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Multi-criteria screening of chemicals considering thermodynamic and life cycle assessment metrics via data envelopment analysis: Application to CO₂ capture

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Abstract

With the growing trend of incorporating sustainability principles in the chemical industry, there is a clear need to develop decision-making tools to quantify and optimise the sustainability level of chemical products and processes. In this study, we propose a systematic approach based on Data Envelopment Analysis (DEA) for the multi-criteria screening of molecules according to techno-economic and environmental aspects. The main advantage of our method is that it does not require any articulation of preferences via subjective weighting of the assessment criteria. Furthermore, our approach identifies the most efficient chemicals (according to some sustainability criteria) and for the ones found to be inefficient it establishes in turn improvement targets that can be used to guide research efforts in green chemistry. Our method was applied to the screening of 125 amine-based solvents for CO₂ capture considering 10 different performance indicators, which are relevant to technical, health, safety and environmental aspects, including CO₂ solubility, molar volume, surface tension, heat capacity, viscosity, vapour pressure, mobility, fire & explosion, acute toxicity and Eco-indicator 99. Our approach eliminates 36% of the solvents (as they are found to be inefficient), identifies the main sources of inefficiency (e.g., properties displaying poor values that should be improved) and ranks the best chemicals according to an objective criterion that does not rely on weights. Overall, our proposed DEA-based framework offers insightful guidance to make chemicals more sustainable.

1. Introduction

The growing trend towards incorporating sustainability principles in product and process design has created a clear need for decision-making tools to assist in the assessment and optimisation of the sustainability level of a system. The pressure for more sustainable processes is particularly strong in the chemical industry, in which a large number of new products is being developed and launched at a very fast pace, raising the question (before their industrial scale-up takes place) of

whether they contribute to enhance the overall level of sustainability or not.

Particularly, in green chemistry applications, engineers and scientists are confronted with the problem of screening chemicals (e.g. mainly solvents, additives, etc.) taking into account economic, technical and environmental aspects simultaneously.^{1,2} In practice, the wide range of sustainability criteria to be considered at the very early stages of the product development makes it quite hard, if not impossible, to identify a single chemical performing best in all of them. This is because there might be inherent trade-offs between conflictive thermodynamic properties and environmental and safety metrics, so improving one of them might be accomplished at the expense of compromising another one. As an example, amine-based solvents are the most commonly used absorbents in CO₂ capture applications, mainly due to their high capacity to chemically react with CO₂ thereby enhancing the carbon uptake.³ However, they are highly volatile and require large amounts of energy during their regeneration, which causes operational problems, safety concerns

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and environmental impacts. This has driven both academia and industry to search for alternative solvents with improved health, safety, and environmental profiles. In fact, during the last decade, novel ionic liquid (IL) solvents are receiving increasing attention as a greener alternative to conventional volatile organic solvents because of their appealing features including remarkable low volatility and tunable physico-chemical properties for carbon capture and other applications.^{4–12} Their downside is that at present they are still rather expensive and further research on their long-term impacts and toxicity is still needed.^{13,14} More recently, deep eutectic solvents (DES) has also been put forward as an alternative to ILs for carbon capture owing to their similar features but enhanced properties, such as lower toxicity, higher biodegradability and renewable nature.^{15–18} Although certainly the application of the aforementioned solvents for CO₂ capture purposes is promising, at present there are only a limited number of studies available and therefore a comprehensive assessment and evaluation of DES solvents is not yet possible.

It is therefore very likely that given a particular application for which a variety of chemicals can be selected, some will perform well in certain properties and poorly in others and vice-versa. In this context, the screening of chemicals becomes quite challenging, as it requires the simultaneous assessment of a wide variety of performance indicators so as to ultimately discard suboptimal alternatives and retain the most promising ones for further inspection and potential commercialisation.

There has been a substantial amount of research on the field of multi-criteria assessment of chemical processes and products.^{2,19–21} In contrast, the problem of screening chemicals according to several criteria has received much less attention to date, albeit some contributions in multi-objective molecular design.^{22–25} In the absence of any rigorous and systematic method for screening chemicals, practitioners assess them by defining, in either an implicit or explicit manner, subjective weights that are attached to every category of interest (e.g. viscosity, density, solubility, etc.). These weights enable the calculation of aggregated indicators on the basis of which the chemicals can be ranked.^{21,26} However, while this approach is easy to implement, it shows significant limitations. First, value judgements expressing preferences cannot be fully articulated prior to understanding the trade-offs between different criteria. In addition, valuable information on the performance of a system in a particular dimension might be lost during aggregation, thereby eliminating some good alternatives before the trade-offs have been understood and explored by decision-makers. Finally, the use of weights provides no insight into the underlying multi-criteria problem itself, as the inherent trade-offs that lie at its heart are not analysed, and consequently, no recommendations on how to improve the suboptimal chemicals are provided.

In this work, we propose a new method to screen and select chemicals in green chemistry applications based on Data Envelopment Analysis (DEA), a technique developed in economics for assessing the efficiency level of a system.

Essentially, DEA is a non-parametric analytical tool for quantifying the relative efficiency of units that makes use of linear programming techniques.^{27,28} DEA serves two purposes: (i) it identifies, among a set of units – each producing a set of outputs from a set of inputs – the efficient ones (i.e. those showing the best ratio between desired outputs and required inputs); and (ii) it establishes efficient targets for the units deemed inefficient that if achieved would make them efficient. Hence, compared to other approaches for screening chemicals based on weights, DEA shows two main advantages: (i) it does not require any aprioristic articulation of preferences via quantitative weights, and (ii) it provides insight into how to improve the suboptimal (inefficient) chemicals so as to make them optimal (efficient). DEA has found many applications in energy and environmental studies and more recently in chemical engineering problems, in which it was combined with life cycle assessment (LCA) principles to assess the eco-efficiency level of several technologies.^{29–33} Despite its advantageous characteristics, which will be explained in detail later during the article, to the best of our knowledge DEA has never been used in the area of green chemistry. We here exploit the capabilities of DEA through its application to the screening of solvents for CO₂ capture, focusing on chemical absorption with amine-based solutions.

