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Challenges and opportunities of Solar thermal energy towards a sustainable chemical industry

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ABSTRACT

The most abundant energy on Earth is solar and it is a versatile resource that is to be used to improve the sustainability of the chemical and process industry. Two main pillars support these industries, the raw materials and energy. Energy in the chemical industry is to be provided in the form of utilities such as steam, thermal energy and power. All of them can be provided by transforming solar thermal energy. This work presents the perspectives on the process integration of solar thermal plants and/or solar thermal energy within the chemical industry, describing the state of the art and the technology readiness level of units and facilities as well as the challenges and opportunities that the integration of solar thermal energy in the chemical industry generate for the process system engineering community, aiming at reaching the goals of the agenda 2030.

1. Introduction

Over the last decades there has been a trend towards sustainability looking for alternative technologies and resources that can help meet the ever growing demand for energy and products. Sustainable chemical industry can be addressed by evaluating the raw materials and utilities. With regards to resources such as coal and crude oil, renewable ones are to increase their share as raw materials in the chemical industry. This is where biomass, the nature's way to absorb solar energy, is playing a role in the production of bulk and specialty chemicals (Corma et al., 2007). However, as important as raw materials, the energy required for the transformations must be renewable to achieve the goal of sustainability. Chemical processes require energy in different forms such as steam, thermal energy and electricity. The production of renewable electricity has been the focus of numerous works involving different resources such as hydro (https://www.irena.org/hydropower), ocean and its different alternatives including waves, tidal among others (https://www.irena.org/ocean), or wind (https://www.irena.org/wind). However, chemical transformation requires thermal energy above all. So far, natural gas-powered boilers is the technology of choice. The production of steam using electrical reboilers is typically limited to small scale and lab scale applications. In addition, resistance heaters at large scale are still at their infancy, even though current efforts are going in this way (Rieks et al., 2015). Geothermal and solar thermal are the best alternatives. However, geothermal aims at lower temperature steam, leaving solar thermal as the technology that is capable of providing both steam and power. Concentrated solar power plants can be integrated within the chemical industry to improve its sustainability, to help meet the sustainable goals of the 2030 agenda of the UN. The targets proposed by the UN directly linked to the chemical industry are the production of affordable and clean energy, responsible consumption and production as well as inclusive and sustainable industrialization and climate action (UN, 2021). Therefore, in this work we go over the structure of solar thermal facilities, the challenges and opportunities for their use and integration within the chemical industry to provide the different forms of energy towards the production of bulk and specialty chemicals. We have divided the work in 4 sections to cover the use of solar thermal energy in all possible forms within the chemical industry. Section 2 comments on the structure of CSP plants, current work and technology readiness level as well as the challenges and improvements expected. Section 3 evaluates the design of integrated power plants and even polygeneration facilities that allow producing steam and power on demand. Process integration plays an important role that go beyond process synthesis to operation and control of such facilities. Section 4 presents the use of thermal energy as an alternative to carry out chemical transformations, typically endothermic reactions as well as the types of steam required in biorefineries as a function of the products. Section 5 points out the need for technology development, the challenges that process system engineering can help address and the room for modeling, simulation and optimization towards the more efficient use of solar thermal energy for a sustainable chemical industry. Finally, Section 6 draws some conclusions.

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Acronyms

CSP	Concentrated solar power
CFD	Computational Fluid Dynamics
CT	Cooling tower
DME	Dimethyl ether
DIAPR	directly irradiated annual pressurized receiver
HTF's	Heat Transfer Fluids
HP	high Pressure turbines.
HRSG	heat recovery steam generation
HBC	hydrocarbon
LCA	Life cycle assessment
LHV	Low heating value
LOCE	Levelized cost of electricity
LP	Low pressure turbines.
MP	Medium pressure turbines.
MILP	Mixed integer linear programming
MINLP	mixed integer nonlinear programming
PV	Photovoltaic
PSE	Process System Engineering
RD	Reactive distillation column
SSP	Solar steam plant
SORC	solar-organic Rankine cycle
$scCO_2$	Super critical CO_2
TAC	Total Annualized cost
TES	Thermal energy storage
TCES	Thermochemical energy storage
VRC-RD	vapor recompression technology assisted RD

2. Solar thermal plants: sections and pse opportunities

Concentrated solar power (CSP) facilities have the capability of producing all types of utilities a chemical plant requires including low, medium and high pressure steam and power. However, they are to be located in regions with high solar availability, Fig. 1. This fact affects directly the use of the steam produced as an utility, since the facilities served must be adjacent. While it can be of no problem for the current chemical complexes located in Saudi Arabia or Texas for instance, it may not be a solution for those located in other places, affecting the sustainability of current chemical hubs. An entire new complex could decide on the location of the new facilities. However, the chemical industry has already a number of hubs all around the globe whose supply of sustainable steam and thermal energy may be a challenge.

CSP facilities consist of four sections: the solar field, the energy storage system if any, the power island and the cooling system. A number of studies have covered each one individually and / or the analysis of the entire facility. Reviews on the configuration and design of solar plants can be found in the literature (IEA 2010; NREL, 2010; He et al., 2020). Different packages have also been developed for the design of the different sections and only a few consider the entire facility, among them DELSON, SAM or SOLENERGY (Ho, 2008). Models for the receivers, the solar field and even detailed cooling towers are not yet integrated within process simulators typically used in the chemical industry such as ASPEN Plus, ASPEN HYSYS or CHEMCAD, which represents an opportunity for the Process System Engineering (PSE) community towards the analysis of solar aided facilities for the development of models and process modeling and optimization tools. Over this section we present the features of the design of the different sections that are responsible for the operation and the performance of these facilities.

Solar field: The solar irradiance the Earth receives per square meter is not enough to be used for most industrial applications. It must be concentrated to reach high temperatures and generate steam or to provide thermal energy. That is the task of the solar field. There is a number of solar capture / concentration technologies such as parabolic troughs, parabolic solar dishes, solar towers and linear Fresnel reflectors (IEA, 2010). Among them, parabolic troughs and solar towers are the most extended designs for large scale operation, being capable of concentrating from 30 up to 1000 times solar radiation ((NREL 2010); Zhou et al., 2019). However, the Earth motion and the geographic location of the solar field affect the direction of the rays and the energy capture efficiency. For the design of the parabolic throughs (Harrigam, 1981), their geometry (Pavlovic et al., 2017; Islam et al., 2015) and the collector field, determining the separation, the array of collectors in series and the parallel rows (Silva et al., 2014), have been optimized. Some of the important parameters are shading and tracking the solar radiation over time (Silva et al., 2014, Montes et al., 2009a,b; Kong et al., 2020). The design of a heliostats field presents similar difficulties, but the lay-out shows more flexibility. The heliostats direct the solar radiation to a receiver where the thermal energy is used to heat up a fluid/system or to produce steam directly. The optimization has been addressed by different groups using mathematical or algorithmic approaches to locate each mirror reducing shading and blocking (Mutuberria et al., 2015; Noone et al., 2012; Barnerena et al., 2016; Leonardi et al., 2019; Collado and Guallar, 2019; Schell, 2011). The methods can

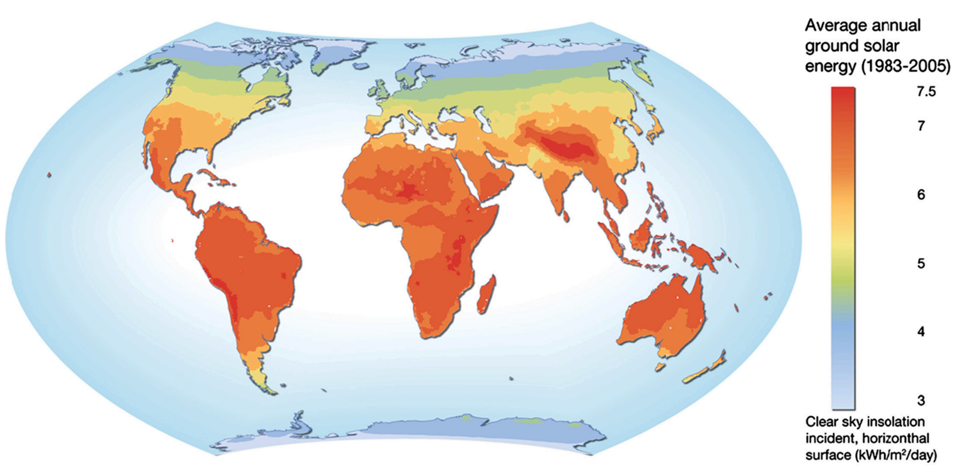

Fig. 1. Isolation of the Earth surface. NASA 2008 (IEA, 2021a).

be classified by the approach followed for the design of the layout such as the cellwise method, the Campo code, heliostat minimum radial spacing method, MUUEN algorithm, HGM methodology, and Greedy algorithm and biomimetic (Wei et al., 2010). The three most common are: DELSOL (Lipps and Vant-Hull, 1980), an extended version of the MUEEN (Siala and Elayeb, 2001) algorithm, and BIOMIMETIC (Noone et al., 2012). These algorithms are currently used in the design of the current CSP facilities but are yet to be integrated with process design tools. The design of solar fields relies on the availability of solar irradiation information, a big data kind of problem. Databases have been developed over the years and most governments collect the information (https://re.jrc.ec.europa.eu/pvg_tools/es/#MR, https://power.larc.nasa.gov/).

