Data envelopment analysis approach to targeting in sustainable chemical process design: Application to liquid fuels

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Abstract. This paper presents a framework for combining data envelopment analysis with process systems engineering tools, aiming to improve the sustainability of chemical processes. Given a set of chemical processes, each characterised by performance indicators, the framework discriminates between efficient and inefficient processes regarding those indicators. We develop an approach to quantifying the closest targets for an inefficient process to become efficient, while preventing unrealistic targets by accounting for its thermodynamic limitations represented as mass and energy flow constraints. We demonstrate the capabilities of the framework by assessing a methanol production process with captured CO_2 and fossil-based H_2, in comparison to ten alternatives. The methanol fuel is found to be suboptimal in comparison with other fuels. Making it competitive would require a significant (unrealistic in the short term) reduction in H_2 price. Alternatively, the methanol fuel could become competitive upon combining fossil-based H_2 with sustainably produced H_2 via wind-powered electrolysis.

Keywords: data envelopment analysis; chemical process targeting; sustainability; practical closest targets; process synthesis; liquid transportation fuels

Introduction

Nowadays chemical engineers are facing the challenge of embedding sustainability principles into the design of new, or the retrofit of existing, processes and products[1–8]. The area of process design has been receiving increasing attention in this context, given its potential role in underpinning the transition towards a greener chemical industry. It is well known that decisions taken at an early stage of development of chemical systems can have a dramatic influence on their techno-economic and environmental performance, making process design paramount to achieving sustainable development goals [9–11].

Incorporating sustainability principles into process design is nevertheless challenging, as it requires the simultaneous consideration of a wide range of economic, environmental and social criteria[12,13]. Defining adequate sustainability metrics in the form of key performance indicators (KPIs) is essential to effectively support the decision process[14,15]. The need to consider all of these KPIs simultaneously leads to complex multi-criteria decision-making problems, whereby identifying the best decisions over a wide range of potential alternatives becomes critical. A handful of techniques and tools have been developed by the Process Systems Engineering community to assist in this type of problems[4,16–18]. Among those techniques, multi-objective optimisation (MOO) has recently emerged as the preferred paradigm to design and plan more sustainable chemical systems[1,4,18,19], but its application to process design presents several limitations. Firstly, the complexity of MOO increases with the number of objectives, both in terms of computational burden and the difficulty of analysing and interpreting Pareto optimal solutions[20–22]. Secondly, in the context of process design, MOO models tend to focus on a single chemical route and to optimize decisions pertaining to the plant topology and operating conditions only. Instead, one may wish to compare multiple designs based on different chemical pathways, while simultaneously considering multiple indicators. Lastly, in process and product design, and particularly in superstructure optimisation, the emphasis is always on identifying a globally optimal solution from a set of feasible designs, often in the sense of a unique objective [23,24]. Suboptimal designs are systematically discarded without trying to understand the reasons of their

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underperforming compared to other designs. This information could provide valuable insight on how to improve emerging chemical routes that are deemed suboptimal, but have the potential to become optimal via targeted modifications.

Bearing these limitations in mind, this paper proposes a framework combining data envelopment analysis (DEA) and process simulation in order to assess different process flowsheets in terms of multiple KPIs, while also providing clear quantitative guidelines on how to improve potential suboptimal designs. This framework is meant to complement standalone MOO tools to assist in the transition towards a greener chemical industry.

DEA is a non-parametric linear programming (LP) method, originally introduced in operations research and economics[25–28]. It has recently found applications in the environmental assessment of products and processes[29–33]. Broadly speaking, DEA quantifies the relative efficiency of a set of comparable decision-making units (DMUs, the equivalent of chemical processes herein) that transform multiple inputs into outputs (the equivalent of sustainability KPIs herein). DEA allows discrimination between efficient (optimal) and inefficient (suboptimal) DMUs by computing an efficiency score for each DMU. DEA furthermore computes quantitative targets for an inefficient DMU to become efficient, by projecting it onto the frontier made by the efficient DMUs.

The original DEA[25,34] was not developed to assess chemical processes, and its application in the chemical industry has remained scarce so far[32,35]. Notwithstanding its capabilities, DEA presents two shortcomings with regards to computing improvement targets, which could hinder its direct application to process design: the usual radial projection approach could target a point on the efficiency frontier that would require significant process modifications to reach, as opposed to a closest projection approach; and this target may be unattainable in practice since the thermodynamic limitations of the underlying process system are not taken into account during the projection. Herein, we shall tailor DEA to address the specific needs of the process design problem, with a view to providing meaningful and practical improvement targets for suboptimal designs. Notice that in the context of chemical engineering, the term targeting traditionally refers to the identification of limits

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(typically thermodynamic) that cannot be exceeded by any design alternative [36]. These targets often apply to subparts of a flowsheet, such as the minimum utilities requirements in heat integration[37–39], maximum yields in reactor networks[40,41], and minimum freshwater consumption in water exchange networks[42,43]. As will be explained in more details later on, we take a broader view of targeting here, based on benchmarking alternatives against one another to establish performance targets according to multiple criteria. To the best of our knowledge, this work is the first of its kind to apply such targeting in chemical process design for sustainability. In the reminder of the paper, we introduce a motivating example and use it to illustrate the limitations of existing DEA in process design and the workings of the proposed DEA model for targeting of chemical processes. Then, we demonstrate the capabilities of our approach on a case study assessment of liquid fuels for transportation.

Targeting for sustainable process and product design: motivating example

To motivate our approach, we consider the design of a new chemical process for producing a given amount of final product (functional unit of 1 kg used as reference in the calculations). This chemical route consumes 2.84 kg of raw material and 1.01 MJ of energy for each unit of product. Its environmental impact is measured in terms of the global warming potential per unit of raw material and unit of energy, which are 0.57 kgCO_2eq/kg and 3.35 kgCO_2eq/MJ, respectively; and the unit costs of raw material and energy are 0.94 US$/kg and 0.32 US$/MJ, respectively. The process furthermore has a theoretical minimal consumption of raw material of 1.25 kg and a theoretical minimal energy requirement of 1.01 MJ for each unit of product, respectively dictated by the stoichiometry of the reaction and the minimum utilities consumption.

Given this information, we are interested in assessing this new design (denoted by G) in comparison with six existing process alternatives (denoted by A – F), which may follow different chemical routes. All of these processes are assessed in terms of two KPIs, representing a specific cost (measured in US$) and an environmental impact (global warming potential, measured in kgCO_2eq) in reference to the functional unit of 1 kg of final product (see Table 1). We reiterate that all seven

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processes produce the same amount of final product, but may follow different routes involving specific unit operations, equipment, etc.

In our capacity as decision-makers, we would like to compare the new design G with the other routes A – F and elucidate whether the former can be economically and environmentally (and, when possible, socially as well) competitive in the market. If the new design G were to be identified as non-competitive with respect to the other options, we would furthermore like to set improvement targets in order to make it a competitive option. Therefore, the main questions we wish to address here are:

(i) How might we decide which chemical processes perform best when both KPIs (cost and environmental impact) are considered simultaneously?

(ii) How might we improve a suboptimal process design in order to make it competitive with other existing efficient routes?

The approach presented in the following section combines DEA with process simulation tools in order to shed light on these two questions. The idea is to develop a simplified model of the process under investigation, e.g. based on mass and energy flow inventories, and introduce it as constraints in a DEA model formulation to provide both nearest and realistic targets for that process.

Note that MOO fails to answer the foregoing questions. Firstly, because MOO aims to generate solutions within the limits of some constraints, whereas the alternatives are already given in our context. Secondly, because MOO simply discards suboptimal alternatives during the search, which does not allow for a further analysis of these alternatives.

To contextualise the use of DEA in the field of chemical engineering, henceforth we will consider every chemical process to be a DMU, characterised by several (economic, environmental or social) KPIs that capture the sustainability performance of the processes all together (see Figure 1). In DEA terminology, these KPIs will be categorised as either inputs or outputs, and then aggregated into a single overall performance measure, called efficiency score, which provides a means of calculating improvement targets for each KPI in return.

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Methodology

This section starts with a review of the traditional DEA approach, where we highlight its limitations for process design applications. In response to this we propose a novel formulation, where a simplified model (surrogate) derived from process simulation is introduced as constraints in a nearest-projection type DEA model. We also illustrate these concepts step-by-step with the motivating example introduced earlier.

Traditional DEA approach

DEA is a data-oriented, non-parametric approach based on mathematical programming for the assessment of the relative efficiency a set of peer entities, referred to as decision-making units (DMUs)[25,26]. Each DMU converts multiple inputs into multiple outputs, where an input traditionally refers to an indicator to be minimised and an output to an indicator to be maximised. DEA provides two main pieces of information: efficiency scores and improvement targets. The first step of DEA entails the construction of a polyhedral envelope, called *efficient frontier* or *best-practise frontier*, which comprises all the Pareto-optimal units; that is, non-dominated units producing more of certain outputs while using less of certain inputs. A DMU lying on the efficient frontier is said to be *efficient*, otherwise it is deemed *inefficient*. In the second step, DEA determines quantitative targets for an inefficient unit to become efficient, via the projection of that unit onto the best-practise frontier, so it is no longer dominated by any other units. Owing to its flexibility, ease of use and decision-aiding capabilities, DEA has been applied to a wide variety of systems, including hospitals, universities, cities, banks, countries, molecules and technologies[44–48].