Our ultimate goal with this piece of work is to pose the task of screening chemicals as a multi-criteria decision-making problem. By framing the task of solvent screening in mathematical terms, we aim to open new research avenues in green chemistry concerning the use of systematic tools to assess and optimise chemicals according to sustainability criteria, including techno-economic, health, safety and environmental aspects. This conceptual framework can help create roadmaps to select chemicals in the development of more sustainable chemical processes, as illustrated herein for the specific case of solvent selection for carbon capture applications.

The paper is organised as follows. A motivating example is introduced in Section 2. The fundamentals of DEA are described next. A case study based on the screening of amine-based solvents for CO₂ capture is presented in Section 4, followed by the corresponding DEA results that are put forward and discussed in Section 5. Finally, the conclusions of the study are drawn at the end of the paper.

2. Motivating Example

A simplified decision-making problem based on hypothetical solvents is introduced to motivate our approach. Solvents are typically characterised and assessed according to a set of features related to their economic, operational and environmental performance. Let us consider seven hypothetical solvents for CO₂ capture to be assessed in terms of five main performance indicators: vapour pressure (-), viscosity (-), surface tension (-), acute toxicity (-) and CO₂ solubility (+) (where +/- indicates whether the property value should be

maximised or minimised, respectively). Note that the data we use in this example, which is summarised in Figure 1, are made up for the purposes of a better illustration only (the numerical values without normalisation are given in Table 1 of the supplementary material) and consider hypothetical solvents that do not exist in practice. Ideally, the aim of the screening task is to select the solvent minimising simultaneously the vapour pressure (so as to lower the potential of explosion hazard and fugitive losses), the viscosity and surface tension (which enhances mass and heat transfer thereby facilitating the plant operation), and the acute toxicity (to reduce a major safety hazard and environmental impact), while at the same time maximising the CO₂ solubility (a major technical target). Note that the data in Figure 1 have been normalised so as to ensure that all the values fall within the interval 0-1. In this figure, the lines connecting the normalised performance attained by every solvent in each criterion intersect in at least one point. Hence, it is clear that there is no single Pareto “optimal” solvent, that is, none of the solvents performs better than the rest simultaneously in all of the properties of interest.

Given that there is no single superior solvent, we aim to answer the following two questions: (a) which solvents behave “globally” better and which ones perform “globally” worse? (b) How could we define quantitative targets for enhancing the performance of the worst solvents? Here we use DEA to shed light on these fundamental issues. More precisely, DEA will be employed to determine the relative efficiency and super-efficiency of each solvent, on the basis of which the solvents will be classified as efficient or inefficient and later ranked without the need to define weights for each criterion. Furthermore, DEA provides quantitative targets that if achieved can make the inefficient solvent efficient. The following section describes the fundamentals of DEA and illustrates how it can be applied in the context of solvent screening.

Fig. 1 Motivating Example – Radar Plot of normalised observation data of five properties for seven hypothetical solvents.

3. Methodology – DEA

DEA is a mathematical methodology that employs linear programming to quantitatively evaluate the relative performance of a group of homogenous entities considering multiple criteria simultaneously.³⁴ In DEA, linear optimisation problems for every single entity (i.e., in our case, a solvent/chemical), or commonly known as Decision Making Unit (DMU), are individually solved to obtain the set of best-performed entities, which form the efficient frontier. DEA identifies in turn sources of inefficiency and offers recommended enhancement targets for the inefficient units that reflect improving directions to achieve the efficient frontier.

3.1 Fundamentals of DEA

DEA analyses a set of DMUs (i.e. solvent/chemical in our case), each one defined as an entity consuming an amount of inputs to generate a certain level of outputs. DEA was originally derived from a traditional concept of efficiency measurement, defined as the ratio between the amount of output to the amount of input. In practical problems, there might be multiple inputs and outputs. This situation makes the analysis more complex and therefore requires the definition of a multi-objective efficiency expressed as the ratio of the weighted sum of outputs to the weighted sum of inputs.

One of the advantages of DEA is its non-parametric nature by which no relationships between inputs and outputs (note that we clarify the meaning of input and output for solvent selection later during the article) need to be assumed in the calculations. Hence, variable weights are optimised to obtain the best possible efficiency value for each entity rather than fixed based on subjective criteria.³¹ This set of weight values maximises the relative efficiency of each entity.³⁵ Hence, the analysis relies on the data only rather than on a fixed number of unknown parameters. In contrast, multi-linear regression is an example of parametric approach based on determining a given number of unknown parameters (i.e., linear regression coefficients) via a least squares error minimisation.

In the context of DEA, the relative efficiency of each DMU_o is defined as the maximum ratio of weighted sum of outputs to weighted sum of inputs subjected to the condition that the analogous ratio, or efficiency, of every DMU is less than or equal to 1.³⁴ For a given DMU_o, a specific fractional problem is formulated to determine its efficiency as follows:

Primal problem

$$\begin{aligned} \max_{u_r, v_i} \theta_o &= \frac{\sum_{r=1}^s u_r y_{ro}}{\sum_{i=1}^m v_i x_{io}} \\ \text{subject to: } &\frac{\sum_{r=1}^s u_r y_{rj}}{\sum_{i=1}^m v_i x_{ij}} \leq 1; \quad j = 1, \dots, n. \quad (M.1) \end{aligned}$$

$$u_r, v_i \geq 0; \quad r = 1, \dots, s; \quad i = 1, \dots, m.$$

Where

- n Number of DMUs
 o Index for the DMU being assessed for $o = 1, \dots, n$
 j Index for the other DMUs for $j = 1, \dots, n$
 m Number of inputs consumed by DMU _{j}
 x_{ij} Amount of input i ($i = 1, \dots, m$) consumed by DMU _{j} (given value)
 s Number of outputs produced by DMU _{j}
 y_{rj} Amount of output r ($r = 1, \dots, s$) produced by DMU _{j} (given value)
 v_i Linear weights assigned to input i (calculated by the LP)
 u_r Linear weights assigned to output r (calculated by the LP)
 θ_o Relative efficiency score of DMU _{o} (calculated by the LP)

