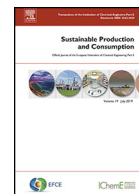




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Sustainable process synthesis, design, and analysis: Challenges and opportunities

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ABSTRACT

In this perspective paper, we present challenges and opportunities that the chemical, biochemical and related industries pose to the process system engineering community to help deliver reliable and novel sustainable alternatives. More specifically, we highlight the need for a systems approach where model-based sustainable process synthesis, design, and analysis serve as opportunities to tackle the challenges. Three technology areas (interlinked to each other) that impact the sustainability of earth, namely, chemical processes linked with CO₂ capture and utilization, biorefineries and water desalination are selected to highlight our views as well as the need for further development of computer-aided tools to efficiently solve the large and complex mathematical systems the problems represent. Analysis of these problems and their reported solutions indicate that opportunity exists for development of a new class of model-based methods and tools and their integration with the currently available ones to obtain the desired sustainability development goals.

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1. Introduction

A core activity of chemical and biochemical engineering is the conversion of resources to needed products through synthesis, design, analysis, and operation of an appropriate process (Gani et al., 2020). The objective of process synthesis is to find the optimal process flowsheet from among numerous alternatives, that converts given raw materials to desired products, subject to a set of process specifications and performance criteria. The objective of process design is to determine optimal values for the variables related to design and operation of the unit operations present in the process flowsheet subject to the same set of process specifications and performance criteria as in process synthesis (Westerberg, 2004). Operation of the process needs utilities such as energy, which directly or indirectly impacts the global warming potential, and, water, which if not treated pollutes the water resources and related environments. Considering the energy-water-environment nexus (García and You, 2016; Shahzad et al., 2017;

Zhao and You 2021), therefore, the objective of process synthesis-design should be to determine process alternatives consisting of hybrid/integrated/intensified options at different scales (unit operation, task, and/or phenomena) that satisfies the same set of process specifications but whose operation is subject to a set of targets with respect to process performance criteria. Therefore, the synthesis and design of processes need to consider which raw material to use, which product to make, what are the environmental impacts due to the operation of the process and many more (Azapagic, 1999; Fan et al., 2019). Achievement of these objectives, would require integration of concepts such as circular economy (Geissdoerfer et al., 2017) and sustainable development goals recently enumerated by the UN in the 2030 agenda (UN, 2021) that address the water-energy-environment nexus by encouraging the recovery and reuse of waste and by-products; significantly improved energy and water consumption efficiencies; alternative chemical (and/or biochemical) synthesis routes, that allow the transformation of resources to added value products.

As the search space for finding the optimal chemical and/or biochemical process is potentially very large due to the numerous alternatives that may need to be investigated, the use of model-based computer aided tools that help to quickly identify promising candidates that can be further studied through experiment-

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Nomenclature

AE	Algebraic equation
AFEX	Ammonia fiber explosion
CCU	Carbon Capture and utilization
CCUS	Carbon Capture, utilization and storage
DA	Dilute acid
DDS	Direct distillation sequence
DG	Direct gasification
DME	Dimethyl ether.
F_{obj}	Objective function
GHG	Green house gas
HDS	Hybrid distillation schemes
IDG	Indirect gasification
IDS	Direct distillation sequence
l_i	Lower bound
LCA	Life cycle assessment
LCI	Life-cycle inventory
LP	Linear programming
MEE	Multieffect evaporator
MILP	Mixed integer linear programming
MINLP	Mixed integer non-linear programming
MS	Molecular sieves
MSF	Multistage flash
NLP	Non-linear programming
ODE	Ordinary differential equation
PI	Process intensification
PSA	Pressure swing adsorption
PSE	Process system engineering.
PDE	Partial differential equation
PO	Partial oxidation
RO	Reverse osmosis
SR	Steam reforming
TVC	Thermal vapour compression
u_i	Upper bound
WGSR	Water gas shift reaction
x	Vector of process variables
Y	Vector of decision variables
z	Vector of process design variables
β	Fitted process model parameter
λ	Property model parameter
θ	Vector of properties

based approaches or through more detailed process analysis is an option worth considering (Nikolopoulou and Ierapetritou, 2012; Chen et al., 2021). Note also that process synthesis-design-operation represents a complex problem, whichever way it is solved. Obviously, the use of an experiment-based trial and error approach while feasible will most likely not provide even a local optimal solution. On the other hand, computer-aided systems approach suffers from availability of the needed validated models as well as the ability to solve the resulting complex mathematical problem. Also, a large collection of models, process synthesis and/or design methods and solver algorithms are needed to cover a wide spectrum of application areas. Therefore, an opportunity exists for use of a systematic computer-aided framework that provides the workflows for different synthesis and/or design problems together with the associated computational tools as well as models and databases. In this perspective paper, this view is highlighted by pointing out the challenges we face and the opportunities they provide with respect to energy-water-environment impacts.

Traditionally, process simulators are used not only to model and simulate the process, but also to solve synthesis and/or design problems. The approach employed for the later, is similar to

experiment-based trial and error approach where the experiment is replaced by a simulator, resulting in reduction of significant time but not necessarily any guarantee of a better solution. The main issues, however, are the need for verification of results (do they match measured data?) and quality of the solution (is it the best solution?). To verify the results, experiments at different scales could be designed, suggesting the use of an integrated experiment and computer-aided solution approach where the search space is first quickly reduced and then of the one or more promising alternatives, experimental verification is performed. To improve the quality of the numerical solution, efficient and reliable numerical solvers are necessary.

Since the early 1980s, when Process Systems Engineering (PSE) was first announced, a large collection of computer-aided methods and associated tools have been developed (Sargent, 2004). Indeed, a process simulator (AspenPlus, gPROMS, Hysys, Aveva Pro/II – to name a few) is a tool that is universally used in education and industrial practice daily all over the world. They include process models, databases, numerical solvers, etc., and allow the modelling and/or simulation of a wide range of processes. Tools for design and analysis (such as economics) are usually available and only recently, tools for synthesis have started to be developed (Chen and Grossmann, 2017). Bertran et al. (2017) proposed a general tool, Super-O, for process synthesis based on superstructure optimization. Tula et al. (2017) reported the development of an integrated tool, ProCAFD, for sustainable process synthesis, design, and innovation. Chen et al. (2021) proposed, Pyosyn, which is especially suited for a wide range of model-based sustainable process synthesis problems. A comprehensive list of computer-aided methods and associated tools developed by researchers from the PSE community is given by Pistikopoulos et al. (2021). Uses of these tools, as pointed out by Guillén-Gosálbez et al. (2019), are continuously increasing and latterly being applied to help in the transition towards a sustainable chemical industry developing transformation paths, energy production and water management and treatment. These targets are in line with the agenda 2030 of the UN in topics such as affordable and clean energy, clean water and sanitation, sustainable cities and communities, responsible consumption, and production among others (UN, 2021). For example, Roh et al. (2016) have employed a combination of process simulation, design, cost analysis, sustainability analysis, etc., for carbon capture and utilization studies; Galán et al. (2019) have applied surrogate modelling, superstructure optimization approach, heat exchanger, and water network design within biorefinery synthesis, design, and analysis studies; Filippini et al. (2019) have applied a first principle based model in gPROMS for salt-free water through economic design of solar powered thermal desalination process; (Martín and Adams, 2019) have highlighted the use of renewable resources. While continuous improvements are being made, the use of these tools in the new sector of renewable energy and products as well as towards the development of a circular economy from wastes indicate challenges that need to be resolved and the opportunities that exist for the PSE community. The following review papers are recommended to obtain an overview on related topics: renewable energy systems (Shi and Chew, 2012), environmental life cycle analysis of water desalination (Cherif and Belhadj, 2018), modelling and optimization of water desalination (Ahmed et al., 2019), circular economy and PSE (Avraamidou et al., 2020), sustainable design of chemical facilities (Meramo-Hurtado and González-Delgado, 2021), biorefinery integrated with carbon capture (Geissler and Maravelias, 2021).

The objective of this perspective paper is to highlight the challenges and opportunities related to model-based sustainable process synthesis, design and analysis through state-of-the-art computer-aided methods and tools, including, a perspective on the tasks that the PSE community faces and opportunity to contribute

towards achieving one or more sustainable development goals. To illustrate these challenges and associated opportunities, the following three types of technologies are considered: a) chemical processes that produce chemicals needed to sustain society but are energy intensive because they are based on non-renewable resources; b) biorefinery processes that currently produce a smaller range of chemicals but are not energy intensive because they are based on renewable resources; c) water desalination processes that produce needed utilities that are not available at specific locations. These examples address some of the UN goals of the 2030 agenda such as affordable and clean energy, responsible consumption and production, climate action or clean water and sanitation. Note, however, they are at different stages of development and therefore, different aspects of PSE model-based tools are highlighted. The paper is organized as follows – after the introduction, brief overviews on the three selected technologies and selected computer-aided methods and tools are given as background information in Section 2; the issues and challenges related to sustainable development within the three selected technologies are highlighted in Section 3; perspectives related to current and future needs are given in Section 4; conclusions are given in section 5.

2. Background information

2.1. Process technologies

Fig. 1 shows a process-A (which can be chemical, biochemical or water desalination) that converts resources (renewable or non-renewable) to desired chemicals (products). It is an example of an energy demanding technology because it needs externally supplied energy to perform its operations. Above process-A, a power plant, which supplies the demanded energy is shown. It is an example of an energy supplying technology. The three types of technologies considered in this paper are related to process-A and some modifications of the total system: a) sustainable chemical process networks including CCU; b) sustainable biomass based biorefinery for chemicals productions; c) sustainable water desalination processes. The objective in each technology is to find solutions through schemes for integration such that the net CO₂ emission is significantly reduced from present values and preferably to zero or negative values. Therefore, these three cases are directly linked to at least 8 of the 17 goals for sustainable development of the UN (UN, 2021) including responsible consumption and production, sustainable cities and communities, industry, innovation and infrastructure, affordable and clean energy, clean water and sani-

tation, life below water, life on land, climate action. Fig. 2 shows the pyramid of the product value/volume. The larger the value, the smaller the production capacity. Within the examples in this paper, biomass can be a source for products within the wide value-chain from energy and bulk chemicals to health products (Espro et al., 2021); commodity chemicals produced at lower energy demands and with renewable energies can significantly contribute to the fight against global warming through reduction of green-house gas (GHG) emissions, direct and/or indirect (Li et al., 2020); water, a commodity that is required from health applications to cooling or raw material in the production of any chemical is obtained from saline water from which salts are extracted for use in different applications of the value chain (Panagopoulos et al., 2019).

2.1.1. Sustainable carbon capture and utilization processes

Most of the chemicals and/or chemicals-based products and desalinated or treated water needed to sustain society are currently obtained by converting non-renewable resources that are energy intensive and thereby contribute to the emission of CO₂. Referring to Fig 1, the objective of a carbon capture (MacDowell et al., 2010) and utilization process is to capture all the CO₂ released by process-A and/or power plant and utilize it in process-A and/or a new process to make chemicals so that the net CO₂ emission is reduced compared to the base case (von der Assen et al., 2014).

