Assessing thermal energy storage technologies of concentrating solar plants for the direct coupling with chemical processes. The case of solar-driven biomass gasification

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1. Introduction

Growing demand to develop and improve upon the sustainable utilization of renewable energies, the environmental outlooks of energy world to follow the clean and free of CO_2 emissions, and the essentiality of the cost effective energy induce to consider different design options, revamps, and replacements to effectively harvest, store, and transform solar into accessible energy or power sinks [1]. Considering the environmental concerns to meet the free emission approaches is the significant purpose of the motivating indication to apply the concentrating solar power (CSP) plants generated power into chemical plants and its intensification [2], which is accomplished not only by designing the new plants [3], also retrofitting the existing in operation plants [4] with joining or replacing the old resources to new and renewable one(s) [5]. The generation of power could be possibly applicable in direct electricity form for on-grid or off-grid or in advance application, for the chemical processes. Therefore, it is needed to investigate the feasibility of integration of CSP plant with storages to support the chemical units and processes. The investigation proposed in this paper deals with the generation of steam from CSP plants adopting different thermal energy storage (TES) technologies so as to assess their benefits/restrictions whenever coupled with chemical processes for direct production of commodities. Specifically, the combustion/gasification of biomass is the selected chemical process [6]. Although, any enhancement in the structure [7], technology and material used in CSP plants would be considerable to sustain the generation of power to demanded market [8], the objective of this work is to assess the operational limitations of TES technologies and CSP related to the chemical processes. In practice, the potential of CSP in storing the heat via heat transfer liquid (HTF) promotes the status of CSP plants to apply and support the chemical units and processes, in comparison with the other renewable energies; hydrogen production [9] and enriched methane stream production [10] are two examples. The drawback of such plants is the thermal restrictions induced by the technology used to store and dispatch the energy [11]. In other words, solar energy is used based on loading heat energy through the daylight – charging period – and

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unloading through the night – discharging period – for constant power generation throughout the day and night. Furthermore, the key role of TES in CSP is dispatching the solar energy in its possible maximum potential and constantly. TES is commonly categorized in terms of functional process and loading method as direct/indirect storage. In direct TES system, HTF acts simultaneously as the storage medium and transferring fluid. However, in indirect TES system, the process would require the secondary medium for storage, which might be selected according to the application [12].

2. Direct thermal energy storage technologies

The common technologies to harvest and concentrate the sunlight and transfer it into the plant are based on the same concept: the sunlight is focused onto a receiver and heats the HTF up by flowing through the pipelines located in the collectors. In general, TES is an intermediate subsystem in CSP plants to store and dispatch the concentrated energy into the power block. CSP plants mainly consist of the solar field, with different streams of collectors, and a power block. In the power block, a series of heat exchangers are installed to heat the water (economizer unit), to generate the steam (boiler unit) and to superheat the steam (superheaters) before sending it to the turbine for power generation. Due to the discontinuous nature of solar energy and the need of supplying the turbine with constant steam conditions, it is favorable to study the process dynamics of CSP and TES on a time scale of at least half a day. Assessing the operating aspects might depend on the proper control strategy and TES technology. In addition, HTF is selected based on application, potential of the process to generate power and the range of temperature for demanded storage. Looking forward the direct use of solar steam into chemical processes (biomass gasification), the molten salt is selected (60% $NaNO_3$ and 40% KNO_3) for its high thermal and chemical capacity and stability around 550 °C, which is rather beneficial than other competitive HTF such as synthetic oils, which provide lower temperature of storage (around 390 °C) and are flammable as well [12].