Thermal Energy transfer. Energy storage and Heat Transfer Fluids (HTF's): The energy captured by the receiver can be used in situ to provide the energy for a particular operation, as it will be described along the text, to produce steam directly or to be stored. Energy storage is key towards the overnight operation of solar based facilities or the effect of clouds (Crespi et al., 2018a). Direct and indirect storage systems are available, whether the heat transfer fluid is the same as that used for power production or not. Indirect storage is the most common technology based on its higher efficiency (NREL, 2010). Thermal energy storage (TES) systems for CSP facilities can be classified into three types: sensible heat storage, latent heat storage and thermochemical energy storage (TCES) (Gil et al., 2010; Kuravi et al., 2013).

-Within the first alternative lies the use of HTF's that provide a volumetric energy density in the order of 50 kWh/m^3 (Gil et al., 2010; Kuravi et al., 2013). Synthetic fluids, molten salts or even water are the ones used at commercial scale CSP facilities (Pelay et al., 2017). Molten salts are widely used due to the high operating temperature leading to a higher performance of the thermodynamic cycle. However, they present operating issues because the salts crystalize at 238 °C and solidify at 221 °C (NREL, 2010), and they are corrosive (Fernández et al., 2012). Alternatively, synthetic fluids, oils and silicones, can be used, but their operating temperatures are limited to 425 °C (Dowling et al., 2017), reducing the energy yield and increasing water consumption per kWh produced (García and Martín, 2021). Novel molecules could be developed to withstand higher operating temperatures so that the performance of the cycle improves and avoid disadvantages such as corrosion or fluidability issues. Molecular design and simultaneous process and product design, a topic that is gaining attention, can play a major role. The storage systems also present several additional challenges, due to the energy losses that limit the storage period and the process performance (Prieto et al., 2016; Sole et al., 2018), presenting the need for insulation (Riahi et al., 2020), and issues related to the dynamics of the storage (Crepi et al., 2018; Lappalainen et al., 2019). 3D modeling of the tanks has also been attempted to deal with some of these challenges (Ravaghi-Ardebili, et al., 2013; Riahi et al., 2020). In addition, the integration of these models with those of the operation of the facility either as the dynamic operation or the scheduling of the facility is still a matter of study (Pérez-Uresti et al., 2021).

-Latent heat storage shows a volumetric energy density of around 100 kWh/m^3, but the operating temperature is reduced compared to the use of HTF's (Gil et al., 2010; Kuravi et al., 2013) presenting similar challenges in the design of the storage devices in terms of thermal losses. The technology development is at pilot scale level.

-Thermo chemical storage systems are based on endothermic chemical reactions that use solar energy to produce a chemical that is later decomposed releasing energy. It was first proposed long ago (Ervin, 1977). The chemical produced can be stored for an unlimited period of time reaching up to 500 kWh/m^3 and used on demand. Fig. 2 shows the general idea of the operation of TCES. The operation in closed loops requires the storage of gaseous species, while open loop operation is appropriate for the production of steam or oxygen reaction systems. Among them, the main examples of systems are ammonia, methane, hydrides, carbonates and hydroxides (Kuravi et al., 2013; Pelay et al., 2017). The reactions are presented below:

-The ammonia system. While the production is exothermic, the

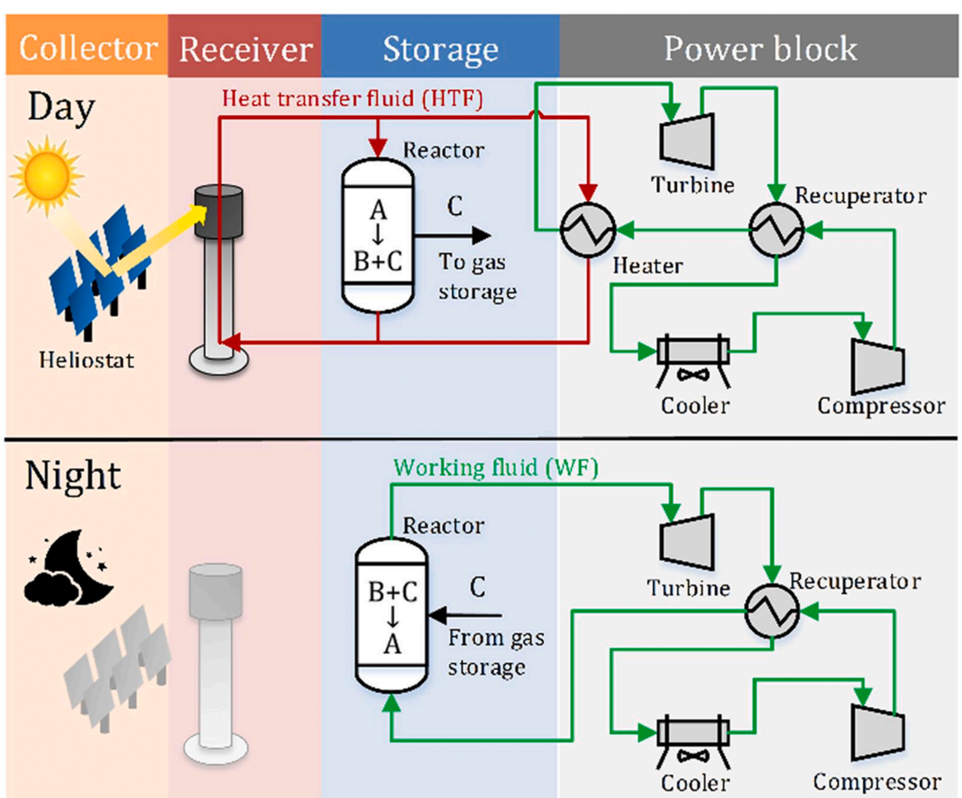

Fig. 2. Scheme of the operation of a CSP facility with TCES (with permission, Peng et al., 2020).

decomposition requires thermal energy. In addition, the equilibrium results in low conversions in the synthesis stage:

$$NH_3 \rightleftarrows 0.5N_2 + 1.5H_2 \ \Delta H_r = 45.7kJ/mol$$

-The production of methane from syngas is exothermic while the decomposition is endothermic. It is the only system whose economics has been evaluated at large scale (Edwards et al., 1996)

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \ \Delta H_r = 206kJ/mol$$

-Metal hydrides can be used as a means to store hydrogen in the form of powder, capable of storing 5% by weight of hydrogen.

$$MgH_2 \rightleftarrows Mg + H_2 \ \Delta H_r = 78kJ/mol$$

-Carbonates, metal oxides or hydroxides based systems are also used:

$$CaCO_3 \rightleftarrows CaO + CO_2 \ \Delta H_r = 178kJ/mol$$
$$Ca(OH)_2 \rightleftarrows CaO + H_2O \ \Delta H_r = 104kJ/mol$$

The design of reactors for the production of ammonia or methanol is common engineering practice (Martín, 2016a), but scale-down represnts a challenge. However, not so common chemicals require alternative designs to address scale up problems. Several studies evaluate the geometries and reactor configurations (fixed beds, moving beds, entrained flow reactors and fluidized beds, Angerer et al. (2018), for various systems, Chen et al. (2018)) to provide the proper heat transfer rates (Schmidt and Linder, 2020). First principles models including the use of Computational Fluid Dynamics (CFD) can be helpful. So far, only pilot scale has been achieved (Pelay et al., 2017; André and Abanades, 2020)

The operation of such facilities has been optimized over time by Peng et al. (2017), highlighting the costs related to gas compression, and further extended in Peng et al. (2020) considering redox, hydroxides and carbonate systems operating within fixed bed reactors.