Fig. 1 also highlights several other issues. For example, where is the real boundary of the system? If only the chemical process, or biorefinery or the desalination is the boundary, then most likely, it is possible to find solutions that do not release CO₂ directly. However, if the power-plant supplying the required energy is employed, then depending on the energy source used, can the CO₂ released (indirectly) be reduced? This will depend on which energy sources are used, for example, distributed small scale desalination plant can be designed to operate fully based on renewable energy sources with zero net addition to CO₂ emission and thus reduction of global warming (Maleki, 2018; Karimanzira, 2020). Also, Li et al. (2020) and Mongkhonsiri et al. (2021) have shown the reduction of direct and indirect CO₂ emissions through a network of the process (for commodity chemicals or waste pulp based biorefinery), the power plant supplying the energy demanded by the process and the water (supply and treatment). An integrated approach of the two types of technologies as well as improving the economic potential through more efficient synthesis-design to reduce the energy demand of the process could result in more sustainable solutions. Using the method of Frauzem (2017), a list of likely reaction synthesis paths for CO₂ utilization has been gener-

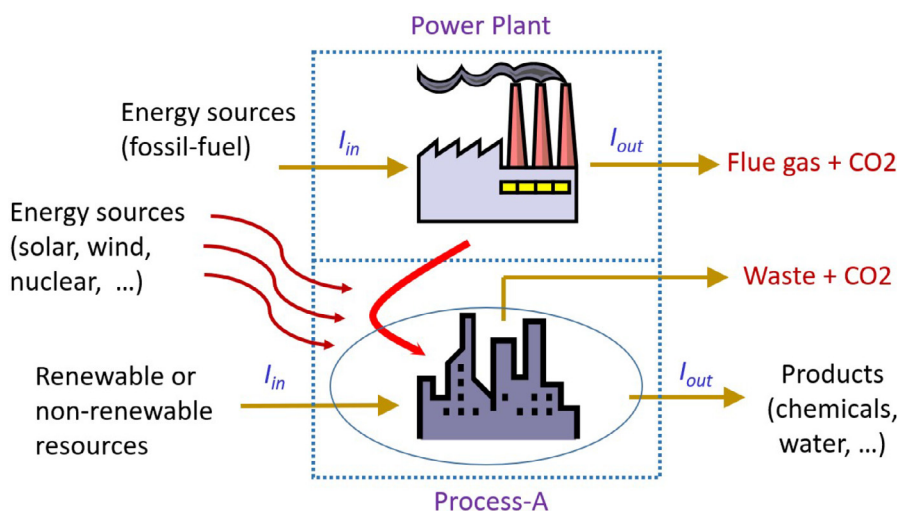


Fig. 1. Integrated chemical process and power-plant.

ated – a partial list is shown in Fig. 3 (a larger list can be obtained from the authors). Note that in all the reaction synthesis paths highlighted, CO₂ is a reactant and never a product. In the figure, mainly single step and some two step conversions (and one three-step conversion) of CO₂ to different products are shown. Therefore, for production of these chemicals, there will not be any direct emission of CO₂, but there will be indirect emission of CO₂ because of the energy demands of the resulting processing steps. Also, even though the stoichiometric coefficients in the reactors satisfy the atomic balance, some of the reactions may still be infeasible. The objective is to find a sustainable design where the amount of captured and utilized CO₂ is greater than the total indirect CO₂ emission. In this regard, a combination of the use of renewable and non-renewable energy sources can contribute to a reduction of the indirect CO₂ emission.

2.1.2. Sustainable biomass based biorefinery for chemicals production

A biorefinery is a chemical complex aiming at the processing of biomass towards the production of chemicals (Cherubini, 2010). The raw material, consisting of a wide range of possible species, is a mixture of compounds including cellulose, hemicellulose, lignin, starch, lipids, and proteins, as shown in Fig. 4. Consequently, considering process-A in Fig. 1 to be a biorefinery, it is by definition, a multiproduct facility that receives the raw materials and aims at being self-sustained in terms of energy requirements. To process such a complex and diverse mixture, the structure of any biorefinery consists of a series of processing steps as shown by the general scheme of biomass processing in Fig. 5. The biomass, depending on the intermediates required, is pre-processed into intermediates, sugars, or syngas. The molecular weight of the intermediates can vary between two, for hydrogen, to thousands for the case of polymers. The preparation of such intermediates requires clean-up and/or adjustments of compositions and temperatures. Next, the intermediates are used to synthesize other chemicals, since most of the times biomass does not contain the desired products as such. The synthesis step can be catalytic-, fermentation- or digestion-based. The final steps involve separation of the synthesis effluent for product recovery and purification to meet the

product specifications. The synthesis of products by conversion of the intermediates has evolved from processes converting one single raw material to a single main product, for example, ethanol or diesel, to the integration of by-products and to biochemical complexes (Bond et al., 2014).

The wide range of biomass resources available on Earth, indicates that it can be converted to a wide range of products, such as, ethanol (Martín and Grossmann, 2011), platform chemicals (Martin and Grossmann, 2015), high value-added products for the pharma and food industry (for example, essential oils (Dávila et al., 2015)), antioxidants towards a sustainable production system and a responsible use of residues for a circular economy as targeted in the UN goals. That is, biomass can be the base for a greener chemical industry capable of substituting the current crude oil-based status quo. Apart from high value biomass, such as crops, algae, and seeds, lower value biomass such as waste also provides opportunities to convert them to a wide spectrum of products and to determine their sustainable processing technologies. Over the years, the value of biomass and the trend to decarbonize the power and transportation sectors, have led to the search for additional uses of biomass from the typical biofuels, the starting point of the biorefinery industry (Jacques et al., 1999), to the production of platform chemicals, biomaterials, food supplements, and health products (highlighted also in Fig. 2 by the pyramid of value chain of products). Society has pushed towards this change of paradigm. Note, however, the biomass resources are not uniformly distributed on earth and therefore, these solutions are likely to be location dependent.

2.1.3. Sustainable water desalination processes

Water is absolutely essential, directly and indirectly, for all living beings on the earth to survive. Food, agriculture, energy, industrialization and transportation are all contributing to the sustenance and quality of life and require significant amounts of water. According to the 2030 Water Resources Group report published in 2009 (<https://www.2030wrg.org/wp-content/uploads/2014/07/Charting-Our-Water-Future-Final.pdf>), 6900 billion m³/day of water will be needed by 2030 compared to 4500

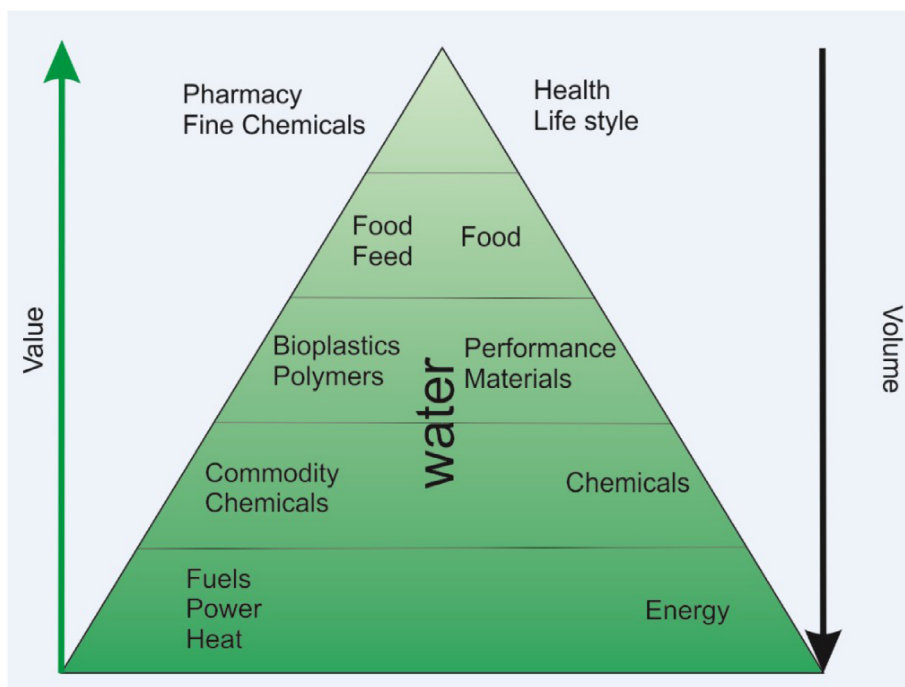


Fig. 2. Pyramid of Value chain of products.

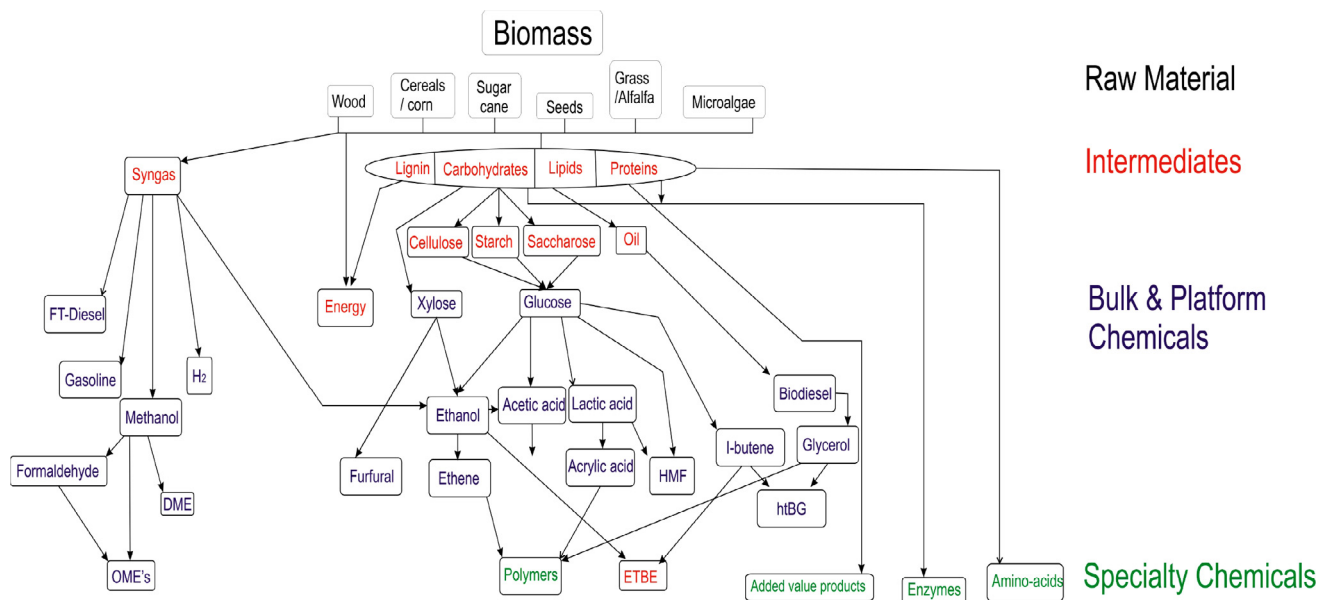


Fig. 4. Biomass based products.

