BOOK OF ABSTRACTS

Workshop on Simulation and Optimization for Sustainable Engineering

Santander, Cantabria, Spain
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Workshop on Simulation and Optimization for Sustainable Engineering

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Book of Abstracts. Workshop on Simulation and Optimization for Sustainable Engineering

**Marcos Fallanza Torices, Gabriel Zarca Lago,
Carolina Tristán Teja, Gloria González Lavín,
Miguel Viar Fernández, Lucía Gómez Coma,
Guillermo Díaz Sainz
(eds.)**

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Miguel Viar Fernández

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Preface

Welcome to the Workshop on Simulation and Optimization for Sustainable Engineering!

It is our pleasure to welcome you to this Workshop on Simulation and Optimization for Sustainable Engineering, which is held in Santander (September 28th-29th), on the occasion of the visit of Prof. Ignacio Grossmann to the Department of Chemical and Biomolecular Engineering of the Universidad de Cantabria in the framework of the Fulbright U.S. Specialist Program.

This workshop is organized in collaboration with AQUIQÁN, the Association of Chemistry and Chemical Engineering of Cantabria, with the aims of serving both as a forum of discussion of the recent advances in the topic and a meeting point of the closest collaborators of Prof. Grossmann in Spain over the last years. Overall, 30 researchers will take part in this event coming from several universities (Alicante, Cantabria, Rovira i Virgili, Salamanca, Sevilla, and Valladolid) and the IMDEA Materials Institute. The program includes a plenary lecture imparted by Prof. Grossmann, one keynote presentation representative of each institution and around 15 oral presentations from young researchers.

We hope that you will enjoy the activities and look forward to meeting you in Santander.

Inmaculada Ortiz, Marcos Fallanza and Gabriel Zarca

Workshop on
Simulation and Optimization for Sustainable Engineering

WSOSE Program

Time	Thusday, 28th	Time	Friday, 29th
8:40 – 9:00	Registration of participants		
9:00 – 9:10	Welcome		
9:10 – 10:00	*PL: Ignacio Grossmann (CMU)*	9:30 – 10:00	*KN4: Miguel A. Pozo (US)*
10:00 – 10:30	*KN1: Mariano Martín (USAL)*	10:00 – 10:30	*KN5: Cesar de Prada (UVA)*
10:30 – 10:50	O1: Sofía González (USAL)	10:30 – 10:50	O10: Erika Oliveira (UVA)
10:50 – 11:10	O2: Carolina Tristán (UC)	10:50 -11:10	O11: Gloria González (UC)
11:10 – 11:50	COFFEE BREAK		
11:50 – 12:20	*KN2: Christina Schenk (IMDEA)*	11:50 – 12:10	O12: Richard Cabrera (URiV)
12:20 – 12:40	O3: José Roldán (USAL)	12:10 – 12:30	O13: Rogelio Rivero (UVA)
12:40 – 13:00	O4: Irina Bausa-Ortiz (UVA)	12:30 – 12:50	O14: Miguel Viar (UC)
13:00 – 13:20	O5: Daniel Montes (UVA)	12:50 – 13:10	O15: Javier Viguri (UC)
13:20 – 13:40	O6: Berta Galán (UC)	13:10 – 13:30	O16: Carlos Prieto (USAL)
13:40 – 15:00	LUNCH		
15:00 -15:30	*KN3: José A. Caballero (UA)*		
15:30 – 15:50	O7: Zinet Mekidiche (UA)		
15:50 – 16:10	O8: Tomás García (UVA)		
16:10 – 16:30	O9: Javier Fernández (UC)		

PL: Plenary Lecture
KN: Keynote
O: Oral Presentation

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PLENARY LECTURE

KEYNOTES

ORAL PRESENTATIONS

Plenary Lecture

Optimization of Reliable and Resilient Power Systems Planning with High Renewables Penetration

Ignacio E. Grossmann[1,*]

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With recent trends in decarbonization, the optimization of electric power systems is receiving increased attention. We consider in this talk the long-term planning of electric power infrastructures involving coal, natural gas and nuclear power with high renewable penetration (wind, solar). We propose a multi-period mixed-integer linear programming (MILP) model that incorporates both the investment decisions on the generating units, storage units, and transmission lines, and short-term unit commitment decisions to capture the variations of the renewables. To make the large-scale MILP model tractable, we first propose several spatial and temporal aggregation schemes. Next, we adapt the Benders decomposition algorithm to solve the problem efficiently. Case studies of the ERCOT, the independent system operator in Texas, are provided to demonstrate the capabilities of the proposed approaches. Finally, we also discuss an extensions or expansion planning of reliable and resilient power generation and transmission systems. The model is formulated using Generalized Disjunctive Programming (GDP). The proposed model can be decomposed into a reliability-constrained expansion planning model and a scenario-based resilient evaluation model. The reliability-constrained expansion planning model first determines the optimal number of back-up units and maintenance/inspection schedules to maximize the power system reliability while satisfying electricity demand over the planning horizon. We finally evaluate the resilience of the design and operation obtained from the expansion planning model by solving multiple contingency scenarios with different extreme weather conditions.

Keynote Lectures

Sustainable Process and product Engineering: Towards the process and chemical industry of the future

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The Sustainable Products and Process engineering group of the University of Salamanca aims to develop mathematical tools towards the design of a more sustainable chemical and process industry. It uses a multi-scale methodology combining the rigor of the analysis of transport phenomena to understand the operation of the process units, and the systematic aspect of process systems engineering. They are applied to three lines of work, *consumer products*, in particular, the design of formulated products in which product performance must be integrated with processes and the supply chain [1], the *design of biorefineries*, where valorization of residual biomass is taken as the main objective (for example, residues from the production of olive oil, orange juice, wine or coffee) with the aim of obtaining high value-added products by creating a circular economy [2,3,4] and *renewable energy storage and transformation processes*, extending of the power to x concept to include the production of energy with an integrating methodology of planning, scheduling and design of the process without forgetting to evaluate the best use of energy depending on the location[5,6,7].

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Regional Government of Castilla y León (Junta de Castilla y León) and by the Ministry of Science and Innovation MICIN and the European Union NextGenerationEU / PRTR (H2MetAmo project - C17.I01.P01.S21), P&G, Mirat Fertilizantes SA, European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 778168, MINECO, JCyL

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Physical model-based, probabilistic, and data-driven methods for a sustainable energy and materials future

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The Earth's finite resource pool presents a tremendous challenge in light of escalating energy consumption and the relentless demand for manufacturing. A sustainable future hinges on innovations in alternative energy resources and materials, particularly bio-based and recyclable materials.
In this talk, we will navigate a diverse landscape of approaches encompassing physical model-based, probabilistic, and data-driven solutions and discuss their advantages and drawbacks. Our focus will center on the development of computational models, algorithms, and software tailored for design and optimization.
In more detail, we will discuss robust computational fluid dynamics-based optimization, and design of experiments, and Bayesian optimization techniques.
The findings are highlighted by numerical results for real-world applications. These case studies include the design of biogas power plants, a step towards sustainable energy production [1]. We will also shed light on the strategic planning and execution of experiments for materials laboratory automation, showcasing the transformative potential of these methodologies.

Acknowledgements
This work is joint work with Jonas Müller, Rainer Keicher, Dominik Schmidt, Kai Velten (Hochschule Geisenheim University), Volker Schulz (Trier University), Miguel Hernández-del-Valle, Lucía Echevarria-Pastrana, Burcu Ozdemir, Enrique Dios-Lázaro, Jorge Ilarraza-Zuazo, De-Yi Wang and Maciej Haranczyk (IMDEA Materials).
For the part related to biogas power plant design, we acknowledge the funding by the German Federal Ministry of Education and Research (Bundesministerium für Bildung und Forschung) within the collaborative project ROENOBIO with contract number 05M2013UTA and the German Research Foundation within the research training group 2126 Algorithmic Optimization. For the materials part, we acknowledge the support from the "(MAD2D-CM)-IMDEA Materials" Project funded by Comunidad de Madrid by the Recovery Transformation and Resilience Plan and by NextGenerationEU from the European Union.

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An overview of advances in zeotropic distillation systems

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The energy consumption in the industrial sector accounts for a third of the global energy use with 156 EJ in 2020 and a prevision of 207 EJ in 2050 [1]. In the industrial sector, the chemical and petrochemical industries account for around 20-30% of the energy consumption (e.g. in the European Union it was 21.5% in 2021, around 2.159 EJ [2]). Inside the chemical and petrochemical industries, distillation is the predominant method used for approximately 90 to 95% of all separation and purification, and this scenario is expected to persist in the foreseeable future. It has been estimated that distillation contributes to around 40-60% of the energy consumption in the petrochemical industries [2], i.e. [2.5-5.6] 10^{18} J/year equivalent to [47 – 105] million tons of oil per year.

With the numbers of the previous paragraph in mind, it is easy to understand that any improvement in distillation technologies can eventually have a huge economic (and environmental) impact at a global level.

In this presentation, we present an overview of some of the most relevant advances in the separation of zeotropic mixtures, with a focus on conceptual advances and mathematical programming models that allow us to get (or approximate) optimal separation sequences. Although the separation of mixtures containing azeotropes is conceptually more complex, the space of alternatives is considerably larger in zeotropic distillation, and most of the results can be directly extended to azeotropic distillation.

First, we present an overview of the first approaches to solve the «*sequencing problem*» considering only conventional distillation columns and sharp split of components adjacent in relative volatilities. Even though, those models are relatively simple and only consider a reduced subset of all possible alternatives they were the base of future advances and contributed to the development of superstructures.

The extension to the sharp separation of non-consecutive key components was closely related to the development of «Thermally Coupled Distillation» (TCD) involving mixtures of more than three components. So, we do a short overview of the advantages and drawbacks of TCD and the main structural considerations to generate the feasible set of TCD sequences. Here we will show that not all the feasible sequences can be optimal, but just the subset of 'regular configurations', which in turn can be generated from the set of basic sequences [3-5].

Once a thermal couple appears it is possible to generate «thermodynamically equivalent configurations» (TEC) [6]. While from the point of view of cost and environmental impact TECs have, in general, a marginal effect, and therefore it is not convenient to consider them if we try to optimize cost or environmental aspects, they have important effects over the operability with configurations that could eventually be very difficult to operate.

TCD configurations are also the starting point to generate intensified distillation sequences. We will show how to generate some intensified alternatives. We also will show that TCD can be integrated with classical heat integration alternatives and combined with other separation technologies to generate hybrid systems. We will illustrate all previous points with some academic and industrial examples.

In the last years, as a consequence of the climatic emergency, the question of how to use renewable energy sources in the chemical industry has acquired more relevance [1]. Among other alternatives, electrification is gaining interest. In the case of distillation, the integration of heat pumps/engines seems an attractive alternative. We will show some ideas of how vapor recompression, bottom flashing, and internally heat-integrated distillation (and maybe other alternatives) can be integrated with TCD to substitute total or partially the classical utilities based on fossil fuels.

Acknowledgments
The authors acknowledge financial support from the Ministerio de Ciencia e Innovación, Spain, under project PID2021-124139NB-C21.