2.1. Two-tank storage CSP plant

A common technology in direct storage of CSP plants is the two-tank storage [13]. This TES technology is based on the accumulation of hot and cold molten salt daytime and in the night. A layout can be seen in Fig. 1. The external supply of molten salt is adopted for the plant start-up and for the maintenance of the plant only, whereas it is normally no-flow for the typical operations. An appropriate holdup of molten salt is loaded the first time in the cold tank at a temperature of about 290 °C, whereas the hot tank starts without any holdup. Then, a pump and a flowrate controller manage the molten salt flowrate to be sent to the solar collectors; the flowrate is positive daytime and null during the night, according to the presence of solar energy to be harvested. Daytime, the cold molten salt flows into the solar field and is progressively heated up to 550 °C, which is the limit of molten salt degradation. Once achieved the desired temperature, the hot molten salt enters the hot tank, which progressively increases its holdup during the day, in spite of the holdup of the cold tank. The hot molten salt stored into the hot tank is then sent to the heat exchanger train of the power block to produce power [14]. Also in this case, a pump and a flowrate controller manage the flowrate supplied to the power block. Specifically, Fig. 1 shows the layout of the Archimede CSP plant operating in Sicily (Italy) [15], where the molten salt enters in series the second superheater, the first superheater, the tube side of the boiler, and the economizer, providing gradually the heat to the steam/water flowing in countercurrent in the economizer for preheating, in the boiler for phase change, in the superheaters for steam temperature increase. A temperature controller manages the flowrate of fresh water inside the water/steam loop so as to prevent too-low temperature in the outflowing molten salt as well as to exploit at best the harvested solar energy. The cold molten salt exits the power block and flows back to the cold tank at 290 °C, ready to start a new loop the following day. Conversely, the steam generated in the power block is sent to a turbine for electrical energy generation and after condensation is recycled back to the economizer is closed-loop. With two fully capacitive tanks placed on the process (molten salt) lines, the flowrate of the molten salts in the power block could be different from the flowrate of the solar field and this is the key-point of the TES technology in study. The flowrate of molten salt supplied to the solar field is usually double with respect to the flowrate supplied to the power block since, facing the presence of the sunlight for about 12 h on one hand, there is the need to produce steam and/or energy for 24 h (in continuous) on the other hand.

2.2. Thermocline (single-tank) storage CSP plant

The other configuration in TES technology consists of a single storage tank which contains simultaneously hot and cold HTF in stratified way by appropriately feeding them to the tank from the

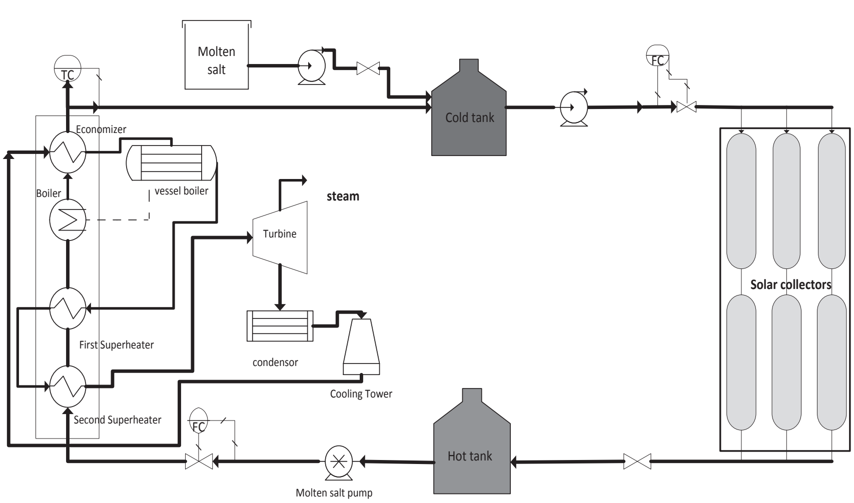


Fig. 1. Direct two-tank TES technology.

top or the bottom, accordingly. This single storage tank is also called thermocline tank [16] due to the thermal stratification phenomena in it [8]. Decreasing the extra volume for storing and related economic issues (the capital cost, maintenance and operational costs associated to the second tank) are the significant motivation of utilizing this single-tank TES technology in CSP plant [11]. As in Fig. 2, the hot fluid is loaded into the tank from the top daytime and, at the same time, the cold fluid is pumped out from the bottom into the solar field to harvest solar energy; by doing so, energy is progressively collected in the thermocline tank [14]. During the night, the cold fluid line is off and no hot fluid is supplied to the thermocline. Conversely, the hot fluid in the tank is continuously (day and night) pumped out from the top and releases the stored heat to the power plant before returning back to the bottom. For this stratified configuration, at any time during the operation, a portion of the medium inside the thermocline tank is at high temperature, and the other portion is at low temperature. The hot and cold temperature regions induce a temperature gradient or thermocline. Buoyancy effects create thermal stratification of the fluid within the tank, which helps to stabilize and maintain the thermocline [17]. This process moves the thermocline region downward daytime and increases the thermal energy potential in the storage. In the night, reversing the flow moves the thermocline upward and depletes the thermal energy [16]. Facing the complexity to predict the thermocline outlet temperature of the hot fluid, the promising economic aspects motivate industrial and technical efforts to consider it as the beneficial alternative technique. On the other hand, a more detailed simulation is needed in this case, to better assess the energy potential of the thermocline, especially when the target is not the power generation, but the direct supply of steam to chemical processes. The next section illustrates the computational fluid-dynamic study of the thermocline with the aim of quantifying the outlet fluid temperature during the day.