The original DEA derives from the concept of efficiency[49], broadly defined as the ratio between weighted outputs and weighted inputs in a production entity. Given a set of n DMUs ($k = 1 \ldots d$), each consuming m inputs $x_{k,i}\,(i = 1 \ldots I)$ and generating n outputs $y_{k,j}\,(j = 1 \ldots J)$, the question about whether or not the DMU ℓ is efficient can be answered via the solution of the following CCR factional model[27]:

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$$\theta_\ell^* := \max \frac{\sum_{j=1}^{J} v_j y_{\ell,j}}{\sum_{i=1}^{I} u_i x_{\ell,i}} \quad (1)$$

$$\text{s.t. } \frac{\sum_{j=1}^{J} v_j y_{k,j}}{\sum_{i=1}^{I} u_i x_{k,i}} \leq 1,\ k = 1 \ldots K,\ k \neq \ell \quad (2)$$

$$u_i, v_j \geq 0,\ i = 1 \ldots I,\ j = 1 \ldots J \quad (3)$$

where u_i and v_j denote the linear weights of outputs and inputs, which are treated as variables to be optimised; and the relative efficiency score θ_ℓ^* indicates whether the DMU ℓ is efficient ($\theta_\ell^* = 1$) or inefficient ($\theta_\ell^* < 1$) in comparison to the other DMUs. The best-practice frontier consists of the subset of all efficient DMUs and may be used as a benchmark to define improvement targets for the inefficient units.

The CCR fractional model (1)-(3) is nonlinear, but it may be conveniently reformulated into an equivalent linear program (LP) by applying fractional programming and duality theory[26,27]. The following model is commonly known as the input-oriented dual CCR model[27]:

$$\theta_\ell^* := \min\ \theta_\ell - \varepsilon\left(\sum_{i=1}^{I} S_i^- + \sum_{j=1}^{n} S_j^+\right) \quad (4)$$

$$\text{s.t. } \sum_{k=1}^{K} \lambda_k x_{k,i} = \theta_\ell x_{\ell,i} - S_i^-,\ i = 1 \ldots I \quad (5)$$

$$\sum_{k=1}^{K} \lambda_k y_{k,j} = y_{\ell,j} + S_j^+,\ j = 1 \ldots J \quad (6)$$

$$\lambda_k \geq 0,\ k = 1 \ldots K \quad (7)$$

$$S_i^- \geq 0,\ i = 1 \ldots I \quad (8)$$

$$S_j^+ \geq 0,\ j = 1 \ldots J \quad (9)$$

In addition to indicating whether or not the DMU ℓ is efficient based on the relative efficiency score θ_ℓ^*, the optimal variable values λ_k, S_i^- and S_j^+ provide improvement targets in case this DMU is inefficient[50]. Positive weights $\lambda_k > 0$ are attached to the subset of efficient DMUs against which the inefficient DMU ℓ is compared, called the reference set or peer group R_ℓ of DMU ℓ. These weights yield a linear combination of efficient DMUs, which corresponds to the radial projection of the DMU ℓ onto the best-practise frontier. The slacks variables S_i^- (resp. S_j^+) represent the surplus amount by which an input (resp. output) could be reduced (resp. increased) to become a non-dominated solution,

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i.e. a strongly efficient DMU[25,26,51]. The infinitesimal $\varepsilon > 0$ in the objective function (Eq. 4) pre-empts the optimisation of the slacks S_i^- and S_j^+. When the optimal efficiency score is $\theta_\ell^* = 1$ and the slacks S_i^- and S_j^+ are all equal to zero, the DMU ℓ is said to be strongly efficient; with an optimal efficiency score of $\theta_\ell^* = 1$ but one or more non-zero slacks S_i^- and S_j^+, the DMU ℓ is said to be weakly efficient. The part of the best-practise frontier comprised of facets interpolating between strongly efficient DMUs is called the strongly efficient frontier, and the remaining part comprised of unbounded facets constitutes the weakly efficient frontier (see Figure 2 for an illustration). Lastly, when the optimal efficiency score is $\theta_\ell^* < 1$ and the slacks S_i^- and S_j^+ are all equal to zero, the radial projection of the DMU ℓ lies on the strongly efficient frontier; with an optimal efficiency score of $\theta_\ell^* < 1$ and one or more non-zero slacks S_i^- and S_j^+, the radial projection of the DMU ℓ lies on the weakly efficient frontier. The corresponding hypothetical targets for the inputs and outputs along this radial projection are given by:

$$x_{\ell,i}^{\text{proj}} = \theta_\ell^* x_{\ell,i} - S_i^- = \sum_{k \in R_\ell} \lambda_k x_{k,i} \tag{10}$$

$$y_{\ell,j}^{\text{proj}} = y_{\ell,j} - S_j^+ = \sum_{k \in R_\ell} \lambda_k y_{k,j} \tag{11}$$

All of these DEA concepts and principles will be illustrated below for the motivating example introduced earlier.

Note that the LP model (4)-(9) is input-oriented (IO) and of *constant returns to scale* (CRS) type, since an inefficient unit is turned into efficient through a proportional radial reduction of its inputs, while keeping the same proportional level of outputs. Alternative output-oriented (OO) models may be considered instead, which maximise the outputs while keeping the inputs constant. The efficiency frontier is identical in both IO and OO models, yet the targets and reference sets for the inefficient units can differ. Others DEA models are of *variable returns to scale* (VRS) type, whereby the inputs and outputs are no longer required to change proportionally. For instance, a VRS type model may be derived from a CRS type one by adding the scalar linear constraint $\sum_{k=1}^{K} \lambda_k = 1$ into the LP

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dual CCR model (Eqs. 4-9). Ultimately, the selection of the appropriate DEA model is of course dependent on the case study at hand and the main purpose of the analysis[25,44,52,53].

In the context of process synthesis and design, inputs often represent intakes of the process to be minimised (undesirable) while outputs are outlets to be maximised (desirable). There are exceptions to this rule nonetheless, such as pollutant emissions which are outlets that need minimising. In applying DEA as part of a life cycle assessment (LCA), it is convenient to normalize all of the efficiency indicators with respect to a functional unit, e.g. representing the production of 1 kg of product. Furthermore, this functional unit may be considered as the sole DMU output, with all the other efficiency metrics being regarded as DMU inputs via ad hoc linear transformations[53–57]. It is important to note that such a normalization does not affect the DEA results as radial projections are unit invariant[51,58], and makes a VRS type model with constraint and a CRS type model identical.

Motivating example revisited: limitations of traditional DEA

We apply the input-oriented dual CCR model (Eqs. 4-9) to the motivating example introduced earlier (Table 1). In reference to the functional unit, we define the production indicator of 1 kg as the only output. Then, we treat both the cost and GWP as inputs to be minimised, despite the second being an undesirable output of the process[59].

According to the DEA results in Figure 2, the designs A, B, C and D are efficient ($\theta_\ell^* = 1$) since neither of these units have both a higher cost and higher GWP than any other unit (for the same output level). These units correspond to the vertices of the strongly efficient frontier and can be used as benchmarks for the inefficient designs. Conversely, the designs E, F and G are inefficient ($\theta_\ell^* < 1$) since they have a higher cost and GWP than one or more units on the efficient frontier A – D; that is, they are dominated.

Take the inefficient unit G as an example. The hypothetical target for G to become efficient is obtained via radial projection onto the efficiency frontier, which gives rise to the hypothetical unit g. The efficiency score of $\theta_{\mathrm{G}}^* = 0.75$ quantifies the ratio between the distance $\overline{\mathrm{Og}}$ from the projected target to the origin and the distance $\overline{\mathrm{OG}}$ from the actual unit to the origin. The hypothetical design g

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is a linear combination of the efficient designs B and C, which define the peer group R_{G} for G. The weights in this linear combination are computed as $\lambda_{\mathrm{B}} = \lambda_{\mathrm{C}} = 0.5$, and so reducing both the cost and GWP of the design G by 25%, that is down to 2.25 US$ and 3.75 $kgCO_2eq$, would make G competitive with B and C.

In some cases, the radial projection may lead to weakly efficient units, as in the case of the design E. The projection of E lies on the weakly efficient frontier since it is dominated by A. The slack variable for the cost is equal to $S^{-}_{\mathrm{cost}} = 1\ \mathrm{US\$}$ at this point, indicating the need for a further cost reduction of 1.00 US$ before the projection can become strongly efficient; the corresponding target e is identical to the design A in this case.

Clearly, the targets derived from DEA can play a key role in process design by spotting weaknesses of candidate processes. Unfortunately, two major limitations arise on applying the standard DEA to the assessment of chemical flowsheets. Firstly, a radial projection might not be the best choice since the projected solutions could lie far away from the original operating conditions of the unit and thus require drastic changes. Alternative projections could be employed instead, e.g. based on other metrics[60–66]. Secondly, and perhaps more importantly, a projected target could be unreachable in practice since the entire DEA study is carried out using data points only, without any knowledge about the physical limits of the underlying process system.

Turning our attention back to the motivating example and considering the theoretical minimum consumption of raw material and energy, we find that the minimal attainable GWP is $1.25 \times 0.57 + 1.01 \times 3.35 = 4.1\ \mathrm{kgCO_2eq}$. Therefore, the radial projection target of 3.75 $kgCO_2eq$ cannot be reached here. This calls for a new DEA model that is tailored to process synthesis and design, whereby more information about the process is exploited to render the targets as realistic as possible. The following section describes one such framework in order to overcome these two limitations.

Novel DEA approach tailored to process synthesis and design

The proposed DEA framework comprises three steps, which are depicted in Figure 3 and detailed next.

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Step 1. The first step consists of gathering information from a detailed process simulation of the candidate design in order to develop a simplified input-output model representation to be used in the DEA model in Step 2. The detailed simulation can be conducted in any process simulation environment, such as Aspen HYSYS®[67] or gPROMS[68]. The simplified input-output model describes the elementary mass and energy streams entering and leaving the control system. In essence, these equations should relate a set of elementary mass and energy flows Z_f ($f = 1 \ldots F$) to the KPIs, treated either as DMU inputs $x_{\ell,i}(\mathrm{Z}_1,\ldots,\mathrm{Z}_F)$ or outputs $y_{\ell,j}(\mathrm{Z}_1,\ldots,\mathrm{Z}_F)$. For instance, Z_f could comprise the flows of raw materials and utilities (e.g. thermal energy and electricity) in connection to DMU inputs, or products, emissions and wastewater in connection to DMU outputs. In turn, thermodynamic limits in the system can be enforced by restricting the flows, e.g. in the form of inequality constraints $g(\mathrm{Z}_1,\ldots,\mathrm{Z}_F) \leq 0$, and these restrictions are then reflected on the KPIs. For instance, these constraints could represent the minimum amount of raw materials and energy that the process would consume under the assumption of a 100% yield and a full heat integration of streams to meet the minimum utility requirements dictated by a composite curve. In practice, one may also wish to vary certain parameters, such as unit prices or impact intensities, based on which the KPIs are calculated. Restrictions could be imposed on the range of these parameters, in a similar manner as the inequality constraints on the mass and energy flows before.