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Process optimization in uncertain environments

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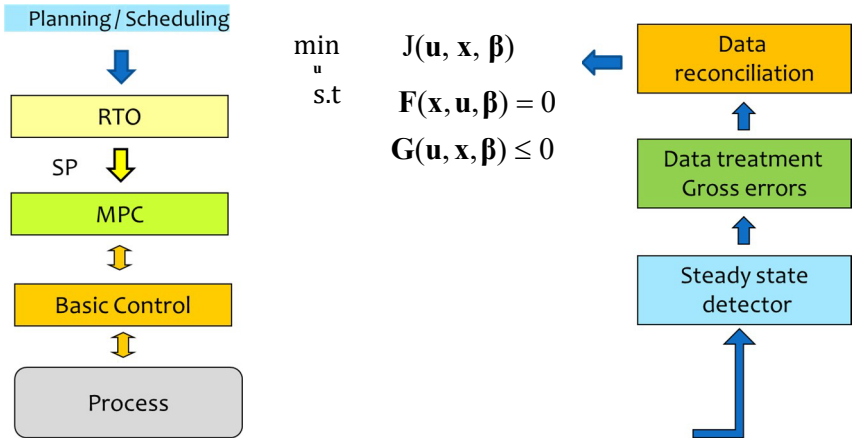
The paper provides an overview and reviews different methods to deal with the optimal operation of processes that function in uncertain environments. Uncertainty can be associated to different sources ranging from errors in the models to unexpected changes or disturbances on the process, unknown future events, etc. Process optimization covers also a wide range of topics. In the paper we will focus on the optimization of the operation, where measurements are available and time may be important, leaving aside other topics such as optimal process design. Of course, both topics are not fully independent as we can consider a plant design where dynamic aspects related to the future operation of the plant are considered so that plant designs are generated that guarantee a certain level of operability, that is, easiness of control, robustness against disturbances, etc. in what is known as integrated process and control design.

In that context, process optimization is carried out traditionally by using production scheduling or Real Time Optimization (RTO) systems that are implemented as large MIP or NLP codes based on a cost function J that reflects the economic operation aims, a process model F that reflects the relations among the process variables x, u (continuous and discrete) and a set of constraints G that condense ranges, rules of operations, safety margins, etc. following an architecture similar to the one on the left hand side of Figure 1.

The optimization problem is solved periodically incorporating the most recent information from the process to provide a certain value for the uncertain variables or parameters $\boldsymbol{\beta}$ in order to compute the optimal actions $\mathbf{u}^*$. Nevertheless, this way of incorporating uncertainty into the decision problem does not consider the different values that $\boldsymbol{\beta}$ may have when $\mathbf{u}^*$ is applied to the process. One way of taking them into account is incorporating to the optimization problem all possible values of $\boldsymbol{\beta}$, in what is known as robust optimization, but this leads to very conservative solutions. Instead, one may consider the set of possible uncertain scenarios and formulate a two-stage optimization problem where decisions are partitioned between what should be done now and what can be done when the uncertainty is revealed providing more degrees of freedom that improve the solution. Also, it is possible to incorporate the concept of risk, penalizing the probability of obtaining very bad solutions if certain scenarios are materialized.



In the same way, the so-called Chance Constraint approach deals with the problem of uncertain variables by formulating the equations where they appear in terms of probability of fulfillment, transforming the problem in a deterministic one. In the latest years, another approach has emerged that do not use mathematical programming but Artificial Intelligence (AI) and data-based models obtained with Machine Learning and optimizer the problem with evolutive algorithms or Reinforcement Learning methods. It is gaining a lot of visibility and will be reviewed in the presentation.

Obviously, the way in which the model is updated according to the current or predicted state of the process plays a central role in the outcome of the optimization, as we compute the optimum of the model as the real one of the process is unknown. But notice that there are always errors between models and the real process. If these errors refer only to the value of the model parameters, then an approach like the one in the previous figure will be fine. But most of the cases the errors will be structural ones and, then, it is well known that the optimum of the model will be different from the one of the process.

To avoid this important problem there are several approaches that, instead of updating the model, try to formulate the optimization problem incorporating direct process information, so that the result of the modified optimization corresponds to the real process optimum in spite of the fact that the model is not perfect. Extremum Seeking (ES) and Modifier Adaptation (MA) stand among the most promising approaches, but they present practical problems when implemented in the process industry. In particular, they need to disturb the process to obtain the required information, which response may delay several hours in many processes and sometimes create problems.

To avoid this problem, and referring to MA methods, in our research group we have been working in the integration of MA with MPC and RTO, to generate eMPC controllers that using an economic aim and a model with errors can provide the real process optimum working in real time. Two algorithms, Dynamic Modifier Estimation (DME) and Transient Modifier Adaptation (TMA) were developed with that purpose and tested in different cases that will be also reviewed in the presentation.

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The pipelines and cable trays location problem in naval design

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This presentation deals with the determination of optimal locations for pipelines and cable trays in naval design. The problem consists of finding the number and types of cable tray routes to be created between various devices in order to minimize a user defined cost function. We reduce the problem to an ad hoc min-cost multicommodity flow problem with additional constraints imposed by technical requirements. This problem is solved for small-sized instances by using off-the-shelf optimization solvers. We also develop an exact relax-and-cut strategy that allows to handle medium-sized instances. For larger instances, we propose a family of heuristic algorithms consisting on the combination of two phases: (I) Construction of initial cable trays paths; and (II) Transformation to feasible cable trays verifying the technical requirements. For each of them, we also propose different strategies which give rise to several algorithms. These algorithms are compared on a computational experience using two types of instances: the first one based on random instances of different sizes and the second one based on instances with well-defined corridors to asses the availability of our methodology to enforce the creation of cable trays. Finally, we also analyze a real size case study provided by our industrial partner, Ghenova, a leading Naval Engineering company, validating our proposal to find solutions for this problem.

Acknowledgements
The authors of this research acknowledge financial support by the Spanish Ministerio de Ciencia Tecnología, Agencia Estatal de Investigación, and Fondos Europeos de Desarrollo Regional (FEDER) via project PID2020-114594GB-C21. The authors also acknowledge partial support from projects: FEDER-US-1256951; Junta de Andalucía, Spain P18-FR-1422; CEI-3-FQM331; B-FQM-322-UGR20; AT 21_00032; NetmeetData: Ayudas Fundación BBVA a equipos de investigación científica 2019; Contratación de Personal Investigador Doctor (Convocatoria 2019) 43 Contratos Capital Humano Línea 2. Paidi 2020, supported by the European Social Fund and Junta de Andalucía; UE-NextGenerationEU (ayudas de movilidad para la recualificación del profesorado universitario); VII PPIT-US (Ayudas Estancias Breves, Modalidad A); and the IMAG-Maria de Maeztu grant CEX2020-001105-M /AEI /10.13039/501100011033.

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Oral Presentations

Optimal integrated plant for renewable surfactants production from manure and CO2

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The sustainable development goals pose a number of challenges to the traditional industry. The sustainable production and consumption from the UN require a complete transformation of the chemical and consumer goods industry. Chemicals traditionally produced from crude fractions must find another raw material that is renewable and alternative production routes. Surfactants are specialty chemicals whose purpose is to wet, emulsify, help solubilize or soften species. They are used in laundry as well as in other industries such as gas recovery from fracture and, so far, they have been typically produced form crude oil. Washing clothes or dishes means that sooner or later the species end up in a water body. Even if the wastewater treatment plants are capable of processing and removing surfactants from water, including the two major ones such as linear alkylbenzene sulphonates (LAS) and the alkyl phenol ethoxylates (APE), that are aerobically degraded and partially absorbed to the sewage sludge, biodegradable ones can certainly help in the sustainability of products such as detergents. There are already synthetic paths for sustainable biosurfactants [1,2]. In most linear processes that transform biomass into the biosurfactants are presented. Surfactants consist of two sections, a hydrophilic head group and a hydrophobic alkyl chain. Alternatively, it is possible to generate both fractions from biomass to build alkyl poluglucosides, APG's, [3] and that can be produced from manure and CO2.

This study presents the conceptual design for the production of sustainable surfactants from waste, including CO_2 and manure. An integrated facility is designed to process the waste employing it to grow algae and produce biogas. From the algae, intermediates such as glucose and lipids are obtained. From biogas, hydrogen is produced. Next, alcohols are produced via lipids hydrogenation so as to synthesize the APG's from them and the glucose. No further raw material is required, at the expense of a large investment. Figure 1 shows a scheme of the process, which is divided into the 7 sections depicted before, such as biogas production, biogas reforming stage, syngas composition adjustment, algae processing, glucose production, glucose crystallization, algae oil section, synthesis of APG. The design problem is formulated as a large NLP for the selection of processing route of the intermediates and final product as well as the operating conditions. Such formulation allows for the selection of the algae growing and its composition for the limited use of additional utilities and chemicals.

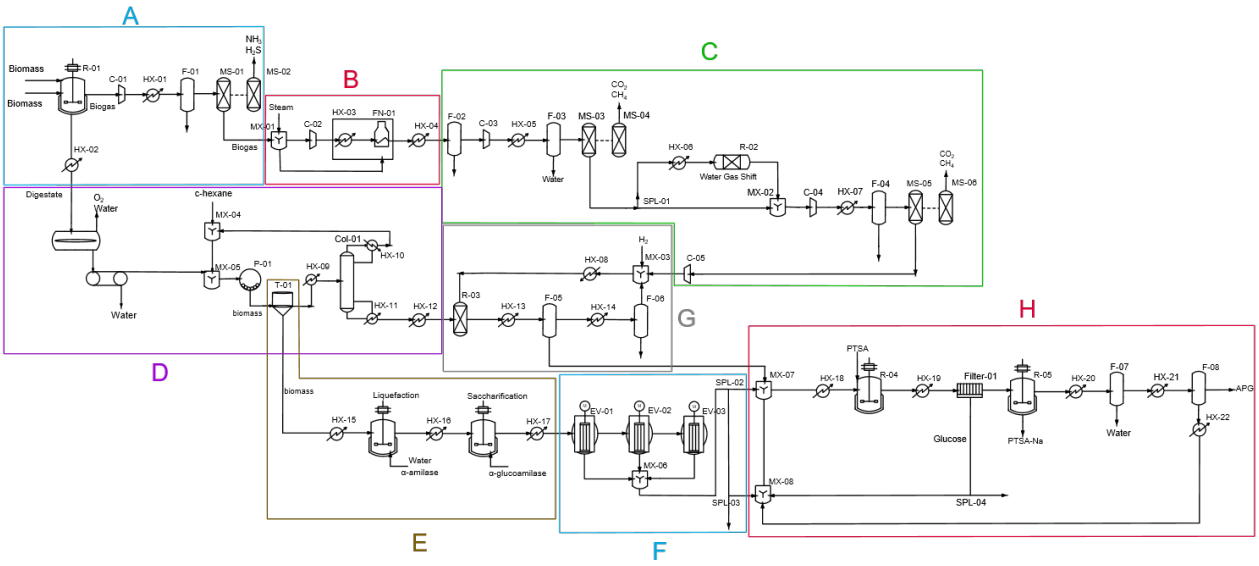

Figure 1. Integrated process for APG production from manure and CO2 : A: Biogas production, B: Biogas reforming stage, C: Syngas composition adjustment, D: Algae processing, E: Glucose production, F: Glucose crystallization, G: Algae oil section, H: Synthesis of APG

The algae composition recommended consists of 60% lipids and 27% carbohydrates. The yield of the facility reaches 0.47 kg/kg of algae (0.08 kg/kg manure). To produce 252 kt/yr of APG the facility consumes 17.7 MW of thermal energy and steam and 7.9 MW of electricity, absorbing 788 kt/yr of CO2 after discounting the emissions related to thermal and power consumption. The investment adds up to 196 M€ for the production cost of 0.17 €/kgAPG. The large amount of manure to be processed, corresponding to 300k cows, suggests a scale down study to evaluate the effect on the investment and production costs. Current market price of APG can be achieved processing the waste of over 2.5k animals.