The above non-linear programming model can be reformulated into a simpler equivalent linear programming (LP) model as follows:

$$\max_{u_r, v_i} \theta_o = \sum_{r=1}^s u_r y_{ro}$$

$$\text{subject to: } \sum_{i=1}^m v_i x_{io} = 1$$

$$\sum_{r=1}^s u_r y_{rj} - \sum_{i=1}^m v_i x_{ij} \leq 0; \quad j = 1, \dots, n. \quad (M.2)$$

$$u_r, v_i \geq 0; \quad r = 1, \dots, s; \quad i = 1, \dots, m.$$

Model M.2 is solved for every DMU. If the efficiency score θ_o is 1, then the DMU is deemed efficient, while inefficient units show efficiency scores below 1.

Dual problem

The dual problem is an equivalent form of the primal LP that provides valuable insight into how to carry out an efficiency enhancement in the inefficient entities. More precisely, the dual LP provides efficient targets based on a reference set of efficient entities. This dual problem is expressed as below.

$$\min_{\lambda_j, S_i^-, S_r^+} \theta_o - \varepsilon (\sum_{r=1}^s S_r^+ + \sum_{i=1}^m S_i^-)$$

$$\text{subject to: } \sum_{j=1}^n \lambda_j x_{ij} + S_i^- = \theta_o x_{io}; \quad i = 1, \dots, m.$$

$$\sum_{j=1}^n \lambda_j y_{rj} - S_r^+ = y_{ro}; \quad r = 1, \dots, s. \quad (M.3)$$

$$\lambda_j, S_i^-, S_r^+ \geq 0; \quad \forall i, j, r; \quad \theta_o \text{ unconstrained.}$$

Where the notation used is as follows:

- θ_o Relative efficiency score of DMU _{o}
 ε Non-Archimedean infinitesimal value to enforce the variables to be strictly positive

- S_i^- Slack variables for input i , surplus amount of input needed to be reduced to become efficient
 S_r^+ Slack variables for output r , additional amount of output to be increased to become efficient
 λ_j Linear weights attached to every single DMU _{j} to form a linear combination

In more rigorous and technical mathematical terms, the goal of this dual problem is to determine the minimum θ_o that reduces each consumed input radially to $\theta_o x_{io}$ while at least the same output level is still accomplished (this is known as input-oriented model). Hence, the efficiency of the inefficient entities is improved through the shrinkage in inputs by moving radially toward the efficient frontier. This means that for the inefficient units the closer we approach to the frontier, the more input needs to be reduced with respect to the observed data (initial point), and therefore, the greater efficiency will be reached. The maximum reduction in inputs that is necessary for such an inefficient DMU to turn into efficient corresponds to the difference between the observed data and its radial projection on the frontier. The theoretical target for input i in any given inefficient DMU _{o} is obtained as follows.

$$\text{Input target} = \sum_{j=1}^n \lambda_j x_{ij} = \theta_o x_{io} - S_i^- \quad (M.4)$$

In this equation, λ_j are the weights used to construct the composite unit that serves as benchmark for the inefficient units, while v_i and u_r are weights appended to the inputs and outputs to maximise the efficiency score of the unit.

Figure 2 provides an example for the case of two inputs and one constant output, where the inefficient units (white circles) are radially projected on the efficient frontier (blue solid line) to obtain their efficient targets (red circles). The relative efficiency score is then estimated from the ratio between the distance from the origin to the projected targets, and the distance from the origin to the inefficient data point.

Fig.2 DEA radial projection for a two-input illustration (the output is assumed to be the same for both units and therefore not shown in the figure).

inefficient unit), yielding a reference target point f for efficiency improvement (depicted as a red circle in Figure 3). This reference target f is essentially a composite unit obtained through a linear combination of the efficient units D and G with weights 61.4% ($\lambda_D = 0.614$) and 38.6% ($\lambda_G = 0.386$), respectively. These linear coefficients provide therefore the improvement targets. Hence, the acute toxicity of solvent F should be reduced from 0.28 to 0.2125 ($0.614 \times 0.17 + 0.386 \times 0.28$). In this context, D and G are the so called peer group or the reference set for the inefficient solvent F . Note that point f might not correspond to any feasible solvent (i.e., as will be later discussed in the case study section, it might be impossible to make changes in solvent F such that it will reach point f lying on the efficient frontier). However, the analysis of such a point f provides insight into which of its properties should be improved (via improvement targets) and how to attain the projected point (via benchmark of its peers).

Likewise, all inefficient entities can be improved in their efficiency level via projection onto the efficiency frontier. However, we might experience, in some cases, the weakly efficient composite unit, as occurs in solvent E , where it is horizontally projected onto the weakly efficient frontier (represented by the cyan line in Figure 3), instead of onto the strongly efficient one. The weakly efficient frontier is basically an extended frontier extrapolated from the strongly efficient frontier. This occurs when the values of inputs and/or outputs fall outside the range of the strongly efficient frontier, which is essentially formed by strongly efficient units. We next apply the DEA to the same data considering this time all the criteria simultaneously. The primal model identifies solvents A, C, D and G as efficient, and solvents B, E, F as inefficient, with efficiency values of 84.0 (B), 77.6 (E) and 87.1 (F), respectively. Figure 4 is a heat map that displays the percentage improvement required in each inefficient unit in order to become efficient, which takes a zero value in the efficient solvents.

Fig. 4 Motivating Example – Heat map displaying the percentage improvement in all of the properties across inefficient solvents.

