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CHEMICAL PROCESS SUSTAINABILITY ASSESSMENT VIA PLANT-WIDE AND UNIT-OPERATIONS INTEGRATED ANALYSES

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Tese de Doutorado apresentada ao Programa de Engenharia Ambiental, Escola Politécnica & Escola de Química, da Universidade Federal do Rio de Janeiro, como parte dos requisitos necessários à obtenção do título de Doutor em Ciências.

Orientadores:
José Luiz de Medeiros, DSc
Ofélia de Queiroz Fernandes Araújo, PhD

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RESUMO

DE FARIA Daniela Ramos Guimarães. **Chemical Process Sustainability Assessment via Plant-Wide and Unit-Operations Integrated Analyses.** Rio de Janeiro, 2020. Tese de Doutorado (Doutor em Ciências) – Programa de Engenharia Ambiental, Escola Politécnica e Escola de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, 2020.

A sustentabilidade deve ser sempre garantida no projeto de processos. A decisão é confusa em função dos vários indicadores medindo diferentes questões de sustentabilidade, enquanto os métodos de avaliação de sustentabilidade existentes não são abrangentes, seja com foco no desempenho do ciclo de vida e nas métricas corporativas ou apenas no processo. O presente trabalho inclui uma revisão de literatura que analisa métodos existentes de avaliação de sustentabilidade para a indústria química. A revisão revelou a necessidade de uma análise integrada de sistemas unindo todos os aspectos dos sistemas industriais. Esta tese busca aproximar a indústria de processos do caminho da sustentabilidade, respondendo as seguintes questões: (i) como engenheiros químicos podem saber se um processo é mais sustentável que outro? (ii) como engenheiros químicos podem identificar as maiores barreiras para sustentabilidade dentro de um processo? (iii) como podemos avançar na direção de uma análise de sustentabilidade mais confiável para processos químicos? O principal objetivo deste trabalho é apoiar o projeto e a operação de processos sustentáveis, desenvolvendo um método hierárquico para avaliar sua sustentabilidade, introduzindo as seguintes vantagens: (i) dimensões ambientais/sociais/econômicas e indicadores específicos de tecnologia; (ii) sustentabilidade global da planta; (iii) gargalos de sustentabilidade em operações unitárias; (iv) ferramentas computacionais; (v) índices de sustentabilidade compostos para tomada de decisão multicritério (vi) avaliação ambiental do berço ao portão; (vii) composição de fluxogramas; (viii) testes estatísticos para seleção de indicadores; e (ix) atendimento à Agenda 2030, integrando a análise de processos à estratégia corporativa. O método é demonstrado em três estudos de caso: (i) o primeiro avalia a sustentabilidade do processo convencional de produção de óxido de etileno; (ii) o segundo investiga a sustentabilidade de uma nova rota para produzir óxido de etileno empregando separadores supersônicos com injeção de água para reduzir perdas de óxido e a compara com a sustentabilidade da rota convencional; e (iii) o terceiro investiga configurações de bio-refinarias e seleciona, em termos de sustentabilidade, a melhor rota conectando três possíveis bio-matérias primas – óleo de soja, óleo de palma e óleo de microalga – a três possíveis bio-produtos – biodiesel, diesel verde e propilenoglicol. O estudo de caso (i) indicou impactos devido a perdas de óxido de etileno, operações intensivas em energia e utilidades intensivas em materiais. O estudo de caso (ii) constatou que a rota do separador supersônico reduz as perdas de óxido de etileno em 95%, resultando em um valor presente líquido 2,5% maior por 20 anos de operação e, consequentemente, exibindo o desempenho mais sustentável. Os resultados do estudo de caso (iii) evidenciam a rota do óleo de palma para biodiesel como a mais sustentável, principalmente devido às menores emissões do berço ao portão e ao custo de operação.

Palavras-chave: Sustentabilidade; Sistemas Industriais; Óxido de Etileno; Projeto de Processos Sustentáveis; Tomada de Decisão.

ABSTRACT

DE FARIA Daniela Ramos Guimarães. **Chemical Process Sustainability Assessment via Plant-Wide and Unit-Operations Integrated Analyses.** Rio de Janeiro, 2020. DSc Thesis (Doctor of Science) – Environmental Engineering Program, Escola Politécnica and Escola de Química, Federal University of Rio de Janeiro, Rio de Janeiro, 2020.

Sustainability must be always assured in process design. Decision is blurred by multiple indicators measuring several sustainability issues, while existing sustainability assessment methods are not comprehensive, either focusing on environmental life-cycle performance and corporate metrics or solely on the process. The present work includes a large-spectrum literature review that evaluates existing methods for sustainability assessment of the chemical industry. The review unveiled the need for integrated systems analysis for life-cycle and company-levels. This thesis is an attempt to bring the chemical process industry closer to the path of integrated sustainability analysis by providing solutions to the following questions: (i) how can chemical engineers know if a process is more sustainable than other? (ii) how can chemical engineers identify major barriers for sustainability performance within a process? (iii) how can we move towards more objective sustainability analysis for chemical process design and production? The main goal of this work is to support sustainable process design and production by developing a hierarchical method to assess sustainability of industrial systems, introducing the following advantages: (i) environmental/social/economic dimensions and technology-specific indicators; (ii) plant-wide/supply-chain overall sustainability; (iii) unit-operation sustainability hotspots diagnosis; (iv) computer-aided tools; (v) composite sustainability-indexes for multi-attribute decision-making (vi) cradle-to-gate environmental assessment; (vii) composition of flowsheets; (viii) statistical tests to select indicators; and (ix) compliance with 2030 Agenda, integrating process analysis to corporate strategy. The method is demonstrated in three main case-studies: (i) The first studies the sustainability of the conventional ethylene oxide process; (ii) the second investigates the sustainability of a novel route for ethylene oxide production employing supersonic separators to prevent ethylene oxide losses using liquid-water injection and compares it with the conventional route counterpart; and (iii) the third investigates biorefinery configurations and screens, on sustainability grounds, the best pathway connecting three possible raw bio-materials – soybean-oil, palm-oil and microalgae-oil – to three possible bio-products – biodiesel, green-diesel and propylene-glycol. Case-study (i) indicated impacts due to ethylene oxide losses, energy-intensive operations and material-intensive utilities. Case-study (ii) found that supersonic separator route reduces ethylene oxide losses by 95%, entailing 2.5% higher net value for 20 operation years, and consequently exhibiting the most sustainable performance. Case-study (iii) results evince the route from palm-oil to biodiesel as the most sustainable, mainly due to lower cradle-to-gate emissions and manufacturing cost.

Keywords: Sustainability; Industrial Systems; Ethylene Oxide; Sustainable Process Design; Decision-Making.

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CHAPTER I - INTRODUCTION

I.1 Contextualization and Motivations

Modern society is facing a tipping point in its history, when it is forced to face the results of more than 100-years of anthropogenic interferences in nature. The idea of ‘Sustainable Development’ emerged in the second half of the 20th Century as an attempt to offer an answer and deal with such problems in a balanced and comprehensive way. Yet, the world had to come a long way until it started to admit the need to act upon the negative impacts caused by modern living standards.

In 1984, LAGO and PÁDUA (1984) discussed the differences between what they called Natural Ecology – emerged in the second half of 19th Century dedicated to study the behavior of natural systems – and Social Ecology – focused on anthropocentric ecosystems, and gained strength from 1960. Whereas Natural Ecology is governed by the interdependence of its elements, its dynamic nature and self-regulated equilibrium, its resilience under a continuous flow of matter and energy, its self-regeneration and long-term survival; Social Ecology changed the time and spatial scale of the world, bringing an escalated pressure on natural resources and disrespecting the natural temporality of ecosystems; i.e., privileging short-term gain. Modern economy fabricates needs that go beyond basic human needs, which generates a rampant consumption (i.e. consumerism) that the environment is not capable to assimilate with its self-regulatory mechanisms. These differences were intensified by three Industrial Revolutions that finally forced economy and human society to go into shock with natural systems.

GEORGESCU-ROEGEN (1971) related the Second Law of Thermodynamics with the economic process by pointing out that the latter uses raw materials and transforms it into something useful (product) for the consumer, disregarding the unavoidable generation of wastes along the way, according to the Law of Entropy Growth. These distortions of current socio-economic models lead to unsustainable long-term scenarios. On one hand, economic thinking starts from the premise of a closed, infinite in terms of resources, reversible system, which could be predicted by mathematical models. On the other hand, Thermodynamics shows that this rationality is impossible and unsustainable because the economic process actually involves an open finite system that generates waste. The thermodynamic economic thinking, by its turn, defends a quantitative and qualitative model that considers the irreversibility of our processes. In this way, it criticizes the justification of growth to purely inflict development and the belief that human variables need to fit the model and not the other way around.

Natural and Social Ecology are more academic strands of ecologic thinking. Ecologism has appeared as a political effort to transform society, based on ecological principles and the ideal of a non-oppressive and communitarian society (LAGO; PÁDUA, 1984), in order to respect the environment. It is a practical movement that criticizes the industrial civilization model, but that also goes beyond the ecological dimension; i.e., early flirting with sustainable development ideas. They pointed inherent contradictions in the relationship Human-Nature-Society, such as ‘unlimited growth’ ideology, gross domestic product (GDP) idolatry, ‘the more the merrier’ belief, structural unemployment, and inequality. These basic contradictions make the economic model unsustainable in the long term, leading to the so-called "ecological crisis" and the inevitable social and ecological collapse.

LA ROVERE (1992) provided an overview on the evolution of development concepts, pointing that neoclassical economists, CEPAL Latin-American economists and other schools failed to question the ideas of progress being related to development. The definition of development only started to be questioned by countries that, even though considered ‘developed’ by the neoclassic conception, continually faced problems of social inequality, resource waste, environmental destruction, among others. As a consequence, alternative meanings of development started to emerge in the second half of the 20th Century; e.g., ecodevelopment encouraged policies targeting the harmonization between economic, social and ecological goals (SACHS, 2004). Finally, in 1987, the Brundtland Commission carved the term ‘Sustainable Development’, with its most frequently cited definition to date: “Sustainable development is the development that meets the needs of the present without compromising the ability of future generations to meet their own needs” (WORLD COMMISSION ON ENVIRONMENT AND DEVELOPMENT, 1987). This definition led the way to more than 30 years of efforts to bring the world closer to the three traditional pillars of sustainable development: environment, society and economy (triple bottom line – TBL).

More recently, ROCKSTRÖM *et al.* (2009) defined the planetary boundaries, a safe operating space for humanity. In theory, such limits should not be transgressed if we want to prevent unacceptable environmental damage caused by human activity. Unfortunately, the world has already crossed the safe operating boundaries for four out of nine planetary systems (STEFFEN *et al.*, 2015): biodiversity loss (genetic diversity), biochemical flows (nitrogen and phosphorus cycle), land-system change, and climate change. Another alarming study presents climate projections from the Intergovernmental International Panel on Climate Change (IPCC) and possible consequences of an increase in global temperature by 1.5°C or more above pre-industrial levels (IPCC, 2018). Potential effects include increase of mean temperature in land and ocean, hot extremes, heavy precipitation, the probability of drought and precipitation deficits in some regions. Some scientists even believe that it is probable that some of these effects are already being experienced on some parts of the world. Such findings call for an urgent response to the threat of climate change, sustainable development, and efforts to eradicate poverty.

In this context, the Agenda 2030 for the sustainable development arose in 2015 as an attempt to guide the world towards a possible peaceful and prosperous future, for people and the Planet. It contains 17 ‘sustainable development goals’ (SDGs) and 169 targets, oriented to eradicate poverty and promote a dignified life for all, within the limits of the Planet (UNITED NATIONS, 2015). They are clear objectives and goals that all countries can adopt according to their own priorities. With the motto of not leaving anyone behind, the Agenda is the most inclusive commitment the world, in a global partnership, has ever taken to get closer sustainable development.

It is evident that multiple efforts are continuously emerging from various ends, and the industry is no exception. Sustainable development issues come as a challenge also for the chemical sector, which have been dueling over a century with the negative – but also positive – impacts from its operations (MAROUŠEK *et al.*, 2015). Clearly, industrial production is being driven to comply with safe operating limits for the Planet and humanity (ROCKSTRÖM *et al.*, 2009), and technologies have been progressing along the past decades from waste disposal (1950’s and 1960’s), to treatment (1970’s and 1980’s) and finally to prevention (1990’s and on) (AYRES and AYRES, 2002).

Modern approaches are contributing to bring industry closer to sustainable development, with examples such as industrial ecology, cleaner production, green chemistry, green engineering, process intensification, life-cycle assessment (LCA) and sustainable process design. Usually, what they all have in common is the application of ‘systems thinking'; i.e., a holistic visualization of a system that understands the connections and interactions between its elements (KIM, 1999). Without systems thinking, it is harder to look at the big picture and realize synergies or trade-offs, the role each actor plays in that system and how it can actually help the improvement of the whole. This applies perfectly to complex or 'wicked' problems like sustainable development (AZAPAGIC and PERDAN, 2014), in which it is crucial to identify the interactions between different elements.

Industrial ecology can be defined as an approach to the design of products and processes and the implementation of sustainable industrial production systems strategies (AYRES; AYRES, 2002). It is a concept in which industrial systems are seen in interaction with the surrounding environment and the goal is to optimize the cycle of materials, from extraction to final disposal. Two popular branches of industrial ecology are cleaner production and LCA. The first was defined by UNEP (United Nations Environment Programme) in 1990 as a "continuous application of an integrated environmental strategy to processes, products and services to increase efficiency and reduce risks to humans and the environment" (UNEP, 2019); the latter consists in the assessment of potential environmental impacts across the life-cycle of a product, process or service (SETAC, 1994).

Nevertheless, these approaches have their own limitations. For instance, while LCA considers the entire life-cycle, it only evaluates environmental burdens and considers industrial processes as 'black boxes'; i.e., with input and output, but no engineering details about unit operations (JACQUEMIN, PONTALIER and SABLAYROLLES, 2012). Cleaner production can be more appealing to engineers, but it lacks the life-cycle perspective. Sustainable process design, on the other hand, offers the advantage of assessing triple bottom line impacts and of being detail-specific with regards to unit operations. Still, although process metrics could be used to foster business analysis and vice-versa, these levels often remain isolated from each other (SIKDAR *et al.*, 2017). The acknowledgement and solution to these gaps offer the potential to shift chemical industry sustainability from fundamentally fragmented approaches to holistic frameworks.

In face of the many methodologies available to evaluate isolated aspects of the sustainability performance of the industry and its impacts, some questions can be posed: (i) how can chemical engineers assess if a process is more sustainable than other via integrated system analysis? (ii) how can chemical engineers identify major barriers for sustainability performance within a process? (iii) how can we move towards more objective sustainability analysis for chemical process design and production? This work is an attempt to provide solutions to those gaps, guiding the chemical process industry closer to the path of sustainability.

I.2 The Present Work and Achievements

The main goal of this work is to support sustainable process design and production. In this context, this Thesis developed a two-level hierarchical method – the Sustainable Process System Engineering (S-PSE) method – to assess sustainability of industrial systems. The first level of S-PSE selects the most sustainable plant-wide feedstock-product configuration, while the second level diagnoses sustainability hotspots across unit-operations within the most sustainable configuration at hand. As an effort to move even closer to comprehensive assessments, an extra corporate level breaks the limits of process boundaries, closing the company loop for industrial systems by adding 2030 Agenda indicator correlation for corporate strategic analysis. The process method offers the advantage of coupling different processing units to provide a plant-wide overall result without the need to simulate them altogether, mainly because it is based on material and energy flows, such as LCA. Despite being essentially gate-to-gate – with some cradle-to-gate environmental indicators for resource selection, the method is stackable along the supply chain – the coupling across processing units could also be extended to the value chain – at the same time that it does not consider unit-operations as black-boxes, hence it can contribute to the development of industrial-level integrated approaches. Another crucial part of any assessment method is the decision-making. The literature review identified that most works on sustainable industrial production do not address decision-making issues, which might lead to biased conclusions. In order to address this gap, one further goal of this work is to apply straightforward decision-making techniques to build the composite index used by the S-PSE method. This includes using statistical tools to retrospectively select relevant indicators and the use of composite sustainability-indexes for multi-attribute decision-making.

Various activities were conducted in this Thesis. The literature review was conducted from the beginning, first in an exploratory stage to search for initial concepts and general state-of-the-art about sustainable process design and production. The exploratory stage also worked as basis for the idealization of the S-PSE method. Subsequently a more structured literature review began on systematic criteria which disembogued in a full review paper that was published in 2020 in the J. of Cleaner Production (JCLEPRO). This material constitutes the **CHAPTER II** of this Thesis. A preliminary version of this review paper was firstly submitted as an archival paper to SDEWES 2019 Conference, and was later invited for keynote presentation in the Conference (*Appendix F, F.3*).

The development of the S-PSE method and tool also began early in this doctorate, with the method conception based on literature review, identified gaps and authors previous experience. The design of the tool was one of the most laborious works of this Thesis, because it involved general spreadsheet formulation, data collection, spreadsheet connection with MATLAB and HYSYS, and mathematical programming. The first version of the S-PSE tool was completely ready by the first semester of 2018. The results of its first case-study on Ethylene Oxide (EO) production were presented in FOCAPD 2019 and published as a Book Chapter in the 2019 issue of Computer Aided Chemical Engineering book series (*Appendix F, F.5*), which constitutes the body of **CHAPTER III**. At this stage, S-PSE was still limited to identifying sustainability hotspots within unit-operations.

The EO case-study evolved towards the comparison of the conventional process with an alternative process developed in this Thesis employing supersonic separators for reducing EO losses. For this assessment, S-PSE method evolved to become a hierarchical method capable to compare plant-wide alternatives in terms of sustainability and still identifying hotspots within unit-operations. This work was also firstly submitted and presented as a conference paper to SDEWES 2019 (*Appendix F, F.2*) and evolved to a full research paper published in 2020 in the J. of Environmental Management (JEMA) assessing both alternatives and comparing them. This work constitutes the **CHAPTER IV** of this Thesis.

The last case-study - the biorefinery design – was firstly presented in the SDEWES 2018 Conference (*Appendix F, F.1*) and then expanded to use the most complete version of S-PSE tool generating another presentation in SDEWES 2019 Conference (*Appendix F, F.4*). This case-study is far more complex than the EO case-studies. It required the simulation of six different processes, several adjustments in the S-PSE tool, data collection for the involved substances, statistical screening of indicators to select an optimized set of relevant parameters, and finally the calculation of composite indexes. The expansion of S-PSE method also included corporate strategic assessment, which was developed under the light shed by the 2030 Agenda and its 17 Sustainable Development Goals (SDGs) using correspondent indicators from GRI (Global Reporting Initiative – GRI, 2020) Standards. The analysis of this case-study is being submitted as a full research paper to the J. of Environmental Management (JEMA), which constitutes the **CHAPTER V** of this Thesis.

In the light of the variety of publications originated, this Thesis has achieved significant results, contributing to the literature of sustainability, industrial systems and sustainable process design, with insights and innovations for scientific technological advances.

I.3 Thesis Structure

The Thesis is organized into six chapters, wherein each chapter from II to V presents one main contribution of this research that was published (or to be published) in a recognized international scientific journal or book. Consequently, Chapters from II to V have their own specific nomenclature, abbreviations, bibliographic review, methods, conclusions and table/figures/equations indexation. Their format has been adapted to obtain a homogeneous structure in this document, with all figures, tables and equations renumbered according to their chapter.

CHAPTER I introduces the subject of this Thesis, contextualizing and discussing key aspects of the research lines, and demonstrating the motivations, achievements and structure of the Thesis.

CHAPTER II presents an up-to-date literature review of broad-spectrum as published in the JCLEPRO (2020).

CHAPTER III presents the first version of Sustainable Process System Engineering (S-PSE) method, identifying sustainability hotspots within unit-operations of Ethylene Oxide conventional production as published in the 2019 issue of the Computer Aided Chemical Engineering book series.

CHAPTER IV presents the hierarchical version of S-PSE method, developed to preliminarily evaluate gate-to-gate sustainability of alternative pathways and to identify hotspots in unit-operations. The method is applied to compare two different processing routes for EO production, conventional processing and the supersonic separator alternative route, as published in the JEMA (2020).

CHAPTER V further develops S-PSE method to preliminarily evaluate cradle-to-gate sustainability of alternative feedstock-process-product pathways and to identify hotspots in unit-operations, and applies it to a biorefinery design case-study consisting of three possible bio-oil feedstocks (soybean-oil, palm-oil and microalgae-oil) and three possible bio-products (biodiesel, green diesel and propylene glycol). This material is currently being submitted to the JEMA.

CHAPTER VI brings an overview of this work, with concluding remarks about the results achieved in this Thesis.

Lastly, Appendix A comprehends published Supplementary Materials belonging to the published paper in the JCLEPRO (2020) as presented in CHAPTER II. Analogously, Appendices B, C and D involve published Appendices belonging to the published paper in the JEMA (2020) (CHAPTER IV) contemplating new SS-UOE Algorithm for simulating and designing the supersonic separator unit operation, calibration of EO-H2O binary interaction parameter of Cubic-Plus-Association Equation-of-State (CPA-EOS), and economic assessment. Appendix E shows published Supplementary Materials containing S-PSE indicators and data used to calculate case-study indicators belonging to the paper currently being submitted to the JEMA (CHAPTER V). Finally, Appendix F gathers the entire production derived from this Thesis, organized chronologically, encompassing published papers, conference proceedings, and book chapter, namely:

Section F.1 – A Sustainability Composite Index for Biorefineries. Proceedings of the 1st SDEWES Latin American Conference on Sustainable Development of Energy, Water and Environment Systems, 2018.

Section F.2 – Sustainability assessment of conventional and innovative supersonic processes for ethylene oxide production. Proceedings of the 14th SDEWES Conference on Sustainable Development of Energy, Water and Environment Systems, 2019.

Section F.3 – A Review on Chemical Process Sustainability Assessment: Boundary, Production, Level, Sustainability Dimensions and Decision-Making Analyses. Proceedings of the 14th SDEWES Conference on Sustainable Development of Energy, Water and Environment Systems, 2019.

Section F.4 – Impact of Biomass Feedstock on Biodiesel Process Sustainability: Assessment from an Extended to a Reduced Set of Indicators via Principal Component Analysis. Proceedings of the 14th SDEWES Conference on Sustainable Development of Energy, Water and Environment Systems, 2019.

Section F.5 – Sustainability Assessment of an Ethylene Oxide Process with Carbon Capture. Computer Aided Chemical Engineering. 1ed.Amsterdam: Elsevier, 2019, v. 47, p. 433-438.

Section F.6 – Novel ethylene oxide production with improved sustainability: Loss prevention via supersonic separator and carbon capture. Journal of Environmental Management, v. 269, 2020.

Section F.7 – Sustainability assessment for the chemical industry: Onwards to integrated system analysis. Journal of Cleaner Production, v. 278, 2021.

Abbreviations

FOCAPD Foundations of Computer-Aided Process Design; EO Ethylene Oxide; GDP gross domestic product; IPCC Intergovernmental International Panel on Climate Change; JEMA Journal of Environmental Management; JCLEPRO Journal of Cleaner Production; LCA Life Cycle Assessment; SDEWES Sustainable Development of Energy, Water and Environment Systems; SDGs Sustainable Development Goals; TBL triple bottom line.

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CHAPTER II - SUSTAINABILITY ASSESSMENT FOR THE CHEMICAL INDUSTRY: ONWARDS INTEGRATED SYSTEM ANALYSIS

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Sustainability assessment for the chemical industry: onwards to integrated system analysis

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Abstract

The chemical industry has been struggling to conduct sustainable operations within safe planetary limits, while being socially sound and profitable. Industrial systems are composed of complex arrangements that can vary from system's boundary, production phase, management level and sustainability dimensions. The integration of such concepts is essential for sustainable development. Another crucial point is the procedure for unbiased decision-making. Contrarily to past works that separately address these concepts, this work integrates all aspects under a system's perspective. This review covers methods applicable to the chemical industry seeking to answer the following question*: are the existing sustainability assessment methods able to comparatively discriminate complex chemical industry arrangements to support design and corporate decisions?* The adopted framework encompasses definition of focus and scope; investigation of prior reviews; definition of literature classification; search and screening the literature; classification of the literature extract; analysis, review and findings; and identification of gaps for future developments. The framework identified 60 methods on sustainable chemical process design and production up to the present date. A sharp increase of articles occurred from 2010, but reported methods are seldom fully integrated and are mostly applied to gate-to-gate boundaries. The main identified literature gap is the lack of simultaneous coverage of all sustainability dimensions within the life-cycle boundaries. Additionally, decision-making is mostly arbitrary, either overlooking indicator screening or critical evaluation of the proposed techniques. This review unveiled the need for integrated systems analysis for product/process life-cycle and company-levels.

Keywords

Sustainability Assessment; Chemical Process Engineering; Sustainable Production; Sustainable Process Design; Decision-Making; Review.

II.1 Introduction

The chemical industry enables modern lifestyles not only by transforming raw materials into commercial goods and electricity, but also processing wastes and degraded resources (e.g., wastewater, black-liquor, flue-gases) into harmless effluents or valuable products (Maroušek et al., 2015). On the other hand, it accounts for 7% of global industrial greenhouse gas emissions (Martinez-Hernandez, 2017), rendering sustainability a critical issue. The ever-growing social awareness of Earth´s limited capacity to maintain a resilient and accommodating state has been steering industry towards sustainable development (Ghosh and Bakshi, 2017). As boundaries have already been crossed for climate changes, biochemical flows, genetic diversity and land-system changes (Steffen et al., 2015), it is of the utmost importance that business takes forward-looking actions for local and planetary safety (Labuschagne et al., 2005). Clearly, industrial production is being driven to comply with safe operating limits for planet and humanity (Rockström et al., 2009), and technologies have been progressing along the past decades from end-of-pipe solutions and in-site pollution prevention (Bakshi, 2014) towards reducing impacts along the life cycle. Performance evaluation tools include, among others, pinch analysis, process graph, artificial intelligence and computer-aided modelling (Fan et al., 2020).

Concerns with sustainability are expected to grow across company's operations, encompassing process and plant workers, engineers, support staff, business management and leadership (Krajnc and Glavic, 2003). The engagement eventually impacts distinct company levels: product, process, corporate or even macroeconomic (Tonelli et al., 2013), which evolve to typify capital as not only economic, but natural and social as well (Dyllick and Hockerts, 2002). Although process metrics could be used to foster business analysis and vice-versa (Arena et al., 2009), these levels often remain isolated from each other (Sikdar et al., 2017). All of these socio-environmental concerns grow while new technology trends arise – such as industry 4.0, smart manufacturing and machine learning (Udell et al., 2019) – forcing industry to adopt innovative business models (Ludbrook et al., 2019).

These perspectives push the chemical industry to a state of more 'integrated sustainability' (Gonzalez-Garay and Guillen-Gosalbez, 2018) and 'sustainable supply chains', shifting fundamentally fragmented and functional approaches to holistic frameworks (Tonelli et al., 2013). Therefore, the effort of life cycle assessments (LCA) with multiple boundaries (equipment, process, site, company, state, country and world) has a greater potential for value-enhancement benefit than isolated efforts (Parthasarathy et al., 2005). Sizing these concepts require sustainability assessment methods to aid decision-making (Sikdar et al., 2017), which still relies on expert judgement instead of structured procedures (Mani et al., 2014).

Prior reviews targeting these topics can be divided into two groups. The first one addresses sustainability asssessment in industry. Tanzil and Beloff (2006) overviewed sustainability indicators and metrics for the chemical industry, focusing on eco-efficiency metrics and examples of company-specific metrics. García-Serna et al. (2007) approached sustainability and green engineering from a chemical engineering perspective, compiling definitions, philosophies and disciplines of sustainable process design, frameworks and tools for green engineering and process design, and regulation aspects. Arena et al. (2009) reviewed company-wide industrial sustainability from an operational perspective, covering definitions, indicators, guidelines and means to achieve and improve sustainability, although not oriented to chemical process systems engineering (PSE). Mulvihill et al. (2011) presented green chemistry metrics to assess the impact of materials efficiency throughout the product’s life cycle, with an example from nanotechnology. Jacquemin et al. (2012) analysed the contribution of LCA to evaluate environmental performance in process design and optimization. Bakshi (2014) reviewed developments in sustainable process design highlighting shortcomings and opportunities. Mani et al. (2014) compiled approaches for analysing environmental sustainability of manufacturing processes; they reported classifications, indicators and metrics, models and software tools. Čuček et al. (2015) listed the mostly used approaches in environmental assessments (especially LCA), main measurements and environmental footprints. Martinez-Hernandez (2017) focused on a system’s view of expanding process design boundaries from molecular to global scale, and how this might shape current methods of designing sustainable processes. Argoti et al. (2019) presented recent developments on Triple Bottom Line (TBL) metrics classified according to the process design phase, disregarding the systems perspective, merely addressing indicators.

Athar et al. (2019a) reviewed inherent assessments methods for sustainable process design considering the scope of health, safety and environment. The authors observed a trend moving towards minimizing hazard rather than avoiding hazard and concluded that most methodologies consider solely the safety dimension. Their analysis focused on sustainable process design, without systems thinking, and missed the social and economic dimensions. Bezerra et al. (2020) reviewed the literature in a systematic and integrated framework to analyse corporate sustainability, relating strategic organizational capabilities to the expected corporate benefits.

The second group of prior reviews emerge when considering sustainability metrics and decision-making procedures. Singh et al. (2012) reviewed composite indexes and frameworks for sustainable development including indices formulation strategy – scaling, normalization, weighting and aggregation. Ahlroth (2014) mapped valuation and weighting techniques used in LCA and indicated which method to choose according to the application. Gan et al. (2017) covered methods for weighting and aggregating sustainability indices, proposing an approach for selecting the most appropriate technique depending on the assessment objectives. Pizzol et al. (2017) critically analysed normalization and weighting techniques employed in LCA, indicating advantages and limitations, using five criteria: scientific robustness, documentation, coverage, uncertainty and complexity. Santos et al. (2019) reviewed the literature on the Analytic Hierarchy Process (AHP), a widely used multi-criteria technique to support decision making, remarking manufacturing as the area in which AHP is most applied. Zarte et al. (2019) reviewed decision-support systems used in designing sustainable product and production life cycle in the manufacturing industry. As in Arena et al. (2009), despite comprising applications of chemical processes, the review by Zarte et al. (2019) was not specific for chemical PSE, covering mechanical systems as well.

II.1.1 The Present Work

In general, although the domains of past reviews may overlap, a common methodologic characteristic of them is to focus on an ensemble of specific approaches, failing to set an integrated system analysis. Their scope is not sufficiently broad to identify whether the reviewed methods comprehend all aspects pertinent to complex industrial systems. A crucial missing issue is to highlight the importance of systems thinking. Rockström et al. (2009) state that planetary capacities offer a limit for every human activity, including industrial, and they are all interlinked. The most modern concepts of sustainable development, e.g., the Doughnut Economics (Raworth, 2017), point out the need of integrated systems analysis. To understand how industrial systems function, it is essential to map their complexity first. Minding this gap and targeting developments in sustainability assessment, this work reviews methods applicable to industrial chemical systems to answer the "Research Question": *are the existing sustainability assessment methods able to comparatively discriminate complex chemical industry arrangements to support design and corporate decisions*? To this end the literature is reviewed addressing if and how the system complexity is considered, focusing issues of boundary selection, production phases, levels of analysis, and sustainability dimensions. Indicators and decision-making procedures are also covered to evaluate how the methods embody design and corporate judgments. The frontline goal is to combine concepts – both consolidated and innovative within the chemical industry and the field of process systems engineering (PSE) – identifying shortcomings and discussing major gaps. Simultaneously, a back-line goal is to shed light on the evolution of the degree of integration of different kinds of sustainability assessments regarding the multiple facets that a complex chemical system often has.

II.2 Methods

The methods employed in this review are discussed regarding screening, classification, analysis and perspectives of the literature on sustainability assessment.

II.2.1 Literature Screening

The review is conducted through the 6 steps in Fig. II-1, adapted from Akbar and Irohara (2018) and Zarte et al. (2019). The literature search starts by defining the gap that motivates the review – the "Research Question" – and its boundaries (Step 1).

The focus on chemical industry systems (mainly PSE) formats the scope of boundary selection, definition of production phases, levels of analysis, sustainability dimensions, indicators and decision-making procedures. Step 2 investigates prior reviews on sustainability assessment of industrial systems (Step 2a) and on measuring sustainability and decision-making procedures (Step 2b), two subjects often addressed separately rather than simultaneously.

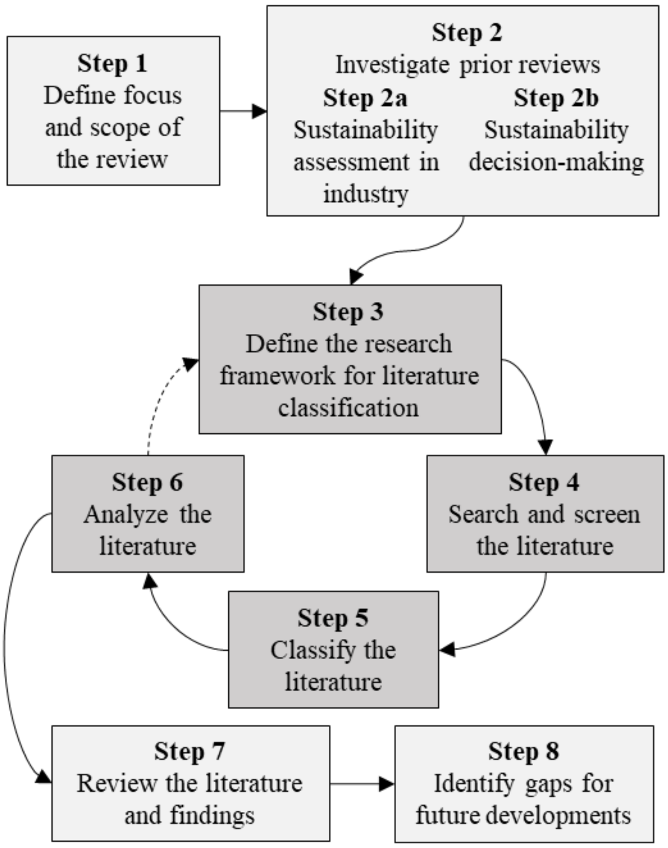

Figure II-1. Stepwise method for literature review.

With the perspective of prior reviews set, the framework for literature classification (Step 3) is defined iterating Steps 4, 5 and 6. Literature is screened (Step 4) in the time window from 2000 to 2020, with complexity added by the large number of expressions and heterogeneous definitions used in reference to sustainability. In fact, an important motivation of this review is the definition of common and unambiguous terminology. In this direction, Garretson et al. (2016) propose a set of harmonizing terms associated to sustainable production. Moldavska and Welo (2017) evaluate current definitions and understandings of sustainable manufacturing. Pang and Zhang (2019) assess the evolutionary progress of green manufacturing and its several synonyms, remarking the increasing use of "green manufacturing" and "sustainable manufacturing" in the past years.

This work pre-evaluates titles, keywords and abstracts using the following words and expressions: ‘sustainability’, ‘sustainability assessment’, ‘sustainability metrics’, ‘chemical processes’, ‘process systems engineering’, ‘sustainable production’, ‘sustainable manufacturing’, ‘sustainable design’, ‘industrial sustainability’, ‘gate-to-gate’, ‘measurement’, ‘normalization’, ‘weighting’, ‘composite indicator’, ‘aggregation’, ‘multi-criteria decision-making’ and ‘decision-making’. The selected works are classified with the research framework criteria (Step 5) and the analysis moves to the full texts (Step 6). The literature classification is revised when needed, and the screening is repeated iteratively, resulting in 60 works for analysis (Step 7). Findings are synthesized to pinpoint gaps for future developments (Step 8).

II.2.2 Literature Classification

Literature is categorized using the criteria in Fig. II-2, comprising Sustainability Dimensions, Assessment Level, Production Phase, Boundaries, Decision-Making procedures and aspects to support categorization. Categories aid evaluating if and how the methods can address complex arrangements, their focus and scope, indicators used, and decision-making procedures applied to identify most sustainable alternatives. The investigated methods relate either to chemical industry, chemical processes, chemical products or chemical PSE.

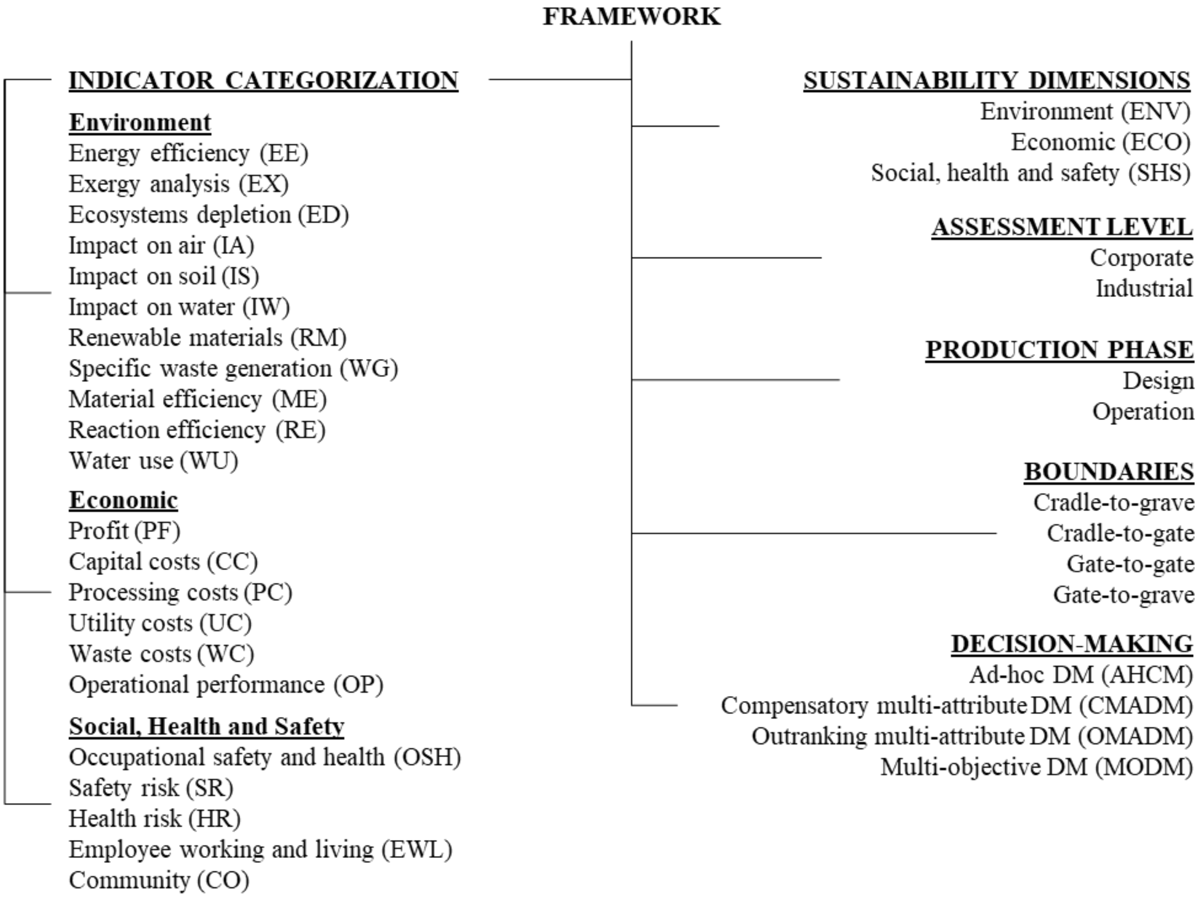

Figure II-2. Framework for literature classification into systems arrangements.

II.2.3 Assessment Methods

The assessment may be at industrial or corporate levels. Multiple expressions have been used to represent this concept, especially for the latter, which is also referred to as ‘strategic level’ or ‘company level’ (Labuschagne et al., 2005), and ‘enterprise level’ (Huang and Badurdeen, 2018). It is a strategic evaluation encompassing the organization, overlooking engineering issues. The corporate level treats the industrial processing system as a black box screening the contribution of firms to sustainable development (Nikolaou and Tsalis, 2020). An analysis at this level might aim at shifting the company´s sustainability strategy or marketing a new product. The ‘industrial level’ refers to the plant floor, the operational and technical spheres, focusing on the process. It is basically an engineering-based assessment that considers unit operations. Labuschagne et al. (2005) refer to the ‘industrial level’ as ‘operational level’, but this is not a clear-cut terminology, since other authors use the expression when referring to the production phase (Zarte et al., 2019). Huang and Badurdeen (2018) name it ‘line level’, a terminology more common to the manufacturing industry than to the chemical industry. A possible outcome of such industrial analysis could be the change in process temperature or reaction yield, selection of alternative technologies or definition of efficient process conditions.

The ‘Boundaries’ set the limits of the assessment from a product life-cycle perspective, and are named ‘cradle-to-grave’, ‘cradle-to-gate’, ‘gate-to-gate’ and ‘gate-to-grave’. The ‘Production Phase’ differentiates methods from a process viewpoint, also regarding the stage of life cycle. This classification targets only the design and operation phases and cover most of the sustainability scope in the literature. Conventional process design uses techno-economic metrics to generate and select production pathways (Othman et al., 2010), usually applying either hierarchical methods based on heuristic rules or mathematical programming (Martinez-Hernandez, 2017). Sustainable process design seeks to improve process sustainability by incorporating environmental, health and safety criteria into design decisions from its conceptualization, besides conventional economic goals (Bakshi, 2014). The operation phase comprises the production and manufacturing stages of the plant. Often, the term ‘sustainable manufacturing’ refers to operation rather than design, comprising activities for creation and provision of manufactured products that balance environmental, social and economic benefits (Zhang et al., 2015), aiming at continuous improvements. In this work, the terms ‘sustainable manufacturing’ and ‘sustainable production’ are used only for the operation phase.

‘Decision-Making’ is the choice among multiple courses of action (Majumder, 2015), and the procedures used are classified as ‘*ad-hoc* decision-making’ (AHDM), ‘compensatory multi-attribute decision-making’ (CMADM), ‘outranking multi-attribute decision-making’ (OMADM), and ‘multi-objective decision-making’ (MODM). AHDM depends on individual or expert judgement, neither providing an overall result nor a systematic approach for final selection of alternatives. It is based on heuristic knowledge, common in process design. CMADM, OMADM and MODM are multiple-criteria decision-making (MCDM) consisting in a structured approach to determine preference amongst alternatives. Multi-attribute decision-making problems are composed of a finite number of discrete alternatives, explicitly known at the beginning (Mardani et al., 2015). The difference between the compensatory and outranking approaches is the possibility of trade-offs, allowed for CMADM but not for OMADM (OECD, 2008). In MODM, the alternatives are not known upfront and it generates a higher sustainability state via mathematical programming (Kumar et al., 2017).

'Sustainability Dimensions' are conventionally accepted as the Triple Bottom Line (TBL), i.e. the *Environmental*, *Social* and *Economic* dimensions. Energy and material efficiency are usually considered in the *Environmental* dimension. This work considers health and safety aspects within the *Social* dimension, expanding it to *Social, Health and Safety* (*SHS*), contrarily to life-cycle derived approaches. Consequently, methods self-classified as *Environmental* are herein reclassified as *SHS*.

Apart from the classification into sustainability dimensions, the framework categorizes the concepts covered by the reviewed methods into relevant aspects inside each dimension, resulting in a pool of indicators available in the literature. *Environmental* is the dimension with more categories of indicators (eleven). *Impacts on Air*, *Soil* and *Water* account for emission and waste impacts on each environment compartment. *Ecosystem Depletion* considers impacts originated from resources destruction and ecosystem stress and can be measured via emergy-related indicators (Baral and Bakshi, 2010), LCA endpoints or *Exergy Analysis* (Teixeira et al., 2018). *Renewable Materials* rewards the use of renewable raw materials. Industrial-level assessments demand categorization capable of recognizing operation nuances in the environmental pillar, while targeting efficient use of resources, mitigating environmental impacts. *Material Efficiency* and *Energy Efficiency* can account for differences in unit operations. Process engineers are more familiar with *Material Efficiency*, often used to quantify efficiency of unit operations or overall process mass balances. *Water Use*, *Reaction Efficiency* and *Specific Waste Generation* are particular aspects of material efficiency that are decoupled from *Material Efficiency* due to their relevance.

Social indicators are here treated into the *SHS* dimension. Conventional social aspects are covered by *Employee Working and Living* and *Community*, while issues related to health and safety are represented by *Occupational Safety and Health*, *Health Risk* and *Safety Risk*.

Occupational Safety and Health uses real industry statistics to, for instance, account for occupational accidents or diseases, and does not apply to the design phases. *Health Risk* and *Safety Risk* address industrial issues of inherent safety and health, possibly generating impacts. *Economic* indicators are classical performance indicators used in process design to maximize profit of a project and remain the ultimate criteria for design decision-making. The *Economic* dimension comprises *Profit*, *Capital Costs*, *Processing Costs*, *Utility Costs*, *Waste Costs* and *Operational Performance*. *Utility Costs* and *Waste Costs* are specific components of *Processing Costs* that indicate the level of details of an assessment method. *Operational Performance* is a measure of productivity that is often time-dependent, capturing operational efficiency along the production line (Huang and Badurdeen, 2018), only applicable to the operation phase.

II.3 Results and Discussion

To review the literature, aspects regarding most-used terminology are discussed before presenting the results under the proposed framework.

II.3.1 Terminology

The most-used keywords in the reviewed literature are compiled in five clusters: indication of industrial-level, indication of corporate-level, life-cycle perspective, decision-making and sustainability, shown in Table AI-1 of Appendix A. Searching in the Web of Science, from 2000 to 2019, for topics containing at least one keyword for industrial-level, one for decision-making and one for sustainability resulted in 592 publications, as presented in Fig. II-3. Removing the decision-making keywords from the survey increased the total of publications to 2761, indicating that most works on sustainable industrial production do not address decision-making issues. Nevertheless, it is noteworthy the increasing trend in the last decade, with a boost from 2010, both for works including decision-making or not.

