

On the path toward day and night continuous solar high temperature thermochemical processes: A review



Sylvain Rodat ^{a,*}, Stéphane Abanades ^a, Houssame Boujjat ^{b,c}, Srirat Chuayboon ^a

^a Processes, Materials and Solar Energy Laboratory, PROMES-CNRS, 7 Rue Du Four Solaire, 66120, Font-Romeu, France

^b Univ. Grenoble Alpes, INES, BP 332, 50 Avenue Du Lac Léman, F-73375, Le-Bourget-du-lac, France

^c CEA-LITEN, Solar and Thermodynamic Systems Laboratory (L2ST), F-38054, Grenoble, France

ARTICLE INFO

Keywords:

Day and night continuous processes
Concentrated solar power
Solar reactor
Hybridization
Solar fuels
Solar chemicals

ABSTRACT

High temperature solar thermochemical processes for fuels and chemical commodities production have been studied for decades and their feasibility is now proven. However, industrial deployment is limited and one of the main reasons is that the variability of solar energy hinders a priori day and night continuous solar process operation. Nevertheless, solar intermittence is now very well managed for Concentrated Solar Power (CSP) electricity production. Indeed, thermal storage up to 600 °C is demonstrated and CSP electricity is base-load capable. However, far beyond electricity, heat supply is the major need in industry. This work reviews the recent works published or patented in the field of continuous operation of high temperature solar thermochemical processes (>600 °C). There is currently a strong commitment toward day and night solar processes operation since it could improve durability, quality of the products, efficiency and economics of such technologies. Indeed, industrial processes are mainly continuous, and daily start up and shut down strongly limit the production capacity of the solar-driven processes, which represents a major lock for scale up. For the first time in this paper, day and night continuous high temperature solar processes are reviewed and categorized. The reported works show the great innovation activity in this field and the various options investigated to date. The main outcomes show that continuous heat supply is possible thanks to hybridization or thermal energy storage.

1. Introduction

Solar energy is the most abundant energy on Earth. As it is diluted, optical solar concentration has been developed in order to increase the available solar heat flux density and thus the maximum achievable temperatures. Solar energy is also highly variable, in time and in space. In order to tackle temporal variability or intermittency, thermal energy storage based on sensible heat (i.e. two-tank storage [1] or thermocline [2]) have been developed. Other options including latent or thermochemical heat storage are also investigated [3]. Solar thermal power plants are currently being deployed commercially for 24 h/day electricity production at temperatures of up to nearly 600 °C [4]. Hybridization with other energy sources (renewable or not) has also been investigated [5]. In order to address the non-homogeneous distribution of solar power on the globe, solar chemical fuels are being envisioned in order to provide a long-term storable and dispatchable renewable energy [6]. For that purpose, it is necessary to reach even higher solar concentration factors in order to obtain the required temperature level

for the endothermal reactions, generally above 800 °C. It concerns pyrolysis, gasification, reforming along with water or CO₂ splitting reactions. High temperature chemical processes like solar production of lime and cement [7] or solar metallurgical carbothermic reduction of metal oxides [8] are also potential candidates for Concentrated Solar Power (CSP) because they require high temperature process heat. Indeed, heat demand in industry is much higher than electricity needs; thus, it is of primary importance to develop methods to run such systems with renewable heat sources. Solar heat is a promising candidate and many studies have been carried out in order to demonstrate the feasibility of solar fuels [9] or solar materials production [10]. However, in general, industrial processes are continuous (day and night operation). To date, in contrast with electricity production from CSP, high temperature solar thermochemical processes have mainly been investigated for daily operation during on-sun periods and shut down at night. This implies high thermal losses related to the reactor preheating in the morning and cooling down at night, low stability of the production outputs affecting the products quality, issues in terms of material

* Corresponding author.

E-mail addresses: sylvain.rodat@promes.cnrs.fr (S. Rodat), stephane.abanades@promes.cnrs.fr (S. Abanades).