In addition, it is possible to develop power facilities using these chemicals. The conceptual design of facilities that produce and store renewable energy in the form of chemicals has also been addressed for some examples, i.e. ammonia (Sánchez and Martín, 2018; Sanchez et al., 2021); methane (Davis and Martín, 2014); metal hydrides (Heras and Martín, 2021). While the use of ammonia or methane is at a higher state of development, the reversibility of the reaction is an issue, and turbines using ammonia are still under development, requiring further experimental studies (Sanchez et al., 2021). The case of the metal hydrides presents a number of additional challenges. The regeneration of the H_2 from the metal hydride results in the need for the reduction of the oxide, decreasing the yield of the cycle. Future developments and cost reductions in solar equipment affect the cost of the electricity produced, but the large investment in the entire facility, since it includes a larger number of sections than current power plants, represents a barrier for the implementation. Power production costs can become competitive if the facility is integrated with a city/town so that the fuel cell also provides district heating (Heras and Martín, 2021). In addition, the scheduling of the operation of such facilities is to be evaluated and simultaneous design and operation problems must be addressed (Zhang et al., 2019).

Thermodynamic cycle: Most of the work so far on CSP aims at the production of power. Solar thermal shows larger efficiencies than photovoltaic transformation. Thermal cycles show efficiencies around 40% while PV panels efficiency reach 20–25%. The energy absorbed by the thermal fluid is used to produce steam in a set of heat exchangers (indirect storage). The performance of the thermodynamic cycle determines the yield to power. A Rankine cycle is the basic structure. Cycles with regeneration, where extractions from the turbine reheat the condensed steam, and reheating, where the solar energy is used to heat the extraction from the high pressure turbine, are among the most used, see Fig. 3. The seasonal operation of the facilities affect the efficiency of the turbine and that of the cycle (García and Martín, 2021). Several approaches have been used to study it including simulation (Janjai et al., 2011; Halb et al., 2012; Li et al., 2019, Martin and Martín, 2017) or optimization based approaches. Within the optimization one, model-based optimization (Morin et al., 2010; Montes et al., 2009a; Montes et al., 2009b; Mahmoudimehr and Sebhati, 2019; Yagli et al., 2019), neural networks (Richter et al., 2011) and mathematical optimization (Martin and Martín, 2013; Ghobeity et al., 2011; Slocum et al., 2011) have been reported. Simulation based studies evaluate more complete cycles, while optimization approaches tend to simplify the turbine modeling due to the large number of extractions to be evaluated, jeopardizing the estimation of the cycle performance. Therefore, more detailed optimization studies on the cycle can help improve the yield. It is possible to argue that the cycle is similar to current coal-based facilities, using the same units, and therefore, in principle, it would be possible to reuse most of the units from a coal thermal plant to a CSP one. However, there are a number of challenges involved. The location of the original facility was typically selected due to the presence of coal and the actual solar irradiance of the region may not be enough for the production of power. In addition, the solar field requires a large area.

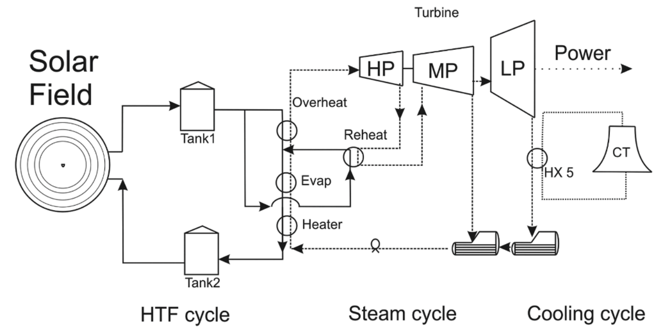

Fig. 3. Regenerative and reheating Rankine cycle with regeneration. HP (high Pressure); MP (Medium pressure); LP(Low pressure) turbines. CT: Cooling tower.

Alternatively, a Brayton cycle can be used. Closed Brayton cycles are used where the concentrated solar radiation and/or the energy stored by a TES can be used to heat up the compressed gas instead of a combustion (Rovense et al., 2019), see Fig. 4. Different receiver designs have been developed, mostly for direct heating of the compressed air with a central receiver as the most proven hybridization. The most developed technologies are tube receivers such as SOLUGAS or PEGASE designs. In addition, pressurized volumetric receivers including SOLGATE, and directly irradiated annual pressurized receiver (DIAPR) are working prototypes that use porous structures for solar absorption and heat transfer (Stein and Buck, 2017). Apart from air as working fluid, He,

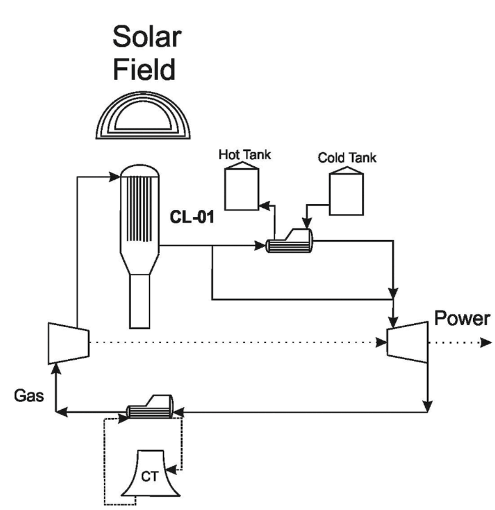

Fig. 4. CSP facility based on a Brayton cycle.

nitrogen, Xe, ammonia, ethane, sulfur hexafluoride or water, the use of supercritical CO_2 is among the most used fluids for this cycle (Zhang et al., 2005; Stein and Buck, 2017), since it is capable of showing an efficiency even larger than superheated or supercritical steam cycles (Ma and Turchi, 2011; Hinze et al., 2017). The analysis of the power block has been performed in recent works (Ma and Turchi, 2011; Hinze et al., 2017; Stein and Buck, 2017), including the comparison of the operation, over a year, of several configurations of a hybrid solar-assisted combined cycle modelled using ASPEN (Milani et al., 2017a), the dynamic modeling and control of the facility (Milani et al., 2017b), the optimization of the cycle using a equation based model simulation optimization approach of the cycle with energy storage (Wang and He, 2017) as well as the use of artificial neural networks for the multiobjective optimization of the key parameters of the cycle. (Deng et al., 2017). However, work is still needed within the turbine industry evaluating different building materials before there is any certainty on the performance of the $scCO_2$ power block. The use of gasses as working fluids has presented the use of particle beds as thermal storage systems (Rovense et al., 2019). The thermodynamics of the fluids, the effect of pressure and temperature on the heat capacity, enthalpy and entropy, is of special interest towards the optimal design and operation of these cycles presenting a process and product design problem (García and Martín, 2021).

Cooling system: A thermodynamic cycle has a hot end, in this case the receiver, and a cold end, the cooling system. The current path towards desertification and water scarcity problems have attracted the attention to the Water-energy nexus in the power industry as a mayor water consumer sector (Rosegrant et al., 2002). The consumption of water actually depends on the cycle, the cooling technology and the facility location. While there are a number of technologies, the classification can be made between dry and wet technologies. The units have been studied in the context of thermal plants (Zhai and Rubin, 2010), and latterly also for solar thermal facilities (Kelly and Price, 2006, Turchi et al., 2010; Blanco-Marigorta et al., 2011; Barigozzi et al., 2011; Palenzuela et al., 2013) because of their location. There is an inverse relationship between solar irradiance and water availability that can jeopardize the operation of solar power facilities (Macknick et al., 2011). In general, wet cooling systems, Fig. 5a, allow high efficiency and lower production costs benefiting from economies of scale, but present a large consumption of water (Martín and Martín, 2013; García and Martín, 2021) that depends on the weather of the region (Guerras and Martín, 2020). In case of using the dry systems, their operation requires the consumption of approximately 5 to 10% of the energy produced to power the fans of the A-frame type of cooling, Fig. 5b (Martín, 2015a). Even from the Greenhouse Gas emissions point of view, considering the CO_2 saved due to the energy produced and the CO_2 consumed per cubic meter of water used, wet systems looked promising (Luceño and Martín, 2018a). However, careful consideration must be taken to reduce water consumption for a more sustainable operation. Solar thermal as a source to produce power can be limited by the capability of cooling. Rankine cycles require a cold and the capability of condensing the steam determines the cycle efficiency. Dry cooling designs are being the focus of recent research. The design is to be performed simultaneously with its operation, due to issues like fouling (Luceño and Martín, 2018b) or the effect of weather episodes, such as sand storms, requiring de development of solution algorithms that would allow the selection of the mechanical features of the unit (i.e. number of pipes, diameters, pitch) as well as its operation further developing previous work on this topic (Lozano Santamaría et al., 2020, 2021).