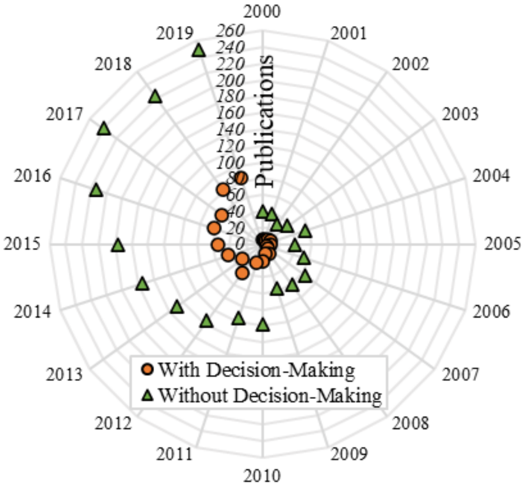

Figure II-3. Publications from 2000 to 2019 with one keyword for industrial-level and one for sustainability. For the data marked with circles one decision-making keyword is added.

II.3.2 Literature Classification Results

Table II-1 presents literature contributions for the chemical industry and process engineers, reporting 60 methods reviewed by this work to assess sustainability. They are divided via the classification given in Fig. II-2. Approximately 50% of the methods address all dimensions of sustainability (TBL), followed by 38% for two dimensions – 20% for *Environmental* and *SHS*, and 17% for *Environmental* and *Economic*, as depicted in Fig. II-4. This shows that the *Environmental* dimension is massively present in the assessments (93%), which is an expected outcome since *Environmental* is often and inappropriately interpreted as the only relevant dimension in sustainable development. The outcome that most of the methods comprise TBL is strongly related to the criteria of health and safety indicators being categorized as social impacts (*SHS*).

Previous reviews did not reach the same conclusion because they classified health and safety issues as environmental burdens. Singh et al. (2012) reported that most works are one-dimensional, mainly targeting environment, and fail to interlink different issues. Zarte et al. (2019), on the other hand, concluded that decision-making is mostly driven by *Environmental* and *Economic* dimensions at the industrial level. If the same classification were applied in the present work, the *SHS* methods would decrease from 45 to 21 and TBL methods would drop from 30 to 17, resulting in predominance of two-dimensional *Environmental* and *Economic* methods, in agreement with past works.

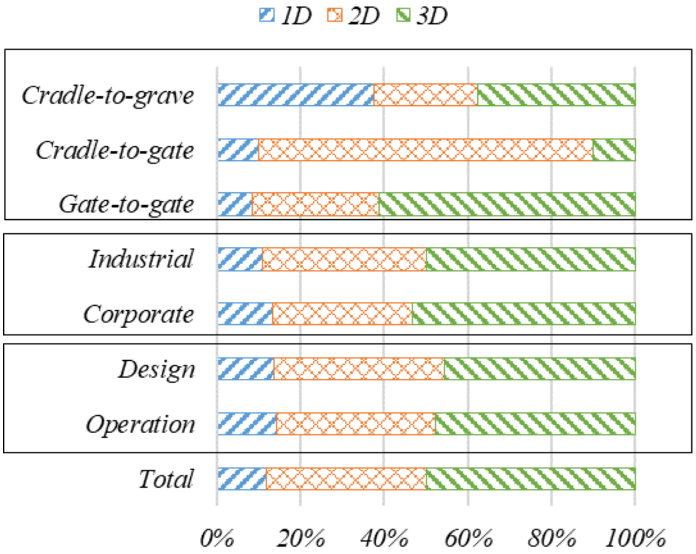

Figure II-4. Percentage of one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) methods in the literature reviewed. Boxes compare the distribution inside the following categories: boundaries, assessment level, production phase.

Table II-1. Literature classification.

Reference	Sustainability Dimensions[1]			Assessment Level	Production Phase	Boundaries	Decision-Making[2]
	ENV	ECO	SHS				
de Faria et al., 2020	x	x	x	Industrial	Design	Gate-to-gate	CMADM
Ee et al., 2020			x	Industrial	Design	Gate-to-gate	CMADM
Lin et al., 2020	x	x	x	Industrial	Design	Gate-to-gate	MODM
Athar et al., 2019b			x	Industrial	Design	Gate-to-gate	AHDM
Garg et al., 2019	x	x	x	Industrial	Design	Gate-to-gate	AHDM
Richter et al., 2019		x	x	Corporate	Operation	Cradle-to-gate	AHDM
Saad et al., 2019	x	x	x	Industrial	Design	Gate-to-gate	DU
Gonzalez-Garay and Guillen-Gosalbez, 2018	x	x		Industrial	Design	Defined by user	MODM
Huang and Badurdeen, 2018	x	x	x	Corporate/Industrial	Operation	Gate-to-gate	CMADM
Xu et al., 2018	x	x	x	Industrial	Design	Cradle-to-grave	CMADM
Agarwal et al., 2018	x	x		Industrial	Design	Gate-to-gate	CMADM
Moradi-Aliabadi and Huang, 2018	x	x	x	Industrial	Operation	Gate-to-gate	MODM
Kreuder et al., 2017	x		x	Industrial	Design	Gate-to-gate	CMADM
Ordouei and Elkamel, 2017	x	x	x	Industrial	Design	Gate-to-gate	CMADM
Sepiacci et al., 2017	x	x		Industrial	Design	Gate-to-gate	MODM
Ghosh and Bakshi, 2017	x	x		Industrial	Design	Cradle-to-grave	MODM
Saavalainen et al., 2017	x	x	x	Industrial	Design	Gate-to-gate	CMADM
Gao and You, 2017	x	x		Corporate	Design/ Operation	Cradle-to-gate	MODM
Alder et al., 2016	x		x	Industrial	Design	Cradle-to-gate	CMADM
Gopalakrishnan et al., 2016	x			Industrial	Design/ Operation	Gate-to-gate	AHDM
Liew et al., 2016, 2015, 2014	x	x	x	Industrial	Design	Gate-to-gate	MODM
Serna et al., 2016	x	x	x	Industrial	Design	Gate-to-gate	CMADM
Ocampo et al., 2016	x	x	x	Corporate	Operation	Gate-to-gate	CMADM
Ren et al., 2016	x	x	x	Industrial	Design	Gate-to-gate	OMADM
Ruiz-Mercado et al., 2016	x	x	x	Industrial	Design	Gate-to-gate	AHDM
Moradi-Aliabadi and Huang, 2016	x	x	x	Industrial	Operation	Gate-to-gate	MODM
Dočekalová and Kocmanová, 2016	x	x	x	Corporate	Operation	Not defined	CMADM
Phan et al., 2015	x		x	Industrial	Design/ Operation	Gate-to-gate	CMADM
Araújo et al., 2015	x	x		Industrial	Design	Gate-to-gate	CMADM
Jia et al., 2015	x	x	x	Industrial	Design	Gate-to-gate	CMADM
Yang et al., 2015	x	x		Industrial	Operation	Cradle-to-gate	CMADM
Leseurre et al., 2014	x		x	Industrial	Design	Gate-to-gate	CMADM
Carvalho et al., 2013	x	x	x	Industrial	Design	Gate-to-gate	AHDM
Shadiya and High, 2013	x	x	x	Industrial	Design	Gate-to-gate	AHDM
Yue et al., 2013	x	x		Corporate	Design	Cradle-to-gate	MODM
Ruiz-Mercado et al., 2012	x	x	x	Industrial	Design	Gate-to-gate	AHDM
Ouattara et al., 2012	x	x		Industrial	Design	Cradle-to-gate	MODM
Brondi and Carpanzano, 2011	x		x	Industrial	Design	Gate-to-gate	CMADM
Torres et al., 2011	x		x	Industrial	Design	Gate-to-gate	CMADM
Othman et al., 2010	x	x	x	Industrial	Design	Gate-to-gate	CMADM
Hossain et al., 2010	x	x		Industrial	Design	Cradle-to-gate	CMADM
Cobb et al., 2009	x		x	Corporate	Operation	Cradle-to-grave	CMADM
Monteiro et al., 2009	x	x	x	Industrial	Design	Gate-to-gate	CMADM
Sugiyama et al., 2008	x	x	x	Industrial	Design	Cradle-to-gate	CMADM
Zhang et al., 2010	x			Corporate	Operation	Cradle-to-grave	CMADM
Curzons et al., 2007	x			Industrial	Design	Cradle-to-gate	CMADM
Martins et al., 2007	x		x	Industrial	Design/ Operation	Gate-to-gate	AHDM
Hossain et al., 2007	x		x	Industrial	Design	Cradle-to-gate	CMADM
Khan and Amyotte, 2005	x	x	x	Industrial	Design	Gate-to-gate	CMADM
Labuschagne et al., 2005	x	x	x	Corporate	Operation	Not defined	AHDM
Saling et al., 2005	x	x	x	Corporate	Operation	Cradle-to-grave	CMADM
Narodoslawsky and Krotscheck, 2004	x			Industrial	Design	Cradle-to-grave	CMADM
Jensen et al., 2003	x	x	x	Industrial	Design	Gate-to-gate	AHDM
Saling et al., 2002	x	x	x	Corporate	Operation	Cradle-to-grave	CMADM
Schwarz et al., 2002	x		x	Industrial	Operation	Gate-to-gate	AHDM
Azapagic et al., 2002	x	x	x	Corporate	Operation	Defined by user	AHDM
Beaver, 2000		x		Corporate	Design/Operation	Cradle-to-grave	CMADM
Young and Cabezas, 1999	x		x	Industrial	Design	Gate-to-gate	CMADM
ICCA, 2015	x		x	Corporate	Operation	Defined by user	AHDM
GRI, 2016	x	x	x	Corporate	Operation	Defined by user	AHDM

[1] *ENV≡Environmental; ECO≡Economic; SHS≡Social, Health and Safety.*

[2] *AHDM≡Ad-hoc decision-making; CMADM≡Compensatory multi-attribute decision-making; OMADM≡Outranking multi-attribute decision-making; MODM≡Multi-objective decision-making; DU≡Defined by user.*

Regarding the distribution of sustainability dimensions in each category, the main difference occurs for boundaries: TBL is much more present in gate-to-gate assessment methods (above 60%) than in others. In fact, as the life cycle boundaries expand, one-dimensional analysis become much more frequent – 8% to gate-to-gate, 10% to cradle-to-gate and 38% to cradle-to-grave. For instance, the Sustainable Process Index (Narodoslawsky, 2015) is an ecological evaluation system for process engineering that measures the area necessary to embed an industrial process into the ecosphere. Unlike most methods, it uses natural concentrations of substances as reference, which can be especially relevant to estimate local environmental impacts and assess how an enterprise conforms with the 'safe planetary boundaries' (Rockström et al., 2009). Nevertheless, like most life cycle methods that adopts a 'planetary perspective', it is limited to the *Environmental* dimension. This suggests, as already pointed by other works (e.g., Parthasarathy et al., 2005), that a trade-off exists between life-cycle boundaries and the number of sustainability dimensions of the method. Even though the life-cycle perspective is desirable, it comes with loss in either the comprehensiveness of TBL or in robustness (implicitly associated to number of dimensions), pinpointing that barriers to integrate complex systems arrangements are yet to be overcome (Martinez-Hernandez, 2017).

Most publications reviewed target industrial-level analysis and unit operations (Fig. II-5a). The only reference comprising industrial and corporate levels is from a hierarchical method for sustainable manufacturing (Huang and Badurdeen, 2018) divided in 'line' (industrial) and 'plant' (corporate) levels, with the latter comprising a broader scope, including metrics such as *Community Diversity* and *Development*. As noted by Sikdar et al. (2017), there is a gap between two types of practitioners that assess process sustainability performance within chemical process engineering: one that resorts to computer-aided tools (e.g., process simulation) to evaluate limited technical aspects (i.e., industrial-level), and another attempting to expand the analysis' frontiers to assess TBL impacts without detailed process information, at corporate-level. This gap restrains industry from addressing suitably sustainability in a comprehensive way (Wan Alwi et al., 2014), considering that sustainability issues are rather complex and not merely 'engineering problems' (Azapagic and Perdan, 2014).

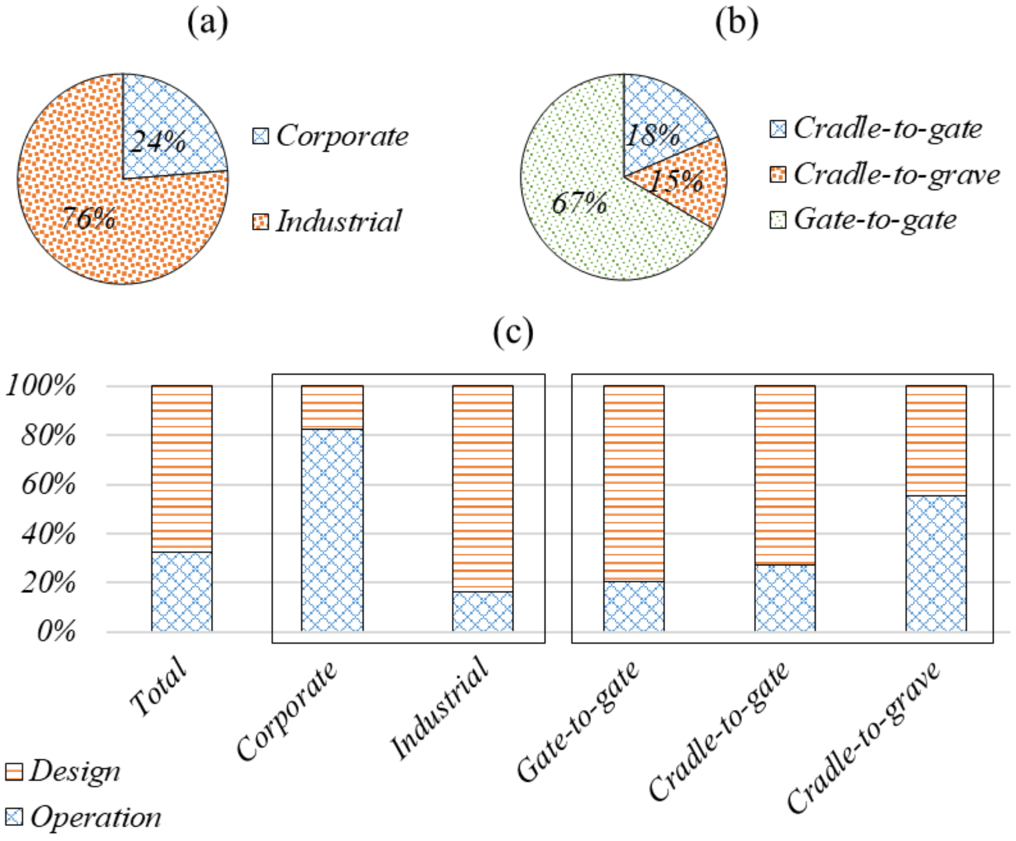

Figure II-5. Literature distribution according to assessment levels (a), boundaries (b), and production phases (c) across different system arrangements.

Comprehensive assessment methods to evaluate operational sustainability are still rarely applied by companies due to the lack of systems perspective (Arena et al., 2009). Most methods focus on corporate-level strategy and management (Fig. II-5c). Company sustainability reports have become an investors’ requirement in the past decades and all major corporations have responded with general methods such as Global Reporting Initiative (GRI, 2016). GRI is a framework composed of various indicators that measure the performance of each dimension of corporate sustainability (Nikolaou and Tsalis, 2020). The chemical sector proposed specialized approaches to assess company’s sustainability, such as the AIChE’s Sustainability Index (Cobb et al., 2009), IChemE's Sustainability Metrics (Azapagic et al., 2002) and Responsible Care® (ICCA, 2015). Despite some business indicators being scalable down from corporate to process design, most of the corporate-level indicators are not valuable metrics at technical scales (Ruiz-Mercado et al., 2012). Unlike industrial-level methods, most corporate-level approaches expand the frontier of analysis beyond the manufacturing site to include the value-chain: 89% of the reviewed literature for corporate-level against 23% for industrial-level, not considering methods with boundary “not defined” or “defined by user”. Gao and You (2017) propose an optimization framework for noncooperative supply chains and product systems; as other examples for supply chain evaluation (e.g. Yue et al., 2013), the assessment disregard details about the process (unit-operations).

In the industrial-level, the production phase dominance shifts from operation to design (Fig. II-5c), in agreement with previous reviews (Zarte et al., 2019), and gate-to-gate limits become the dominant analysis (Fig. II-5b) with 47% of the reviewed design methods. Clearly, to assess sustainability from a PSE perspective, constraining the boundaries of analysis to gate-to-gate requires less information, is simpler and faster to apply, while providing an effective evaluation of the industrial process (Finnveden et al., 2009). A well-established gate-to-gate tool used in many reviewed works (e.g., Jia et al., 2015) is US EPA's Waste Reduction (WAR) algorithm (Young and Cabezas, 1999), which estimates environmental/health potential impacts. Sepiacci et al. (2017) applied WAR algorithm to estimate plant design environmental impacts in addition to predictive conceptual design with market uncertainty for economic aspects. GREENSCOPE (Ruiz-Mercado et al., 2012) assesses gate-to-gate sustainability of chemical process designs employing 140 indicators lumped in four areas – environment, efficiency, energy, and economic. Later, Ruiz-Mercado et al. (2016) proposed a systematic combination of WAR Algorithm for conceptual design, GREENSCOPE for detailed design, and SustainPro for retrofit and modification (Carvalho et al., 2013). Ordouei and Elkamel (2017) developed a composite sustainability index for cradle-to-cradle process design, i.e. designing a circular (inside-gate) process where all wastes are recovered and reused in the process. It is worth noting that, although the authors considered a waste-free process as 'cradle-to-cradle', the methodology does not include supply chain steps or lifecycle stages outside the manufacturing gate. The *Sustainability Degree* (Araújo et al., 2015) compares performance of process alternatives, combining *ad-hoc* criteria (*Green Design Criteria*, GDC) and sustainability indicators to provide a single indicator. Other methods applicable to process design stages propose hierarchical approaches to optimize sustainability of production pathways in research and development (Liew et al., 2014), in preliminary engineering (Liew et al., 2015) and in basic engineering (Liew et al., 2016). The method Chimex Eco-footprint (Leseurre et al., 2014), despite being gate-to-gate, attempts a more comprehensive analysis by adding metrics from the supplier gate to the company gate. Ee et al. (2020) present an index-based analysis to allow comparison between chemical and biological routes using a single assessment framework. A state-of-the-art sustainability assessment with PSE perspective is the Sustainable PSE method (de Faria et al., 2020) that provides a hierarchical assessment, featuring TBL technology-specific indicators, plant-wide overall sustainability; unit-operation sustainability hotspots diagnosis; computer-aided tools; and composite sustainability-indexes for multi-attribute decision-making. The hotspots diagnosis identifies the main unit-operations with sustainability issues early in process design. This feature is illustrated in Fig. II-6 for an ethylene oxide process (de Faria et al., 2020).

The majority of PSE industrial-level gate-to-gate methods in the literature focus on enhancing sustainability during process design. Other approaches expand the gate-to-gate frontier in process design, but only few works consider simultaneously *Environmental*, *Economic* and *SHS* dimensions (Fig. II-4). Alder et al. (2016) developed an LCA-based framework for solvent selection considering *Environmental* and *SHS* issues but neglecting the *Economic* pillar. On the other hand, Ouattara et al. (2012) employed cradle-to-gate approach and considered the *Economic* dimension but ignored *SHS*. Xu et al. (2018) presented a vector-based algorithm applicable for screening chemical process alternatives under uncertainties considering life-cycle TBL. Most of these methods couple LCA with engineering metrics – a trend highlighted by Jacquemin et al. (2012). For instance, Process to Planet combines features of integrated hybrid LCA and process design (Ghosh and Bakshi, 2017); SusDesign generates and analyses design alternatives using pollution prevention heuristic guidewords, cradle-to-grave LCA of materials and/or exergy analysis (Hossain et al., 2010); and GSK FLASC^{TM} tool evaluates a cradle-to-gate life cycle environmental impacts of synthetic processes (Curzons et al., 2007). Even though LCA studies are often for corporate decision-making, they are also applicable to industrial scale.

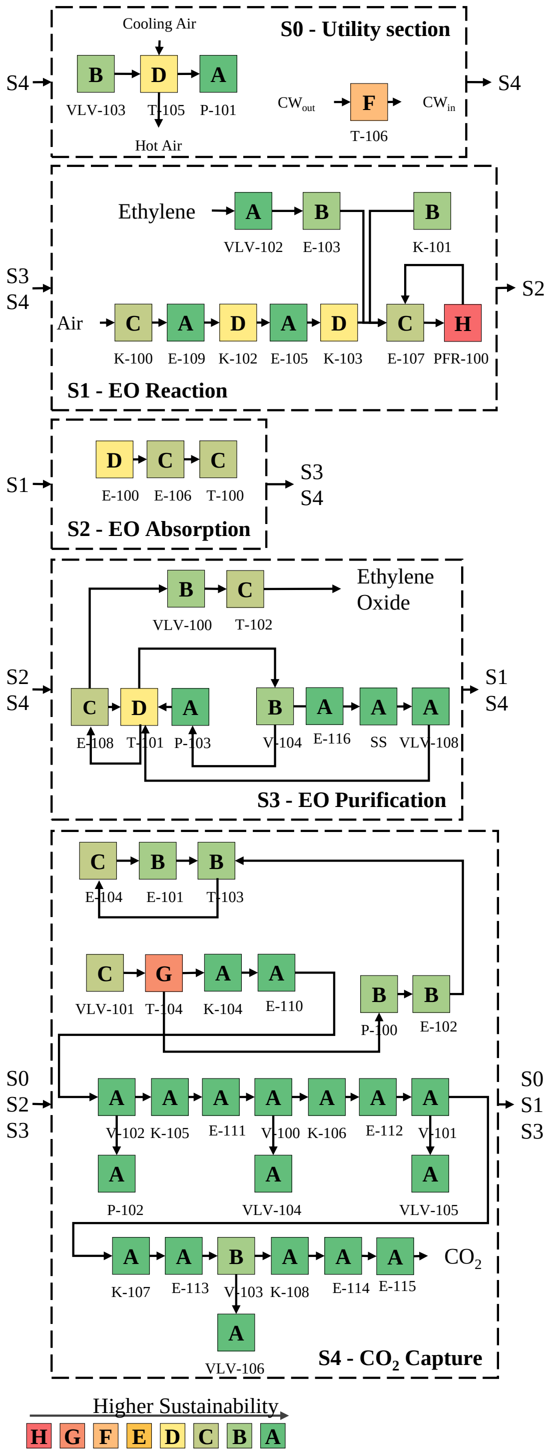

Figure II-6. Unit-operation sustainability hotspots diagnosis of an ethylene oxide (EO) process via the Sustainable PSE method: VLV=valve, T=separation-tower, P=pump, E=heat-exchanger, K=compressor, PFR=plug-flow-reactor, SS=supersonic-separator, V=flash-vessel. (adapted from de Faria et al., 2020).

In a minor extent when compared to design methods, there is an increasing effort to achieve 'sustainable production' or 'sustainable manufacturing' at industrial-level operation. These traditionally estimate 'performance efficiency', related to green chemistry, green engineering and industrial ecology. Green Motion^{TM} is a simple questionnaire inspired in the twelve principles of green chemistry to promote continuous improvements (or design new processes) (Phan et al., 2015). Another approach to assess sustainable production evaluates whether services demanded by manufacturing processes are within the local systems capacity (Gopalakrishnan et al., 2016).

II.3.3 Indicators

Indicators capture the inherent ideas associated to sustainability and transform collected data into manageable information for decision-making. The number of indicators proposed in the literature is often overwhelming, e.g. GREENSCOPE uses 140 indicators (Ruiz-Mercado et al., 2012). Although a proper selection of indicators to be used in the analysis is needed, there is a lack of methods for parameter screening and selection, an issue recognized in past reviews (Martinez-Hernandez, 2017). This subject is discussed in the Suplementary Material, Part B.

In general, assessment methods select their indicators either from the literature or via expert judgement, mostly dismissing systematic procedures for indicators screening, or statistical evaluation to avoid redundancies. Most of the methods that screen indicators resort to sensitivity analysis. Carvalho et al. (2013) target indicators with highest potential for design improvements via sensitivity analysis, while Ren et al. (2016) aim at the most critical and sensitive ones. Saling et al. (2002) also applied sensitivity analysis to check stability of results.

Fig. II-7 presents the main indicators found in the reviewed methods. Four out of the five most common indicators belong to the *Environmental* dimension: *Impact on Air, Impact on Water, Impact on Soil*, and *Energy Efficiency*. Of these four, the first three cover traditional LCA impact categories in many methods, such as: (i) global warming potential for *Impact on Air*; (ii) aquatic toxicity potential for *Impact on Water*; and (iii) terrestrial toxicity potential for *Impact on Soil*. In the *SHS* dimension, *Health Risk* shares classical LCA impact categories (e.g., human toxicity potential). LCA metrics can be applied both to industrial- and corporate-level analyses. *Impact on Air*, *Impact on Water*, *Impact on Soil* and *Health Risk* contain parameters from the WAR algorithm (Young and Cabezas, 1999).

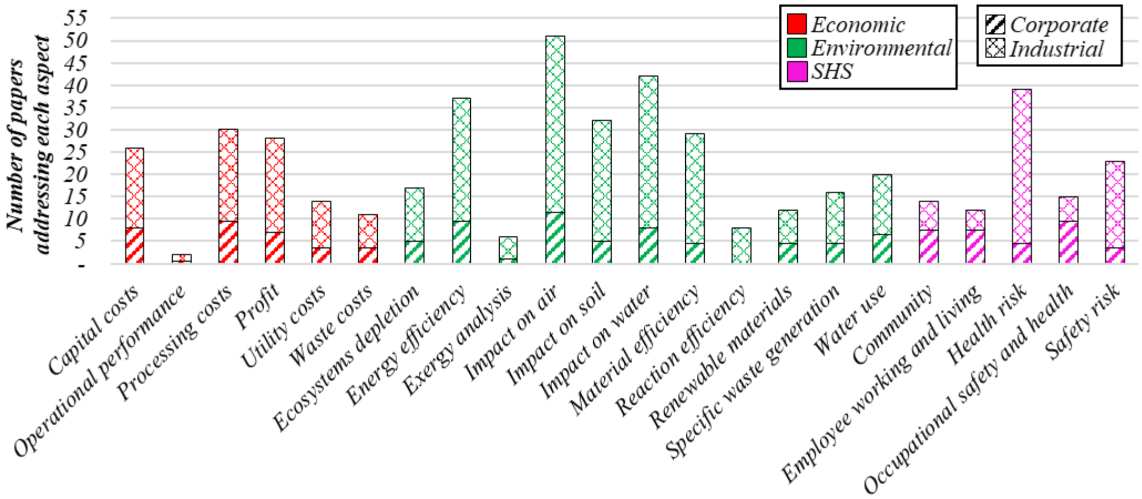

Figure II-7. Indicators aspects most covered by assessment methods.

Moldavska and Welo (2017) identified environment, economic benefits, and safety as the most cited features in the literature with potential to improve sustainable manufacturing. Indeed, along with *Environmental* indicators, *Energy Efficiency* and its related aspects (*Processing Cost*, *Material Efficiency*, *Profit*, *Capital Cost* and *Safety Risk*) not only corroborate findings by Moldavska and Welo (2017) but are traditionally used in engineering assessments, especially in industrial designs. Examples of indicators from these groups are in Appendix A, Part AII.

Corporate-level and industrial-level sustainability assessments present largest differences in the category *SHS* (Fig. II-7), mainly in *Occupational Safety & Health*, *Community*, and *Employee Working & Living*. Computation of such indicators demands development of company-level policies reaching a broader range of stakeholders and actions than those restricted to process aspects, hampering their inclusion in evaluations of industrial-systems sustainability. This is an additional driver to integrate industrial and corporate assessments in hierarchical methods, leading to a comprehensive analysis.

II.3.4 Decision-Making

Decision-making aims at identifying the most sustainable system among the evaluated options. Clearly, from Fig. II-8a, CMADM is the leading procedure among the reviewed methods, indicating that most of them allow compensability or trade-off between indicators. CMADM is followed by AHDM approaches, which are more employed in operation analysis than in design, possibly because the former is mostly a corporate assessment and hence rely heavily on expert judgement (Mani et al., 2014). Especially for AHDM, issues related to the behaviour of decision-makers may arise. Maroušek (2013) showed that the next generation of agriculture decision-makers will be more interested in sustainability and ethical issues than the current one. In general, design evaluations seek a more structured approach than the operation counterpart, and even when using *ad-hoc* decisions those are organized in a systematic way (e.g., using hierarchical heuristic rules).

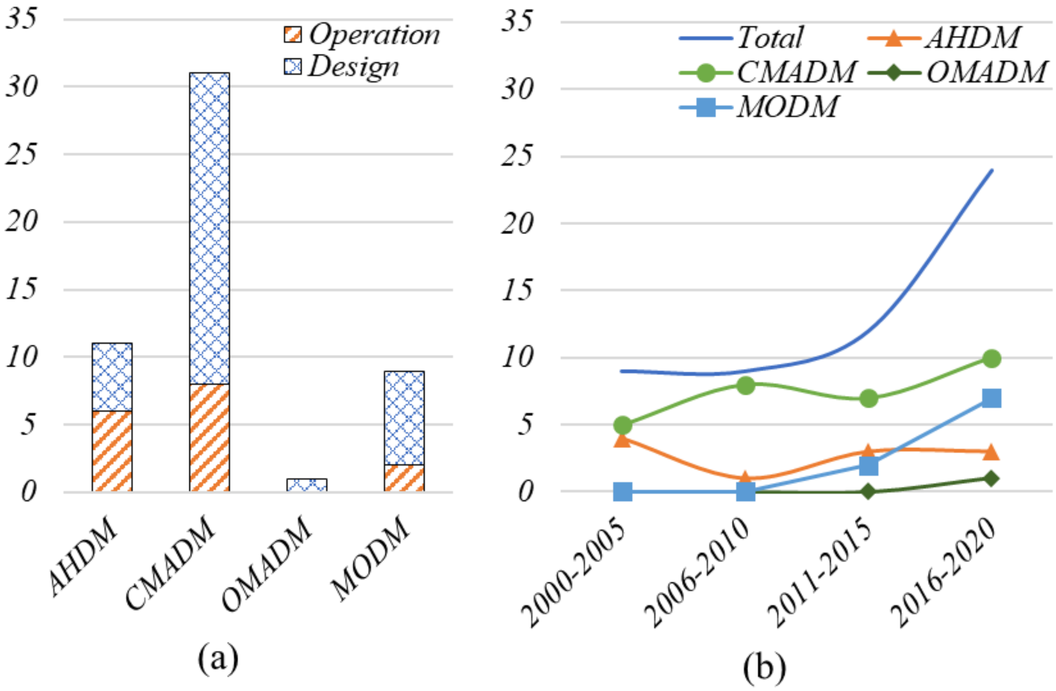

Figure II-8. Decision-making: (a) most used techniques in reviewed methods; and (b) their time-evolution.

Sustainpro (Carvalho et al., 2013) is an example of a systematic method to generate new design alternatives based on well-defined heuristic rules, which leaves the final decision to engineering expert judgement. In Jensen et al. (2003), the alternative processing paths evolve towards improving performance, being evaluated with a set of sustainability metrics; in the end no trade-offs are allowed. Garg et al. (2019) generate intensified alternatives using a rule-based methodology, which are first analysed in terms of economics, sustainability parameters and LCA, and then screened through predefined criteria. In Athar et al. (2019b), final decision uses a process equipment risk matrix to identify whether the risk is within the acceptability range or not. The final decision on AHDM methods can also be based on graphical representations of individual indicators, e.g. Richter et al. (2019), or on interpreting values of indicators displayed in tables, e.g. Martins et al. (2007).

The evolution of decision-making techniques over time (Fig. II-8b) shows that *ad-hoc* approaches were slightly more common in the past, while CMADM always prevails and MODM utilization is increasing. Lin et al. (2020) use interval goal programming to screen sustainable biorefinery technologies under uncertain conditions. Moradi-Aliabadi and Huang (2018) and Moradi-Aliabadi and Huang (2016) use genetic algorithm and Monte Carlo simulation technique. The time-series also confirm the findings from Fig. II-3 that shows a sharp increase in literature on sustainable design and manufacturing after 2010.

Along with the selection of indicators, the choice of the decision-making technique is crucial to evaluate if an assessment method achieves the goal of supporting design and corporate judgements. CMADM additive aggregation method – with predominance of linear summation (e.g. Saavaleinen et al.,2017) is the most common (Appendix A, Table AIII-1) in agreement with previous reviews (Gan et al., 2017), followed by geometric aggregation – e.g. geometric mean of the ratios of categorized indices for pairwise comparisons (Torres et al., 2011) and ½ potency (Khan and Amyotte, 2005). Additive methods have the advantage of simplicity, but they imply full compensability and preferably independent indicators. Nonetheless, geometric aggregation is a less compensatory approach which favors indicators with lower performance rather than already well-scored indicators (OECD, 2008). Another way of mitigating compensability is to resort to tools that support trade-off management (de Magalhães et al., 2019).

Some works define their own functions for CMADM. Agarwal et al. (2018) apply an aggregate metric estimating the contribution of sustainability relative to project capital investment. Zhang et al. (2010) aggregate indicators in terms of physical property. Beaver (2000) consider monetization of societal and environmental impacts. Narodoslawsky and Krotscheck (2004) consider total area necessary for embedding an industrial process into the ecosphere.

Normalization is required prior to any indicator aggregation, and the method chosen impacts the outcome (Sikdar et al., 2017). For instance, Monteiro et al. (2009) use the min-max normalization, and Huang and Badurdeen (2018) employ benchmarking normalization. Most CMADM techniques rely on equal weighting (Singh et al., 2012), which implies no preference among indicators. If a non-compensatory approach is sought, then outranking (OMADM) should be used to override preference dependence. In general, non-compensatory techniques are seldom employed in sustainability indices (Gan et al., 2017). In this review, OMADM is performed only by Ren et al. (2016) with the sustainability prioritization framework and Saad et al. (2019) with multiple MCDM techniques.

Another structured way of making sustainable decisions is to submit multiple goal-attainment problems to mathematical programming, i.e., multi-objective optimization. This approach is more suitable to process design than operation, as the designer seeks the best solution among processing alternatives. Table AIII-2 in Appendix A presents nine MODM works and the employed methods. Most studies fail to clarify whether the chosen decision-making technique was indeed the most suited; with few exceptions critically discussing and comparing alternative approaches. Ocampo et al. (2016) discuss their multi-criteria framework employing fuzzy analytic hierarchy process for weighting. Serna et al. (2016) discuss MCDM techniques combining indicator weights and influences. Xu et al. (2018) and Huang and Badurdeen (2018) compare their results to others obtained from alternative decision-making techniques through robustness analysis. In Saad et al. (2019), the practitioner chooses between CMADM, OMADM and MODM and then performs a sensitivity analysis to verify robustness and reliability of final score. This shortcoming has also been identified by Pizzol et al. (2017) that pinpointed the further need for statistical significance, sensitivity and uncertainty analyses to test index efficacy and robustness.

II.4 Conclusions and Implications

A review of procedures for sustainability assessment applicable to industrial chemical systems is presented, aiming at identifying if the existing methods can *comparatively discriminate complex chemical industry arrangements to support design and corporate decisions*. The work gathers 60 methods from 2000 to 2020, identifying – despite the sharp increase of publications in the last decade – the existence of a research gap regarding harmonization of terminology.

With respect to complex arrangements, the analysis shows that most methods comprise the three dimensions of sustainability (mainly because health and safety are considered as metrics for evaluating social impacts). As the life-cycle boundaries expand, one-dimensional analyses become much more frequent, which clearly indicates a lack of research works considering the entire product life-cycle while preserving the tri-dimensional scope (TBL). The analysis also shows that industrial-level methods are more common than corporate-level, with the latter being dominant only for the operational phase, and most of the literature assessed is dedicated to industrial gate-to-gate process design. This indicates absence of systems perspective within companies, disconnecting the industrial-level from the corporate-level.

Evaluation of how the reviewed methods bear design and corporate judgments contemplates the indicators and decision-making procedures used. Moreover, the reviewed works seldom employ in-depth analysis of indicators, and the range of decision-making procedures mostly apply equal weighting additive aggregation, which imply in compensability (or trade-off) of impact indicators. *Ad-hoc* approaches are more frequent for operational assessment methods, dominated by corporate-level expert-based decision-making. The review could not identify the reasons why researchers choose a specific decision-making method, but rather noted the scarce amount of works comparing different decision-making approaches. One last research gap drawn from this finding regards the degree of arbitrariness that rules the final decision.

Overall, the existing sustainability assessment methods are unable to comparatively discriminate complex chemical industry arrangements since none of the works reviewed consider simultaneously all the issues necessary for a comprehensive evaluation. Furthermore, most of them fail in supporting design and corporate decisions, because they lack critical evaluation either in indicator screening and selection, or in decision-making procedure. These gaps point out future efforts to developing a decision-support method fit to building a sustainable chemical industry.

As a first recommendation, this review identifies the need of comprehensive methods that are fully integrated; i.e., covering chemical process sustainability from design to operation, from industrial to corporate-level and from gate-to-planet, considering all sustainability dimensions. Although the consolidation of the notion that environmental management should not end within corporation boundaries (Akhtar, 2019), it needs to embrace the other factors enumerated in this review, which add up to the complexity of industrial arrangements. Initiatives like the 2030 Agenda helps undertaking the challenge ahead, since its goals include a comprehensive and inclusive perspective towards sustainability – the Sustainable Development Goals. Only two reviewed works cited Sustainable Development Goals, both in corporate-level assessments (GRI and Responsible Care®). In fact, there is an unexplored opportunity to link sustainable design and production indicators to the 2030 Agenda to map compliance of industrial processes with Sustainable Development Goals.

Another research opportunity concerns more transparent decision-making, demanding development and application of methods for indicator screening and selection. Such actions would produce reliable results to support design and corporate judgements. More attention could also be paid to non-compensatory methodologies to avoid unnecessary trade-offs.

It is worth noting that the choice of keywords for literature screening is a ubiquitous review limitation. The present work focused on keywords to search the chemical or manufacturing industries. Works covering other areas with their own terminology – e.g. fuels, energy, biorefineries and pharmaceuticals – might have been left out of this analysis. Additionally, the employed keywords are explicit on sustainability topics. Hence, works that comprehend only one sustainability dimension (social or economic or environmental) were not included. Again, the choice of keywords obviously bears subjective choices.

Lastly, the main fact unveiled here is the need for integrated systems analysis. Even though some methods already try to move alongside, the literature has not yet succeeded in terms of finding a single unified solution. This discovery is materialized in the numbers uncovered in this review: Environmental, Economic and SHS are considered together only in 38% of life-cycle assessments, mainly for corporate-level. Only one reference addressed simultaneously industrial and corporate-levels. Design (65%) and operation (27%) are often separately considered; and the methods tend to evaluate either solely industrial gate-to-gate process design (47%) or corporate operation beyond the gate (20%). Thus, there is a pattern, hopefully fainting, still neglecting the system perspective for product/process life-cycle and company-levels.

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Abbreviations

AHDM *ad-hoc* decision-making; CMADM compensatory multi-attribute decision-making; MCDM multiple-criteria decision-making; MODM multi-objective decision-making; OMADM outranking multi-attribute decision-making; PSE process systems engineering; SHS social, health and safety; TBL triple bottom line.

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CHAPTER III - SUSTAINABILITY ASSESSMENT OF AN ETHYLENE OXIDE PROCESS WITH CARBON CAPTURE

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Sustainability Assessment of an Ethylene Oxide Process with Carbon Capture

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Abstract

Sustainability criteria must be integrated to computer-aided design tools. To assess sustainability in a straightforward and unbiased way it is necessary to rely on indicators, supporting design decisions among alternative processing routes. The set of meaningful sustainability indicators should be representative of the process system under assessment and not resort to generic databases, which commonly exclude process-specific conditions from the analysis, treating unit-operations as black boxes. Methods that rely on technology-specific indicators are preferred in-depth analysis of process systems. The Sustainable Process Systems Engineering (S-PSE) approach is herein proposed to fulfill the gap of composite-index methods for sustainability assessment at process systems engineering level targeting on performance quantification and ranking of alternatives. By integrating computer-aided design environments, S-PSE appoints sustainability hotspots within unit-operations and strongly brings sustainability information to the process engineering discipline while still maintaining traditional process design routine. This work applies S-PSE method to evaluate the sustainability of the conventional ethylene oxide process as working example to demonstrate its efficacy in identifying unit-operations requiring retrofitting to enhance sustainability performance. Of relevance to a sustainability-oriented design is the side-product CO_2, which is separated from unreacted ethylene before recycling to the reactor, yielding a nearly pure CO_2 product, which, upon proper destination, contributes to enhance process sustainability. Furthermore, due to its toxicity and flammability, ethylene oxide process has inherent health and safety vulnerability. Submitted to S-SPE analysis, ethylene oxidation reaction, distillation tower for CO_2 desorption, cooling water tower and cooling tower air-blower are disclosed as the main sustainability hotspots. Reaction drawbacks are associated with energy consumption, health and safety and environmental impacts, the distillation tower is the most energy-intensive operation, and the cooling water tower and air-blower are the most material-intensive. The case study clearly demonstrates coordination of computer-aided design tools (Aspen HYSYS, Excel and MATLAB) to sustainable process design.

Keywords

Process design, Sustainability assessment; Composite index; Index aggregation; Ethylene oxide; Process systems engineering.

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III.1 Introduction

It is increasingly necessary to include sustainability criteria early in process design to deal with complex issues since conceptualization, when the window for improvements is wider (Diwekar, 2015). In order to conduct sustainability assessment in a straightforward unbiased way, it is necessary to rely on indicators and on an objective decision-making procedure.

The large number of indicators available for measuring sustainability aspects is the first difficulty when assessing sustainability. For example, GREENSCOPE method (Ruiz-Mercado et al., 2012) has more than 100 indicators. A proper choice of indicators to include in the evaluation is a necessary condition to analyze sustainability, and there is a lack of proven effective methods for parameter screening and selection. The set of meaningful indicators should be representative of the system under assessment (Böhringer and Jochem, 2007).

Another problem for sustainability assessment in process design is that many approaches resort to generic databases, which takes process-specific conditions out of the analysis. This is the case of Life Cycle Assessment (LCA). Even though LCA is an useful tool to analyze systems environmental impacts, it has a natural limitation to assess technology-specific aspects (Bakshi, 2014). On the other hand, methods not limited to treat unit-operations as black-boxes, i.e. with just input and output known (Jacquemin et al., 2012), are required for in-depth analysis of process systems. This is the case of existing methods such as GREENSCOPE (Ruiz-Mercado et al., 2012) and SustainPro (Carvalho et al., 2009).

The final step in a sustainability assessment is the decision-making. Given that sustainability is a relative concept, a “sustainable state” of a system is not an absolute condition (Sikdar et al., 2017), requiring a reference state as comparison. Decision-making in this context is the process of identifying the most sustainable system among selected options to solve a (design) problem. It can be achieved through composite indexes, multi-objective optimization or other decision-making procedures. Several *ad hoc* criteria for decision-making are proposed in the literature (Abraham and Nguyen, 2003; Anastas and Zimmerman, 2003). A range of tools for decision-making are available, e.g. multi-criteria decision analysis (Azapagic and Perdan, 2014).

The Sustainable Process Systems Engineering (S-PSE) method fulfills the gap of composite-index methods for sustainability assessment at process systems engineering level targeting on performance quantification and ranking of alternatives (de Faria et al., 2018). S-PSE interlinks the application of process technology-specific indicators with aggregation procedures to put forth a relevant gate-to-gate sustainability composite-index. This work applies S-PSE method to evaluate the sustainability of a conventional ethylene oxide process and identifies unit-operations sustainability hotspots. Of relevance to a sustainability-oriented design is the side-product CO_2, which is separated from unreacted ethylene before recycling to the reactor, yielding a nearly pure CO_2 product, which, upon proper destination, contributes to enhance process sustainability. Ethylene oxide is a flammable and explosive commercial chemical that is very reactive, which makes it a broadly versatile chemical intermediate (Lou et al., 2006). It is used to manufacture ethylene glycol, poly(ethylene oxide), glycol ethers, ethanolamines, and surfactants, etc. Due to its toxicity and flammability characteristics, ethylene oxide processes have inherent health and safety vulnerability.

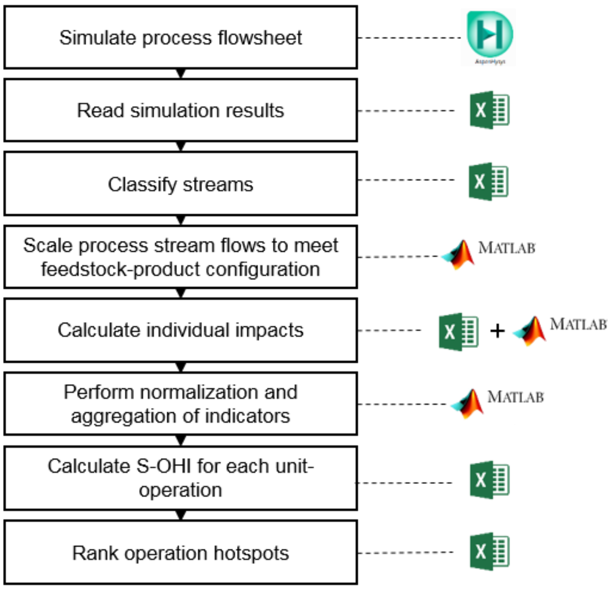

Figure III-1. Main steps of S-PSE assessment method to calculate S-OHI and respective CAD used in each step.