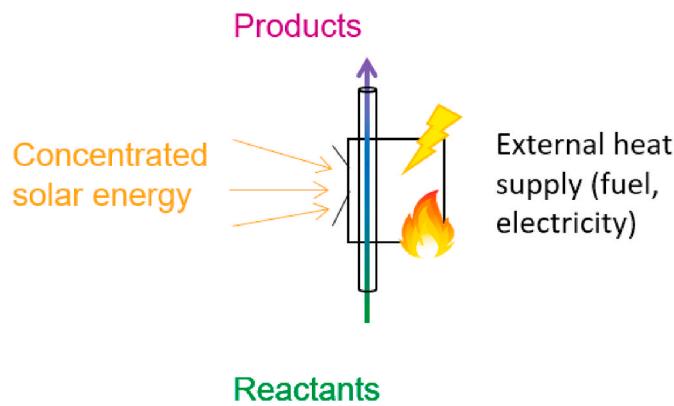


Fig. 1. External heating of a hybrid solar process.

resistance to thermal shocks, and low profitability as the process runs about 30% of the time thereby affecting the production capacity. The main control variable of a thermochemical process is the temperature that directly impacts kinetics. Several works have focused on the daily variation of solar energy for diurnal control of the process temperature. Obviously, the main investigated input variable has been the reactant flow rate that has a direct impact on the receiver temperature. The works are mainly based on simulation results [11]. Saade et al. [12] also numerically investigated model predictive control including DNI (Direct Normal Irradiance) nowcast to control the receiver temperature. The other way for temperature control is to adapt the incoming flux density. The main drawback is that it results in heat spillage and thus oversizing of the heliostat field that represents about 40% of the investment cost for a solar power plant [13]. Ophoff et al. [14] reported about a new iris mechanism for solar thermal receivers in which temperature is controlled thanks to a shutter. Roca et al. [15] proposed to control the heliostat field for a two-step solar hydrogen production plant. Eventually, it is also possible to add thermal inertia to the receiver tanks to thermal storage. Gokon et al. [16] developed a double-walled reformer tube containing high-temperature thermal storage to reduce the impact of solar transients. All these works do not enable around-the-clock operation. Recent works can also be found with the aim to ensure continuous solar processes. The objective of this review is to provide a state-of-the-art (gathering publications and patents) about day and night continuous solar thermochemical processes in order to expose the various proposed solutions and encourage further developments of technological breakthroughs. Noticeably, most of the cited references are dated after year 2000 showing the new and growing interest in this field. Low temperature hybridization ($T < 600^{\circ}\text{C}$) such as steam generation for coal gasification or methane reforming [5] is out of the scope of this study focusing on high temperature solar heat. Four main

categories about the possible options for 24-hour operation have been identified. The first option is to deliver heat at night to the reactor tanks to external heating modules (mainly electric heater or burner) (part 2). The heat requirements can also be provided by internal partial combustion of the feedstock inside the process, which relates to autothermal processes (part 3). Besides, thermal storage remains an option even if the high temperature needs require special investigations. High temperature heat can be stored and supplied either directly or indirectly to the process (part 4). Finally, the "solar flame" using a heat transfer fluid is discussed as it can provide heat in the very same way as a combustion flame so that it can be adapted to almost any process and it can be especially useful for volumetric heat supply (i.e. not at the wall surface) (part 5).

2. External heating for continuous solar processes

In order to offer continuous operation, it is possible to operate solar reactors during low DNI periods or at night thanks to an external heat supply (allothermal process), as depicted in Fig. 1. Power can come from a fossil fuel burner (methane, fuel ...) or from electricity (Joule effect). Hybrid solar/combustion has firstly been considered on a theoretical point of view by Sudiro et al. [17] to investigate a solar hybrid configuration coupling coal to liquid and gas to liquid processes. Advantages of integrated hybrid operation (solar and/or external heater) as compared to systems with separate cavity and boiler are numerous [18]. First, a unique heat exchanger is needed, leading to lower capital expenditures along with a better utilization rate. Thermal losses linked to start up and shut down are avoided. Low DNI period can be valorized. Thermal shocks can be avoided leading to lower mechanical stress on the receiver material. Moreover, the heat supply zone is separated from the reaction chamber, thus avoiding any contamination of the reaction products by the combustion products. Nathan et al. [19] estimated that as compared to the stand-alone solar power plant, the hybrid plant can reduce the capital cost of up to 51% while achieving a solar share of about 50%.