Step 2. In the second step, the simplified input-output model from Step 1 is combined with a closest-target DEA model, based on work by Aparicio et al.[63]. Our enhanced DEA model projects inefficient DMUs onto the efficient frontier by minimising the distance to target (according to a given metric), while accounting for the thermodynamic limits of the process so as to prevent unrealistic targets. A certificate of infeasibility for this model is an indication that the candidate design may not be projected onto the efficient frontier within the design envelope dictated by the thermodynamic limits. The model takes the form of a mixed-integer program, either linear (MILP) or nonlinear (MINLP) depending on the nature of the simplified input-output model. Given the of all strongly efficient

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processes and $E \subset \{1,\ldots,K\}$, as determined from the repeated solution of the LP model (4)-(9), the targets for an inefficient DMU $\ell \notin E$ are computed from:

$$\min \sum_{f=1}^{F} \left| \frac{Z_f - Z_f^{\text{ref}}}{Z_f^{\text{ref}}} \right| \tag{12}$$

$$\text{s.t.} \sum_{k \in E} \lambda_k x_{k,i} = x_{\ell,i}(\mathrm{Z}_1,\ldots,\mathrm{Z}_F), \quad i = 1\ldots I \tag{13}$$

$$\sum_{k \in E} \lambda_k y_{k,j} = y_{\ell,j}(\mathrm{Z}_1,\ldots,\mathrm{Z}_F), \quad j = 1\ldots J \tag{14}$$

$$g(\mathrm{Z}_1,\ldots,\mathrm{Z}_F) \leq 0 \tag{15}$$

$$\sum_{i=1}^{I} u_i x_{k,i} = \sum_{j=1}^{J} v_j y_{k,j} + d_k = 0, \quad \forall k \in E \tag{16}$$

$$d_k \leq M(1 - b_k), \quad \forall k \in E \tag{17}$$

$$0 \leq \lambda_k \leq M b_k, \quad \forall k \in E \tag{18}$$

$$b_k \in \{0,1\}, \quad \forall k \in E \tag{19}$$

$$d_k \geq 0, \quad \forall k \in E \tag{20}$$

$$u_i \geq 1, \quad i = 1\ldots I \tag{21}$$

$$v_j \geq 1, \quad j = 1\ldots J \tag{22}$$

The main degrees of freedom in this model are the modified mass and energy flows Z_f in order to make the DMU ℓ efficient. The objective function in Eq. (12) minimises relative deviations between Z_f and the original flows Z_f^{ref}. The improvement targets are enforced in Eqs. (13)-(14), where the weights λ_k have the same interpretation as in the dual CCR model (4)-(9). These targets are constrained by thermodynamic limits in the system via the generic inequality constraints in Eq. (15). The linear constraints in Eq. (16) combined with the big-M constraints in Eqs. (17) and (18) determine the peer group of the DMU ℓ. A binary variable b_k equal to 1 indicates that the DMU k belongs to the peer group, in which case $d_k = 0$ and $\sum_{i=1}^{I} u_i x_{k,i} = \sum_{j=1}^{J} v_j y_{k,j}$, and the corresponding weight λ_k can be adjusted freely (provided that the constant *M* is set to a large enough positive value)[63]. Otherwise, having b_k equal to 0 forces $\lambda_k = 0$ when the DMU k does not belong to the peer group of the DMU ℓ.

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Figure 4 presents a flowchart summarizing the workflow in the second step of the proposed framework (Figure 2), which is broken down into three sub-steps:

- **Step 2.1. Definition and normalization of attributes.** The attributes are classically labelled as inputs or outputs according to whether they are to be maximised (DMU outputs) or minimised (DMU inputs). A tailored approach to sustainability assessment in process synthesis and design entails the selection of a single DMU output, corresponding to the functional unit in LCA; while all of the economic, environmental and social indicators are normalized in reference to the functional unit, possibly with a negative sign to enable their minimisation.
- **Step 2.2. Characterization of efficient frontier.** Determine the set E of (strongly) efficient alternatives from the repeated solution of the dual CCR model (4)-(9). This set serves as benchmark in setting improvement targets for an inefficient candidate design.
- **Step 2.3. Target setting within thermodynamic limits.** Quantify improvement targets for any inefficient design by solving the closest-target mixed-integer optimisation model (12)-(22), which embeds the simplified model obtained in Step 1 of the framework. The targets given by Eqs. (13)-(14) are guaranteed to be consistent with the thermodynamic limits of the process; or, else a certificate of infeasibility is returned, which indicates that the candidate design cannot be projected onto the efficient frontier without violating the process thermodynamic limits.

Step 3. This final step seeks to exploit the results of the previous Step 2 in either one of two ways. In case the closest-target mixed-integer optimisation model (12)-(22) is feasible, one may feed the optimised mass and energy flows back into a detailed process simulator and take further corrective actions as appropriate. Naturally, one could also investigate process updates in order to move beyond the efficient frontier and make a candidate design more sustainable than its peers. If the projection is otherwise proven to be infeasible, one may identify the main factors that prevent the process from reaching the efficient frontier, and be in a position to provide guidelines for further technological developments.

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Motivating example revisited: application of enhanced DEA

We now revisit the motivating example and follow the enhanced DEA framework delineated in Figure 3. In Step 1, we consider a simplified input-output model of the candidate process G relating the GWP indicator and specific cost to the mass and energy flows:

$$x_{\mathrm{G,GWP}} = Z_{\mathrm{rm}} I_{\mathrm{rm}} + Z_{\mathrm{en}} I_{\mathrm{en}} \tag{23}$$

$$x_{\mathrm{G,cost}} = Z_{\mathrm{rm}} C_{\mathrm{rm}} + Z_{\mathrm{en}} C_{\mathrm{en}} \tag{24}$$

$$Z_{\mathrm{rm}} \geq 1.25\ \mathrm{kg/kg} \tag{25}$$

$$Z_{\mathrm{en}} \geq 1.01\ \mathrm{MJ/kg} \tag{26}$$

The GWP impact and cost associated to design G ($x_{\mathrm{G,GWP}}$, $x_{\mathrm{G,cost}}$) in Eqs. (23)-(24) are functions of the elementary flows of raw material (Z_{rm}) and energy (Z_{en}), treated as degrees of freedom next; whereas their respective environmental impact intensities ($I_{\mathrm{rm}} = 0.57\ \mathrm{kgCO_2eq/kg}$, $I_{\mathrm{en}} = 3.35\ \mathrm{kg\ CO_2eq/MJ}$) and unit cost ($C_{\mathrm{rm}} = 0.94\ \mathrm{US\$/kg}$, $C_{\mathrm{en}} = 0.32\ \mathrm{US\$/MJ}$) are treated as parameters in the model. The restrictions in Eqs. (25)-(26) account for the physical limits of design G, which were described earlier in the example definition.

The results of Step 2 are presented in Figure 5. We first solve the dual CCR model (4)-(9) to characterize the efficient frontier. The designs A – D are found to be efficient, while the designs E – G are inefficient. To quantify the feasible improvement targets and the peer designs to be used as benchmark, we apply the enhanced closest-targets model (12)-(22) and compare the projected point to the radial projection from model (4)-(9). We have reported earlier that the radial projection target (point g) has a GWP impact of 3.75 $kgCO_2eq$ and a specific cost of 2.25 US$, which lies outside the theoretical limits of the system. By contrast, the enhanced closest-target DEA (point G^*) yields a GWP impact of 4.42 $kgCO_2eq$ and a specific cost of 2.03 US$. The latter target is consistent with the physical limits that govern the process and accordingly, the candidate design G may reach the efficient frontier under realistic flow conditions. Nevertheless, since a simplified input-output representation of the flowsheet is employed in the calculations, these targets could still be infeasible in the original simulation model. More detailed models could be used instead in the enhanced DEA problem (12)-

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(22) to yield more reliable predictions, yet at the price of introducing nonlinearity and nonconvexity in the optimisation. Note that target G^* reaches the efficient frontier, and so these targets will ensure that G becomes competitive.

Case study in liquids fuels for transportation

We illustrate the capabilities of the enhanced DEA framework through the sustainability assessment of liquid fuels for transportation, which could be potentially employed in the automotive fleet powered by internal combustion engines. According to the International Energy Agency[69], the total volume of emissions has kept increasing over the last two decades, showing an average annual growth rate of 2.2% since 2002. Out of the total CO_2 emission reported in 2015, the transport sector was responsible for 24%, which represents 7.7 $GtCO_2eq$[69].

Our main objective is to assess methanol with H_2 derived from fossil fuels, and compare it with ten alternative transportation liquid fuels (see Table 3), including gasoline, bio-gasoline, Fischer-Tropsch naphtha from natural gas, ethanol produced from three different processes and feedstocks (i.e. corn, sugarcane, switchgrass), liquid hydrogen produced from three fuel sources (i.e. natural gas, coal, biomass), and methanol employing electrolysis powered by wind as a source of H_2. The methanol production process of interest is based on work by Gonzalez-Garay and Guillén-Gosálbez[70], where CO_2 captured from power plants using amines reacts with H_2 generated from the cracking of fossil fuels[71]. If this process were found to be inefficient, a further objective is to quantify practical improvement targets that would make it competitive.

The scope of our analysis follows a well-to-wheel (WTW) approach, which is further decomposed into well-to-pump (WTP) and pump-to-wheel (PTW) contributions[72]. This approach assesses a fuel from the procurement of its feedstock until its combustion in the engine, thus neglecting the emissions associated with the manufacturing and recycling of the vehicles.