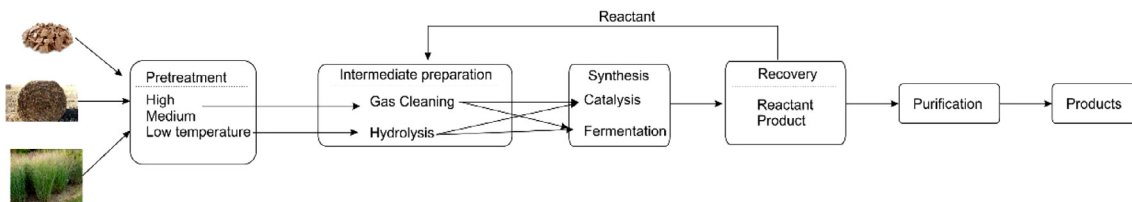


Fig. 5. General scheme of biomass processing.

able to meet the increasing water demand (Al-hotmani et al., 2020; Martino et al., 2021). The ongoing objective is still the improvement in design, operation, and control of desalination processes to ensure quality water (in terms of salinity and other dissolved solids such as boron) at cheaper price with lower environmental impact. However, exploitation of the full potential of model-based techniques in such solutions can hardly be seen.

2.2. Computer-aided methods and tools

First a generic problem formulation covering various types of synthesis-design problems is given, followed by a brief discussion on the modelling issues. Next, the current state of the art of the solution approaches is discussed related to the three types of process technologies considered in this paper.

2.2.1. General problem definition

The general product-process synthesis-simulation-design problems formulated as a mathematical optimization by Zhang et al. (2016) is adopted in this paper and described through Eqs. (1)–(6):

$$\text{Minimize or maximize, } F_{Obj} = F \{ C^T Y + f(z, x) \} \tag{1}$$

Subject to

Y (vector of decision variables); x (vector of process variables); z (vector of design variables, integer or real), and,

Constraints

* Process model ($D = 0$ for steady state; $D = dx/dt$ for dynamic for example, for a first order lumped parameter model; $D = \delta x / \delta t$ distributed model for example, for a one-dimensional dynamic distributed parameter model)

$$h_1(x, z, \theta, \beta, Y) = D \tag{2}$$

* Property model

$$h_2(x, \lambda, Y) - \theta = 0 \tag{3}$$

* Process equality constraints (specifications)

$$h_3(x, z) = 0 \tag{4}$$

* Process inequality constraints (limiting values)

$$l_1 \leq g_1(x, z, Y) \leq u_1 \tag{5}$$

* Process configuration

$$l_2 \leq p_1(x, z, Y) \leq u_2 \tag{6}$$

With,

$$Y = 0 \text{ or } 1; x \geq 0; z \geq 0.$$

In the above equations, x represents a vector of continuous variables, for example, mixture compositions, stream flow rates, stream temperatures; Y represents a vector of binary integer (0, 1) decision variables, for example, unit operation identity; $h_1(x, z, \theta, \beta, Y)$ represents equality constraints related to the process model equations, that is, mass and energy balance equations of different types, where θ represents properties and β represents fitted model parameters; $h_2(x, \lambda, Y)$ represents equality constraints related to chemical properties where λ represents a vector of property model parameters (including kinetic model parameters) and θ represents a vector of physico-chemical properties, including environmental impacts and sustainability related properties (note that different sets of properties may be used in Eqs. (2) and (3)); $h_3(x, z)$ represents equality constraints related to specifications for process design, for example, fixed operating pressure, and/or utility usage (heat addition); $g_1(x, z, Y)$ represents inequality constraints related to process design specifications, for example, lower bounds

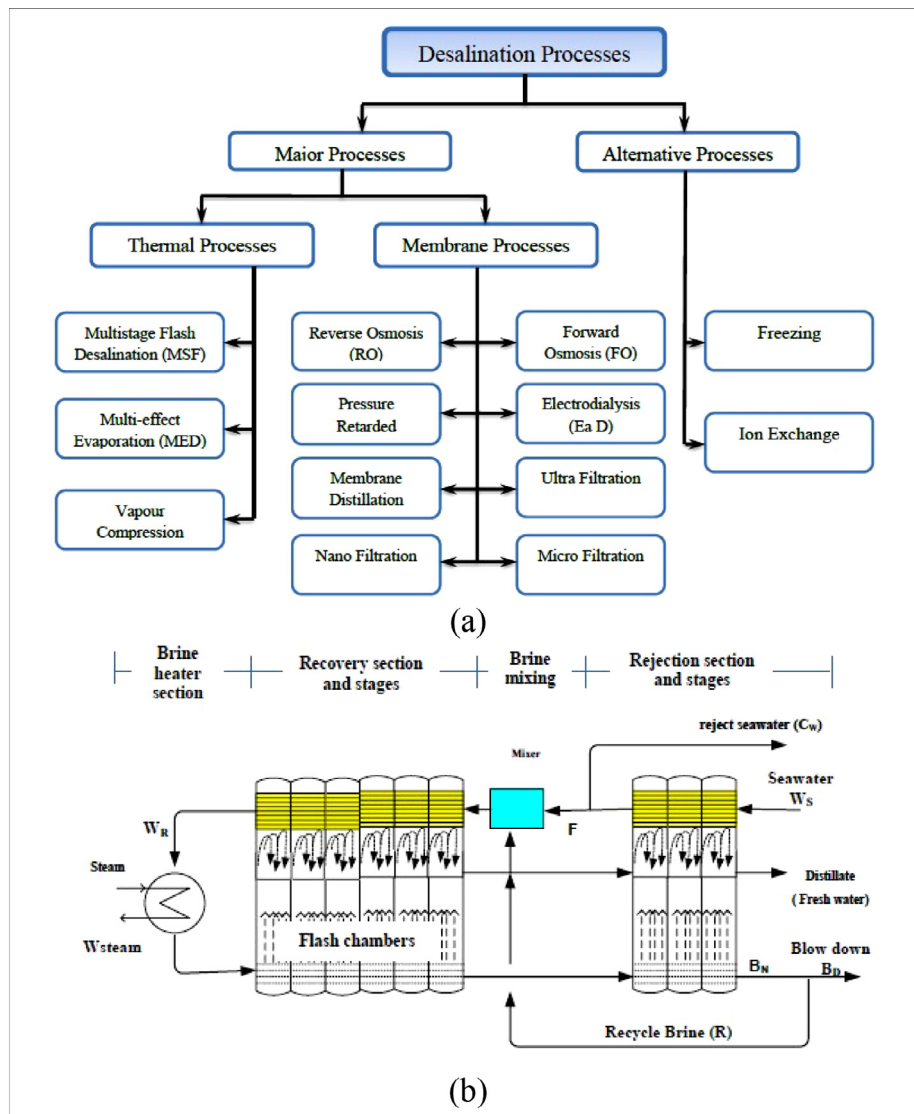


Fig. 6. Desalination technologies; Overview of alternatives (a); MSF desalination thermal process (b) (adopted from El-Dessouky and Ettouney, 2002).

on product purity, sustainability indicators, and, process environmental impacts; and $p_1(x, z, Y)$ represents process network (superstructure) configurations and/or constraints, for example, connections between two processing steps (unit operations); l_1, l_2 , and u_1, u_2 are lower and upper bounds for Eqs. (5) and (6), respectively. The objective function defined in Eq (1), where $f(x)$ represents a vector of linear and/or nonlinear functions and $C^T Y$ represents some cost function, is given as an example. Different forms of the objective function may be used depending on the objectives of the problem being studied. Also, based on the problem definition, Eq. (1) can be either maximized or minimized.

Different combinations of Eqs. (1)–(6) represent various types of mathematical problems representing process simulation, synthesis, design and/or integrated problems. Also, any specific sets of equations can be solved by the direct approach (all the equations are solved simultaneously, as in process synthesis); decomposition-based approach (divides the problem into a set of hierarchical sub-problems, which are solved sequentially, as in sustainable process design); hybrid-approach (divides the problem into sub-problems where models of different scales and types are used, as in combined product and process design). Uncertainties in the model parameters (β and λ) can also be considered as part of the solution method.

2.2.2. Modelling and simulation

Process simulation problems involve the solution of Eqs (2) and (3) with values of all decision variables fixed, input variables and design variables specified (de Prada et al., 2019). Note that the property model equations (Eq. (3)) are usually embedded within the process model equations Eq (2). The model equations can be of various types (such as algebraic, ordinary differential, partial differential) and of various forms (such as, empirical-mechanistic, continuous-discontinuous, discrete-distributed). The modelling and/or simulation objective determines the model type and form. The solution of the model equations need appropriate numerical solvers. For steady state process simulation, the process model equations are represented by algebraic equations (AEs), while for dynamic simulation the process model equations are usually represented by ordinary differential equations (ODEs) and for multi-dimensional simulation (steady state or dynamic), partial differential equations (PDEs). Note that in Eq. (2), the ODEs and PDEs can appear on the left hand sides with respect to other independent variables.

A process simulator is a computer aided tool that guides the user through steps of a simulation work-flow consisting of (as main steps) process definition, model generation and analysis, model parameter retrieval, model equation solution and simulation

Table 1
Process simulators and their uses.

Type	Typical uses	Model type	Examples
Steady state	Mass and energy balance, verify steady state operation; verify unit operation design	Algebraic equations	AspenPlus, ChemCad, gPROMS, Hysys, Aveva Pro/II
Dynamic	Transient response, control system verification, operability-controllability analysis	Ordinary differential and algebraic equations	AspenPlus (dynamics), gPROMS, Dynsim
Distributed	Detailed 3-D modelling of equipment during operation, verification of sizing parameters	Partial differential and algebraic and/or ordinary differential equations	COMSOL, ANSYS-Fluent EDEM

Table 2
Process synthesis tools and their uses.

Type	Typical uses	Problem types	Tools
Synthesis of networks of similar unit operations	Synthesis of heat exchanger networks,	MILP, MINLP	SYNHEAT (Yee and Grossmann, 1990)
Synthesis of processing routes	Determines the optimal processing routes from a superstructure of alternatives, synthesis of RO networks for water desalination	MILP, MINLP	Super-O (Beltran et al., 2017)
Integration and synthesis of processing routes	Determines the optimal integrated networks and also the optimal processing routes from a superstructure of alternatives	MILP, MINLP	Pyosyn (Chen et al., 2021)

results analysis. The scope and application range of the process simulator depends on the models and solvers the simulator has in its libraries of models and solvers. Table 1 lists three types of process simulators together with their main uses. Note that Table 1 is used to highlight the message and is not intended to give a comprehensive list of available tools.

2.2.3. Process synthesis

Process synthesis involves the solution of Eqs. (1)–(6) usually with simpler forms of the process model equations than process design or optimization, and the models are of the steady state type. Eq. (6) represents constraints within a superstructure of processing routes. The objective of the process synthesis problem is usually to determine the optimal processing route to obtain one or more chemical products by converting one or more available raw materials. The property models (Eq. (3)) in process synthesis may also include environmental properties and sustainability metrics so that these effects can also be assessed for the optimal processing routes. Depending on the complexity of the process model equations, the process synthesis problem is usually MILP (mixed integer linear programming) or MINLP (mixed integer nonlinear programming). Together with a solver for the model equations, a solver for optimization is also needed. Usually the solvers for MILP and MINLP also solve the model equations. In MILP problem formulations, the process models are linearized or simple (surrogate) models of the original nonlinear model. Table 2 lists a selection of process synthesis tools. Note that Table 2 is used to highlight the message and is not intended to give a comprehensive list of available tools.