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Optimizing Reverse Electrodialysis Energy Recovery from Desalination Brines through Disjunctive Programming

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Introduction

Desalination is a growing, drought-proof, but energy-intensive water source whose rejected brine is also gaining recognition as a potential source of energy rather than a mere waste stream. Salinity Gradient Energy (SGE) technologies, which retrieve energy from the mixing of two water streams of different concentrations, can provide clean, base-load electricity to desalination supporting their decarbonization and circularity. Reverse Electrodialysis (RED) is one of the most developed SGE technologies to power desalination but needs to prove it is economically feasible to make RED-based electricity a full-scale reality [1].

Estimating the techno-economic feasibility of the RED process involves incorporating detailed models, and balancing trade-offs in design and operation that heuristics can hardly address. An alternative to making decisions about RED process design is to use optimization-based methods. This work provides the cost-optimal design of a large-scale RED system capturing SGE from a medium-capacity desalination plant's brine using Generalized Disjunctive Programming (GDP)that yields the hydraulic topology and working conditions of the RED units that maximize the net present value (NPV) of the RED process.

Problem Statement and Superstructure Definition

The problem addressed is to determine the number and hydraulic arrangement of the RED units and their working conditions (e.g., electric current, inlet flow velocities, and high- and low-salinity (HC and LC) streams' molar concentrations and flow rates) that yield the NPV-optimal flowsheet design of the RED process for a given concentration, volume, and temperature of the HC and LC feed streams, and a fixed design of the RED stacks.

The superstructure in Fig. 1 displays the feasible design alternatives for the stated problem, with Nr candidate RED units, a set of units that source the HC and LC feedwaters and sink and discharge units that collect the unused and exhausted HC and LC streams from the RED units.

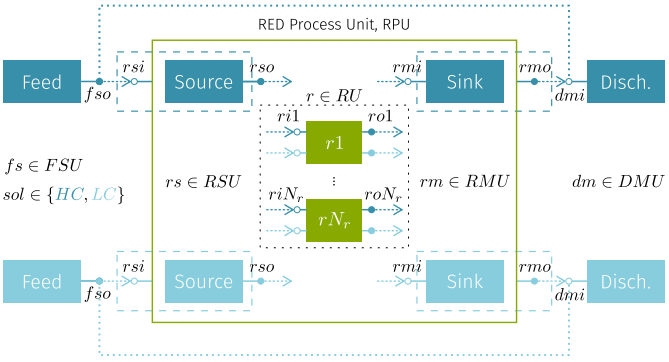

Figure 1. Superstructure of the RED process with Nr candidate RED units.

Optimization model

The set of equations (1) describes the general form of the GDP optimization model [2] for the superstructure in Fig. 1. The Nr two-term disjunctions represent the discrete activation and deactivation of the Nr candidate RED units. The objective is to maximize the NPV of the RED process that considers electricity sales and carbon pricing revenues.

$$\begin{aligned} \max NPV = \quad & f(x) \\ s.t. \quad & g(x) \leq 0 \\ & \begin{bmatrix} Y_r \\ h_r(x) \leq 0 \end{bmatrix} \veebar \begin{bmatrix} \neg Y_r \\ B^r x = 0 \end{bmatrix} \quad \forall\, r \in RU \\ & \Omega(Y_r) = True \\ & x \in X \subseteq R^n \\ & Y_r = \{True,\ False\} \quad \forall\, r \in RU \end{aligned} \tag{1}$$

Bilinear mass balances in the mixers and nonlinearities in the rigorous RED unit model give rise to a nonlinear GDP model. Nonconvexities yield multiple optimal local solutions, therefore requiring global optimization techniques. As such, we apply the Global Logic-based Outer Approximation (GLOA) algorithm to solve the GDP problem. The GLOA algorithm decomposes the solution to the GDP into a sequence of mixed-integer linear programming (MILP) master problems and reduced nonlinear programming (NLP) subproblems. We solve the MILP master problems with CPLEX and the NLP subproblems with the multistart heuristic algorithm MSNLP using IPOPTH as a local NLP solver.

Using the GDP model, this work explores how electricity and emissions allowances prices, membranes price, desalination plant capacity, and the use of high-performing membranes, may affect the cost-optimal design, economic competitiveness of the RED process. To evaluate the benefits of the GDP model over heuristics, we also compare the conventional series parallel configuration with the optimal solution to the GDP problem. This case study serves to estimate the emissions and energy savings from the water- and carbon intensive grid mix that the RED system can offer to desalination in the most cost-effective way. For instance, in the context of soaring electricity prices and strong green financing support, with the use of high-performing, affordable membranes (~10 €/m2), RED could save 8% of desalination plant energy demand from the grid, earning profits of up to 5 million euros and LCOE of 66–126 €/MWh, which is comparable to other renewable and conventional power technologies. In such conditions, the optimization model finds profitable designs for the entire range of medium-capacity desalination plants, providing energy and emission savings from the grid.

Conclusions

These assessments show that mathematical programming is an efficient and systematic modeling and optimization tool to assist early-stage research, and to identify optimal design and operation guidelines for full-scale RED implementation. Future studies should incorporate in decision-making uncertainty from electricity and emission allowances prices and membrane cost through stochastic optimization and sustainability criteria through multi-objective optimization coupled with life cycle assessment principles.

Acknowledgements

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Stability Kinetic Study for Amylase and Protease Enzymes

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Abstract
Surfactants are one of the main ingredients in the formulation of detergents as they reduce the surface tension of water and promote the solubility of soil in the liquid medium. However, they are marketed as disposable products, entering a negative impact on the environment due to its lack of biodegradability. For this reason, the design of detergent formulations is currently focused on employing ingredients that satisfy the cleaning needs respecting the environment [1]. Nowadays enzymes such as amylases and proteases are considered as a potential alternative ingredient due to their biodegradability capability [2]. These proteins are able to improve the cleaning performance, reducing the cleaning time together with the fresh water and energy consumption [2]. In this way, more environmentally friendly cleaning process is carried out, promoting the achievement of the objectives set by United Nations in terms of sustainability and responsible consumption and production [3].

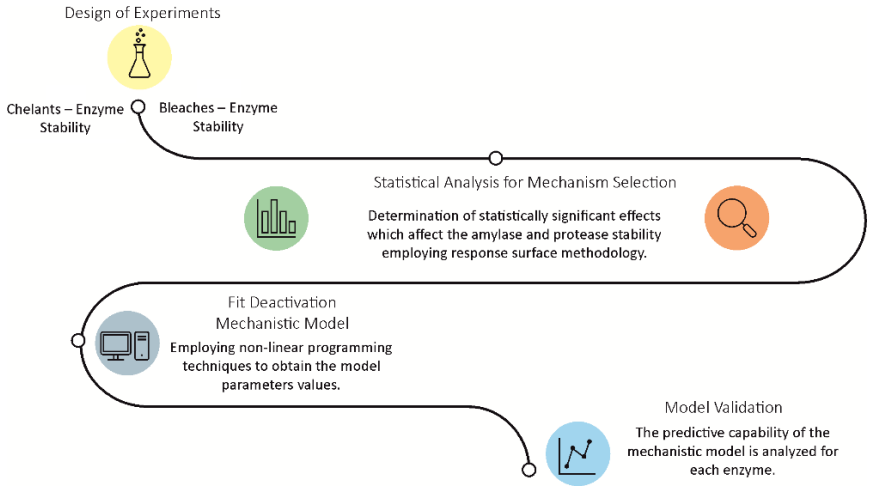

Figure 1. Modelling Methodology for Amylase and Protease.

The stain removal performance might be affected by the stability of the enzymes. For this reason, this work proposes a methodology in order to study the amylase and protease stability, showed in Figure 1. Two designs of experiments were carried out to evaluate the impact of pH, temperature, hardness, bleaching agents such as peroxide and peracid-based bleaches, manganese-based bleaching catalyst, chelating and builder compounds on enzyme stability. Then, response surface methodology was performed to identify the most significant variables which affect the stability of each enzyme, proposing a kinetic mechanism. Next, a mechanistic model is formulated as non-linear differential equations for each enzyme. Subsequently, a parameter estimation problem is solved, using non-linear programming techniques, to obtain the model parameters values. Finally, the predictive capabilities of each mechanistic model were validated employing experimental data.

The statistical analysis shows a thermal decomposition of amylase led by pH – temperature interaction. Additionally, deprotonated peracid-based bleach promotes the amylase decomposition together with the protonated peroxide base bleach, being the last one, activated by the manganese bleaching catalyst. On the other hand, the protease presents an abrupt thermal decomposition from a temperature of 50 °C, regardless of pH. In contrast to amylase, the protease is decomposed by the protonated and deprotonated forms of peracid and peroxide-based bleaches respectively. Figure 2 and figure 3 show the validation at 95% confidence of the mechanistic models, providing a training determination coefficient of 0.84 and 0.90 for amylase and protease respectively. In addition, the validation determination coefficient is 0.90 for both enzymes, showing a large capability of the models to predict the amylase and protease stability as a function of variation sources, being not overfitted models.

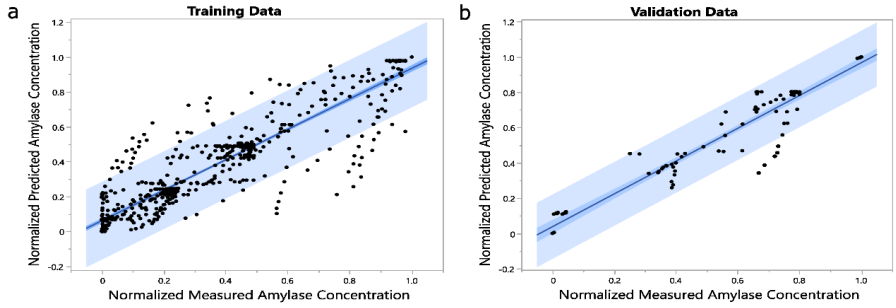

Figure 2. Validation Amylase Stability Model: (a) Training Data, (b) Validation Data.