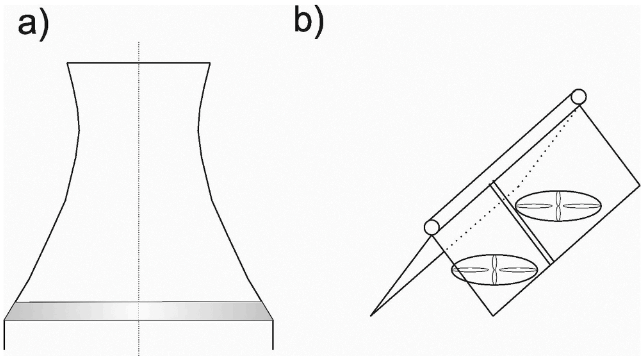

Fig. 5. Wet and dry (A-Frame) cooling systems.

The life cycle assessment of CSP facilities has been performed towards comparing different cooling systems, showing that dry systems reduce 77% water consumption but increase the greenhouse gasses emissions by 8% (Heath et al., 2011). Due to the differences in plant design from one location to another, another work presents differences of sustainability of around 10% just due to the solar availability in different locations (Corona et al., 2016). The comparison of the thermal energy storage systems has also been addressed. The use of salts and even mined salts is favored since their impact is lower than for synthetic fluids (Heath et al., 2011; Casa et al., 2021). Together with the sustainability assessment, social indexes play an important role in a more comprehensive definition of sustainability. The installation of such facilities creates wealth and jobs in any particular region. Studies show that CSP facilities increase the social welfare in Spain, especially in terms of socioeconomic sustainability and fairness of relationships (Corona et al., 2017). Further studies are needed for the selection of facilities and their configurations towards a sustainable transition of the power system.

3. Integrated multisource power facilities

In the previous section the basic structure of CSP facilities has been presented. In spite of the storage systems, the capability of the facility to meet a certain demand over a year long is still a challenge. Two approaches can be followed to address this issue. Either the storage of power in the form of chemicals, already presented above, or the integration of resources (Tovar-Facio et al., 2021). Solar can be coupled with fossil resources (Pramanik and Ravikrishna, 2017; Sheu et al., 2012). Beyond fossil ones, the possibility of using renewables has also been presented (Yuan and Chen, 2012; Weekman, 2010). Conceptual studies integrating biomass, following a gasification process to syngas and a gas turbine (Vidal and Martín, 2015), or the use of waste, to avoid the diversification of the use of highly valuable biomass that can be further used for high added value chemicals production, have been presented (Colmenar-Santos et al., 2015; Corré and Conijn, 2016; de la Fuente and Martín, 2019, 2020). Beyond these studies, pilot plants have already been installed in Spain (Sanz, 2012) or Italy (Kramer, 2014).

The strategies in the integration depend on the biomass/waste humidity. Drier feedstocks can be gasified. The production of syngas allows the use of a gas turbine to produce power to mitigate the limited solar radiation at times. The use of thermal energy to heat up the salts of the CSP facility is not selected due to the lower efficiency, not even the hot flue gas from the gas turbine. In addition, when solar energy can meet the demand, the syngas can be used to produce hydrogen/methane/methanol, storing the excess while being able to operate most of the biomass section of the plant under steady state, see Fig. 6a (Vidal and Martín, 2015). If the feedstock contains no more that 15% solids, anaerobic digestion is recommended producing biogas, Fig. 6b. The use of a gas turbine within cogeneration schemes in any of the cases would allow the further use of the hot gas to heat up the molten salts and still top up the energy provided by the Sun (Vidal and Martín, 2015; de la Fuente and Martín, 2019). The production costs of these integrated systems can become competitive for the gasification based use of biomass (340 MW, at 0.073 €/kWh and 97kt/yr of hydrogen, Vidal and Martín, 2015) but not for the use of waste, whose distributed availability and low organic concentration also limits the size/production capacity of the facility (25 MW at 0.17 €/kWh de la Fuente and Martín, 2019).

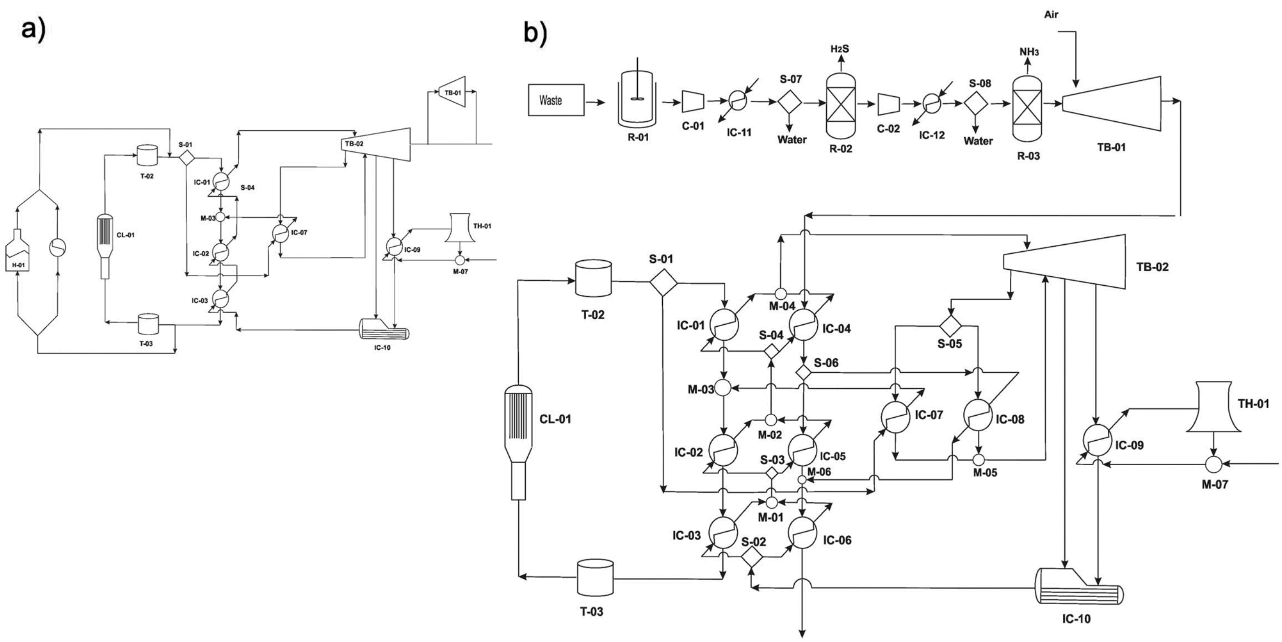

Fig. 6. CSP integrated with a) Biomass gasification plant; b) Anaerobic digestion.

Facility location studies have revealed that waste availability in rural areas can provide enough backup power to maintain a certain power production capacity, but the collection of waste can be a challenge depending on the farm size and distribution across the territories. Urban areas have the advantage of having in operation a municipal solid waste (MSW) collection and management infrastructure, but only larger cities generate enough waste to produce the power required to back-up CSP facilities of small /medium sizes (de la Fuente and Martín, 2020). As a result, the investment in a full size facility may be barrier for their installation. The investment costs increase to secure a certain production capacity over time. In any case, these facilities are more complex to operate than fossil based thermal power plants. In addition, the wide range of feedstocks composition call for detailed studies on the performance of the facilities processing each type of residue and control of the integrated facilities is a challenge requires novel approaches (Dowling et al., 2018).

The distributed production of solar energy is also another challenge, therefore the integration of small devices such as a micro gas turbine and a solar dish system (Ragnolo et al., 2015) or heliostats using biodiesel as fuel (Aichmayer et al., 2013), as well as small scale steam turbines combining solar and biogas as fuel (Garcia-Ferrero, et al., 2020; Bustamante et al., 2021) and combined cycles (Ferriere et al., 2019) can be a solution to provide utilities to remote areas for off the grid applications (Giovannelli. 2015) as well as polygeneration. The performance of gas micro turbines has been evaluated in recent literature including the heliostat field design and the gas turbine model achieving LOCE of 150 €/kWh for production capacities of 100–200 kW (Giostri et al., 2020). Small scale hybrid Rankine and Brayton cycles have also been evaluated for 30 kW, where the Rankine cycle shows 10% larger efficiency (Bustamante et al., 2021).