The first demonstration of a hybrid solar reactor was published by Chinnici et al. [18] (Fig. 2). Solar power was about 1 kW while burner was able to provide about 10 kW. The receiver featured a cavity (30 cm inner diameter) with an aperture of 6 cm to let solar radiation indirectly enter the reactor cavity receiver. A burner, run in the moderate or intense low oxygen dilution regime, was also introduced into the cavity for hybridization. The co-annular heat exchanger enabled both the preheating of the combustion air and the recirculation of flue gases (to lower NO_x emissions). The shutter allowed heat losses to be mitigated during the combustion-only mode of operation. Results showed successful operation and potential to avoid CO₂ emissions. Temperatures above 600 °C in the heat transfer fluid were reached, opening the way toward continuous solar thermochemistry such as low temperature solar thermal reforming of methane [20]. A patent was associated to this work

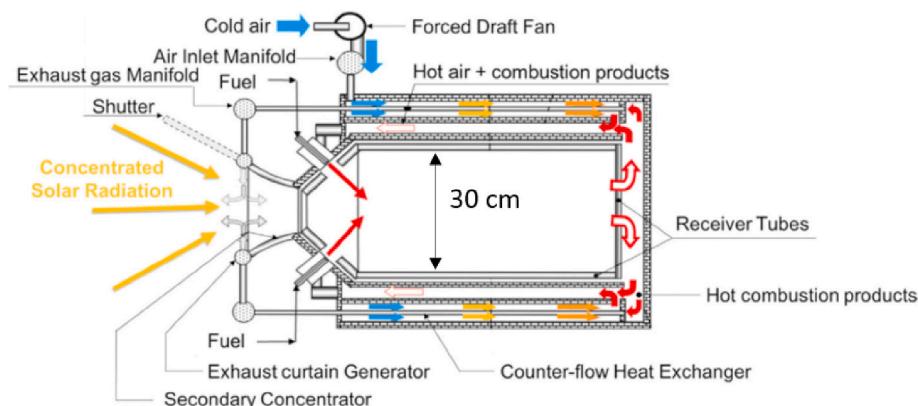


Fig. 2. Schematic diagram of a heat solar receiver combustor (Reprinted from Ref. [18] with permission from Elsevier).

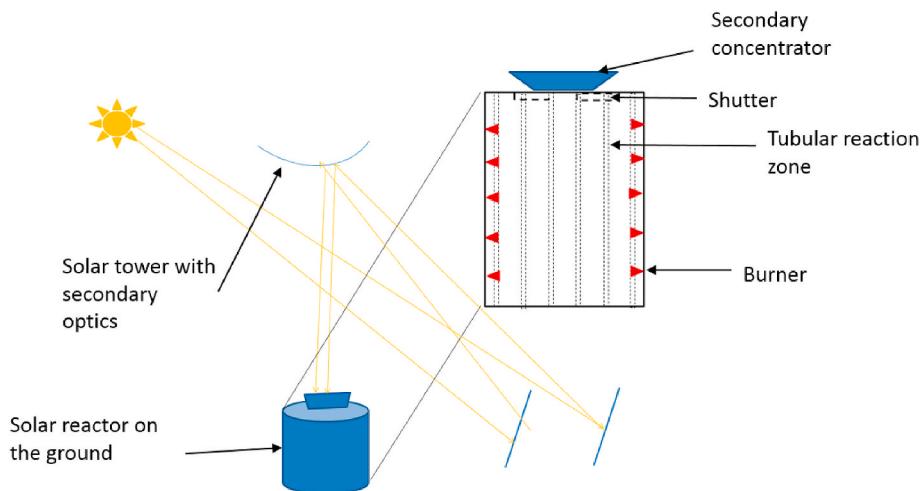


Fig. 3. Hybrid tubular solar reformer with external heating [23].