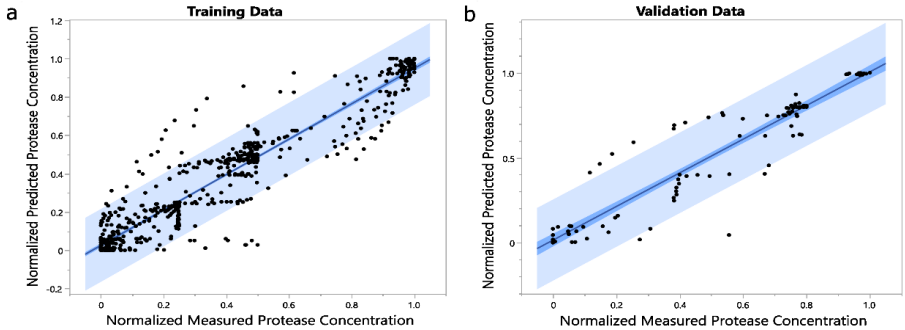

Figure 3. Validation Protease Stability Model: (a) Training Data, (b) Validation Data.

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An alternative for parameter estimation in biological processes

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The main goal of this study is to propose an improved methodology for parameter estimation in biological processes. Biological processes are frequently described using several nonlinear differential equations and several parameters to represent the complex dynamics of these processes. Particularly, in wastewater treatment processes based on microalgae- bacteria consortia, some of the values of the parameters are previously known and can be assumed from the values reported in the literature. Instead, other parameters largely depend on environmental conditions, the scale of the reactors, and the specific strains involved in wastewater treatment. In microalgae-bacteria models, these model parameters are generally obtained through calibration or parameter estimation [1], [2].

The proposed methodology represents an alternative to dealing with large optimization problems in parameter estimation. The proposed approach solves increasing-complexity optimization problems to estimate process parameters gradually, avoiding convergence problems. The idea is first to formulate one easier parameter estimation problem involving a subset of system outputs and parameters, replacing the other outputs variables with their experimental values, and then use these estimated values as a starting point for the next step of the optimization problem. The approach is oriented to increase the sub-set dimension until all the system outputs are being included the optimization problem.

An experimental microalgae-bacteria photobioreactor for wastewater treatment was used here as the study case to apply the proposed methodology. The model BIO_ALGAE 2 [3] has been used to describe the photobioreactor. In this work, five model outputs were considered: Total Suspended Solids (TSS) concentration, dissolved Total Organic Carbon (TOC) concentration, dissolved Inorganic Carbon (IC) concentration, dissolved ammonium concentration ($S\_NH^{+}_4$), and dissolved oxygen (S_O_2) concentration. Photobioreactor modeling and simulation are coded in dynamic simulation software PROOSIS®.

A sensitivity analysis was conducted to identify the parameters with the greatest impact on the model outputs. In the sensitivity analysis, the model parameters involved in the processes of microalgae, heterotrophic bacteria, and nitrifying bacteria, as well as in gas transfer processes, were considered. The results of sensitivity analysis indicated that model outputs are especially sensitive to the maximum specific growth rate of microalgae (μ_{ALG}) and heterotrophic bacteria (μ_H); the decay rate of microalgae ($k_{death,ALG}$) and heterotrophic bacteria ($k_{death,H}$); and the gas-liquid mass transfer coefficients for ammonia ($K_{la,NH3}$), oxygen ($K_{la,O2}$), and carbon dioxide ($K_{la,CO2}$). Results of sensitivity analysis are used here also as a guide to determine the best selection of groups of model outputs to consider. Furthermore, for the appropriate selection of the pairs model parameters - model outputs, prior knowledge of the dynamics of the system and the dependencies between the parameters and the model outputs should be considered. Figure 1 shows the subsets of output variables used in the parameter estimation problem through dynamic optimization, as well as the stages necessary to include all outputs in the optimization problem.

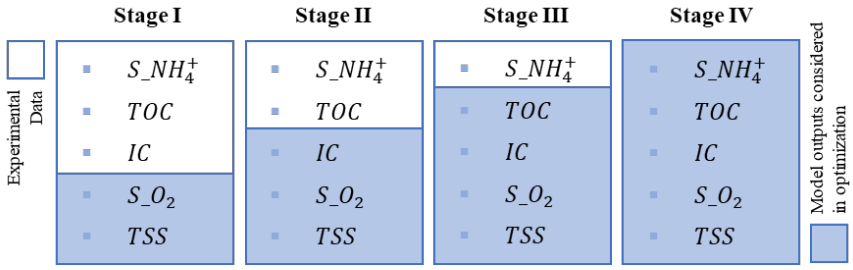

Figure 1. Stages of the optimization problem in the photobioreactor

Parameter estimation has been performed in a four-stage optimization sequence. In the first stage of the optimization problem, two model outputs were considered: TSS concentration and S_O2 concentration. Both model outputs depend mainly on the maximum specific growth rate of microalgae, the decay rate of microalgae, and the mass transfer coefficient for oxygen. Inorganic carbon is included as model output in the second stage of the optimization. As expected, μALG is the parameter with the greatest influence on IC concentration. Also, IC is highly affected by the gas-liquid mass transfer coefficient for carbon dioxide. In the third stage, TOC concentration is also considered as model output. TOC concentration is mainly affected by μH and kdeath,H. Finally, dissolved ammonium concentration is included as model output in the fourth stage. Ammonium concentration is mainly affected by μALG, kdeath,ALG, and Kla,NH3.

In this work, the fair function estimator [4] is used as a robust objective function in the parameter estimation problem. Unlike Least Square Method, the fair function estimator reduces the effect of outliers, thus making it more robust in nature. Parameter estimation results for each optimization step were provided in Table 1. The proposed optimization approach results in a better fit between experimental and simulated data and lower convergence time compared to considering the whole optimization problem at once.

Table 1. Values of estimated parameters in photobioreactor

Parameter	Value				Limits for Optimization
	Stage 1	Stage 2	Stage 3	Stage 4	
μ_{ALG} [d^{-1}]	1.627	0.990	1.062	1.062	0.4 – 2
$k_{death,ALG}$ [d^{-1}]	0.101	0.050	0.050	0.050	0.05 – 0.21
μ_H [d^{-1}]	1.656	1.000	1.210	1.211	1 – 6
$k_{death,H}$ [d^{-1}]	0.895	0.900	0.900	0.900	0.12 – 0.9
$K_{la,\,O2}$ [d^{-1}]	13.081	4.000	4.000	4.000	4 – 30

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Decomposition of continuous-time two-stage stochastic scheduling problems using the Similarity Index

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Scheduling deals with the optimal assignment of a series of finite resources to tasks over a defined time horizon. This allocation problem is frequently cast as a mixed-integer optimization problem, where binary variables are utilized to represent decisions such as resource assignments or operational states. Additionally, as scheduling deals with making decisions over time, it is closely related to uncertainty on some parameters, such as the weather, the price and availability of raw materials, demands, prices, etc. If uncertainty is not taken into account, the decisions can be suboptimal or could even lead to production problems (infeasible operation). There are several approaches for incorporating uncertainty in scheduling problems, among them, is two-stage stochastic programming. In which, the decision variables are split into two categories: first and second stage. The first-stage decisions are known as "here and now", and they are made without knowledge of the future value of the uncertain parameters. The second-stage decisions are known as "wait and see" as they are made once the actual value of the uncertain parameters is revealed. The probability distribution function of the uncertain parameters is discretized in a series of scenarios, $\xi = \{\xi 1, \xi 2, \dots, \xi N\}$, with associated probabilities, $p = \{p1, p2, \dots, pN\}$. The main difficulty associated with two-stage stochastic programming is the size of the resulting problems. The number of variables and constraints is directly proportional to the number of scenarios N considered in the uncertainty discretization. As MIP problems are NP-hard in general, their computational time scales exponentially in the worst case. Hence, the solution time becomes prohibitive when uncertainty is considered in industrial-scale scheduling problems. The authors have recently presented a decomposition method that allows solving each uncertainty scenario ξi as an independent optimization problem, which allows accelerating the computational time of two-stage stochastic scheduling problems based on a discrete-time representation in up to two orders of magnitude [1]. For this, they use a similarity index (SI) that allows comparing the first- stage solution of each scenario. Such index is maximized in each iteration until all first-stage solutions are equal and the non-anticipation criteria is met. However, the authors' previous proposal could not deal with scheduling problems based on continuous-time representations. That is, problems in which the number and duration of the time periods are fixed beforehand. This time representation can lead to sub-optimal solutions by definition and increases the number of binary variables associated with each time interval [2]. To overcome these issues, continuous time representations were developed over the years. With this approach, the time period durations are additional variables in the optimization problem. Although these continuous-time models are harder to develop, they yield more precise solutions and shorter solution times as they require fewer binary variables. To extend the use of the Similarity Index decomposition to continuous-time scheduling problems, it is necessary to meet the non-anticipation constraints on the time slot duration variables. A first approach could be to incorporate the slot duration into the similarity index itself. However, nonlinear nonconvex terms would appear, which complicates the solution and breaks the linearity of the usual scheduling MILPs.To overcome this issue, we propose to compute the similarity index only for binary variables with no influence on the continuous ones. Then, the Progressive Hedging Algorithm (PHA) could be used to make the time slot durations non-anticipative

[3]. This algorithm is based on the augmented Lagrangean and penalizes deviations from the expected value, computed from all the scenarios solutions. In this way, both the SI maximization and the corresponding PHA terms could be incorporated into the objective function of the problem to enable its decomposition. Our proposal was tested on literature case study that consists in the hybrid scheduling and planning of a multiproduct continuous plant with a single processing unit [4]. The case study was originally deterministic (no uncertain parameters), but it was extended to a two-stage formulation assuming the product demand as uncertain. The resulting problem has a time horizon of four weeks, with due dates at the end of each week. Additionally, each week is split into five variable duration slots for processing the different materials. Considering five different products, and eight equally probable scenarios, the optimization problem has 8801 continuous variables, 1120 binary variables, and 9155 constraints. It was coded on GAMS 40.2.0 and solved with Gurobi 9.5. The traditional monolithic approach was compared to our proposal for solving the optimization problem. The monolithic approach arrived at a solution $z^P = 10685$ in 10 CPU hours. On the other hand, the combined SI+PHA method at a solution $z^P = 9883$ in 2141 CPU seconds and 269 iterations. Although the proposed SI+PHA yielded a worse solution, these results seem to show that the decomposition approach allows obtaining high quality feasible solutions much faster than its monolithic counterpart. Figure 1 shows the SI and scaled PHA error evolution over the iterations. The SI converges quickly to the maximum possible value of 1 (the first-stage binary variables are equal among the scenarios), while the PHA error takes a lot of iterations to meet the established convergence criterion.

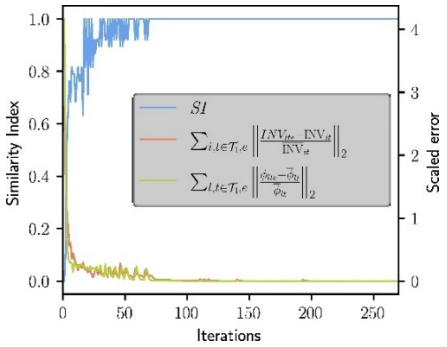

Figure 1. Scaled error and SI evolution until convergence.