3. Computational fluid-dynamic (CFD) study of thermocline technology

The key parameter to assess the performances of the TES technologies is the outlet fluid temperature, which is directly related to the steam/electric energy generated in the turbine. While the outlet temperature is clearly identified in the two-tank storage technology, since it corresponds to the temperature of the molten salt within the tank, the temperature profile for the thermocline needs a detailed analysis in terms of the height (depth of the fluid) in input and output of the tank. Specifically, the estimation is easy daytime, since the hot fluid fed at the top of the thermocline tank is partially sent to the power block and the temperature is quite close to the temperature of the hot fluid coming from the solar field; conversely, a computational fluid-dynamic (CFD) study is necessary to assess the temperature profile during the night. It is worth remarking that in the night there is not any hot feed to the tank and that the fluid exits from the top (hottest fluid) to feed the power block and comes back to the tank at the bottom as cold fluid. The numerical results of the CFD simulation for the night 12 h are reported in Figs. 3 and 4. The specification of molten salt such as density, viscosity, and the thermal conductivity of the applied molten salt is defined by experimental-based temperature-functions [18]. The computational domain is discretized into the finite volumes. A second-order scheme is used to solve the pressure spatial discretization, third-order MUSCL method for momentum and energy. Pressure–velocity coupling is implemented through the SIMPLE algorithm available in Ansys Fluent package. The overall transient formulation (time discretization) is based on the second-order implicit method of solution. The temperature profile of the thermocline is plotted in terms of the depth of thermocline inside the storage tank. Initially, by storing the complete filled thermocline tank with hot HTF (550 °C) at charging period, we start to predict the temperature behavior of the tank through the discharging period, which is not loading the tank anymore. Therefore, storage tank is solely discharge the hot stored HTF from the top of the tank. Due to night conditions, the amount of the hot HTF is decreased and the thermocline region moves upwards. As shown in the night dynamics of Fig. 3a–c, after 1 h the temperature of HTF at top is still rather high (545 °C) and thermocline line, which roughly corresponds to the flex of the temperature profile along the tank height, is almost at 1/3 from the bottom of the tank. In this region, the average temperature of the colder HTF is around 480 °C. After 6 h (Fig. 3b), the thermocline line is raised up to the middle of the tank height and the lowest temperature at the bottom is about 400 °C. At last, it is shown that before the sunrise (at 7:00 AM) the cold HTF is governed over the tank and the average temperature of the tank is approximately 350 °C (Fig. 3c); the temperature at the top of the tank is about 460 °C.

It is obvious that the temperature of stored molten salt entering into the tank and afterward, passing through the heat exchanger block decreases in heat exchangers to transfer the heat to supplementary water and produce steam. For this purpose, in double-tank technology, because of the ease in the separation of hot and cold fluids in the different tanks and the consistency in the temperature of fluid, there is no remarkable tendency of decrease in

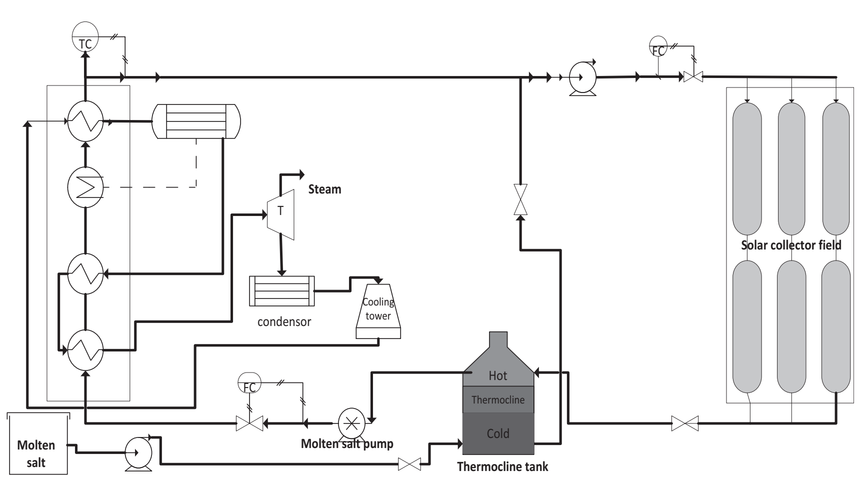
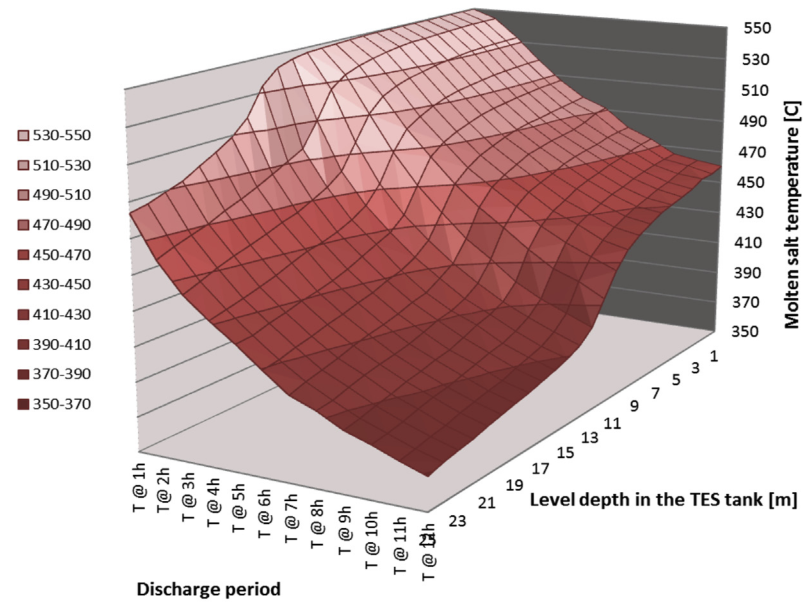