Two indicators are used to assess the performance of the liquid fuels: the total driving cost (DC) and the global warming potential (GWP) per driven mile. Both indicators are defined as inputs to

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be minimised, while the output is set to 1 driven-mile. The choice of 1 driven-mile as the functional unit (rather than 1 kg of fuel) is motivated by the need to compare different types of fuels fulfilling the same function. Notice that GWP is physically an undesirable output of the process, but we treat it as a desirable input to be minimised instead, based on earlier considerations. This analysis could be extended by considering other economic, environmental and social aspects.

The DC of fuel comprises the total costs of production (TC) and the transportation costs (TrC). The former includes the costs associated with procuring the fuel feedstock, its transportation to the conversion facility as well as the capital and operation and maintenance costs of the conversion facility. The second includes the capital and infrastructure costs required to transport the fuel from the refinery to end-users. Cost data for all the fuels were sourced from the International Energy Agency report on production cost of alternative liquid fuels[73]. For our methanol process of interest, the TC was estimated from detailed process simulations[70], while the TrC was obtained from a report of the International Energy Agency report[73].

The GWP indicators that quantify the environmental impact of the fuels follow a WTW approach and account for the emissions of CO_2, CH_4 and NO_x, expressed as CO_2-equivalent and projected to 100 years. GWP data for all the fuels were obtained from the GREET Software®[72], except for methanol employing electrolysis (85-$MeOH_{re}$) which is sourced from the LCA study by Bhandari et al.[74]. For our methanol process of interest, WTP emissions were calculated based on a simplified model derived from detailed process simulations[70], and their associated environmental impact intensities were sourced from the Ecoinvent database[71]. PTW emissions were computed from the Greet Software[72]. More details about the simplified input-output models are given in the results section below.

Results

We present and discuss the case study results by following the steps in the enhanced DEA framework (Figure 3 and Figure 4).

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Step 1. A linear model relating both selected KPIs (DC and GWP) to mass and energy flows is derived from detailed simulations[70] of the methanol production process of interest (85-$MeOH_f$). The flows Z_f (Figure 6) comprise the two feedstocks CO_2 and H_2, the thermal and electric energy utilities, the methanol product, the water by-product (to be treated), and the CO_2 emissions attributed to the energy generation. The complete set of costing and impact parameter values are reported in Table 2, alongside the corresponding data source.

The total driving cost (Eqs. 27-30) reflects the cost of the fuel per driven distance from the acquisition of raw materials up to the stage where the fuel is burnt in the engine:

$$\mathrm{DC} = 0.85\ \mathrm{DC_{MeOH}} + 0.15\ \mathrm{DC_G} \tag{27}$$

$$\mathrm{DC_{MeOH}} = \mathrm{TPC} + \mathrm{TrC} \tag{28}$$

$$\mathrm{TPC} = \mathrm{VPC} + \mathrm{FPC} + \mathrm{ACC} \tag{29}$$

$$\mathrm{VPC} = \frac{Y_\mathrm{v}}{Z_\mathrm{MeOH}\ \mathrm{LHV_{MeOH}}} \sum_f Z_f C_f \tag{30}$$

For a blend containing 85% of methanol (M85), DC consists of the cost of the methanol ($\mathrm{DC_{MeOH}}$) and gasoline ($\mathrm{DC_G}$). $\mathrm{DC_G}$ is considered a constant, while $\mathrm{DC_{MeOH}}$ is calculated as the sum of the total production cost (TPC) and transportation cost (TrC) of the methanol. TrC is considered a constant since it is not influenced by design or operation decisions, whereas TPC is computed as the sum of the variable production cost (VPC), the fixed cost of production (FPC), and the annualised capital cost (ACC). The latter two are considered constants since they represent only around 20% of the TPC[70]. VPC is calculated from the mass and energy flows Z_f and their associated unitary costs C_f. The parameters Z_MeOH, $\mathrm{LHV_{MeOH}}$ and Y_v representing the methanol flow, methanol lower heating value, and vehicular yield, respectively, are used as conversion factors.

The GWP of the methanol-gasoline blend (Eqs. 31-33) is computed according to:

$$\mathrm{GWP} = \mathrm{GWP^{WTP}} + \mathrm{GWP^{PTW}} \tag{31}$$

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$$\mathrm{GWP}^{\mathrm{WTP}} = 0.85\ \mathrm{GWP}^{\mathrm{WTP}}_{\mathrm{MeOH}} + 0.15\ \mathrm{GWP}^{\mathrm{WTP}}_{\mathrm{G}} \tag{32}$$

$$\mathrm{GWP}^{\mathrm{WTP}}_{\mathrm{MeOH}} = \frac{Y_{\mathrm{v}}}{\mathrm{Z}_{\mathrm{MeOH}}\ \mathrm{LHV}_{\mathrm{MeOH}}} \sum_f Z_f I_f \tag{33}$$

The GWP of the fuel relies on a WTW approach, summing the emissions from the stages of WTP ($\mathrm{GWP}^{\mathrm{WTP}}$) and PTW ($\mathrm{GWP}^{\mathrm{PTW}}$). $\mathrm{GWP}^{\mathrm{PTW}}$ is considered constant since PTW emissions are not influenced by changes in the manufacturing phase. $\mathrm{GWP}^{\mathrm{WTP}}$ is made up by emissions related to the production of methanol ($\mathrm{GWP}^{\mathrm{WTP}}_{\mathrm{MeOH}}$) and gasoline ($\mathrm{GWP}^{\mathrm{WTP}}_{\mathrm{G}}$). Finally, $\mathrm{GWP}^{\mathrm{WTP}}_{\mathrm{MeOH}}$ is calculated from the mass and energy flows Z_f and their associated unitary impact (I_f) [71,74].

Step 2. We link the simplified model (Eqs.27-33) for the methanol process obtained previously with the closest-target DEA model (Eqs. 12-22), and we solve it to identify the mass and energy flows that enable the projection of our fuel 85-$\mathrm{MeOH_f}$ onto the efficient frontier with minimum changes with respect to the original flows or costs. This step entails the following sub-steps:

Step 2.1. All of the fuel alternatives (DMUs) are shown in Table 3, along with their respective attributes. DC and GWP are considered as inputs, while the output is defined as a 1 constant mile for the whole set of fuels. As mentioned before, instead of considering one kilogram of product/fuel, here we consider one driven mile since it enables comparison of different fuels meeting the same function. It also takes into account the efficiency of the fuels during the combustion in the type of car engine employed (spark-ignition internal combustion engine vehicle)[72]. Some liquid fuels are blends containing 15% of regular gasoline. This assumption is made in order to consider the same engine efficiency and type of car, thereby avoiding the need to include the impact embodied in the manufacturing of the car in all of the cases (such impact now cancels out as all the fuels require the same type of vehicle).

Step 2.2. We solve the dual CCR model (4)-(9) for all 11 fuels in order to identify the set *E* of (strongly) efficient alternatives. The results in Figure 7a show that 4 fuels are efficient ($\theta_\ell^* = 1$), namely gasoline, EtOHsc-85, Bio-gasoline and 85-$\mathrm{MeOH_{re}}$. Gasoline shows the lowest price, but the

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second highest GWP, being overcome only slightly by FT-naphtha. Ethanol from sugarcane has a very similar cost to gasoline, but a lower GWP. Bio-gasoline and methanol based on H_2 from renewable electrolysis are the cleaner fuels, showing the lowest GWP. On the other hand, ethanol from corn or switchgrass, liquid hydrogen from coal, natural gas or biomass, and our fuel of interest (85-$MeOH_f$) are all deemed inefficient. The comparison in Figure 7b confirms that liquid H_2 from coal, natural gas and biomass perform significantly worse than the other fuels, both in terms of DC and GWP. This is principally due to the high cost and energy consumption associated to the transport and storage stages[72,73]. Observe also that our fuel 85-$MeOH_f$ shows the second highest DC, just behind methanol employing renewable electrolysis as source of H_2 (85-$MeOH_{re}$).

Step 2.3. Having determined the reference set *E* of efficient fuels, we now turn to the task of determining improvement targets for our fuel 85-$MeOH_f$, by embedding the simplified model of the fuel attributes in terms of the process mass and energy flows (Eqs. 27-33) into the enhanced closest-targets DEA model (Eqs. 12-22). We consider the following three illustrative cases:

Case 1: The flow of H_2 is a variable, with lower-bound given by:

$$Z_{\mathrm{H}_2} \geq Z^{\mathrm{L}}_{\mathrm{H}_2} \tag{34}$$

This lower bound $Z^{\mathrm{L}}_{\mathrm{H}_2}$= 10.34 tH_2/h is derived from the stoichiometry ratio between H_2 and methanol in reaction R1 and the production rate of methanol (see Figure 6). All the other flows Z_f and costs C_f are fixed.

Case 2: The cost of H_2 is a variable, without setting any lower-bound on this cost, while all the mass and energy flows and the other cost are constant. Also modify the objective function in Eq. (12) to minimise the deviation with respect to the current hydrogen cost, $\left|\frac{C_{\mathrm{H}_2} - C^{\mathrm{ref}}_{\mathrm{H}_2}}{C^{\mathrm{ref}}_{\mathrm{H}_2}}\right|$.