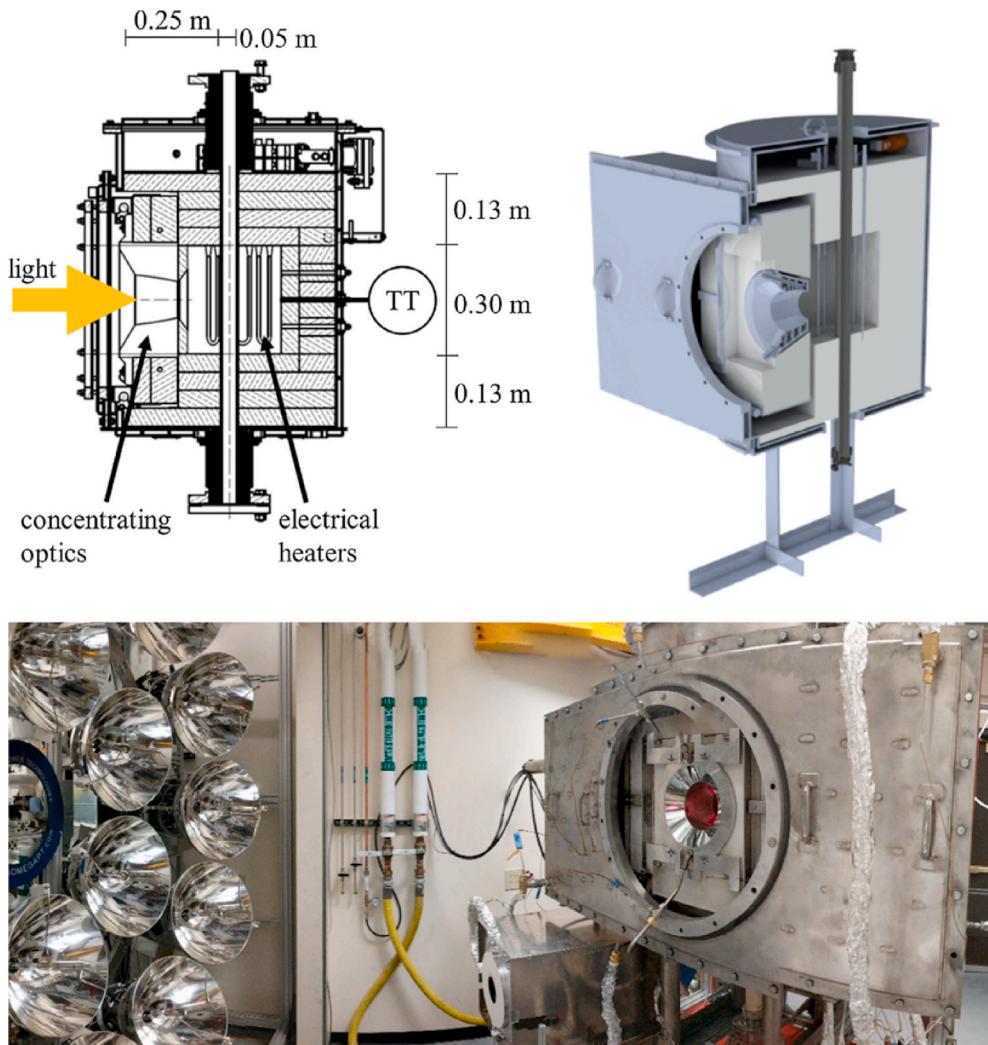


Fig. 4. Cutaway, rendering, and picture of a solar-electric reactor (Reprinted from Ref. [25] with permission from Elsevier).

[21] along with a techno-economic assessment demonstrating the cost effectiveness of the hybrid solar receiver combustor as compared to a separate solar-only cavity receiver and a boiler [22]. In the same vein, Dupassieux et al. [23] patented a solar hybrid reactor concept with

external heat supply, as displayed in Fig. 3. It featured a beam down optics with a secondary concentrator that lets solar concentrated radiation enter a tubular cavity type receiver on the ground. The envisioned reaction was methane reforming. The cavity was also equipped with

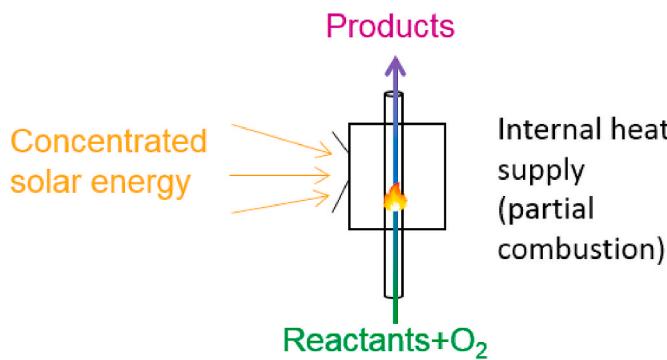


Fig. 5. Internal heating of a hybrid solar process.

burners for off-sun operation as in conventional reformers. A shutter enabled to avoid radiative losses at night. The hybrid solar ground reformer concept was previously raised by Segal et al. [24] but without details about nighttime operation.