In future work, we aim to replace the PHA to meet the non-anticipation criteria on the time slot duration variables. With these preliminary results, we could observe that the algorithm was mainly limited by the convergence of the continuous variables.

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Green Ammonia Production Plant: Small-Scale Preliminary Design and Simulation

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Abstract
Although shipping has proven to be the most energy efficient mode for mass transport, according to the International Maritime Organization (IMO), emissions from ship engines are harmful to the environment at both regional and global scales [1. Many development projects have settled the goal of substituting fossil fuels for other clean and renewable energy sources; hydrogen, ammonia, methanol, liquid biomethane or synthetic diesel are investigated as renewable fuels (Sea of innovation Cantabria Cluster 2021). Ammonia seems to be the best option as a renewable fuel [2] and in addition, it doesn't present any problematic property, which makes it an easy working and transporting component.

The objective of the ***Bahía H2 Offshore:*** *Ammonia as a marine fuel* is the development of a pioneering and innovative system for the generation, in marine conditions, of fuels in the form of hydrogen and green ammonia through floating renewable energy (offshore wind and/or solar photovoltaic) as shown in Figure 1. Initially the project will focus on the design, construction, installation and monitoring of a floating platform at the public domain of the Santander Port Authority integrating alkaline electrolysis technologies for the production of green hydrogen and the *simulation of the Haber-Bosch process* for the generation of ammonia (NH_3). Although in this first phase the technological solutions will be tested in a port area of Santander, the final application will be in conditions far from the coast. This project seeks to provide a solution to two main drawbacks faced by offshore renewable energy projects: the intermittency and seasonality of the solar or wind energy they produce and the need to transport the energy generated to the surface for its final use.

The project of Marine Sciences of the Cantabria University titled ***Planta de producción de amoniaco sostenible a pequeña escala como combustible renovable de buques "Amonsos"*** simulates and evaluates different alternatives to produce small scale ammonia (25 kg/h ammonia of 98% purity) in floating platform at the port of Santander to be used as fuel for cargo ships, selecting the best sustainable alternative for ammonia production from seawater and air as raw material.

The alternatives consist of four stages: power collection, considering wind turbines or solar PV panels, air separation for which membranes or, PSA are evaluated, water electrolysis and ammonia synthesis [3]. The analysis of the state of the art of small-scale ammonia production plants allows the Haber-Bosch process to be selected as the most suitable in terms of accessibility of raw materials, working conditions, efficiency, costs, and LRT, including the obtaining of hydrogen through seawater electrolysis and nitrogen from air separation.

The project is organized in three parts:

1. Design of a small-scale production process (25 kg/h ammonia of 98% purity) from raw materials and renewable energies, modelling of the proposed diagram and simulation of the diagram to subsequently optimize the operating conditions based on an objective function of minimizing installation and operation costs. This information allows the sizing of equipment and the establishment of an overall area for the floating platform. Preliminary estimation indicates the necessity of 300 m^2 of area for the floating platform and €2.1 MM as necessary cost inversion using modular methods.

2. Definition of the optimal configuration of the process; this includes a superstructure, optimising the superstructure and selecting the best alternatives in accordance with economic, environmental and social objectives.

3. Integration of the models for power collection units considering wind turbines and/or solar PV panels is carried out [4].

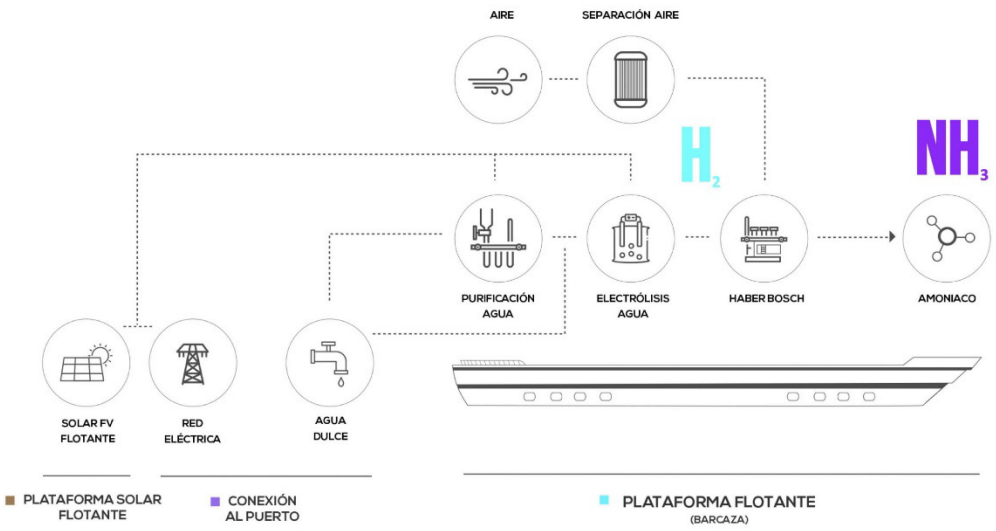

Figure 1. Set-up of ***Bahía H2 Offshore:*** *Ammonia as a marine fuel* (www/bahiah2.com/proyecto).

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Empowering Distillation Columns: A Green Revolution in Energy Efficiency and Environmental Impact

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In the context of sustainable development and environmental protection, with a particular focus on reducing atmospheric CO2 emissions, the transition from fuel-based to electrified processes stands as a pivotal objective for industries striving to decarbonize. Concurrently, the increased utilization of renewable energy sources is imperative. However, this transition is not without its challenges, driven by the imperative of energy efficiency and the diverse requirements of various industrial processes.

Within this context, the chemical and pharmaceutical sectors, significant contributors to energy consumption and CO2 emissions, heavily rely on a critical unit operation - the distillation process - for purification and component recovery. Initially characterized by low thermodynamic efficiency, the distillation process poses a considerable challenge.

Fortunately, advanced distillation configurations, such as thermally coupled distillation, vapor recompression, heat pumps, and internally heat-integrated distillation, have emerged as viable options offering substantial sustainability improvements. This study investigates the simultaneous integration of these alternatives to enhance energy efficiency, reduce overall energy demands in high-energy-demand separation processes like distillation, and promote greater electrification of the process by converting thermal heat into mechanical work and electricity.

However, it's crucial to acknowledge that directly substituting combustion-generated heat with electrical sources may escalate operational costs. Therefore, this study adopts a comprehensive approach encompassing both economic and environmental perspectives. The economic assessment includes an analysis of the total annualized cost, while the environmental assessment incorporates a life cycle analysis utilizing the ReCiPe metric at both midpoint and endpoint levels.

By exploring these facets, this research aims to provide valuable insights into the feasibility and viability of a multi-pronged approach to enhance energy efficiency, reduce energy consumption, and promote sustainable electrification in energy-intensive separation processes like distillation.

Optimizing the monthly scheduling of crude oil operations at a refinery

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The present work focuses on solving the optimization of crude oil operations scheduling carried out in a real system composed of a refinery and a marine terminal, over a monthly horizon. To address this problem, we introduce a large-scale mixed-integer non-linear programming (MINLP) model that faithfully represents the operation and characteristics of the system. Considering the model's complexity and its non-linear and non-convex nature, the challenge lies in solving the model in a time frame that meets the user's needs. Therefore, we develop a temporal decomposition method in conjunction with a linear approximation.

In the literature, there is a great variety of works that tackle this issue, many of them using a discrete-time formulation approach ([1], [4], [5]) and a smaller number using a continuous-time formulation ([2], [3]). However, there is a common point among these works, and it is that almost all of them solve the problem for a short scheduling horizon or apply to simplified refineries compared to the real ones. It can be said that few works address the monthly crude oil scheduling problem by using relatively detailed models, as in [6].

Figure 1 shows a simplified representation of the refinery under study. There is a terminal where vessels arrive to unload the crude oil. Also, there is a pipeline that connects the terminal and the storing section. The storing section consists only of storage tanks but, within it, it is possible to distinguish two types of tanks, called discharge tanks and refinery tanks. The difference between both types is that the discharge tanks cannot feed the crude distillation units (CDUs) since they are not physically connected to them, so they can only store crudes and transfer them to the refinery tanks. The discharge tanks are located halfway between the port and the refinery tank area. Finally, there is the processing section, where the CDUs process the crude blends to meet the demand for final products. In this case study, there are three discharge tanks, eight refinery tanks, and two CDUs.

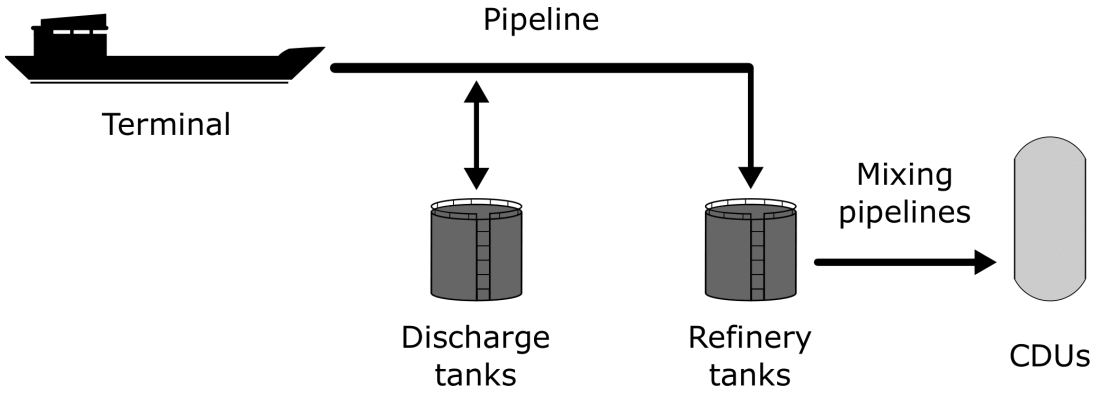

Figure. 1. Schematic of system

There are seven grades to classify both tanks and crude oils: T1, T2, T3, T4, T5, T6, T7. The classification of tanks is based on rules that evaluate their composition (i.e., types and volumes of crude oil). Each tank has only one grade associated with it at a time, but it may vary over the horizon. A key point related to crudes is their unloading from ships since the grade of the receiving tanks must be taken into account. Crude oil can be unloaded into tanks of different classes, but there is a priority scale that relates crude oil grades to receiving tank grades.

Moreover, three types of crude processes are carried out in the refinery (i.e., standard, asphaltic, and low-sulfur fuel oil) and for each of them, there are recipes that indicate the grades and proportions of tanks allowed in the preparation of the feed blends. Concerning the asphaltic process, it is important to mention that only one campaign is carried out during the month, whose start and end dates are known at the beginning of the horizon and must be considered at the time of solving the scheduling. For the rest of the processes, the campaign dates are not fixed and are obtained as a result of the optimization.

An important aspect in feeding CDUs is the need to avoid frequent changeovers, as they lead to inefficient operation. Consequently, once a feed mixture is created, a minimum period of uninterrupted operation in the participating tanks must be adhered to. Furthermore, the feed mixture must meet quality specifications.

As previously mentioned, the refinery has two crude distillation units. However, these CDUs are not identical. In CDU 1, it is possible to carry out standard or asphaltic processes but not low-sulfur fuel oil campaigns. On the other hand, in CDU 2, it is possible to carry out standard or low-sulfur fuel oil processes, but asphaltic campaigns are not allowed.