3.3 DEA framework to the problem of screening chemicals

In this section we introduce a DEA-based methodology for screening chemicals that comprises the following steps (see Figure 5):

1. **Definition and classification of attributes:** This step specifies the criteria on the basis of which the screening will be carried out. Every criterion/attribute is labelled as input or output according to its nature (attributes to be minimised are regarded as inputs, while attributes to be maximised are outputs). Note that if all the attributes need to be minimised/maximised, we can still define a dummy output/input that takes a value of one in all of the DMUs and which enables the application of the DEA models.
 2. **Data collection:** In this step, the attributes are given values based on experimental measurements and/or in silico calculations.
 3. **Data normalisation:** This step is required when some attributes take zero and/or negative values in some solvents, a situation that can cause numerical problems in the DEA models.²⁸ To this end, different normalisation strategies can be applied, some of which might affect the DEA results.²⁸
 4. **DEA application:** This step involves two sub-steps:
 - Efficiency assessment (primal problem): The primal model M.2 is applied to the raw data (or normalised data, depending on the existence of zero/negative values), thereby providing the efficiency scores for every chemical.
 - Inefficiency assessment (dual problem): The dual model M.3 is solved in order to establish, for every inefficient chemical, improvement targets and members of its peer group.
 5. **Interpretation of results:** The solutions computed with the primal and dual models are analysed, and a set of recommendations and guidelines are provided. This step may require solving a super-efficiency model to further discriminate between the efficient chemicals.^{28,35,37}
- Several remarks should be made at this point regarding the application of our methodology.
- The traditional DEA determines whether a unit is efficient or not but provides no ranking of efficient units. This limitation can be overcome using super-efficiency models, as discussed earlier in the article.
 - DEA is very sensitive to the number of criteria considered in the analysis. Increasing the number of criteria/attributes leads to a poor discrimination (i.e. many units are deemed efficient). In general, the rule for a proper discrimination is that the number of DMUs should be $n \geq \max\{m \times s, 3 \times (m + s)\}$,

Fig.5 Flow diagram of the DEA-based framework for the solvent screening problem.

- where m and s are the number of inputs and outputs, respectively.³⁵ To reduce the number of inputs, we could apply a correlation analysis or discard those that show very low variability (small differences between the maximum and minimum values).
- Different normalisation strategies can be applied in step 3 of the methodology, which may affect the outcome of the DEA models.
- DEA is a very well established methodology that can be easily implemented in widely used software packages like Excel, MATLAB, etc.
- It is possible to define bounds on the weights attached to the attributes (variables v_i, u_r) in order to better reflect the decision makers' preferences (i.e., vapour pressure might be given more importance than viscosity, etc.).

4. Case study – An application to solvent screening

We illustrate the capabilities of our approach through a case study where we aim to screen 125 aliphatic, acyclic amine-based solvents that could be used in CO₂ capture (a list of solvent names and CAS numbers can be found in Table2 in the supplementary material). Despite their promising operational performance, amine-based solvents show some disadvantages, mainly due to high energy-consumption during their regeneration along with other specific environmental impacts. Intensive research on more sustainable solvents for CO₂ capture has laid emphasis on one single aspect: either the i) technical performance^{38,39} (quantified through the CO₂ capture capacity, CO₂ absorption/desorption rate and regeneration energy); or ii) the environmental performance^{40–43}, assessed via ecotoxicity, chemical stability and biodegradability. Both aspects have been therefore typically studied separately and rarely assessed following an integrated approach like the one proposed here. Recent research has attempted to integrate these dimensions, but through the definition of aggregated scores showing the limitations mentioned before.^{44–46}

There are several attributes that can be used for the selection of CO₂ capture solvent candidates.^{36–38} In our calculations, we use a set of properties that can be broadly categorised into the following groups:

- Technical properties related to the performance and cost of the carbon sequestration facility (i.e., CO₂ solubility, molar volume, heat capacity, surface tension and viscosity).
- Indicators directly related with health and safety aspects of the solvent itself (i.e., vapour pressure, mobility, fire & explosion and acute toxicity).
- A life cycle environmental performance indicator (i.e., Eco-indicator 99) that quantifies the environmental burdens associated with the production of the solvent from cradle-to-gate (from the extraction of the necessary raw materials required to produce the solvent, until the point where the solvent is ready for use). Note that this LCA indicator does not consider the operation of the carbon sequestration plant

neither the management of the waste produced once the solvent cannot be regenerated any further.

Concerning the technical properties (group 1: molar volume, surface tension, heat capacity and viscosity), the performance indicators employed in this work were selected bearing the following criteria in mind. First, they capture the molecular effects of the absorption/desorption process that governs the capture sequestration system in which the solvents will eventually be used. Second, there are predictive models available that enable quick calculations for these properties. Third, there are sufficient data available to apply these models to a wide range of molecules.

It is therefore desired to identify solvents that exhibit the following values of the properties:

Technical aspects:

- Maximum CO₂ solubility, as this property indicates the ability of a solvent to efficiently dissolve CO₂. Higher solubility values imply lower capital and operating costs of the absorption/desorption system, less energy consumption and better CO₂ selectivity.
- Minimum molar volume, which leads to higher solvent density and therefore lower absorption/desorption equipment sizes and consequently smaller capital costs.
- Minimum liquid heat capacity, as lower heat capacities imply lower sensible heat addition and therefore smaller regeneration energy requirements and operating costs.
- Minimum viscosity and surface tension, as low values of these properties favour mass transfer in the packing material, thereby reducing the capital costs of carbon sequestration.

Health and safety:

- Minimum vapour pressure, as this leads to lower solvent losses and therefore smaller operating costs and environmental impact (i.e., less fugitive emissions).
- Minimum fire & explosion, mobility and acute toxicity, as lower values of these metrics involve better health and safety conditions when producing the solvent and also during the operation of the carbon sequestration plant.

Environmental performance:

- Minimum Eco-indicator 99, as lower values of this indicator involve lower impacts quantified considering all the stages in the life cycle of the solvent (but omitting the operation of the carbon sequestration plant and the management of the waste generated after using the solvent).