Case 3: The flow of H_2 is a variable, with the same lower-bound as in Eq. (34), and H_2 may be produced from two different sources (Eq. 35), namely fossil fuels ($Z_{\mathrm{H}_2,\mathrm{ff}}$) and wind-powered electrolysis[74] ($Z_{\mathrm{H}_2,\mathrm{re}}$):

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$$Z_{H_2} = Z_{H_2,ff} + Z_{H_2,re} \quad (35)$$

The results for the three case studies are shown in Figure 7 and Table 4. Case 1 is proved to be infeasible. Therefore, our fuel 85-$MeOH_f$ cannot be projected onto the efficient frontier by modifying the sole flow of H_2 subject to the stoichiometric limit given by Eq. (34). In Case 2, it is found that 85-$MeOH_f$ could reach the target defined by its peers, 85-$EtOH_{sc}$ and Bio-gasoline, on the efficient frontier, but this would call for a 60% reduction in H_2 price, down to 1.17 US$/kg (see Figure 7b). In practice however, such a large drop in H_2 price is unlikely in the foreseeable future given the current state-of-the-art in H_2 production technology[73,74]. In case 3, it is found that 85-$MeOH_f$ could also reach the target set by its peers, 85-$MeOH_{re}$ and Bio-gasoline, on the efficient frontier, by allowing for a mix of H_2 from fossil fuels and wind-powered electrolysis in addition to reducing the flow of H_2 to the production process (see Figure 7b). This projection increases DC by 7.9% and reduces GWP by 9.4% with respect to their initial values in Table 3. It is enabled by: (i) the reduction of the total H_2 flow to the stoichiometric lower bound $Z^{\mathrm{L}}_{\mathrm{H}_2}$ $(\mathrm{Eq.}\ 34)$, which represents a decrease of 14.5% compared with the initial H_2 flow in Figure 6; and (ii) the use of a 26-74% mix of H_2 from fossil fuels and wind-powered electrolysis, respectively, which suggests that our fuel 85-$MeOH_f$ may only become competitive upon substituting a majority of the H_2 feedstock from fossil fuels by a more sustainable production route, despite the resulting increase in fuel price. Notice that one cannot extend the projection beyond the efficient frontier in this case, because it would result in a violation of the stoichiometric constraint $(\mathrm{Eq.}\ 34)$. However, a modified projection can be assessed, whereby the flow of H_2 is maintained at the stoichiometric lower bound $Z^{\mathrm{L}}_{\mathrm{H}_2}$, while sourcing 100% of this flow from wind-powered electrolysis ($Z_{H_2} = Z_{H_2,re},\ Z_{H_2,ff} = 0$). The resulting projection crosses the best-practise frontier and improve on the existing fuel 85-$MeOH_f$ (which is not operating at stoichiometric minimal H_2 flow), by reducing both its DC and GWP.

Step 3. With the results of the closest-target DEA model in hand, we may either identify the main limitations that prevent the methanol fuel 85-$MeOH_f$ from becoming sustainable and establish

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work guidelines for promoting its competitiveness; or else update the methanol process conditions (H_2 flow and price herein) that render our fuel 85-$MeOH_f$ competitive.

Discussion

Our results show that the methanol fuel 85-$MeOH_f$ could become competitive with other fuels, either by allowing a significant reduction in the H_2 price, or by considering alternative sources of H_2 with a lower GWP across their entire life-cycle. The finding that 85-$MeOH_f$ becomes competitive upon combining H_2 flows from fossil-fuel and renewable feedstocks in order to reduce the GWP at the cost of a higher DC, is new. Moreover, the finding regarding the H_2 price concurs with the results of other studies[70,75] looking at the production of methanol from captured CO_2 and H_2, which have also identified the H_2 price as a major impediment to economic competitiveness. Although the projected H_2 price of 1.17 US$/kg appears unrealistic as of today, our results help identify technological gaps and bottlenecks in the methanol production, where further efforts should be directed to enhance its competitiveness. For instance, our results suggest that one mechanism could be sponsoring research programs concerned with the lowering of H_2 production costs. Furthermore, it is worth pointing out that many renewable energy sources, such as wind, solar photovoltaic and biofuels, rely on policies such as consumption subsidies, mandated minimum levels of consumption and other market incentivisation[76–78], in order to be economically competitive with fossil fuels. In that sense, another approach which is gaining attention could be to penalise fossil fuels, or to compensate cleaner fuels, according to their externalities[76,79–82], thereby accounting for the real cost. Fossil fuels could be subjected to emission taxes on the basis of the negative externalities related to travelled miles, such as local air pollution and GHG emissions, land use, water pollution and loss in biodiversity[82]. Conversely, cleaner fuels such as biofuels and methanol could be subsidised on the basis of their positive externalities, such as decreasing harmful emissions, increasing energy independency and other social benefits. We have shown that another approach to making the methanol fuel 85-$MeOH_f$ competitive could be sourcing H_2 from renewables, for instance wind-powered electrolysis, instead of (or in combination with) fossil-derived H_2. This corresponding reduction in GWP could indeed

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compensate for the higher methanol fuel price. To sum up, all of these approaches could be deployed to boost the methanol fuel 85-$MeOH_f$, whose widespread use would not only help mitigate climate change, but also help reduce reliance on fossil fuels until electric cars eventually take off.

We have already pointed out that the transportation sector is responsible for 24% of the total CO_2 emissions, coming second after the electricity sector[69]. In this context, our framework provides a valuable tool for researchers and decision-makers to: (i) assess new or emerging processes that could potentially produce more sustainable fuels and therefore help tackle the reduction target in CO_2 emissions (based on their comparison with current fuels technologies while considering several sustainability KPIs simultaneously); (ii) understand why a certain fuel underperforms in comparison with others, thereby providing useful insight on how to improve emerging fuels which have the potential to become sustainable through targeted modifications; and (iii) provide realistic conditions during the targeting phase, which do not violate the thermodynamic limits of the underlying fuel production process and therefore make the targeting more reliable.

Conclusions

This paper has presented a systematic framework for improving the sustainability of chemical processes, based on the synergistic combination between DEA and process synthesis tools. Our framework improves the capabilities of standard DEA models and process targeting methodologies by providing realistic targets for suboptimal processes. Its main advantages are four-fold: (i) It remains applicable in the presence of multiple sustainability KPIs; (ii) It discriminates between the efficient and inefficient options among a set of candidate process designs, thereby defining a best-practise frontier which can be used as a benchmark for improving the inefficient process designs; (iii) It identifies quantitative targets for the inefficient process, which are at a minimum distance of the best-practise frontier in terms of mass and energy flow modifications; and (iv) It defines realistic targets that account for the thermodynamic limits of the underlying process, by embedding a (simplified) model

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of the sustainability KPIs in terms of the process mass and energy flows into the enhanced closest-targets DEA model.

The framework has been demonstrated on a real-life case study, for assessing the economic and environmental performance of a new methanol fuel (85-$MeOH_f$) utilizing CO_2 captured from power plants and H_2 sourced from fossil fuels, in comparison with ten existing liquid fuels employed in the automotive fleet powered by internal combustion engines. Application of the DEA framework reveals that gasoline, ethanol from sugarcane-gasoline blend, bio-gasoline, and methanol employing H_2 from wind-based electrolysis result are efficient and thereby define the best-practise frontier. On the other hand, none of FT-naphtha, ethanol from switch grass-gasoline blend, ethanol from corn-gasoline blend, the three H_2-based fuels from biomass, natural gas and coal, and the methanol fuel 85-$MeOH_f$ are competitive in view of their higher cost and GWP. Regarding the methanol fuel 85-$MeOH_f$ more specifically, the closest-targets DEA model has helped to quantify realistic and attainable operational targets that would make it competitive with all its peers in terms of cost and GWP. The current price of H_2 is a major impediment to the economic competitiveness of $MeOH_f$, a finding which is in agreement with other research studies. The sole reduction of the flows of H_2 from fossil fuels does not allow to reach the best-practise frontier when the stoichiometric limits are taken into account. However, if flexibility is introduced in the H_2 source by mixing H_2 from fossil fuels and wind-powered electrolysis, it is found that $MeOH_f$ could indeed become competitive due to a reduction in GWP despite an increase in price.

Apart from employing the enhanced DEA framework to promote a more sustainable chemical industry, applications could be in other areas of sciences and engineering as well. This framework aims to support decision- and policy-makers in the systematic assessment and selection of the best alternatives, but also to provide practical targets for improving the sustainable level of current alternatives. In the context of this work, it provides a tool for decision-makers to discriminate among a set of process designs, the principal sources of inefficiency, the definition of improvement targets, and the quantification of feasible material and energy flows to reach those targets. Lastly, subject to

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further analysis, the proposed framework could provide valuable insight for identifying technological gaps that deserve future research efforts.

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References

1. Pieragostini C, Mussati MC, Aguirre P. On process optimization considering LCA methodology. *J Environ Manage*. 2012;96(1):43-54.

2. Pope J, Annandale D, Morrison-Saunders A. Conceptualising sustainability assessment. *Environ Impact Assess Rev*. 2004;24(6):595-616.

3. Azapagic A, Perdan S. Sustainable chemical engineering: Dealing with “wicked” sustainability problems. *AIChE J*. 2014;60(12):3998-4007.

4. Jiménez-González C. Embedding Sustainability in Product and Process Development—The Role of Process Systems Engineers. In: *Sustainability in the Design, Synthesis and Analysis of Chemical Engineering Processes*. Elsevier; 2016:353-378.

5. García-Serna J, Pérez-Barrigón L, Cocero MJ. New trends for design towards sustainability in chemical engineering: Green engineering. *Chem Eng J*. 2007;133(1-3):7-30.

6. Byrne EP, Fitzpatrick JJ. Chemical engineering in an unsustainable world: Obligations and opportunities. *Educ Chem Eng*. 2009;4(4):51-67.

7. Hanes RJ, Bakshi BR. Sustainable process design by the process to planet framework. *AIChE J*.

For peer review only

2015;61(10):3320-3331.

8. Hanes RJ, Bakshi BR. Process to planet: A multiscale modeling framework toward sustainable engineering. *AIChE J*. 2015;61(10):3332-3352.

9. Towler G, Sinnott R. *Chemical Engineering Design*. 2nd ed. Elsevier; 2000.

10. Towler G, Sinnott RK. Economic Evaluation of Projects. In: *Chemical Engineering Design Principles, Practice and Economics of Plant and Process Design*. ; 2013:1303.

11. Grossmann IE. Challenges in the new millennium: product discovery and design, enterprise and supply chain optimization, global life cycle assessment. *Comput Chem Eng*. 2004;29(1):29-39.

12. Keeble BR. The Brundtland report:"Our common future." *Med War*. 1988;4(1):17-25.

13. WCED. *Our Common Future – The Brundtland Report. World Commission on Environment and Development.* Geneva; 1987.

14. Reniers GLL, Sörensen K, Vrancken K. *Management Principles of Sustainable Industrial Chemistry: Theories, Concepts and Indusstrial Examples for Achieving Sustainable Chemical Products and Processes from a Non-Technological Viewpoint*. John Wiley & Sons; 2013.