III.2 S-PSE Method

The Sustainable Process Systems Engineering method (S-PSE) is a hierarchical approach to assess gate-to-gate sustainability of process systems, composed of two levels: Sustainable Plant-Wide Index (S-PWI) and Sustainable Operation Hotspot Index (S-OHI) (de Faria et al, 2018). S-PSE evaluates aspects across five sustainability dimensions – environment (ENV), economic (ECO), health and safety (HS), material efficiency (ME) and energy efficiency (EE), and is capable of interlinking process technology-specific indicators with aggregation procedures to put forth a sustainability composite-index highly relevant to process design and analysis. Additionally, it integrates computer-aided design (CAD) environments (Excel, MATLAB and Aspen HYSYS) as shown in Figure III-1, bringing sustainability information to the process engineering discipline while still maintaining traditional process design routine.

S-PWI preliminarily evaluates alternative production pathways to select most sustainable plant-wide configuration and S-OHI appoints sustainability hotspots within unit-operations. The second-level evaluation does not comprise economic aspects (considered in the first level) and is used to compare unit-operations (UO) performances and identify process hotspots. Unit-operations are classified as reaction, separation, heating/cooling, compression, and expansion.

S-OHI is an aggregate parameter that measures the Canberra distance (Sikdar et al., 2017) of S-PSE indicator set to their reference point and is calculated according to:

$$S-OHI = \frac{1}{v}\sum_{\mathrm{r}=1}^{v}\left(\frac{1}{n_r^{ap}}\sum_{y=1}^{n_v} X_{y,r}\right) = \frac{1}{v}\sum_{v} SI_v \tag{III-1a}$$

$$X_y = 1 - \frac{|x_y - r_y|}{|x_y - x_{y0}| + |r_y - x_{y0}|} \tag{III-1b}$$

where v represents the number of dimensions, four; $X_{y,r}$ is the normalized value of applicable indicator y in dimension r; n_r^{ap} is the number of applicable indicators in each dimension r; SI_v is the sustainability aggregate index for each dimension v, x_y are the indicators describing the system, r_y are the reference values for each indicator, and x_{y0} is a value set as the origin.. “Applicable” means all indicators being calculated for a specific type of UO - each outlet and inlet streams of a UO have components impacts that are attributed to it depending on its type (Table III-1).

Table III-1. Indicators applicable to each type of unit-operation.

Indicator[a]	UO type
Smog, Ec_{aq}, *HW*	Assigned UO for component outlet impacts
EI, *GWP*, $Fail_{F/E}$, $Fail_{R/D}$, *Mob*, *Acute*	All
MI, *E*	Separation, cooling/heating and reaction UOs
SMLI	Separation UO
Haz_{in}	Assigned UO for component inlet impacts

[a] *Smog* stands for photochemical oxidation, Ec_{aq} for ecotoxicity for aquatic fresh water, *HW* for hazardous waste, *EI* for energy intensity, *GWP* for climate change, $Fail_{F/E}$ for risk of fire/explosion, $Fail_{R/D}$ for risk of reaction/decomposition, *Mob* for mobility, *Acute* for acute toxicity, *E* for E factor, *SMLI* for separation mass loss index, Haz_{in} for hazardous raw materials input.

[b] Except pumps and valves.

S-OHI includes the calculation of 13 indicators as shown in Table III-1 – a simplification of the framework full-version (de Faria et al., 2018) not comprising exergy destruction solid waste mass, and reaction molar efficiency, but including E factor (Ruiz-Mercado et al., 2012). Since S-OHI has the goal of identifying worst sustainable performances among unit-operations in a process, UO reference points are set as the worst values among second-level indicators. Hence, S-OHI ranges from 0-1 with zero (0) indicating higher sustainability and one (1), lower sustainability, i.e. hotspots.

III.3 Case Study: Ethylene Oxide Production

This work applies S-PSE second-level assessment, i.e. S-OHI, to evaluate the sustainability of ethylene oxide conventional processing.

III.4 Process Simulation

A conventional ethylene oxide (EO) process was simulated using Aspen HYSYS and its process flow diagram is presented in Figure III-2. Table III-2 presents the main operating conditions. The process comprises four units: EO reaction, EO absorption, EO purification, and CO_2 treatment (Bayat et al., 2013), besides an Utility Section. In the first section, EO is produced by direct catalytic oxidation of ethylene with pure oxygen or air (used in this case study) in the gas phase. The reactor is a vertical shell and tube multitubular containing a fixed catalytic packed bed, and surrounded by water to produce steam and to remove the growing heat of the exothermic reaction (Rebsdat and Mayer, 2001).

After reaction, the reactor outlet stream is scrubbed countercurrently with cool water, being absorbed in the liquid phase and hence separated from non-condensable gases. High pressures are preferred to facilitate absorption, and short residence time is required to prevent formation of ethylene glycol. Two-steps distillation are required to achieve EO purification. The first column separates a small fraction of light-end gases, which are absorbed in the previous unit. The second is responsible for sharp separation of water and EO, producing a stream with 99.5% of purity (Borhani et al., 2015).

Table III-2. Ethylene oxide process operating conditions.

UO	Conditions
PFR-100	23 bar; 250 °C
T-101	21.7 bar; 41 °C (top); 210 °C (bottom)
T-102	4bar; 40 °C (top); 144 °C (bottom)
T-104	1.1 bar; 68 °C (top); 112 °C (bottom)
T-105	1 bar; 75 °C (top); 29 °C (bottom)
T-106	1 bar; 50 °C (top); 35 °C (bottom)

CO_2 is a by-product of the reaction and to avoid its build-up in the recycle stream, it is separated in Hot Potassium Carbonate (HPC) – on of the most used chemical absorption-desorption processes to capture acid gases, such as CO_2 and H_2S. HPC consists of the absorption of CO_2 in a hot potassium solution at high pressure, followed by desorption at atmospheric pressures and lower temperatures than absorption (Lou et al., 2006). The lean-gas stream, composed mostly of ethylene and nitrogen, is recycled to the reactor after partially purged for preventing build-up of inert gases in the process. In this work, the stream of CO_2 captured goes to a fifth unit composed of five compressors, interleaved with tanks to remove water to pressurize the gas to 100 bar and 60 °C and sold at a purity of 98%, hence avoiding emission.

Table III-3 shows the distribution of inlet and outlet impacts across ethylene oxide processing unit-operations. Impacts for cooling water make-up stream are allocated along all heat exchangers using cooling water. The allocation is based on material flow proportion.

Table III-3. Unit-operations with inlet or outlet impacts assigned.

Inlet/outlet stream	Impact attributed to UO
MakeUp Water	T-103
Purge	PFR-100
Ethylene (sphere)	PFR-100
Air	PFR-100
MkUp Water	T-100
Hot Air	T-105
Cooling Air	T-105
Cooling Air-2	T-106
Hot Air-2	T-106
MkUp CW	Allocation[a]
Air-1	Blower
Air-5	Blower
Air-3	Blower 2
Air-4	Blower 2
CO2	PFR-100

[a] This stream has impacts allocated across UOs that use cooling water: E-105, E-106, E-109, E-110, E-111, E-112, E-113 and E-114.

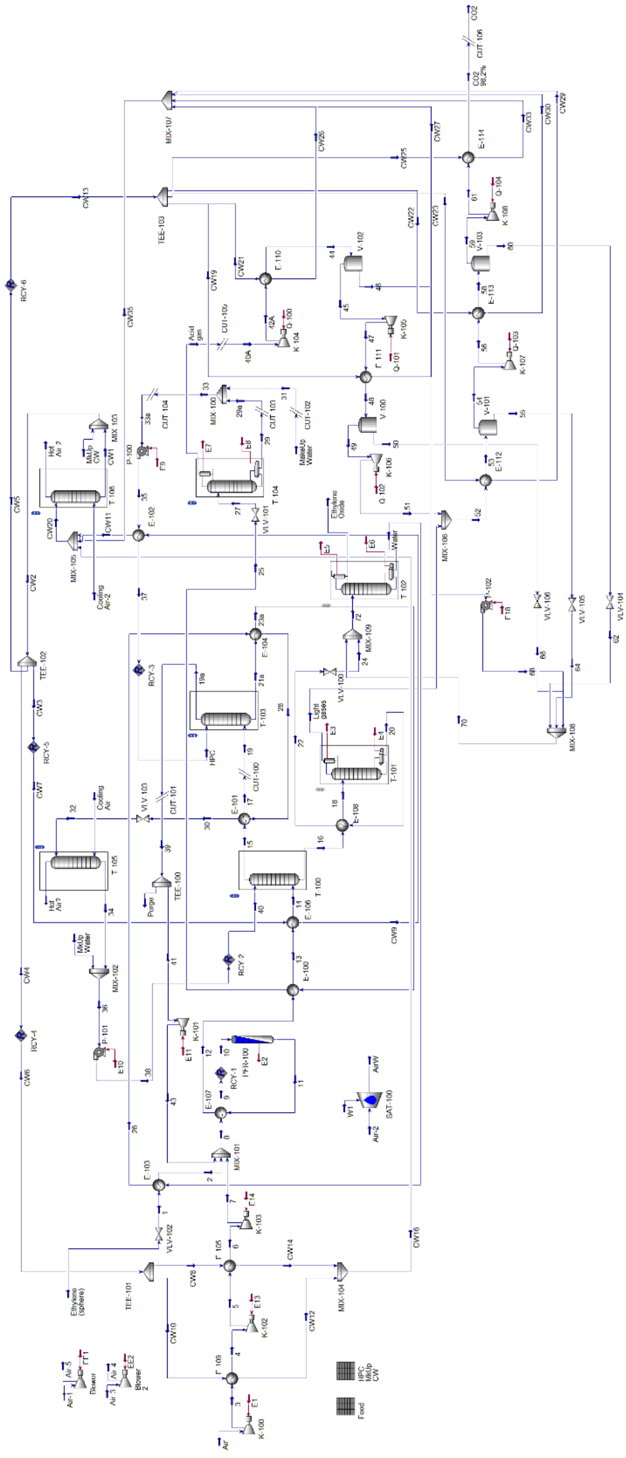

Figure III-2. Aspen HYSYS simulation of ethylene oxide processing.

III.5 Results and Discussion

Figure III-3 shows that ethylene oxidation reaction (PFR-100), distillation tower for CO_2 desorption (T-104), cooling water tower (T-106) and cooling tower air-blower (Blower 2) are the main unit-operations with sustainability hotspots.

PFR-100 reaction operation presents the worst drawbacks in the entire unit. Hotspots are mainly associated with high energy consumption, due to increased pressure and pre-heat the feed to 250 °C, HS and ENV impacts. HS problems are due to acute toxicity (*Acute*) and risk of reaction/decomposition ($Fail_{R/D}$). They are both associated to PFR-100 outlet stream, the first being due to the high ethylene oxide content, which is a substance likely to inflict health effects on humans exposed to a hazardous airborne concentration, and the latter because of stream high temperatures, what imposes a greater risk of reaction and decomposition. Regarding ENV concerns, PFR-100 presents high greenhouse gas emissions (*GWP*) and great impacts associated to the release of non-reacted ethylene, causing photochemical oxidation (*Smog*), and losses of ethylene oxide during the purification stage, resulting an increase in ecotoxicity for aquatic fresh water (Ec_{aq}). The remaining UOs present considerably lower impacts. T-104 distillation tower is the most energy-intensive operation, condition that also results in HS hotspots. The cooling water tower and air-blower are the most material-intensive.

In terms of sections, it is possible to see from Figure III-3 that the major impacts reside in EO Reaction and Utility Section. The first presents mentioned hotspots associated to PFR-100 and significant HS drawbacks in E-107. The main issues with E-107 are acute toxicity and the risk of reaction/decomposition, both due to reactor outlet composition. The latter is responsible for the second most intensive unit-operations: cooling water tower and cooling tower air-blower. In general, the utility section was the most intensive in material, which is a natural conclusion because it is associated to utility inputs and outputs. Overall, all distillation towers present relevant drawbacks, mainly associated to EE and HS risks. For instance, they are responsible for bringing down the sustainability of EO Purification stage. High temperatures and pressure services often end up not only consuming a large amount of energy but also causing risks of mobility, fire/explosion and reaction/decomposition.

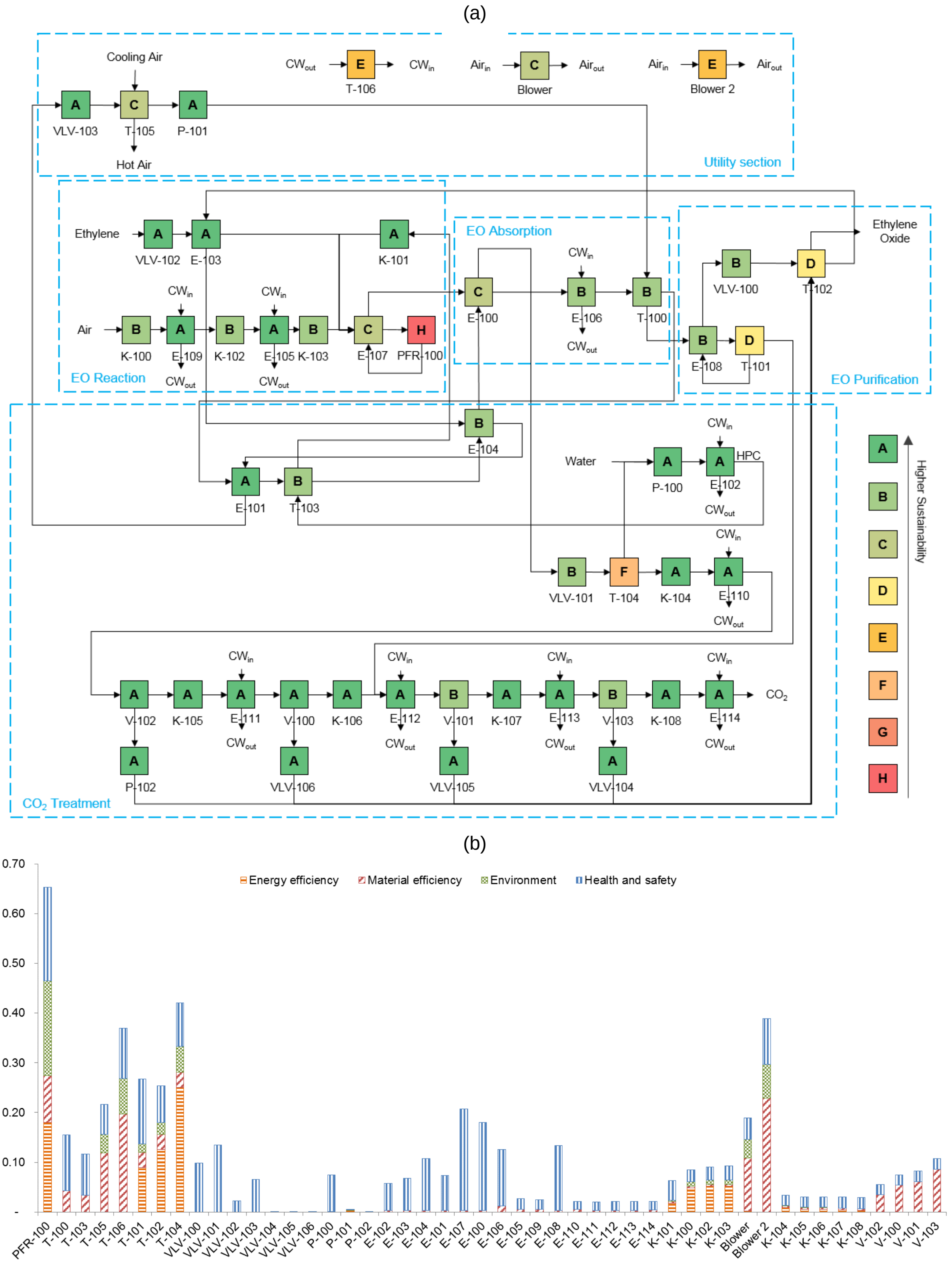

Figure III-3. S-OHI results: (a) flow diagram showing the level of sustainability of each unit-operation; (b) S-OHI values for each UO, pointing major hotspots across all dimensions.

The least intensive in sustainability hotspots is EO Absorption. In addition, the sustainability of operations in the carbon capture stage range from A to B level, indicating that this section not only avoids greenhouse gas emissions, but in fact contributes to the overall sustainable performance of the plant with low-intensive operations.

III.6 Conclusions

This work applies the Sustainable Process Engineering (S-PSE) method to assess the sustainability of ethylene oxide processing and identify major hotspots within the process. The case study clearly demonstrates coordination of computer-aided design tools (Aspen HYSYS, Excel and MATLAB) to sustainable process design. The main problems reside in ethylene oxidation reaction, distillation tower for CO_2 desorption, cooling water tower and cooling tower air-blower. The impacts associated to the reaction operation are much greater than others. Reaction drawbacks include high energy consumption, HS and ENV impacts. Given that many HS and ENV impacts are linked to the release of non-reacted ethylene and losses of ethylene oxide during the purification stage, a possible way of increasing process sustainability would be to enhance ethylene oxide recovery, reducing product losses. While a gate-to-gate approach for process design offers the advantage of deepening into fundamental process engineering models and comprehensively considering all sustainability dimensions when standard LCA does not, it still should be applied coupled with a life cycle method to avoid shifting impacts outside the system boundary.

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CHAPTER IV - NOVEL ETHYLENE OXIDE PRODUCTION WITH IMPROVED SUSTAINABILITY: LOSS PREVENTION VIA SUPERSONIC SEPARATOR AND CARBON CAPTURE

This paper was published in Journal of Environmental Management, Volume 269, 2020. doi: doi.org/10.1016/j.jenvman.2020.110782 (*Appendix F.6*).

Novel Ethylene Oxide Production with Improved Sustainability: Loss Prevention via Supersonic Separator and Carbon Capture

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Abstract

Sustainability must be always assured in process design. Not rarely, multiple sustainability criteria point oppositely, entailing a need for more systematic and coherent assessments. The Sustainable Process Systems Engineering method is introduced as a two-level hierarchical evaluation of process designs. The first level selects the best design via four-dimensional indicators (environment, efficiency, health-&-safety, and economic), while in the second level, sustainability hotspots of the best design are pinpointed to unveil possible improvements. The method is applied for sustainability assessment of two ethylene oxide processes: the conventional and a novel route employing supersonic separator to prevent ethylene oxide losses using liquid-water injection. Supersonic separator route reduces oxide losses by 83.33 kg/h, representing +0.9% greater ethylene oxide production, 95% less ethylene oxide losses, entailing 2.5% higher net value for 20 operation years despite 0.11% higher investment, and consequently exhibiting the best environmental, technical, health-&-safety and economic performances. Photochemical-oxidation and aquatic-ecotoxicity are environmental indicators with highest improvement due to supersonic separator inclusion. Ethylene oxidation reactor, carbon dioxide stripping-column and cooling-water tower are the main unit-operations with sustainability hotspots.

Keywords

Sustainability Assessment; Composite Index; Supersonic Separator; Ethylene Oxide; Cubic-Plus-Association; Loss Prevention.

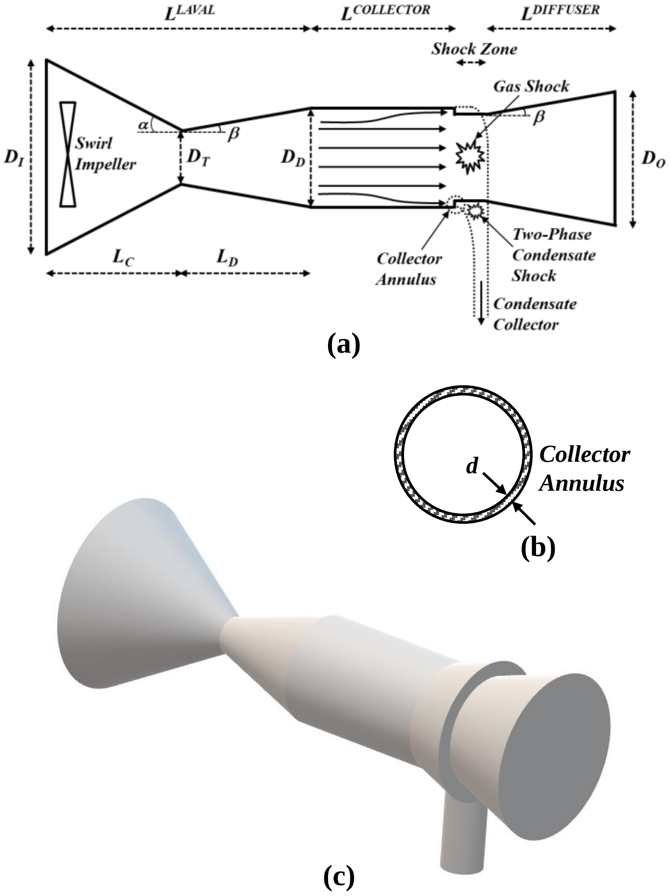
IV.1 Introduction

Ethylene oxide (EO) is a versatile intermediary with high reactivity and flammability issues (Lou et al., 2006). Glycols, poly(ethylene-oxide), glycol-ethers, ethanolamines, and surfactants are manufactured with EO, a worldwide massively produced chemical with $26*10^6$ tons in 2018 and expected $36*10^6$ tons in 2023 (Reseacrh and Markets, 2019). Due to EO toxicity/flammability, EO processes have inherent health-safety-environment vulnerability, with environmental burdens from harmful releases, energy-intensity and exergy-destruction. EO life-cycle impact assessment (LCIA) reports climate-change, human-health, ecosystems and particulate-formation concerns (Ghannadzadeh and Meymivand, 2019). Recent works investigated alternative EO production routes to mitigate its potential Health-Safety-Environment impacts. Ghannadzadeh and Sadeqzadeh (2017) coupled exergy and pinch analyses to reduce exergy losses. Lu et al. (2016) investigated titano-silicate/H_2O_2 catalysts for EO synthesis. Lee et al. (2010) studied a gas-expanded liquid-based process to reduce CO_2 emissions. De Faria et al. (2019) investigated carbon capture to boost sustainability of EO process and identified major unit-operations drawbacks.

IV.1.1 Supersonic Separator for EO Recovery

Supersonic separators (SS) are compact devices comprising static swirling-vanes, converging-diverging Laval nozzle, liquid-collector and diffuser. Fig. IV-1a discloses SS with rectilinear diameter profile where L_C, L_D, L^{Laval}, $L^{Collector}$, $L^{Diffuser}$, L respectively represent converging, diverging, Laval, collector, diffuser and total lengths; α, β, D_I, D_T, D_O, D_D, d respectively represent converging/diverging wall angles, inlet/throat/outlet/liquid-collector diameters, and collector annulus (Fig. IV-1b). Fig. IV-1c is a three-dimensional view. Fluid expands accelerating to supersonic velocities in the Laval, creating intense cooling that liquefies condensable species, where the Mach Number, $Ma=v/c$, has a special role – v is axial velocity and c is sound speed. Flow is subsonic ($Ma<1$) in the converging section, becomes sonic ($Ma=1$) at the throat, and supersonic ($Ma>1$) in the Laval diverging section. The supersonic liquid mist is centrifugally separated in the liquid-collector with constant flow-section (Fig. IV-1a) through the collector annulus accompanied by a slip-gas – part of the uniform gas flow that slips through the annulus; i.e., collected condensate is actually two-phase (L+V), or three-phase (e.g., water-hydrocarbon-gas). Supersonic flow is a metastable condition with rising instability through the Laval diverging section as the difference between outlet pressure (P^{Outlet}) and supersonic pressure increases. Therefore, after condensate withdrawal, an irreversible sudden adiabatic transition – the normal shock – occurs in the dry-gas supersonic flow, turning it into subsonic, sharply increasing entropy, pressure and temperature, while conserving mass/momentum/energy. Ideally, shock should occur at the supersonic shock zone, just after the liquid-collector annulus. The after-shock recompressed flow is hot and subsonic, and decelerates through the ending diffuser, recovering pressure and temperature until the SS outlet. Since shock is highly irreversible, even for isentropic expansion (Laval nozzle) and compression (diffuser) steps, SS cannot recover *100%* of the inlet pressure ($P^{Outlet} < P^{Inlet}$). SS head-loss increases, and the minimum temperature at Laval outlet (T^{Laval}) decreases with increase of the maximum attained supersonic *Ma*, referred to as $Ma^{Shock} = Ma^{Laval}$ (*Ma* just-before-shock-and-condensate-withdrawal). After condensate withdrawal, the sound speed increases as compressibility and density are lower in dry-gas. Hence, *Ma* decreases at constant flow-section to a lower supersonic *Ma*; namely, Ma_{BS} (*Ma* just-before-shock-and-after-condensate-withdrawal) at temperature and pressure (T_{BS}, P_{BS}). Ma_{BS} determines if shock occurs ($Ma_{BS} > 1$) or not ($Ma_{BS} \leq 1$). Furthermore, as the L+V condensate flow is normally supersonic through the collector annulus, it also experiences a shock transition at the curved collector *panhandle* (Fig. IV-1a). Thus, there is an analogous Ma_{BCS} (*Ma* just-before-condensate-shock) for the L+V condensate flow, implying shock occurrence ($Ma_{BCS} > 1$) or not ($Ma_{BCS} \leq 1$). If so, the multiphase-condensate also passes through supersonic-subsonic flow transition, increasing entropy, temperature and pressure.

Arinelli et al. (2017) proposed a rigorous thermodynamic SS model as a HYSYS unit-operation extension for SS design and simulation (SS-UOE) in which the multiphase sound speed is obtained via a phase-equilibrium *c* unit-operation extension (PEC-UOE) from de Medeiros et al. (2017). Precise multiphase sound speed is primordial for correct *Ma* calculation, a necessity for accurate SS design. Arinelli et al. (2017) applied SS-UOE for CO_2-rich natural gas water and hydrocarbon dew-points adjustments and CO_2 removal. Several works also used SS-UOE for simulation of offshore gas processing (de Medeiros et al., 2019), mainly dew-points adjustment. However, there are SS applications for polar liquid recovery as in Teixeira et al. (2018) who explored an innovative SS recovery of methanol, ethanol and monoethylene-glycol from raw gas simultaneously adjusting gas dew-points. In this case a new liquid-water injection through SS inlet increased the capture of hydrophilic methanol, ethanol and glycol, and was the first utilization of Cubic-Plus-Association Equation-of-State (CPA-EOS) in SS simulation, a necessity in aqueous-hydroxylate systems. Teixeira et al. (2019) deepened the SS-methanol-recovery case proving an economic leverage that affords a post-combustion capture plant. Following this track, a new SS application with liquid-water injection for EO recovery from vent-vapors is here devised and designed with CPA-EOS.



(a)

(b)

(c)

Figure IV-1. SS with linear diameter profiles: (a) lateral view with geometric parameters; (b) collector annulus axial view; (c) three-dimensional view.

IV.1.2 Sustainable Process Design

Sustainability criteria must be included early in process design to handle complex issues when the window for changes is wider (Diwekar, 2015) and should encompass process indicators and corporate triple-bottom-line aspects to support decision-making. LCA is a consolidated methodology for sustainability performance evaluation (Finnveden et al., 2009). Sadhukhan et al. (2017) applied cradle-to-gate LCA to access environmental impacts of four alternatives for magnetite nanoparticles production with average black-boxes representing aggregated processes. Man et al., (2020) applied multi-criteria decision-making to find most sustainable papermaking process also using average black-boxes and LCIA, without social dimension. Pell et al. (2019) conducted a cradle-to-gate and process simulation-based LCA for environmental assessment of mining rare-earth elements. A major limitation of traditional LCA for process design is that it relies on simple input-output black-box models ignoring process complexity (Jacquemin et al., 2012). Hence, it becomes unappealing to engineers and limited to corporate levels (Ocampo et al., 2016). Moreover, when considering unit-operations, LCA is constrained to environmental impacts, rendering difficulties to handle Triple-Bottom-Line issues through life-cycle. On the other hand, gate-to-gate assessments require less information, are easier, can evaluate unit-operations (Finnveden et al., 2009) and simplify addressing Triple-Bottom-Line.

Recent works corroborate these claims utilizing multiple dimensions in gate-to-gate assessments. García et al. (2017) performed a techno-economic, energy and environmental assessment for biorefinery hydrogen production using process simulation. In a cradle-to-cradle approach Ordouei and Elkamel (2017) developed a composite sustainability-index for process design, comprising environment, energy, safety and cost-benefit but without including supply-chain or lifecycle stages outside the gate, thus benefiting from the perks of a gate-to-gate approach. In general, the literature lacks comprehensive approaches for process sustainability assessment. As a rare example, the method of Saad et al. (2019) ranks sustainability of processes using all three sustainability dimensions and creating a social well-being indicator category.

IV.1.3 The Present Work

It is investigated the innovative use of supersonic separators (SS) to boost EO production sustainability by annihilating EO losses in the Conventional-Route. Both Conventional-Route and SS-Route execute carbon capture and sequestration (CCS) – originally for removing CO_2 from reactor loop; not for environmental concerns, but favoring sustainability anyways. There is a literature gap regarding sustainability impacts of SS application in EO production. Moreover, the strategy of liquid-water SS injection used for SS-methanol-recovery (Teixeira et al., 2019) is also a keystone here to enhance EO capture. The new EO SS-Route competitiveness is demonstrated against the Conventional-Route via simulation-based economic and sustainability analyses. The sustainability analysis introduces the new Sustainable Process Systems Engineering (S-PSE), a hierarchical process sustainability assessment, featuring: (i) environmental/social/economic dimensions and technology-specific indicators; (ii) plant-wide/supply-chain overall sustainability; (iii) unit-operation sustainability hotspots diagnosis; (iv) computer-aided tools; and (v) composite sustainability-indexes for multi-attribute decision-making.

IV.2 Technical Background

To implement economic and sustainability analyses of EO Conventional-Route and SS-Route, theoretical aspects are discussed.

IV.2.1 Supersonic Separator Model

A more complete SS-UOE – different from the original SS-UOE of Arinelli et al. (2017) – is used for SS HYSYS simulations. For the phase-equilibrium sound speed PEC-UOE (de Medeiros et al., 2017) is used. SS-UOE finishes SS design matching sonic-throat flow and executing supersonic expansion, condensate withdrawal, shock transition and diffuser compression. Main improvements on the original SS-UOE comprise: (i) feed, Gas-Product and Condensate-Product are stagnated HYSYS streams; (ii) realistic annulus liquid-collector; and (iii) normal shock occurrence in the liquid-collector *panhandle*. Appendix B presents the new SS-UOE algorithm. The original SS-UOE (Arinelli et al., 2017) was validated with literature data in Teixeira et al. (2019) and is the basis of new SS-UOE. SS-UOE designs SS with linear diameter profiles (Fig. IV-1), but any diameter profile also works. SS-UOE inputs comprise: (i) stagnated-feed data (T^{Feed},P^{Feed}, flow rate, composition) automatically retrieved from HYSYS flowsheet; (ii) number of parallel SS's; (iii) inlet/outlet diameters (D_I,D_O); (iv) converging/diverging wall angles (α,β); (v) liquid-collector annulus (d); (vi) adiabatic expansion/compression efficiencies ($\eta^{EXP}\%,\eta^{CMP}\%$); and (vii) Ma^{Shock} (maximum attained Ma). SS-UOE calculates SS head-loss and remaining geometric parameters: throat diameter (D_T), converging/diverging lengths (L_C,L_D), liquid-collector length ($L^{Collector}$), diffuser length ($L^{Diffuser}$); and exports stagnated gas-product and condensate to HYSYS flowsheet. Stagnation/de-stagnation calculations are required because HYSYS streams are stagnated at given (T,P) and flow rates, while SS inlet/outlet fluids are not; i.e., in HYSYS the feed (T^{Feed},P^{Feed}) has negligible molar kinetic energy ($\bar{K} \approx 0$), such that new (T^{Inlet},P^{Inlet}) have to be calculated at SS inlet. Analogously from SS outlet at (T^{Outlet},P^{Outlet}), a new stagnated ($T^{Gas\text{-}Product}$,$P^{Gas\text{-}Product}$) state is calculated in HYSYS flowsheet. Inlet de-stagnation solves conservation of total molar energy ($\bar{K}+\bar{H}$) and molar entropy ($\bar{S}$), subject to SS inlet flow-section, hence assuming an isentropic transition from the stagnated-feed state to SS inlet state. In SS-UOE (T^{Feed},P^{Feed}) refers to stagnated-feed in the flowsheet, with properties $\bar{S}^{Feed}$, $\bar{K}^{Feed} \approx 0$, $\bar{H}^{Feed}$; while (T^{Inlet},P^{Inlet}) refers to SS inlet state satisfying $\bar{K}(T^{Inlet},P^{Inlet})+\bar{H}(T^{Inlet},P^{Inlet})=\bar{H}^{Feed}$ and $\bar{S}(T^{Inlet},P^{Inlet})=\bar{S}^{Feed}$. Arinelli et al. (2019) discussed this procedure, so-called KHS-Bridge. It represents reversible and adiabatic expansion/compression along a flow-section change subjected to flow rate and composition. SS outlet stagnation to ($T^{Gas\text{-}Product}$,$P^{Gas\text{-}Product}$) is also a KHS-Bridge and, for $\eta^{EXP}\%=\eta^{CMP}\%=100\%$, Laval expansion and diffuser compression are KHS-Bridges as well.

IV.2.2 Ethylene Oxide Production: Conventional-Route

In 1931 a better EO process replaced the old Chlorohydrin Process (Berty, 1983): the direct air (or pure oxygen) oxidation of ethylene to EO. Despite technology evolution, environmental concerns remain: the direct ethylene oxidation route can have fugitive EO emissions, lowering profitability with hazardous releases. Furthermore, an EO plant generates

$\approx 3.4*10^6$ ton^{CO2}/y (Lee et al., 2010), and goals have been established against CO_2 emissions (Skagestad et al., 2017).

Air-based Conventional-Route EO production (Fig. IV-2) has four main units: EO reaction, EO absorption, EO purification and CCS unit (Lou et al., 2006). EO reactor PFR-100 produces undesirable by-product CO_2 at huge rates demanding a CCS unit to remove it from the reactor-loop and to compress it for exportation (Rebsdat and Mayer, 2001). Conventional-Route also includes a Cooling-Tower T-106 that sends cooling-water (CW) at 35°C to all condensers, coolers and compressor intercoolers after a make-up to compensate evaporation. CCS unit uses chemical-absorption with Benfield hot potassium carbonate (HPC) process (Milidovich and Zbacnik, 2013). HPC chemical-absorption has high efficiency, low cost, and is a mature technology vis-à-vis other CCS methods. The most common chemical-absorption solvents are aqueous-amines – monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and their blends – despite well-known shortcomings: corrosion, high regeneration heat duty and oxidative-thermal degradation (Borhani et al., 2015). In EO production, main comparative advantages of HPC to aqueous-amines comprise lower health-environment-safety impacts (non-flammable, non-toxic solvent);, solvent chemically inert to EO (differently from amines), high CO_2 loading; low regeneration heat-ratio; and absorption/regeneration at higher temperatures without solvent degradation entailing efficient and cost-effective regeneration (Vega et al., 2020). The major HPC drawback is a slower liquid-phase reaction rate, requiring larger stage numbers and kinetic-enhancer additives. Similarly to aqueous-amines, HPC has also corrosion issues (Smith et al., 2012).

EO Conventional-Route in Fig. IV-2 highlights CCS unit and SS-EO-Recovery block for the SS-Route; i.e., both routes are simultaneously described since the only difference between them is the SS-EO-Recovery. The vertical shell-and-tube multi-tubular reactor PFR-100 generates EO via highly exothermic air oxidation of ethylene in the catalyst-packed tubes at 23bar and 260°C, while in the shell pressurized-water boils absorbing reaction heat and generating medium-pressure steam to all heat-demanding reboilers of columns T-101, T-102 and T-104 (Bayat et al., 2013). The reactor effluent, after preheating reactor feed, is cooled with CW, and goes to column T-100 where EO is absorbed into water at 22bar without ethylene glycol formation thanks to short residence-time. EO purification involves two distillation columns: T-101 has a total-reflux condenser venting light gases (absorbed in T-100) and its degassed water-EO bottoms go to T-102 which sharply splits EO-H_2O at 4 bar producing liquid distillate EO ($>99.5\%mol$) and pure-water bottoms that go to cooling-tower T-105, returning to absorber T-100 after make-up. Light gases from T-101 go to CO_2 compression train. T-100 lean-gas follows to CO_2 HPC absorber T-103 at 20 bar. HPC-rich is regenerated in stripper T-104 at $P=1atm$ with a total-reflux condenser venting water-saturated CO_2. T-103 top gas is mostly unreacted ethylene and nitrogen, which is recycled to EO reactor after partial purge to avoid inert gases build-up. CO_2 from stripper T-104 passes through five-stage intercooled compression train becoming supercritical CO_2 ($T=40^oC$, $P=100bar$, $98\%mol$ CO_2) exported to geological destinations.

IV.2.3 Novel Supersonic Separator Route

EO SS-Route (Fig. IV-2) is the Conventional-Route plus a SS with double water-injection at 40°C (shaded SS-EO-Recovery block) processing vent-gas from T-101 condenser to recover some EO originally evaporated by light gases and subsequently lost in Conventional-Route. In SS-Route, SS-EO-Recovery exploits water-EO affinity correctly modeled by CPA-EOS which was calibrated in Appendix C. First water-injection ($H_2O:EO=30mol:mol$) contacts T-101 vent-gas at 21 bar in flash-drum V-104, partially capturing EO in V-104 aqueous bottoms that is pumped to T-101. The second water-injection ($H_2O:EO=10mol:mol$) joins V-104 top-vapor at SS inlet ($P=21bar$). SS produces a gas-product ($P\approx18bar$) that goes to an intermediate CO_2 compressor and a liquid-vapor (L+V) condensate compressed in the collector *panhandle* shock to 27 bar (Fig. IV-1a) allowing its direct recycle to T-101.

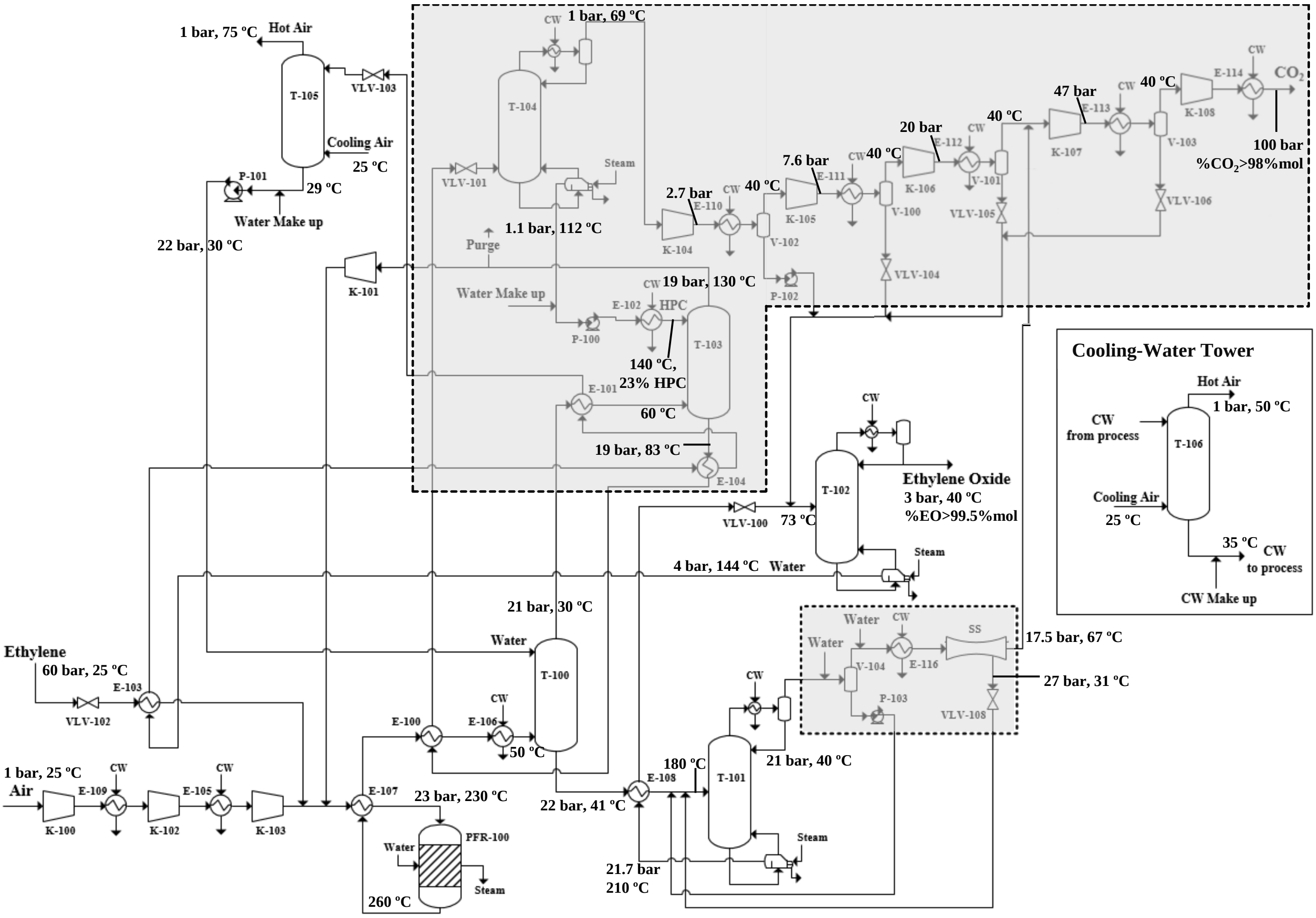


Figure IV-2. EO Conventional-Route and EO SS-Route (SS-EO-Recovery and CCS unit highlighted).

IV.2.4 Simulation Assumptions

SS-UOE and PEC-UOE run with any HYSYS equation-of-state. The thermodynamic modeling of the SS unit of SS-Route is provided by CPA-EOS which was chosen because it is adequate for water-alcohol and water-EO systems, and was already successfully used with SS (Teixeira et al., 2019). Since the CPA-EOS $k_{EO\text{-}H2O}$ binary parameter is not available, it was adjusted in Appendix C with literature EO-H_2O vapor-liquid equilibrium (VLE) data. Table IV-1 presents simulation assumptions for EO Conventional-Route and SS-Route. Power consumption, utilities and stream data are obtained via simulations. Economic evaluation follows Turton et al. (2009) (Appendix D). Table IV-2 shows how inlet/outlet impacts distribute across unit-operations. CW make-up impacts are allocated on CW exchangers.

Table IV-1. Simulation assumptions.

Assumption	***Item***	***Description***
{A1}	*Process Modeling*	*Simulation: HYSYS 10; Thermodynamic Package: HYSYS-NRTL;* *HPC:Aspen-Properties E-NRTL;* *SS:new SS-UOE (Appendix B) with CPA-EOS (adjusted* $k_{EO\text{-}H2O,}$ *Appendix C);* *Phase-Equilibrium Sound Speed: PEC-UOE (de Medeiros et al., 2017).*
{A2}	*Inlets*	*Air:* $F=2609$ *kmol/h;* $T=25^{\circ}C$; $P=1.013$ *bar;* $N_2=73.84\%$*mol,* $O_2=24.55\%$*mol,* $H_2O=1.6\%$*mol; Ethylene:* $F=368$ *kmol/h;* $T=25^{\circ}C$; $P=60$ *bar.*
{A3}	*EO-Reaction*	*PFR-100:* $P=23$ *bar,* $T^{in}=230^{\circ}C$; $T^{out}=260^{\circ}C$.
{A4}	*EO-Absorption*	*Water:* $F=11{,}100$ *kmol/h;* $P=22$ *bar;*$T=29.6^{\circ}C$; *Absorber T-100: Stages=10;* $P=21$ *bar;* $T^{TOP}=29.6^{\circ}C$; $T^{BOTTOM}=41.3^{\circ}C$.
{A5}	*CCS*	*Absorber T-103: Stages=10;* $P=20$ *bar;* $T^{TOP}=130^{\circ}C$; $T^{BOTTOM}=83^{\circ}C$; *HPC:* $H_2O=76.68\%$*mol,* $K_2CO_3=23.32\%$*mol;* *Stripper T-104: Stages=10;* $P=1.013$ *bar;* $T^{TOP}=68.9^{\circ}C$; $T^{BOTTOM}=112^{\circ}C$; $CO_2 \geq 98\%$*mol; Compression-Train: Stages=5,* $P^{Export}=100$ *bar.*
{A6}	*EO-Purification*	*Light-Gases T-101: Stages=20;* $P=21.70$ *bar;* $T^{TOP}=40^{\circ}C$; $T^{BOTTOM}=210^{\circ}C$; *EO-*H_2O *T-102: Stages=50;* $P=4$ *bar;* $T^{TOP}=40^{\circ}C$; $T^{BOTTOM}=144^{\circ}C$; *EO=99.5%mol*
{A7}	*SS*	$D_I=80$*mm;* $D_O=60$*mm;* $d=0.25$*mm;* $\alpha=12.67^{\circ}$; $\beta=2.66^{\circ}$; $\eta^{EXP}=\eta^{CMP}=100\%$; $Ma^{Shock}=1.35$.
{A8}	*Cooling-Towers*	*Process-Water T-105: Stages=10;* $P=1.013$ *bar;* $T^{TOP}=75.3^{\circ}C$; $T^{BOTTOM}=29.3^{\circ}C$; *Air: 3226 kmol/h;* $T=25^{\circ}C$; $P=1.013$ *bar.*

		CW T-106: Stages=10; P=1.013 bar; T^{TOP}*=49.7ºC;* T^{BOTTOM}*=34.9ºC;* *Air: 11,619 kmol/h; T=25ºC; P=1.013 bar.*
{A9}	*Heat Exchangers*	ΔP^{SHELL}*=0.2 bar;* ΔP^{TUBES}*=0.2 bar;* $\Delta T^{APPROACH}$*=5ºC;* *Intercoolers:* T^{GAS}*=40ºC.*
{A10}	*Compressors* *Pumps*	*Adiabatic Efficiency:* η*=75%;* *Driver: Electric.*
{A11}	*Heating-Utility*	*Medium-Pressure Steam: T=195ºC; P=13 bar.*
{A12}	*Cooling-Utility*	*CW:* $T \epsilon [35°C,50°C]$*; P=1.013 bar.*

Table IV-2. Unit-operations with inlet/outlet assigned impacts.