In conclusion, we can say that the presented method allows us to solve the monthly scheduling problem of a real case in a sensible time. A solution with relative gap less than 5% has been found (11187 binary variables, 395098 real ones, and 685827 constraints) in about 17 minutes using GAMS with GUROBI 9.5.2 over an Intel Core i7-10510U 2.30 GHz CPU machine with 16GB of RAM.

Acknowledgements
Financial support received from the Spanish Government with projects a-CIDiT (PID2021-123654OB-C31) and InCo4In (PGC 2018-099312-B-C31), and from European Social Fund. Furthermore, this work was supported by the Regional Government of Castilla y León and the EU-FEDER (CLU 2017-09, CL-EI-2021-07, UIC 233).

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CO_2-based formic acid by emerging electrochemical reduction: A multi-objective optimization approach

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The economy's defossilization needs the implementation of alternative production approaches, being the carbon utilization technologies promising routes to valorize carbon dioxide (CO_2) into valuable products. Among alternatives, CO_2-based formic acid (HCOOH) by electrochemical CO_2 reduction (ER) suits as a direct and flexible route to form a chemical vector from CO_2, water, and electricity. While promising, several doubts exist in the potential trade-offs that implementing the ER route may entail and under which scenarios it becomes competitive over other routes. This work aims to assess the economic and environmental prospects of the CO_2-based HCOOH by ER compared to conventional fossil-based production. The levelized cost of production (€/kg) and the carbon footprint (kg CO_{2e}/kg) are used in a multi-objective optimization function. A mathematical model to solve the mass and energy balances around the ER pathway is developed from previous studies, serving as equalities [1]. Constraints for each process unit regarding capacities and thermodynamic limits are considered. Screening of scenarios is performed to evaluate uncertainties regarding technology performance and system considerations. The problem is formulated as a Mixed Integer Non-Linear Program (MINLP). The economic and environmental trade-offs are envisioned in Pareto's solution for producing alternative CO_2-based HCOOH.

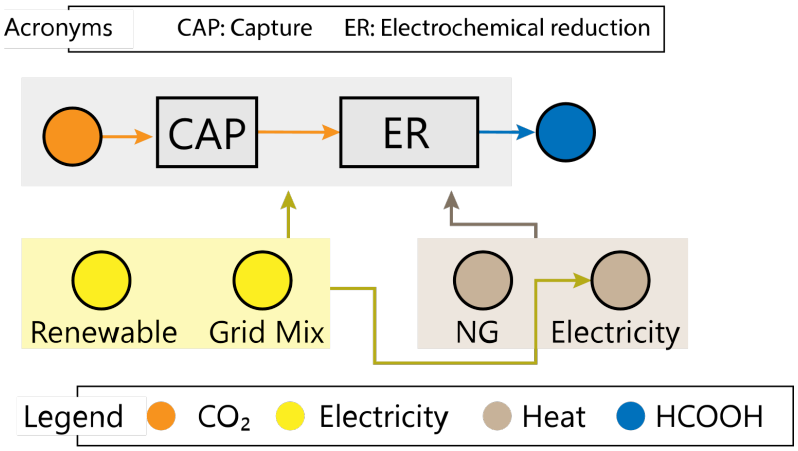

Figure 1. Cradle-to-gate system boundaries for producing CO_2-based HCOOH by ER.

Acknowledgments
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Application of Dynamic Modifier Estimation to an Industrial Propane-propylene Splitter

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This paper presents a study on the implementation of a Dynamic Real-Time Optimization (dRTO) layer integrated with Modifier Adaptation (MA) on an industrial propane-propylene splitter of a refinery in Spain. A propane-propylene splitter is a superfractionator, i.e. a distillation column that performs the separation of components with rather low relative volatility (<1.2) among the components. For this reason, the column requires a high number of equilibrium stages, taking more than 10 hours to reach steady state. The objective of the splitter studied is to produce high purity propylene from a stream of propylene, propane and a small amount of impurities. A DMC controller maintains the propylene concentration in the distillate within a range by manipulating the distillate flow and the steam flow to the kettle.

Since the two manipulated variables of the DMC are directly related to the main costs (steam) and benefits (distillate production), it seems logical to add an RTO layer capable of calculating the process optimum (the setpoints for the DMC) as shown in Figure 1. Normally, a rigorous first principles model is used in RTO, but in our case, due to the large size (more than 12000 DAE equations), and the complexity and required development/maintenance time of such a model, its use is not recommended. Instead, the linear model already developed for the DMC is used for this purpose. However, the use of a model with large parametric and structural uncertainties, such as the linear model of the DMC, can lead to suboptimality in the process. To avoid this problem, MA methods intend to solve the process-model mismatch problem and, with that purpose, MA concepts (Marchetti et al., 2009) have been incorporated into dRTO. MA modifies the optimization problem so that the necessary optimality conditions (NCO) of the problem are matched to those of the real plant, regardless of the presence of model-process uncertainties [1]. In addition, we present a method, Dynamic Modifier Estimation (DME) [2], where the estimation of MA modifiers is made using transient measurements as required by the slow dynamics of the splitter.

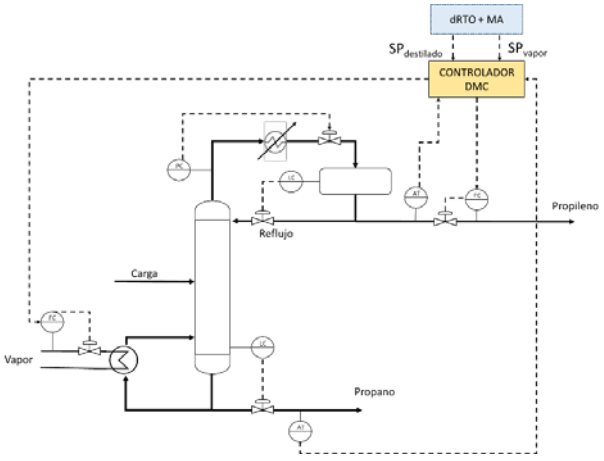

Figure 1. Flow diagram of the actual process with the proposed inclusion of a dRTO+MA layer.

The behavior of the system of Figure 1, which includes a dynamic optimization layer, was tested in a virtual plant environment that mimics the real plant, and allows different operating modes, as shown in Figure 2. The virtual plant uses a rigorous first-principles dynamic model in place of the splitter. The virtual plant is integrated with the same DMC controller as the real plant, and communication between the different layers of the automation pyramid is performed using OPC-UA [3]. The economic cost function of the RTO layer considers the profit obtained from propylene and propane minus the cost of steam. The price of the distillate depends on the propylene concentration (≥97.5% molar), i.e., below this value, the price decreases as a function of composition.

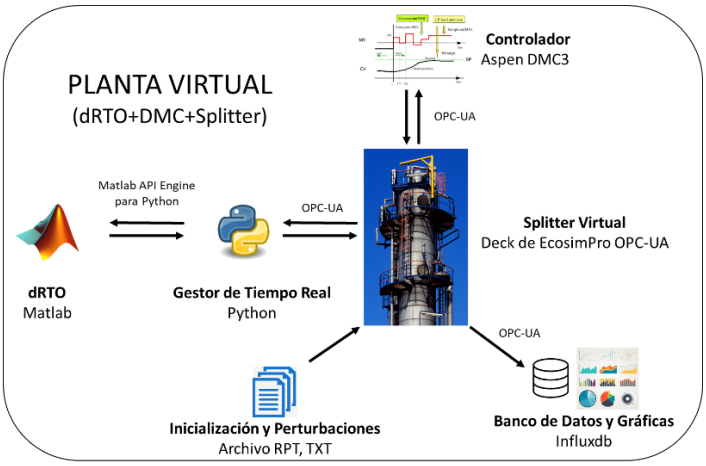

Figure 2. Virtual plant architecture.

The results show that the application of MA using DME stays at the optimal value of the cost function for a longer period of time, because the MA algorithm is able to satisfy the constraint for most of the operating time. In conclusion, the dRTO architecture with MA using transient data and DMC controller was able to improve the overall economic performance of the plant compared to not using the MA methodology.

Acknowledgements
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Euler-Lagrange mathematical framework for the design of microfluidic solid-liquid systems

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Solid-liquid systems have been traditionally modeled using the Euler-Euler approach that describes the two phases as interpenetrating continua, considering a distribution of the particle phase properties and neglecting the specific position in space and time. Resorting to Population Balance Models, which can be merged with the former, particles can be included in the modeled system. Hence, their size distribution and properties are often predicted relying on non-deterministic methods and providing statistical outcomes. The Euler-Lagrange mathematical formulation comes up as an attractive alternative that tracks the position of every particle in every moment. The erosion of ducts and surfaces or the interaction of drugs or pollutants with biological structures are common applications for the use of this approach. Models that include both particles tracking and fluid-solid mass transfer are available in the literature to assess the performance of fluidized beds, bubble columns or bioreactors. However, to the best knowledge of the authors, there are no previous studies that apply this approach to predict the performance of solid-liquid microfluidic systems with fluid-solid interfacial mass transfer. This work aims to apply a Eulerian-Lagrangian approach to predict the fluid dynamics and the mass transfer in microfluidic particulate solid-liquid systems. Therefore, a powerful and versatile tool will be available to assist in the design of contactors to achieve selective separations and processes where the interaction between solid and liquid phases is of primary importance. For this purpose, a Euler-Lagrange model is developed for a tridimensional complex domain and solved under a Computational Fluid Dynamics (CFD) framework.

The continuous liquid phase flow is modeled in a fixed frame of reference, following the Eulerian formulation. The Navier Stokes equations are solved for laminar regime using the finite volume method (FVM). To account for the transport of the different chemical species involved in the system, a conservation equation which describes the convection and diffusion phenomena related to the individual species is included [1]. The flow field is solved under steady state conditions using the pressure-based segregated algorithm SIMPLE (Semi-Implicit Method for Pressure Linked Equations). To discretize the convective and diffusion terms, the second-order upwind scheme is selected, while the least squares cell-based scheme is chosen to evaluate the gradient terms. Meanwhile, the dispersed solid phase is modeled employing the Lagrangian approach. A Discrete Phase Model is used in the Lagrangian inertial reference frame to track in steady state fashion the motion of a large number of particles through the continuous flow field. The particles are assumed to be spherical, rigid, non-rotating and of uniform size. Critical forces acting over the particles and, therefore, affecting their trajectories, such as the Saffman's lift force, the pressure gradient force and the added-mass force, are considered in this model. As the discrete phase is present in a low volume fraction, the particle-particle interactions are neglected. To account for the mass transfer between both phases, a user-defined function (UDF) coded in C language is developed and implemented in the ANSYS Fluent software. This submodel tracks the particles over the computational grid and assesses the interfacial transfer of the species between both phases. The problem is solved following a two-way coupling approach to consider the effect of the contact of the liquid on the solid and vice versa. This implies that, first, the continuous phase flow field has to be solved without introducing the discrete phase. Then, the discrete phase is approached; to this end the particle trajectories are computed, besides the mass, momentum and energy effects resulting from the biphasic

interaction are calculated. Next, the liquid phase conservation equations are updated and the particle trajectories, properties and exchange terms are recalculated in the modified continuous flow field iteratively until convergence is reached.