15. Ruiz-Mercado GJ, Gonzalez MA, Smith RL. Sustainability indicators for chemical processes: III. Biodiesel case study. *Ind Eng Chem Res*. 2013;52(20):6747-6760.

16. Grossmann IE, Westerberg AW. Research challenges in process systems engineering. *AIChE J*. 2000;46(9):1700-1703.

17. Johns WR. Process Synthesis: Poised for a wider role. *Chem Eng Prog*. 2001;97(4):59-65.

18. Grossmann IE, Guillén-Gosálbez G. Scope for the application of mathematical programming techniques in the synthesis and planning of sustainable processes. *Comput Chem Eng*. 2010;34(9):1365-1376.

For peer review only

19. Azapagic A. Life cycle assessment and its application to process selection, design and optimisation. *Chem Eng J*. 1999;73(1):1-21.

20. Wheeler J, Caballero JA, Ruiz-Femenia R, Guillén-Gosálbez G, Mele FD. MINLP-based Analytic Hierarchy Process to simplify multi-objective problems: Application to the design of biofuels supply chains using on field surveys. *Comput Chem Eng*. 2017;102:64-80.

21. Jaimes AL, Martınez SZ, Coello CAC. An introduction to multiobjective optimization techniques. *Optim Polym Process*. 2009:29-57.

22. del Rio-Chanona EA, Zhang D, Shah N. Sustainable biopolymer synthesis via superstructure and multiobjective optimization. *AIChE J*. 2018;64(1):91-103.

23. Henao CA, Maravelias CT. Surrogate-based superstructure optimization framework. *AIChE J*. 2011;57(5):1216-1232.

24. Yuan Z, Eden MR. Superstructure optimization of integrated fast pyrolysis-gasification for production of liquid fuels and propylene. *AIChE J*. 2016;62(9):3155-3176.

25. Cooper WW, Lawrence M. Seiford, Zhu J, Hillier FS. *Handbook on Data Envelopment Analysis*. Vol 164. (Cooper WW, Seiford LM, Zhu J, eds.). Boston, MA: Springer US; 2011.

26. Cook WD, Seiford LM. Data envelopment analysis (DEA) - Thirty years on. *Eur J Oper Res*. 2009;192(1):1-17.

27. Charnes A, Cooper WW, Rhodes E. Measuring the efficiency of decision making units. *Eur J Oper Res*. 1978;2(6):429-444.

28. Banker RD, Charnes A, Cooper WW. Some models for estimating technical and scale inefficiencies in data envelopment analysis. *Manage Sci*. 1984;30:1078–1092.

29. Vázquez-Rowe I, Iribarren D. Review of life-cycle approaches coupled with data envelopment analysis: Launching the CFP + DEA method for energy policy making. *Sci World J*. 2015;2015.

For peer review only

30. Galán-Martín Á, Guillén-Gosálbez G, Stamford L, Azapagic A. Enhanced data envelopment analysis for sustainability assessment: A novel methodology and application to electricity technologies. *Comput Chem Eng*. 2016;90.

31. Ewertowska A, Galán-Martín A, Guillén-Gosálbez G, Gavaldá J, Jiménez L. Assessment of the environmental efficiency of the electricity mix of the top European economies via data envelopment analysis. *J Clean Prod*. 2015;116.

32. Mio A, Limleamthong P, Guillén-Gosálbez G, Fermeglia M. Sustainability evaluation of alternative routes for fine chemicals production in an early stage of process design adopting process simulation along with data envelopment analysis. *Ind Eng Chem Res*. 2018.

33. Limleamthong P, Gonzalez-Miquel M, Papadokonstantakis S, Papadopoulos AI, Seferlis P, Guillén-Gosálbez G. Multi-criteria screening of chemicals considering thermodynamic and life cycle assessment metrics via data envelopment analysis: application to CO 2 capture. *Green Chem*. 2016;18(24):6399-6696.

34. Liu JS, Lu LYY, Lu WM. Research fronts in data envelopment analysis. *Omega (United Kingdom)*. 2016;58:33-45.

35. Limleamthong P, Guillén-Gosálbez G. Mixed-Integer Programming Approach for Dimensionality Reduction in Data Envelopment Analysis: Application to the Sustainability Assessment of Technologies and Solvents. *Ind Eng Chem Res*. March 2018:acs.iecr.7b05284.

36. Biegler LT, Grossmann IE, Westerberg AW. *Systematic Methods of Chemical Process Design*. 1st ed. New Jersey: Prentice Hall; 1997.

37. Bandyopadhyay S, Sahu GC. *Energy Targeting in Heat Integrated Water Networks with Isothermal Mixing*. Vol 29. Elsevier B.V.; 2011.

38. Dimian AC, Bildea CS, Kiss AA. *Pinch Point Analysis*. Vol 35.; 2014.

For peer review only

39. Furman KC, Sahinidis N V. A Critical Review and Annotated Bibliography for Heat Exchanger Network Synthesis in the 20th Century. *Ind Eng Chem Res*. 2002;41(10):2335-2370.

40. Al-Otaibi M, El-Halwagi M. Targeting Techniques for Enhancing Process Yield. *Chem Eng Res Des*. 2006;84(10):943-951.

41. Feinberg M. Optimal reactor design from a geometric viewpoint - III. Critical CFSTRs. *Chem Eng Sci*. 2000;55(17):3553-3565.

42. Ahmetović E, Ibrić N, Kravanja Z, Grossmann IE. Water and energy integration: A comprehensive literature review of non-isothermal water network synthesis. *Comput Chem Eng*. 2015;82:144-171.

43. Ahmetovich E, Kravanja Z. Solution strategies for the synthesis of heat-integrated process water networks. *Chem Eng Trans*. 2012;29(October):1015-1020.

44. Emrouznejad A, Yang G. A survey and analysis of the first 40 years of scholarly literature in DEA: 1978–2016. *Socioecon Plann Sci*. 2018;61:4-8.

45. Liu JS, Lu LYY, Lu W-M. Research Fronts and Prevailing Applications in Data Envelopment Analysis. In: *Data Envelopment Analysis*. Springer; 2016:543-574.

46. Liu JS, Lu LYY, Lu W-M, Lin BJY. A survey of DEA applications. *Omega*. 2013;41(5):893-902.

47. Martín-Gamboa M, Iribarren D, García-Gusano D, Dufour J. A review of life-cycle approaches coupled with data envelopment analysis within multi-criteria decision analysis for sustainability assessment of energy systems. *J Clean Prod*. 2017;150:164-174.

48. Chalos P. An Examination of Budgetary Inefficiency in Education Using Data Envelopment Analysis. *Financ Account Manag*. 1997;13(1):55-69.

49. Farrell MJ. The measurement of productive efficiency. *J R Stat Soc*. 1957;Series A(General 120):253-281.

For peer review only

50. Cooper WW, Seiford LM, Zhu J. *Data Envelopment Analysis: History, Models and Interpretations.* (W.W. Cooper, L.M., Seiford, Zhu J, ed.). Boston: Kluwer Academic Publishers; 2004.

51. Tone K. A slacks-based measure of efficiency in data envelopment analysis. *Eur J Oper Res*. 2001;130(3):498-509.

52. Lozano S, Iribarren D, Moreira MT, Feijoo G. The link between operational efficiency and environmental impacts. A joint application of Life Cycle Assessment and Data Envelopment Analysis. *Sci Total Environ*. 2009;407(5):1744-1754.

53. Cook WD, Tone K, Zhu J. Data envelopment analysis: Prior to choosing a model. *Omega*. 2014;44:1-4.

54. Seiford LM, Zhu J. Modeling undesirable factors in efficiency evaluation. *Eur J Oper Res*. 2002;142(1):16-20.

55. Westermann G. *Data Envelopment Analysis in the Service Sector*. Springer; 1999.

56. Korhonen PJ, Luptacik M. Eco-efficiency analysis of power plants: An extension of data envelopment analysis. *Eur J Oper Res*. 2004;154(2):437-446.

57. Dyson RG, Allen R, Camanho AS, Podinovski VV, Sarrico CS, Shale EA. Pitfalls and protocols in DEA. *Eur J Oper Res*. 2001;132(2):245-259.

58. Edelstein B, Paradi JC. Ensuring units invariant slack selection in radial data envelopment analysis models, and incorporating slacks into an overall efficiency score. *Omega*. 2013;41(1):31-40.

59. Liu WB, Meng W, Li XX, Zhang DQ. DEA models with undesirable inputs and outputs. *Ann Oper Res*. 2010;173(1):177-194.

60. Cherchye L, Van Puyenbroeck T. Comment on multi-stage DEA methodology. *Oper Res Lett*.

For peer review only

2001;28(2):93-98.

61. González E, Alvarez A. From efficiency measurement to efficiency improvement : The choice of a relevant benchmark. *Eur J Oper Res*. 2001;133:512-520.

62. Silva Portela MCA, Borges PC, Thanassoulis E. Finding Closest Targets in Non-Oriented DEA Models: The Case of Convex and Non-Convex Technologies. *J Product Anal*. 2003;19(2-3):251-269.

63. Aparicio J, Ruiz JL, Sirvent I. Closest targets and minimum distance to the Pareto-efficient frontier in DEA. *J Product Anal*. 2007;28(3):209-218.

64. Jahanshahloo GR, Vakili J, Zarepisheh M. A linear bilevel programming problem for obtaining the closest targets and minimum distance of a unit from the strong efficient frontier. *Asia-Pacific J Oper Res*. 2012;29(2):1250011.

65. Amirteimoori A, Kordrostami S. A Euclidean distance-based measure of efficiency in data envelopment analysis. *Optimization*. 2010;59(7):985-996.

66. Baek C, Lee J-D. The relevance of DEA benchmarking information and the least-distance measure. *Math Comput Model*. 2009;49(1-2):265-275.

67. Aspen Technology Inc. Aspen Hysys User's Guide. 2016:533.

68. Process System Enterprise. gPROMS. 2004.

69. International Energy Agency. CO2 Emissions from Fuel Combustion: Overview. *IEA Stat*. 2017:14.

70. Gonzalez-Garay A, Guillen-Gosalbez G. SUSCAPE: A framework for the optimal design of SUStainable ChemicAl ProcEsses incorporating data envelopment analysis. *Chem Eng Res Des*. 2018;137:246-264.