Stream	***Impact attributed to unit-operation***	***Unit-operation description***
Inlet – Water	*T-103*	CO_2 *HPC-Absorber*
Outlet – Purge	*PFR-100*	*EO-Reactor*
Inlet - Ethylene	*PFR-100*	*EO-Reactor*
Inlet - Air	*PFR-100*	*EO-Reactor*
Inlet – Make-up Water	*T-100*	*EO-Absorber*
Outlet – Hot air	*T-105*	*Process-Water Cooling-Tower*
Inlet – Air	*T-105*	*Process-Water Cooling-Tower*
Inlet – Air	*T-106*	*CW-Tower*
Outlet – Hot Air	*T-106*	*CW-Tower*
Inlet – Make-up Water	*Allocation*[a]	*Note*[a]
Inlet – Water-Injection	*SS*	*SS*
Inlet – Water-Injection	*V-104*	*Light-gases separator*

[a] *Allocates impacts across CW-exchangers: E-105, E-106, E-109, E-110, E-111, E-112, E-113, E-114, E-116.*

IV.2.5 Sustainability Assessment: S-PSE

S-PSE assesses process sustainability via a two-level hierarchical procedure (Fig. IV-3): (i) plant-wide or production-unit and (ii) unit-operations. First-level selects the most sustainable plant-wide feedstock-process-product configuration. Second-level locates unit-operation sustainability hotspots.

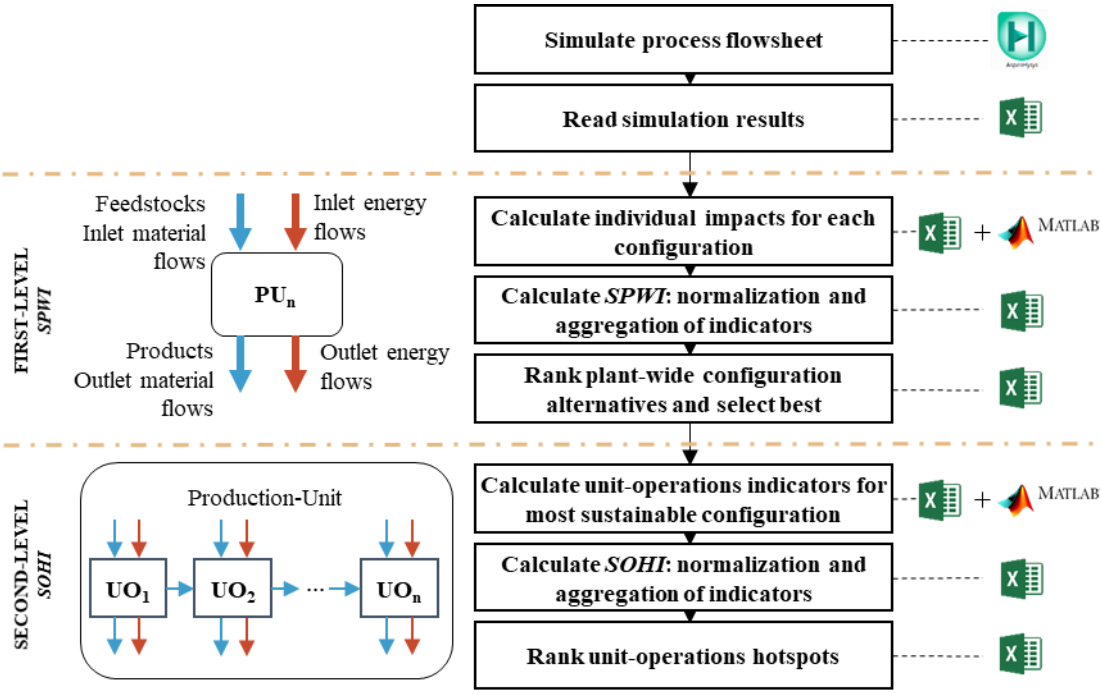


Figure IV-3. Hierarchical S-PSE and computer-aided tools (PU≡production-unit; UO≡unit-operation).

S-PSE ranks alternatives with the Sustainable Plant-Wide Index (*SPWI*, first-level) and the Sustainable Operation Hotspot Index (*SOHI*, second-level). Although previous works comprise similar features from *SPWI* calculation – e.g., indicators (Ruiz-Mercado et al., 2012), modular design (Gao and You, 2017), computer-aided tools (Carvalho et al., 2013), or ranking process alternatives (Kreuder et al., 2017; Ordouei and Elkamel, 2017) – the hierarchical combination of S-PSE steps from supply-chain to gate-to-gate unit-operations is an original aspect of this work. Using input-process-output models, product units are combined into a production structure, comprising performance data and resource flows. Hence, S-PSE is modular, flexible, and extensible, supporting the arrangement of production-units to provide plant-wide or value-chain overall configuration. S-PSE integrates three computer-aided tools: HYSYS simulator, MATLAB, and MS-Excel interface (Fig. IV-3). S-PSE starts simulating each production-unit solving mass/energy balances. Data is exported to MS-Excel/MATLAB that calculate indicators using built-in property database, process characterization factors and classification labels.

Sustainability indicators are classified into four dimensions: (i) *Environment*; (ii) *Efficiency*; (iii) *H&S* (Health-and-Safety); and (iv) *Economic*. For ranking, indicators are normalized and aggregated into two composite-indexes: *SPWI* (first-level) and *SOHI* (second-level), calculated via Canberra-distance metric (Brandi and dos Santos, 2016), which estimates similarity/dissimilarity between two systems and is invariant under ratio/scale transformations, has translational symmetry (Sikdar et al., 2017) and adopts a reference to measure the relative sustainability of systems (Brandi et al., 2017). A normalized (range 0-1) indicator X_n is given by Canberra-distance in Eq. (IV-1), where x_n is an indicator, N_I is number of indicators, r_n represents a reference, x_{n0} is set as origin that guarantees translational symmetry and is a fraction of the indicator ideal value through sensitivity analysis. In first-level assessment, the reference is chosen as the best (i.e., most sustainable) value of an indicator among all production-units. Hence, $X_n=1$ and $X_n=0$ respectively represent best and worst sustainability. Table IV-3 shows that, depending on the indicator, best sustainability can correspond to its maximum or minimum value. Eqs. (IV-2)-(IV3) calculate *SPWI*, where $X_{n,d}$ represents normalization of indicator x_n in dimension *d*; *Nd* is number of indicators in dimension *d*; $SPWI_d$ is the sustainability aggregate-index for dimension *d*; and *D* is number of dimensions.

$$X_n = 1 - \frac{\left|x_n - r_n\right|}{\left|x_n - x_{n0}\right| + \left|r_n - x_{n0}\right|} \quad , \quad n = 1..N_I \tag{IV-1}$$

$$SPWI_d = \frac{1}{Nd}\sum_{n=1}^{Nd} X_{n,d} \tag{IV-2}$$

$$SPWI = \frac{1}{D}\sum_{d=1}^{D} SPWI_d \tag{IV-3}$$

The second-level assessment identifies worst sustainability performances and differentiate unit-operations regarding bottlenecks, as opposed to *SPWI* that seeks the best process. Therefore, unit-operation references are set as worst values among second-level indicators, with zero/one standing for higher/lower (i.e., hotspots) sustainability. It is worth noting that would the reference be set to the best performer, unit-operations with lowest sustainability would be closely ranked. This is a drawback of Canberra-distance, as it distinguishes points closer to the reference, while worse points seem flocked, regardless their original mutual differences. Second-level assessment classifies unit-operations into five categories: Reaction, Separation, Heating/Cooling, Compression and Expansion. *SOHI* does not contemplate the *Economic* dimension, focusing on *Environment*, *Efficiency* and *H&S*. Some indicators are not applicable to all unit-operations (Table IV-4). Eqs. (IV-4)-(IV-5) calculate *SOHI*, where $X_{n,d}$ represents normalization of indicator x_n in dimension *d*; Nd^{Ap} is number of applicable indicators for a given unit-operation in dimension *d*; $SOHI_d$ represents the sustainability aggregate-index for dimension *d*; and *D* is number of dimensions.

$$SOHI_d = \frac{1}{Nd^{Ap}} \sum_{n=1}^{Nd^{Ap}} X_{n,d} \qquad \text{(IV-4)}$$

$$SOHI = \frac{1}{D} \sum_{d=1}^{D} SOHI_d \qquad \text{(IV-5)}$$

IV.2.6 Sustainability Indicators

SPWI and *SOHI* respectively involve calculating 16 and 12 technology-specific process indicators (Table IV-3), where some indicators appear in both assessments. *Environment* accounts for resource/waste impacts using LCA impact metrics: global-warming (*GWP*), aquatic-ecotoxicity (Ec_{aq}), photochemical-oxidation (*Smog*), and hazardous-waste (*HW*), which are pertinent to ethylene/EO contexts. *Efficiency* accounts for technicalities of unit-operations, identifying bottlenecks and improvements in early-stage design. *Efficiency* indicators are mainly from green-chemistry (Anastas and Warner, 1998) and green-engineering (Anastas and Zimmerman, 2003) principles: energy-intensity (*EI*), material-intensity (*MI*), E-factor (*E*), water-intensity (*WI*) and separation mass-loss index (*SMLI*). Chemical plants offer inherent risks to workers and populations; hence, process social impacts are assessed through *H&S* human-health indicators – hazardous-input (*Hazin*), acute-toxicity (*Acute*) – and safety indicators – fire/explosion ($Fail_{F/E}$), mobility (*Mob*). *Economic* estimates early-stage economic viability via cost of manufacturing (*COM*), fixed capital investment (*FCI*), gross annual-profit (*GAP*) and economic-potential (*EP*), defined in Appendix D. *Economic* dimension only exists in first-level assessment, assisting plant configuration.

Table IV-3. S-PSE for first-level (*SPWI*) and second-level (*SOHI*) assessments.

Indicator	*Calculation*[a]	*Unit*	*SPWI*	*SOHI*	*Best*[b]
Environment					
Global-Warming (GWP)[c,d]	$GWP = \sum_i \left(m_{out,i}\ CF_i^{GWP} \right) + \sum_k \left(En_k\ C_f\ EF \right)$	$kgCO_2e$	x	x	Min
Photochemical-Oxidation (Smog)[d]	$Smog = \sum_i \left(m_{out,i}\ CF_i^{smog} \right)$	$kgNO_xe$	x	x	Min
Aquatic-Ecotoxicity (Ec_{aq})[d,h]	$Ec_{aq} = \sum_i \left(m_{out,i}\ CF_i^{Ec_{aq}} \right)$	$PAF.m^3d$	x	x	Min
Hazardous-Waste (HW)[e]	$HW = \sum_i \left(m_{out,i}\ CF_i^{HW} \right)$	kg/h	x	x	Min
Efficiency					
Energy-Intensity (EI)	$EI = \sum_k \left(En_k\ C_f \right) / m_{prod}$	J/kg	x	x[f]	Min
Material-Intensity (MI)	$MI = m_{in} / m_{prod}$	kg/kg	x	x[f]	Min
E-factor (E)	$E = (m_{in} - m_{prod}) / m_{prod}$	kg/kg	x	x	Min
Water-Intensity (WI)[c]	$WI = (m_{in,water}\ \lambda) / m_{prod}$	kg/kg	x		Min
Separation mass-loss index (SMLI)	$SMLI = \left(\sum_F m_{sep,in,F} / m_{sep,prod} \right) - 1$	kg/kg		x	Min
H&S					
Hazardous-Input (Haz_{in})[d]	$Haz_{in} = \sum_i \left(m_{in,i}\ CF_i^{Haz} \right) / m_{prod}$	kg/kg	x	x[f]	Min
Fire/explosion ($Fail_{F/E}$)[g]	$Fail_{F/E} = Max_F \left\lfloor \sum_i \left(m_{i,F}\ IndVal_{i,F}^{F/E} \right) \right\rfloor$		x	x	Min
Mobility (Mob)[g]	$Mob = Max_F \left\lfloor \sum_i \left(m_{i,F}\ IndVal_{i,F}^{Mob} \right) \right\rfloor$		x	x	Min
Acute-Toxicity (Acute)[g]	$Acute = Max_F \left\lfloor \sum_i \left(m_{i,F}\ IndVal_{i,F}^{Acute} \right) \right\rfloor$		x	x	Min
Economic					
COM	*Appendix D*	MMUSD/y	x		Min
FCI	*Appendix D*	MMUSD	x		Min
GAP	*GAP=REV-COM (Appendix D)*	MMUSD/y	x		Max
EP	*EP=REV-CRM-CUT (Appendix D)*	MMUSD/y	x		Max

[a] Ruiz-Mercado et al. (2012). [b] Best: indicator value for best sustainability (reference-point). For first-level assessment, best value among production-units; for second-level, worst value among unit-operations. [c] GREENSCOPE (Ruiz-Mercado et al., 2012).

[d] LCIA: GWP (energy usage emissions). [e] LCIA: CF=1(hazardous species); CF=0(non-hazardous). [f] SOHI: absolute numerator.

[g] Koller et al. (2000) and Sugiyama et al. (2008): probability of release effects for each species in each stream times species mass. H&S indicator value is the highest among streams. [h] PAF: Potentially Affected Fraction of Species.

Some second-level indicators are attributed to specific unit-operations. Table IV-4 determines which indicators apply to each unit-operation; hence, being “Applicable” or not in Eq. (IV-4). Component inlet/outlet impacts correspond to burdens associated to its consumption/release and are credited to unit-operations responsible for such presence; e.g., reactant impacts are assigned to the respective reactor. They are *Environment* or *H&S* parameters related to component physical properties. *Efficiency* indicators of material-intensity are not calculated for compression/expansion unit-operations which are not material-intensive. Impacts can be allocated through multiple unit-operations; e.g., utility streams can undergo a material allocation throughout unit-operations consuming them.

Table IV-4. Indicators applicable to unit-operations.

Indicator	**Unit-operation type**
$Smog$, Ec_{aq}, HW	Assigned unit-operation for component outlet impacts
EI, GWP, $Fail_{F/E}$, Mob, $Acute$	All
MI, E	Separation, Cooling/Heating, Reaction
$SMLI$	Separation
Haz_{in}	Assigned unit-operations for component inlet impacts

IV.3 Results and Discussion

Table IV-5 exhibits SS specifications/results where different (T,P) states are seen. SS feed is supposed stagnated at (T^{Feed},P^{Feed}). At SS inlet a new (T^{Inlet},P^{Inlet}) state is calculated via KHS-Bridge. Analogously, there is a KHS-Bridge converting SS outlet state (T^{Outlet},P^{Outlet}) to stagnated Gas-Product ($T^{GasProduct}$, $P^{GasProduct}$). T^{Laval},P^{Laval} and $Ma^{Shock}=Ma^{Laval}$ refer to the multiphase fluid at Laval-end, upstream the liquid-collector, while Ma_{BS} refers to dry-gas downstream the liquid-collector (after $x=L^{Laval}+L^{Collector}$, Fig. IV-1) at ($T_{BS}$,$P_{BS}$). Ma reduces from $Ma^{Shock}=1.35$ to $Ma_{BS}=1.15$ due to higher c of dry-gas. After liquid removal via annulus at (T^{Laval},P^{Laval}), the L+V condensate Ma increases to $Ma_{BCS}=1.81$, due to lower c from higher liquid-fraction. After condensate shock, the L+V state in the collector *panhandle* is (T_{ACS},P_{ACS}, Ma_{ACS}), which gives a final stagnated L+V Condensate-Product state ($T^{Cond-Product}$,$P^{Cond-Product}$).

Table IV-5. SS specifications and design.

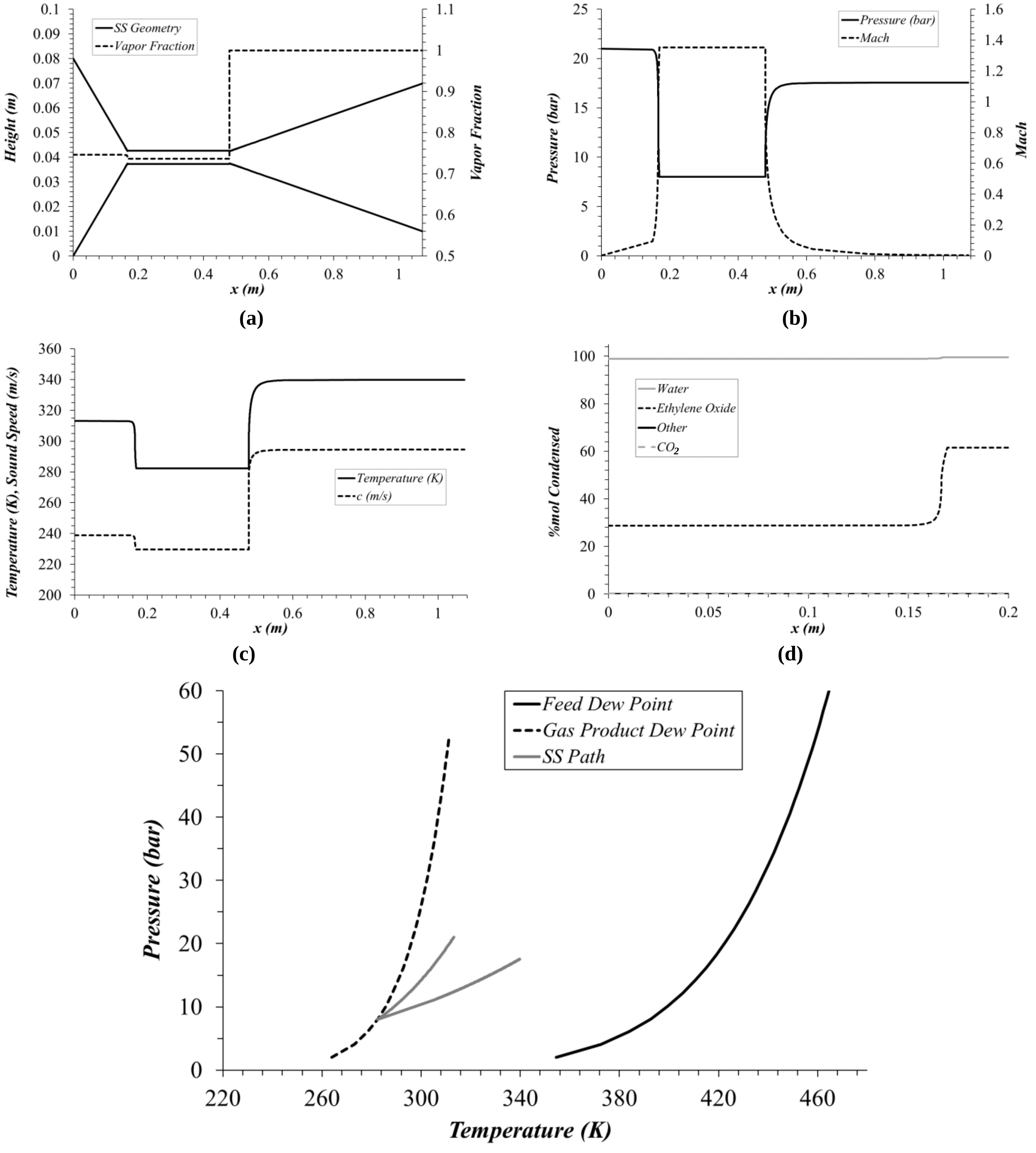
Specified Items	***Value***	***Calculated by SS-UOE***	***Value***
No.of SS's	*1*	$D_T(m)$	*0.0051*
$D_I(m)$	*0.08*	$L_C(m)$	*0.1665*
$D_O(m)$	*0.06*	$L_D(m)$	*0.0030*
$\alpha(^o)$	*12.67*	$L^{Laval}(m)$	*0.1695*
$\beta(^o)$	*2.66*	$D_D(m)$	*0.0054*
d(mm)	*0.25*	$L^{Collector}(m)$	*0.3103*
Ma^{Shock}	*1.35*	$L^{Diff}(m)$	*0.5926*
$\eta^{EXP}\%$	*100*	*L(m)*	*1.0724*
$\eta^{CMP}\%$	*100*	$P^{Laval}(bar)$	*8.01*
$P^{Feed}(bar)$	*21.0*	$T^{Laval}(^oC)$	*9.25*
$T^{Feed}(^oC)$	*40.00*	Ma_{BS}	1.15^*
Feed $MMsm^3/d$	*0.0071*	$P^{Outlet}(bar)$	*17.55*
Feed %EO	*2.45%*	$T^{Outlet}(^oC)$	*66.64*
Feed $\%H_2O$	*24.85%*	$P^{Gas\text{-}Product}(bar)$	*17.55*
$P^{Inlet}(bar)$	*21.00*	$T^{Gas\text{-}Product}(^oC)$	*66.64*
$T^{Inlet}(^oC)$	*40.00*	Ma_{BCS}	*1.809*
		$P_{ACS}(bar)$	*27.20*
		$T_{ACS}(^oC)$	*29.30*
		$P^{Cond\text{-}Product}(bar)$	*27.20*
		$T^{Cond\text{-}Product}(^oC)$	*30.68*
		%P Recovery	*83.57%*
		%mol Condensate	$39.31\%^{\#\&}$
		$REC\%H_2O$	*99.58%*
		REC%EO	*61.54%*

**After condensate withdrawal.* #*Total condensate* ($63\%molH_2O+4\%molEO+25\%molCO_2+7\%molN_2+1\%molO_2$).&*Vapor-Fraction=0.3302.*

IV.3.1 SS Performance

Fig. IV-4 depicts SS profiles via SS-UOE for dependent variables versus SS axial position *x(m)*. Fig. IV-4a exhibits SS silhouette and molar vapor-fraction versus *x(m)* with throat position at $x=L_C=0.1665m$. Figs. 4b-4c respectively depict (*P*,*Ma*) and (*T*,*c*) profiles. The sound speed *c* continuously decreases from *x=0* to $x=L^{Laval}=0.1695m$ due to increasing condensation and cooling, both augmenting the multiphase density (ρ) and multiphase isothermal compressibility ($\varXi_P = (\partial\rho / \partial P)_{T,\underline{Z}}$), which decrease the multiphase *c* (de Medeiros et al., 2017). SS signatures – i.e., throat $\pm\infty$ gradient singularities (de Medeiros et al., 2017) – are seen in SS profiles, since $\left(\frac{dA}{dx}\right)^{Throat} \neq 0$ thanks to linear diameter-position dependence (Fig. IV-1a). Fig. IV-4d shows condensation profiles (%mol condensed) of $H_2O/EO/CO_2$ versus $x(m)$, while Fig. IV-4e depicts SS path on plane PxT with feed and Gas-Product dew-point loci rendered by CPA-EOS.

SS inlet is 74.60%mol vapor (Fig. IV-4a), due to liquid-water injection for higher EO recovery. This is also noted in Fig. IV-4d, showing $\approx 98.89\%$ of water and 28.7% of EO condensations at $x=0$. Therefore, the SS path in Fig. IV-4e starts beyond the feed dew-point locus, confirming the two-phase SS inlet. As fluid accelerates (T,P,c) decrease, while Ma increases until $x=L^{Laval}=0.1695m$, where Ma attains the specified maximum $Ma^{Shock}=1.35$ with minimum ($T=T^{Laval}=9.25^oC,P=P^{Laval}=8.01bar$) (Table IV-5) condensing 61.54% EO and 99.58% water (Fig. IV-4d). Water-EO condensate is withdrawn through the collector annulus ($d=0.25mm$) (Fig. IV-1) at $x=L^{Laval}+L^{Collector}=0.4798m$ under constant (T^{Laval},P^{Laval}). The Slip-Gas is the fraction of SS vapor (17.6%) accompanying condensate through the annulus and is given by annulus area per flow-section area; i.e., $4(d/D_D)(1–d/D_D)$. After condensate and Slip-Gas removal, Ma falls to $Ma_{BS}=1.15$, still supersonic and causing shock, which occurs at $x=L^{Laval}+L^{Collector}=0.4798m$ as sudden compression/heating and Ma decrease to subsonic (Figs. IV-4b-IV-4c). On plane PxT, shock appears as a rectilinear jump back to higher (T,P) (Fig. IV-4e). After normal shock, the flow is a superheated compressed dry-gas whose (T,P) smoothly increase and Ma decreases through the ending diffuser until SS outlet. Outlet dry-gas attains a Gas-Product stagnated state ($T^{Gas\text{-}Product}=66.64^oC,P^{Gas\text{-}Product}=17.55bar$). Table IV-5 shows small (T,P) changes for feed and Gas-Product de-stagnation/stagnation due to low $v^{Inlet}=0.59m/s$ and $v^{Outlet}=1.14m/s$. In the liquid-collector *panhandle*, condensate shock occurs since $Ma_{BCS}=1.81$, producing after-condensate-shock state ($T=T_{ACS}=29.30^oC,P=P_{ACS}=27.20\ bar$). Stagnation of such state gives a two-phase Condensate-Product ($T^{Cond\text{-}Product}=30.68^oC,P^{Cond\text{-}Product}=27.20bar$).



(a)

(b)

(c)

(d)

(e)

Figure IV-4. SS results: (a) SS silhouette & vapor-fraction vs *x(m)*; (b) *P(bar)* & *Ma* vs *x(m)*; (c) *T(K)* & *c(m/s)* vs *x(m)*; (d) %mol condensed H_2O/EO/CO_2 vs *x(m)*; (e) plane *PxT* with SS path including feed and Gas-Product dew-point loci.

IV.3.2 Techno-Economic Comparison: Conventional Route versus SS Route

Table IV-6 presents results for EO Conventional-Route and SS-Route. SS utilization successfully increases EO production by *0.9%* (*+1.71kmol/h*), besides obtaining a purer EO or *+2t/d* (*+83.33kg/h*) greater EO production. Concerning CCS, SS-Route obtains *2%* less CO_2 product, with higher purity (*98.7%mol vs 98.2%mol*). Since revenues derive from EO/CO_2 sales and EO is more expensive than CO_2 (Appendix D), Table IV- 6 shows SS-Route higher revenues (*REV*) and gross annual-profit (*GAP*) for same feed and raw-materials cost (*CRM*). SS-Route requires slightly less power and somewhat higher CW make-up. SS indirectly affects CCS, since T-101 vent-gas passes through SS before reaching CO_2 compressors. Therefore, vent-gas molar flow rate to CO_2 compressors is lower than Conventional-Route counterpart. SS pressure-recovery is *83.6%*, thus Gas-Product has lower pressure than SS feed (*17.6 bar vs 21 bar*); but, the compressor suction pressure admitting vent-gas is *≈15 bar*. Hence, SS reduces power consumption due to lower vent-gas flow rate. Concerning CW make-up, its increase in SS-Route comes from E-116, a CW cooler at SS inlet. Considering these opposite SS effects in utility usages, costs of utilities (*CUT*) of both routes are similar (Table IV-6), implying similar *COM's*. The added SS unit – comprising SS, V-104, E116 and P-103 – has little investment impact: SS-Route increases *FCI* by *ΔFCI≈0.11MMUSD* (*≈0.11%* increment). Therefore, SS-Route net present value (*NPV*) after 20 operational years increases by *ΔFCI≈6.92MMUSD*, a reasonable *2.5%* increase (Fig. IV-5).

Table IV-6. Results: EO production routes.

Results	*Conventional-Route*	*SS-Route*	*Variation*
EO (t/d)	*223.4*	*225.4*	*0.895%*
EO (kmol/h)	*211.5*	*213.2*	*0.895%*
EO Purity (%mol)	*99.90%*	*99.93%*	*---*
CO_2 Product (kmol/h)	*296.0*	*290.0*	*-2.03%*
CO_2 Purity (%mol)	*98.23%*	*98.70%*	*+0.48%*
Power Consumption (MW)	*12.77*	*12.73*	*-0.31%*
CW Make-up (t/d)	*604.9*	*608.7*	*+0.63%*
FCI (MMUSD)	*104.54*	*104.65*	*+0.11%*
CRM (MMUSD/y)	*33.92*	*33.92*	*---*
CUT (MMUSD/y)	*7.68*	*7.65*	*-0.39%*
COM (MMUSD/y)	*71.74*	*71.73*	*---*
REV (MMUSD/y)	*155.70*	*157.06*	*+0.87%*
GAP (MMUSD/y)	*83.96*	*85.33*	*+1.63%*
20years NPV (MMUSD)	*280.70*	*287.62*	*+2.5%*

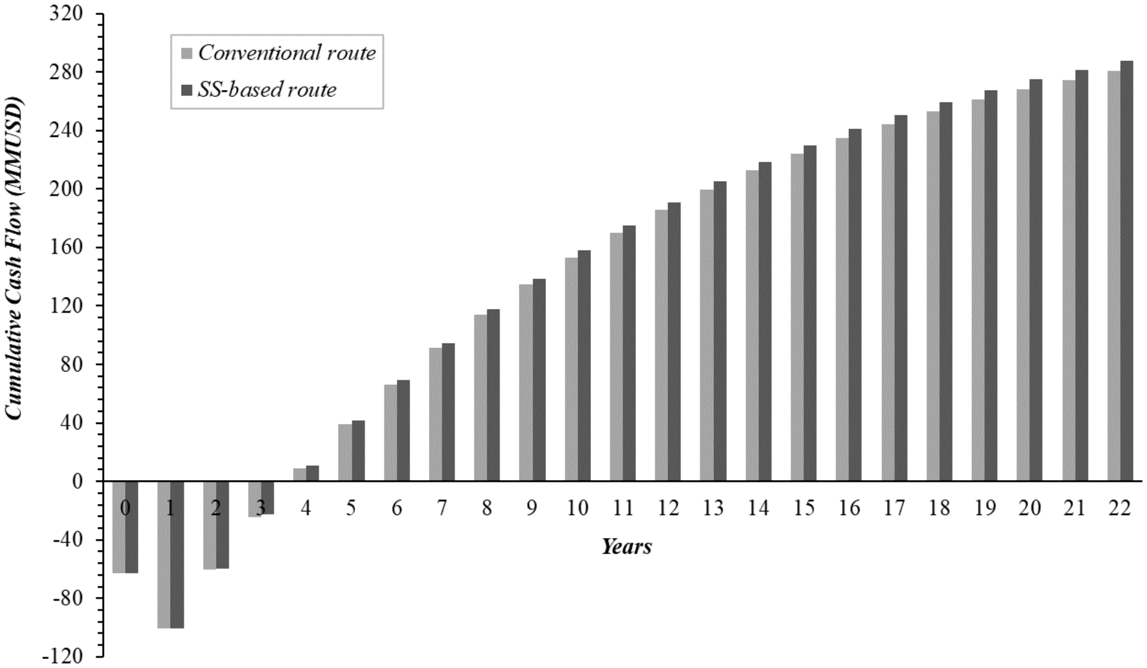


Figure IV-5. ***NPV*** **vs years: Conventional-Route and SS-Route.**

IV.3.3 Sustainability Analysis: Conventional-Route and SS-Route

SS requires some additional compression and temperature correction, but results do not show massive disparities between the processes. This hampers identifying which option is better via traditional composite indexes. Fortunately, Canberra-distance distinguishes close performances, but this requires choosing an appropriate origin in Eq. (IV-1). To this end, a sensitivity analysis was performed to seek the best origin in Fig. IV-6, set as percent of reference. Fig. IV-6 shows that the difference between Conventional-Route and SS-Route composite indexes (*SPWI*) is small for origins at low reference percent; i.e., with similar results for both routes, after normalization they become indistinguishable if the origin is not close to results; in other words, Canberra-distance distinguishes close performances for origins also close to them. Hence, Fig. IV-6 shows best contrast for origins from 80% to 95% of references. Above such range, the normalization becomes radical; i.e., a result close to both reference and origin, normalizes as ≈1 (false best sustainability) and the other as ≈0 (false worst sustainability), almost a binary normalization regardless the proximity of performances. Thus, for *SPWI* the origin is set as 95% of reference. *SPWI* indicates SS-Route as more sustainable than the Conventional-Route (Fig. IV-7). Conventional-Route and SS-Route perform similarly for various indicators (Table IV-7); i.e., distinction resides on few indicators, with greatest discrimination obtained on *Environment* dimension (Fig. IV-7a).

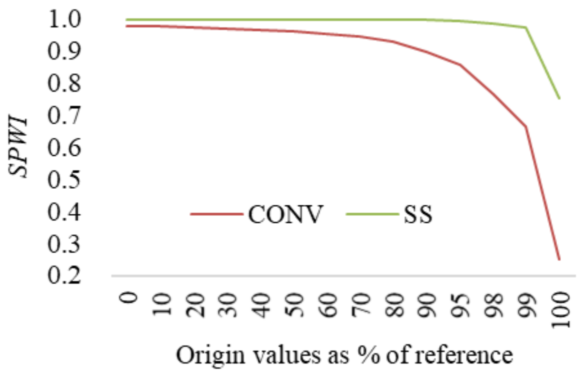


Figure IV-6. *SPWI* sensitivity to Canberra-distance origin (CONV=Conventional-Route, SS=SS-Route).

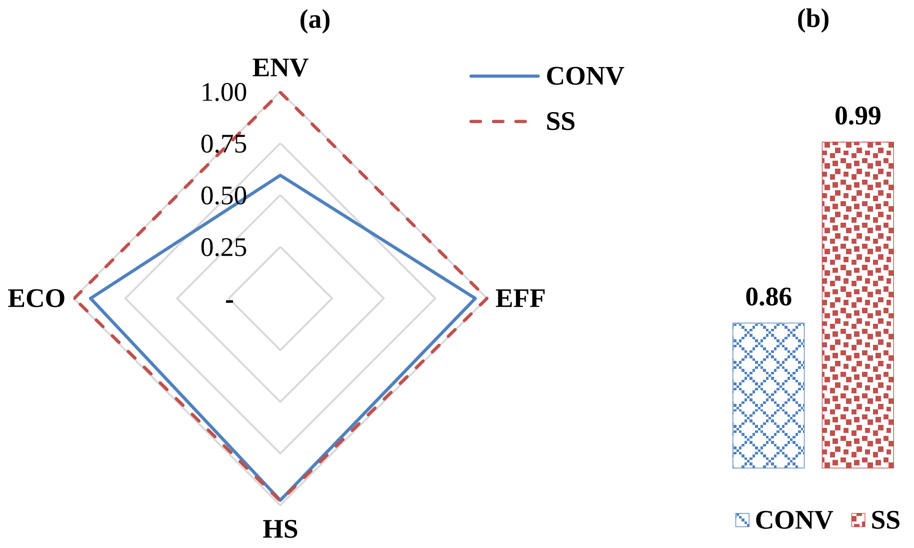


Figure IV-7. *SPWI* results (CONV=Conventional-Route, SS=SS-Route, ENV=*Environment*, ECO=*Economic*, EFF=*Efficiency*, HS=*H&S*).

SS-Route is consistently better than Conventional-Route in all dimensions and most indicators. In *Environment*, the main difference is for Ec_{aq} reflecting higher EO losses in Conventional-Route. *Efficiency* also reports SS-Route superiority. Excepting *WI*, all other indicators are better for SS-Route, mainly because they are all intensities and SS-Route produces 0.895% more EO. For *EI* and *WI*, the difference is smaller since SS-Route actually consumes more water and slightly more energy. In *H&S*, the main distinction happens for Haz_{in} and *Acute*, because Haz_{in} is a ratio per product generated; i.e., both routes have same consumptions of hazardous ethylene and SS-Route produces more EO giving better Haz_{in} for SS-Route. On the other hand, *Acute* evaluates impacts of chemical release and EO streams score negatively thanks to low EO human exposure limit. In Conventional-Route, the maximum EO concentration occurs in the reactor outlet, but in SS-Route EO concentration is even higher in T-101 inlet – because it combines reactor outlet with V-104 and SS recoveries. This makes *Acute* the worst SS-Route indicator of all 16 sustainability parameters, conveying a EO-recovery/sustainability trade-off. Nevertheless, Haz_{in} and *Acute* opposite results balance *H&S* overall index, which is similar for both routes. In *Economic* SS-Route main advantages occur in *GAP* and *EP*. Even though *FCI* is higher in SS-Route, it also produces more. SS *FCI* increases plant *FCI* by $\Delta FCI \approx 0.11 MMUSD$ ($\approx 0.11\%$ increase). On the other hand, SS-Route produces *83.33kg/h* more EO than Conventional-Route, increasing *EP* by

$\Delta EP \approx 1.4 MMUSD/y$; i.e., revenues make SS-Route economically better. These results evince SS-Route as technically, environmentally, socially and economically sounder.

Table IV-7. First-level assessment normalized indicators.

Indicator	*Conventional-Route*	*SS-Route*
Environment		
Global-Warming (GWP)	*0.95*	*1.00*
Photochemical-Oxidation (Smog)	*0.25*	*1.00*
Aquatic-Ecotoxicity (Ec_{aq})	*0.19*	*1.00*
Hazardous-Waste (HW)	*1.00*	*0.99*
Efficiency		
Energy-Intensity (EI)	*0.94*	*1.00*
Material-Intensity (MI)	*0.93*	*1.00*
E-factor (E)	*0.91*	*1.00*
Water-Intensity (WI)	*1.00*	*1.00*
H&S		
Hazardous-Input (Haz_{in})	*0.93*	*1.00*
Fire/explosion ($Fail_{F/E}$)	*0.98*	*1.00*
Mobility (Mob)	*1.00*	*1.00*
Acute-Toxicity (Acute)	*1.00*	*0.92*
Economic		
Cost of Manufacturing (COM)	*1.00*	*1.00*
Fixed Capital Investment (FCI)	*1.00*	*0.99*
Gross Annual-Profit (GAP)	*0.81*	*1.00*
Economic-Potential (EP)	*0.86*	*1.00*

After establishing SS-Route with highest sustainability, S-PSE identifies its bottlenecks. EO reactor PFR-100, CO_2 stripper T-104 and cooling-tower T-106 are unit-operations with main sustainability hotspots (Fig. IV-8). PFR-100 has the worst drawbacks of EO plants. Since reactions are associated with reactants/products impacts, ethylene/EO inlet/outlet burdens entail *H&S* and *Environment* PFR-100 hotspots. *H&S* issues derive from *Acute* (high EO content) and *Mob* (high-pressure) of PFR-100 effluent, while *Environment* issues are high *GWP* and *Smog* associated to unreacted ethylene releases, and high Ec_{aq} from EO losses in purification. PFR-100 also has *Efficiency* issues like high *EI* from cooling for isothermal reaction. With less, but still high impacts, CO_2 stripper T-104 has second highest *EI* and *GWP* (greenhouse-gas emissions), besides fire/explosion risks ($Fail_{F/E}$) from high inlet temperature.

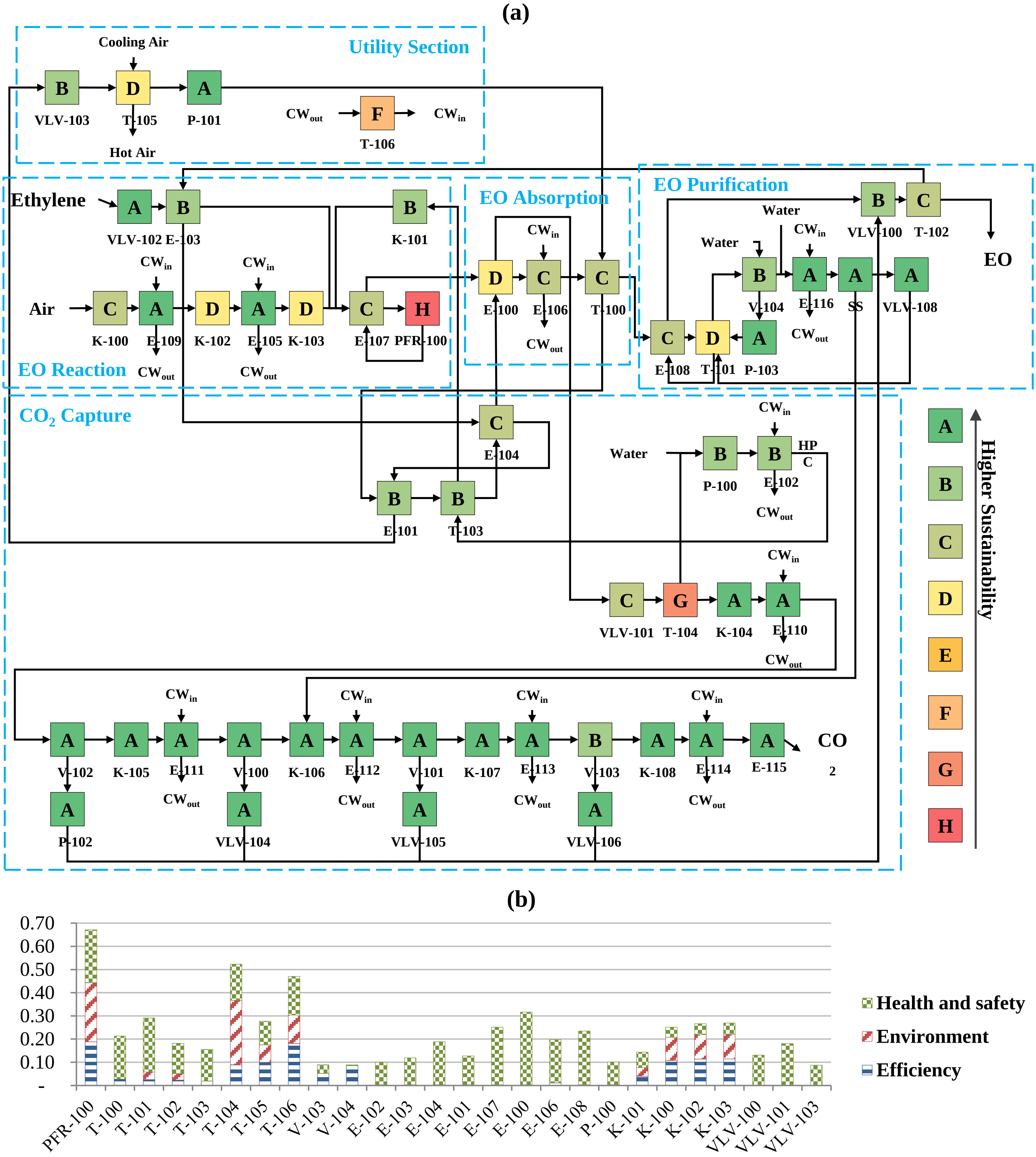


Figure IV-8. ***SOHI*** **results: (a) sustainability level of unit-operations; (b)** ***SOHI*** **across dimensions for unit-operations with sustainability level worse than "A".**

The remaining unit-operations have lower impacts, notwithstanding the existence of hotspots in all sections, with major impacts residing in EO Reaction (PFR-100 hotspots, E-

107 *Acute* issues from reactor outlet composition), CCS (high *EI* of compressors) and Utility (cooling-tower T-106 has highest material-intensity with hazardous inlet/outlet and *Mob* issues) sections. If it was not for CO_2 stripper T-104, CCS section would bear low-intensity sustainability hotspots, since its operations range from A to C sustainability levels (Fig. IV-8a); i.e., CCS not only avoids emissions, but also contributes to overall sustainable performance with low-intensity operations. In EO Purification section, distillations and some exchangers have issues, mainly from high cooling loads and/or high temperature/pressure: T-101 (*Acute*/*Mob*), T-102 (*EI*/*GWP*/*Acute*) and E-108 (*Acute*/*Mob*) respond for bringing down EO Purification sustainability. In EO Absorption section, the high temperature/pressure of E-100 creates *H&S* burdens ($Fail_{F/E}$, *Mob*, *Acute*).

Main opportunities to improve sustainability of both EO routes comprise avoiding unreacted ethylene releases, further reducing EO losses, lowering CW usage (CO_2 stripping and EO distillations).

IV.4 Conclusions

The Sustainable Process Engineering (S-PSE) method was applied to assess sustainability of two EO producing routes and to identify their sustainability hotspots. EO Conventional-Route and the alternative SS-Route with lower EO losses were compared technically, environmentally, socially and economically. SS-Route recovers *95%* of original EO losses – via SS unit and pre-flash V-104 combined – in EO Purification section, representing *+0.895%* greater EO production, or *83.33 kg/h* more EO for same feed. Higher SS-Route revenues rise profit, despite its *≈0.11%* higher *FCI*, giving a *2.5%* higher *NPV* for 20 operation years.

Sustainability analysis evinces better *Environmental*, technical (*Efficiency*), social (*Health-and-Safety*) and *Economic* performances of SS-Route comparatively to Conventional-Route. The main sustainability issues of both routes reside in EO reactor, CO_2 stripper and cooling-tower, though reaction impacts are far greater. Reaction drawbacks mainly comprehend *H&S* and *Environment* impacts linked to unreacted ethylene and EO losses from purification; the latter reasonably mitigated by including SS to reduce EO risks and losses in the new SS-Route.

Supplementary Data

Supplementary data to this chapter can be found online at https://doi.org/10.1016/j.jenvman.2020.110782.

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Abbreviations

CCS Carbon Capture and Sequestration; CPA-EOS Cubic-Plus-Association Equation-of-State; CW Cooling-Water; EO Ethylene Oxide; HPC Hot Potassium Carbonate; LCA Life-Cycle Analysis; MMUSD Million US-Dollar; S-PSE Sustainable Process Systems Engineering; SS Supersonic Separator; VLE Vapor-Liquid Equilibrium.