The selected performance indicators have been calculated using the following models:

- The CO₂ solubility has been calculated based on the Hansen solubility parameter taken from Stefanis and Panayiotou.⁴⁷
- The liquid-liquid molar volume was calculated following the work by Constantinou et al.⁴⁸
- The heat capacity was estimated via a group-contribution method following the work by Rayer et al.⁴⁹
- The viscosity and surface tension were determined according to the work by Conte et al.⁵⁰

- The vapour pressure was obtained using the Riedel correlation.⁵¹

- The mobility, fire & explosion and acute toxicity were determined using the Estimation Program Interface (EPI) Suite and the Toxicity Estimation Software Tool (TEST).⁵²

- The Eco-indicator 99 was determined using the FineChem tool (Wernet et al., 2009), which predicts several LCA metrics from a set of molecular descriptors (e.g., number of hydroxy groups, number of carboxy groups, etc.).²⁰ These LCA metrics are calculated from cradle-to-gate (i.e., from the extraction of raw materials to the production of the necessary amount of chemical, but omitting the operation of the carbon sequestration plant and the management of the waste generated once the solvent cannot be regenerated any more). The functional unit used in the analysis is 1 kg of solvent produced

Overall, we believe that these indicators and the level of abstraction of the models used to estimate them are good enough for the purposes of our analysis. Note that our approach could be easily adapted to work with other indicators if they become available at some point in the future.

5. Results and discussion

The results obtained with our approach are discussed next.

Step 1: In the first step, we define the attributes, classify them as inputs and outputs and collect the necessary data to establish their values. The following technical, safety, health and environmental criteria are considered as inputs to be minimised (-) in our analysis:

- Technical: molar volume (-), heat capacity (-) (related to the energy required for regeneration processes), viscosity (-) and surface tension (-) (related to mass transfer limitations).^{53,54}
- Health and safety: vapour pressure (-) (related to fugitive emissions), fire & explosion (-) (related to explosion hazard)⁵⁵, mobility (-) and acute toxicity (-).
- Environmental: Eco-indicator 99 (-) (one of the most widely used impact assessment methods in LCA that accounts for damage in human health and ecosystems as well as resources depletion).

The CO₂ solubility is the output to be maximised. **Step 2:** The attributes values were retrieved from Papadopoulos et al. (2016).⁴⁶

Step 3: The normalisation step was not applied in this case since no negative values. However, a small epsilon value was added to the null values to avoid numerical problems.

Step 4: The VRS DEA model features 147 variables and 136 constraints. It was implemented in GAMS 24.4.5 and solved with CPLEX 12.6.1.0 on an Intel® Core™ i5-4570 processor operating at 3.20 GHz.^{56,57} It took around 1.4-1.6 CPU seconds to solve every instance to global optimality.

Step 5: Interpretation of results. According to the solution of the primal problem, there are only 80 strongly efficient solvents (80 out of a total of 125 solvents, that is, 64% of them), as shown in

Figure 6. Hence, the primal problem allows discarding 36% of the solvents. Figure 7 shows the histogram of efficiency values. As observed, inefficient solvents show large efficiency values (between 86 and 99%), which indicates that they are close to the efficient frontier.

The dual problem is solved next. Figure 8 shows a heatmap that summarises the percentage improvements required for the 45 inefficient solvents to become efficient. They have been calculated as the ratio between the value of the property in the original inefficient solvent minus the value in the projected efficient solvent, divided by the property value in the original solvent. The rows display the attributes, while the columns show the CAS number of the solvent. Note that all the categories (except for solubility) must be minimised. A more intense red/blue colour reflects a stronger target, and therefore the need to minimise/maximise further the corresponding category so as to become efficient.

This analysis provides very valuable insight for chemists and engineers, as it pinpoints the most critical parameters to guide future research efforts. In our case, vapour pressure is found to be the most critical property, requiring an average reduction of around 42%, as shown in Figure 9. This analysis is consistent with the fact that several amines are quite volatile due to their high vapour pressure (which represents a potential hazard). Eco-indicator 99 and acute toxicity come next in importance,

with average reductions of around 25% and 21%, respectively, followed by heat capacity (14%), which may correlate with the amount of energy consumed in the regeneration process.

A deeper analysis of some inefficient solvents reveals that Diethylenetriamine (with CAS No. 111-40-0) needs reductions of around 100%, 99% and 80% in acute toxicity, vapour pressure and Eco-indicator 99, respectively. It is followed by 1,6-Hexanediamine (124-09-4) with 100%, 97% and 42% reductions in acute toxicity, vapour pressure and Eco-indicator 99, respectively. Likewise, 4-(Diethylamino)butylamine (27431-62-5) also behaves poorly in acute toxicity, vapour pressure and Eco-indicator 99 (100%, 95% and 43% reductions, respectively).

Note that as a general rule, the boiling points of the amines are always lower than the boiling points of the analogues containing alcohol functions (i.e., hydroxyl groups). This is because the intermolecular interactions of alkanes are driven by van der Waals forces, whilst in alcohols they are mainly based on hydrogen bonds,

Fig.6 Relative overall efficiency score of 125 conventional solvents.

Fig.7 Histogram of efficiency score of all 125 conventional solvents.

Fig.8 Improvement percentage required for each inefficient solvent.

Fig.9 Average improvement percentage in each indicator.

which are stronger compared to the former. Accordingly, amine-based solvents present lower boiling points (i.e., higher vapour pressures) than alkanolamine-based solvents. Hence, vapour pressure clearly needs to be improved to increase the overall efficiency of these amine solvents (without alcohol functions), as pinpointed by the DEA.