Fig. 2. Direct thermocline TES technology.



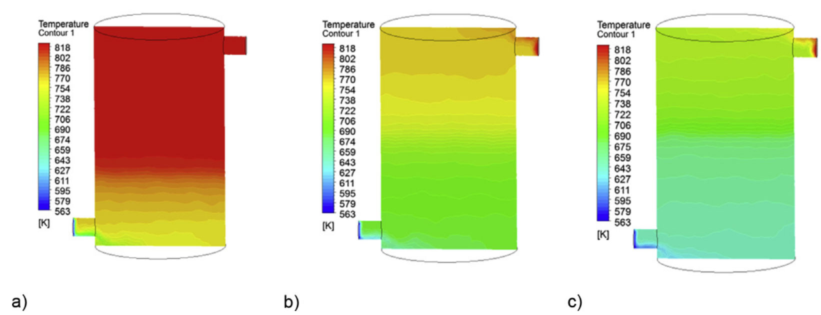


Fig. 3. Temperature distribution of thermocline in discharging period (night cycle) in terms of the depth of thermocline: a) 1 h, b) 6 h, and c) 12 h after the sunset.

temperature, except of some disturbances caused in facing with less quantity holdup in storage tank remained from last discharge, as it is seen in Fig. 5. On the other hand, the single-tank TES technology presents significant and wide range variation of the temperature due to the thermocline (Fig. 6). This thermocline temperature variation is therefore implemented in the Dynsim suite by Invensys Simulation Science for the detailed process simulation of the single-tank TES technology so as to estimate the power potential of the two solutions. The calculated temperature of steam for the two cases is reported in Figs. 7 and 8.

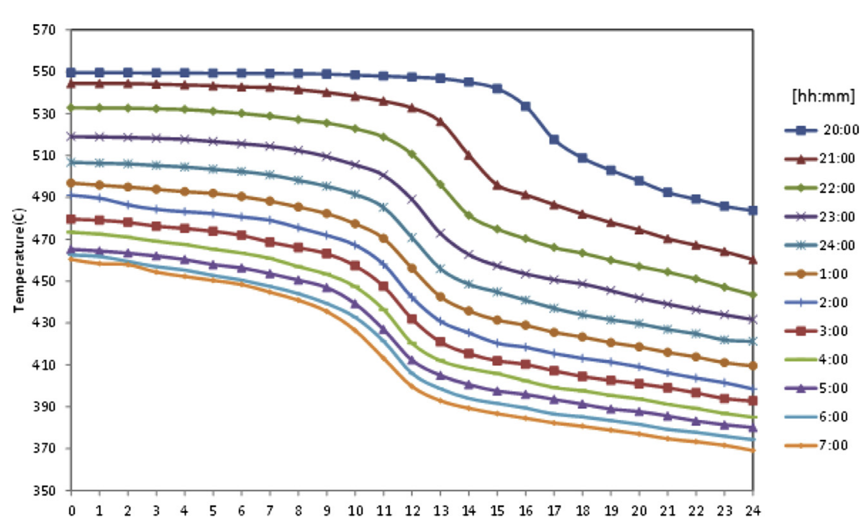


Fig. 4. Dynamic profiles of thermocline during the night hours.