Most of the works on renewable energy have focused on the production of power, but utility plants producing both power and steam have been studied within the process system engineering field for decades. In general, a utility plant consists of a set of steam generators, turbines, steam headers and cooling systems, which can be combined in several arrangements to supply the steam and electricity. The problem of designing and optimizing a utility plant based on fossil resources was first addressed by Papoulias and Grossmann (1983). The superstructure is formulated as a mixed integer linear programming (MILP) model to find the optimal configuration that minimized the annual cost of the utility plant to produce fixed steam and electricity demands. This model was extended including the effect of the temperature on the steam production, as well as the efficiency of the steam turbine as a function of the load, Bruno et al. (1998), while Mavromatis and Kokossis (1998) incorporated the concept of Turbine Hardware Model (THM). This concept has been extended in other works (Medina-Flores and Picón-Núñez, 2010; Luo et al., 2011). Renewables have mostly been considered within the concept of the Locally Integrated Energy Sector (LIES) (Kostevšek et al., 2015; Liew et al., 2017) for instance in district heating to provide low temperature heat or hot water at households (Fang et al., 2015). However, at industrial scale standard steam in terms of pressure and temperature must be supplied.

A renewable based utility plant consists of the same sections as presented before, the major difference is the source of the energy and the units related to process them. Due to the variability in solar irradiance, not only over a day but seasonally, CSP facilities can be integrated with biomass and waste. Following the discussion above, waste is digested to produce biogas that is later used in a gas turbine. The hot flue gas is further used to produce steam in a heat recovery steam generation (HRSG) system. Biomass, due to its lower water content, can be either burned in a boiler to produce the steam, or gasified. The syngas can be burned or used in a gas turbine followed by a HRSG system. To make it more flexible, wind turbines can also be integrated. The superstructure, see Fig. 7, was formulated as a mixed integer nonlinear programming (MINLP) model by Pérez-Uresti et al. (2019a) modeling unit by unit. However, to include the seasonality Pérez Uresti et al. (2020) and uncertainty the model is reformulated as an MILP and different approaches can be used including stochastic programming as well as the use of representative days in order to address the variability and solve such a large problem Pérez Uresti et al. (2021, 2022). The results show that the more flexible the facility, the higher the investment cost required, as expected. The methodology presented by Pérez-Uresti et al. (2022) allows selecting a design based on a in-sample-out of sample analysis to validate the robustness of the solution. The selection of technologies is location dependent. For the case of study, biomass gasification, CSP and wind turbines are the ones selected with investments costs around 550 M $ and operating costs around 37 M$/yr. Further work is still required due to the statistical nature of the selection of representative days as well as the computational challenges of include hourly variability in process design.

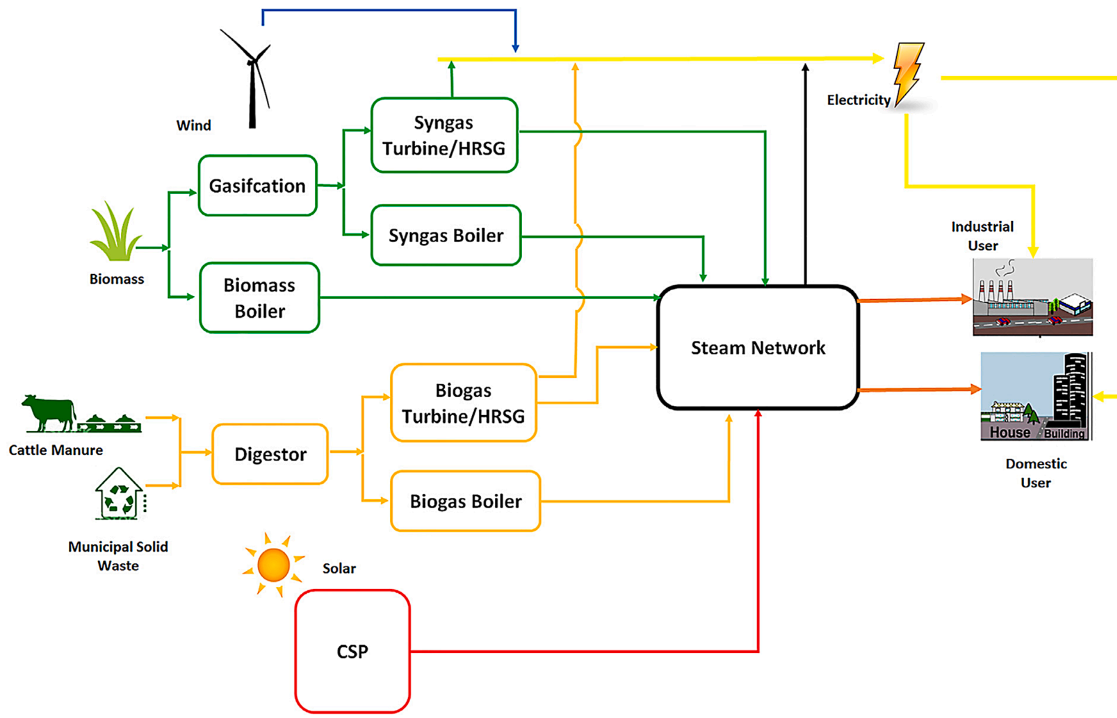

Fig. 7. Renewable based utility plant (With permission from Pérez Uresti et al.,- 2019a).

The analysis of the renewable based utility plants allows estimating the cost of the renewable steam as a function of the resource and the steam quality (Pérez Uresti et al., 2019b). It is paramount information for the technoeconomic analysis of chemical facilities. Furthermore, for biofuels to be actually sustainable not only the raw materials must be renewable but also the utilities, power and, above all, steam (Martín and Grossmann, 2018). For instance, the production of bioethanol requires steam in pretreatment stages, i.e. dilute acid, as well as in the preparation of the feed to the synthesis reactor or the concentration of alcohol (Martín and Grossmann, 2011, 2012a). Similarly, biodiesel requires steam as heating agent across the flowsheet as well as in the recovery of the excess of methanol (Martín and Grossmann, 2012b).

4. Chemical assisted plants by solar thermal energy

The need for a renewable power system to substitute the current dependency on fossil resources, and the target of decarbonization has focused the efforts and studies in the use of solar thermal energy (IEA, 2021b). However, there are a number of processes and unit operations whose demand for thermal energy can be provided directly by the Sun. This chapter is divided into unit operations, in particular drying, evaporation or distillation, and chemical reactions assisted by solar energy, such as gasification, reforming or water splitting.

4.1. Unit operations

The separation or water removal from a mixture or compound is the most important task that can be performed using solar energy. In this section solar drying and water desalination are presented as the most common uses of solar thermal energy in separation processes.

Solar drying: For centuries food as well as cloths are dried in the Sun, especially in the southern European or equatorial countries enjoying better weather. It is a low temperature operation. Water evaporation requires around 2200 kJ/kg at room temperature resulting in a highly demanding operation that affects the economy as well as the sustainability of the processes. An example within the biofuels industry is algae drying. The algae grow in a dilute pond. Harvesting the algae is a complex and expensive process that jeopardizes the economy of the production of biodiesel, but at the same time poses an additional challenge in the attempt to produce sustainable diesel (Martín and Grossmann, 2012b). Solar drying is an alternative for certain raw materials. In this section two cases are discussed, sludge and food drying.

Sludge drying: Sludge is the residue from waste water treatment. It typically contains 5% solids (IWA, 2022) and up to 25% after dewatering (Garanto, 2016). Dried sludge has a large LHV, comparable with wood. The organic content can be interesting as a raw material for agricultural land application, as a source for nutrients, and as a source of energy via biogas production or incineration. In addition, solar drying has the potential of reducing the pathogens of the sludge. Dewatering and specially drying is energy intense. Several technologies have been developed for such a task including open solar dryers and covered ones, the last ones being the most used Thermo-System, 2022; Huber Technology, 2022; Garanto, 2016). Basically they consist of a greenhouse where the sludge is exposed to the solar radiation on top of belts. The sludge can be anaerobically digested, that is endothermic in most cases. As a result of the need for thermal energy, integrated systems have been proposed to process sludge aiming at the self-sufficiency of wastewater treatment plants. Solar energy is used to dry the sludge and to provide for the energy required for the digestion of the waste. In addition, both the biogas and solar energy are used to dry the sludge (Di Fraia et al., 2018). Further studies at process level of the integrated process are required to compare technologies and scale them up.