2.2.4. Process design

This problem is also commonly known as flowsheet optimization, unit operation (equipment) design and/or process design-specification Westerberg, 2004; Janus and Engell, 2021). The later two problem types may not involve optimization. As the flowsheet is fixed, the optimization involves solution of Eqs. (1) and (5) with

decision variables with respect to flowsheet configuration as fixed. Therefore, the flowsheet optimization problems are usually nonlinear programming (NLP) or linear programming (LP) depending on whether the process model equations Eqs. (2) and (3) are nonlinear or linear, respectively. Some unit operation (equipment) design problems may involve optimization, if the design problem involves matching the process specifications as well as minimization of costs, for example. The other design problems also involving integer variables, such as the number of stages in a distillation column, are regarded as reverse simulation problems where given the input-output variables, determine the equipment design parameters. The different design problems are usually available as design-options with process simulators and information on them can be found in all process simulator manuals.

2.2.5. Framework for sustainable process design

Tula et al. (2017) proposed a 12-step workflow for sustainable process synthesis, design, and innovation, which consists of a synthesis stage (first 3 steps), a design stage (the next 6 steps) and an innovation stage (last 3 steps). In this paper, application of this 3-stages (or 12-steps) method and associated tools are highlighted through the case studies. Fig. 7 shows an adopted version of a framework, proposed earlier by Tula et al. (2017) that could be suitable for sustainable chemical process synthesis, design, analysis and innovation through an integrated set of computer-aided methods and tools (ProCAFD).

It can be noted in Fig. 7 that a number of methods and associated tools are needed for various steps of the solution procedure. Also, it can be noted that tools for process simulation is an important tool, but it is one of many other needed tools. As the problems are becoming larger and multidisciplinary, need for data of chemicals (properties, hazardous effects, uses in products, etc.), of materials (membranes, adsorbents, catalysts, etc.), product types (blends, functional, formulated, etc.), cost-economics (prices, tax, interest rates, etc.), reaction paths (CO₂ utilization, active pharmaceutical ingredients, bio-conversion); biomass (type, availabil-

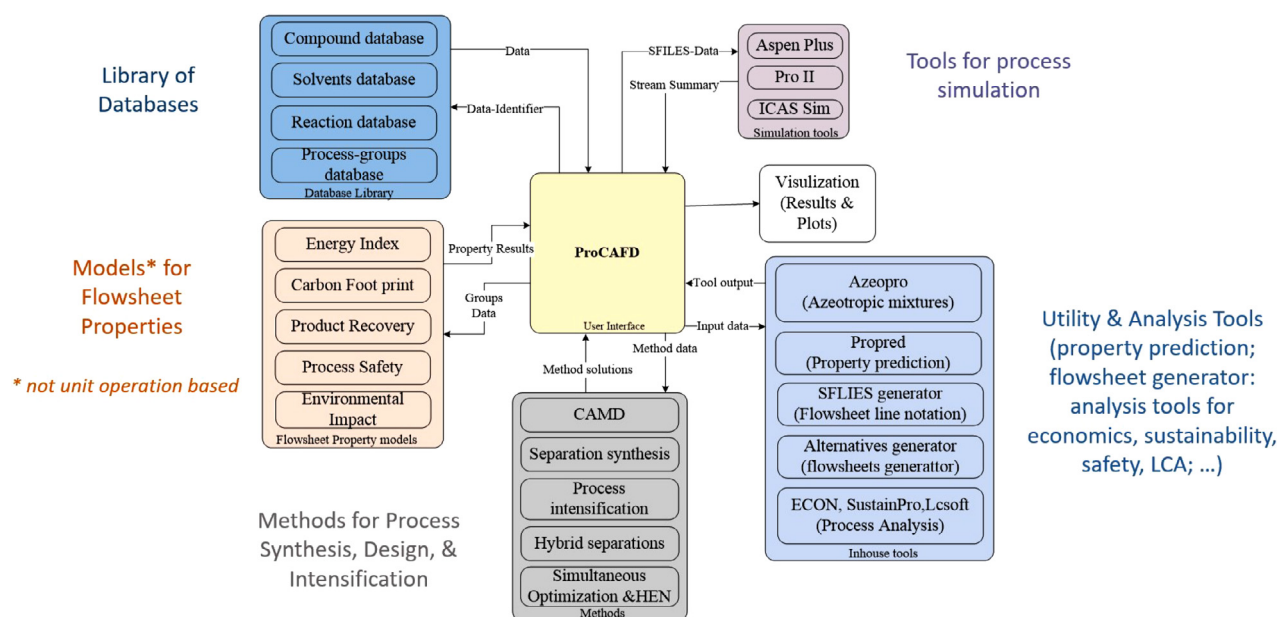


Fig. 7. Framework for integrated (adopted from Tula et al., 2017).

ity, location, etc.) and many more are also increasing. The systems being considered are also becoming more complex, requiring multiple models of different scales. Methods for process design need to be integrated not only with process synthesis, operability, etc., but also with aspects of product design (chemicals, materials, devices, etc.). Analysis of the problem as well as the problem solution always remains an important issue. It is not enough to find a converged numerical solution; the solution needs to be sustainable as well. Finally, to verify the design decisions and generate data for analysis, process simulators of various types are also needed. Note that synthesis, design, etc., can also be performed through a trial-error approach where for every set of decisions, the simulator is used to evaluate the decision (forward approach) and based on the results, the decision is adjusted until convergence is achieved. In the reverse approach, design decisions are made directly, and the process simulator is used only for the final verification.

Life cycle assessment (LCA) is an ISO 14040 standardized method which help evaluating the environmental impacts of a process (Zhou et al., 2014). It is based on the life-cycle inventory (LCI) of the inputs (energy, raw materials, chemicals) and outputs (products) induced by the process construction, operation, and decommissioning. The environmental impacts of a process can be calculated as the sum of the impacts the inputs and outputs will have. For example, the RO process is responsible for more than 90% of the impacts if the energy supplied in the form of electricity is generated using fossil fuel. The local electricity production mix and the value of electric consumption at plant will therefore significantly influence on the impacts of desalination processes. Pre-treatment of seawater, addition of anti-fouling agents and subsequent post-treatment of freshwater, disposal of brine, decision on the energy sources to be used all lead to environmental impact and sustainable issues which needs to be analyzed via Life Cycle Analysis (Vince et al., 2008). In general, all process synthesis design alternatives should be checked for social, economic, and environmental sustainability (Martín, 2016). Recently several tools have been developed for sustainability analysis such as COMANDO, a framework for energy systems optimization (Langiu et al., 2021); DESIRES, a framework that integrates social economic and environmental metrics for decision support towards sustainable design (Azapagic et al., 2016); GreenScope, a tool developed at the US-

EPA for quantifying process sustainability and Life cycle inventory (Smith et al., 2015); and WAR, algorithm that aims at the reduction of waste for the design of sustainable processes (Young and Cabezas, 1999), to list a few.

3. Sustainable technologies, issues & challenges

In this section, using three technologies, the problem formulation, their solution as well as challenges and associated issues are highlighted with respect to model-based computer-aided solution techniques. These three technologies are selected because they all need energy, produce or need fresh water and impact the environment. These technologies are at different levels of development, and so, different aspects of the same set of methods and tools are highlighted. For example, models are fairly well developed in the chemical processing areas, therefore, the highlight is on issues related to combination of sub-networks (process, water, energy, CO₂ capture) into an optimal sustainable integrated network. In the biorefinery area, synthesis of the optimal network is still an issue and therefore, the modelling needs related to synthesis of the optimal processing route are highlighted. In the desalination area, the focus is the optimal design-configuration of a selected set of alternative desalination processes. Therefore, the focus is on the detailed modelling issues. Also, the highlighted issues and challenges are based on the experience gained by the authors in studies involving them. By addressing the identified issues, we aim to highlight how PSE methods and associated tools can help achieve UN sustainable goals such as responsible consumption and production of chemicals, clean water by efficient use of potential energy sources while reducing environmental impact via CO₂ capture and reuse.

3.1. Sustainable carbon capture and utilization

Numerous examples of CCU can be found in the published literature (for example, see (Ghiat and Al-Ansari, 2021a)). In this paper, a few that have employed integrated solution approaches covering process synthesis, design and analysis are discussed. Fig. 8 highlights the main idea of CCU alternatives in the form of a superstructure of alternatives. Note that in Fig. 8, there are also alternatives for the CO₂ capture process (not shown in the figure);

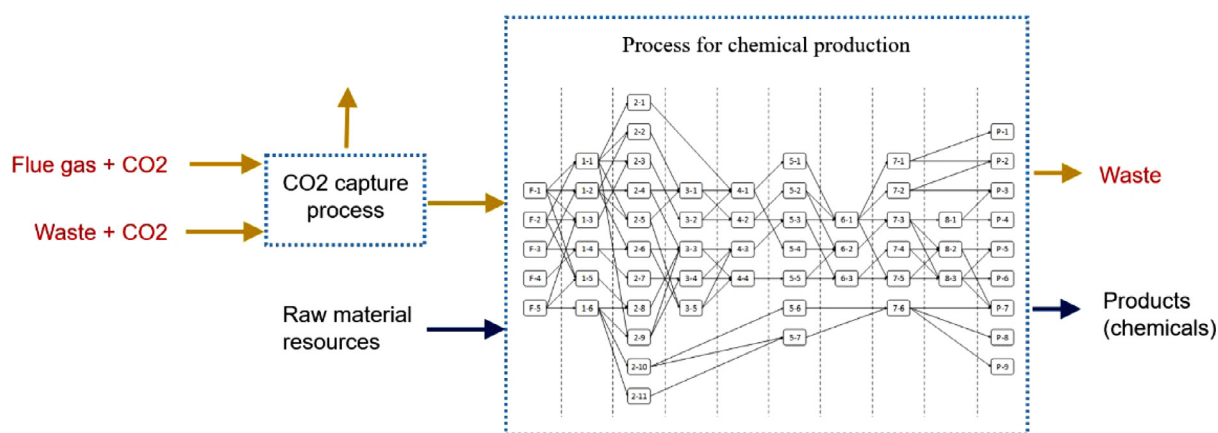


Fig. 8. Superstructure of alternatives for CCU.

Table 3

List of chemical processes with CO₂ reduction studied by authors.

CCU problem	Process type	Chemical process	Impact
Problem 1 (Kongpanna et al., 2015)	Use of captured CO ₂	DMC from various sources	Net reduction of CO ₂ , increased profit
Problem 2 ((Roh et al., 2016))	Use of captured CO ₂	DMC production; methanol synthesis	Net reduction of CO ₂ , increased profit
Problem 3 (Frauzem 2017)	Use of captured CO ₂	DME & succinic acid production	Net reduction of CO ₂ , increased profit
Problem 4 (Wisutwattana et al., 2017)	Process intensification	Ethylene glycol production	Net CO ₂ reduction, increased profit
Problem 5 (Castillo-Landero et al., 2018)	Process intensification	Dioxalane production	Reduction of energy demand, carbon-footprint
Problem 6 (O'Connell et al., 2019)	Hybrid separation	Various hybrid separation schemes	Reduction of energy, carbon-footprint
Problem 7 (Li et al., 2020)	Use of captured CO ₂	Xylitol production	Net reduction of CO ₂ , increased profit

the waste from the chemical production process should not include any CO₂; and, although the power and other utilities (steam, water, etc.) are not shown in the figure, they should be integrated as shown in Fig. 1. A solved example of this integration with and without uncertainty can be found in Li et al. (2020). Table 3 lists a selection of CCU, and intensified problems solved with the methods and tools listed in Section 2 and highlighted in Fig. 7. Appendix A gives details of the models used for solving process synthesis-design problems.