To validate the model, the capture of Cr (VI) from aqueous solutions using functionalized magnetic nanoparticles (MNPs) in microfluidic devices is selected as case study. The experimental results published in the literature [2] were obtained in a spiral microfluidic device, which is replicated, meshed and implemented in the model to carry out a series of simulations varying the concentration of particles involved in the Cr (VI) capture. Figure 1 depicts the extent of chromium capture depending on the MNPs load or mass flow rate. The simulated chromium capture is in good agreement with the experimental results, being the divergence between experimental and simulated data inferior to 12% in all the cases. Consequently, the Euler-Lagrange approach is successfully proven as an adequate tool to predict the fluid dynamics and mass transfer phenomena in microfluidic multiphasic systems.

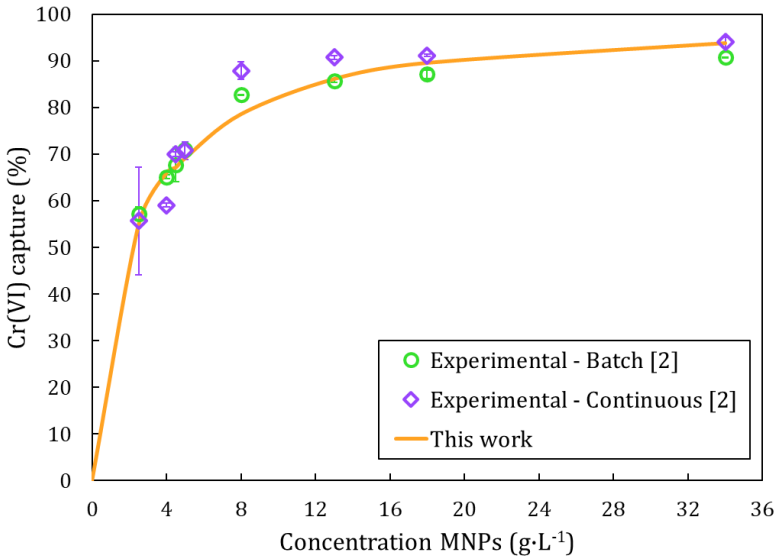

Figure 1. Comparison of the experimental [2] and simulated chromium (VI) capture outcomes.

Acknowledgements
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Which biofuels have the best sustainability performance? A Data Envelopment Analysis approach

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Liquid biofuels offer an alternative to a more sustainable transport sector, reducing carbon emissions and keeping in use the existing vehicle fleet. Today, there are a multitude of options for biofuel production, and the choices made regarding fuel type, blend, conversion process, and carbon source can significantly influence the ultimate cost and environmental footprint of the final product.

Our study proposes a multi-criteria approach that combines Life-Cycle Assessment with Data Envelopment Analysis to evaluate the performance of 72 biofuel production routes in 12 metrics that cover the three pillars of sustainability, i.e., economic, environmental, and social. Biofuel routes are assessed from a cradle-to-wheel perspective, thus including the whole production supply chain spanning from biomass farming to biofuel combustion in vehicle engines.

The findings indicate that around 50% of the analyzed biofuel routes perform better than the rest, with renewable diesel being a better alternative than ethanol-based blends or biodiesel. Additionally, waste biomass emerges as a preferable choice compared to cellulosic biomass or bio-oil. Notably, the choice of carbon source emerges as a key decision, underscoring the importance of considering regional/local factors such as soil and climate conditions before promoting a specific biofuel option.

Overall, this work provides a powerful framework for holistic assessments that could help policymakers develop better-informed regulations and achieve, in this way, the emission reduction targets of current environmental policies for the transportation sector.

Implementation of Multivariable Predictive Control Strategies (MPC) in Programmable Logic Controllers (PLCs)

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Model Predictive Control (MPC) is an advanced control strategy that has found widespread application in large-scale industrial processes. This control methodology relies heavily on computing resources, exceptionally high storage memory capacities, and computational power. To fulfill these demands, personal computer PC-based systems have been harnessed and seamlessly integrated into existing commercial distributed control systems (DCS). Equally, the industrial landscape also features a prevalent control architecture characterized by greater accessibility, lower economic overheads, and widespread acceptance centered around programmable logic controllers (PLCs). These PLCs have traditionally found utility in simple ON-OFF and PID control strategies.

This work aims to investigate predictive control strategies and the accompanying optimization algorithms that could be adapted for implementation within the constraints of PLCs. The prevalent challenge arises from the inherent limitations of PLCs, which encompass their storage and computational capabilities, rendering the scaling of MPC strategies for multivariable process systems a daunting industrial feat.

MPC is based on models. Mathematical models of multivariable process systems at the laboratory scale have been obtained by experimental tests and analytical identification methods described in [1], [2]. Furthermore, the deployment of optimization algorithms hinges on efficient resource management, program memory, and scanning cycle management, which are the primary considerations in PLC. Therefore, there is a pressing need to devise a strategy that harmonizes storage memory management and programming oversight, ensuring that the calculations executed by the chosen algorithms remain within the bounds of the available program memory of commercial PLC devices. In addition, several algorithms for solving the cost function optimization problem have been evaluated. Given the intricate computational demands inherent to these algorithms when executed on PC-based systems, genetic algorithms [3] emerge as a viable choice to solve the optimization problem.

The first coding and design tests of the controller and the selected optimization algorithm were performed on a Siemens S7-1200 CPU 1214 AC/DC/RLY PLC [4]. This PLC model is distinguished by its limited program memory and programming constraints, which have presented hurdles in the development of the controller. However, there has been preliminary success in generating cost function calculations from the prescribed values of the MPC controller.

Currently, the selected optimization algorithm and the controller are being developed in a virtual PLC device, Siemens S7-1500 PLC, which simplifies the programming management and optimizes the use of the device's internal memory, which is necessary for further development. The communication between the PLC and the process systems will be performed using the proposed virtual environment [5]. In addition to the genetic algorithms, the Hildreth Method will be used to compare the performance of the optimization solver. On the other hand, control algorithms such as DMC and GPCGPAD will be considered to compare the designed controller.

Acknowledgements
This work was funded by the Spanish MCIN/AEI as part of the a-CIDiT (PID2021-123654OB-C31) research project and also supported by the Regional Government of Castilla y León and the EU-FEDER (CL-EI-2021-07, UIC 233). Rivero-Contreras, R. has received financial support from the 2019 call of pre-doctoral contracts of the University of Valladolid and Banco Santander.

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Design of an Ionic Liquid-based Extractive Distillation Process to Mitigate F-Gas Emissions

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Hydrofluorocarbons (HFCs) are fluorinated gases (F-gases) used extensively in the refrigeration and air conditioning (RAC) sector. HFCs exhibit a high global warming potential (GWP), up to 13,000 times higher than CO_2, which coupled to the projected increase in installed cooling capacity, 4 to 5 times by 2050, represents a contribution to climate change [1]. As a consequence, international agreements have been adopted with the aim of reducing the production of HFCs. Among them, the Kigali Amendment to the Montreal Protocol and the European Regulation 517/2014 are highlighted as they set the progressive phase-down of HFCs with the goal of reaching an 85% of reduction by mid-century. They also established the term 'reclamation', that is, the reprocessing of a F-gas recovered during maintenance or prior to disposal, to match the equivalent performance of a virgin substance [2]. Applying the reclamation of HFCs requires the development of new technology to overcome the typical azeotropic behavior of refrigerant mixtures, in order to separate and reuse their constituents.

This work focuses on the design and simulation of an extractive distillation (ED) process using ionic liquids (ILs) as entrainers to separate the refrigerant blend R-410A. This mixture is widely employed at present in RAC equipment, and it is composed of 50/50 wt % of difluoromethane (R-32) and pentafluoroethane (R-125). To date, only a few studies have addressed this separation challenge, presenting process layouts that assume equilibrium conditions on the whole system. However, given the relatively high viscosity of the ILs, it is expected that the mass transfer phenomena play a key role in the separation of the mixture. Thus, the goal of this work is to assess the importance of this phenomena and to propose new guidelines to select the IL entrainer.

For this purpose, a selection of three ILs was first made based on the availability of vapor-liquid equilibrium data over a wide range of temperatures and pressures, the IL viscosity, the absorption capacity and the ideal solubility selectivity. The next step was to evaluate the ED design under two approaches: the equilibrium and the rate-based models. Figure 1 shows the workflow followed. The equilibrium design (Figure 1A) was performed by fine-tuning three process variables: the R-410A feed stage, the solvent/feed ratio, and the reflux ratio, with the objective of reaching a product purity of 99.5 wt % and the minimum theoretical stages. Next, the performance of the resulting design was evaluated with the rate-based model (considering the mass transfer rate of the gas component within the bulk of liquid), and compared to the equilibrium model. Then, the design was initialized with the rate-based model by increasing the height equivalent to a theoretical plate (HETP) until achieving the 99.5 wt % product purity (Figure 1B). Afterwards, the rate-based design was obtained by performing sensitivity analyses of the main process variables, namely, R-410A feed stage, the solvent/feed ratio and the HETP with the focus on minimizing the energy requirements (Figure 1C). Finally, the ED process of each IL was compared in terms of energy requirements and economics [3].

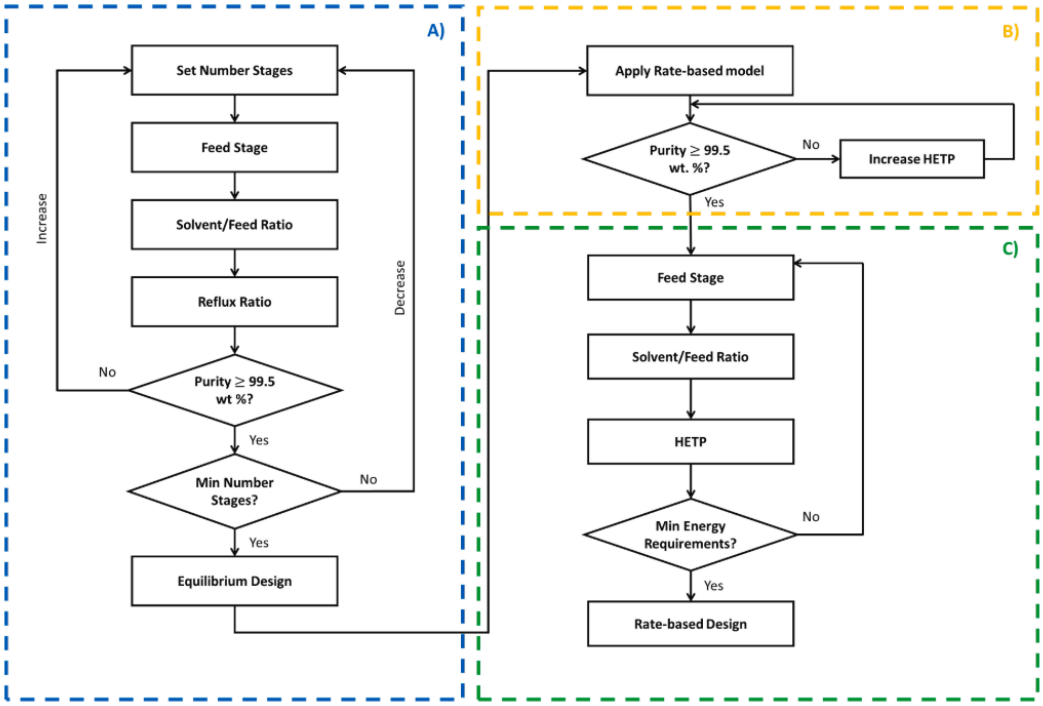

Figure 1. Design workflow: A) Equilibrium design, B) Rate-based initialization, and C) Rate-based design.