Electrical external heat supply was also investigated by Rowe et al. [25] who developed a hybrid solar electrical reactor by introducing electrical heater directly inside the cavity (Fig. 4). Electrical power was 15 kW while solar power was 3.8 kW. Carbon gasification was carried out at 925 °C even if operation up to 1700 °C was claimed. The prototype was mainly operated to demonstrate the continuous control of the reactor temperature by using different control schemes (PI, PI + feed-forward, model predictive control and model predictive control + nowcast). The authors showed that it was possible to continuously maintain the reactor temperature in the range ±10 °C thanks to model predictive control + nowcast, provided that forecasts are accurate.

3. Internal partial combustion for continuous solar processes

Depending on the solar process, it is also possible to directly supply heat inside the reaction zone by partial combustion of the feedstock (Fig. 5).

This type of process heat supply is mainly suitable for the reactions of gasification and reforming, two well-known processes that can operate autothermally thanks to the oxy-combustion of a part of the reactive load (biomass, coal or methane). Fig. 6 illustrates the principle of solar hybrid biomass gasification. During on-sun periods, the enthalpy of the reaction is provided by concentrated solar energy (allothermal operation) so that biomass is integrally converted into syngas. During off-sun periods, oxygen is introduced into the system in order to burn a part of

the biomass and to provide the heat required to gasify the remaining part (autothermal mode). In between, during cloud passages inducing transients, a smart dynamic control of oxygen injection can enable to maintain a stable reactor temperature. It has to be noticed that products flow rate and composition are not maintained with this operation strategy, since combustion products are emitted along with the reaction products, thus possibly requiring an additional downstream separation step (post-combustion CO₂ capture).

The oldest work identified regarding hybrid solar gasification concerns the study of Baykara et al. [26]. It focused on the economics of the conventional, hybrid solar and solar coal gasification processes. Results showed that solar hybrid coal gasification could offer continuous process with estimated product costs at reasonable levels with respect to conventional ones (H₂ costs of 7.89, 8.77 and 12.85 \$/GJ for the conventional, hybrid solar and solar coal gasification processes, respectively). Kaniyal et al. [27] were among the firsts to investigate the hybrid solar gasification process by taking into account seasonal, diurnal, and stochastic variability of the solar resource. An entrained flow reactor was selected. A comparison was proposed between the conventional autothermal coal gasification process (40 bars) and the solar hybrid gasification process (1 bar) to convert 1 kg/s of biomass. Beyond the fact that continuous solar process was ensured, solar hybridization enabled a boost of total energy production by 21% and a 30% decrease in CO₂-equivalent emissions on a mine-to-tank basis. The process analysis showed that a syngas storage was required in order to limit the frequency and the amplitude of the fluctuations on the downstream Fisher-Tropsch unit. In the same way, Li et al. [28] studied the solar hybrid biomass gasification in an indirectly-heated fixed bed reactor with the objective to optimize oxygen-to-feedstock and steam-to-feedstock ratios for redwood feedstock and to maximize cold gas efficiency. They claimed that the solar-to-fuel efficiency in solar-/hybrid mode was significantly lower than the cold gas efficiency in the autothermal gasification because a large part of solar power was remitted or lost to the environment. However, the syngas quality was definitely upgraded by solar energy. Muroyama et al. [29] developed a dynamic model of the solar hybrid gasification process and showed cold gas efficiency of 0.87 in autothermal mode and 1.2 in allothermal mode. They were the firsts to experimentally study solar hybrid gasification in a 1.5 kW_{th} tubular reactor irradiated by artificial light in a solar simulator. Activated charcoal or lignite coal was introduced in the fluidized bed. They demonstrated that it was possible to control the reactor temperature by adjusting the oxygen feeding rate [30]. Hybrid solar-/autothermal processing was also studied during on sun experiments by Boujjat et al. [31] in an innovative 1.5 kW_{th} spouted bed reactor for