In the solution of the problems listed in Table 3, the 3-stages sustainable design methodology (Tula et al., 2017) has been applied, although, the problems solved did not employ all three stages of the methodology. In stage 1, superstructure-based MILP model has been formulated and solved to obtain the optimal processing route for CO₂ utilization. In stage 2 process simulator-based flowsheet optimization has been performed. The objective function has been to minimize costs and CO₂ emission. Even though significant improvements and negative net CO₂ emissions have been achieved for the CCU alternatives listed in Table 3, as pointed out by Frauzem (2017), it is not clear whether the needed global net CO₂ emission reduction can be achieved through CCU, while CCUS only delays the problem of global warming on earth. A superstructure of alternatives for CCU and a specific CCU solution are highlighted in Fig. 9, where one processing route for CO₂ capture (coal_MEA_CO2), hydrogen supply (M1.1), methanol synthesis (Meohdir-syn plus Flash1.1; Dist2.1 & 3.1) and DME synthesis (Dmemeoh plus Flash6.1; Dist7.1 & 8.1) are shown together with other likely alternatives. A further improvement than what was reported previously, is possible by adding hybrid and PI options to the original solutions of Frauzem (2017). Detailed results of synthesis, design, simulation, and analysis for the processes listed in Table 3 can be obtained from the authors. Solved problems on similar topics have also been reported by others, for example, reactive distillation (Kiss, 2011), hybrid separation (Skiborowski et al., 2014), carbon capture and utilization (von der Assen et al. 2014),

integrated process synthesis, design, analysis (Tusso-Pinzón et al., 2020), to name a few.

3.1.1. Issues and challenges

The main challenge and issue are how to reduce the CO₂ emission from the operation of chemical processes, which are generally, energy intensive. As the resources on earth are not distributed uniformly, a challenge is to find solutions that benefit earth globally and not a specific region. Use of renewable as well as non-renewable sources of energy need to be combined to supply the energy demand of the chemical processes such that the CO₂ emitted indirectly by the power plants could be captured and utilized. Mixing renewable with non-renewable sources, could provide a solution to tackling global warming by the chemical and related industry. Process intensification and hybrid distillation schemes (HDS) for energy consumption reduction have been proposed. There are solutions that could be immediately employed, such as membrane-based hybrid distillation schemes, instead of waiting for total replacement of distillation columns, which is a long-term solution. As pointed out by (O'Connell et al., 2019), distillation is highly energy intensive only if high purity products are desired. Through HDS, the energy demand for distillation columns can be significantly reduced. Also, the DS or other innovative hybrid schemes should be considered for problems that are energy intensive and not those that are difficult but not really energy intensive.

3.2. Sustainable biorefinery

3.2.1. Biorefinery

The synthesis of a biorefinery is a problem typically addressed in three stages. The first one is pre-screening or synthesis of processing routes, that can be performed based on literature information to narrow the search of technologies or using high level modelling approaches. Next is the selection and design of promising

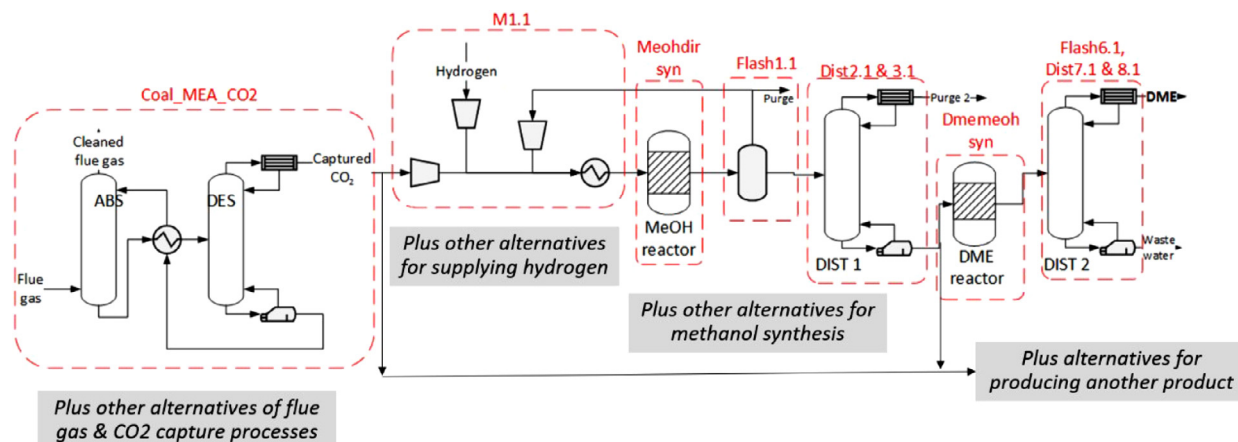


Fig. 9. Example of a superstructure of CO₂ capture and utilization (adopted from Frauzem, 2017).

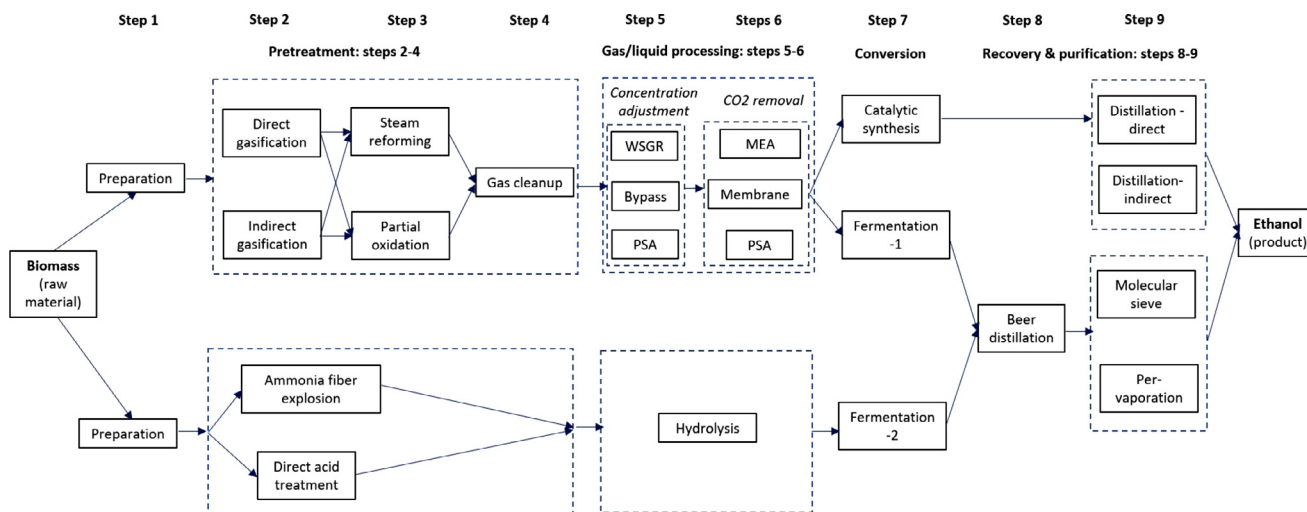


Fig. 10. Example of a superstructure for ethanol production from biomass (lignocellulose).

flowsheet alternatives containing preselected technologies, which can be optimized again within the framework of a superstructure. The problem solved at this stage is classified as design and analysis of the process and gives a base case design. The third stage consists of innovation or improvement of the base case through detailed modelling as well as the integration of energy and water networks, more efficient separation sequences and/or process intensification (Kraemer et al., 2011; Tian et al., 2018).

The formulation of the synthesis–design–innovation problem for a lignocellulose based biorefinery with ethanol as the main product involves two different paths, the gasification and the hydrolysis one as shown in Fig. 10, where a superstructure of alternative processing routes are highlighted. The gasification path (thermochemical route) produces syngas, which serves as raw material for conversion to value-added chemicals, while sugars (from hydrolysis path) serve as raw material for production of bulk and specialty chemicals (Aden et al., 2004). As shown in Fig. 10, each path consists of several processing steps and each step has multiple options for performing the associated task. The thermochemical path includes 9 processing steps consisting of preparation step 1 (biomass washing and grinding); pretreatment steps 2–4 (either direct (DG) or indirect (ID)); followed by reforming, either steam reforming (SR) or partial oxidation (PO); followed by gas cleanup. Under gas processing steps 5–6, alternative technologies can be used to adjust the H₂ to CO ratio (Water Gas Shift Reaction, WSGR), a bypass or Pressure Swing Adsorption, PSA) followed by CO₂ removal (Amine

based absorption, MEA; membrane-based separation or PSA). For conversion step-7 two alternatives are highlighted (fermentation or catalytic synthesis). Note that the recycle of the unconverted gases is not shown in Fig. 10. The recovery and purification steps 8–9 depend on the options used for conversion. In the case of fermentation, first a beer column is used first to concentrate ethanol in the product stream and then to purify (dehydrate) through molecular sieves or pervaporation. In the case of catalytic synthesis, recovery and purification are done either through directly sequenced or indirectly sequenced distillation.

The hydrolysis path consists of biomass washing and grinding (preparation step 1), followed by pretreatment (steps 2–4), where several technologies can be used, such as Ammonia fiber explosion (AFEX) or dilute acid treatment (DA). Steps 5–6 represent hydrolysis of cellulose to sugars. In conversion (step 7) fermentation of the sugars to ethanol occurs. The recovery and purification of ethanol follows the same as highlighted above for the thermochemical path.

For any model-based synthesis and/or design and optimization, each of the alternatives for the processing steps within the processing route (process flowsheet) need to be represented by an appropriate model. A combination of simple mass and energy balance-based models, correlations based on rules of thumb, surrogate models, etc., can be derived to represent Eqs. (2)–(4). The development of surrogate models to estimate, for example, the product yields in conversion steps requires regressed model parameters

Table 4
Biorefinery design problems. Technologies and portfolio of products.