Food Drying: Water is responsible for the decay of crops as a result of the growth of microorganisms leading to putrefaction. Thus, crops, vegetables and grains drying is essential for its preservation and storage, especially in developing countries. Water content of fruits, vegetables and other foods can reach 90% which makes its drying a highly demanding operation. Solar dryers can be classified among direct, indirect, either natural or forced circulation, and mixed type (Mustayen et al., 2014). Direct solar dryers consist of a transparent cover exposed to the solar radiation. Different designs can be highlighted such as the solar cabinet, the staircase solar dryer or the glass roof solar dryer. The humid air goes up and is released from the top. Among the indirect solar designs, based on the generation of an air flow, natural and forced technologies are used. Natural convection is based on density difference while a fan is used to force the air flow (Singh et al., 2012). Typically, indirect forced convection is faster than natural (Baradey et al., 2016). The design and systematic comparison of the designs is to be further evaluated.

Water desalination. Solar distillation: The need for fresh water across the globe has created the need to develop efficient and sustainable technologies for sea water desalination. The operation is also characterized as low temperature. While there is a number of technologies for water desalination (Martín, 2016a), the demand of water in areas with high solar irradiation has pushed towards the use of solar energy as a resource for marine water desalination. Optimization studies of desalination plants have been performed lately to reduce energy consumption (Alsarayreh et al., 2020). In addition, the coupling of CSP facilities with desalination plants, can provide the power required for the operation (Palenzuela et al., 2011, 2013). Direct solar distillation can be performed either via passive or active distillation. The first of the two uses direct solar radiation. However, the production rate is lower. Active distillation combines, in the form of solar stills, external sources such as a solar collection, evacuated tube receiver, heat pipe and even solar panels that provide thermal energy to the water in the basin along with the direct sun rays (Manchanda and Kumar, 2017). The geometry of the greenhouse plays a role in the efficiency, where asymmetric designs show 20% larger efficiency (Al-Hayek and Badran, 2004). In addition, double basin designs increase the production 85%, and the use of a solar tracking system shows a 380% improvement (Manchanda and Kumar, 2015). The coating of the glass cover can improve the productivity of the still by 5–25% (Shanmugan et al., 2020). Solar still has been deemed as a cost-effective technology to produce fresh water. A recent study has evaluated the economics of different designs (Katekar and Deshmukh, 2021) comparing active and passive stills and different collectors. According to that work, the low concentrating photovoltaic-thermal solar still is the most economical design and the cascade solar still is the one with the largest production capacity. The sustainability of integrated CSP – Reverse-osmosis processes has been evaluated using LCA analysis presenting the environmental advantages od such integration with small increases in the cost (Salcedo et al., 2012). Even though the technology is being used, the commercialization of such systems is still a challenge.

4.2. Reaction engineering

There is a number on endothermic reactions widely spread in the chemical and energy industry. Typically that energy at high temperature has been provided by the combustion of a fuel or using a nuclear reaction. Whether this fuel is renewable or not can affect the sustainability of the process. CO_2 emissions come anyway associated with the combustion of fossil fuels or biomass. In a path towards decarbonization, the use of solar energy to provide that energy can be a step forward. In this section a number of cases are presented. The technology readiness level is still it their infancy in most cases, but the preliminary results at laboratory and pilot plant scale are promising. The operation takes place at medium to high temperature depending on the reaction taking place, which requires high solar concentration in some cases. Most of the reactions studied are related to the production of hydrogen aided by concentrated solar power due to the expected importance of hydrogen economy (Steinfeld, 2005).

Solar based reforming. Reforming of a hydrocarbon (HBC) is the reaction with steam or CO_2 (dry reforming) for the production of syngas (Martín, 2016a). It is a highly endothermic process that typically consumes a fraction of the feedstock to provide for the energy. For the use of methane as hydrocarbon the reactions for steam and dry reforming are as follows:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \Delta H_r = 206 kJ/mol$$

$$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2 \Delta H_r = 247 kJ/mol$$

Steam reforming achieves higher conversion at the same temperature and therefore, higher conversion at lower temperature than dry reforming (Sheu et al., 2015). The HBC reforming using solar thermal energy requires a system consisting of two main parts, a solar collector and a chemical reactor. The solar collector can be any of the ones presented in the description of the CSP facility such as a trough, a central receiver tower, a linear Fresnel reflection or a parabolic dish. The solar receiver heats up a HTF that is used to provide the energy required for the reaction or else directly heats the reactor. However, the high temperature required for the reforming, above 800ºC, suggests the use of directly irradiated systems. The reformer is an integrated unit that combines the solar receiver and the catalytic bed in one system where the most appropriate collectors are solar towers and dishes. Only in low temperature reforming systems indirectly heated technologies are used since they are based on the use of solar to heat up a HTF that is not stable at high temperature and each time heat is transferred losses occur. The advantage on this alternative is that these reactors resemble current industrial reformers. A comprehensive review of configurations and catalysts can be found in Simakov et al. (2015).

The use of solar reforming results in the storage of 26–31% of solar energy within the product gas (Agrafiotis et al., 2014) that can be further used to produce chemicals and fuels (Martín, 2016a). If the production of hydrogen is the final aim of the reforming, the need for a water gas shift reaction, also endothermic, reduces this value to 21% (Agrafiotis et al., 2014). The production of fuels can provide higher efficiency to power that Rankine based facilities where the solar energy produces steam, due to the larger efficiency of combined cycle plants (45–50%). The technoeconomic analysis of the use of solar energy for the reforming of methane is reported to reduce 85% the lifecycle emissions of CO_2 as well as increase the methane to fuel conversion (He and Li, 2014). Since the idea is the reforming of hydrocarbons, it is possible to perform dry reforming of biogas, that contains in itself all the ingredients. Su et al. (2018) evaluated the performance of such a facility that uses natural gas as backup to maintain the operation when the solar irradiance is below a threshold. By using solar energy savings of 3.3% of natural gas and 77.8% in electricity are reported. From the 1980s there have been efforts for the dry (Sandia Nat lab) and steam reforming from 1990′s (DLR, CIEMAT) at small scale. TRL's from 3 to 5 are reported for several reactor designs (USDOE, 2015). The operation and design of such plants under solar variability with no fossil backup is still to be addressed.

Solar based gasification: Gasification of carbonous matter is an endothermic process that consumes a fraction of the feedstock to provide for the energy required for the decomposition of the raw material into raw syngas producing CO_2. The reactions taking place and the various designs available in the market can be seen elsewhere (Martín, 2016a)

−Oxygen based reactions

$$C + O_2 \rightarrow CO_2$$

$$C + 0.5O_2 \rightarrow CO$$

$$CO + 0.5O_2 \rightarrow CO_2$$

−Steam based reactions
$C + H_2O \rightarrow CO + H_2$
$C + 2H_2O \rightarrow CO_2 + 2H_2$
$CO + H_2O \rightarrow CO_2 + H_2$
−Methane formation
$C + 2H_2 \rightarrow CH_4$
$2C + 2H_2O \rightarrow CH_4 + CO_2$
$CO + 3H_2 \rightarrow CH_4 + H_2O$
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$
−Boudouard reaction
$C + CO_2 \rightarrow 2CO$
−Others (hydrocarbon producion)
$H_2 + 0.5O_2 \rightarrow H_2O$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$
$C_nH_{2n} + H_2 \rightarrow C_nH_{2n+2}$
$C_nH_m + nH_2O \rightarrow nCO + (n + m/2)H_2$

However, solar reactors use cavity-type configurations to capture the solar radiation, see Fig. 8. Two different designs of solar gasification reactors are available, either directly irradiated reactors, Fig. 8a, where the feedstock is directly exposed to the concentrated solar irradiation or indirectly irradiated reactors, Fig. 8b, where the carbonous matter receives the heat through an opaque wall. Directly irradiated reactors provide an efficient heat transfer, however, they require a transparent window for the access of the solar radiation. This is an issue when operating at high pressures and for large scales, requiring conical or hemispherical shaped windows. Among the indirectly irradiated reactors, packed and fluidized beds are used. Packed beds are easy to operate, robust and relatively cheap, however, they present limitations to the heat/mass transfer across the packed bed while the buildup of ash reduces the absorptivity of the surface, see Fig. 8b. On the other hand, fluidized beds provide efficient heat and mass transfer at the cost of the proper size reduction of the feedstock, as well as an excess of steam or fluidification gas (Piatkowski et al., 2011; Romero and Steinfeld, 2012)

Over the last decades several experimental studies have reported the solar gasification of diverse materials using a fluidized bed reactor (Taylor et al., 1983; Murray and Fletcher, 1994). Numerical simulations of different reactor designs have been developed reaching energy efficiencies of 28% and net solar to electric efficiency of 20% (Bai et al., 2017). The first generation of industrial solar gasification pilot plants using solar tower concentrating systems is coming into operation. Solar assisted gasification has the potential to produce high-quality synthesis gas with almost 50% higher output per unit of feedstock and, as a result, around 66% larger production of liquid fuels. The better utilization of the feedstock improves the energetic performance of the system and lower specific CO_2 emissions, as the calorific value of the feedstock is upgraded through the solar energy input by an amount equal to the enthalpy change of the reaction. Recent works have reported the technoeconomic analysis of these facilities. Zhong et al. (2021) performed the simulation of the system using SAM software to determine the solar field and ASPEN plus for the simulation of the chemical process to the production of FT liquids. However, the solar variability is to be further included in the analysis. Solar thermal is used to assist an integrated gasification combined cycle to achieve cycle efficiencies of 55%, beyond those of the Rankine or Brayton cycles. The work is performed by simulating the chemical section using ASPEN (Ansari et al., 2020).