Nomenclature

A, AP, $c(P,T,\underline{Z})$	*Area (m^2), Annual Profit (MMUSD/y), Multiphase sound speed property (m/s)*
CF, C_f	*Impact-characterization(kg/kg) & utility-conversion(J/J) factors*
COM, CRM, CUT	*Annual costs of manufacturing, raw-materials and utilities (MMUSD/y)*
d, D_I, D_O, D_D, D_T	*Annulus and inlet/outlet/collector/throat diameters (m)*
$DEPR$, E, $\bar{E}$	*Depreciation (MMUSD/y), E-factor (kg/kg), molar energy of multiphase fluid (J/mol)*
Ec_{aq}, EF	*Aquatic-Ecotoxicity (PAF m^3d), Power-Emission Fator (kgCO2e)*
EI, En, EP	*Energy-Intensity (J/kg), Energy-Flow (J/h), Economic-Potential (MMUSD/y)*
F, $Fail_{F/E}$, FCI	*Molar flow rate (kmol/s), Fire/Explosion, Fixed Capital Investment (MMUSD)*
GAP, GWP	*Gross Annual Profit (MMUSD/y), Global-Warming (kgCO_2e)*
$\bar{H}$, $\bar{K}$	*Multiphase Molar Enthalpy and Molar Kinetic Energy (J/mol)*
Haz_{in}, HW, $IndVal$	*Hazardous-Input (kg/kg), Hazardous-Waste (kg/h), probability of release occurrence*
L_C, L_D, $L^{Collector}$	*Converging/Diverging/Collector lengths (m)*
$L^{Diffuser}$, L^{Laval}, L, m	*Diffuser/Laval/Total lengths (m), Material flow (kg/h)*
Ma, Ma^{Shock}	*Mach Number, Ma before-shock-and-condensate-withdrawal*
MI, M_M	*Material-Intensity (kg/kg), Molar Mass (kg/mol)*
Mob, N, NPV	*Mobility, Horizon (years), Net Present Value (MMUSD)*
P, q, REV	*Pressure (bar,Pa), Mass flow rate (kg/s), Revenues (MMUSD/y)*

$\bar{S}$, SMLI	*Molar entropy (J/mol/K), Separation Mass-Loss index (kg/kg)*
Smog, SOHI	*Photochemical-Oxidation (kgNO$_x$e), Sustainable Operation Hotspot Index*
SPWI, T	*Sustainable plant-wide index, Temperature (K)*
v, WI, x, $\underline{Z}$	*Axial velocity (m/s), Water-Intensity (kg/kg), axial position (m), Vector of mol fractions*
Greek Symbols	
$\alpha, \beta, \delta_P, \delta_M, \delta_L$	*SS converging/diverging wall angles(deg), pressure-step(Pa); Mach/length tolerances*
$\eta^{EXP}\%, \eta^{CMP}\%, \lambda$	*SS expansion/compression adiabatic efficiencies (%), CW/steam make-up (%)*
$\rho,\ \Xi_P = \left(\frac{\partial \rho}{\partial P}\right)_{T,\underline{Z}}$	*Multiphase density (kg/m^3), Multiphase isothermal compressibility (kg/m^3.Pa)*
Subscripts	
AS, ACS	*Just-after-shock, just-after-condensate-shock*
BCS, BS	*Just-before-condensate-shock, just-before-shock-and-after-condensate-withdrawal*
F, i, in, k, L+V	*Stream, component, inlet, unit-operation, two-phase condensate*
prod, sep, V	*Product-stream, separation-operation, vapor*

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CHAPTER V - SCREENING BIOREFINERY PATHWAYS TO BIODIESEL, GREEN-DIESEL AND PROPYLENE-GLYCOL: A HIERARCHICAL ASSESSMENT OF PROCESS SUSTAINABILITY

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Screening biorefinery pathways to biodiesel, green-diesel and propylene-glycol: A hierarchical assessment of process sustainability

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Abstract

Plant design implies to choose the best among a set of feedstock-to-product process pathways. Multiple performance indicators measuring several sustainability issues can blur the decision, and existing sustainability assessment methods usually focus only on environmental life-cycle performance and corporate metrics or solely on the gate-to-gate process. It is relevant to incorporate integrated system analysis to address sustainability comprehensively. This work expands a previously proposed framework for sustainable process design adding new features: (i) cradle-to-gate environmental assessment; (ii) composition of flowsheets; (iii) new indicators; (iv) statistical screening of indicators; and (v) compliance with 2030 Agenda. A biorefinery case-study demonstrates the framework: to select the best pathway from soybean-oil, palm-oil, and microalgae-oil to produce biodiesel, green-diesel, and propylene-glycol. Statistical screening reduces the indicator set by 62%. Results evince all routes from microalgae-oil as economically unfeasible due to oil cost, despite superior environmental performance. On the other hand, palm-oil-to-biodiesel is the most sustainable due to lower cradle-to-gate emissions and manufacturing cost. 2030 Agenda analysis also outlines palm-oil-to-biodiesel as best for 5 out of 10 Sustainable Development Goals linked to the reduced indicator set. Process sustainability hotspots are associated to hazardous methanol input, energy-intensive distillations and high pressure/temperature hydrogenation reactors.

Keywords

Sustainability Assessment; Sustainable Process Design; Sustainable Development Goals; Biodiesel; Green-Diesel; Biorefinery.

V.1 Introduction

The importance of integrated systems analysis is present in modern sustainable development concepts, such as the Doughnut Economics (Raworth, 2017) and 2030 Agenda (UN, 2015). Nevertheless, in the literature on chemical process sustainability there is a research line exploring computer-aided engineering to provide a prospective design methodology for sustainable processes (Mukherjee et al., 2015), and another research line relying on simple input-output black-box models not suitable for process engineers (Jacquemin et al., 2012). These different approaches restrain industry from addressing sustainability in a comprehensive way (Wan Alwi et al., 2014). Sikdar et al. (2017) pointed the existence of these two research lines as a gap since sustainability assessment cannot evolve while industry remains evaluating limited technical aspects or analyzing life-cycle impacts and corporate metrics without detailed process information.

Recent works demonstrate how sustainable process design literature is more focused on computer-aided engineering than corporate life-cycle aspects. El-Halwagi (2017) proposed an economic metric based on the conventional return on investment to include sustainability impacts early in process design. García et al. (2017) presented a techno-economic, energy and environmental assessment for hydrogen production using process simulation. Jia et al. (2015) developed an integrated system composed of three hierarchical layers (overall goal, sustainability dimensions and indicators) for assessing and comparing sustainability of alternatives coupled to process simulation. In another work on process design, Liew et al. (2014b) proposed a systematic framework to evaluate the sustainability of production pathways in research and development stage using a fuzzy multi-objective representing trade-offs among economic, environmental, and health-and-safety aspects. In general, gate-to-gate assessments simplify addressing multi-dimensional sustainability while still being able to evaluate unit-operations (Finnveden et al., 2009). Nevertheless, value-chain impacts should not be disregarded especially for biorefineries, since using renewable resources has a major role in their sustainability (Liew et al., 2014a).

Biorefinery feedstocks may raise concerns regarding the biomass used (Capodaglio and Callegari, 2018). Edible vegetable oils are readily accessible for utilization but evidently ignite concerns on food versus biofuels/bioenergy competition, a problem also existent in non-edible resources due to land competition with food-related crops (Seraç et al., 2019).

However, using expensive food-related crops makes biodiesel economically non-competitive with diesel as feedstock represents ~70% of biodiesel production costs (Kwon et al., 2013), entailing that feedstock selection is the most important aspect to avoid “over budget biodiesel production” (Anuar and Abdullah, 2016). Furthermore, many biodiesel feedstocks require arable lands competing with food crops, increasing prices among other consequences – the food-energy nexus (Cuberos Balda et al., 2017). Alternative oil feedstocks aim at minimizing the use of expensive food-grade oils, with varying physicochemical properties (Avhad and Marchetti, 2015). Additionally, intensive monocultures change the landscape and surrounding ecosystems, besides interfering with food supply-chains, and intensifying fertilizer utilization and consequent water eutrophication (Gasparatos et al., 2018).

De Faria et al. (2021) outlined an unexplored opportunity to link sustainable design and production indicators to the 2030 Agenda for Sustainable Development (UN, 2015) to map compliance of industrial processes with its 17 Sustainable Development Goals (SDGs) against poverty and environment issues considering the three dimensions of sustainability. SDGs can be integrated into business strategies via the SDG Compass guide (García-Sánchez et al., 2020). It is still not common to find literature connecting sustainable process design to the 2030 Agenda. Exceptions include the work from Guillén-Gosálbez et al. (2019), highlighting the potential role of process systems engineering to meet SDGs, and Van Bochove et al. (2019) that performed techno-economical evaluation at early design phase to check safety of chemicals and project impacts on SDGs.

As stakeholders are dealing with many indicators, they are facing multidimensional complex systems without an accepted methodology for sustainability assessment and indicator screening (Brandi and dos Santos, 2020). Taking metrology into account, Brandi and dos Santos (2016) suggested using statistics to select indicators according to their reliability, dimensionality, and validity. Huysman et al. (2015) addressed indicators in the literature and proposed a systematized framework to evaluate indicators for different levels of economic activity, boundaries and national/global perspective. Sutherland et al. (2016) used space-temporal process-based models to project indicator response, as well as correlation assessment to examine independence, and principal components analysis (PCA) to identify indicator redundancy/dominance. These works focus respectively on supply-chain, resource efficiency indicators and cumulative effects assessment, but the idea is applicable to sustainable process design. Sustainability assessment methods for the chemical industry were reviewed by de Faria et al. (2021) concluding that sustainability works seldom employ in-depth indicator analysis.

V.1.1 The Present Work

The Sustainable Process Systems Engineering (S-PSE) method (de Faria et al., 2020) provides a hierarchical gate-to-gate assessment, featuring technology-specific indicators, plant-wide overall sustainability; unit-operation sustainability hotspot diagnosis; computer-aided tools; and composite sustainability-indexes. As an effort to move even closer to reliable and integrated analysis in sustainable process design, the present work aims at expanding S-PSE. An extra corporate level breaks the limits of process boundaries, closing the company loop for industrial systems by adding 2030 Agenda indicator correlation for corporate strategic analysis. The process method offers the advantage of coupling different processing units to provide a plant-wide overall result without the need to simulate them altogether.

In addition, de Faria et al. (2021) unveiled that most works on sustainable industrial production usually do not address decision-making issues, which might lead to biased conclusions. In order to address this gap, one further goal of this work is to apply straightforward decision-making techniques to build composite indexes used in the method. This includes using statistics to retrospectively select relevant indicators besides the use of composite sustainability-indexes for multi-attribute decision-making. Therefore, this work explores the following new resources of S-PSE: (i) cradle-to-gate environmental assessment; (ii) composition of flowsheets; (iii) new indicators; (iv) statistical indicator screening; and (v) compliance with 2030 Agenda, integrating process analysis to corporate strategy.

S-PSE is demonstrated in a biorefinery case-study to evaluate the most sustainable feedstock-process-product pathways connecting three bio-oil feedstocks (soybean-oil, palm-oil and microalgae-oil) to three bio-products (biodiesel, green-diesel and propylene-glycol). S-PSE further identifies sustainability bottlenecks within the most sustainable pathway.

V.2 Methods

Methods implemented to assess sustainability and biorefinery processes are discussed.

V.2.1 Sustainability Assessment

The S-PSE method (de Faria et al., 2020), is expanded to assess biorefinery sustainability. S-PSE is composed of two levels: (i) plant-wide or production-unit; and (ii) unit-operations. The first-level selects the most sustainable feedstock-process-product configuration, while the second-level locates unit-operation sustainability hotspots in the most sustainable proposal. S-PSE hierarchical procedure ranks alternatives with the Sustainable Plant-Wide Index (*SPWI*) in the first-level and the Sustainable Operation Hotspot Index (*SOHI*) in the second-level. S-PSE allows considering two types of production-units: single (single flowsheet) and composed (flowsheet hybrids). Production-units composition makes S-PSE stackable along the value-chain, contributing to integrate the industrial-level to its life-cycle. A functional-unit scales a production-unit based on its material flow (e.g., a specified raw-material demand *f*), generating a scaling-factor in Eq. (V-1), where *FU* refers to the functional-unit of production-unit *k*; S_k is the scaling-factor of production-unit *k*; *f* is the functional-unit demand; *m* is the material flow and N_{PU} is the number of production-units.

$$S_k = \frac{f_{FU,k}}{m_{FU,k}} \ , \ k = 1..N_{PU} \tag{V-1}$$

The procedure is similar to the computational basis of life-cycle assessment (LCA) of Heijungs and Suh (2002). The resulting scaled process matrix (scaled flows) is used to calculate indicators. The simulation/economic results scale linearly to the rate of feedstock/product consumed/manufactured.

S-PSE classifies sustainability indicators into four dimensions – *Environment, Efficiency, Health & Safety (H&S)* and *Economic* – but here they are further subdivided into two sub-dimensions: (i) *Environment – cradle-to-gate* and *gate-to-gate*; (ii) *Efficiency – material* and *energy*; (iii) *H&S – health* and *safety*; and (iv) *Economic – profit* and *costs*. The classification in sub-dimensions enables statistical analysis of indicators as discussed ahead. The new S-PSE jumps from 17 indicators in de Faria et al. (2020) to the present 42 technology-specific process indicators (Tables EI-1 to EI-4, Appendix E). Table V-1 presents all indicators, their dimension and sub-dimension.

Despite being essentially gate-to-gate, S-PSE boundaries are expanded regarding raw materials considering to some extent environmental impacts related to feedstocks and introducing *Environment/Cradle-to-gate* differentiation among alternatives. The major sources of biofuel LCA impact categories (Liew et al., 2014a) are selected: cradle-to-grave greenhouse-gas emissions (*CG-GWP)*, land-use (*LU*), cradle-to-grave eutrophication (*CG-Eu*), cradle-to-grave acidification (*CG-Ac*) and cradle-to-gate biodiversity-loss (*CG-Bio*).

Table V-1. S-PSE indicators: dimensions, sub-dimensions and SDG correlation.

Indicator	*Dimension*	*Sub-Dimension*	*SDGs linkage*
Global-Warming (GWP)	Environment	Gate-to-gate	3,12,13,14,15
Ozone-Depletion (ODP)	Environment	Gate-to-gate	3,12
Aquatic-Ecotoxicity (Ec_{aq})	Environment	Gate-to-gate	3,6,12,14,15
Photochemical-Oxidation (Smog)	Environment	Gate-to-gate	3,12,14,15
Atmospheric-Acidification (Acid)	Environment	Gate-to-gate	3,12,14,15
Aquatic-Eutrophication (Eut_A)	Environment	Gate-to-gate	3,6,12,14,15
Renewability Material Index (RMI)	Environment	Gate-to-gate	8,12
Hazardous-Waste (HW)	Environment	Gate-to-gate	3,6,12,14,15
Cradle-to-Gate GWP (CG-GWP)	Environment	Cradle-to-gate	3,12,13,14,15
Land-Use (LU)	Environment	Cradle-to-gate	6,14,15
Cradle-to-Gate Eutrophication (CG-Eu)	Environment	Cradle-to-gate	3,6,12,14,15
Cradle-to-Gate Acidification (CG-Ac)	Environment	Cradle-to-gate	3,12,14,15
Cradle-to-Gate Biodiversity-Loss (CG-Bio)	Environment	Cradle-to-gate	6,14,15
Energy-Intensity (EI)	Efficiency	Energy	7,8,12,13
Resource Energy-Efficiency (ηE)	Efficiency	Energy	7,8,12,13
Exergy-Destruction ($\Delta\dot{B}$)	Efficiency	Energy	7,8,12,13
Product Exergy-Efficiency ($\eta\dot{B}_{prod}$)	Efficiency	Energy	7,8,12,13
Water-Intensity (WI)	Efficiency	Energy	6,8,12
Resource Exergy-Efficiency ($\eta\dot{B}$)	Efficiency	Energy	7,8,12,13
Material-Intensity (MI)	Efficiency	Material	8,12
E-factor (E)	Efficiency	Material	3,6,12,14,15
Final-product concentration (C_{prod})	Efficiency	Material	8,12
Solid-Waste Mass (m_S)	Efficiency	Material	3,6,12,14,15
Reaction Molar-Efficiency (ηR)	Efficiency	Material	8,12
Reaction-Yield (ε)	Efficiency	Material	8,12
Separation Mass-Productivity (SMP)	Efficiency	Material	8,12
Separation mass-loss index (SMLI)	Efficiency	Material	8,12
Human Toxicity-cancer-effects ($HTox_c$)	H&S	Health	3,8,16
Human Toxicity- non-cancer-effects ($HTox_{nc}$)	H&S	Health	3,8,16
Hazardous-Input (Haz_{in})	H&S	Health	3,8,16
TRI-Input (TRI_{in})	H&S	Health	3,8,16
Acute-Toxicity (Acute)	H&S	Health	3,8,16
Irritation-Factor (Irrit)	H&S	Health	3,8,16
Particulate-Matter (PM)	H&S	Safety	3,12,14,15
Fire/explosion ($Fail_{F/E}$)	H&S	Safety	3,8,16
Decomposition ($Fail_{R/D}$)	H&S	Safety	3,8,16
Mobility (Mob)	H&S	Safety	3,8,16
Cost of Raw-Materials ($Cost_{RM}$)	Economic	Cost	8,9
Cost of Manufacturing (COM)	Economic	Cost	8,9
Fixed Capital Investment (FCI)	Economic	Cost	8,9
Gross Annual-Profit (GAP)	Economic	Profit	8,9
Economic-potential (EP)	Economic	Profit	8,9

A new S-PSE feature uses statistics to retrospectively select non-redundant indicators from the original 42 indicators in order to generate an optimized set. The statistical screening (Fig. V-1) follows dos Santos and Brandi (2015), and is applied to the sets of normalized indicators of all sub-dimensions. It consists in performing: (i) corrected item-total correlation and Cronbach Alpha Test (Hair et al., 2014) to check for internal consistency and reliability; (ii) inter-item correlation to test correlation and representativeness; and (iii) PCA to assess redundancy. The redundancy test performs a PCA on the entire set of indicators, without division into sub-dimensions. Hence, indicators highly correlated within each sub-dimension are considered redundant. Each step consecutively reduces the dimension of the previous set of indicators. Since the original set of 42 indicators is not sufficiently ample to select a general optimal set of indicators (Hair et al., 2014), the solution is always case-specific.

For ranking purposes, the optimized set of indicators is normalized and aggregated, generating two composite-indexes: *SPWI* (first-level) and *SOHI* (second-level). Due to the new sub-dimensions classification, *SPWI* calculation was adapted from de Faria et al. (2020) in Eqs. (V-2) and (V-3), where $X_{n,c,d}$ is the normalized value of indicator x_n in sub-dimension c of dimension d (normalization uses Canberra distance, de Faria et al. 2020); Ncd is the number of indicators in sub-dimension c of dimension d; $SPWI_d$ is the sustainability aggregate index for dimension d; Cd is the number of sub-dimensions of dimension d, and D is the number of dimensions.

$$SPWI_d = \frac{1}{Cd}\sum_{c=1}^{Cd}\left(\frac{1}{Ncd}\sum_{n=1}^{Ncd} X_{n,c,d}\right) \tag{V-2}$$

$$SPWI = \frac{1}{D}\sum_{d=1}^{D} SPWI_d \tag{V-3}$$

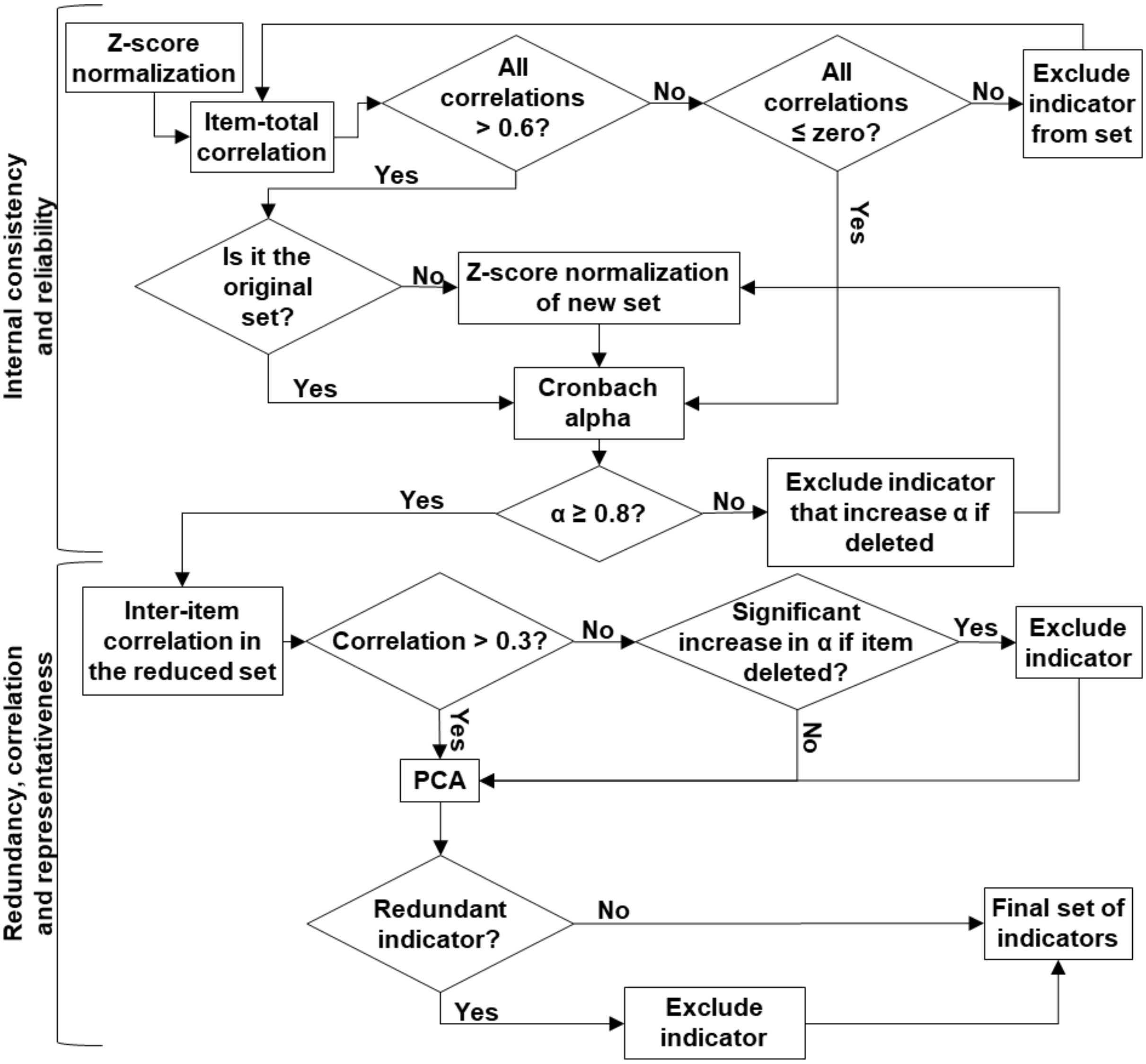

Figure V-1. Statistical screening of indicators.

The second-level assessment classifies unit-operations into five categories: reaction, separation, heating/cooling, compression and expansion. Table V-2 gives the updated list of indicators (defined in Table V-1) from de Faria et al. 2020, wherein some indicators are not applicable to all types of unit-operations. This adds complexity to the analysis and precludes the second-level from having its own statistical analysis of indicators and classification in sub-dimensions. Hence, *SOHI* calculation is performed here as in de Faria et al. (2020).

Table V-2. Indicators applicable to unit-operations.

Indicator	*Unit-Operation Type*
ODP, $Smog$, Ec_{aq}, $Acid$, Eut_{A}, HW, m_{s}, PM, $HTox_{c}$, $HTox_{nc}$	*assigned unit-operation for component outlet impacts*[a]
EI, ηE, $\Delta\dot{B}$, GWP, $Fail_{F/E}$, $Fail_{R/D}$, Mob, $Acute$	*all*
MI, WI	*separation, cooling/heating, reaction*
ηR, ε	*reaction*
SMP, $SMLI$	*separation*
Haz_{in}, TRI_{in}	*assigned unit-operation for component inlet impacts*[a]

[a] *Outlet/inlet impacts calculated for each component; component impacts are assigned to the unit-operation responsible for its presence in the process.*

With the purpose of integrating process analysis to corporate strategy, this work evaluates how each plant-wide alternative comply with the 2030 Agenda. This new S-PSE feature is based on GRI Standards (GRI, 2020a) and SDG Compass linkage document outlining the connections between SDGs and GRI Standards (GRI, 2020b). In order to arrive at the correspondence between S-PSE indicators and SDGs, the following procedure applies: (a) link S-PSE indicators to relevant indicators in GRI Standards (Table EI-5, Appendix E); and (b) take the SDG/GRI Standard connection (SDG Compass) and make S-PSE/SDG connection. Table V-1 presents the final linkage between S-PSE indicators and SDGs. Adherence to 2030 Agenda is evaluated by taking the arithmetic mean of all indicators linked to each SDG giving an average value for each SDG. This procedure also allows assessing production-unit alternatives from a business perspective; i.e., favoring configurations more aligned to management goals and assisting communication or corporate reporting.

V.2.2 Biorefinery Processes

S-PSE is applied to a biorefinery case-study in Fig. V-2 contemplating three exclusive biomass feedstocks (soybean-oil, palm-oil, microalgae-oil) and three exclusive bio-products (biodiesel, biodiesel-and-propylene-glycol, green-diesel) totaling eight configurations in Table V-3. Production-unit PU#9 is not a biorefinery, but combined with other production-units generates configurations PU#6 to PU#8. Table V-4 presents process modeling assumptions for HYSYS 8.8 simulations that are necessary to gather power/utilities consumptions and stream data. Data for calculating indicators are in Part II, Appendix E. Bio-oil feed at 1000 kg/h is the functional-unit for each alternative. Oil compositions reported in the literature as triacylglycerol (TAG) are used, instead of describing oils by major fatty acids in triacylglycerols.

Table V-3. Production-units input/output for biorefinery case-study.

Production-Unit	***Feedstock***	***Product***	***Production-Unit Type***	***Production-Unit Composition***
PU#1	*soybean-oil*	*biodiesel*	*single*	---
PU#2	*palm-oil*	*biodiesel*	*single*	---
PU#3	*microalgae-oil*	*biodiesel*	*single*	---
PU#4	*soybean-oil*	*green-diesel*	*single*	---
PU#5	*microalgae-oil*	*green-diesel*	*single*	---
PU#6	*soybean-oil*	*biodiesel-&-propylene-glycol*	*composed*	*PU#1+PU#9*
PU#7	*palm-oil*	*biodiesel-&-propylene-glycol*	*composed*	*PU#2+PU#9*
PU#8	*microalgae-oil*	*biodiesel-&-propylene-glycol*	*composed*	*PU#3+PU#9*
PU#9	*glycerol*	*Propylene-glycol*	*single*	---

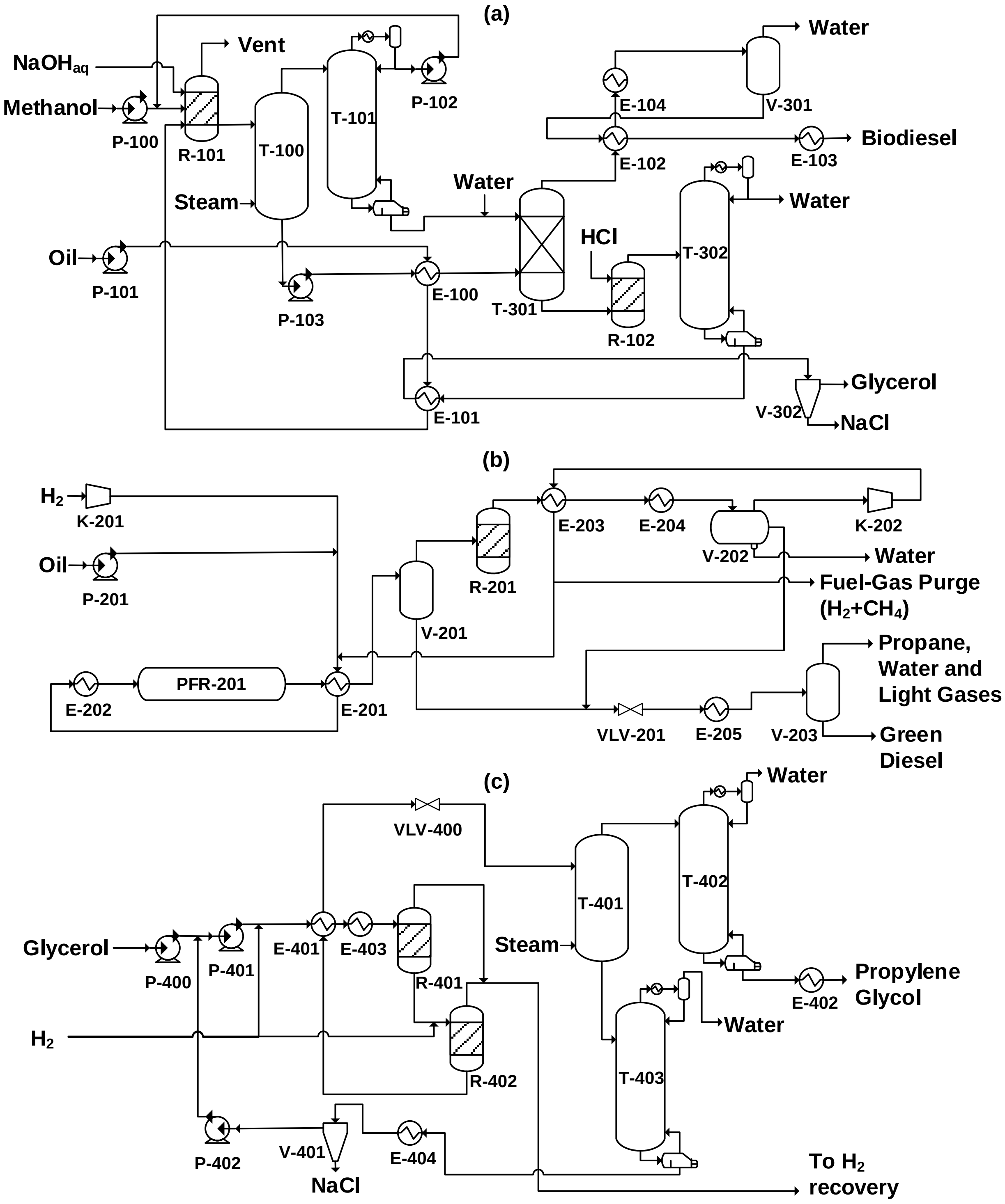

Figure V-2. Single-product production-units flowsheets: (a) biodiesel (PU#1, PU#2, PU#3); (b) green-diesel (PU#4, PU#5); (c) propylene-glycol (PU#9).

Methanol transesterification with glycerol by-product (Zhang et al. 2003) is employed in biodiesel product-units comprehending: (i) transesterification; (ii) methanol recovery; (iii) glycerol-biodiesel separation; (iv) glycerol purification; and (v) biodiesel purification. The thermodynamic model NRTL-Electrolyte (Non-Random Two Liquids) is used for liquid phase activity coefficients, while vapors are supposed ideal gas since biodiesel process operates at low-pressure. Transesterification occurs in R-101 reactor (60°C, 4bar, Methanol:Oil=6mol/mol, Oil:NaOH=100kg/kg), converting 99% soybean-oil, 99% palm-oil and 95% microalgae-oil. A lower microalgae-oil conversion is set for better economic/energy performances (Posada et al., 2016). Soybean-oil attains highest conversion rate due to its high linolenic content, followed by palm-oil with its high stearic content, while microalgae-oil has lower content of linolenic/stearic chains (Likozar and Levec 2014). The reactor outlet contains methanol, fatty-acid methyl esters (FAME), glycerol, aqueous-NaOH, small fraction of non-converted TAGs and goes to T-100 steam-stripping column (10-staged, 130°C, 1.1bar) producing methanol-water top product and glycerol-biodiesel bottoms. The methanol-water stream goes to T-101 atmospheric distillation (25-staged, reflux-ratio=3, 1.013bar) where methanol is recovered as distillate (99%mol) and recycles to transesterification reactor. The T-100 glycerol-biodiesel stream is separated in the T-301 liquid-liquid extractor (4-staged) using water solvent. After this point, the NaOH in T-100 bottoms is stoichiometrically neutralized to NaCl using aqueous-HCl (37%w/w) in reactor R-102. Subsequent T-302 distillation splits glycerol-water producing aqueous-glycerol-NaCl bottoms (67%mol glycerol NaCl-free basis) whose water content stabilizes glycerol and lowers its bubble-point preventing thermal degradation. Due to its small ≈4%w/w content in T-302 feed, NaCl is soluble in the hot 67%mol glycerol-water (90%w/w glycerol) bottoms, but after cooled in E-101 to 30^{o}C, NaCl partially precipitates in the cyclone V-302 since its solubility in 67%mol glycerol-water is 7%w/w at 30^{o}C (Velez et al., 2019) and the NaCl content in T-302 bottoms is 11%w/w. The liquid NaCl-glycerol-water V-302 effluent (67%mol glycerol NaCl-free basis) is the final NaCl-saturated aqueous-glycerol product (NaCl=7%w/w). V-301 flash-vessel (150°C, 1bar) strips water from biodiesel. Soybean-oil and palm-oil produce 97%mol pure biodiesel, while microalgae-oil produces 76%mol biodiesel. Differently from Zhang et al. (2003), biodiesel purification does not comprise FAME-TAG vacuum-distillation; i.e., all distillations are atmospheric.

Green-diesel high-pressure process (Kalnes et al., 2011; Sotelo-Boyás et al., 2012) comprises: (i) bio-oil hydrotreatment; (ii) methanation; (iii) hydrogen recovery; and (iv) green-diesel purification. Hydrotreatment is followed by a high-pressure flash-vessel (V-201, 250°C, 50bar) producing gas (H_2, H_2O, propane, CO, CO_2) and raw green-diesel. After cooled to 80°C, raw green-diesel is stripped of gas, propane and water in vessel V-203 (80°C, 1.013bar). Simulation uses Peng-Robinson Equation-of-State (PR-EOS) for predicting thermodynamic properties of vapors and liquids. The hydrotreatment reaction deoxygenates triglycerides producing propane, H_2O, CO, CO_2 and long-chain paraffins as green-diesel (Sotelo-Boyás et al., 2012). Hydrotreatment is simulated as an isothermal plug-flow reactor (PFR-201, 340°C, 50bar) with H_2 in excess (H_2:Oil=0.05kg/kg). PFR-201 feed is preheated with PFR-201 outlet, which cools down to 250°C and follows to V-201 (250°C, 50bar). V-201 produces a top gas (paraffin, CO/CO_2, propane, H_2, water); and raw green-diesel bottoms (with propane and lights) which is mixed with liquid hydrocarbons (mostly propane) from V-202 and depressurized to V-203 flash-vessel (80°C, 1bar) giving the final green-diesel product and a stream of lights (mostly propane). The top gas from V-201 passes through a gas-phase methanation reactor R-201 (conversion reactor, 250°C, 50bar) where CO and CO_2 are converted to CH_4. R-201 gas effluent preheats the H_2 recycle and is cooled to 45°C, and sent to a 3-phase separator V-202 (45°C, 40bar), where H_2 is recovered (with CH_4), water is separated as bottoms and an intermediate hydrocarbon phase (paraffin, propane and CH_4) is recovered and added to raw green-diesel. The recovered H_2 is recompressed to 50bar, preheated with R-201 effluent and recycled to PFR-201 after a purge (fuel-gas) accounting for the produced CH_4. The difference between green-diesel processes PU#4 and PU#5 resides on the obtained paraffin range: C15-C18 for soybean-oil PU#4 and C13-C22 for microalgae-oil PU#5.

Propylene-glycol process (Sengupta and Pike, 2013) comprehends: (i) glycerol hydrogenolysis (200°C, 13.8bar); (ii) propylene-glycol purification via atmospheric steam-stripping and distillation; and (iii) glycerol recovery via atmospheric distillation. Simulation adopts NRTL-Electrolyte and ideal gas as liquid and vapor thermodynamic models respectively. Glycerol is fed to the process as the 7%w/w NaCl-saturated aqueous-glycerol stream from biodiesel production-units with 67%mol glycerol (NaCl-free basis). Glycerol two-phase hydrogenolysis occurs in R-401/R-402 reactors (200°C, 13.8bar, 55% conversion each). Glycerol feed is mixed with H_2 and preheated with hot R-402 effluent. Purification comprehends: (i) propylene-glycol/glycerol separation in T-401 steam-stripper (10-staged); (ii) water-glycerol atmospheric distillation T-403 (6-staged); (iii) T-403 bottoms are cooled to 30°C precipitating NaCl collected in cyclone V-401, and producing 7%w/w NaCl-saturated aqueous-glycerol (67%mol glycerol NaCl-free basis) as recycle to R-401; and (iii) water-propylene-glycol atmospheric distillation T-402 (10-staged).

Table V-4. Process simulation assumptions.

Assumption	*Item*	*Description*
{A1}	*Process Simulation*	*HYSYS 8.8.*
{A2}	*Thermodynamic Modeling*	*NRTL: liquids (Biodiesel/Propylene-glycol processes);* *Ideal Gas: vapors (Biodiesel/Propylene-glycol processes);* *PR-EOS: liquids/vapors (Green-Diesel process).*
{A3}	*Feeds*	*Oil: F=1000 kg/h; T=25ºC; P=1.013bar;* *Methanol: T=25ºC; P=1.013bar;* *Aqueous-NaOH (50%w/w): T=25°C; P=1.013bar;* *Aqueous-HCl (37%w/w): T=25°C; P=1.013bar;* H_2 *(Green-Diesel): T=25°C; P=20.77bar;* *Aqueous-Glycerol (67%mol NaCl-free basis; NaCl=7%w/w): F=233kg/h; T=30ºC; P=1.013bar;* H_2 *(Propylene-glycol): T=25°C, P=13.8bar.*
{A4}	*Transesterification Reactor*	*R-101: P=4bar; T=60ºC; Methanol:Oil=6mol/mol; Oil:NaOH=100kg/kg;* *Conversions: Soybean-Oil=99%; Palm-Oil=99%;Microalgae-Oil=95%.*
{A5}	*Methanol Distillation*	*T-100: 10-Staged; P=1.1bar; T=130ºC;* T^{TOP}*=108ºC;* T^{BOTTOM}*=117ºC;* *T-101: 25-Staged; P=1bar;* T^{TOP}*=64ºC;* T^{BOTTOM}*=102ºC;* *Reflux-Ratio=3; Distillate: Methanol=99%mol;*
{A6}	*Glycerol-Biodiesel Liquid Extraction*	*T-301: 4-Staged; P=1.1bar;* T^{TOP}*=66ºC;* T^{BOTTOM}*=96ºC.*
{A7}	*NaOH Neutralization*	*R-102: HCl:NaOH=1mol/mol.*
{A8}	*Glycerol Purification*	*T-302: 10-Staged; P=1bar;* T^{TOP}*=100ºC;* T^{BOTTOM}*=149ºC;* *Glycerol=67%mol (NaCl-free); NaCl=7%w/w*
{A9}	*Biodiesel Purification*	*V-301: P=1bar; T=150ºC.*
{A10}	*Hydrotreatment Green-Diesel*	*PFR-201: P=50bar; T=340°C;* H_2*=4.76%w/w; Conversion=100%;* *V-201: P=50bar; T=250ºC.*
{A11}	*Methanation* H_2 *Recycle Green-Diesel*	*R-201: P=50bar; T=250°C; Conversions: CO=100%;* CO_2*=100%;* *V-202: P=40bar; T=45ºC.*
{A12}	*Green-Diesel Stripping*	*V-203: P=1bar; T=80ºC.*
{A13}	*Glycerol Hydrogenolysis*	*R-401:P=13.8bar; T=200°C; Conversion=55%;* *R-402: P=13.8bar; T=200°C; Conversion=55%;*
{A14}	*Propylene-glycol Purification*	*T-401: 10-Staged; P=1bar;* T^{TOP}*=155ºC;* T^{BOTTOM}*=121ºC;* *T-402:10- Staged; P=1bar;* T^{TOP}*=100ºC;* T^{BOTTOM}*=188ºC;* *T-403:6- Staged; P=1bar;* T^{TOP}*=100ºC;* T^{BOTTOM}*=146ºC;*

V.3 Results and Discussion

S-PSE results for the biorefinery case-study follow. Detailed simulation and indicators results are in online Supplementary Data.

V.3.1 Economic and Environment Pre-Assessment of Biorefinery Pathways

First-level results in Table V-5 show that several production-units are economically unfeasible: *EP* is negative for PU#3, PU#5, and PU#8; and *GAP* is negative for PU#1, PU#3, PU#4, PU#5, and PU#8. Microalgae-oil processes are economically unfeasible for *Economic/profit* indicators due to the cost of raw-materials ($Cost_{RM}$). Despite of the growing interest in microalgae biofuels (Wiesberg et al., 2017), *COM* of microalgae biomass processing is high; e.g., only harvesting and drying respond for ≈50% of *COM* (Sahoo et al., 2017). Consequently, microalgae-oil price is ≈15 times higher than palm-oil and soybean-oil counterparts (Supplement B, Supplementary Materials). It is thought that microalgae-oil price has to drop below 1USD/kg – like it is for palm-oil and soybean-oil – to allow economic feasibility of algal biofuels (Laurens, 2017). Indeed, $Cost_{RM}$ is the most significant tributary to *COM* for biodiesel production, turning the economic performance of single-product biodiesel plants more vulnerable to conjuncture changes (Živković et al., 2017). Hence, PU#3, PU#5 and PU#8 are considered unfeasible and discarded from analysis since their results are not suitable for statistical screening, indicator normalization and aggregation.

Table V-5 also shows results of *Environment/Cradle-to-gate* indicators. Soybean-oil climate change impacts come mostly from CO_2 emissions associated to changes of land utilization – soybean-oil is the most land-use intensive feedstock (Matsuura et al. 2017). N_2O and fossil CO_2 emissions are the reasons behind soybean-oil high scores in climate change impact category due to high consumption of nitrogen fertilizer and extensive use of diesel-fired machines in soybean agriculture. On the other hand, Table V-5 shows that the GWP impacts of palm-oil are comparatively much lesser than the soybean-oil counterpart due to unnecessary utilization of nitrogen fertilizers in native or planted forests of perennial palm trees. Regarding microalgae-oil Table V-5 results, the greenhouse gas balance of the microalgae biomass cultivation stage entails an excellent net negative GWP. On the other hand, despite of the potential of microalgae-oil for drastic reduction of biodiesel greenhouse gas emissions and land-use, and its advantage of being non-edible, the high *CG-Eu* and *CG-Ac* translate high electricity consumption during algal cultivation (i.e., water recirculation pumps, suspension agitators, and blowers to deliver flue-gas to culture) and nutrients consumption in the microalgae growth cycle that have eutrophication impacts via culture effluents (Grierson et al. 2013).

Table V-5. Results: *Economic* and *Environment/Cradle-to-gate* indicators.

Production-Unit & Feedstock*	***PU#1*** *sb-oil*	***PU#2*** *p-oil*	***PU#3*** *ma-oil*	***PU#4*** *sb-oil*	***PU#5*** *ma-oil*	***PU#6*** *sb-oil*	***PU#7*** *p-oil*	***PU#8*** *ma-oil*
Economic indicators								
$Cost_{RM}$ (MMUSD/y)	5.9	5.3	88.0	6.3	88.5	6.9	6.2	88.9
COM (MMUSD/y)	8.1	7.4	96.7	8.5	97.3	10.4	9.8	99.0
FCI (MMUSD)	6.2	6.2	6.2	6.8	6.6	10.6	10.6	10.6
GAP (MMUSD/y)	-0.6	0.1	-81.1	-1.6	-90.5	1.2	1.9	-79.3
EP (MMUSD/y)	1.5	2.1	-72.4	0.6	-81.8	4.6	5.3	-69.3
Environment/Cradle-to-gate indicators								
CG-GWP (tCO_2e)	11.83[a]	2.00[a]	-0.83[a]	12.29[b]	-0.32[b]	11.90[a,b]	2.07[a,b]	-0.75 [a,b]
LU ($km^2.y$)	18.31	3.12	0.04	18.31	0.04	18.31	3.12	0.04
CG-Eu (kgPe)	1.42	0.81	4.40	1.42	4.40	1.42	0.81	4.40
CG-Ac ($kgSO_2e$)	8.72	12.20	99.60	8.72	99.60	8.72	12.20	99.60
CG-Bio (species-eq-lost.y)	1E-12	2E-11	NA[c]	1E-12	NA[c]	1E-12	2E-11	NA[c]

[a] *Including indirect GWP of methanol inlet from its production via natural gas steam-reforming and syngas synthesis (Chen et al., 2019).* [b] *Including indirect GWP from H_2 inlet from its production via natural gas steam-reforming (Mehmeti et al., 2018).* [c] *Not available. *sb-oil=soybean-oil; p-oil=palm-oil; ma-oil=microalgae-oil.*

V.3.2 Statistical Screening of Indicators

The final result of the statistical screening allowed reducing the original indicator set (Table V-1) to the following 16 indicators (62% reduction): *GWP*, *Smog* (*Environment/Gate-to-gate*); *CG-GWP* (*Environment/Cradle-to-gate*); ηE, *WI* (*Efficiency/Energy*); *E*, ε, *SMLI* (*Efficiency/Material*); *Mob*, $Fail_{F/E}$ (*H&S/Safety*); *Acute*, Haz_{in} (*H&S/Health*); *FCI*, *COM* (*Economic/Cost*); *GAP*, *EP* (*Economic/Profit*).