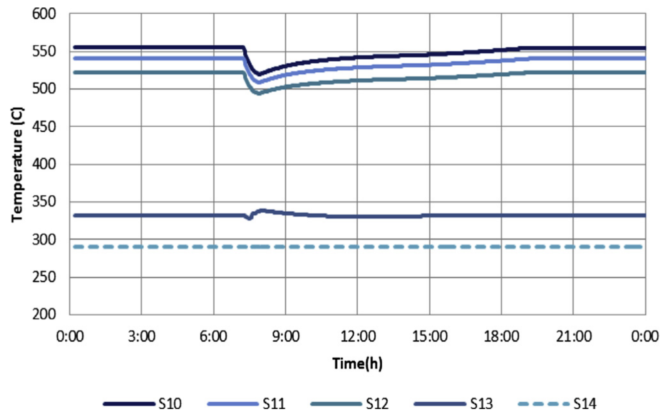


Fig. 5. Outlet temperature trend of molten salt from the two-tank TES technology (S10 is the outflow of the hot tank and the inlet of the power block; S11 is the outflow of the second superheater; S12 is the outflow of the first superheater; S13 is the outflow of the boiler; S14 is the outflow of the power block and the inlet of the cold tank).

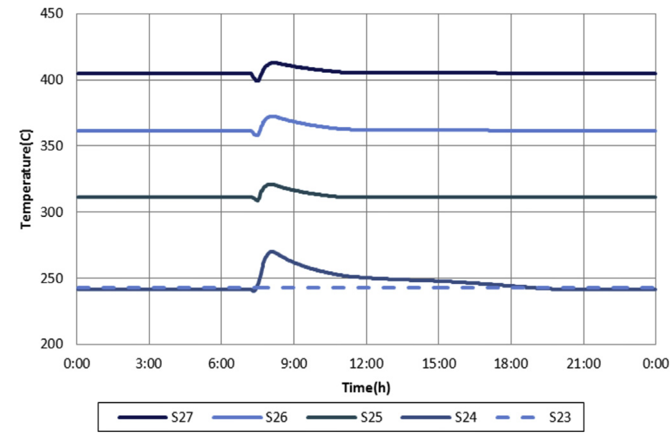


Fig. 7. Temperature trend of steam generated with the two-tank TES technology (S27 is the outflow of the second superheater and the inlet of the turbine; S26 is the outflow of the first superheater; S25 is the outflow of the boiler; S24 is the outflow of the economizer; S23 is the inflow of the power block and the economizer as well).

In practice, as also demonstrated in the scientific literature, the thermocline TES technology for CSP is a promising technology in power generation owing to its potential in reduction of capital cost to 35% with respect to the two-tank TES technology due to eliminating an extra storage tank and merging them into one volume [18]. Nevertheless, additional investigations are needed to assess possible current limitations of the thermocline when CSP plants are coupled with chemical processes for direct steam supply.

4. Coupling CSP/TES technologies with chemical processes. The case of biomass gasification

The idea of applying the CSP plant generated steam into the chemical units is motivated by the clean and free emission source of energy, which is on the crest of energy sectors' discussions and outlooks. Therefore, to take an advantage of the clean power generated by the solar power plant, it is necessary to assess its effects on the process thermal treatments. Nowadays, coal and natural gas are the main fuels to produce steam power for combustion systems. Environmentally speaking, reducing the carbon footprint [19] from the chemical plants requires the extensive attempts in reducing the energy requirement of the chemical plants [20], and reducing the carbon emissions associated with what remaining energy is required. Moreover, changing the process to alter the relative requirements for thermal energy is the other approach for energy reducing purposes [4]. Following these approaches, replacing fuel-based power plants to renewable and clean source of energy could bring the beneficial challenging in comparison with the traditional ways of steam generation processes. Biomass gasification/combustion is a traditional and well-known process in power and chemical production with several process layouts such as fluidized bed gasifiers [21], updraft gasifiers [22], and traveling grate gasifiers [23] to quote a few. In general, biomass gasification [24] is the thermo-chemical conversion of organic (waste) feedstock in a reduced oxygen medium (partial oxidization) [25], whereas the combustion takes place completely in the presence of oxygen [26]. The common operating temperature for gasification is rather high, commonly varies from 750 °C to 1000 °C, depending on the type of feedstock [18] and operating conditions [27]. The resulting products are fuel gases (mainly syngas including carbon monoxide, carbon dioxide, hydrogen, and methane) and slag, ash and solid residues as by-products. The syngas is the fundamental base chemical for the synthesis of energy carriers such as methanol [28] and dimethyl ether [29], for auto-traction fuels via gas-to-liquid (Fischer–Tropsch) process [30], and