71. Wernet G, Bauer C, Steubing B, Reinhard J, Moreno-ruiz E, Weidema B. The ecoinvent

For peer review only

database version 3 (part I): overview and methodology. *Int J Life Cycle Assess*. 2016;3:1218-1230.

72. Centre for Transportation Research-Energy Systems Division. GREET. 2016.

73. International Energy Agency (IEA). Production of alternative transportation fuels: Influence of crude oil price and technology maturity. 2013:46.

74. Bhandari R, Truddewind CA, Zaap P. *Life Cycle Assessment of Hydrogen Production Methods – A Review*. Jülich: Cambridge University Press; 2012.

75. Pérez-Fortes M, Schöneberger JC, Boulamanti A, Tzimas E. Methanol synthesis using captured CO2 as raw material: Techno-economic and environmental assessment. *Appl Energy*. 2016;161:718-732.

76. de Gorter H, Just DR. The social costs and benefits of biofuels: The intersection of environmental, energy and agricultural policy. *Appl Econ Perspect Policy*. 2010;32(1):4-32.

77. Rajagopal D, Sexton SE, Roland-Holst D, Zilberman D. Challenge of biofuel: Filling the tank without emptying the stomach? *Environ Res Lett*. 2007;2(4).

78. Bourgeon JM, Tréguer D. Killing two birds with one stone: US and EU biofuel programmes. *Eur Rev Agric Econ*. 2010;37(3):369-394.

79. Ogden JM, Williams RH, Larson ED. Societal lifecycle costs of cars with alternative fuels/engines. *Energy Policy*. 2004;32(1):7-27.

80. Tong F, Hendrickson C, Biehler A, Jaramillo P, Seki S. Life cycle ownership cost and environmental externality of alternative fuel options for transit buses. *Transp Res Part D Transp Environ*. 2017;57(October):287-302.

81. Anil M, Saygin D, Miketa A, Gielen D, Nicholas W. the True Cost of Fossil Fuels : Saving on the Externalities of Air. 2016:1-12.

For peer review only

82. Birur DK, Beach RH, Loomis RJ, et al. Externalities of Transportation Fuels : Assessing Trade-offs Between Petroleum and Alternatives. *RTI Press Publ No OP-0013-1307*. 2013;(July).

83. Saur G, Ainscough C. *U.S. Geographic Analysis of the Cost of Hydrogen from Electrolysis*.; 2011.

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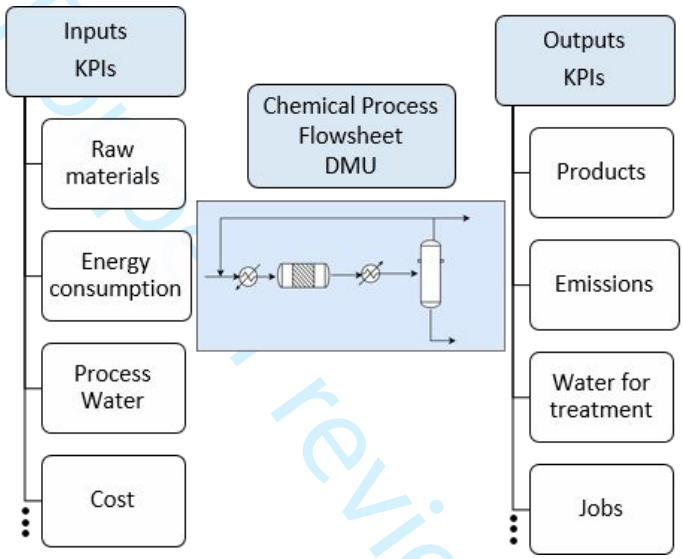


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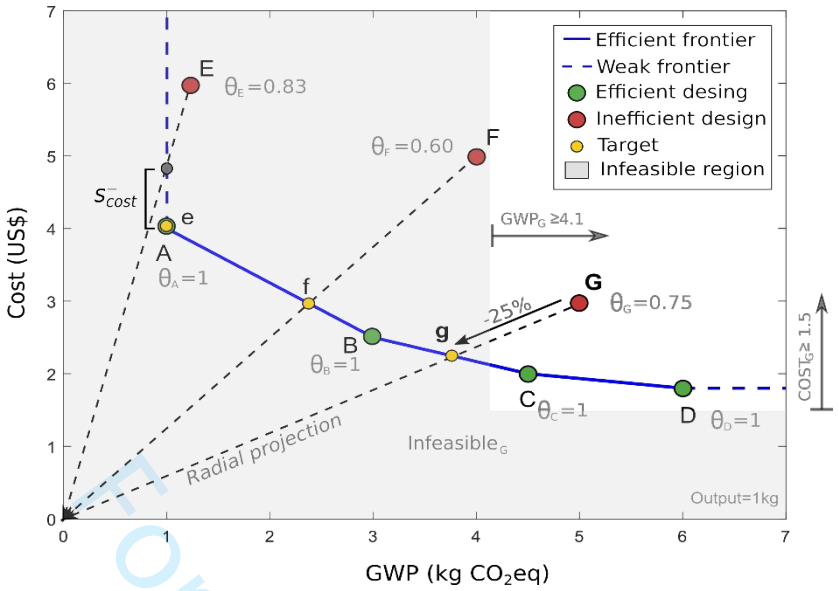


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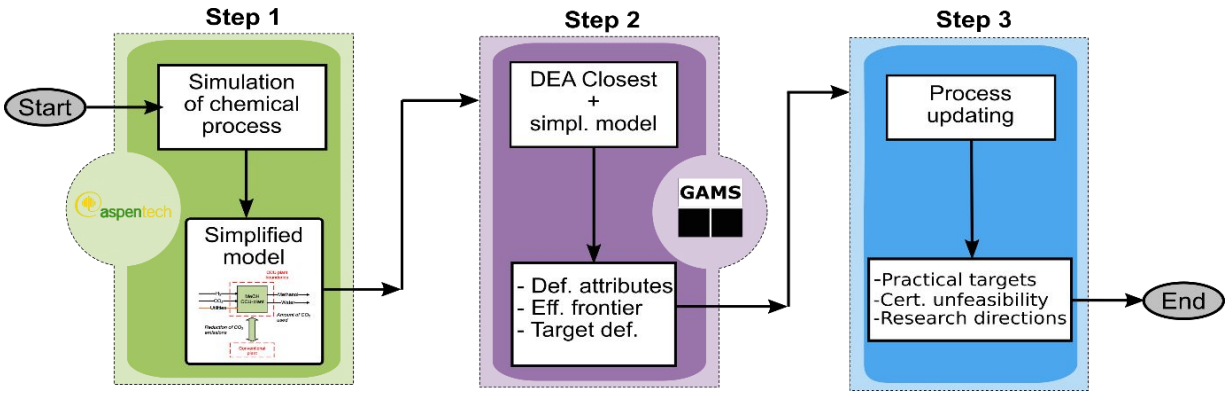


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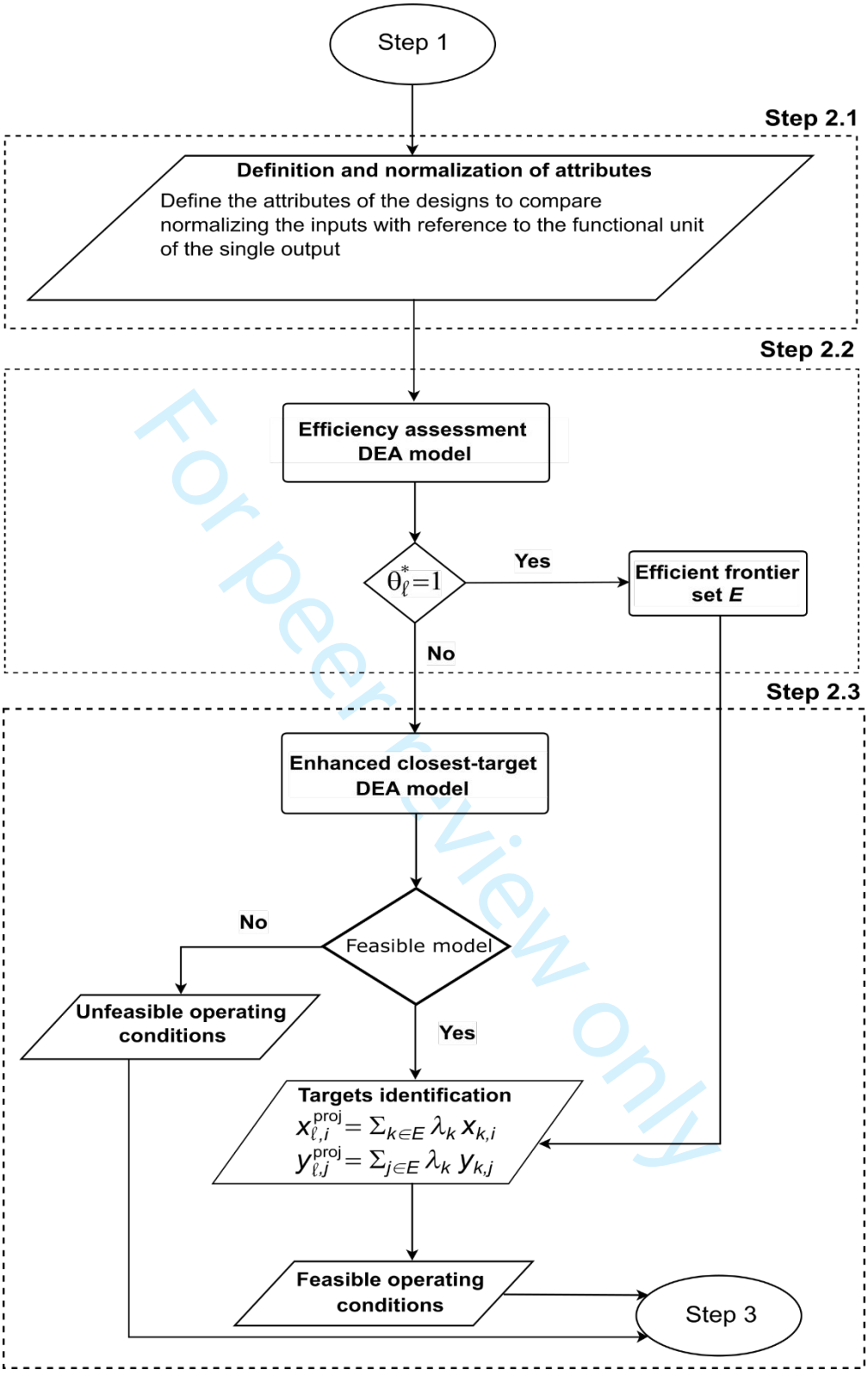