The results revealed that the equilibrium model overestimates the separation efficiency in the ED column, regardless of the IL properties, which placed the rate-based model as the most rigorous model to undertake the design of IL-based ED processes to separate F-gases. In addition, a non-fluorinated IL, $[C_2C_1im][SCN]$, has been proposed for the first time as the best entrainer. This is mainly due to its high solubility selectivity, which allows to obtain a design with a lower energy and economic demand in comparison with the other ILs evaluated. Overall, the IL-based ED process becomes a promising technology to mitigate the effect of the F-gases on the climate change and boost their reclamation. As future work, it is intended to perform a rigorous optimization of the rate-based design using surrogate models given the complexity of the simulations.

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Analysis, modelling and simulation of trace elements release from solid matrices to the marine environment

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The release analysis and behavior prediction of the potentially polluting elements from processes, products and natural matrices to environmental compartments is relevant to achieving sustainability. Process as Carbon Capture and Sequestration technology, marine chemical spills and Oceanic Acidification; products as sunscreen and natural matrices as penguin guano and volcanic ashes from remote areas as Antarctica can release elements to the natural environment. Biogeochemical cycling of nutrients and trace elements are vital for marine ecosystems. Some elements are essential for marine life and, therefore, influence the dynamics of ocean ecosystems. On the other hand, these elements can be present in excess, and together with other compounds, can negatively affect the health of ecosystems.

In the present work, the evolutionary application of the release modeling of elements and compounds from different solid matrices to the marine environment is showed. The modelling and the estimation of the corresponding parameters in all cases are completed using Aspen Custom Modeler software which solves rigorous models and simultaneously estimates parameters. The adjustment of the model parameters was performed using an NL2SOL algorithm for the least-square minimization of the deviation between the experimental and theoretical data. Several statistical parameters together the parity plot obtained allows display the validation of the model proposed in terms of the experimental and simulated concentrations of elements.

Release of trace metals from waste and contaminated sediment to water has been modelled widely according to the two compartments model [1]. However, this approach is neither suitable to explain initial release delay of elements, nor the elements that are adsorbed or precipitated after an initial release. To overcome these limitations the research group modelled the release of contaminants from polluted estuarine sediment in contact with water considering that trace metals are associated with oxidised compartment and with a reduced compartment of the sediment (Fig 1a). These models have been validated working under variable conditions of experimental contact, liquid and solid phase characteristics. Modelling and simulation are useful in predicting sediment behavior under different scenarios as CCS technology, chemical spills and OA. Maximum concentrations of released elements from sediment and the kinetic coefficients are estimated for each scenario [2,3].

Under the same approach, trace metals and inorganic nutrients release rate from sunscreens to seawater has been determined by a kinetic scheme that considers transfer between elements in organic material, colloidal suspension and seawater compartments (Fig. 1b). Release and adsorption of the components in seawater have been modelled under total or equilibrium reaction considering pseudo-first-order kinetics. This model has been extended successfully to a three-compartment (organic colloidal residues, seawater and clams) biokinetic model to interpret the bioaccumulation of Zn in clams exposed to seawater with different concentrations of a commercial sunscreen containing ZnO nanoparticles [4,5].

Recently, the research group has addressed the analysis, simulation and validation of the experimental release of dissolved metals from Gentoo (*Pygoscelis papua*) penguins guano to seawater from Livingston Island, Antarctica. Penguin guano has been considered as a suitable bioindicator of the exposure to environmental contaminants in Antarctic environment. A mathematical model using two metal pools guano and seawater compartments considering pseudo-first-order kinetics, is proposed in order to interpret and predict the release of trace metals (Fig. 1c). Proposed modelling aims to obtain the flow and mass of the released elements from the Gentoo penguin guano to the Southern Ocean; this may be of crucial relevance given the increasing presence of this species south of the 60 °S parallel due to its diet and the effects of climate change in Antarctica [6].

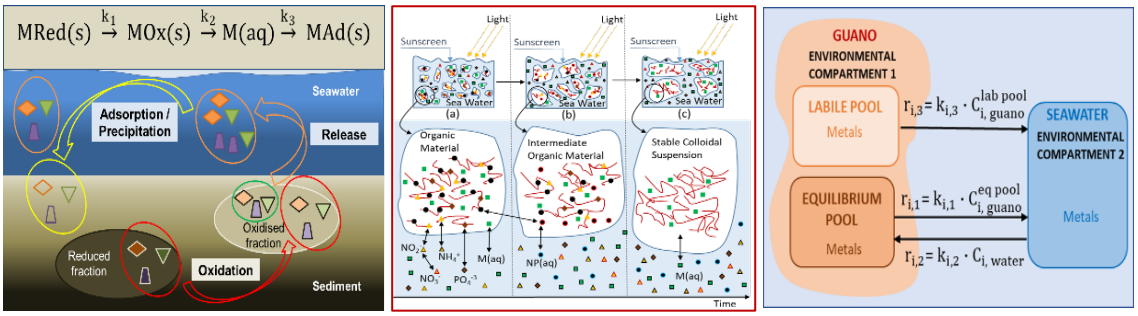

Figure 1. Kinetic scheme of studied chemical elements release to seawater from a) sediments, b) sunscreen, c) penguin guano.

Currently batch and column leaching tests are being designed to model and simulate elements mobility from ornithogenic soils and volcanic ashes in Deception Island, Antarctica. The Aspen Custom Modeler software will be used for model resolution and estimation of the transport parameters useful as inputs to the hydrodynamic model identify, characterize and quantify physical and mixing processes that control circulation and biogeochemical flows within Deception Island, by combining both observational and modeling approaches [7].

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Three-phase reactors assessment for the hydrogenation and dehydrogenation of Liquid Organic Hydrogen Carriers (LOHCs) in the energy transition

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Over the last years, a series of demanding climatic goals have been set to face the environmental impacts. To accomplish them, a large increase of renewable resources is expected. However, the main renewable resources (wind and solar) introduce fluctuations jeopardizing the stability of the energy system. In order to overcome this challenge, the use of energy carriers such as hydrogen is proposed. Its utilization presents a wide range of benefits and applications to be considered in the energy transition. Nevertheless, hydrogen use introduces some drawbacks. For instance, it presents a low volumetric energy density. At the same time, it can leak out many materials. Both features hinder this energy carrier transport and storage. Traditionally, different alternatives have been used such as compression and liquefaction for its transportation and storage. However, lately other promising options have emerged to store it under ambient conditions. One of them is the use of Liquid Organic Hydrogen Carriers (LOHCs). Some of its benefits are found in the mild operating conditions, the availability of chemicals and the possibility to be used during several reaction cycles [1].

The LOHCs technology allows to increase hydrogen volumetric density as it is introduced in the chemical structure of a liquid trough a hydrogenation reaction. Afterwards, it can be released on demand with the inverse dehydrogenation reaction. It seems clear that the main stage of the process is the reaction. At this point, in order to understand the complexity of these reactions systems, the development of rigorous reactor models is required. However, available reaction studies for these LOHCs systems include only kinetic rates [2]. In this work, slurry and trickle bed (Figure 1) 1-dimension models are developed to accurately represent the hydrogenation and dehydrogenation of some of the most attractive LOHCs systems that involve three-phase reactions. In particular, two promising LOHCs have been analyzed: dybenzyltoluene [3] and an indoles mixture [4,5]. As a novelty, relevant mass, heat and momentum transfer are included apart from kinetics. Otherwise, the reactor performance may be oversized if mass or heat transfer have a relevant impact on progress of the reaction.

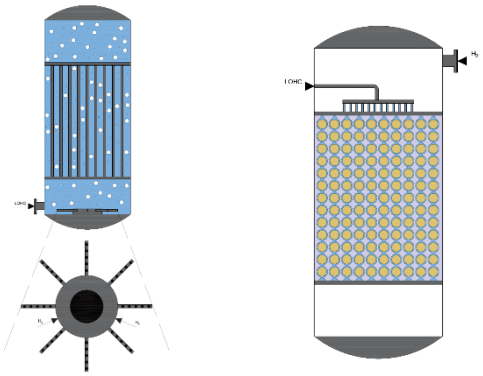

Figure 1. Slurry and trickle bed reactors

The importance of considering the mass transfer is shown in the hydrogenation reactors. For instance, the slurry reactors presented a first operating region where mass transfer is the controlling step. Then, in a second zone, kinetics eventually become the main reaction resistance. The results show a better performance for the first one (from 2 to 5 times). In the case of trickle bed reactors, it was found that almost the entire unit is controlled by the mass transfer. Therefore, considering these phenomena on these units is essential too. On the contrary, dehydrogenation reactors are clearly dominated by kinetics. Its associated endothermicity was presented as one of the reactor bottlenecks due to the importance of the temperature in the reaction progress.

Once analyzed each reactor, the development of surrogate models based on the original ones was also possible. It allows to obtain simpler expressions useful for process scale formulations and optimization. Hence, the isolate unit optimization was performed in this work. The results show a higher cost in trickle bed reactors (18.14-50.98 M$·s $/kg_{H_2}$) compared to slurry ones (0.78-1.99 M$·s/$kg_{H_2}$) for the hydrogenation. This is mainly caused by a worst catalyst use. With regards to dehydrogenation, trickle bed design (107.14-262.66 M$·s $/kg_{H_2}$) is also more expensive than slurry kind (4.63-31.33 M$·s $/kg_{H_2}$). Notwithstanding, trickle bed units, in spite of being more expensive, may be used for lower capacity applications. This is due to its easier operation compared to slurry reactor units.

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September, 2023

The Workshop on Simulation and Optimization for Sustainable Engineering is held in Santander (September 28th-29th) on the occasion of the visit of Prof. Ignacio Grossmann to the Department of Chemical and Biomolecular Engineering of the Universidad de Cantabria in the framework of the Fulbright U.S. Specialist Program.

This workshop is organized in collaboration with AQUIQÁN, the Association of Chemistry and Chemical Engineering of Cantabria, with the aims of serving both as a forum of discussion of the recent advances in the topic and a meeting point of the closest collaborators of Prof. Grossmann in Spain over the last years. Overall, 30 researchers will take part in this event coming from several universities (Alicante, Cantabria, Rovira i Virgili, Salamanca, Sevilla, and Valladolid) and the IMDEA Materials Institute. The program includes a plenary lecture imparted by Prof. Grossmann, one keynote presentation representative of each institution and around 15 oral presentations from young researchers.

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