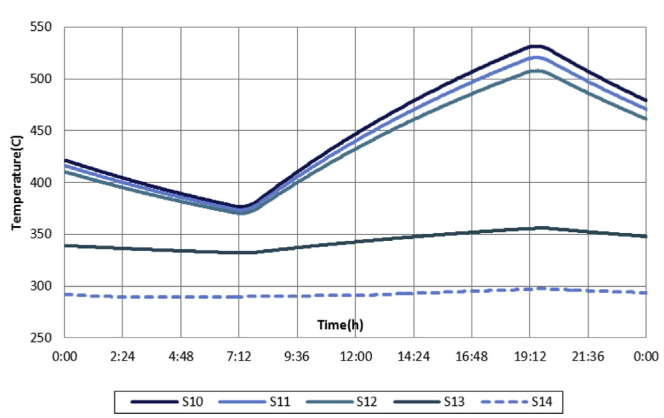


Fig. 6. Outlet temperature trend of molten salt from the thermocline TES technology (S10 is the outflow of the hot tank and the inlet of the power block; S11 is the outflow of the second superheater; S12 is the outflow of the first superheater; S13 is the outflow of the boiler; S14 is the outflow of the power block and the inlet of the cold tank).

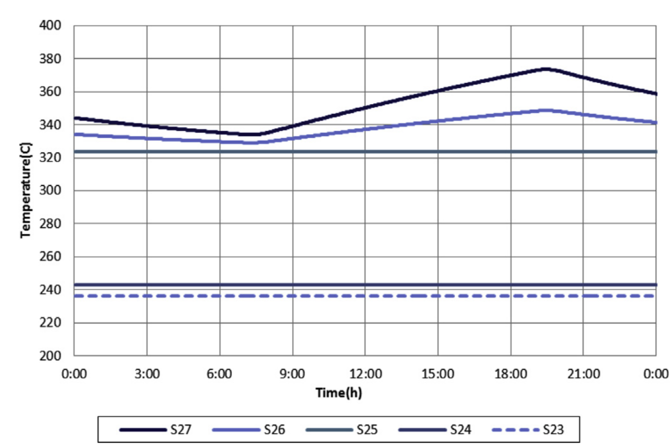


Fig. 8. Temperature trend of steam generated with the thermocline TES technology (S27 is the outflow of the second superheater and the inlet of the turbine; S26 is the outflow of the first superheater; S25 is the outflow of the boiler; S24 is the outflow of the economizer; S23 is the inflow of the power block and the economizer as well).

hydrogen [26] and energy generation [31]. Although, gasification is conceptually high-temperature process with the need of providing high-temperature steam, it is possible to operate a gasifier with low-temperature steam with the adaptation of effective operational parameters, operating conditions and adopting special design options in the configuration of reactor as well [32]. The oxidizing agents are commonly oxygen/air and steam, which could be fed in countercurrent. The use of countercurrent gasifier allows exploiting the high temperature of ashes slowly coming down from the top of the unit to further heat the steam provided at the bottom. The residence time of the biomass within the gasifier is longer and the conditions are milder as well, but the low-temperature (solar) steam supply is effective for biomass gasification. In this context, it is mandatory to assess the effects of the use of the direct TES technologies on the biomass gasification process. In the acquaintance of the authors, this is the first paper that is integrating the dynamic simulation of CSP, the CFD model for thermocline systems, and the detailed dynamic model for biomass gasifiers. The proposed approach is therefore a possible way to effectively assess the TES performances when the CSP plants are adopted to intensify chemical plants.

4.1. Biomass characterization

It is well known that cellulose (40–50 wt%), hemicellulose (25–35 wt%) and lignin (15–35 wt%) are the building blocks of woody biomass [33]. The multi-step kinetic model adopted elsewhere by the same authors [23] characterizes the biomass as a mixture of these three major components, together with moisture and inert ashes. Since the biochemical analysis of biomass is usually unavailable, the method proposed by Ranzi et al. [34] has been adopted to characterize the biomass feedstock on the basis of the bare elemental analysis. If only the elemental analysis in terms of C, H, and O content is available, then a suitable combination of the reference species is simply derived from the three atomic balances. For this reason three mixtures of the reference components (cellulose, hemicellulose, and lignin) are proposed, and the biomass feedstock is characterized as the linear combination of these reference mixtures.

4.2. Modeling of the gasifier

The overall kinetic scheme is integrated in a mechanistic model that accounts for the intra- and inter-phase heat and mass transfer phenomena that must be considered and coupled with the kinetics when modeling reactors treating thick particles. According to the literature [35], a convenient way to present the mass and energy balance equations is to distinguish the particle and the reactor scale. The particle model should be able to predict temperature profiles and product distribution as a function of time. This model requires not only reaction kinetics, but also reliable rules for estimating transport properties to account for morphological changes during the pyrolysis process. The intra-particle mass and heat transfer resistances are simply described by assuming an isotropic sphere. The particle is discretized into several sectors to characterize the temperature and concentration profiles, and the dynamic behavior of the particle under pyrolysis, gasification and combustion regimes. The gradients of temperature and volatile species inside the particle are evaluated by means of the energy and continuity equations. N sectors are assumed to discretize the particle. The mass balance of the solid phase is:

$$\frac{dm_{j,i}}{dt} = V_j R_{j,i} \tag{1}$$

where $m_{j,i}$ is the mass of the ith solid component; V_j is the volume of the jth sector; $R_{j,i}$ is the net formation rate of the ith component resulting from the multi-step devolatilization model and from the heterogeneous gas–solid reactions in the jth sector; finally, t is the time variable. The mass balance of the gas phase is:

$$\frac{dm_{j,i}}{dt} = J_{j-1,i}S_{j-1} - J_{j,i}S_j + V_j R_{j,i} \tag{2}$$

where $m_{j,i}$ is the mass of the ith volatile species within the jth sector; S_j is the external surface of the jth sector; and J are the total fluxes generated by diffusion and pressure gradients. The energy balance is:

$$\frac{d\sum_{i=1}^{NCP} m_{j,i}h_{j,i}}{dt} = JC_{j-1}S_{j-1} - JC_jS_j + S_{j-1}\sum_{i=1}^{NCG} J_{j-1,i}h_{j-1,i} - S_j\sum_{i=1}^{NCG} J_{j,i}h_{j,i} + V_j HR_j \tag{3}$$

where $h_{j,i} = c_{P_{j,i}}T_j$ is the component partial enthalpy; T_j is the temperature of the jth sector. The term JC accounts for the heat conduction; the term $V \cdot HR$ accounts for the total reaction heat; NCP is the total number of components; and NCG is the number of gas components.

Mass exchange between adjacent sectors is only allowed for the volatile species, whereas solid compounds are constrained to remain inside the sector. The density profile inside the particle is evaluated as the sum of all the densities of different species $m_{j,i}$ present in each sector. Similarly, the shrinking and porosity of each sector are calculated. Mass and heat fluxes within the particle follow the constitutive Fick, Fourier, and Darcy laws [23]:

$$J_{j,i} = -D_{j,i}^{eff} MW_i \left.\frac{dc_{j,i}}{dr}\right|_{r_j} - \frac{Da_j}{\mu_j}\left.\frac{dP_j}{dr}\right|_{r_j} c_{j,i}MW_i \tag{4}$$

where $D_{j,i}^{eff}$ is the effective diffusion coefficient of the ith component inside the jth sector; MW and c are the molecular weight and the concentration; r is the radius; Da is the Darcy coefficient of the solid; μ is the viscosity of the gas phase; P is the pressure.

$$JC_j = -\kappa_j^{eff}\left.\frac{dT_j}{dr}\right|_{r_j} \tag{5}$$

where κ_j^{eff} is the effective conduction coefficient inside the jth sector. The boundary conditions at the gas–solid interface become:

$$J_{N,i} = k_{ext}MW_i\left(c_{N,i} - c_i^{bulk}\right) + \frac{Da_N}{\mu_N}\left.\frac{\Delta P}{\Delta r}\right|_N c_{N,i}MW_i \tag{6}$$

$$JC_N = h_{ext}\left(T_N - T^{bulk}\right) + JR_N + \sum_i^{NCG} J_{N,i}h_{N,i} \tag{7}$$

where k_{ext} and h_{ext} are the convective transfer coefficients [36] and JR_N is the net radiation heat. The overall model is solved by means of differential–algebraic solvers [37] of BzzMath library [38].