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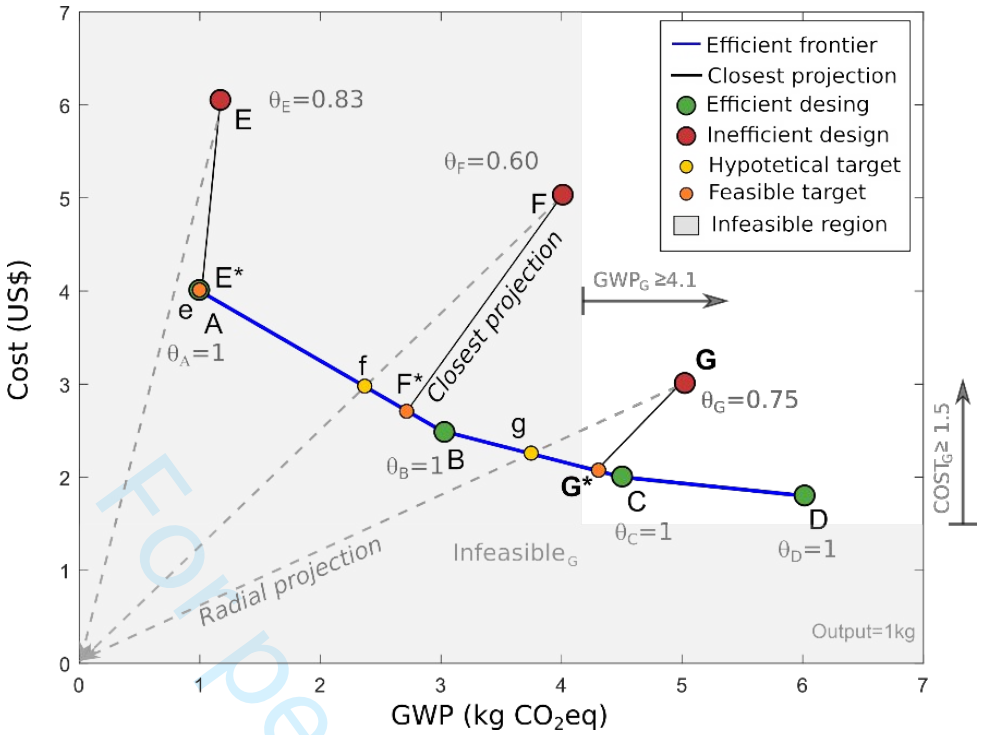


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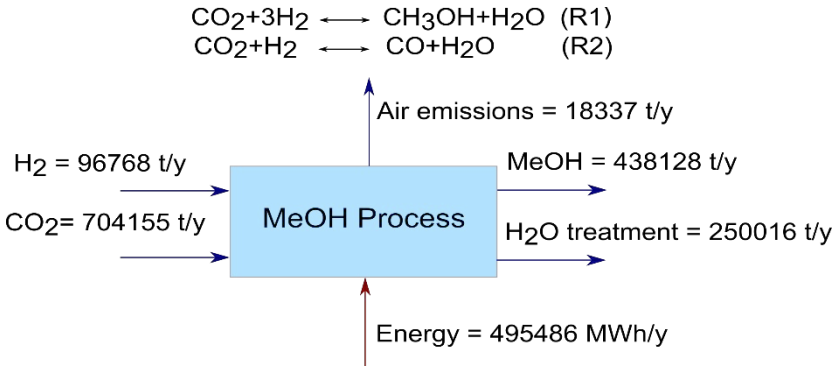


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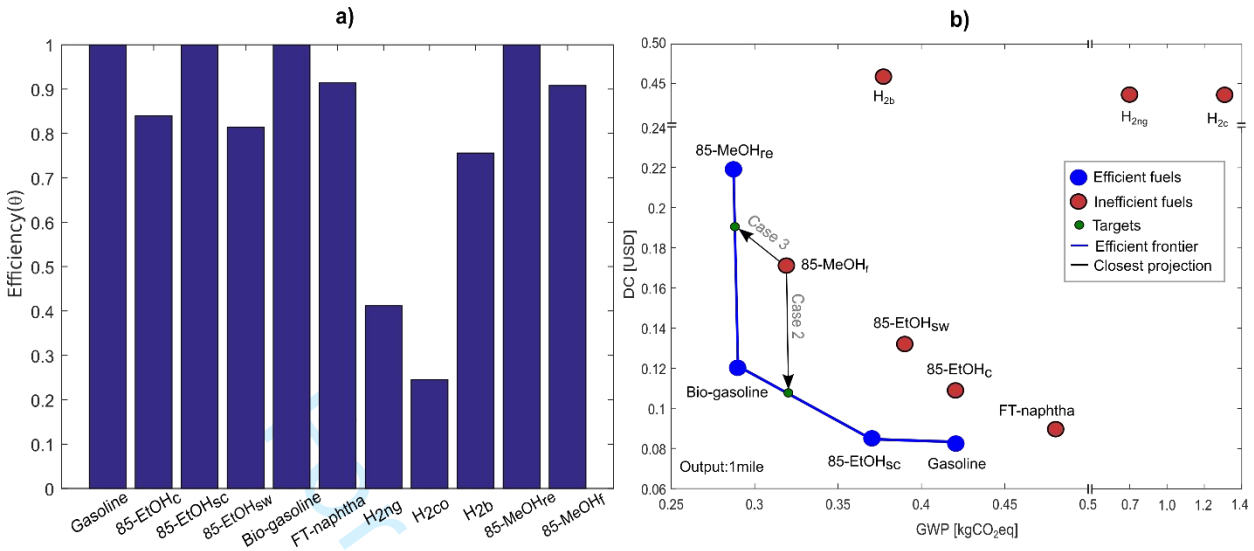


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Table 1. List of chemical processes in the motivating example. All seven chemical process designs are characterised by two indicators to produce a given amount of final product. The assessment focusses on Process G.

Processes	Cost (US$)	GWP ($kgCO_2eq$)	Production (kg)
A	4.00	1.00	1.00
B	2.50	3.00	1.00
C	2.00	4.50	1.00
D	1.80	6.00	1.00
E	6.00	1.20	1.00
F	5.00	4.00	1.00
G	**3.00**	**5.00**	**1.00**

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Table 2. Economic and environmental information employed for computing the DC and GWP associated to methanol fuel.

Component	Impacts	
	C_k[a]	I_k[d]
CO_2	0 (US$/kg)	-322.290 (kg CO_2eq/t)
H_2 cracking of fossil fuels	2680 (US$/t)	1700 (kg CO_2eq/t)
H_2 wind electrolysis	3804 (US$/t)[e]	970 (kg CO_2eq/t)[f]
Heat recovery	-0.008 (US$/MJ)	-0.082 (kg CO_2eq/MJ)
Electricity	0.015 (US$/MJ)	0.166 (kg CO_2eq/MJ)
Cooling water	0.023 (US$/t)	0.303 (kg CO_2eq/t)
H_2O (treatment)	1.50 (US$/t)	0.501 (kg CO_2eq/t)
Air emissions	0	1000 (kg CO_2eq/t)
Parameters		
VCP (US$/mi)[a]		0.127
FCP (US$/mi)[a]		0.013
ACC (US$/mi)[a]		0.021
TrC (kgCO_2eq/mi)[b]		0.015
GWP^{PTW} (kgCO_2eq/mi)[c]		0.320
GWP_G^{WTP} (kgCO_2eq/mi)[c]		0.101
Z_{MeOH} (t/h) [a]		54.766
LHV_{MeOH} (MJ/t)[c]		34366
Y_v (MJ/mi) [c]		4.525

a[70], b[73], c[72], d[71], e[83], f[74]

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Table 3. DMUs and the attributes considered for the case study

Liquid Fuel	Description	DC (US$/mi)	GWP ($kgCO_2eq/mi$)
Gasoline	Petroleum refinery operation	0.083	0.420
85-$EtOH_c$*	85% of ethanol from corn	0.110	0.420
85-$EtOH_{sc}$*	85% of ethanol from sugarcane	0.085	0.370
85-$EtOH_{sw}$*	85% of ethanol from switch grass	0.133	0.390
Bio-gasoline	Renewable gasoline from pyrolysis of residual forest	0.121	0.290
FT-naphtha	Fischer-Tropsch naphtha from natural gas	0.091	0.480
H_{2ng}	Liquid hydrogen from natural gas	0.438	0.700
H_{2co}	Liquid hydrogen from coal	0.437	1.310
H_{2b}	Liquid hydrogen from biomass	0.460	0.380
85-$MeOH_{re}$*	85% of methanol from CO_2 and H_2 from renewable electrolysis	0.2192	0.2873
85-$MeOH_f$*	**85% of methanol from CO_2 and H_2 from fossil fuels**	**0.162**	**0.3320**

*Liquid fuels blending 15% of regular gasoline.

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Table 4. Results of the closest-target DEA framework applied to the transportation fuels case study.

Case	Variable	Target
1	Z_{H_2} (kg/h)	Infeasible
2	C_{H_2} (US$/kg)	1.17
3	$Z_{H_2\mathrm{ff}}$ (t/h)	2.70
	$Z_{H_2\mathrm{re}}$ (t/h)	7.64

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