Hybrid solar-redox: The use of thermochemical cycles to split water gained attention under the umbrella of the nuclear energy aiming at producing hydrogen (Martín, 2016a; Agrafiotis et al., 2015). Under this scheme, two main products are aimed at, hydrogen and fuels. The production of hydrogen uses water as raw material and metal oxides. The production of fuels involves a carbon resource, either methane or CO_2. In both cases there exists a reduction zone operated at high temperature, to run the endothermic reactions using solar irradiance, and an oxidation zone, where the exothermic reaction takes place. It is possible to dissociate up to 20% of H_2O and CO_2 at 1 bar operating over 2600 K and 3100 K respectively (Galvez et al., 2008). However, thermochemical water splitting takes place at 1200º-1600 ºC, compatible with concentrated solar power (Abanades, 2019). These facilities can produce up to 1424 ton/day using a tower of 28 MW, coproducing power (Kumar Budama et al., 2021).

For the production of hydrogen, the endothermic reaction is as follows:

$$M_xO_y \rightarrow M_xO_{y-1} + 0.5O_2$$

While the exothermic reaction is

$$M_xO_{y-1} + H_2O \rightarrow M_xO_y + H_2$$

The US Department of Energy (DoE) pointed out that solar thermochemical water splitting was the most promising solar technology to produce hydrogen at a cost that was expected to reach \$2–3/kg in 2025 (Kromer et al., 2011). This technology is reaching commercialization level for sites receiving 1 MWh/m^2yr of annual irradiation and prototypes have been developed and show a lifetime comparable with nuclear facilities (Vogel and Kalb, 2010).

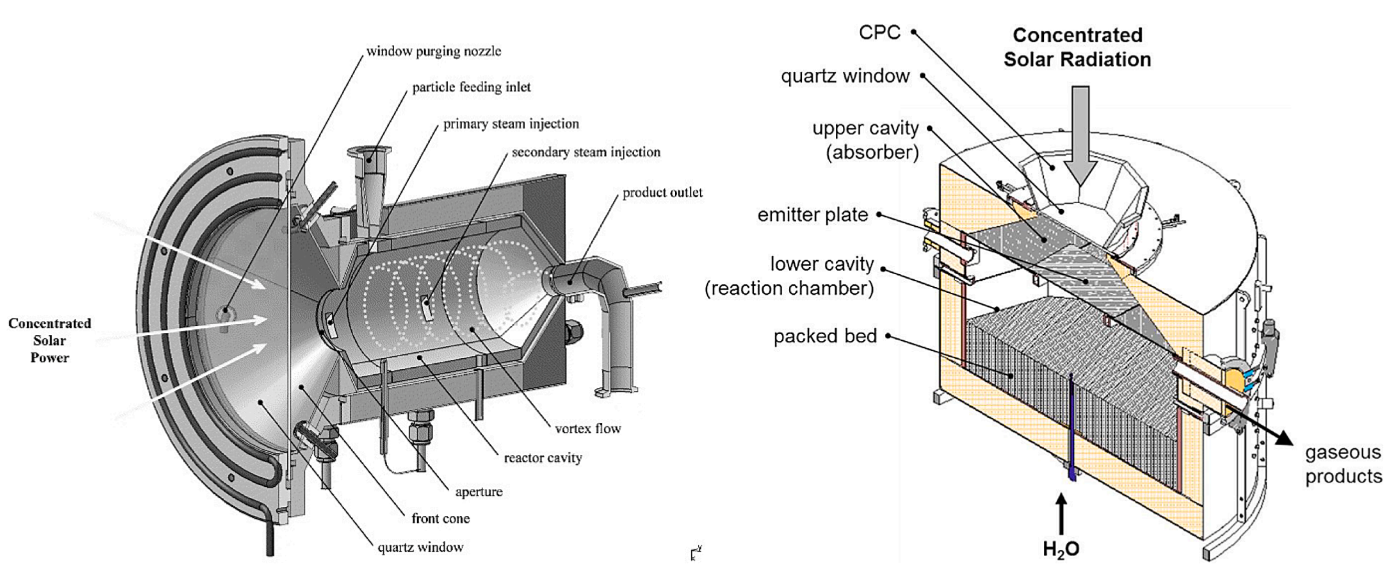

Fig. 8. Scheme of a) Directly irradiated reactor b) indirectly irradiated packed-bed solar reactor configuration (With permission Z'Graggen et al., 2006; Loutzenhiser and Muroyama, 2017).

For the production of fuels it is possible to use two sources of carbon, either splitting CO_2 where the endothermic reaction is the same as before:

$$M_xO_y \rightarrow M_xO_{y-1} + 0.5O_2$$

While the exothermic reactions are shown below:

$$M_xO_{y-1} + H_2O \rightarrow M_xO_y + H_2$$

$$M_xO_{y-1} + CO_2 \rightarrow M_xO_y + CO$$

Or methane, in which case the set of reactions is as follows:

$$M_xO_y + yCH_4 \rightarrow xM + y(H_2 + CO)$$
$$xM + yH_2O \rightarrow M_xO_y + yH_2$$

All these schemes allow the easy separation of products, so that the H_2 can be used in a fuel cell or just produce a syngas with the proper H_2 to CO ratio. Different metal/oxide systems are been studied. The use of iron based systems come always first since they are cheaper. However, the reduction temperature is relatively high. Several prototype reactors have been designed. In the German Aerospace Center two designs have been developed, one using a single coated monolith located in a single reaction chamber. The redox material coats a multi-channeled honey comb. The second reactor consists of two separate chambers with fixed honeycomb absorber in both chambers. In the US, a design consisting of a counter-rotating ring receiver / reactor / recuperator has been demonstrated. The unit utilizes two sets of moving beds packed with ferrite reactant material in close proximity, moving in opposite directions to achieve high efficiency. Another system is the ZnO/Zn. However, temperatures over 2000 K are required for the dissociation of the ZnO. Several prototypes have been developed such as the ROCA, or the ZIRRUS. Other systems such as SnO_2/SnO, GeO_2/GeO or the MgO/Mg have also been considered. Comprehensive reviews of the different systems can be found in (Lapp et al., 2012; Xiao et al., 2012; Scheffe and Steinfeld, 2014). Kim et al. (2011) presented a techno economic analysis for the production of methanol from the reduction of CO_2 to CO using the Fe_3O_4 /FeO system and a CR5 heat engine (Counter-rotating-ring receiver/reactor/recuperator). The CO produced is further used via WGS to produce syngas and with it synthesize methanol. A breakeven price of the methanol is estimated to be 1.22 USD/kg, a little above current market prices (Methanex, 2022) but comparable to other renewable-resource-based alternatives.

Solar thermal decomposition. Apart from the use of thermochemical cycles for the decomposition of carbonous matter, it is possible to directly decompose methane avoiding any production of CO_2, as it is produced in the steam reforming. The reaction is highly endothermic:

$$CH_4 \rightarrow C + H_2 \; \Delta H_r = 74.9 kJ/mol$$

Apart from hydrogen, the quality of the carbon black obtained is expected to make it a marketable product as well. The decomposition can be carried out with no catalyst beyond 1300 ºC, therefore metallic and carbonaceous catalysts have also been evaluated to reduce the operating temperature and improve the kinetics (Abanades et al., 2014). The reactor design for such purpose uses directly irradiated particle-laden flows and indirect irradiated graphite/ceramic absorber tubes (Abanades and Flamant, 2008a,b; Hirst and Seindfeld, 2004; Rodat et al., 2010). The challenge is the design of the reactors, its geometry, evaluated using ANSYS Fluent, and the deposition of C on the surfaces (Abanades et al., 2014). The thermodynamics and the kinetics of the reactors are also a matter of study to determine the yield of the reaction (Ozalp and Shilapuran, 2010). Conversions over 80% can be achieved. However, the integration of the reactor within the process is to be further evaluated.