At this point of the discussion it is important to clarify that the attributes can reflect either intrinsic or extrinsic properties. As an example, heat capacity is an intrinsic property that cannot be modified unless the molecular structure of the solvent is altered or the solvent itself is blended with other chemicals. On the other hand, the Eco-indicator 99 is an example of an extrinsic property that can be altered through modifications in the solvent's supply chain (e.g., changes in the production, storage and transportation technologies can reduce the life cycle impact of the solvent). Note also that even after implementing the aforementioned strategies, it might still be impossible to attain the improvement targets determined by the DEA, as they do not necessarily reflect a feasible solution. Thus, our approach focuses on pinpointing the main sources of inefficiency, but without getting into the details on how to attain the improved performance. Further work will focus on this topic, paying special attention to the use of blends of different solvents as an effective strategy to improve the properties of a solvent.

We now investigate how to make the inefficient solvents efficient. Figure 10 depicts a heat map of linear coefficients (projection of inefficient units on the efficient frontier taking as reference the efficient solvents) while Figure 11 shows the number of times each efficient solvent is defined as peer (by the inefficient units) along with the corresponding summation of linear coefficients (summation of the rows elements in Figure 10). To offer an insightful illustration of these results, consider the inefficient solvent Diethylenetriamine (111-40-0), which would become efficient by approaching to the linear

combination of 2-Amino-2-methyl-1,3-propanediol (115-69-5), 2-amino-2-methylhexan-3-ol (63765-79-7), and 1,2-Bis(dimethylamino)-2-methylpropane (68955-53-3), with linear multipliers 0.788, 0.140 and 0.072, respectively.

To further discriminate among the efficient units, we carried out a super-efficiency analysis, which in essence solves the dual problem again but this time removing each efficient unit from the model once at a time. The goal of this model is to study how the efficient frontier changes when one efficient unit is left out of the analysis. Figure 12 shows the super-efficiency scores, which are consistent with the findings mentioned above, as sterically hindered amines show high super-efficiency values. Note that there is one efficient solvent, Triethanolamine (102-71-6), for which the super-efficiency model renders unfeasible. This is a common situation arising when a variable returns to scale super-efficiency model is used.⁵⁸

As mentioned earlier, one of the main advantages of alkanolamines is that they contain hydroxyl groups which help to reduce the vapour pressure and increase the solubility in aqueous solution. On the one hand, aqueous solutions of primary amines (e.g., monoethanolamine, MEA 141-43-5) and secondary amines (e.g., diethanolamine, DEA* 111-42-2) present fast reaction kinetics with CO₂ to form very stable carbamate ions, which enhance the CO₂ absorption rate but increase the cost required for solvent regeneration. Moreover, despite their thermodynamic selectivity towards CO₂ being very high, the capacity of CO₂ absorption is restricted by stoichiometry to a maximum of 0.5 mole CO₂ per mole of amine.⁵⁹ On the other hand, tertiary amines (e.g., methyl diethanolamine, MDEA 105-59-9) present an equimolar reaction stoichiometry with CO₂ via bicarbonate anion mechanism. However, the indirect reaction between tertiary amine and CO₂ through bicarbonate formation is much slower than the direct reaction of primary and secondary amines with CO₂ for carbamate formation.

Fig.10 Linear weights for the peers chosen by each inefficient solvent.

Fig.11 Summation of linear weights and frequency of use for all the efficient solvents.

Fig.12 Super-efficiency score of all the efficient solvents.

Furthermore, tertiary amines allow for stoichiometrically higher equilibrium loadings and they present a lower regeneration cost, while the kinetic selectivity of tertiary amine towards CO_2 is very low. With regards to sterically hindered amines (e.g. 2-amino-2-methyl-1-propanol, AMP 124-68-5), they also present equimolar reaction stoichiometric as one mole of CO_2 is absorbed per mole of amine through direct carbamate formation. However, this carbamate form is unstable and it undergoes carbamate reversible reaction. The steric effect influences the stability of the carbamate formed due to the reaction of the amine with CO_2 , reducing the energy penalty for solvent regeneration. Therefore, sterically hindered amines exhibit highly reversible kinetics with CO_2 via direct carbamate formation, high stoichiometric loading capacity and require less energy for regeneration, plus they show better stability because of higher degradation resistance.⁶⁰ Hence, our

mathematical results explain why inefficient solvents seek to get closer to them and mimic their behaviour.

Finally, we investigate the relationship between chemical structure and performance. To this end, we encode the chemicals using UNIFAC structural groups.⁶¹ We then calculate Spearman coefficients that correlate the values of the properties with the number of functional groups of each type present in the solvent (see Figure 13). Note that this analysis neglects interactions between groups, yet it provides valuable insight into the link between molecular structure and properties. As seen in Figure 13, the number of OH groups positively correlates with solubility, surface tension and viscosity, while negatively correlates with Eco-indicator 99, vapour pressure and fire & explosion (and also with the other

Fig.13 Spearman's Correlation Coefficient between functional groups and solvent properties. The sign of the preference is as follows: molar volume (-), heat capacity (-), viscosity (-), surface tension (-), vapour pressure (-), fire & explosion (-), mobility (-), acute toxicity (-), eco-indicator 99 (-), solubility (+).

properties but to a lesser extent). The length of the chain represented by the number of CH₂ and CH₃ functional groups also shows positive correlation with molar volume and the heat capacity. Furthermore, CH₂ negatively correlates with mobility and vapour pressure, while CH₃ negatively affects surface tension and solubility.

6. Conclusions

With the growing trend of incorporating sustainability principles in the chemical industry, there is a clear need to develop decision-making tools to quantify and optimise the sustainability level of chemical products and processes. In this paper, we have proposed a systematic methodology for screening chemicals according to a set of techno-economic and sustainability criteria which is based on DEA, a tool originally developed in economics and widely used in science and engineering. This approach, which can be easily implemented in standard software packages, provides valuable insight into the screening problem by identifying optimal and suboptimal (efficient/inefficient) chemicals and by providing improvement targets for the inefficient ones that can guide research efforts of chemists and engineers during the early stages of the development of new products and processes.