4.3. Solar-driven steam biomass gasification

Therefore, in order to provide the consistent and effective operation, the process is controlled by thermochemical heat of reaction along with related key parameters. However, it is crucial to consider the restrictions and limitations due to the steam generated in the CSP plant and TES technologies. The main focus of this section is concentrated on thermocline as a promising technology due to its economic advantageous. The key-elements to assess the benefits of TES technologies are the ratio of H_2:CO in produced syngas as well as the solid residue after the gasification (considering an even volume and geometry of the gasifier). Especially, in the case of application for synthesis of a chemical such as methanol or dimethyl ether, it would be appropriate to adjust the ratio of H_2:CO as a main benchmark of efficiency of gasification. On the other hand, the amount of solid residue is in the produced gases is the other considerable benchmark to evaluate the efficiency of the plant, which presents the quality of the gasification due to the thermal treatment and completion of the gasification process in the unit. As oxygen and steam are applied as oxidizing agents in the gasification process, it is compensable for the process to change the amount of oxygen fed into the process and assessing the behavior of the process with low-temperature steam injected to gasifier. Owing to the definition of equivalent ratio (ER or λ), it is the oxygen to biomass ratio divided by the stoichiometric oxygen to biomass ratio [39]. This term is crucial because a high λ value results in a lower concentration of H_2 and CO as well as in a higher CO_2 content in the product gas, due to the more combustion governed on gasification. The other relevant parameter is the steam to biomass ratio (SBR), which could affect the efficiency of the plant, though should be taken into account that SBR is due to the limitation of the potential of power generated in CSP plant cannot be as a degree of freedom. As it can be seen from Fig. 9, the total amount of gasification residue decreases while increasing the gasification temperature and, therefore, while the steam temperature supply is high. Increasing λ, also the ratio of H_2:CO increases as shown in Fig. 10, which means the efficiency of the plant is increasing. At temperature lower than 370 °C, which are easily obtained with thermocline TES technology, it is observed that plant is dangerously close to the shutdown conditions as it can be seen from the high amount of solid residue. In other words, the two-tank TES technology ensures constant conditions for the direct link of CSP to chemical processes, whereas the thermocline TES technology still requires certain plant overdesign to achieve the same results. This means that the hypothetical benefits coming from the thermocline TES technology could be zeroed whenever chemical processes requiring high-temperature steam are directly intensified with a CSP plant.

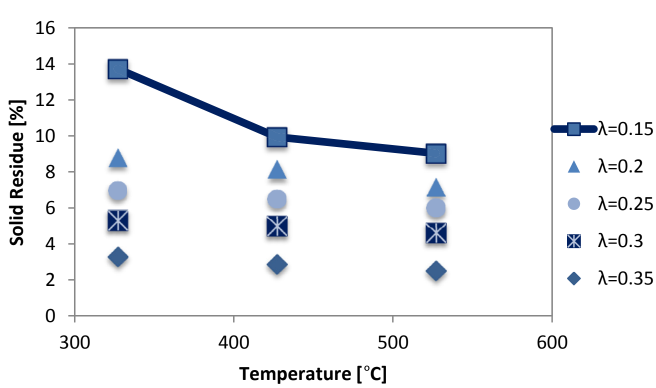


Fig. 9. Solid residue percentage with respect to the solar steam temperature.

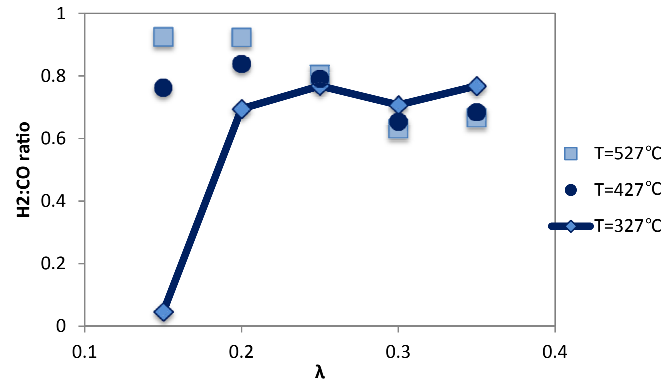


Fig. 10. H_2:CO ratio with respect to the solar steam temperature.

5. Conclusions and future developments

This work proposed the assessment of the performance of two different direct thermal energy storage (TES) technologies commonly adopted in concentrating solar power (CSP) plants: the two-tank storage and the thermocline storage. The comparison is performed at different levels, in terms of steam generation, electrical energy generation, and direct supply of steam for chemical processes. The dynamic simulation of an overall CSP plant is coupled with CFD codes for the detailed description of thermocline systems and, thus, for the reliable assessment of the plant performances in terms of solar energy harvested and thermal energy conversion and usage. The assessment of the pros and cons of the direct TES here considered is carried out not only accounting for investment, operational, and key performance indices, but also simulating their integration with a biomass gasification process. A detailed first-principles dynamic model for the biomass gasifier is given and solved with dedicated numerical methods.

The resulting solar-driven and low-temperature steam-supplied biomass gasification process is studied in detail by providing interesting trends on the solid residue of biomass and the H_2/CO ratio with respect to the steam temperature available from the heat thermal fluid stored in the thermal energy storage tank. Feasibility of solar steam-supplied biomass gasification is demonstrated, although deeper studies are necessary to define the optimal design of unit operations and the overall process layout as well. This study has also shown that the potential economic benefit of the thermocline TES technology is defeated by the need of preserving constant operating conditions in the steam supply to the chemical process, highlighting its restrictions for direct intensification of chemical plants. It unavoidably leads to novel studies on design and operations of TES and its unit operations. Advanced and predictive control techniques could be a possible viable way to manage a priori the temperature variations of steam generated with the thermocline system, making it more appealing TES technology for the integration of chemical plants.

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