Problem	Raw Material	Biomass treatment	Product	Authors
Synthesis	Switchgrass	Biochemical / gasification Thermal/ biochemical Thermal/ biochemical	FT/ hydrogen/ ethanol Portfolio Portfolio	Martín and Grossmann (2011) Ponce-Ortega et al. (2012) (Kelloway and Daoutidis, 2014)
	Various	Biochemical Pyrolysis/ gasification Biochemical	Portfolio Propylene/liquid fuels Portfolio	Bertran et al., 2017 Yuan and Eden (2016) Ng et al. (2019)
Design	Corn Stover	Biochemical	Ethanol	Aden and Foust (2009)
	Ligno		Ethanol	Piccolo and Bezzo (2009)
	Corn Stover		Ethanol	Kazi et al. (2010)
	Switchgrass		Ethanol	Tao et al. (2011)
	Switchgrass		Butanol	Malmierca et al. (2017)
	Corn stover	Gasification	Ethanol	Phillips et al. (2007)
Process integration	Corn stover		Ethanol	Dutta and Phillips (2009)
	Corn	Biochemical/	Ethanol	Cucek et al. (2011)
Process- product	Sugar cane	Gasification	Methanol/ethanol	Albarelli et al. (2017)
			ETBE/ethanol	Galán et al. (2019)

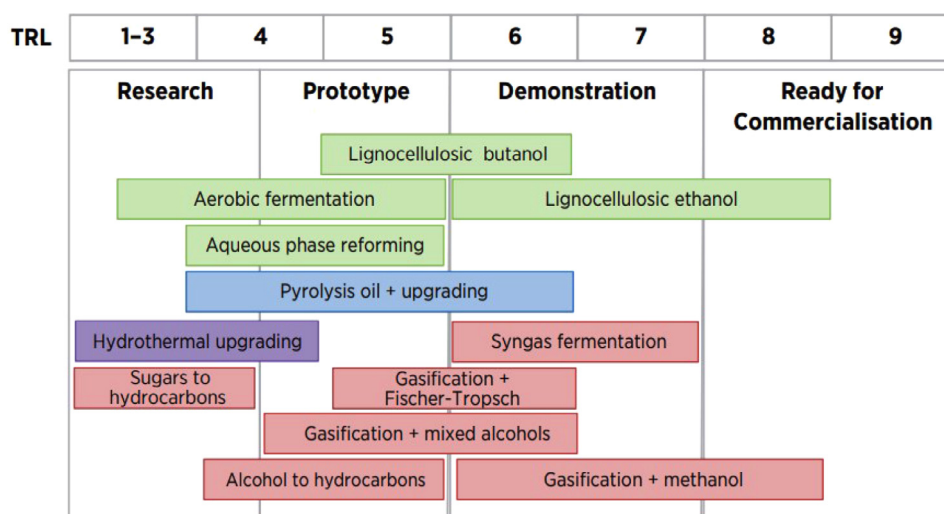


Fig. 11. Status of biobased processes. Colors represent the principal conversion process, hydrolysis (green), pyrolysis (blue), hydrothermal upgrading (purple) and gasification (red). (With permission from IRENA 2016).

through fitting of collected data. Models for separation tasks usually require phase equilibria predictions, while for energy balance calculations, properties such as heat capacities, heats of formation, etc. (represented by Eq. (3)) are needed. In addition, to avoid decomposition of species, catalyst poisoning, improper feed compositions for reaction, etc., bounds need to be imposed (represented by Eq. (5)). A selected set of technologies for each of the processing steps constitutes the process flowsheet (the superstructure is represented through Eq. (6)). The superstructure optimization model is formulated as an MINLP optimization problem using as objective function the total annualized cost (objective function represented by Eq. (1)), with special interest in the cost of the utilities. In appendix B, examples of the superstructure model, the kinetic model and the separation model are given to highlight the modelling issues related to biorefinery synthesis and optimization.

The complexity of the synthesis-design problem formulation increases if integration of water and energy (Duran and Grossmann, 1986b), heat exchanger network (Yee and Grossmann, 1990) and water network (Martín et al., 2011) are considered or simultaneous process synthesis, heat and power integration (Baliban et al., 2011).

A collection of selected biorefinery synthesis-design-innovation (integration) problems based on literature survey is given in Table 4. The listed biorefinery problems are organized in terms of problem type, raw material, biomass treatment, products and

references. However, as shown in Fig. 11, the technology readiness level of the biorefineries is mostly at prototype and demonstration levels, while only lignocellulosic ethanol and gasification-based methanol has reached commercialisation.

3.2.2. Issues and challenges

Biorefineries can be considered the future chemical complexes for sustainable production of chemicals, fuels and energy aiming at a responsible production system so as to address the UN development goals. Conversion of biomass into a desired product (often termed as an intermediate chemical), which could serve as the starting material for a wide range of higher-value products is highly species specific, requiring different equipment and technologies as well as operating conditions for a desired intermediate chemical of choice. For example, breaking down biomass into lipids, sugars or proteins requires different operating conditions as a function of the biomass structure and composition (as highlighted in Fig. 4). Since biomass availability is location dependent, therefore, choice of the appropriate biomass to produce the desired product, employing a collection of technologies configured into an optimal processing route is a challenge that needs to be resolved.

Another challenge (and issue) to the development of an optimal biorefinery is the lack of data to evaluate the performance of the designed process. As first-principles based models are not available for many of the operations, model parameters need to be esti-

ated with measured data from planned experiments. A particular example of this issue is the kinetic model for the co-fermentation of C5 and C6, which requires a large number of adjustable parameters. The formulation of this problem should include models that are predictive but at the same time simple, consistent, and having acceptable accuracy. For this reason, use of appropriate thermodynamic models, experimental data and surrogate models developed from rigorous simulation models or through regression with measured data from experiments are encouraged.

The number of possible alternatives for a biorefinery synthesis-design problem increases as many technologies can be employed for specific operations of a processing route. For example, from gasification to gas cleanup, the number of possible alternatives increases as it is possible to find many technologies to perform these operations. Also, from the data in Table 4, it can be noted that different raw materials can be used in a biorefinery to produce the same product. Therefore, the selection and evaluation of different alternatives is another challenge (and issue) since tradeoffs between different factors such as costs, yields, waste, resources, etc., need to be considered.

New technologies and new chemicals whose model and/or data are not found in process simulators commonly employed for synthesis-design related calculations, require the development of models that can be added through flexible software architecture. As most of the traditional biorefineries have not yet reached commercial exploitation, improvement in terms of innovation and/or integration is necessary to make them more attractive (IRENA 2016).

As biomass is a living organism whose actual composition depends on how it is grown, it is a challenge (and issue) to either grow the biomass towards a certain composition that allows an optimal operation of a biorefinery, or use the model of the biorefinery to look for the type or species of the biomass that best suits the process. For example, use of algae (Martin and Grossmann, 2013) and lignocellulosic (Galán et al., 2019) biorefineries have been presented. This inverse problem is especially interesting and suitable for of interest in the biorefinery industry, especially, the one that links process and product design.

3.3. Sustainable water desalination

3.3.1. Desalination process

The supply of water using different energy sources and different desalination processes for different purposes and the associated demands are highlighted in Fig. 12. Note, that Fig. 12 illustrates a specific application of the concept highlighted in Fig. 1, namely, options available in water desalination. Fig. 12 also shows the link between the 3 technology areas and their effect on the energy-chemicals-water-environment-nexus presented in this paper. Note, that wastewater treatment of the used water is an important topic, that could also be integrated with the process to reduce the demand on fresh water, as pointed out by Li et al. (2020). Many reviews on wastewater treatment technologies can be found, for example, (Pesqueira et al., 2020) and Rout et al. (2021).

The starting point in water desalination optimization problems is Seawater defined conditions (in terms of salinity, temperature, pH), variable freshwater demand profile, the selected desalination process (for example, MSF) plant configurations, fixed design specification of each stage of MSF, equipment sizing parameters (volume of the storage tank, seawater flow), freshwater demand profile, operating time horizon of 24 h; different grades of water and many more (depending on the problem complexity).

The objective of the typical design problem is to find the optimal process configuration (MSF/RO/MEE) representing the desalination process. For example, for MSF, it is the number of stages,

the recycled brine flow rate, R ; the make-up seawater, F ; and the equipment design of stages (size, condenser tubes, venting).

The optimal solution is obtained by formulating an optimization problem as described in Section 2.2.1 Eqs (1)–(6). A more specific example of Eqs. (1)–(6), applied to desalination process optimization is given below. Additional details are given in Appendix C.

$$\text{Minimize, } F_{OBJ} = F \{ C^T Y + f(z, x) \} = \begin{cases} \text{(total annualised cost)} \\ \text{or, (production cost)} \\ \text{or (specific energy cost)} \end{cases} \quad (7)$$

Subject to,

- Y (MSF: brine recycle; RO: by-pass/recycle, energy recovery device; fossil fuel/solar/wind/biofuel/geothermal);

- z (MSF: brine recycle rate, make-up seawater, top brine temperature, steam temperature, number of recovery stages; RO: Feed pressure, number of stages, number of pumps, number of turbines, number of pressure vessels, number of membranes in a pressure vessel; MEE: number of effects, number of pre-heaters, top brine temperature, steam temperature, final effect temperature)

- x (stream flowrates, stream temperatures, stream concentrations), and,

Constraints,

- Eq. (2) (process model): The steady state process model consists of mass and energy balances and the total number of equations depends on the process configuration (number of stages, number of pressure vessels and number of effects) of the MSF, RO and MEE processes, respectively.

- Eq. (3) (property models): The models consist of the estimation of mixture boiling point temperature elevation, calculations of overall heat transfer coefficients subject to fouling, thermodynamic losses in MSF and MEE processes, temperature depended permeability constants, physical properties such as density, viscosity.

- Eq. (4) (process specifications): Specifications, for example, water demand of different grades, are given as constraints.

- Eq. (5) (process constraints): Constraints such as on Top Brine Temperature, and steam temperature are imposed.

- Eq. (6): The process configuration relates to number of stages, number of pressure vessels, number of evaporation effects, energy recovery device, as well as specific connections. Note that the processing route is fixed but the configuration within the processing step needs to be determined.

Table 5 gives a list of problems considered in the past in terms of problem type, energy sources, type of process, raw material, and products. The general process formulation presented in Section 2 directly applies to these problems.

3.3.2. Issues and challenges

Water-energy-food-chemicals-environment are essential components of a sustainable smart city. Fig. 1 implicitly has all these required components. Regarding water, Fig. 13 shows the various possible components of water management in a smart/sustainable city while Fig. 12 describes only a facet of the water management problem i.e., the sustainable production of freshwater using renewable energy and sustainably produced chemicals.

The researchers listed in Table 5 only considered a subset of the problem shown in Fig. 13. For example, (Hawaidi and Mujtaba, 2011) considered fossil fuel as the source of energy but considered detailed MSF process model and variable water demand. Filippini et al. (2019) considered solar energy and detailed MEE and RO process model but without fouling. Karimanzira (2020) considered wind as the energy source but considered a detailed RO process model with variable membrane fouling. Martino et al. (2021) considered renewable sources of energy, simple surrogate-based RO process model and different grades of water.

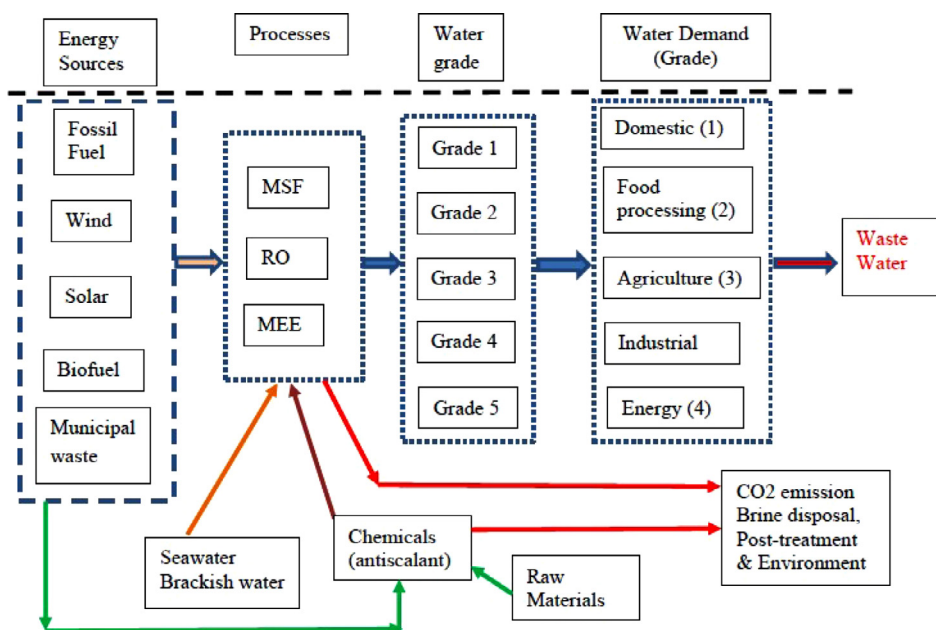


Fig. 12. Superstructure of water desalination (expanded from Fig. 1).