We have illustrated the capabilities of our methodology through its application to the screening of 125 amine-based solvents utilised in CO₂ capture in terms of 10 criteria. Our method discards 36% of the solvents, and highlights the need to improve some critical properties like vapour pressure, acute toxicity and total weighted life cycle impact (quantified via the Eco-indicator 99) as a necessary step to increase their overall level of efficiency. While these limitations of amine-based solvents are well known, our approach quantifies in a systematic manner improvement targets and identifies in turn

sources of inefficiency. More precisely, our analysis reveals that sterically hindered amines are particularly appealing solvents in terms of overall performance, as they tend to be used by many inefficient solvents as peers and also show high super-efficiency scores.

By studying the link between chemical structure and properties, we found that adding OH groups enhances most of the properties of interest, an insight that explains why alcohol amines tend to show better global performance. Moreover, hindered amines present lower energy penalty for solvent regeneration as well as higher CO₂ loading capacity, which explains why they are chosen by many inefficient chemicals as efficient peers in the DEA analysis.

Overall, we found that the DEA-based framework is a very effective approach to screen chemicals, identify primary sources of inefficiency and provide quantitative targets for further improvements. The pressing need to develop more sustainable chemicals calls for advanced decision-support tools that should be ultimately integrated in computer aided molecular design programs. Our final aim is to encourage a widespread use of systematic tools for sustainability assessment and optimisation in green chemistry applications, so the experimental and modelling communities join efforts in the transition towards a greener chemical industry.

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Reference

- 1 P. G. Jessop, *Green Chem.*, 2011, **13**, 1391–1398.
- 2 L. Moity, M. Durand, A. Benazzouz, C. Pierlot, V. Molinier

* DEA here refers to the acronym of the solvent, which by chance coincides with the acronym for the method we use.