In Table EIII-1 (Part EIII, Appendix E) Corrected Item-Total Correlations (*CITC*) – the correlations between scores on each item and the total scale scores – were used in each sub-dimension to eliminate redundant indicators. C_{prod}, m_s, ηR, *ODP*, Ec_{aq}, *Acid*, Eut_A, *LU*, *CG-Eu*, *CG-Ac*, *CG-Bio*, $HTox_c$ and *Irrit* were eliminated in the Round#1 of screening due to *CITC<0.6* (Table EIII-1, Part EIII, Appendix E). *SMP* was excluded in Round#2 for its *CITC<0.6* in the *Efficiency/material* reduced set from Round#1. For *Efficiency/Energy* indicators all correlations were negative or zero (Fig. V-1), then statistical screening moved to Cronbach Alpha Test in Table EIII-2 (Part EIII, Appendix E). Consequently, $\Delta\dot{B}$, $\eta\dot{B}_{prod}$ and $\eta\dot{B}$ were removed to increase the Cronbach Alpha of *Efficiency/Energy* above 0.8. For this partially-reduced set of 25 indicators, PCA unveiled the first two principal components accounting for more than 80% of the total variance, translating a large redundancy. PCA results in Fig. V-3 identified the following redundant clusters: (*GWP*, *RMI*, *HW*), (*EI*, ηE), (*MI*, *E*), ($HTox_{nc}$, Haz_{in}), (*Acute*, TRI_{in}), (*PM*, $Fail_{F/E}$), ($Fail_{R/D}$, *Mob*), and ($Cost_{RM}$, *COM*). Hence, the following indicators were deleted in the PCA step: *HW*, *RMI*, *EI*, *MI*, $HTox_{nc}$, TRI_{in}, *PM*, $Fail_{R/D}$ and $Cost_{RM}$. Despite their different sustainability dimensions, pairs (*GWP*, Haz_{in}), (*CG-GWP*, $Fail_{F/E}$) and (*COM*, ηE) also had high correlation, a symptom that they also represent similar aspects.

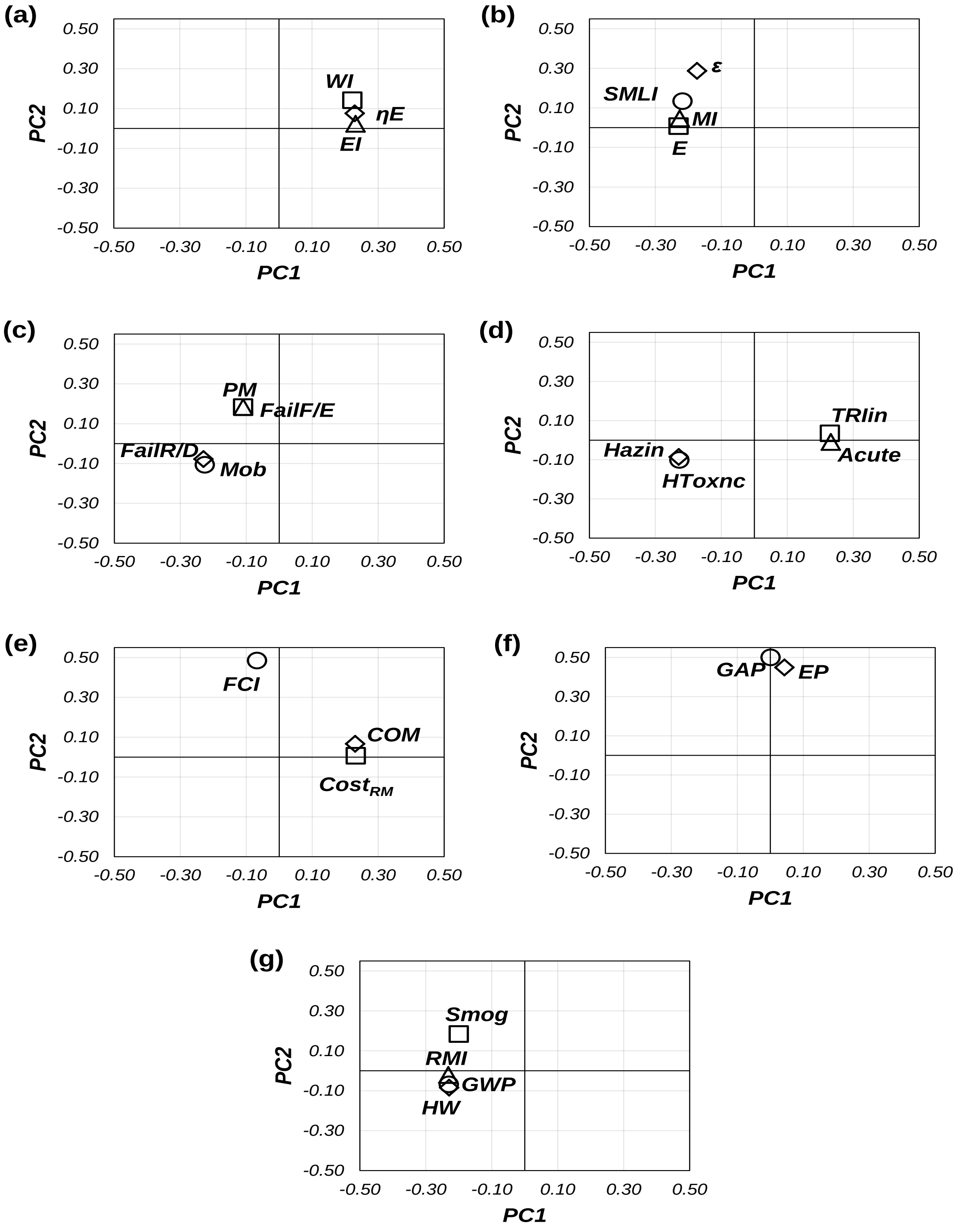

Figure V-3. Indicators scatter plot via principal components (PC1,PC2) for sub-dimensions: (a) *Efficiency/Energy*; (b) *Efficiency/Material*; (c) *H&S/Safety*; (d) *H&S/Health*; (e) *Economic/Cost*; (f) *Economic/Profit*; (g) *Environment/Gate-to-gate.*

V.3.3 First-Level Assessment of Biorefinery Pathways: Plant-Wide Sustainability

After a sensitivity analysis, the statistically optimized set of 16 indicators (Sec. V.3.2) was normalized by setting the origin at 25% above the ideal value for maximum-target indicators and at 25% below the ideal value for minimum-target indicators.

Fig. V-4 presents comparative *SPWI* results in each dimension (Eq. V-2) and overall (Eq. V-3) for valid production-units in Table V-3 after deleting microalgae-oil processes PU#3, PU#5, PU#8. For *Efficiency* (Fig. V-4a), major discrepancies happen for *WI* and ηE. Green-diesel process (PU#4) is the only one without stripping-columns, carrying out cooling in fan-coolers or process heat exchangers, diminishing water consumption while increasing energy demand. Nevertheless, the water-glycerol distillation in biodiesel processes has high heat-load, increasing the energy intensity in these production-units. The best *Efficiency/Material* performances are for biodiesel processes (PU#1, PU#2) due to low *E*-factor and high ε. Since green-diesel PU#4 presents much superior *WI* values, the counterparts of all other production-units fall far from the reference point, entailing that *WI* heavily influences their *Efficiency* index. Similar effects occur for other indicators in different dimensions. This is a drawback of setting the reference as the best value among alternatives. However, since this is a comparative analysis and the remaining indicators have similar values, *WI* becomes the most discriminating indicator for *Efficiency* performance.

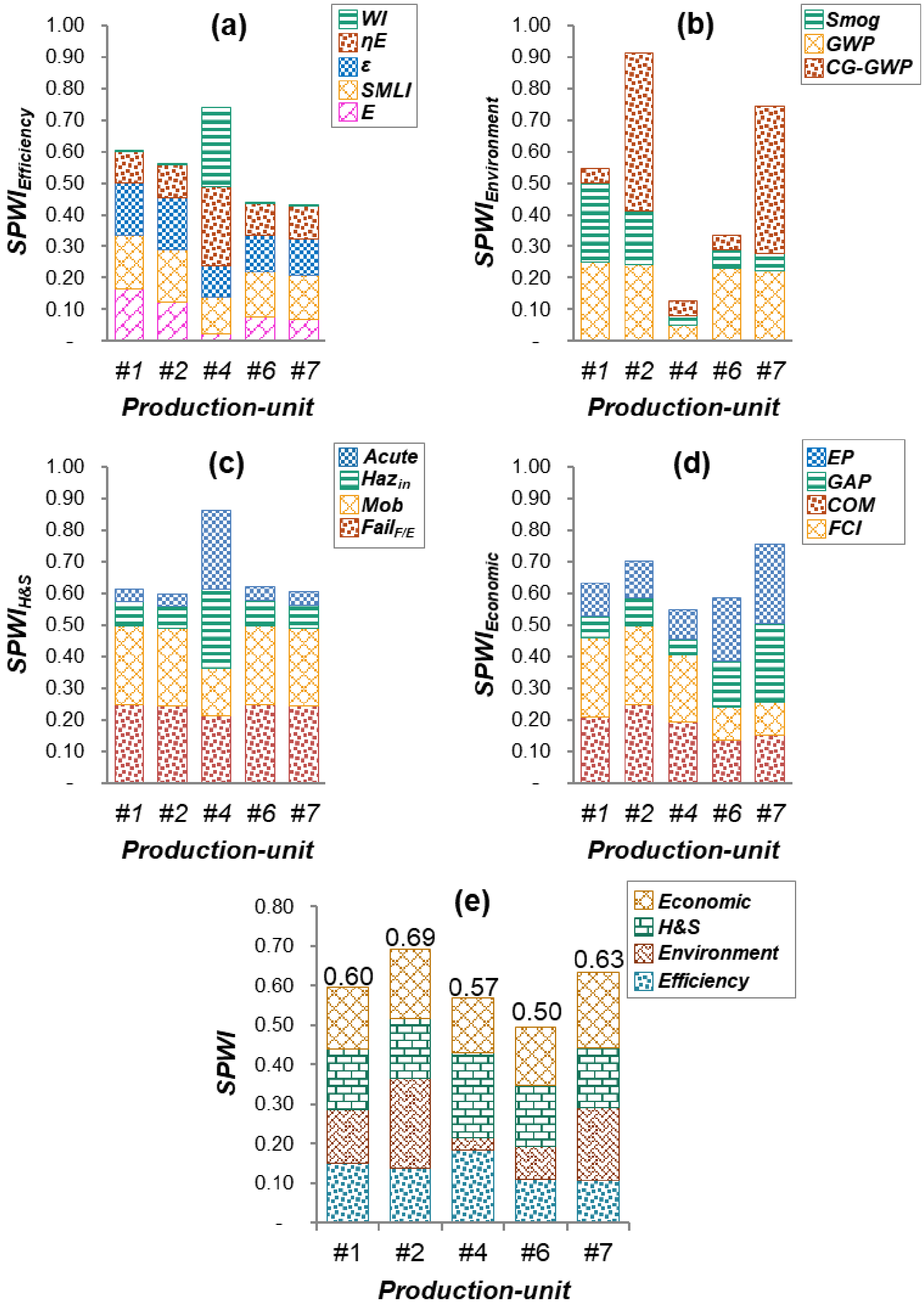

Figure V-4. First-level results for each sustainability dimension (normalized values): (a) *Efficiency*; (b) *Environment*; (c) *H&S*; (d) *Economic*; and (e) overall.

Fig. V-4b evinces palm-oil (PU#2, PU#7) as the most environmentally friendly feedstock. Soybean-oil (PU#1, PU#4, PU#6) is the feedstock with highest *Environment* impacts as discussed in the pre-assessment (Sec. V.3.1). Consequently, and also due to its high agricultural yield, palm-oil is a much less intensive feedstock than soybean-oil and a lower land-intensive biomass (Carneiro et al. 2017). Since the biggest differences of *Environment* indicators among production-units are for *Cradle-to-gate*, feedstock aspects become more important than the process itself. In terms of *Environment* indicators green-diesel process (PU#4) is the worst performer due to its *GWP* (CH_4/CO_2 emissions) and *Smog* (C_3H_8/CH_4 releases). *Smog* is also the underlying reason why biodiesel processes are better than biodiesel-and-propylene-glycol processes: emitted propylene-glycol inflicts photochemical-oxidation.

For *H&S* indicators, green-diesel process (PU#4) is the worst in *H&S*/*Safety* (Fig. V-4c). PU#4 scores poorly for $Fail_{F/E}$ and *Mob*, because it operates hydrotreatment reactors using H_2 at severe pressure/temperature conditions. The use of methanol in biodiesel processes (PU#1, PU#2, PU#6, PU#7) also impacts the respective *H&S* results, but PU#4 has the highest *H&S/Health*. Apart from PU#4, *H&S* results are similar among processes and feedstocks.

Feedstock cost is the most significant variable for *Economic/Profit*. The best economic results are for biodiesel-and-propylene-glycol composed production-units where palm-oil is the best feedstock (PU#7). Propylene-glycol adds revenue and compensates for low-priced biodiesel; i.e., valorization of glycerol increases revenues, contributing to biodiesel biorefinery sustainability (Gonzalez-Garay et al. 2017).

SPWI overall result (Fig. V-4e) unveils that the most sustainable biorefinery configuration is PU#2 (palm-oil to biodiesel) with PU#7 (palm-oil to biodiesel-and-propylene-glycol) close behind. In terms of process type, biodiesel and biodiesel-and-propylene-glycol processes scored first in *Environment* and, regarding feedstock, palm-oil results as the most sustainable alternative. Green-diesel PU#4 performs poorly in *Economic*, *Environment* and *H&S/Safety*. *SPWI* results are in line with previous works comparing the viability of biomass-derived products from different sources. For instance, Tan et al. (2009) highlighted palm-oil as attractive in terms of economic and environmental performances in face of its high yield and low production cost. In the end, *Economic* and *Environment* play a decisive role in choosing the best feedstock-product route, due to the great differences among configurations, which impact Canberra distances.

V.3.3.1 Compliance of Biorefinery Pathways with Sustainable Development Goals

The affinities of soybean-oil and palm-oil biorefinery pathways with the Sustainable Development Goals (SDGs) of 2030 Agenda were measured in Fig. V-5. The following ten SDGs are linked to the final set of S-PSE indicators (UN, 2015): SDG3 “*Ensure healthy lives and well-being*”; SDG6 “*Ensure access to water and sanitation*”; SDG7 “*Ensure access to affordable, sustainable and modern energy*”; SDG8 “*Promote inclusive and sustainable economic growth, employment and decent work*”; SDG9 “*Promote resilient infrastructure, sustainable industrialization and innovation*”; SDG12 “*Ensure sustainable consumption/production*”; SDG13 “*combat climate-change and impacts*”; SDG14 “S*ustainably use the oceans, seas and marine resources*”; SDG15 “*Sustainably manage forests, combat desertification, reverse land and biodiversity degradation*”; and SDG16 “*Promote just, peaceful and inclusive societies*”. Two ways of assessing production-units compliance with SDGs are used: (i) calculating (Sec. V.2.1) the average value of all indicators linked to each SDG (Fig. V-5a) to compare production-unit performances; and (ii) calculating the number of indicators from S-PSE optimized set that are linked to each SDG (Fig. V-5b), thus evaluating the presence of SDGs in the analysis (Table EII-5, Appendix E).

Most S-PSE indicators correlate with SDG3, SDG8 and SDG12, but SDG8 does not connect to *Environment* and *E*-factor indicators, while SDG12 is not linked to *H&S* and *Economic* indicators, and SDG3 does not relate only to *Efficiency* and *Economic* indicators. Comparing performances, PU#2 again stands out for many SDGs, excepting SDG6, SDG7 and SDG16. The main reasons are the high water-intensity and energy-intensity of PU#2 regarding SDG6 and SDG7, and its hazardous methanol input regarding SDG16. SDG9 results confirm the need for PU#2 improvement regarding *Economic* indicators, when compared to biodiesel-and-propylene-glycol process PU#7. In general, PU#2 is best in terms of good health and well-being, responsible consumption/production, climate-change action, marine life and life in general.

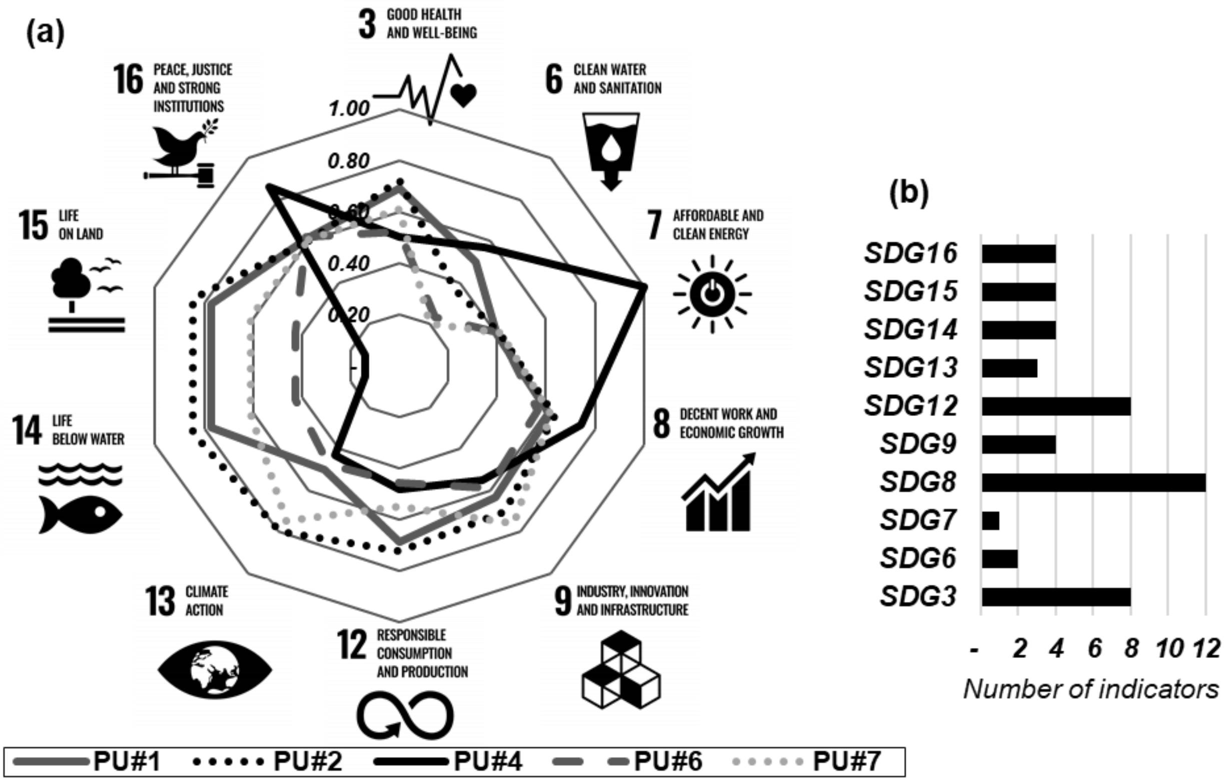

Figure V-5. Production-units PU#1, PU#2, PU#4, PU#6 and PU#7: (a) average value of all indicators linked to each SDG; and (b) number of S-PSE indicators linked to each SDG.

V.3.4 Second-Level Assessment: Unit-Operation Sustainability Hotspots of PU#2

Second-level analysis of PU#2 considered 10 indicators: *GWP*, *Smog* (*Environment*); *EI*, *WI*, *MI*, *SMLI* (*Efficiency*); $Fail_{F/E}$, *Mob*, Haz_{in}, *Acute* (*H&S*) – ε was excluded since there is only one reaction in PU#2. Fig. V-6 presents the results. Since the NaOH catalyst feed ratio is very small ($100kg^{Oil}/kg^{NaOH}$) comparatively to other PU#2 inlets (e.g., methanol), the neutralization reaction, reactor R-102 and all NaOH and HCl streams were discarded from the hotspots analysis. In the same way, the small solid NaCl streams and related operations were considered harmless and of low impact and were discarded from the analysis.

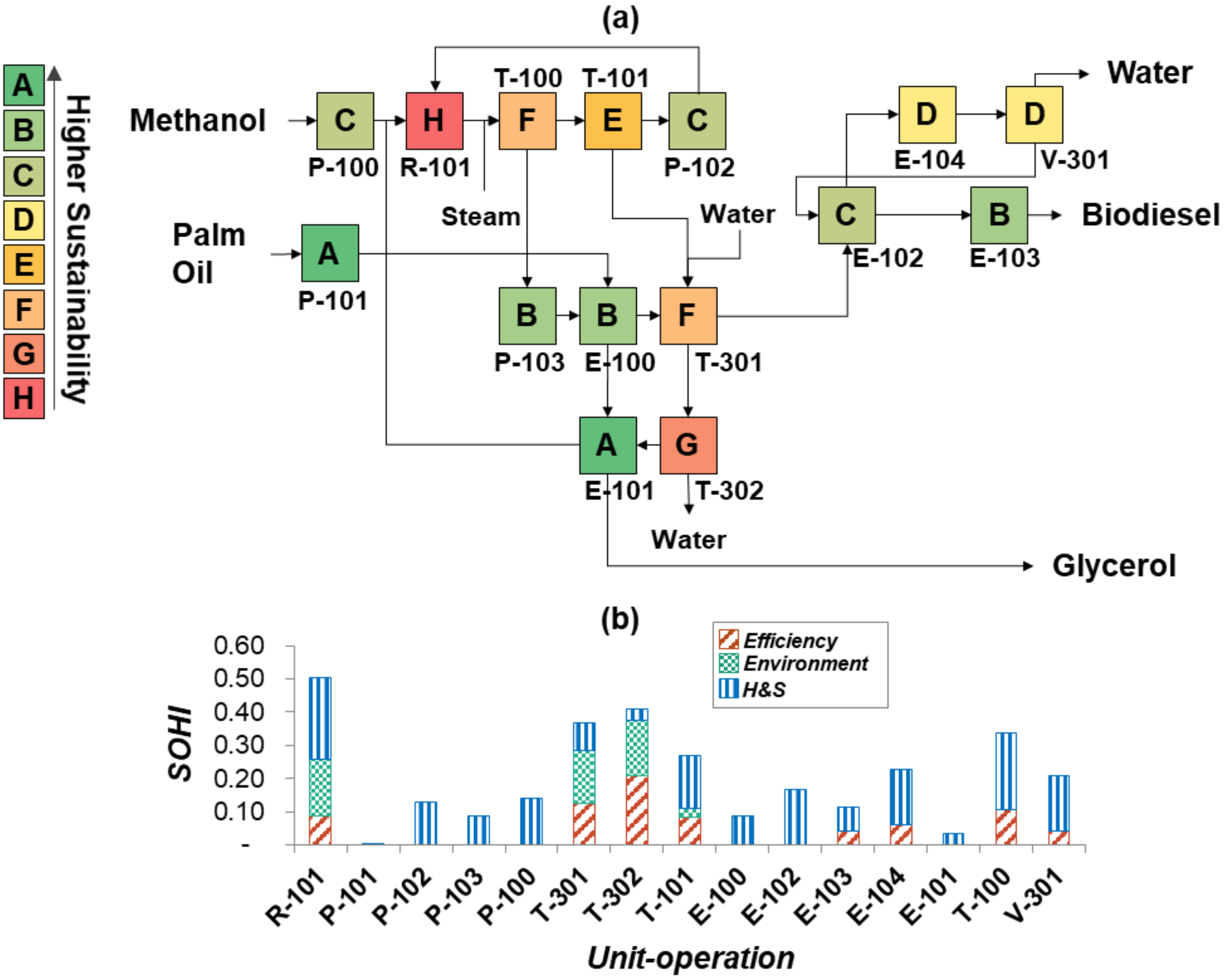

Figure V-6. Second-level results: (a) Sustainability of PU#2 and its unit-operations; (b) *SOHI* values of PU#2 unit-operations.

Major hotpots are in reactor R-101, and separators T-100, T-301 and T-302. T-302 is a distillation tower showing heavy impacts associated to *Efficiency* with high *EI* values. This is an expected outcome since distillation is energy-intensive, but the underlying reason for the impressive heat consumption of T-302 – even if compared to other distillations such as T-402 and T-403 – is its large water-glycerol feed from the liquid-liquid extractor. R-101 poses heavy *Environment* and *H&S* risks. Reactions are associated with environmental impacts of chemicals (reactants and products), greatly impacting characterization factors. Hence, all inlet/outlet triglycerides and methanol impacts are attributed to R-101, making it highly material-intensive (*MI*) and responsible for methanol inlet/outlet poor Haz_{in}, *Acute* and *Smog* results. A similar reasoning – this time associating fatty acid methyl-esters and glycerol outlet impacts to T-301 – contributes to highlight T-301 as poorly sustainable. T-301 is responsible for the biodiesel-glycerol split via water extraction, inheriting the impacts from biodiesel/glycerol traces in waste streams. T-301 also has high water-intensity (*WI*). High bottom temperature and top methanol output makes T-100 the second highest score for *H&S* burdens with risks of failure ($Fail_{F/E}$) and methanol toxicity (*Acute*). Other worth mentioning unit-operations are T-101, E-104 and V-301 (Fig. V-6a). Overall, minor hotspots are observed for pumps/valves, whereas greatest hotspots are related to reaction/separation, and heating/cooling bottlenecks are mainly for *H&S* issues associated to $Fail_{F/E}$ and *Mob* (due to process atmospheric pressure and high temperature), attributing to E-104 the worst scores for this type of unit-operation (level D of sustainability, Fig. V-6a).

V.4 Conclusions

A hierarchical method, S-PSE, is applied to assess sustainability at early-design of biorefinery configuration contemplating soybean-oil, palm-oil and microalgae-oil as candidate bio-oil feedstocks and biodiesel, green-diesel, and biodiesel-and-propylene-glycol as candidate bio-products. New and original features of S-PSE method were presented, such as statistical screening of indicators and analysis of compliance with the 2030 Agenda. Results showed that microalgae-oil based biorefinery pathways are not economically feasible yet due to high oil costs, despite of being environmentally much superior in terms of greenhouse gas emissions and land-use than soybean-oil and palm-oil biorefineries because microalgae-oil is a prominent reducer of biorefinery *Environment* impacts as well as of land competition with food crops. Statistical screening reduced the original set of indicators by 62%, achieving a representative, non-redundant, optimized group of 16 indicators. The palm-oil to biodiesel pathway (PU#2) was the production-unit with the best sustainability results, wherein the *Environment* and *Economic* dimensions played central roles. The palm-oil to biodiesel-and-propylene-glycol biorefinery (PU#7) also showed great potential and was the second more sustainable pathway. Nevertheless, *Efficiency* and *Environment* scores need improvements by reducing waste and photochemical-oxidation via increasing reaction/separation efficiencies.

Compliance with the 2030 Agenda highlighted SDG3, SDG8, and SDG12 as the Sustainable Development Goals most linked to S-PSE indicators. In this regard, palm-oil to biodiesel (PU#2) attained the best performances for most SDGs, notwithstanding the poor results for SDG3 and SDG7 – due to PU#2 high water-intensity and energy-intensity – and SDG16 related to hazardous methanol input. Finally, the second-level assessment corroborated results from compliance with the 2030 Agenda as it identified reaction/separation operations as major sustainability hotspots of PU#2 due to hazardous reactants (e.g., methanol) and energy-intensive distillations.

Supplementary Materials

Parts EI, EII and EIII with indicators, data used, SDG-GRI linkage and results of statistical screening of indicators are found in Appendix E. Supplementary Data to this chapter with simulation and indicator results will be found online in Excel Worksheet Supplementary_Data.xls after publication.

Acknowledgments

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Abbreviations

CITC Corrected Item-Total Correlations; FAME Fatty Acid Methyl Esters; H&S Health and Safety; LCA Life-Cycle Assessment; PCA Principal Component Analysis; PR-EOS Peng-Robinson Equation-of-State; SDG Sustainable Development Goal; S-PSE Sustainable Process Systems Engineering; TAG triacylglycerol.

Nomenclature

Acid, Acute	*Atmospheric-Acidification (kg*SO_2*e), Acute-Toxicity*
CG-Ac	*Cradle-to-Gate Acidification (kg*SO_2*e)*
CG-Bio	*Cradle-to-Gate Biodiversity-Loss (species-eq-lost.year)*
CG-Eu	*Cradle-to-Gate Eutrophication (kgPe)*
CG-GWP	*Cradle-to-Gate Global-Warming (kg*CO_2*e)*
COM, $Cost_{RM}$	*Cost of Manufacturing and Cost of Raw-Materials (MMUSD/y)*
C_{prod}	*Final-product concentration (kg/kg)*

E, Ec_{aq}	*E-factor (kg/kg), Aquatic-Ecotoxicity (PAF.m^3.d)*
EI, EP	*Energy-Intensity (J/kg), Economic-Potential (MMUSD/y)*
$Eut_A, Fail_{F/E}$	*Aquatic-Eutrophication (kgNe), Fire/explosion*
$Fail_{R/D}$	*Decomposition*
FCI, GAP	*Fixed Capital Investment (MMUSD), Gross Annual-Profit (MMUSD/y)*
GWP, Haz_{in}	*Global-Warming (kgCO$_2$e), Hazardous-Input (kg/kg)*
$HTox_c$	*Human Toxicity-cancer-effects (cases)*
$HTox_{nc}$	*Human Toxicity-non-cancer-effects (cases)*
$HW, Irrit$	*Hazardous-Waste (kg/h), Irritation-Factor*
LU, MI	*Land-Use (km^2.y), Material-Intensity (kg/kg)*
Mob, m_s	*Mobility, Solid-Waste Mass (kg/h)*
ODP, PM	*Ozone-Depletion (kgCFC11e), Particulate-Matter (PM2.5e)*
$RMI, SMLI$	*Renewability Material Index (kg/kg), Separation mass-loss index (kg/kg)*
$SMP, Smog$	*Separation Mass-Productivity (kg/kg), Photochemical-Oxidation (kgNO$_x$e)*
$SOHI, SPWI$	*Sustainable Operation Hotspot Index, Sustainable Plant-Wide Index*
TRI_{in}	*TRI-Input (kg/kg)*
WI, ε	*Water-Intensity (kg/kg), Reaction-Yield (kg/kg)*
$\Delta\dot{B}$	*Exergy-Destruction (J/h)*
$\eta\dot{B}, \eta\dot{B}_{prod}$	*Resource Exergy-Efficiency (%),Product Exergy-Efficiency (%)*
$\eta E, \eta R$	*Resource Energy-Efficiency (J/J), Reaction Molar-Efficiency (mol/mol)*

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CHAPTER VI - CONCLUDING REMARKS

The Sustainable Process Systems Engineering (S-PSE) Method was developed to assess process sustainability. S-PSE is a hierarchical method, featuring technology-specific indicators, plant-wide overall sustainability; unit-operation sustainability hotspots diagnosis; computer-aided tools; statistical tests to select indicators; composite sustainability-indexes; and compliance with 2030 Agenda, integrating process analysis to corporate strategy.

S-PSE is composed of two main levels: plant-wide or production-unit; and unit-operations. The first-level selects the most sustainable plant-wide feedstock-process-product configuration, while the second-level locates sustainability hotspots within unit-operations. Sustainability indicators are classified into four dimensions: (i) Environment; (ii) Efficiency; (iii) H&S (Health-and-Safety); and (iv) Economic; and S-PSE hierarchical procedure ranks alternatives with the Sustainable Plant-Wide Index (*SPWI*) in the first-level and the Sustainable Operation Hotspot Index in the second-level (*SOHI*). Using input-process-output models, product units are combined into a production structure, comprising performance data and resource flows. S-PSE integrates three computer-aided tools: HYSYS simulator to generate process mass/energy balances, MATLAB for statistical tests and indicator calculation, and MS-Excel interface to calculate indicators using built-in property database, process characterization factors and classification labels.

S-PSE method and tool has evolved along this doctorate. It started from single process analysis restricted to the evaluation of unit-operations (as it is in the current second-level) presented in **CHAPTER III**. Then it incorporated plant-wide assessment for gate-to-gate sustainability, comparing different feedstock-process-product configuration, as shown in **CHAPTER IV**. The evolution continued and the method added new features, such as cradle-to-gate environmental indicators, indicator statistical screening and, at last, corporate-level integration with the 2030 Agenda assessment, as presented in **CHAPTER V**. The final version of S-PSE method is able to provide an integrated system analysis, as can be concluded from Fig. VI-1.

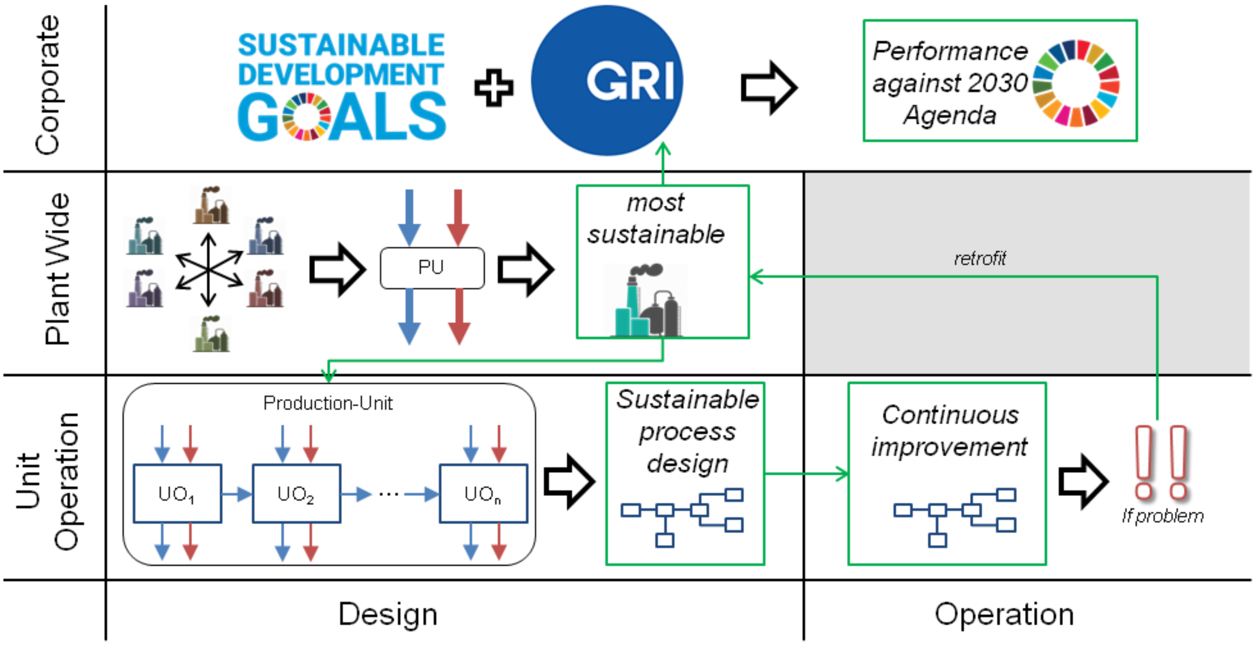

Figure VI-1. Final version of S-PSE method demonstrating its integrated system analysis.

Fig. VI-1 shows how S-PSE method works in different levels (corporate, plant-wide and unit-operation) along design and operation stages, integrating them altogether. In the design phase, S-PSE selects most sustainable plant-wide configuration, then proceeds to identify gaps in unit-operations, with the overall goal of achieving sustainable process design. Unit-operations can continue to be assessed during the plant operation stage, with the goal of continuous improvement. If a major process sustainability problem is detected during operation, the engineers can evaluate if a retrofit is needed. In this case, retrofit can be performed with S-PSE, using the same steps mentioned for the design stage. As an effort to move even closer to comprehensive assessments, an extra corporate level breaks the limits of process boundaries, closing the company loop for industrial systems by adding the operation stage of the production phase and corporate strategic analysis. In the corporate-level, the goal is to monitor company performance against 2030 Agenda, relating S-PSE process indicators to GRI (Global Reporting Initiative) indicators and to Sustainable Development Goals (SDGs).

Besides the integration between industrial assessment levels and production phases, S-PSE is modular, flexible, and extensible, being able to support the arrangement of production-units to possibly provide value-chain overall configuration. Although this feature was not explored in the case studies investigated in this thesis, it can be used to extrapolate gate-to-gate boundaries even further than it is today – with the sole accounting of cradle-to-gate environmental impacts. S-PSE also addresses social, environmental and economic dimensions, which contributes even more to its integrated analysis.

This Thesis attempted to answer three questions posed at the beginning of this work: (i) how can chemical engineers assess if a process is more sustainable than other via integrated system analysis? (ii) how can chemical engineers identify major barriers for sustainability performance within a process? (iii) how can we move towards more objective sustainability analysis for chemical process design and production? The main conclusions derived from S-PSE assessments and the work provided along this Thesis are:

i. The main fact unveiled by the Literature Review is the need for integrated systems analysis for sustainability dimensions, product/process life-cycle and company-levels. As previously stated, S-PSE is an integrated systems analysis solution, mainly for process design, and it brings the chemical industry closer to comprehensive assessments that do not neglect process complexity;
ii. Major barriers for sustainability performance within a process can only be identified if the method applied does not consider unit-operations as black-boxes. By applying technology-specific indicators and not generic databases, and breaking the sustainability assessment in unit-operations, S-PSE is able to quickly outline the main operations that are responsible for a decrease in sustainability;
iii. More objective sustainability analysis claims for non *ad-hoc* decision-making and reliable selection of indicators. Both aspects are covered by S-PSE method since it comprises composite sustainability-indexes for multi-attribute decision-making and statistical tests to retrospectively select an optimized set of indicators.

The content of this Thesis is of great importance to the sustainable process industry, especially in the area of sustainable process design, sustainable production, sustainability metrics and indicators, and environmental management. All the published material clearly states the value of this research. The development of method and tools for evaluating process sustainability integrated to corporate strategy and decision-making opens the horizon of process engineering for sustainable design and production.

Future developments of this work comprehend the inclusion of uncertainty analysis; investigation of alternative decision-making techniques; evaluation of the robustness of S-PSE method; and application of S-PSE in case-studies for operation and retrofit. Other potential developments might encompass S-PSE expansion for life-cycle analysis that is technology-specific; studies for value-chain optimization; investigation of consequential approaches; assignment of weights to indicators according to local reality (e.g. water consumption indicators would be more important for regions with water scarcity); use of S-PSE methods to optimize process conditions and define operational ranges.

APPENDICES

APPENDIX A – CHAPTER II SUPPLEMENTARY MATERIALS

Sustainability assessment for the chemical industry: onwards to integrated system analysis

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SUPPLEMENTARY MATERIALS

PART AI. Assessment Methods

Tables. AI-1, AI-2.

PART AII. Indicators

PART AIII. Decision-Making

Tables. AIII-1, AIII-2.

PART AI. Assessment Methods

Table AI-1. Common keywords in the sustainability literature.

Indication of industrial-level	**Indication of corporate-level**	**Life cycle perspective**	**Decision-making**	**Sustainability**
Design	Business sustainability	Life cycle assessment	Data envelopment analysis	Ecology fingerprint
Industrial systems	Corporate social responsibility	Life cycle inventory	Decision making	Environmental impact
Process design	Corporate sustainability	Life cycle management	Fuzzy set theory	Environmental metrics
Product and process evaluation			Indicator sensitivity algorithm	Potential Environmental impact
Production line simulation			Indicators	Sustainability control
Sustainable manufacturing			Metrics and measurement	Sustainability enhancement
			Multi criteria decision making methods	Sustainability indicators
			Multi objective optimization	Sustainable development
			Multicriteria decision making	
			Multiobjective optimization	
			PROMETHEE	
			Rank	
			Surrogate modelling	

Table AI-2. Literature classification regarding indicator categories.

Reference	ECO-PF	ECO-CC	ECO-PC	ECO-UC	ECO-WC	ECO-OP	ENV-EE	ENV-EX	ENV-ED	ENV-IA	ENV-IS	ENV-IW	ENV-RM	ENV-WG	ENV-ME	ENV-RE	ENV-WU	SHS-OSH	SHS-SR	SHS-HR	SHS-EWL	SHS-CO
de Faria et al., 2020	x	x	x				x			x		x		x	x		x		x	x		
Ee et al., 2020																			x			
Lin et al., 2020	x	x	x				x	x	x	x	x	x		x	x	x	x		x	x	x	x
Athar et al., 2019																			x			
Garg et al., 2019	x		x	x			x			x					x		x			x		
Richter et al., 2019	x																	x			x	
Saad et al., 2019	x	x	x				x		x	x	x	x						x			x	x
Gonzalez-Garay and Guillen-Gosalbez, 2018		x	x	x	x					x	x	x										
Huang and Badurdeen, 2018			x	x	x	x	x			x			x	x	x		x	x	x	x	x	x
Xu et al., 2018	x	x	x				x		x	x										x		x
Agarwal et al., 2018	x	x					x			x					x		x					
Moradi-Aliabadi and Huang, 2018	x						x							x	x			x		x		
Kreuder et al., 2017							x				x	x	x	x	x				x	x		
Ordouei and Elkamel, 2017		x					x			x	x	x						x		x		
Sepiacci et al., 2017	x	x	x	x						x	x	x								x		
Ghosh and Bakshi, 2017	x									x												
Saavalainen et al., 2017	x		x	x	x	x	x			x	x	x	x	x	x	x			x	x		
Gao and You, 2017		x	x							x												
Alder et al., 2016							x		x	x		x		x	x				x	x		
Gopalakrishnan et al., 2016									x	x		x										
Liew et al., 2016, 2015, 2014	x		x							x	x	x							x	x		
Serna et al., 2016	x									x	x	x	x		x				x	x		
Ocampo et al., 2016	x	x	x				x		x	x	x	x		x	x		x	x		x	x	x
Ren et al., 2016		x	x				x	x		x	x	x										x
Ruiz-Mercado et al., 2016	x	x	x	x	x		x	x	x	x	x	x	x	x	x	x	x		x	x	x	
Moradi-Aliabadi and Huang, 2016	x														x			x		x		x

Reference	ECO-PF	ECO-CC	ECO-PC	ECO-UC	ECO-WC	ECO-OP	ENV-EE	ENV-EX	ENV-ED	ENV-IA	ENV-IS	ENV-IW	ENV-RM	ENV-WG	ENV-ME	ENV-RE	ENV-WU	SHS-OSH	SHS-SR	SHS-HR	SHS-EWL	SHS-CO
Dočekalová and Kocmanová, 2016	x	x	x				x			x			x	x			x	x			x	x
Phan et al., 2015							x						x		x	x			x	x		
Araújo et al., 2015	x	x	x				x			x					x		x					
Jia et al., 2015		x	x							x	x	x							x	x		
Yang et al., 2015			x						x	x	x	x								x		
Leseurre et al., 2014										x	x	x	x	x	x		x			x		
Carvalho et al., 2013	x	x	x	x	x		x			x	x	x			x	x	x		x	x	x	
Shadiya and High, 2013	x	x	x		x		x			x		x			x	x	x		x	x		
Yue et al., 2013		x	x							x												
Ruiz-Mercado et al., 2012	x	x	x	x	x		x	x	x	x	x	x	x	x	x	x	x		x	x		
Ouattara et al., 2012		x	x	x						x		x								x		
Brondi and Carpanzano, 2011									x	x	x	x								x		
Torres et al., 2011							x			x	x	x			x		x			x		
Othman et al., 2010							x			x	x	x							x	x		x
Hossain et al., 2010		x	x	x			x	x		x					x					x		
Cobb et al., 2009							x			x		x	x		x		x	x				x
Monteiro et al., 2009	x									x	x	x								x		
Sugiyama et al., 2008	x		x				x		x	x	x	x			x				x	x		
Zhang et al., 2010							x	x	x				x		x							
Curzons et al., 2007							x		x	x		x		x	x							
Martins et al., 2007							x			x	x	x			x					x		
Hossain et al., 2007										x	x	x						x		x		
Khan and Amyotte, 2005		x								x	x	x							x	x		
Labuschagne et al., 2005	x								x	x	x	x						x			x	x
Saling et al., 2005		x	x	x	x		x		x	x	x	x						x	x	x	x	x
Narodoslawsky and Krotscheck, 2004							x		x	x	x	x		x								
Jensen et al., 2003	x			x	x		x			x	x	x			x	x	x		x	x		
Saling et al., 2002		x	x	x	x		x		x	x	x	x							x	x		

Reference	**ECO-PF**	**ECO-CC**	**ECO-PC**	**ECO-UC**	**ECO-WC**	**ECO-OP**	**ENV-EE**	**ENV-EX**	**ENV-ED**	**ENV-IA**	**ENV-IS**	**ENV-IW**	**ENV-RM**	**ENV-WG**	**ENV-ME**	**ENV-RE**	**ENV-WU**	**SHS-OSH**	**SHS-SR**	**SHS-HR**	**SHS-EWL**	**SHS-CO**
Schwarz et al., 2002							x			x		x			x		x			x		
Azapagic et al., 2002	x	x	x				x			x	x	x		x	x		x	x	x	x	x	x
Beaver, 2000	x	x	x	x	x																	
Young and Cabezas, 1999										x	x	x								x		
ICCA, 2015							x			x		x					x	x				
GRI, 2016	x		x				x			x		x	x	x			x	x			x	x

PART AII. Indicators

Key requirements for selecting appropriate sustainable development indicators include (Böhringer and Jochem, 2007): (i) rigorous connection to sustainability definition, (ii) meaningful indicators, and (iii) data reliability and availability. Indicators should be simple, understandable, reproducible, robust and non-perverse (i.e., the higher the metric value is, more sustainable is the performance), cost-effective (in terms of data gathering), stackable along the supply chain, useful to manage decision-making and relevant to business (Tanzil and Beloff, 2006). Proper selection of indicators, avoiding the use of excessive factors (Schwarz et al., 2002), must be conducted retrospectively because there is no effective method to select indicators in advance (Sikdar et al., 2017).

Huysman et al. (2015) address the existence of many indicators in the literature proposing a systematized framework to structure and evaluate indicators selected for different levels of economic activity, boundary and perspective (national or global). The authors aim at identifying which indicators were correctly selected for their purposes. Sutherland et al. (2016) use space-temporal process-based models to project indicator response, correlation assessment to examine independence, and principal components analysis (PCA) to identify possible redundancies and dominant parameters. These works focus respectively on resource efficiency indicators and cumulative effects assessment, but the idea is applicable to sustainable design and production. Mukherjee (2017) applies machine learning algorithms for identification of relevant indicators in sustainable processes. Taking the metrology perspective into account, Brandi and dos Santos (2016) suggest using statistical tools to select indicators according to their reliability, dimensionality, and validity. In general, multivariate analysis and analytical approaches, such as PCA, are applicable to the overall framework and can guide subsequent screening choices (OECD, 2008). However, multivariate analysis techniques should be avoided if the sample is small compared to the number of indicators.