Solar thermal and solar photovoltaic integration. To improve the yield from energy to hydrogen, the solar spectrum can be better harvested if hydrogen is produced from the high-energy spectrum, and electricity is generated from middle spectrum photons using photovoltaic arrays while only the high temperature heat is used to produce electricity in a Rankine cycle using long wave photons. Zamfirescu and Dincer (2014) evaluated such a system using chemical storage in the form of the production of ammonia. The energy released from the ammonia is used in the Rankine cycle. The power produced at the Rankine cycle is used to power an alkaline electrolyzer that produces hydrogen and a photocatalytic reactor is used to produce hydrogen from an aqueous solution of sulfites. The operation over time is performed using DELSOL3 software to evaluate the yield of the heliostat field through SAM package. This system, for a large size facility using a 500 MW heliostat field, is capable to producing a levelized price of hydrogen of 1.65 $/kg., the DOE target.

Power to X. An alternative to integrate solar thermal energy is to provide for the electricity required for the electrolysis of water that is later used for the production of chemicals such as methane (Davis and Martín, 2014), methanol (Martín, 2016b), DME (Martín, 2015b) or ammonia (Sánchez and Martín, 2018). Most of the studies so far have used PV panels or wind turbines to produce the power required. While the investment costs are lower using PV solar in locations at the south of Europe (Martín, 2017), the disadvantage appears in the operation of the facility due to the larger variability of the production of power resulting in the need for the simultaneous process design and scheduling problem (Zhang et al., 2019). The plant design represents the challenge of the hourly variability and the problem size. The use of CSP plants can mitigate the hourly variability of the operation using the thermal storage compared to the use of PV panels, while seasonal variability can be mitigated with the production of the chemical.

Thermo chemical storage systems are based on endothermic chemical reactions and the details have already been presented within the description of the storage of solar energy section.

Thermal energy to distillation. Distillation consumes around 3% of the world's energy (Engelien and Skogestad, 2004). The use of renewable resources can improve the sustainability of the chemical industry just by substituting the energy source that powers the distillation columns. The design and structure of the thermal facilities as presented above result in the need to simultaneously produce thermal energy and power towards a better efficiency of the system. Recent works have presented integrated facilities that include a solar steam plant (SSP) and solar-organic Rankine cycle (SORC) to produce power together with a reactive distillation column (RD) and vapor recompression technology assisted RD (VRC-RD) applied to the methyl acetate hydrolysis process. An hourly discretization is considered over a year horizon and modelled and optimized in MATLAB. This integrated system reports a reduction in the TAC around 45% (Chen et al., 2021).

5. Challenges and opportunities

The use of renewable resources represents an opportunity towards the sustainability of the operation of processes that rely on utilities typically produced from fossil sources, but a number of challenges. However, the variability of major resources, in particular solar energy, presents challenges for its deployment as major energy resource in industry resulting in opportunities for research

-Solar variability is one of the major issues. Industry and society require energy independently of the weather or the time of the day. Even if the energy demand decreases at night, industry operates 24/7 resulting in the need for a robust and reliable source. Energy storage in different forms have established itself as a field of study to mitigate the variability. Alternative systems, materials and fluids are to be further developed to mitigate the disadvantages and challenges presented by the currently used ones.

-Solar variability is linked to both, the time and the location. Each facility design is particular of the location since the heliostat field must make the most of the solar irradiation and the daily profile. Studies on the weather prediction and design under uncertainly are being considered mostly for the facility, but not that extensively for the design of the solar field.

-Process design methodologies, as presented in most design books, date back to the crude oil industry. Novel approaches, tools and methods are required for the design of renewable based processes. Novel procedures that consider uncertainty and weather variability are being developed but the computational burden they require opens a challenge and an opportunity for the PSE community. Several attempts are already integrating process operation, scheduling and design, but further work is required at methodological level and at algorithmic development to address the problems.

-Energy storage system presents challenges in terms of the design of the technology and its yield as well as in the operation. From the technology design standpoint, the use of sensible heat for overnight operation is widely extended either molten salts or synthetic fluids. Energy loses represent a major issue, and simulation studies of the geometry of the storage tanks and the effect of the weather conditions affecting it are to be developed for the specific location of the facility.

-The use of solar energy as a resource for power and steam has focused most of the work and as a result the technology readiness level is higher, with facilities already operating worldwide (TRL 9). In addition, hybrid facilities that make use of a renewable backup resource are already being installed (TRL6–8). However, the use of solar within chemical processes is behind in terms of development. Only solar drying and desalination are already at industrial scale (TRL9). Most of the studies focus on the reactor design at pilot plant level such as reforming, solar based gasification, thermal splitting and thermal decomposition (TRL 1–4), but the design of the process and the operation of the facility is also a major challenge. Scheduling and control are major issues in the operation of these facilities that rely on the integration of several sections to make the most of the energy and solo mitigate the variability over time. The complexity in the operation of solar powered systems is higher than what industry is used to.

-An additional challenge related to the use of solar energy to meet electricity demand is the need for cooling. Solar irradiation availability is inversely related to the availability of water. While wet cooling systems (TRL 9) are the most efficient, even from the emissions point of view, the limited availability of water requires the design of dry systems that require a fraction of the energy produced to power the fans. Cases such as A-frames (TRL-7–9) can be the solution, and the design relies on its integration with he operation, since cleaning the fouling film can affect the performance.

-Reactor design for the use of solar thermal energy to assist the progress of chemical reactions is still at low technology readiness level (TRL-1–4). Computed aided design can play an important role in the optimization of the usage of solar radiation. The need for complex modeling using CFD and structural analysis presents an opportunity for the development of surrogate models and data based optimization techniques.

-The thermodynamics of the species involved in cycles for power production such as organic Rankine cycles, Brayton cycles using supercritical CO_2 and other gasses, is a field open within the process and product design initiative that is gaining support within the process system engineering community. The selection of the fluid is a combination of its properties and the performance of the units and the entire process.

-The design of integrated systems requires further decomposition algorithms to address horizons of operation that range from a year to the strategic substitution of the current power system by facilities that store energy in the form of chemicals and use the later to produce power/ thermal energy to meet a certain demand.

-Process control of large and complex facilities consisting of a number of integrated sections processing variable resources represents a challenge and the need to develop strategies and tools for the industrial scale up and operation of the facilities.

-The sustainability assessment of integrated facilities is limited to the facility itself and aiming at the production of power. Renewable based steam production together with power is to be further evaluated to assess the actual sustainability improvement of the use of renewable based utilities within the chemical industry, including biorefineries.

-The model of solar aided chemical facilities is typically carried out combining process simulators, such as ASPEN Plus or similar, and specialty packages to estimate / design the solar fields. There are opportunities to expand process simulators to include not only solar, but also other renewable resources such as wind or biomass. SAM package from the NREL covers the renewable resources but it is clear that the power of process simulators can help model integrated facilities. Equation-based process models are another alternative, the one used for optimization and control, and over the years many research groups have developed models for different units.

-The scattered resources changes the paradigm of the economies of scale. Even if it can be cheaper to produce using larger facilities, the design of units make be limited due to mass and heat transfer issues as well as the reduced local availability results in a trend towards distributed production and modular design of facilities.

6. Conclusions

The substitution of fossil based energy sources to power industry and society represents a challenge but also an opportunity towards reaching the goal of sustainability presented by the united nations. Solar energy is the largest source of energy that hits the Earth surface. The proper use can make the difference. Over time, the efforts have focused on the production of power and the challenge to address has been dealing with the variability of the resource. Different storage systems have been designed to cover low term variability, i.e. sensible heat, to longer time using renewable backup resources such as biomass or waste, as well a longer term energy storage in the form of chemicals. The progress over the decades has allowed the installation of facilities for the production of power, CSP, that are already at industrial scale of development (TRL 9), where the major challenge beyond the design is the control and operation of integrated facilities that no longer have one energy resource but a number of them. Novel design methods and algorithms are required to address the facility design and operation. In addition, thermal energy is required for many operations in industry, and solar thermal can be used to provide energy to distillation (TRL 1–4), to food drying (TRL 9), hydrocarbon cracking for hydrogen and chemicals production (TRL 1–4), or the production of steam as utility for biorefineries (TRL 9). The solar assisted processes require the design of the reactors that is a challenge itself, but again the operation of such facilities over time plays a major role in the industrial application, where PSE can provide the tools and the expertise.

CRediT authorship contribution statement

Mariano Martín: Conceptualization, Methodology, Writing – review & editing, Supervision, Project administration, Funding acquisition.

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.

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