- and J.-M. Aubry, *Green Chem.*, 2012, **14**, 1132–1145.
- 3 A. B. Rao and E. S. Rubin, *Environ. Sci. Technol.*, 2002, **36**, 4467–4475.
- 4 L. A. Blanchard, D. Hancu, E. J. Beckman and J. F. Brennecke, *Nature*, 1999, **399**, 28–29.
- 5 B. E. Gurkan, J. C. de la Fuente, E. M. Mindrup, L. E. Ficke, B. F. Goodrich, E. A. Price, W. F. Schneider and J. F. Brennecke, *J. Am. Chem. Soc.*, 2010, **132**, 2116–2117.
- 6 J. F. Brennecke and B. E. Gurkan, *J. Phys. Chem. Lett.*, 2010, **1**, 3459–3464.
- 7 J. Palomar, M. Gonzalez-Miquel, A. Polo and F. Rodriguez, *Ind. Eng. Chem. Res.*, 2011, **50**, 3452–3463.
- 8 M. Gonzalez-Miquel, M. Talreja, A. L. Ethier, K. Flack, J. R. Switzer, E. J. Biddinger, P. Pollet, J. Palomar, F. Rodriguez, C. A. Eckert and C. L. Liotta, *Ind. Eng. Chem. Res.*, 2012, **51**, 16066–16073.
- 9 M. Gonzalez-Miquel, J. Bedia, C. Abrusci, J. Palomar and F. Rodriguez, *J. Phys. Chem. B*, 2013, **117**, 3398–3406.
- 10 M. Gonzalez-Miquel, J. Bedia, J. Palomar and F. Rodriguez, *J. Chem. Eng. Data*, 2014, **59**, 212–217.
- 11 M. Gonzalez-Miquel, M. Massel, A. DeSilva, J. Palomar, F. Rodriguez and J. F. Brennecke, *J. Phys. Chem. B*, 2014, **118**, 11512–11522.
- 12 R. I. Canales, M. J. Lubben, M. Gonzalez-Miquel and J. F. Brennecke, *Philos. Trans. R. Soc. A*, 2015, **373**, 20150011.
- 13 M. Ramdin, T. W. de Loos and T. J. H. Vlucht, *Ind. Eng. Chem. Res.*, 2012, **51**, 8149–8177.
- 14 T. P. Thuy Pham, C.-W. Cho and Y.-S. Yun, *Water Res.*, 2010, **44**, 352–372.
- 15 G. Garcia, S. Aparicio, R. Ullah and M. Atilhan, *Energy & Fuels*, 2015, **29**, 2616–2644.
- 16 G. García, M. Atilhan and S. Aparicio, *J. Phys. Chem. C*, 2015, **119**, 21413–21425.
- 17 X. Li, M. Hou, B. Han, X. Wang and L. Zou, *J. Chem. Eng. Data*, 2008, **53**, 548–550.
- 18 L. Cao, J. Huang, X. Zhang, S. Zhang, J. Gao and S. Zeng, *Phys. Chem. Chem. Phys.*, 2015, **17**, 27306–27316.
- 19 C. Capello, U. Fischer and K. Hungerbühler, *Green Chem.*, 2007, **9**, 927–934.
- 20 G. Wernet, S. Papadokonstantakis, S. Hellweg and K. Hungerbühler, *Green Chem.*, 2009, **11**, 1826–1831.
- 21 S. Hellweg, U. Fischer, M. Scheringer and K. Hungerbühler, *Green Chem.*, 2004, **6**, 418–427.
- 22 K.-J. Kim and U. M. Diwekar, *Ind. Eng. Chem. Res.*, 2002, **41**, 4479–4488.
- 23 A. I. Papadopoulos and P. Linke, *AIChE J.*, 2006, **52**, 1057–1070.
- 24 L. Y. Ng, N. G. Chemmangattuvalappil and D. K. S. Ng, *Ind. Eng. Chem. Res.*, 2014, **53**, 17429–17444.
- 25 J. Burger, V. Papaioannou, S. Gopinath, G. Jackson, A. Galindo and C. S. Adjiman, *AIChE J.*, 2015, **61**, 3249–3269.
- 26 M. Tobiszewski, S. Tsakovski, V. Simeonov, J. Namieśnik and F. Pena-Pereira, *Green Chem.*, 2015, **17**, 4773–4785.
- 27 A. Boussofiane, R. G. Dyson and E. Thanassoulis, *Eur. J. Oper. Res.*, 1991, **52**, 1–15.
- 28 W. D. Cook and L. M. Seiford, *Eur. J. Oper. Res.*, 2009, **192**, 1–17.
- 29 P. Zhou, B. W. Ang and K. L. Poh, *Eur. J. Oper. Res.*, 2008, **189**, 1–18.
- 30 Y. Lorenzo-Toja, I. Vázquez-Rowe, S. Chenel, D. Marín-Navarro, M. T. Moreira and G. Feijoo, *Water Res.*, 2014, **68**, 651–666.
- 31 S. Lozano, D. Iribarren, M. T. Moreira and G. Feijoo, *Sci. Total Environ.*, 2009, **407**, 1744–1754.
- 32 J. Ren, S. Tan, L. Dong, A. Mazzi, A. Scipioni and B. K. Sovacool, *Bioresour. Technol.*, 2014, **162**, 1–7.
- 33 D. Iribarren, A. Hospido, M. T. Moreira and G. Feijoo, *Sci. Total Environ.*, 2011, **409**, 1786–1798.
- 34 A. Charnes, W. W. Cooper and E. Rhodes, *Eur. J. Oper. Res.*, 1978, **2**, 429–444.
- 35 W. W. Cooper, L. M. Seiford and K. Tone, *Data Envelopment Analysis: A Comprehensive Text with Models, Applications, References and DEA-Solver Software*, Springer Science & Business Media, 2007.
- 36 R. D. Banker, *Eur. J. Oper. Res.*, 1984, **17**, 35–44.
- 37 K. Tone, *Eur. J. Oper. Res.*, 2002, **143**, 32–41.
- 38 F. A. Chowdhury, H. Yamada, T. Higashii, K. Goto and M. Onoda, *Ind. Eng. Chem. Res.*, 2013, **52**, 8323–8331.
- 39 K. Goto, H. Okabe, S. Shimizu, M. Onoda and Y. Fujioka, *Energy Procedia*, 2009, **1**, 1083–1089.
- 40 I. Eide-Haugmo, O. G. Brakstad, K. A. Hoff, K. R. Sørheim, E. F. da Silva and H. F. Svendsen, *Energy Procedia*, 2009, **1**, 1297–1304.
- 41 I. Eide-Haugmo, H. Lepaumier, A. Einbu, K. Vernstad, E. F. Da Silva and H. F. Svendsen, *Energy Procedia*, 2011, **4**, 1631–1636.
- 42 H. Lepaumier, D. Picq and P. L. Carrette, *Energy Procedia*, 2009, **1**, 893–900.
- 43 E. Gjernes, L. I. Helgesen and Y. Maree, *Energy Procedia*, 2013, **37**, 735–742.
- 44 A. I. Papadopoulos, S. Badr, A. Chremos, E. Forte, T. Zarogiannis, P. Seferlis, S. Papadokonstantakis, C. S. Adjiman, A. Galindo and G. Jackson, *Chem. Eng. Trans.*, 2014, **39**, 211–216.
- 45 S. Papadokonstantakis, S. Badr, K. Hungerbühler, A. I. Papadopoulos, T. Damartzis, P. Seferlis, E. Forte, A. Chremos, A. Galindo, G. Jackson and C. S. Adjiman, *Comput. Aided Chem. Eng.*, 2015, **36**, 279–310.
- 46 A. I. Papadopoulos, S. Badr, A. Chremos, E. Forte, T. Zarogiannis, P. Seferlis, S. Papadokonstantakis, A. Galindo, G. Jackson and C. S. Adjiman, *Mol. Syst. Des. Eng.*, 2016, **3**, 1645–1669.
- 47 E. Stefanis and C. Panayiotou, *Int. J. Thermophys.*, 2008, **29**, 568–585.
- 48 L. Constantinou, R. Gani and J. P. O’Connell, *Fluid Phase Equilib.*, 1995, **103**, 11–22.
- 49 A. V. Rayer, A. Henni and P. Tontiwachwuthikul, *Can. J. Chem. Eng.*, 2012, **90**, 367–376.
- 50 E. Conte, A. Martinho, H. A. Matos and R. Gani, *Ind. Eng. Chem. Res.*, 2008, **47**, 7940–7954.
- 51 B. E. Poling, J. M. Prausnitz and J. P. O’Connell, *The properties of gases and liquids*, McGraw-Hill, New York, 5th edn., 2001.
- 52 EPA (Environmental Protection Agency), <http://www.epa.gov>, (accessed 1st February 2014).
- 53 M. Ramdin, T. W. de Loos and T. J. H. Vlucht, *Ind. Eng. Chem. Res.*, 2012, **51**, 8149–8177.
- 54 S. Ma’mun, H. F. Svendsen, K. a. Hoff and O. Juliussen, *Energy Convers. Manag.*, 2007, **48**, 251–258.
- 55 T. P. T. Pham, C.-W. Cho and Y.-S. Yun, *Water Res.*, 2010, **44**, 352–372.
- 56 GAMS Development Corporation, *General Algebraic Modeling System (GAMS) Release 24.4.5*, Washington, DC, USA, 2015.

- 57 GAMS Development Corporation, *GAMS - The Solver Manuals*, GAMS Release 24.4.5, Washington, DC, USA, 2015.
- 58 L. M. Seiford and J. Zhu, *INFOR*, 1999, **37**, 174–187.
- 59 S. Freguia and G. T. Rochelle, *AIChE J.*, 2003, **49**, 1676–1686.
- 60 A. A. Khan, G. N. Halder and A. K. Saha, *Int. J. Greenh. Gas Control*, 2015, **32**, 15–23.
- 61 A. Fredenslund, R. L. Jones and J. M. Prausnitz, *AIChE J.*, 1975, **21**, 1086–1099.