A few examples of indicators from the most frequent aspects covered by the methods analysed in the review are:

(a) *Impact on Air* (IA): global warming potential, ozone depletion potential, acidification or acid-rain potential, and photochemical oxidation or smog formation potential;

(b) *Impact on Water* (IW): aquatic toxicity potential, and freshwater eutrophication potential;

(c) *Impact on Soil* (IS): terrestrial toxicity potential;

(d) *Health Risk* (HR): human toxicity potential by ingestion, and human toxicity potential by either inhalation or dermal exposure;

(e) *Energy Efficiency* (EE): energy consumption, energy losses, energy index (Ordouei and Elkamel, 2017), energy conversion efficiency (Ren et al., 2016), E-factor for energy production (Araújo et al., 2015), energy accumulation factor (Carvalho et al., 2008);

(f) *Processing Cost* (PC): OPEX, raw material cost, total annualized cost (Gonzalez-Garay and Guillen-Gosalbez, 2018);

(g) *Material Efficiency* (ME): material intensity (Araújo et al., 2015), E-factor (Ruiz-Mercado et al., 2012b), global material economy (Leseurre et al., 2014), accumulation factor (Carvalho et al., 2008);

(h) *Profit* (PF): total or material added value (Carvalho et al., 2008; Serna et al., 2016), net present value, product revenue, dynamic economic potentials (Sepiacci et al., 2017);

(i) *Capital Cost* (CC): CAPEX, cost of equipment, time of return on investment, annualized capital costs (Shadiya and High, 2013);

(j) *Safety Risk* (SR) – explosiveness, reactivity, flammability, heat of reaction, temperature, pressure (Carvalho et al., 2008; Serna et al., 2016; Sugiyama et al., 2008).

PART AIII. Decision-Making

The basic working principles of any MCDM is the selection of criteria (indicators), alternatives, aggregation methods, and result based on weights or outranking (Majumder, 2015). Multi-attribute decision-making problems are composed of a finite number of discrete alternatives, explicitly known at the beginning (Mardani et al., 2015). The difference between the compensatory and outranking approaches is the possibility of trade-offs. CMADM allows a good performance in one aspect to compensate for a poor result in another one, and weights become a measure of preference. In outranking techniques, weights truly represent relevance of the evaluated aspects (OECD, 2008). Usually, CMADM apply indicator weighting and aggregation procedures to produce a single composite indicator. Examples of CMADM are Analytic Hierarchy Process (AHP), additive and geometric aggregation; and OMADM is exemplified by ELECTRE and PROMETHEE.

CMADM can use different criteria (qualitative and/or quantitative indicators), weighting methods and aggregation metrics. Table AIII-1 shows the techniques applied by the reviewed methods. Most CMADM techniques rely on equal weighting, which implies that all variables are equally relevant for the assessment. It is worth noting that equal weights do not mean “no weights”. There is a risk of using variables with a high degree of correlation and end up double-counting correlated aspects, rendering relevant statistical and correlation tests on the indicators (OECD, 2008).

There are various weighting techniques in the literature besides equal weighting, some derived from statistical models – e.g. data envelopment analysis (DEA) – and others from participatory methods – e.g. AHP (Gan et al., 2017). In the literature reviewed, AHP is the most used weighting technique. AHP performs decision trade-off among multiple objectives in a hierarchically organized structure, but it usually depends on subjective expert judgments (e.g., engineering and management team, investors and government offices) to define weighting criteria. Böhringer and Jochem (2007) compare the implications of experts attributing weights versus statistical methods, indicating a risk of rather subjective weights when they are participatory. Nevertheless, weights directly derived from statistics might be less acceptable by policy-makers due to the possibility of addressing a high value for a politically insignificant variable. Pizzol et al. (2017) survey LCA specialists that identified a negative perception regarding weighting techniques and other decision-making procedures, which contributes to practitioners preferring equal weights or even relying on AHDM.

Table AIII-1. Compensatory multi-attribute decision-making (CMADM) techniques used in the methods.

Criteria[1]	**Weighting method**	**Aggregation method**	**Used in**[2]
Quanti	Equal weights	Additive - linear summation	[R4, R26, R33, R38]
Quanti	Equal weights	Additive - arithmetic mean	[R8, R41]
Quali and quanti	Equal weights	Additive - scoring	[R23]
Quanti	Equal weights	Geometric	[R34, R44]
Quanti	Equal weights	Radar chart area	[R27]
Quanti	Scoring	Additive - linear summation	[R22]
Quanti	Not defined	Function defined by author	[R6, R40, R47, R52]
Quanti	Not defined	Additive - linear summation	[R12, R36, R53]
Quanti	AHP[3]	Additive - linear summation	[R9, R25, R35, R43]
Quanti	AHP-DEMATEL[4]	Additive - linear summation	[R17]
Quali and quanti	FDANP[5]	Interval vector-based algorithm	[R5]
Quanti	FUZAHP[6]	Additive - arithmetic mean	[R18]
Quali and quanti	AHP, ANP or Entropy Weight	Additive – GRA[7]	[R2]
Quanti	Based on heuristics	Additive - linear summation	[R39]
Quali and quanti	Based on industry sector relevance	Not specified	[R37]
Quanti	Based on national and societal relevance	Additive[8]	[R46, R48]
Quanti	Based on green design criteria	Additive	[R24]

[1] *Quali≡ qualitative indicators; Quanti≡ quantitative.*

[2] *See Supplementary Material Table A3 for list of references.*

[3] *Analytic hierarchy processes.*

[4] *Decision-Making Trial and Evaluation Laboratory.*

[5] *Fuzzy decision-making trial and evaluation laboratory based analytic network process.*

[6] *Fuzzy AHP.*

[7] *Grey Relation Analysis.*

[8] *Summation for single dimension aggregate index and Graphical representation of single indexes, with overall measure being the distance of the individual alternatives to the portfolio plot diagonal.*

Other weighting methods reported in the literature are AHP-DEMATEL, FDANP and FUZAHP (Table AIII-1). Serna et al. (2016) addressed the relative importance by integration of AHP and the interrelation of the dimensions by the Decision-Making Trial and Evaluation Laboratory (DEMATEL). FDANP is also a combination of techniques – fuzzy set theory, DEMATEL and Analytic Network Process (ANP) – able to tackle the interdependencies and interactions among the criteria system and to address the vagueness and uncertainty existing in human’s judgments (Xu et al., 2018). The fuzzy set theory is also applied in combination with AHP (Ocampo et al., 2016).

Only two methods perform non-compensatory approaches. The sustainability prioritization framework (Ren et al., 2016) can be utilized for selecting the most sustainable chemical process among multiple alternatives, incorporating the FAHP (fuzzy analytic hierarchy process) method to quantify qualitative (soft) criteria and indicators for quantitative (hard) criteria, the FANP (fuzzy analytic network process) method for weighting, and the PROMETHEE method for prioritizing alternatives. Saad et al. (2019) consider multiple MCDM techniques, including OMADM through ELECTRE, that are subject to sensitivity analysis to ensure reliable results. If the scores of the employed MCDM method are very sensitive to slight changes in indicators values or weights, another MCDM method is used.

MODM, or multi-objective optimization (MOO), generates a higher sustainability state via mathematical programming. In this case, the alternatives are not known at the beginning of the problem and it generates a continuous set of possibilities (Kumar et al., 2017), displayed in a ‘Pareto frontier’ whose shape indicates the nature of trade-offs. Some MOO problems stop at the Pareto frontier, while others seek for a single result.

Table C2 presents the nine works that use MODM and which method they employ. They apply fuzzy multi-objective optimisation to trade-off economic aspects with environmental, health and safety (Liew et al., 2016, 2015, 2014); ε–constraint method sets the environmental performance as the primary objective and the economic objectives are inequality constraints to find the Pareto frontier (Ghosh and Bakshi, 2017). Grid-search method is also used to generate the Pareto frontier (Sepiacci et al., 2017). TOPSIS or FUCA are applied for goal-programming and trading-off Pareto-optimal set (Ouattara et al., 2012). Multi-Objective Genetic Algorithms (MOGA) is proposed to find the Pareto frontier, followed by DEA to filter and rank the solutions (Gonzalez-Garay and Guillen-Gosalbez, 2018).

Table C2. Multi-objective decision-making techniques used in the methods.

Optimization method	Used in[1]
Fuzzy MOO	[R16]
ε–constraint method	[R11, R30]
Grid-search method	[R10]
TOPSIS or FUCA	[R2, R32]
MIBLFP[2]	[R13]
MOGA[3]	[R7]
MOGA followed by DEA	[R3]

[1] *See Supplementary Material Table A3 for list of references.*
[2] *Mixed-integer bilevel linear fractional program.*
[3] *Multi-Objective Genetic Algorithms.*

Abbreviations

AHDM *ad-hoc* decision-making; AHP Analytic Hierarchy Process; ANP Analytic Network Process; CC *Capital Costs*; CMADM compensatory multi-attribute decision-making; CO *Community*; DEA Data Envelopment Analysis; DEMATEL Decision-Making Trial and Evaluation Laboratory; ED *Ecosystem Depletion*; EE *Energy Efficiency*; EWL *Employee Working and Living*; EX *Exergy Analysis*; FAHP Fuzzy Analytic Hierarchy Process; FANP Fuzzy Analytic Network Process; HR *Health Risk*; IA *Impact on Air*; IS *Impact on Soil*; IW *Impact on Water*; MCDM multiple-criteria decision-making; ME *Material Efficiency*; MODM multi-objective decision-making; MOGA Multi-Objective Genetic Algorithms; MOO multi-objective; OMADM outranking multi-attribute decision-making; OP *Operational Performance*; OSH *Occupational Safety and Health*; PC *Processing Costs*; PCA principal components analysis; PF *Profit*; PSE process systems engineering; RE *Reaction Efficiency*; RM *Renewable Materials*; SHS social, health and safety; SR *Safety Risk*; TBL triple bottom line; UC *Utility Costs*; WC *Waste Costs*; WG *Waste Generation*; WU *Water Use*.

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APPENDIX B - NEW SS-UOE ALGORITHM FOR SUPERSONIC SEPARATOR DESIGN AND SIMULATION

New SS-UOE algorithm considers isentropic expansion/compression steps ($\eta^{EXP}\%=\eta^{CMP}\%=100\%$). For lower adiabatic efficiencies, the pertinent modifications are discussed elsewhere (Arinelli et al., 2019). Mach-Tolerance=$\delta_M\approx 10^{-3}$, Length-Tolerance=$\delta_L\approx 10^{-3}$m.

[P1] Input Data and Feed Handling. F^{Feed}, T^{Feed}, P^{Feed} and $\underline{Z}^{Feed}$ are rescued from SS feed in HYSYS. D_I, D_O, α, β, Ma^{Shock} are entered via SS-UOE property-window. Calculate M_M^{Feed} and $q^{Feed}=F^{Feed}.M_M^{Feed}$. Feed flow properties are obtained via *Flash(P,T)* for feed stream in Eq. (B.1). Transition from stagnated feed to non-stagnated SS inlet is done via a KHS-Bridge iterating Eqs. (B.2)-(B.5). SS inlet flow properties are defined in Eqs. (B.6)-(B.10) for $(T^{Inlet},P^{Inlet},\underline{Z}^{Inlet})$.

$$Flash\ (P^{Feed},T^{Feed},\underline{Z}^{Feed})\longrightarrow \bar{H}^{Feed},\bar{S}^{Feed},\rho^{Feed} \tag{B.1}$$

---------------------- *Newton-Raphson Block Begins* ----------------

Iterate on (T^{Inlet},P^{Inlet}) until (B.4)≈0 & (B.5)≈0

$$Flash\ (P^{Inlet},T^{Inlet},\underline{Z}^{Feed})\longrightarrow \bar{H}(P^{Inlet},T^{Inlet},\underline{Z}^{Feed}),\bar{S}(P^{Inlet},T^{Inlet},\underline{Z}^{Feed}),\rho(P^{Inlet},T^{Inlet},\underline{Z}^{Feed}) \tag{B.2}$$

Calculate

$$v^{Inlet}(T^{Inlet},P^{Inlet})=\frac{4q^{Feed}}{\pi D_I^2\rho\left(T^{Inlet},P^{Inlet},\underline{Z}^{Feed}\right)} \tag{B.3}$$

$$\bar{H}\left(T^{Inlet},P^{Inlet},\underline{Z}^{Feed}\right)+M_M^{Feed}\,\frac{\left(v^{Inlet}(T^{Inlet},P^{Inlet})\right)^2}{2}-\bar{H}^{Feed} \tag{B.4}$$

$$\bar{S}\left(T^{Inlet},P^{Inlet},\underline{Z}^{Feed}\right)-\bar{S}^{Feed} \tag{B.5}$$

---------------------- *Newton-Raphson Block Ends* -------------------

$$M_M^{Inlet}=M_M^{Feed}\ ,\ \underline{Z}^{Inlet}=\underline{Z}^{Feed}\ ,\ \rho^{Inlet}=\rho(T^{Inlet},P^{Inlet},\underline{Z}^{Inlet}) \tag{B.6}$$

$$\bar{H}^{Inlet}=\bar{H}\left(T^{Inlet},P^{Inlet},\underline{Z}^{Inlet}\right),\ \bar{S}^{Inlet}=\bar{S}\left(T^{Inlet},P^{Inlet},\underline{Z}^{Inlet}\right) \tag{B.7}$$

$$q^{Inlet}=q^{Feed}\ ,\ F^{Inlet}=F^{Feed}\ ,\ v^{Inlet}=\frac{4q^{Inlet}}{\pi D_I^2\rho^{Inlet}},\bar{K}^{Inlet}=M_M^{Inlet}\,\frac{{v^{Inlet}}^2}{2} \tag{B.8}$$

$$PEC-UOE\ (P^{Inlet},T^{Inlet},\underline{Z}^{Inlet})\xrightarrow{Multiphase\ c} c^{Inlet} \tag{B.9}$$

$$\bar{E}^{Inlet}=\bar{H}^{Inlet}+\bar{K}^{Inlet}\ ,\ Ma^{Inlet}=v^{Inlet}/c^{Inlet} \tag{B.10}$$

[P2] Subsonic Expansion. Solved by successive small isentropic expansions (index *n*) in the converging section from inlet state until $Ma=1$, defining the throat diameter D_T. Expansion-Step δ_P ($\leq 10^4 Pa$) is manipulated. Eqs. (B.11)-(B.13) are initializations. Eqs. (B.14)-(B.18) are iterated.

$$n=0,\quad x^{(0)}=0,\ \ P^{(0)}=P^{Inlet},\ \ T^{(0)}=T^{Inlet} \tag{B.11}$$

$$D^{(0)}=D_I\ ,\ \ v^{(0)}=v^{Inlet}\ ,\ \ \delta_P=10^4\,Pa \tag{B.12}$$

$$\bar{K}^{(0)}=\bar{K}^{Inlet},\ \bar{H}^{(0)}=\bar{H}^{Inlet},\ c^{(0)}=c^{Inlet},\ Ma^{(0)}=Ma^{Inlet} \tag{B.13}$$

---------------------- *Loop Begins* ------------------

$$n\equiv n+1,\quad P^{(n)}\equiv P^{(n-1)}-\delta_P \tag{B.14}$$

$$Flash\ (P^{(n)},\bar{S}^{Inlet},\underline{Z}^{Inlet})\longrightarrow T^{(n)},\bar{H}^{(n)},\rho^{(n)} \tag{B.15}$$

$$PEC-UOE\ (P^{(n)},T^{(n)},\underline{Z}^{Inlet})\xrightarrow{Multiphase\ c} c^{(n)} \tag{B.16}$$

$$\bar{K}^{(n)}=\bar{E}^{Inlet}-\bar{H}^{(n)},\ \ v^{(n)}=\sqrt{2.\bar{K}^{(n)}/M_M^{Inlet}} \tag{B.17}$$

$$Ma^{(n)}=v^{(n)}/c^{(n)}\ ,\ D^{(n)}=\sqrt{4q^{Inlet}/(\pi.v^{(n)}.\rho^{(n)})} \tag{B.18}$$

---------------------- *Loop Ends* -------------------

$$D_T=D^{(n)} \tag{B.19}$$

$$if\ \ 1-\delta_M\leq Ma^{(n)}\leq 1+\delta_M\ \ \longrightarrow Stop \tag{B.20}$$

[P3] SS Converging-Section Geometry. With D_T, Eqs. (B.21)-(B.22) determinate SS converging-length and axial locations of diameters in [P2].

$$L_C=\frac{D_I-D_T}{2.\tan\alpha} \tag{B.21}$$

$$For\ all\ D^{(k)}\ (k=1\rightarrow n)\ calculate\quad x^{(k)}=L_C-\frac{D^{(k)}-D_T}{2.\tan\alpha} \tag{B.22}$$

[P4] Supersonic Expansion. Solved by successive small isentropic expansions (index *n*) in the Laval diverging-section from the throat until $Ma=Ma^{Shock}$. Expansion-Step δ_P ($\leq 10^4Pa$) is manipulated. Eq. (B.23) is initialization. Eqs. (B.24)-(B.30) are iterated. Eq. (B.31) defines the Laval-end state (T^{Laval},P^{Laval},Ma^{Shock}). Eq. (B.32) finishes Laval geometry.

$$\delta_P = 10^4\,Pa \tag{B.23}$$

---------------------- *Loop Begins* -----------------

$$n \equiv n+1, \quad P^{(n)} \equiv P^{(n-1)} - \delta_P \tag{B.24}$$

$$Flash\ (P^{(n)}, \bar{S}^{Inlet}, \underline{Z}^{Inlet}) \longrightarrow T^{(n)}, \bar{H}^{(n)}, \rho^{(n)} \tag{B.25}$$

$$PEC-UOE\ (P^{(n)}, T^{(n)}, \underline{Z}^{Inlet}) \xrightarrow{Multiphase\ c} c^{(n)} \tag{B.26}$$

$$\bar{K}^{(n)} = \bar{E}^{Inlet} - \bar{H}^{(n)}, \quad v^{(n)} = \sqrt{2.\bar{K}^{(n)} / M_M^{Inlet}} \tag{B.27}$$

$$Ma^{(n)} = v^{(n)} / c^{(n)}\ , \ D^{(n)} = \sqrt{4q^{Inlet} / (\pi.v^{(n)}.\rho^{(n)})} \tag{B.28}$$

$$x^{(n)} = L_C + \frac{D^{(n)} - D_T}{2.\tan\beta} \tag{B.29}$$

$$if\ Ma^{(n)} > Ma^{Shock} + \delta_M \rightarrow \mathrm{Re}duce\ \delta_P,\ n \equiv n-1, Execute\ Eqs.(A.24)\ to\ (A.30) \tag{B.30}$$

---------------------- *Loop Ends* -------------------

$$T^{Laval} = T^{(n)},\ P^{Laval} = P^{(n)},\ v^{Shock} = v^{(n)} \tag{B.31}$$

$$D_D = D^{(n)}, L_D = \frac{D_D - D_T}{2.\tan\beta}\ ,\ L^{Laval} = L_C + L_D \tag{B.32}$$

$$if\ \ Ma^{Shock} - \delta_M \le Ma^{(n)} \le Ma^{Shock} + \delta_M\ \rightarrow Stop \tag{B.33}$$

[P5] Two-Phase Condensate-Collector: Liquid-collector geometry is defined in Eq. (B.34). Collector length with constant flow-section ($L^{Collector}$) is calculated for $\Delta t_R^{Collector} = 1\,ms$ residence-time (changeable by user). Likewise, the collector annulus (*d*) has default of *2mm* (changeable by user). $Flash(P^{Laval},T^{Laval},\underline{Z^{Inlet}})$ is invoked at x=L^{Laval}+$L^{Collector}$ in Eq. (B.35), obtaining vapor properties and flows. Eqs. (B.36)-(B.37) define the collector annulus area-fraction to give the fraction of vapor accompanying the liquid. Flow rates of vapor kept in SS as working-fluid and of two-phase condensate are calculated via Eqs. (B.38)-(B.39). Eq. (B.40) determines condensate molar fractions vector used in Eq. (B.41) for attaining L+V condensate properties via $Flash(P^{Laval},T^{Laval},\underline{Z}_{L+V})$. Eq. (B.42) calculates velocities of vapor and L+V condensate both equal to v^{Shock}, determined in Eq. (B.31) at x=L^{Laval}.

$$L^{Collector} = v^{Shock}.\Delta t_R^{Collector}\ ,\ d = 2.10^{-3} m \qquad (B.34)$$

$$Flash\ (P^{Shock}, T^{Shock}, \underline{Z}^{Inlet}) \rightarrow F_V, \underline{Y}, \rho_V, \bar{H}_V, \bar{S}_V, M_{M,V} \qquad (B.35)$$

$$A^{CollectorAnnulus} = \frac{\pi \left\lfloor D_D^2 - (D_D - 2d)^2 \right\rfloor}{4} \qquad (B.36)$$

$$prop_V = \frac{A^{CollectorAnnulus}}{A_D} = \frac{D_D^2 - (D_D - 2d)^2}{D_D^2} \qquad (B.37)$$

$$F_V = F_V.(1 - prop_V) \qquad (B.38)$$

$$F_{L+V} = F^{Inlet} - F_V \qquad (B.39)$$

$$\underline{Z}_{L+V} = \frac{\underline{Z}^{Inlet}.F^{Inlet} - \underline{Y}.F_V}{F_{L+V}} \qquad (B.40)$$

$$Flash\ (P^{Laval}, T^{Laval}, \underline{Z}_{L+V}) \rightarrow \rho_{L+V}, \bar{H}_{L+V}, \bar{S}_{L+V}, M_{M,L+V} \qquad (B.41)$$

$$v_V = v_{L+V} = v^{Shock} \qquad (B.42)$$

[P6] Normal Shock Preparation. Properties just-before-shock-after-condensate-withdrawal (*BS*) are recovered from the remaining SS vapor via Eqs. (B.43)-(B.46), while the *BS* diameter is calculated discounting the collector annulus. Eqs. (B.47)-(B.49) consolidate *BS* flow properties.

$$P_{BS} \equiv P^{Laval}\ ,\ T_{BS} \equiv T^{Laval}\ ,\ D_{BS} = D_D - 2d \qquad (B.43)$$

$$M_{MBS} = M_{M,V}\ ,\ \bar{H}_{BS} = \bar{H}_V\ ,\ \bar{S}_{BS} = \bar{S}_V \qquad (B.44)$$

$$\underline{Z}_{BS} = \underline{Y}\ ,\ v_{BS} = v_V\ ,\ \rho_{BS} = \rho_V \qquad (B.45)$$

$$F_{BS} = F_V\ ,\ q_{BS} = F_{BS}.M_{MBS} \qquad (B.46)$$

$$PEC-UOE\ (P_{BS}, T_{BS}, \underline{Z}_{BS}) \xrightarrow{Multiphase\ c} c_{BS} \qquad (B.47)$$

$$Ma_{BS} = v_{BS} / c_{BS} \qquad (B.48)$$

$$\bar{K}_{BS} = M_{MBS}.v_{BS}^2 / 2\ ,\ \bar{E}_{BS} = \bar{K}_{BS} + \bar{H}_{BS} \qquad (B.49)$$

[P7] Normal Shock. Eq. (B.50) checks Ma_{BS} for supersonic flow after condensate withdrawal. If so, shock is solved via mass/energy/momentum balances for after-shock temperature (T_{AS}), pressure (P_{AS}) and velocity (v_{AS}). $Flash(P_{AS},T_{AS})$ provides after-shock properties $\bar{H}, \rho$ in Eq. (B.51). v_{AS} is eliminated via Eq. (B.52), giving Eqs. (B.53)-(B.54) for (T_{AS},P_{AS}). Newton-Raphson Method solves Eqs. (B.53)-(B.54) numerically. Eqs. (B.55)-(B.60) calculate single-phase after-shock properties.

$$if\ \ Ma_{BS} \le 1 \ \longrightarrow\ T_{AS} = T_{BS}\ ,\ P_{AS} = P_{BS}\ ,\ v_{AS} = v_{BS}\ ,\ \ Go\ to\ Eq.(A.55) \tag{B.50}$$

---------------------- *Newton-Raphson Block Begins* ----------------

Iterate on (T_{AS},P_{AS}) *until (B.53)≈0 & (B.54)≈0*

$$Flash\ (P_{AS}, T_{AS}, \underline{Z}_{BS}) \longrightarrow \bar{H}(P_{AS}, T_{AS}, \underline{Z}_{BS}),\ \rho(P_{AS}, T_{AS}, \underline{Z}_{BS}) \tag{B.51}$$

Calculate

$$v_{AS}(T_{AS}, P_{AS}) = \frac{4q_{BS}}{\pi D_{BS}^2\, \rho(T_{AS}, P_{AS}, \underline{Z}_{BS})} \tag{B.52}$$

$$\bar{H}(T_{AS}, P_{AS}, \underline{Z}_{BS}) + M_{MBS} \frac{(v_{AS}(T_{AS}, P_{AS}))^2}{2} - \bar{H}_{BS} - \bar{K}_{BS} \tag{B.53}$$

$$\rho(T_{AS}, P_{AS}, \underline{Z}_{BS}).(v_{AS}(T_{AS}, P_{AS}))^2 + P_{AS} - \rho_{BS} v_{BS}^2 - P_{BS} \tag{B.54}$$

---------------------- *Newton-Raphson Block Ends* --------------------

$$M_{MAS} = M_{MBS}\ ,\ \underline{Z}_{AS} = \underline{Z}_{BS}\ ,\ \rho_{AS} = \rho(T_{AS}, P_{AS}, \underline{Z}_{AS}) \tag{B.55}$$

$$\bar{H}_{AS} = \bar{H}(T_{AS}, P_{AS}, \underline{Z}_{AS})\ ,\ \bar{S}_{AS} = \bar{S}(T_{AS}, P_{AS}, \underline{Z}_{AS}) \tag{B.56}$$

$$PEC-UOE\ (P_{AS}, T_{AS}, \underline{Z}_{AS}) \xrightarrow{Single-Phase\ c} c_{AS} \tag{B.57}$$

$$q_{AS} = q_{BS}\ ,\ F_{AS} = F_{BS}\ \ ,\ D_{AS} = D_{BS}\ \ ,\ v_{AS} = \frac{4q_{AS}}{\pi D_{AS}^2 \rho_{AS}} \tag{B.58}$$

$$\bar{K}_{AS} = M_{MAS} \frac{v_{AS}^2}{2}\ \ ,\ \ \bar{E}_{AS} = \bar{H}_{AS} + \bar{K}_{AS} \tag{B.59}$$

$$Ma_{AS} = v_{AS} / c_{AS}\ \ \ ,\ \ \ \Delta\bar{S}^{Shock} = \bar{S}_{AS} - \bar{S}_{BS} \tag{B.60}$$

[P8] Subsonic Compression. Diffuser subsonic compression is accomplished by successive small isentropic compressions (index *n*) from $x=L^{Laval}+L^{Collector}$ to $x=L$. Compression-Step δ_P ($\le 2.10^3 Pa$) is manipulated. Eqs. (B.61)-(B.63) are initializations. Eqs. (B.64)-(B.71) are sequentially iterated. Eqs. (B.72)-(B.74) define SS outlet conditions at $x=L$.

$$n = n+1,\ \ x^{(n)} = L^{Laval} + L^{Collector}\ ,\ L^{Diffuser} = \frac{D_O - D_{AS}}{2.\tan\beta}\ ,\ \ L = L^{Laval} + L^{Collector} + L^{Diffuser} \tag{B.61}$$

$$P^{(n)} = P_{AS}\ ,\ \ T^{(n)} = T_{AS},\ \ D^{(n)} = D_{AS}\ \ ,\ \ v^{(n)} = v_{AS}\ \ ,\ \ \delta_P = 2.10^3 Pa \tag{B.62}$$

$$\bar{K}^{(n)} = \bar{K}_{AS}\ ,\ \bar{H}^{(n)} = \bar{H}_{AS}\ ,\ c^{(n)} = c_{AS}\ ,\ Ma^{(n)} = Ma_{AS} \tag{B.63}$$

---------------------- *Loop Begins* -----------------

$$n \equiv n+1,\ \ \ P^{(n)} \equiv P^{(n-1)} + \delta_P \tag{B.64}$$

$$Flash\ (P^{(n)}, \bar{S}_{AS}, \underline{Z}_{AS}) \xrightarrow{Single-Phase\ \ Prop.} T^{(n)}, \bar{H}^{(n)}, \rho^{(n)} \tag{B.65}$$

$$PEC-UOE\ (P^{(n)}, T^{(n)}, \underline{Z}_{AS}) \xrightarrow{Single-Phase\ c} c^{(n)} \tag{B.66}$$

$$\bar{K}^{(n)} = \bar{E}_{AS} - \bar{H}^{(n)},\ \ v^{(n)} = \sqrt{2.\bar{K}^{(n)} / M_{MAS}} \tag{B.67}$$

$$Ma^{(n)} = v^{(n)} / c^{(n)},\ D^{(n)} = \sqrt{4q_{AS} / (\pi . v^{(n)} . \rho^{(n)})} \tag{B.68}$$

$$x^{(n)} = L_C + \frac{D^{(n)} - D_T}{2.\tan\beta} \tag{B.69}$$

$$if\ \ x^{(n)} < L - \delta_L \rightarrow \text{Re}vise\ \delta_P\ with\ x^{(n)}, Execute\ Eqs.(A.64)\ to\ (A.71) \tag{B.70}$$

$$if\ \ x^{(n)} > L + \delta_L \rightarrow \text{Re}duce\ \delta_P\ ,\ n \equiv n - 1,\ Execute\ Eqs.(A.64)\ to\ (A.71) \tag{B.71}$$

---------------------- *Loop Ends* --------------------

$$P^{Outlet} = P^{(n)},\ T^{Outlet} = T^{(n)} \tag{B.72}$$

$$\bar{H}^{Outlet} = \bar{H}^{(n)}\ \ ,\ \ \bar{S}^{Outlet} = \bar{S}_{AS} \tag{B.73}$$

$$v^{Outlet} = v^{(n)},\ Ma^{Outlet} = Ma^{(n)} \tag{B.74}$$

$$if\ \ L - \delta_L \le x^{(n)} \le L + \delta_L \xrightarrow{\quad} Stop \tag{B.75}$$

[P9] Gas Finishing Procedures. KHS-Bridge solves transition from SS outlet to stagnated Gas-Product in Eqs. (B.76)-(B.78). Eq. (B.80) creates Gas-Product stream in HYSYS.

---------------------- *Newton-Raphson Block Begins* ----------------

Iterate on (T_{AS},P_{AS}) *until (B.77)≈0 & (B.78)≈0*

$$Flash\ (P^{Gas-Product}, T^{Gas-Product}, \underline{Z}_{AS}) \xrightarrow{\quad} \bar{H}(P^{Gas-Product}, T^{Gas-Product}, \underline{Z}_{AS}), \bar{S}(P^{Gas-Product}, T^{Gas-Product}, \underline{Z}_{AS}) \tag{B.76}$$

Calculate

$$\bar{H}\left(T^{Gas-Product}, P^{Gas-Product}, \underline{Z}_{AS}\right) - M_{MAS}\frac{v^{Outlet^2}}{2} - \bar{H}^{Outlet} \tag{B.77}$$

$$\bar{S}\left(T^{Gas-Product}, P^{Gas-Product}, \underline{Z}_{AS}\right) - \bar{S}^{Outlet} \tag{B.78}$$

---------------------- *Newton-Raphson Block Ends* --------------------

$$Z^{Gas-Product} = \underline{Z}_{AS}\ ,\ F^{Gas-Product} = F_{AS} \tag{B.79}$$

$$Gas\text{-}Product\ to\ HYSYS:\ F^{Gas-Product}, T^{Gas-Product}, P^{Gas-Product}, \underline{Z}^{Gas-Product} \tag{B.80}$$

[P10] Condensate Shock Preparation. Properties before condensate shock are recovered from L+V condensate via Eq. (B.81)-(B.84). Eqs. (B.85)-(B.87) consolidate before-condensate-shock flow properties.

$$P_{BCS} \equiv P^{Laval}\ \ ,\ \ T_{BCS} \equiv T^{Laval}\ , A_{BCS} = A^{CollectorAnnulus} \tag{B.81}$$

$$M_{MBCS} = M_{M,L+V}\ \ ,\ \ \bar{H}_{BCS} = \bar{H}_{L+V}\ ,\ \ \bar{S}_{BCS} = \bar{S}_{L+V} \tag{B.82}$$

$$\underline{Z}_{BCS} = \underline{Z}_{L+V}\ \ ,\ \ v_{BCS} = v_{L+V}\ \ ,\ \ \rho_{BCS} = \rho_{L+V} \tag{B.83}$$

$$F_{BCS} = F_{L+V}\ \ ,\ q_{BCS} = F_{BCS}.M_{MBCS} \tag{B.84}$$

$$PEC - UOE\ (P_{BCS}, T_{BCS}, \underline{Z}_{BCS}) \xrightarrow{Multiphase\ c} c_{BCS} \tag{B.85}$$

$$Ma_{BCS} = v_{BCS} / c_{BCS} \tag{B.86}$$

$$\bar{K}_{BCS} = M_{MBCS}.v_{BCS}^2 / 2 \tag{B.87}$$

[P11] Condensate Shock. Eq. (B.88) checks *Ma_{BCS}* for condensate supersonic flow. If so, multiphase-shock is solved via mass/energy/momentum balances for after-condensate-shock temperature (T_{ACS}), pressure (P_{ACS}) and velocity (v_{ACS}). *Flash(P_{ACS},T_{ACS})* provides after-condensate-shock properties $\bar{H}, \rho$ in Eq. (B.89). v_{ACS} is eliminated via Eq. (B.90), giving Eqs. (B.91)-(B.92) for (T_{ACS},P_{ACS}). Newton-Raphson Method solves Eqs. (B.91)-(B.92) numerically. Eqs. (B.93)-(B.97) calculate after-condensate-shock flow properties.

$$if\ \ Ma_{BCS} \le 1 \ \longrightarrow\ T_{ACS} = T_{BCS}\ ,\ P_{ACS} = P_{BCS}\ ,\ v_{ACS} = v_{BCS}\ ,\ \ Go\ to\ Eq.(A.93) \tag{B.88}$$

----------------------- Newton-Raphson Block Begins -----------------

Iterate on (T_{ACS},P_{ACS}) until (B.91)≈0 & (B.92)≈0

$$Flash\ (P_{ACS}, T_{ACS}, \underline{Z}_{BCS}) \longrightarrow \bar{H}(P_{ACS}, T_{ACS}, \underline{Z}_{BCS}),\ \rho(P_{ACS}, T_{ACS}, \underline{Z}_{BCS}) \tag{B.89}$$

Calculate

$$v_{ACS}(T_{ACS}, P_{ACS}) = \frac{q_{BCS}}{A_{BCS}\,\rho\left(T_{ACS}, P_{ACS}, \underline{Z}_{BCS}\right)} \tag{B.90}$$

$$\bar{H}\left(T_{ACS}, P_{ACS}, \underline{Z}_{BCS}\right) + M_{MBCS}\,\frac{\left(v_{ACS}(T_{ACS}, P_{ACS})\right)^2}{2} - \bar{H}_{BCS} - \bar{K}_{BCS} \tag{B.91}$$

$$\rho\left(T_{ACS}, P_{ACS}, \underline{Z}_{BCS}\right).\left(v_{ACS}(T_{ACS}, P_{ACS})\right)^2 + P_{ACS} - \rho_{BCS} v_{BCS}^2 - P_{BCS} \tag{B.92}$$

----------------------- Newton-Raphson Block Ends --------------------

$$M_{MACS} = M_{MBCS}\ ,\ \underline{Z}_{ACS} = \underline{Z}_{BCS}\ ,\ \rho_{ACS} = \rho(T_{ACS}, P_{ACS}, \underline{Z}_{ACS}) \tag{B.93}$$

$$\bar{H}_{ATPS} = \bar{H}\left(T_{ACS}, P_{ACS}, \underline{Z}_{ACS}\right)\ ,\ \ \bar{S}_{ACS} = \bar{S}\left(T_{ACS}, P_{ACS}, \underline{Z}_{ACS}\right) \tag{B.94}$$

$$PEC-UOE\ (\,P_{ACS}, T_{ACS}, \underline{Z}_{ACS}\,) \xrightarrow{Multiphase\ c} c_{ACS} \tag{B.95}$$

$$q_{ACS} = q_{BCS}\ ,\ F_{ATPS} = F_{BCS}\ \ ,\ A_{ACS} = A_{BCS}, v_{ACS} = \frac{q_{ACS}}{A_{ACS}\rho_{ACS}} \tag{B.96}$$

$$\bar{K}_{ACS} = M_{MACS}\,\frac{v_{ACS}^2}{2}\ \ ,Ma_{ACS} = v_{ACS} \,/\, c_{ACS} \tag{B.97}$$

[P12] Condensate Finishing Procedures. Eq. (B.98) retrieves after-condensate-shock data of $L+V$ condensate. Eqs. (B.99)-(B.100) execute condensate stagnation at constant pressure and total molar energy obtaining Condensate-Product temperature. Eq. (B.101) creates Condensate-Product stream in HYSYS.

$$P^{Cond-Product} = P_{ACS}\ ,\ \underline{Z}^{Cond-Product} = \underline{Z}_{ACS}\ \ ,\ F^{Cond-Product} = F_{ACS} \tag{B.98}$$

$$\bar{H}^{Cond-Product} = \bar{H}_{ACS} + \bar{K}_{ACS} \tag{B.99}$$

$$Flash\ (\,P^{Cond-Product}, \bar{H}^{Cond-Product}, \underline{Z}^{Cond-Product}\,) \longrightarrow T^{Cond-Product} \tag{B.100}$$

$$Condensate\text{-}Product\ to\ HYSYS:\ \ F^{LiqProduct}, T^{Cond-Product}, P^{Cond-Product}, \underline{Z}^{Cond-Product} \tag{B.101}$$

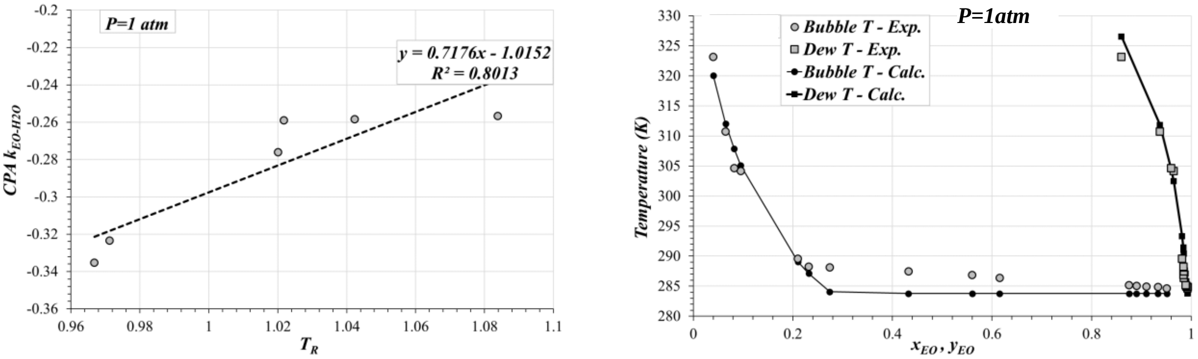
APPENDIX C – CALIBRATION OF EO-H_2O BINARY INTERACTION PARAMETER OF CUBIC-PLUS-ASSOCIATION EQUATION-OF-STATE (CPA-EOS)

CPA-EOS EO-H_2O binary interaction parameter $k_{EO\text{-}H2O}$ was calibrated with EO-H_2O VLE data of Coles and Popper (1950) (Table C.1). Individual CPA-EOS $k_{EO\text{-}H2O}$ values for EO-H_2O were found to match the experimental bubble-point and dew-point data at $P=1\ atm$ in Table C.1, excluding high %mol EO points which lie out of the liquid composition range of interest ($x_{H2O} \geq 0.75$). Temperature dependence of $k_{EO\text{-}H2O}$ was fitted in Eq. (C.1). Fig. C.1 shows the fitting of Eq. (C.1) giving $A_{EO\text{-}H2O}=-1.0152$, $B_{EO\text{-}H2O}=0.7176$ with $R^2=0.80$. Fig. C.2 exhibits the *T*-*x*-*y* diagram for EO-H_2O VLE at 1 atm, displaying experimental data and predictions with adjusted CPA-EOS. Discrepant bubble-points are out of the range of interest ($x_{H2O} \geq 0.75$).

$$k_{EO-H2O} = A_{EO-H2O} + B_{EO-H2O} T_R \quad , \quad T_R = T(K)/298.15 \tag{C.1}$$

Table C.1. Coles & Popper (1950) EO-H_2O VLE data ($P=1\ atm$) and calculated CPA-EOS $k_{EO\text{-}H2O}$.

Temperature (K)	*Liquid EO Mol-Fraction (x_{EO})*	*Vapor EO Mol-Fraction (y_{EO})*	*Adjusted $k_{EO\text{-}H2O}$*
284.65	0.9510	0.9927	--
284.95	0.9100	0.9900	--
285.15	0.8750	0.9888	--
286.35	0.6150	0.9833	--
286.85	0.5600	0.9845	--
287.45	0.4320	0.9853	--
288.15	0.2740	0.9845	--
288.25	0.2320	0.9841	-0.3353
289.55	0.2100	0.9816	-0.3235
304.15	0.0950	0.9648	-0.276
304.65	0.0820	0.9595	-0.259
310.75	0.0650	0.9370	-0.2585
323.15	0.0400	0.8600	-0.2567



(a) (b)

Figure C.1. (a) CPA-EOS $k_{EO\text{-}H2O}$ vs T_R; (b) EO-H$_2$O T-x_{EO}-y_{EO} diagram via fitted CPA-EOS vs data.

APPENDIX D – ECONOMIC ASSESSMENT

FCI (*MMUSD*) is estimated via Turton et al. (2019), with *Six-Tenths Rule* extrapolation for capacities out of correlation range. *COM (MMUSD/y*) is estimated with Eq. (D.1), where *COL*, *CRM*, *CUT*, *CWT* are annual costs (*MMUSD/y*) of labor, raw-materials, utilities and waste-treatment, respectively. Gross annual-profit (*GAP,MMUSD/y*), annual-profit (*AP,MMUSD/y*) and *NPV (MMUSD*) follow in Eqs. (D.2a)-(D.2c), where *ITR*, *DEPR*, *N* and *i* are income tax-rate (%), annual depreciation (*MMUSD/y*), horizon (years) and annual interest-rate (%), respectively. Table D.1 lists economic assumptions.

$$COM = 0.18 * FCI + 2.73 * COL + 1.23 * (CRM + CUT + CWT) \tag{D.1}$$

$$GAP = REV - COM \tag{D.2a}$$

$$\begin{cases} AP = GAP - (ITR / 100) * (GAP - DEPR) & (GAP > DEPR) \\ AP = GAP & (GAP \le DEPR) \end{cases} \tag{D.2b}$$

$$NPV = -\left(0.2 + 0.3 * q^{-1} + 0.5 * q^{-2} \right) FCI + AP \left\{ \sum_{k=3}^{N+3} q^{-k} \right\} \ , q \equiv (1 + i / 100) \tag{D.2c}$$

Table D.1. Economic assumptions.

Assumption	*Subject*	*Description*
{E1}	*FCI (USD)*	*FCI extrapolation: Six-Tenths rule;* *SS@21bar: via capacity/pressure extrapolations from* FCI^{SS}*@80bar, 6MMSm³/d (Machado et al., 2012).*
{E2}	*COM (USD/y)*	$CUT^{CW}=F^{CW,Make\text{-}up}$*(t/y)*(0.03USD/t);* $CUT^{Electricity}$*=Power(MWh/y)*(70USD/MWh);* $CRM^{Water}=F^{Water,Make\text{-}up}$*(kg/y)*(11USD/t);* $CRM^{Ethylene}=F^{Ethylene}$*(t/y)*(360USD/t).*
{E3}	*Prices (USD/t)*	*EO=2,000USD/t;* CO_2*=7USD/t;* C_2H_4*=360USD/t*
{E4}	*Parameters*	*N=20 years; Construction: 2 years, 20%+30%/50% FCI allocation;* *i=10%; ITR=34%; Operation=8322h/y; CEPCI=574 (Sept, 2017).* *DEPR(USD/y)=10%FCI(USD); Working-Capital(USD)=5%FCI(USD).*

APPENDIX E – CHAPTER V SUPPLEMENTARY MATERIALS

Screening biorefinery pathways to biodiesel, green-diesel and propylene-glycol: A hierarchical assessment of process sustainability

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SUPPLEMENTARY MATERIALS

PART EI. S-PSE Indicators
Tables EI-1, EI-2, EI-3, EI-4, EI-5.

PART E-II. Data Used to Calculate Case Study Indicators
Tables EII-1, EII-2.

PART E-III. Statistical Screening of Indicators
Tables EIII-1, EIII-2.

Abbreviations

CITC Corrected Item-Total Correlations; FAME Fatty Acid Methyl Esters; H&S Health and Safety; LCA Life-Cycle Assessment; PCA Principal Component Analysis; PR-EOS Peng-Robinson Equation-of-State; SDG Sustainable Development Goal; S-PSE Sustainable Process Systems Engineering; TAG triacylglycerol.

