 24 (1985) 537–541, <https://doi.org/10.1021/i200030a004>.
- [32] M. Errico, E. Sanchez-Ramirez, J.J. Quiroz-Ramirez, J.G. Segovia-Hernandez, B.-G. Rong, Synthesis and design of new hybrid configurations for biobutanol purification, *Comput. Chem. Eng.* 84 (2016) 482–492, <https://doi.org/10.1016/j.compchemeng.2015.10.009>.
- [33] C. Gutiérrez-Antonio, Multiobjective stochastic optimization of dividing-wall distillation columns using a surrogate model based on neural networks, *Chem. Biochem. Eng. Q.* 29 (2016) 491–504, <https://doi.org/10.15255/CABEQ.2014.2132>.
- [34] R. Storn, Differential Evolution – a Simple and Efficient Heuristic for Global Optimization over Continuous Spaces, 1997, pp. 341–359.
- [35] N.K. Madavan, M. Field, Multiobjective Optimization Using a Pareto Differential Evolution Approach, 2002, pp. 1145–1150.
- [36] F. Glover, Tabu search—Part I, *ORSA J. Comput.* 1 (1989) 190–206, <https://doi.org/10.1287/ijoc.1.3.190>.
- [37] H. Zhang, G.P. Rangaiah, A hybrid global optimization algorithm and its application to parameter estimation problems, *Asia-Pacific J. Chem. Eng.* 6 (2011) 379–390, <https://doi.org/10.1002/apj.548>.
- [38] M. Srinivas, G.P. Rangaiah, Differential evolution with tabu list for solving nonlinear and mixed-integer nonlinear programming problems, *Ind. Eng. Chem. Res.* 46 (2007) 7126–7135, <https://doi.org/10.1021/IE070007Q>.
- [39] G.P. Rangaiah, Stochastic Global Optimization: Techniques and Applications in Chemical Engineering, World Scientific, 2010.
- [40] W.D. Seider, D.R. Lewin, J.D. Seader, S. (Chemical engineer) Widagdo, R. (Rafiqul) Gani, K.M. Ng, Product and process design principles: synthesis, analysis, and evaluation (n.d.).
- [41] M. Goedkoop, R. Spriensma, The Eco-Indicator 99: a Damage Oriented Method for Life Cycle Impact Assessment- Methodology Report, 2001.
- [42] M. Goedkoop, R. Spriensma, The Eco-Indicator 99 a Damage Oriented Method for Life Cycle Impact Assessment- Annex, 2001.
- [43] M. Errico, E. Sanchez-Ramirez, J.J. Quiroz-Ramirez, B.-G. Rong, J.G. Segovia-Hernandez, Multiobjective optimal acetone–butanol–ethanol separation systems using liquid–liquid extraction-assisted divided wall columns, *Ind. Eng. Chem. Res.* 56 (2017) 11575–11583, <https://doi.org/10.1021/acs.iecr.7b03078>.
- [44] Center for Chemical Process Safety, Guidelines for Chemical Process Quantitative Risk Analysis, 2nd ed., John Wiley & Sons, Inc., Hoboken, NJ, USA, 2010 <https://doi.org/10.1002/9780470935422>.
- [45] C. Jiménez-González, D.J.C. Constable, C.S. Ponder, Evaluating the “Greenness” of chemical processes and products in the pharmaceutical industry—A green metrics primer, *Chem. Soc. Rev.* 41 (2012) 1485–1498, <https://doi.org/10.1039/C1CS15215G>.
- [46] R.A. Sheldon, The e factor: fifteen years on, *Green Chem.* 9 (2007) 1273–1283, <https://doi.org/10.1039/b713736m>.
- [47] M. (Mike) Lancaster, Green Chemistry: an Introductory Text, 3rd ed., Royal Society of Chemistry, 2016.
- [48] D.J.C. Constable, A.D. Curzons, V.L. Cunningham, Metrics to ‘green’ chemistry—Which are the best? *Green Chem.* 4 (2002) 521–527, <https://doi.org/10.1039/B206169B>.
- [49] K. Deb, Multi-objective optimisation using evolutionary algorithms: an introduction. Multi-Objective Evol. Optim. Prod. Des. Manuf., Springer, London, 2011, pp. 3–34, [https://doi.org/10.1007/978-0-85729-652-8\\_1](https://doi.org/10.1007/978-0-85729-652-8_1).
- [50] A.P. Dicks, A. Hent, The E Factor and Process Mass Intensity, Springer, Cham, 2015, pp. 45–67, [https://doi.org/10.1007/978-3-319-10500-0\\_3](https://doi.org/10.1007/978-3-319-10500-0_3).