Table 5
Desalination design and operation problems using different energy sources and processes.

Problem Type	Feedwater, energy sources	Process	Authors
Fixed demand; optimize design and operation	Seawater with fixed salinity and temperature, fossil fuel	MSF	Tanvir and Mujtaba (2008)
Variable (daily and seasonal) demand; optimize design and operation	Seawater with fixed salinity but variable temperature, fossil fuel	MSF	Hawaidi and Mujtaba (2011)
Fixed demand; superstructure-based optimization	Brackish and Seawater with variable salinity and temperature, fossil fuel	RO	Sassi and Mujtaba (2012)
Optimize design and operation	Seawater with fixed salinity and temperature, LNG cold energy	Freeze Desalination	Cao et al. (2015)
Optimize design and operation	Seawater with fixed salinity and temperature, wind-solar energy with energy storage	RO	Maleki (2018)
Optimize design and operation	Seawater with fixed salinity and temperature, solar energy	Combined power plant and MSF	Shaaban (2019)
Optimal design and economic evaluation	Seawater with fixed salinity and temperature, Solar energy	Hybrid MEE-RO	Filippini et al. (2019)
Fixed demand; fixed design, optimize operation and minimize energy consumption	Brackish water with fixed salinity and temperature, fossil fuel	Industrial RO	Alsarayreh et al. (2020)
Fixed demand; optimize design and operation	Seawater with fixed salinity and temperature, fossil fuel	Hybrid MEE-TVC-RO	Al-hotmani et al. (2020)
Optimize design and operation	Seawater with fixed salinity and temperature, wind energy	RO	Karimanzira (2020)
Optimize design and operation	Different types of water sources, renewable energy sources	RO	Martino et al. (2021)

Although the solution of the whole problem will require the use of MINLP techniques (which are available) but the issue that remains is the computational power needed to solve such a large-scale problem incorporating very detailed process models (including dynamic fouling models) for each of the components/unit operations of the total system. Even, a superstructure-based RO network optimization can lead to very large-scale mathematical problems. Often, a maximum of two to three stage RO process is considered due to computational burden (Alnouri and Linke, 2012) and limited choices of computational tools available to solve such problems.

The challenges in water management remain in formulating the whole problem (considering all facets of water management (Fig. 13) from systems engineering perspective and develop tools to solve the total problem. Even to formulate a partial problem of a smart city in terms of its water, energy, and chemical requirements (as is the focus of this paper) as a unique systems engineering problem is necessary but is still a long way to resolution.

Guerra and Reklaitis (2018) have pointed out some of the challenges in water management within energy systems.

4. Perspectives

4.1. Based on current trends

Resources recovery and reuse is gaining more importance in all three types of technologies highlighted in Section 3. Biomass and specifically waste biomass and captured CO₂ are intended to be used as feedstocks for the manufacture of value-added products, beyond the traditional use as energy and fuels resources, for a sustainable chemical industry. The change in the raw materials aims at improving not only the sustainability of the facilities by adding products to the portfolio, but also to providing the energy, thermal or electrical, required to run the facility as well as the entire industry. However, this transition to a more sustainable chemical industry and in particular to the production of specialty chemicals

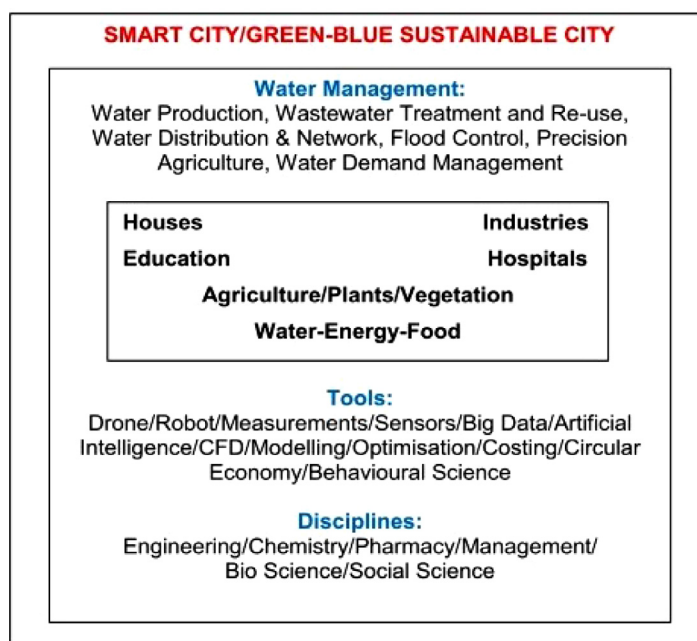


Fig. 13. Smart city, water management and potential tools.

including large molecules poses a challenge for the simulation of the production and purification stages. Commercial process simulation software is not able to model physico-chemical extractions, in particular, to predict the yield as a function of the raw material, nor the thermodynamic properties of these complex compounds. Surrogate or black-box models based on measured data from experiments are being developed to evaluate the performance of such units while higher level molecular structure-based property modelling is gaining support to predict the properties of the species themselves (Bhosekar and Ierapetritou, 2018; McBride and Sundmacher, 2019). Process intensification as well as solution of large integrated synthesis-design problems under uncertainty of data and models are also getting urgent attention. These have been identified as options to obtain sustainability and thereby achieve the goals of circular economy (Pistikopoulos et al., 2021).

In the past, in most cases, the application of renewable energy in desalination has been restricted to the use of one type of renewable energy (solar/wind/geothermal/thermocline/LNG) with one type of desalination process (MSF/MEE/RO/Freeze) (Cao et al., 2015; Shahzad et al., 2018; Karimanzira, 2020). Only handful of work can be found where co-generation of power is also considered with one type of renewable energy and one type of desalination process (Shaaban, 2019). Filippini et al. (2019) considered dual energy sources (solar and fossil) in hybrid (MEE-TVC-RO) desalination using very detailed process models. Only recently a matrix of energy sources (solar/wind/grid) were considered but with only RO desalination process (Maleki, 2018; Martino et al., 2021) but with single or multiple grades of water and using simple process models.

As summary, three additional specific perspectives, not ordered in terms of priority, are highlighted below.

- * Location dependent sustainable integrated systems with net zero or negative CO₂ emission should be extended to other greenhouse gases.
- * Biomass would be the source for chemicals and power towards a new sustainable chemical industry.
- * Sustainable water management will require the use of efficient desalination processes (thermal, membrane) using renewable resources (energy, chemicals) to reduce carbon footprint.

4.2. Based on future needs

Although food has not been explicitly considered, it is directly linked to energy (processing and transportation), water (processing and agriculture) and chemicals (processing and agrochemicals). Any development of future smart cities will require the formulation and solution of the total problem using a more advanced systems approach. There is no single model-based platform currently available, which can facilitate the formulation and solution of such problems.

In the Gulf regions where there are extreme shortages of freshwater, centralized desalination plants are in place for supplying water for domestic and agricultural use and are heavily subsidized by the governments for energy supply. Often these plants have not been designed to take advantage of all available sources of renewable energies (such as wind, biomass, geothermal, thermocline, etc.). Resources on earth are not uniformly distributed. While there is shortage of water in these regions, there is plenty of solar energy sources, which could be used. In other regions, like in Switzerland, a combination of water, wind and solar sources are used to achieve sustainability (Limpens et al., 2019).

The framework highlighted in this work has the potential to allow development of decentralized smart cities by considering energy-water-chemical-environment nexus with the use of locally suitable energy sources (solar, wind, biomass, thermocline, municipal solid wastes, etc.). However, this will only be possible when appropriate model-based techniques are available.

Although the currently available Commercial software such as ASPEN, Aveva PROII and gPROMS have been widely employed for modelling, optimization and control of processes, the application of these tools in new intensified process operations, desalination and biorefinery related processes have not been fully exploited and require further development to reach commercial use for these and other renewable based processes.

The transformation of the chemical industry involves the transition towards biomass as renewable raw material to substitute current bulk and platform chemicals as well as a raw material for value-added products in the food and health industries. While several stages are widely known and already in operation, biomass processing is challenging and sensitive to the different species that

affect the technologies and the operating conditions. The availability of biomass is region dependent and costly transportation results in the need for particularized facilities that are a function of the type of biomass available in the regions of influence of the processing facility. The design becomes an art as well as an engineering work. Supply chain becomes an important issue for the sustainability of the future chemical industry based on renewable resources as well as the shift into distributed production in certain cases to make the most of the available resources (García and You, 2015; Sellitto et al., 2019). In addition, biomass wastes are contributing to create the biocircular economy aiming at providing further use to waste as raw material for that bio based chemical industry while providing the proper treatment and management to the vast amounts of organic wastes generated by human activities. This contribution can help address social issues such as migration to larger cities but fixing population when biorefineries are installed in forest and agricultural areas (Heras and Martín, 2020). This is expected to contribute to the social pillar of sustainability.

As summary, three additional specific perspectives, not ordered in terms of priority, are highlighted below.

- * Biomass species selection can determine the products obtained regionally.
- * Process optimization based on renewable resources requires development of new class of tools.
- * Social welfare will depend on the proper use and distribution of fresh water, and renewable based products and circular economy must become a reality.

5. Conclusions

The resources that allow mankind to thrive through products that are made from them, are being stretched; supply of water, a pivotal requirement for food and energy production, is becoming a major concern; use of fossil fuels, supplying the process energy demands, continue to increase emissions of greenhouse gases and impacting the environment negatively. All these development point to an urgent need for change in the selection, distribution and use resources. Resources such as biomass, energy and water need to be used efficiently through integrated process-utility networks. New and more sustainable technologies need to be developed, taking into account, the uneven distribution of natural resources on earth.

The challenges and opportunities that a model-based systems approach faces related to their application for the development of sustainable alternative technologies for carbon capture and utilization, biorefinery and water desalination have been highlighted and perspectives on their resolution have been presented. These three key technology areas are interlinked with each other through their demands for energy, demands and/or production of fresh water, and impacts on the environment caused by their operations. Even though many examples of carbon capture and utilization, biorefinery and water desalination could be found, the challenges with respect to their sustainable development still exist. This means opportunities exist for the Process Systems Engineering community to not only develop the needed methods and associated tools but also to contribute towards sustainable development through innovative solutions. More efforts are needed to develop new model-based methods and computer-aided tools that are predictive, intelligent, versatile and have the ability to solve a wide range of problems correctly, consistently and efficiently. This means currently available property databases need significant extensions, raw material characterization needs improvements, new process and /or property models need to be developed, etc., so that integrated, novel and more sustainable technologies can be identified, their performances verified, and specific sustainable development goals achieved.

This paper identified specific PSE methods-tools that can help to address the challenges. In particular, PSE methods-tools could serve as the glue that will link models, methods, data, etc., from different sources and disciplines together so that natural resources are utilized efficiently, and the criteria for achieving zero-waste and/or circular economy are satisfied. Methods and associated tools would therefore be able to contribute to the achievement of some of the related sustainable development goals of the United Nations.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix

Note that all references to Eqs. (1)–(6) in appendices A, B and C refer to the equations in Section 2.2.1.