PART EI. S-PSE Indicators

Table EI-1. S-PSE *Environment* indicators for first-level (*SPWI*) and second-level (*SOHI*) assessment

Indicator	**Calculation**[a]	**Unit**	***SPWI***	***SOHI***	**Best**[b]
Gate-to-Gate Sub-Dimension					
Global-Warming (*GWP*)[c,d]	$GWP = \sum_i \left(m_{out,i}\ CF_i^{GWP} \right) + \sum_k \left(E_k\ C_f\ EF \right)$	$kgCO_2e$	x	x	Min
Ozone-Depletion (*ODP*)[d]	$ODP = \sum_i \left(m_{out,i}\ CF_i^{ODP} \right)$	*kgCFC11e*	x	x	Min
Aquatic-Ecotoxicity (*Ec*$_{aq}$)[d]	$Ec_{aq} = \sum_i \left(m_{out,i}\ CF_i^{Ec_{aq}} \right)$	$PAF.m^3d$	x	x	Min
Photochemical-Oxidation (*Smog*)[d]	$Smog = \sum_i \left(m_{out,i}\ CF_i^{smog} \right)$	$kgNO_xe$	x	x	Min
Atmospheric-Acidification (*Acid*)[d]	$Acid = \sum_i \left(m_{out,i}\ CF_i^{Acid} \right)$	$kgSO_2e$	x	x	Min
Aquatic-Eutrophication (*Eut*$_A$)[d]	$Eut_A = \sum_i \left(m_{out,i}\ CF_i^{Eut_A} \right)$	*kgNe*	x	x	Min
Renewability Material Index (*RMI*)[d]	$RMI = \sum_i CF_i^{RMI} \left(m_{in,i} / \sum_i m_{in,i} \right)$	*kg/kg*	x		Max
Hazardous-Waste (*HW*)[e]	$HW = \sum_i \left(m_{out,i}\ CF_i^{HW} \right)$	*kg/h*	x	x	Min
Cradle-to-Gate Sub-Dimension					
Cradle-to-Gate GWP (*CG-GWP*)[f]	*See note f*	$kgCO_2e$	x		Min
Land-Use (*LU*)[f]	*See note f*	$m^2 year$	x		Min
Cradle-to-Gate Eutrophication (*CG-Eu*)[f]	*See note f*	*kgPe*	x		Min
Cradle-to-Gate Acidification (*CG-Ac*)[f]	*See note f*	$kgSO_2e$	x		Min
Cradle-to-Gate Biodiversity-Loss (*CG-Bio*)[f]	*See note f*	*species-eq-lost year*	x		Min

[a] *Ruiz-Mercado et al. 2012. See list of symbols for equation variables meanings and units.*

[b] *Best stands for the indicator targeted goal to maximize sustainability, i.e. the reference point. For first-level assessment, it is set as the best target among all production-units; for second-level, it is the worst value among all unit-operations (opposite from the table).*

[c] *Calculation adapted from GREENSCOPE method* (Ruiz-Mercado et al., 2012).

[d] *Calculated using Life Cycle Impact Assessment (LCIA) methods. For GWP, there is also a term accounting for emissions from energy consumption.*

[e] *Calculated using LCIA logic, but considering CF as being equal to zero if the component is not classified as hazardous, and equal to one if it is.*

[f] *Cradle-to-gate feedstock-related indicators must be looked up in the literature; they are not calculated through this method.*

Table EI-2. S-PSE *Efficiency* indicators for first-level (*SPWI*) and second-level (*SOHI*) assessment

Indicator	**Calculation**[a]	**Unit**	***SPWI***	***SOHI***	**Best**[b]
Energy Sub-dimension					
Energy-Intensity (EI)	$EI = \sum_k \left(E_k\, C_f\right) / m_{prod}$	*J/kg*	x	x[c]	Min
Resource Energy-Efficiency (ηE)	$\eta \mathrm{E} = \dot{H}_{prod} / \dot{H}_{in}$	*J/J*	x		Max
Exergy-Destruction ($\Delta\dot{B}$)[d]	$\Delta\dot{B} = \dot{B}_{out} + \dot{B}_{out}^{W} - \dot{B}_{in} - \dot{B}_{in}^{W}$	*J/h*	x	x	Max
Product Exergy-Efficiency ($\eta\dot{B}_{prod}$)[d]	$\eta\dot{B}_{prod} = \dot{B}_{product} / (\dot{B}_{in} + \dot{B}_{in}^{W})$	*%*	x		Max
Water-Intensity (WI)[e]	$WI = (m_{in,water}\, \lambda) / m_{prod}$	*kg/kg*	x	x[c]	Min
Resource Exergy-Efficiency ($\eta\dot{B}$)[d]	$\eta\dot{B} = (\dot{B}_{out} + \dot{B}_{out}^{W}) / (\dot{B}_{in} + \dot{B}_{in}^{W})$	*%*	x		Max
Material Sub-dimension					
Material-Intensity (MI)	$MI = m_{in} / m_{prod}$	*kg/kg*	x	x[c]	Min
E-factor (E)	$E = (m_{in} - m_{prod}) / m_{prod}$	*kg/kg*	x		Min
Final-product concentration (C_{prod})	$C_{prod} = \sum_{\substack{i=product \\ F=prod\ stream}} \left(m_{i,F}\right) / m_{prod}$	*kg/kg*	x		Max
Solid-Waste Mass (m_s)[e]	$m_s = m_{s,waste}$	*kg/h*	x	x	Min
Reaction Molar-Efficiency (ηR)	$\eta \mathrm{R} = n_{r,prod} / \sum_i n_{r,in,i}$	*mol/mol*	x[f]	x	Max
Reaction-Yield (ε)	$\varepsilon = m_{r,prod} / m_{r\_theoretical,prod}$	*kg/kg*	x[f]	x	Max
Separation Mass-Productivity (SMP)	$SMP = m_{sep,prod} / \sum_F m_{sep\_in,F}$	*kg/kg*	x[f]	x	Max
Separation mass-loss index (SMLI)	$SMLI = \left(\sum_F m_{sep,in,F} / m_{sep,prod}\right) - 1$	*kg/kg*	x[f]	x	Min

[a] *Almost all taken from GREENSCOPE method* (Ruiz-Mercado et al., 2012). *See list of symbols for equation variables meanings and units.*

[b] *Best stands for the indicator targeted goal to maximize sustainability, i.e. the reference point. For first-level assessment (SPWI), it is set as the best target among all production-units; for second-level (SOHI), it is the worst value among all unit-operations (opposite from the table).*

[c] *Calculation for SOHI considers only the numerator (absolute value).*

[d] *Calculation taken from Teixeira et al. (2018).*

[e] *Calculation adapted from GREENSCOPE method* (Ruiz-Mercado et al., 2012).

[f] *For SPWI, it is considered as unit-operation average values.*

Table EI.3 S-PSE *H&S* indicators for first-level (*SPWI*) and second-level (*SOHI*) assessment

Indicator	Calculation[a]	Unit	*SPWI*	*SOHI*	Best[b]
Health Sub-Dimension					
Human Toxicity-cancer-effects ($HTox_c$)[c]	$HTox_c = \sum_i \left(m_{out,i}\ CF_i^{HTox_c}\right)$	*cases*	x	x	Min
Human Toxicity- non-cancer-effects ($HTox_{nc}$)[c]	$HTox_{nc} = \sum_i \left(m_{out,i}\ CF_i^{HTox_{nc}}\right)$	*cases*	x	x	Min
Hazardous-Input (Haz_{in})[d]	$Haz_{in} = \sum_i \left(m_{in,i}\ CF_i^{Haz}\right) / m_{prod}$	*kg/kg*	x	x[e]	Min
TRI-Input (TRI_{in})[d]	$TRI_{in} = \sum_i \left(m_{in,i}\ CF_i^{TRI}\right) / m_{prod}$	*kg/kg*	x	x[e]	Min
Acute-Toxicity (Acute)[f]	$Acute = \max_F \left[\sum_i \left(m_{i,F}\ IndVal_{i,F}^{Acute}\right)\right]$	*Unit*	x	x	Min
Irritation-Factor (Irrit)[g]	$Irrit = \max_F \left[\sum_i \left(IndVal_{i,F}^{Irrit}\right)\right]$	*Unit*	x		Min
Safety Sub-Dimension					
Particulate-Matter (PM)[c]	$PM = \sum_i \left(m_{out,i}\ CF_i^{PM}\right)$	*PM2.5e*	x	x	Min
Fire/explosion ($Fail_{F/E}$)[f]	$Fail_{F/E} = \max_F \left[\sum_i \left(m_{i,F}\ IndVal_{i,F}^{F/E}\right)\right]$		x	x	Min
Decomposition ($Fail_{R/D}$)[f]	$Fail_{R/D} = \max_F \left[\sum_i \left(m_{i,F}\ IndVal_{i,F}^{R/D}\right)\right]$		x	x	Min
Mobility (Mob)[f]	$Mob = \max_F \left[\sum_i \left(m_{i,F}\ IndVal_{i,F}^{Mob}\right)\right]$		x	x	Min

[a] *Almost all taken from GREENSCOPE method* (Ruiz-Mercado et al., 2012). *See list of symbols for equation variables meanings and units.*

[b] *Best stands for the indicator targeted goal to maximize sustainability, i.e. the reference point. For first-level assessment (SPWI), it is set as the best target among all production-units; for second-level (SOHI), it is the worst value among all unit-operations (opposite from the table).*

[c] *Calculated using Life Cycle Impact Assessment (LCIA) methods.*

[d] *Calculated using LCIA logic, but considering CF as being equal to zero if the component is not classified as hazardous or as a TRI substance, and equal to one if it is.*

[e] *Calculation for SOHI considers only the numerator (absolute value).*

[f] *Calculation taken from Koller et al. (2000) and Sugiyama et al. (2008) method that calculates the probability of release occurrence effects for each component in each process stream and then multiplies this probability by the component mass. The final value of each HS indicator is given by the maximum among all streams.*

[g] *For Irrit, we use a unit mass instead of $m_{i,F}$, i.e. 1 kg of substance i in stream F, because this health hazard is independent of the mass to which workers are exposed* (Sugiyama et al., 2008).

Table EI-4. S-PSE *Economic* indicators for first-level (*SPWI*) and second-level (*SOHI*) assessment

Indicator	**Calculation**[a]	**Unit**	***SPWI***	***SOHI***	**Best**[b]
Cost Sub-Dimension					
Raw-Materials Cost ($Cost_{RM}$)	*APEA*[c]	*MMUSD/y*	x		Min
Cost of Manufacturing (COM)	*APEA*[c]	*MMUSD/y*	x		Min
Fixed Capital Investment (FCI)	*APEA*[c]	*MMUSD*	x		Min
Profit Sub-Dimension					
Gross Annual-Profit (GAP)	$GAP = Rev - COM$	*MMUSD/y*	x		Max
Economic-potential (EP)	$EP = Rev - Cost_{RM} - Cost_{utility}$	*MMUSD/y*	x		Max

[a] *Almost all taken from GREENSCOPE method* (Ruiz-Mercado et al., 2012). *See list of symbols for equation variables meanings and units.*

[b] *Best stands for the indicator targeted goal to maximize sustainability, i.e. the reference point. For first-level assessment (SPWI), it is set as the best target among all production-units; for second-level (SOHI), it is the worst value among all unit-operations (opposite from the table).*

[c] *Values are obtained straight from Aspen Process Economic Analyser (APEA).*

Table EI-5. S-PSE indicators linkage to GRI Standards and Sustainable Development Goals (SDGs)

Indicator	*GRI linkage*[a]	*SDGs linkage*[b]
GWP	*305-1: Direct GHG Emissions* *305-2: Energy indirect GHG Emissions*	*3,12,13,14,15*
ODP	*305-6: Emissions of ozone-depleting substances*	*3,12*
Ec_{aq}	*304: Biodiversity* *306: Waste*	*3,6,12,14,15*
Smog	*305-7:* NO_x, SO_x, *and other significant air emissions*	*3,12,14,15*
Acid	*305-7:* NO_x, SO_x, *and other significant air emissions*	*3,12,14,15*
Eut_A	*304: Biodiversity* *306: Waste*	*3,6,12,14,15*
RMI	*301-2: Recycled input materials used*	*8,12*
HW	*306: Waste*	*3,6,12,14,15*
CG-GWP	*305-1: Direct GHG Emissions* *305-2: Energy indirect GHG Emissions*	*3,12,13,14,15*
LU	*304: Biodiversity*	*6,14,15*
CG-Eu	*304: Biodiversity* *306: Waste*	*3,6,12,14,15*
CG-Ac	*305-7:* NO_x, SO_x, *and other significant air emissions*	*3,12,14,15*
CG-Bio	*304: Biodiversity*	*6,14,15*
EI	*302: Energy*	*7,8,12,13*
ηE	*302: Energy*	*7,8,12,13*
$\Delta\dot{B}$	*302: Energy*	*7,8,12,13*
$\eta\dot{B}_{prod}$	*302: Energy*	*7,8,12,13*
WI	*303: Water and Effluents*	*6,8,12*
$\eta\dot{B}$	*302: Energy*	*7,8,12,13*
MI	*301: Materials*	*8,12*
E	*306: Waste*	*3,6,12,14,15*
C_{prod}	*301: Materials*	*8,12*
m_s	*306: Waste*	*3,6,12*
ηR	*301: Materials*	*8,12*
ε	*301: Materials*	*8,12*
SMP	*301: Materials*	*8,12*
SMLI	*301: Materials*	*8,12*
$HTox_c$	*403: Occupational Health and Safety*	*3,8,16*
$HTox_{nc}$	*403: Occupational Health and Safety*	*3,8,16*
Haz_{in}	*403: Occupational Health and Safety*	*3,8,16*
TRI_{in}	*403: Occupational Health and Safety*	*3,8,16*
Acute	*403: Occupational Health and Safety*	*3,8,16*
Irrit	*403: Occupational Health and Safety*	*3,8,16*
PM	*305-7:* NO_x, SO_x, *and other significant air emissions*	*3,12,14,15*
$Fail_{F/E}$	*403: Occupational Health and Safety*	*3,8,16*
$Fail_{R/D}$	*403: Occupational Health and Safety*	*3,8,16*
Mob	*403: Occupational Health and Safety*	*3,8,16*
$Cost_{RM}$	*201-1: Direct economic value generated and distributed*	*8,9*
COM	*201-1: Direct economic value generated and distributed*	*8,9*
FCI	*201-1: Direct economic value generated and distributed*	*8,9*
GAP	*201-1: Direct economic value generated and distributed*	*8,9*
EP	*201-1: Direct economic value generated and distributed*	*8,9*

[a] (GRI, 2020a).

[b] (GRI, 2020b).

PART EII. Data Used to Calculate Case-Study Indicators

The following sources are used to support calculation of indicators for every dimension: IPCC AR5(Myhre et al., 2013) for *GWP*; ReCiPe for *Smog* (Huijbregts et al., 2017); TRACI for *PM* (Bare, 2012); midpoint USEtox 2.02 model for Ec_{aq} (Hauschild et al., 2016); and 2016 ERPG/WEEL Handbook for *Acute* (AIHA, 2016). Triacylglycerol (TAGs) characterization factors (*CF*) for Ec_{aq} are assumed equal to glycerol *CF*; for FAME equal to 'oleic acid'. *Smog*'s *CF* are considered equal to the value provided for 'aliphatic hydrocarbons' for all hydrocarbons present in the simulation. Fats and oils are categorized as solid waste for landfill (Ruiz-Mercado et al., 2012); hence mass of solids (m_s) considers glycerol, TAGs and FAME.

For cradle-to-gate impacts, values are shown in Table EII-1. Table EII-2 presents prices used to generate economic indicators.

Table EII-1. Values for cradle-to-gate (CG) characterization factors.

Indicator	Unit	Soybean-Oil	Palm-Oil	Microalgae-Oil
LU	m^2 *year/kg*[a]	*18.31*(Marzullo 2007)	*3.12*(Marzullo 2007)	*0.04*(Grierson et al. 2013)
CG-GWP	$kgCO_2e/kg$[a]	*11.73*(Matsuura et al. 2017)	*1.89*(Siregar et al. 2015)	*-0.89*(Grierson et al. 2013)
CG-Eu	*kgPe/kg*[a]	*1.4E-3*(Marzullo 2007)	*8.1E-4*(Marzullo 2007)	*4.4E-3*(Grierson et al. 2013)
CG-Ac	$kgSO_2e/kg$[a]	*8.7E-3*(Marzullo 2007)	0.01(Marzullo 2007)	*0.10*(Grierson et al. 2013)
CG-Bio	*Species-eq-lost.year*	*1.06E-15*(Chaudhary et al. 2016)	*2.17E-14*(Chaudhary et al. 2016)	*NA*[b]

[a] *Not all references provides impacts in terms of mass of oil, thus a conversion procedure is applied to these cases. For dry weight biomass, it is assumed 25% extraction efficiency to produce the oil.*

[b] *Not available.*

The mass of product is considered as the mass of biodiesel for Production-Unit #1, Production-Unit #2 and Production-Unit #3; the mass of green-diesel for Production-Unit #4 and Production-Unit #5; and the mass of propylene-glycol and biodiesel for Production-Unit #6, Production-Unit #7 and Production-Unit #8. Glycerol is not accounted for obtaining the total mass of product value, which is used in the denominator of many intensity indicators. For water intensity indicator, a 10% of cooling water and steam make-up is assumed.

Table EII-2. Raw-materials and product prices.

Material	Price (USD/kg)	Reference
Soybean-Oil	0.62	IndexMundi
Palm-Oil	0.54	IndexMundi
Microalgae-Oil	10.00	Laurens 2017
Biodiesel	0.83	Neste
Green-diesel	0.94	ValueOils
Propylene-Glycol	3.90	ChemWorls

PART EIII. Statistical Screening of Indicators

Table EIII-1. Corrected item-total correlations (*CITC*): indicator screening rounds.

Indicator	*Indicator Set*	*CITC Round#1*	*CITC Round#2*	*CITC Final*
GWP	*Environment/Gate-to-gate*	0.92	0.97	0.97
ODP	*Environment/Gate-to-gate*	0.00[c]	---	---
Ec_{aq}	*Environment/Gate-to-gate*	-0.91[c]	---	---
Smog	*Environment/Gate-to-gate*	0.85	0.82	0.82
Acid	*Environment/Gate-to-gate*	0.00[c]	---	---
Eut_A	*Environment/Gate-to-gate*	0.00[c]	---	---
RMI	*Environment/Gate-to-gate*	0.96[b]	1.00	1.00
HW	*Environment/Gate-to-gate*	0.90[b]	0.96	0.96
CG-GWP	*Environment/ Cradle-to-gate*	0.96	0.96	0.96
LU	*Environment/ Cradle-to-gate*	-0.02[c]	---	---
CG-Eu	*Environment/ Cradle-to-gate*	-0.02[c]	---	---
CG-Ac	*Environment/ Cradle-to-gate*	-1.00[c]	---	---
CG-Bio	*Environment/ Cradle-to-gate*	-1.00[c]	---	---
EI	*Efficiency/ Energy*	-0.90[a,b]		0.98[a]
ηE	*Efficiency/ Energy*	-0.90[a]		1.00[a]
$\Delta\dot{B}$	*Efficiency/ Energy*	-0.91[a,c]		---
$\eta\dot{B}_{prod}$	*Efficiency/ Energy*	-0.89[a,c]		---
WI	*Efficiency/ Energy*	-0.73[a]		1.00[a]
$\eta\dot{B}$	*Efficiency/ Energy*	-0.91[a,c]		---
MI	*Efficiency/Material*	0.81[b]	0.91	0.98
E	*Efficiency/Material*	0.73	0.85	0.95
C_{prod}	*Efficiency/Material*	-0.77[c]	---	---
m_s	*Efficiency/Material*	-0.50[c]	---	---
ηR	*Efficiency/Material*	-0.08[c]	---	---
ε	*Efficiency/Material*	0.99	0.96	0.87
SMP	*Efficiency/Material*	0.61[c]	0.53	---
SMLI	*Efficiency/Material*	0.92	0.97	1.00
$HTox_c$	*H&S/Health*	0.00[c]	---	---
$HTox_{nc}$	*H&S/Health*	0.99[b]	0.99	0.99
Haz_{in}	*H&S/Health*	1.00	1.00	1.00
TRI_{in}	*H&S/Health*	1.00[b]	1.00	1.00
Acute	*H&S/Health*	0.99	0.99	0.99
Irrit	*H&S/Health*	0.00[c]	---	---
PM	*H&S/Safety*	1.00[b]		1.00
$Fail_{F/E}$	*H&S/Safety*	1.00		1.00
$Fail_{R/D}$	*H&S/Safety*	1.00[b]		1.00
Mob	*H&S/Safety*	1.00		1.00
$Cost_{RM}$	*Economic/Cost*	0.83[b]		0.83
COM	*Economic/Cost*	1.00		1.00

Indicator	***Indicator Set***	***CITC Round#1***	***CITC Round#2***	***CITC Final***
FCI	*Economic/Cost*	*0.86*		*0.86*
GAP	*Economic/Profit*	*0.98*		*0.98*
EP	*Economic/Profit*	*0.98*		*0.98*

[a]Efficiency/Energy statistical screening used Cronbach Alpha Test (Table L2);[b]Deleted in PCA step; [c]Deleted in CITC step or via Crombach Alpha Test.

Table EIII-2. Results: Cronbach Alpha Test for *Efficiency/Energy* indicators.

Indicator	***Cronbach Alpha after deleting item Trial #1***	***Cronbach Alpha after deleting item Trial #2***	***Cronbach Alpha after deleting item Trial #3***	***Cronbach Alpha after deleting item Trial #4***
EI	*-3.90*	*-16.61*	*-1.90*	*0.99*
ηE	*-4.11*	*-20.87*	*-2.06*	*0.98*
$\Delta\dot{B}$	*-3.75*	*0.10**	*deleted*	*deleted*
$\eta\dot{B}_{prod}$	*-5.11*	*-0.02*	*0.99**	*deleted*
WI	*-5.07*	*-56.17*	*-2.35*	*1.00*
$\eta\dot{B}$	*-3.57**	*deleted*	*deleted*	*deleted*

**Deletion causing highest Cronbach Alpha (item deleted in all subsequent trials).*

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APPENDIX F – PUBLICATIONS RESULTED FROM THIS THESIS RESEARCH

F.1 – A Sustainability Composite Index for Biorefineries. Proceedings of the 1st SDEWES Latin American Conference on Sustainable Development of Energy, Water and Environment Systems, 2018.

Conference on Sustainable Development of Energy, Water and Environment Systems, Rio de Janeiro 28.-31.1.2018

Biofuels and biorefineries

SDEWES.LA2018.0009

A Sustainability Composite Index for Biorefineries

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Abstract

Given the great amount of possible "feedstock-process-product" configurations for biorefineries, there is a natural need for a decision-making procedure in biorefinery design. Many works have considered screening alternatives based on life cycle assessment. Nevertheless, these studies often evaluate only the environmental aspect of biorefineries, considering production processes as black boxes. This paper proposes a systematic method to preliminary assess alternative biorefineries input-output scenarios based on a gate-to-gate sustainability assessment tool. The tool applies a hierarchical procedure composed of two levels: production unit and unit operation. The assessment in the first level comprises evaluating the different scenarios regarding five dimensions of process systems engineering sustainability and generating a composite index to rank alternatives. Next, the second level evaluates the best scenario comparing its specific unit operations to identify hotspots and propose process improvements. The assessment tool has been applied into a case study for biorefinery process design using three possible feedstocks (soy, palm and microalgae oil) and four possible products (biodiesel, green diesel, glycerol and propylene glycol). The goal of this case study was to identify the most sustainable chemical processing pathways and input-output configuration for this biorefinery. Scenario comprising biodiesel and propylene glycol from palm oil was found to be the most sustainable.

F.2 – Sustainability assessment of conventional and innovative supersonic processes for ethylene oxide production. Proceedings of the 14th SDEWES Conference on Sustainable Development of Energy, Water and Environment Systems, 2019.

Conference on Sustainable Development of Energy, Water and Environment Systems, Dubrovnik, 1.-6.10.2019

SDEWES2019.0069

Sustainability Assessment of Conventional and Innovative Supersonic Processes for Ethylene Oxide Production

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Abstract

With increasing environmental concerns, sustainability must be assured in designing new processes. It encompasses multiple criteria that often point to opposite directions demanding objective and systematic procedures for assessing performance quantitatively, to be embodied in algorithmic process design procedures. Hence, application of metrics and indicators to measure the level of sustainability may contribute to straightforward unbiased results. The Sustainable Process Systems Engineering (S-PSE) method fulfills that gap of composite-index methods for sustainability assessment at process systems engineering level targeting on performance quantification and ranking of alternatives. The method is a hierarchical approach composed of two levels. The first-level preliminarily evaluates alternative production pathways to select the most sustainable plant-wide configuration in terms of environment, energy efficiency, material efficiency, health and safety, and economy. The second-level appoint sustainability hotspots within unit-operations. S-PSE interlinks the application of process technology-specific indicators with aggregation procedures to put forth a highly relevant gate-to-gate sustainability composite-index. This work applies S-PSE method to evaluate and compare the sustainability of two plants producing ethylene oxide from alternative technologies: a conventional and an innovative process employing a supersonic separator to enhance ethylene oxide recovery. Due to the supersonic separator geometry, comprising a convergent-divergent nozzle, ethylene oxide can be condensed and recovered in the purification stage, almost free from impurities. Both plants apply carbon capture to reduce the amount of greenhouse gases emitted, recovering a highly pure stream of CO_2. The alternative comprising supersonic separator increases ethylene oxide recovery by 40 kg/h, being the option with best environmental, social (health and safety) and economic performance. Ethylene oxidation reaction, cooling water tower and cooling tower air-blower are the main unit-operations with sustainability hotspots. Reaction drawbacks are associated with environmental, health and safety impacts, and the cooling water tower and air-blower are the most material-intensive. The case study clearly demonstrates coordination of computer-aided design tools (Aspen Hysys, Excel and Matlab) to sustainable process design.

F.3 – A Review on Chemical Process Sustainability Assessment: Boundary, Production, Level, Sustainability Dimensions and Decision-Making Analyses. Proceedings of the 14th SDEWES Conference on Sustainable Development of Energy, Water and Environment Systems, 2019.

Conference on Sustainable Development of Energy, Water and Environment Systems, Dubrovnik, 1.-6.10.2019

Sustainability comparisons and measurements 1

SDEWES2019.0070

A Review on Chemical Process Sustainability Assessment: Boundary, Production, Level, Sustainability Dimensions and Decision-Making Analyses

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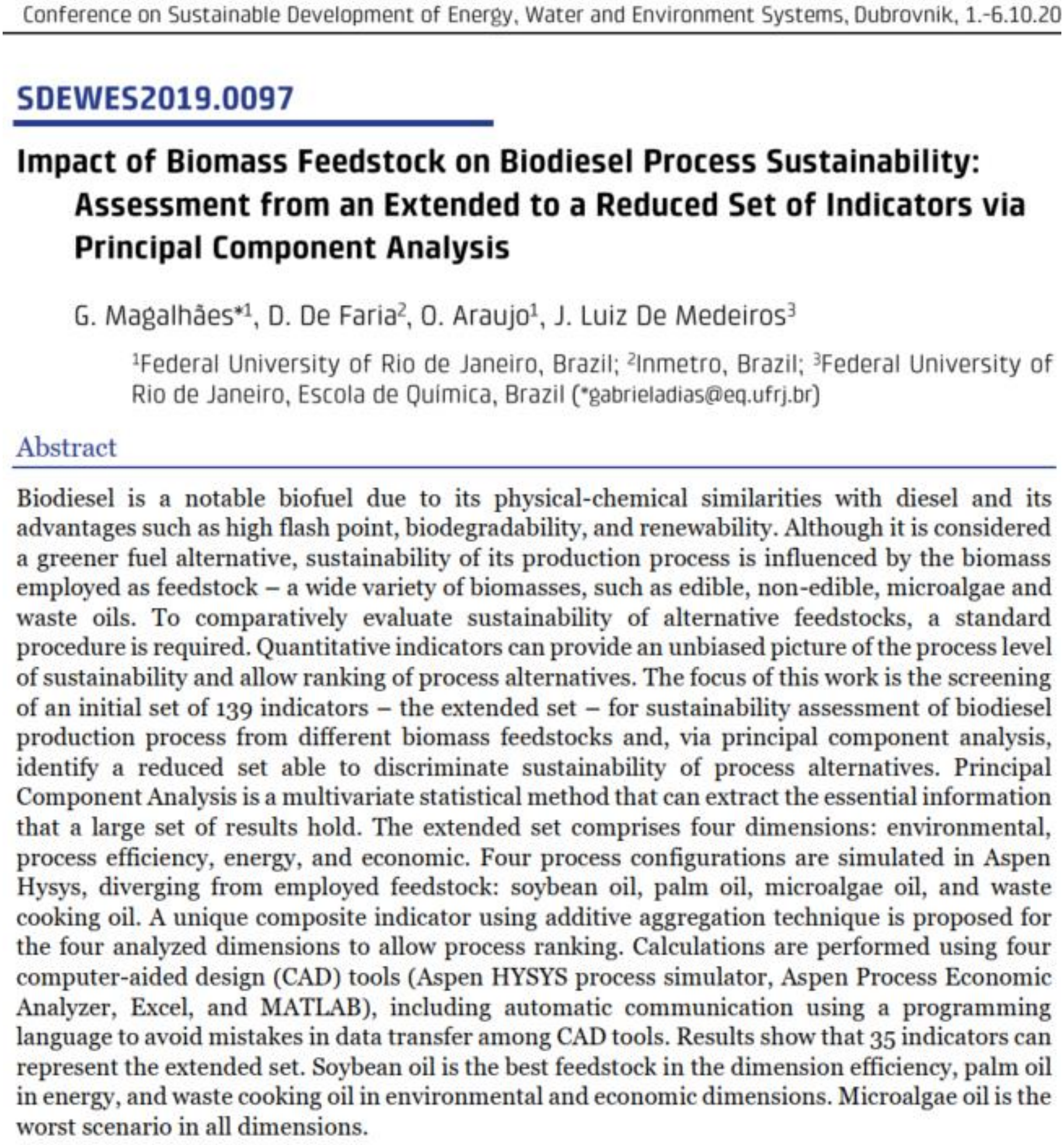
Abstract

To target sustainability of systems and products, environmental, social, and economic issues are to be assessed and, due to inherent antagonisms, trade-offs are posed and decisions must be made. Each system has unique performance aspects that defy procedures to measure, track performance and expand tools that support sustainable processes. Multiple frameworks to support sustainability assessment exist, lacking well-established and straightforward methods, which often brings to biased or non-comparable results. This paper presents a critical review of 46 state-of-the-art methods for sustainability assessment that can be applied to the chemical industry and process systems engineering. The main remark unveiled by this review reports advances in integrating multiple concepts that had not been associated to sustainability within process systems engineering together, such as boundary selection, production phase, level of analysis, sustainability dimensions, and decision-making. Such categories are intended to aid the understanding of each method focus and scope, issues addressed and indicators used, and decision-making procedure applied to identify most sustainable alternative. All the methods investigated must correlate either with chemical industry, chemical process, chemical products or process systems engineering. The methodology used consists of eight steps, namely: definition of focus and scope, investigation of prior reviews, definition of literature classification, literature search and screening, classification, analysis, review and findings, identification of gaps for future research. The evaluation identified a sharp increase of literature about sustainable chemical design and production from 2010, but also pointed how far the field is from developing fully integrated assessment methods for sustainability in process systems. The majority of the literature assessed stood for industrial gate-to-gate design methods. As the life cycle boundaries expanded, single dimension analysis is more frequent, indicating a trade-off between life cycle boundaries, inclusion of sustainability dimensions and quality. The decision-making analysis highlighted the dominance of compensatory approaches, pointing that most methods allow compensability between indicators. In general, the methods did not investigate the application of different aggregation metrics, a shortcoming that pinpointed the further need to apply statistical analysis of sustainability indexes.

F.4 – Impact of Biomass Feedstock on Biodiesel Process Sustainability: Assessment from an Extended to a Reduced Set of Indicators via Principal Component Analysis. Proceedings of the 14th SDEWES Conference on Sustainable Development of Energy, Water and Environment Systems, 2019.



SDEWES2019.0097

Impact of Biomass Feedstock on Biodiesel Process Sustainability: Assessment from an Extended to a Reduced Set of Indicators via Principal Component Analysis

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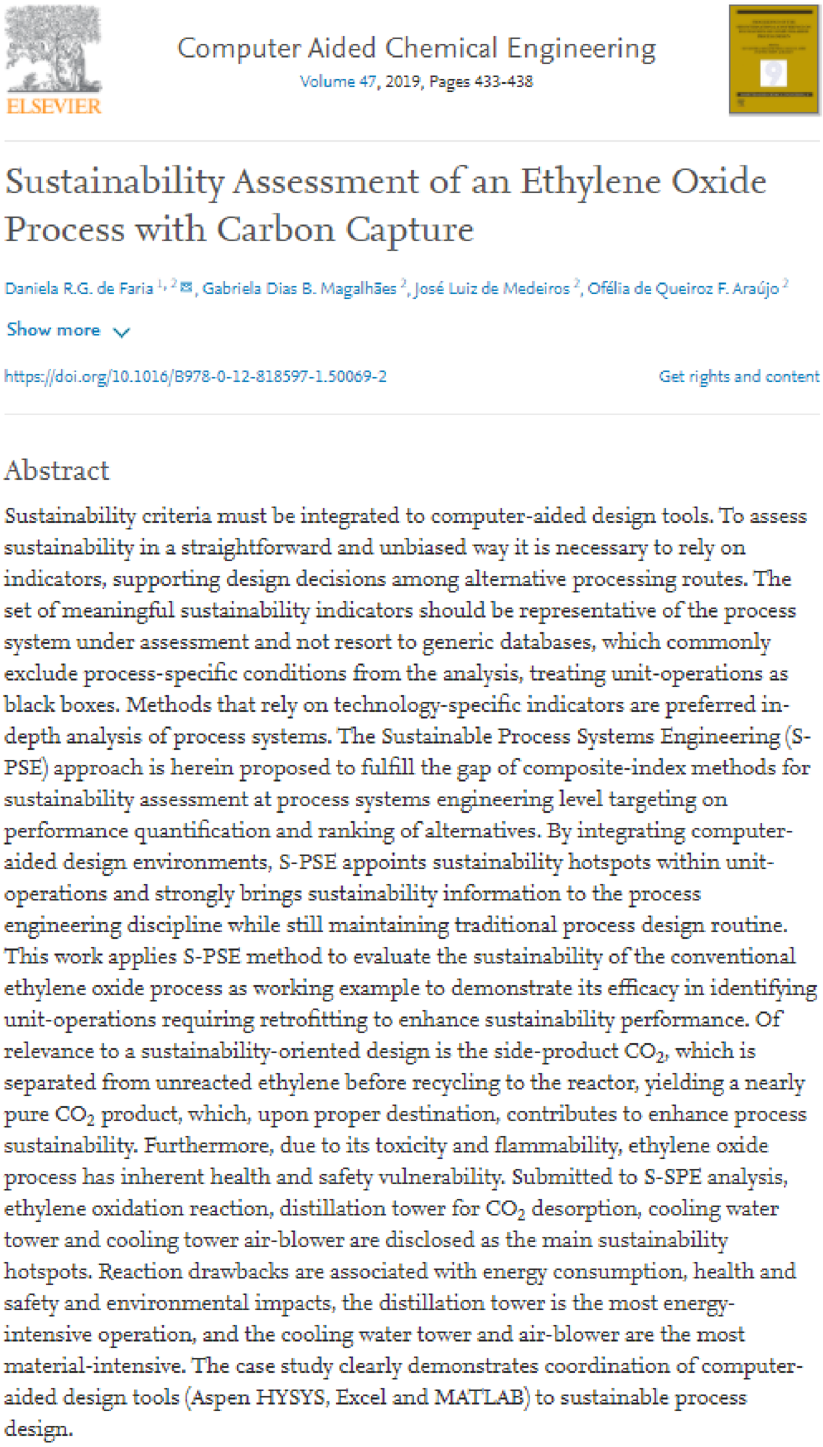
Abstract

Biodiesel is a notable biofuel due to its physical-chemical similarities with diesel and its advantages such as high flash point, biodegradability, and renewability. Although it is considered a greener fuel alternative, sustainability of its production process is influenced by the biomass employed as feedstock – a wide variety of biomasses, such as edible, non-edible, microalgae and waste oils. To comparatively evaluate sustainability of alternative feedstocks, a standard procedure is required. Quantitative indicators can provide an unbiased picture of the process level of sustainability and allow ranking of process alternatives. The focus of this work is the screening of an initial set of 139 indicators – the extended set – for sustainability assessment of biodiesel production process from different biomass feedstocks and, via principal component analysis, identify a reduced set able to discriminate sustainability of process alternatives. Principal Component Analysis is a multivariate statistical method that can extract the essential information that a large set of results hold. The extended set comprises four dimensions: environmental, process efficiency, energy, and economic. Four process configurations are simulated in Aspen Hysys, diverging from employed feedstock: soybean oil, palm oil, microalgae oil, and waste cooking oil. A unique composite indicator using additive aggregation technique is proposed for the four analyzed dimensions to allow process ranking. Calculations are performed using four computer-aided design (CAD) tools (Aspen HYSYS process simulator, Aspen Process Economic Analyzer, Excel, and MATLAB), including automatic communication using a programming language to avoid mistakes in data transfer among CAD tools. Results show that 35 indicators can represent the extended set. Soybean oil is the best feedstock in the dimension efficiency, palm oil in energy, and waste cooking oil in environmental and economic dimensions. Microalgae oil is the worst scenario in all dimensions.

F.5 – Sustainability Assessment of an Ethylene Oxide Process with Carbon Capture. Computer Aided Chemical Engineering. 1ed.Amsterdam: Elsevier, 2019, v. 47, p. 433-438.



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Sustainability Assessment of an Ethylene Oxide Process with Carbon Capture

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Abstract

Sustainability criteria must be integrated to computer-aided design tools. To assess sustainability in a straightforward and unbiased way it is necessary to rely on indicators, supporting design decisions among alternative processing routes. The set of meaningful sustainability indicators should be representative of the process system under assessment and not resort to generic databases, which commonly exclude process-specific conditions from the analysis, treating unit-operations as black boxes. Methods that rely on technology-specific indicators are preferred in-depth analysis of process systems. The Sustainable Process Systems Engineering (S-PSE) approach is herein proposed to fulfill the gap of composite-index methods for sustainability assessment at process systems engineering level targeting on performance quantification and ranking of alternatives. By integrating computer-aided design environments, S-PSE appoints sustainability hotspots within unit-operations and strongly brings sustainability information to the process engineering discipline while still maintaining traditional process design routine. This work applies S-PSE method to evaluate the sustainability of the conventional ethylene oxide process as working example to demonstrate its efficacy in identifying unit-operations requiring retrofitting to enhance sustainability performance. Of relevance to a sustainability-oriented design is the side-product CO_2, which is separated from unreacted ethylene before recycling to the reactor, yielding a nearly pure CO_2 product, which, upon proper destination, contributes to enhance process sustainability. Furthermore, due to its toxicity and flammability, ethylene oxide process has inherent health and safety vulnerability. Submitted to S-SPE analysis, ethylene oxidation reaction, distillation tower for CO_2 desorption, cooling water tower and cooling tower air-blower are disclosed as the main sustainability hotspots. Reaction drawbacks are associated with energy consumption, health and safety and environmental impacts, the distillation tower is the most energy-intensive operation, and the cooling water tower and air-blower are the most material-intensive. The case study clearly demonstrates coordination of computer-aided design tools (Aspen HYSYS, Excel and MATLAB) to sustainable process design.

F.6 – Novel ethylene oxide production with improved sustainability: Loss prevention via supersonic separator and carbon capture. Journal of Environmental Management, v. 269, 2020.

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Research article

Novel ethylene oxide production with improved sustainability: Loss prevention via supersonic separator and carbon capture

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ABSTRACT

Sustainability must be always assured in process design. Not rarely, multiple sustainability criteria point oppositely, entailing a need for more systematic and coherent assessments. The Sustainable Process Systems Engineering method is introduced as a two-level hierarchical evaluation of process designs. The first level selects the best design via four-dimensional indicators (environment, efficiency, health-&-safety, and economic), while in the second level, sustainability hotspots of the best design are pinpointed to unveil possible improvements. The method is applied for sustainability assessment of two ethylene oxide processes: the conventional and a novel route employing supersonic separator to prevent ethylene oxide losses using liquid-water injection. Supersonic separator route reduces oxide losses by 83.33 kg/h, representing +0.9% greater ethylene oxide production, 95% less ethylene oxide losses, entailing 2.5% higher net value for 20 operation years despite 0.11% higher investment, and consequently exhibiting the best environmental, technical, health-&-safety and economic performances. Photochemical-oxidation and aquatic-ecotoxicity are environmental indicators with highest improvement due to supersonic separator inclusion. Ethylene oxidation reactor, carbon dioxide stripping-column and cooling-water tower are the main unit-operations with sustainability hotspots.

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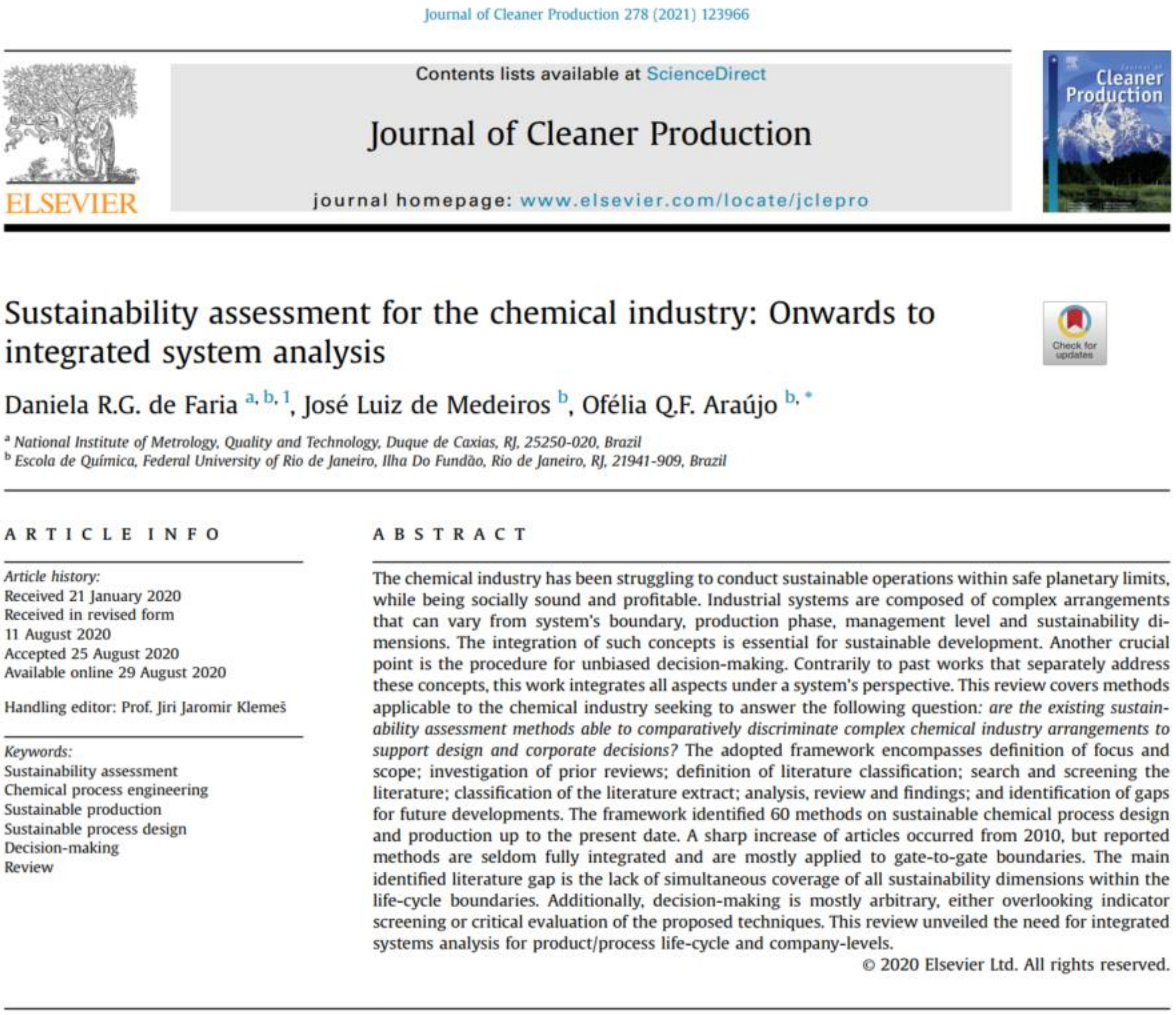

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Sustainability assessment for the chemical industry: Onwards to integrated system analysis

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ABSTRACT

The chemical industry has been struggling to conduct sustainable operations within safe planetary limits, while being socially sound and profitable. Industrial systems are composed of complex arrangements that can vary from system's boundary, production phase, management level and sustainability dimensions. The integration of such concepts is essential for sustainable development. Another crucial point is the procedure for unbiased decision-making. Contrarily to past works that separately address these concepts, this work integrates all aspects under a system's perspective. This review covers methods applicable to the chemical industry seeking to answer the following question: *are the existing sustainability assessment methods able to comparatively discriminate complex chemical industry arrangements to support design and corporate decisions?* The adopted framework encompasses definition of focus and scope; investigation of prior reviews; definition of literature classification; search and screening the literature; classification of the literature extract; analysis, review and findings; and identification of gaps for future developments. The framework identified 60 methods on sustainable chemical process design and production up to the present date. A sharp increase of articles occurred from 2010, but reported methods are seldom fully integrated and are mostly applied to gate-to-gate boundaries. The main identified literature gap is the lack of simultaneous coverage of all sustainability dimensions within the life-cycle boundaries. Additionally, decision-making is mostly arbitrary, either overlooking indicator screening or critical evaluation of the proposed techniques. This review unveiled the need for integrated systems analysis for product/process life-cycle and company-levels.