Appendix A. Combined chemical process with energy supply and wastewater treatment

The full model for superstructure-based optimization to determine the optimal network with net CO₂ emission is given in Li et al. (2020). The objective function used for a 3 sub-network problem is given below:

$$Z = \sum_{n=1}^3 (S_n^{PROD} - C_n^{RAW} - C_n^C - C_n^E - C_n^H - C_n^{water} - C_n^{CAP} / \tau) \quad (A1)$$

Where, Z is the objective function being minimized, subscript n indicates sub-network (chemical process, water supply and energy supply), S indicates revenue from product sale, C_n^{RAW} , C_n^C , C_n^E , C_n^H , C_n^{water} are operating costs for raw material, chemicals, electricity, energy, water respectively for the sub-networks, while C_n^{CAP} is the vector of capital costs for sub-networks and τ is the life time of the project.

The processes in each network are represented by simple mass and energy balance models for mixers, stoichiometric conversion reactors, split factor-based separators and stream dividers and bypass (no change in the entering the leaving streams). With these models, in principle, all sub-networks can be represented. For these simple process models, Eq. (3) is not necessary because the property data is used estimate the split factors for the separators and kinetic data is used to estimate the conversions for the reactors. Eqs. (4) and (5) represent the constraints in terms of raw material availability, product purity, energy demand-supply, etc. Eq. (6) represent the connections not allowed in the superstructure. For example, power for pumps and/or compressors are supplied through electricity sub-network.

Sample mass balance model is given for process unit operations (Eq. (2)): mass balance equations

$$g_{i,k}^M = \sum_{ii} f_{ii,k}^{IN} \mu_{i,ii,k} \quad (A2)$$

mixer:

$$f_{i,k}^M = f_{i,k}^{IN} + g_{i,k}^M \quad (A3)$$

Reactor:

$$f_{i,k}^R = f_{i,k}^M + \sum f_{react,k}^M \theta_{react,r,k} \gamma_{i,r,k} MW_i / MW_{react} \quad (A4)$$

Separator:

$$f_{i,k}^W = f_{i,k}^r (1 - \delta_{i,k}) \quad (A5)$$

$$g_{i,k}^W = f_{i,k}^R - f_{i,k}^W \quad (\text{A6})$$

Divider:

$$f_{i,k}^{OUT,1} = f_{i,k}^W \sigma_{i,k} \quad (\text{A7})$$

$$f_{i,k}^{OUT,2} = f_{i,k}^W - f_{i,k}^{OUT,1} \quad (\text{A8})$$

Process constraints Eq. (4) and (5): raw material (availability):

$$\sum_i F_{i,k,l}^{W,LOC} \leq AVAIL_{k,l} \quad (\text{A9})$$

raw material (demand):

$$\sum_i F_{i,k,l}^{W,LOC} \leq DEM_{k,l} \quad (\text{A10})$$

Superstructure connection (Eq. (6)):

To and from streams of a step:

$$f_{i,k,kk}^1 \leq f_{i,k}^{OUT,1} S_{k,kk}^P \quad (\text{A11})$$

In the above equations, subscripts i, k, kk, l, ii represent component, interval (unit operation) in step k , interval in step kk , interval in step l , respectively; superscripts $LOC, IN, M, OUT, R, W, 1, 2$ indicate location, inlet, mixer, outlet, reactor, waste (separator), outlet exit numbers, respectively; f, g, F are intermediate stream flowrate, generated flowrate and feed flowrate, respectively; θ is conversion; λ is stoichiometric coefficients; δ is component split factors; σ is stream split factor; $AVAIL, DEM, MW$ are short for available, demand and molecular weight, respectively. The full model document including the optimization code as GAMS file can be obtained from the authors. The above problem represents a network synthesis problem.

Appendix B. Biorefinery

The objective function to minimize is given by,

$$\min Cost = \sum_i C_i \cdot U_i \quad (\text{B1})$$

Where, C_i correspond to the cost of the different utilities and U_i the utilities, such as steam or electricity.

Subject to,

*Process constraints (Eq. (2)): Simple mass and energy balance models

Mixers:

$$\sum_{i \in IN} f_{i,k} = f_{out,k} \quad (\text{B2})$$

$$f_{i,k}^{OUT} \cdot H_i = \sum_{j \in IN} f_{i,k}^{IN} \cdot H_j \quad (\text{B3})$$

Heat exchangers:

$$\sum_{j \in IN} f_{i,k}^{IN} = f_{i,k}^{OUT} \forall j \quad (\text{B4})$$

$$Q = \sum_{j \in OUT} f_{i,k}^{OUT} \cdot H_i - \sum_{j \in IN} f_{i,k}^{IN} \cdot H_j \quad (\text{B5})$$

Compressors:

$$\sum_{j \in IN} f_{i,k}^{IN} = f_{i,k}^{OUT} \forall j \quad (\text{B6})$$

$$T^{OUT} = h_{1,Compressor}(T^{IN}, P^{IN}, P^{OUT}) \quad (\text{B7})$$

$$W = h_{1,Compressor}(T^{IN}, P^{IN}, P^{OUT}) \quad (\text{B8})$$

Splitters:s

$$f_{i,k}^{OUT} = (\sigma_{i,k}) f_{i,k}^{IN} \quad (\text{B9})$$

$$\sum_k \sigma_k = 1$$

Reactor (Gasifier)

$$f_{i,k}^{OUT} = f_{i,k}^{IN} + \sum f_{react,k}^{IN} \theta_{react,r,k} \lambda_{i,r,k} (MW_i / MW_{react}) \quad (\text{B10})$$

$$Q = \sum_{j \in OUT} f_{i,k}^{OUT} \cdot H_i - \sum_{j \in IN} f_{i,k}^{IN} \cdot H_j \quad (\text{B11})$$

Separator (i.e., cyclone, flash, distillation column)

$$f_{i,k}^{OUT} = f_{i,k}^{IN} (1 - \delta_{i,k}) \quad (\text{B12})$$

$$Q = \sum_{j \in OUT} f_{i,k}^{OUT} \cdot H_i - \sum_{j \in IN} f_{i,k}^{IN} \cdot H_j \quad (\text{B13})$$

* Property models (Eq. (3)):

Enthalpy H_i of compound i is calculated from the standard formation enthalpy and the Cp_i as a function of temperature T , that is (λ represents Cp_i),

$$H_i = h_2(i, T) \quad (\text{B14})$$

* Process equality constraints (Eq. (4)):

For example, in the thermochemical route, after gasification, the ratio of H_2 to CO is specified as a constraint,

$$H_2/CO = 1 \quad (\text{B15})$$

Or, the separation yields as a function of the operating conditions of the cyclones or the flash operation;

$$\delta_{i,k} = h_3(f, P, T) \quad (\text{B16})$$

* Process specifications (Eq (5)):

For example, the temperature in the gasifier cannot be greater than T_{max} , that is,

$$T_i \leq T_{max} \quad (\text{B17})$$

In the above equations, subscripts i, k , represent component i and the unit operation of processing step k , respectively; superscripts IN, OUT are inlet and outlet, respectively; f is stream flowrate; θ is conversion; λ is vector of stoichiometric coefficients; δ is vector of component split factors; σ is stream split factor. Q is the thermal energy and W the electrical energy. T and P are the temperature and pressure corresponding to the processing step. The detailed models for the biorefinery can be obtained from the authors.

Note that since the flowsheet (processing route), is fixed Eq. (6) is not necessary. The above problem represents a flowsheet simulation design (optimization) problem.

Appendix C: Desalination process

The detailed optimization equations in the context of water desalination problem are presented below.

The objective function (Eq. (1)) minimizes a multi-parametric function of cost terms consisting of Total Annualized Costs for MSF/MEE (multi-stage flash/multi-effect evaporator) and RO (reverse osmosis), Fresh water production cost and Specific energy consumption cost). The $TAC_{MSF/MEE}$ is given below as an example:

$$TAC_{MSF/MEE} (\text{Dollar}/y) = ACC + AOC \quad (\text{C1})$$

Where,

$$ACC = 182HN_{Total}^{0.65} \quad (\text{C2})$$

$$AOC = (C_{Steam} + C_{Chemical} + C_{Power} + C_{Maintenance} + C_{Labour}) \quad (\text{C3})$$

Where ACC and AOC are annualized capital cost and annualized operating cost, respectively. C_i indicates operating costs related to type i . H is the yearly hours of operation and N the number of stages.

*Process Model (Eq. (2)): A typical steady state mass and energy balance model for MSF process is given below:

Mass balance in the flash chamber:

$$B_j = B_{j-1} - V_j; \quad j = 1, N \quad (C4)$$

Salt balance in the flash chamber:

$$B_{j-1} \times CB_{j-1} = B_j \times CB_j; \quad j = 1, N \quad (C5)$$

Where B_j , V_j and CB_j are brine flowrate for MSF stage j , vapor flowrate leaving MSF stage j and concentration of brine leaving MSF stage j , respectively; N is the number of stages.

Energy balance on flashing brine:

$$B_j = \frac{h_{Bj-1} - h_{vj}}{h_{Bj} - h_{vj}} \times B_{j-1}; \quad j = 1, N \quad (C6)$$

Where, h_{Bj} , h_{vj} are enthalpy of brine leaving MSF stage j and enthalpy of vapor leaving MSF stage j , respectively.

* Property model (Eq. (3)): Property models suitable for study of desalination processes are given by El-Dessouky and Ettouney (2002), Tanvir and Mujtaba (2008), Sassi and Mujtaba (2012), and Filippini et al. (2019).

A typical correlation to evaluate boiling point temperature elevation (TE) is given below (El-Dessouky and Ettouney, 2002):

$$TE = AX + BX^2 + CX^3 \quad (C7)$$

With,

$$A = 8.325 \times 10^{-2} + 1.883 \times 10^{-4} \times T + 4.02 \times 10^{-6} \times T^2 \quad (C7a)$$

$$B = -7.625 \times 10^{-4} + 9.02 \times 10^{-5} \times T + 5.2 \times 10^{-7} \times T^2 \quad (C7b)$$

$$C = 1.522 \times 10^{-4} - 3 \times 10^{-6} \times T^{-3} \times 10^{-8} \times T^2 \quad (C7c)$$

Where, T = boiling point temperature in °C and X = salinity in weight percent

* Process specifications (Eq. (4)): This constraint is represented by Freshwater demand, D :

$$D_{grade, 1 to N} = D_{grade, 1 to N}^* \quad (C8)$$

* Process inequality constraints (Eq. (5)): Examples of process inequality constraints is given below in terms of bounds on the top brine temperature for MSF/MEE process.

Bounds on the Top Brine Temperature:

$$TBT^L \leq TBT \leq TBT^U \quad (C9)$$

* Process configuration (Eq. (6)): Example of a process configuration equation is given below in terms of total number of MSF/MEE/RO stages.

Total number of stages or effect:

$$N = \sum y_j \quad (C10)$$

Where, $y_j = 0$ or 1 , and j varies between minimum and maximum number of stages/effects.

The above design-optimization problem formulation results in a Mixed Integer Nonlinear Programming model that can be solved in different ways. Different methods have been developed in the literature to solve these MINLP problems (Duran and Grossmann, 1986a; Fletcher and Leyffer, 1994; Jiang et al., 2015; Martino et al., 2021).

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