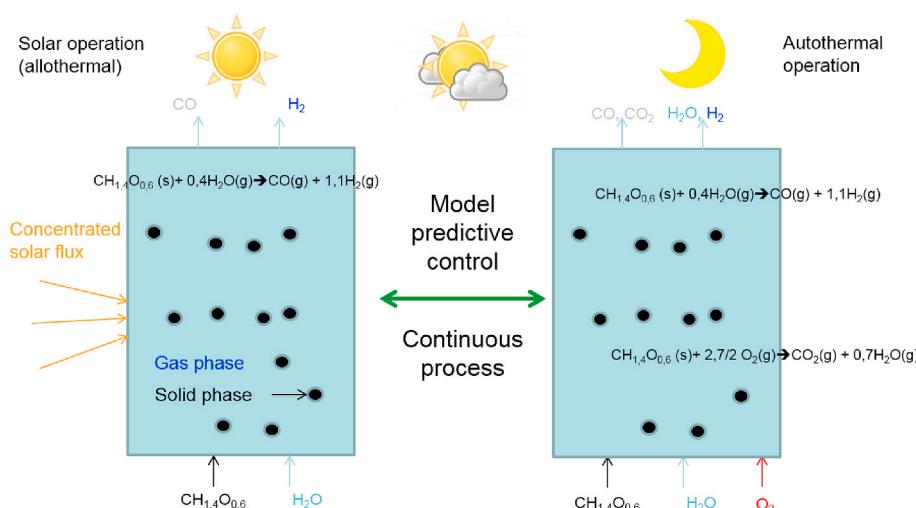


Fig. 6. Principle of the solar hybrid biomass gasification.

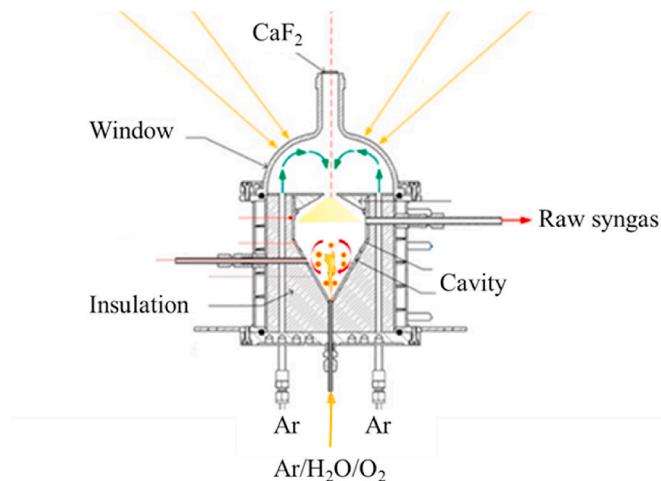


Fig. 7. Schematic of the spouted bed reactor with hybrid operation [34].

wood gasification (Fig. 7). This reactor featured a conical shape into which biomass particles (diameter in the order of 1 mm) were fed. Reactive gases (H_2O and O_2) and jet gas (argon) entered the bottom of the cavity in order to propel the particles toward the reactor cavity top and to absorb direct solar irradiation. Particles then dropped again at the bottom in a circulation loop until complete conversion. A detailed 3D CFD model of the reactor was validated against experimental results for both allothermal and hybrid operation modes. The modelling included thermal, hydrodynamic and chemical considerations. The size distribution of the injected particles was also taken into account. Results highlighted the influence of the oxy-combustion on the temperature distribution as well as the impact of the operation mode on the cold gas efficiency. Due to combustion, the temperature was increased in the cavity center in hybrid mode (Fig. 8). The observed decline of syngas quality (decrease of the Low Heating Value) is in accordance with the work of Goomba et al. [32]. They investigated the influence of the O_2/C ratio in a solar hybrid co-gasifier. Increasing the O_2/C ratio drove to higher reactor temperatures but to lower H_2/CO ratios, while carbon conversion increased and solar-to-fuel efficiency decreased. These results were related to the exothermic combustion reaction. A dynamic

model at 10 MW_{solar} scale was also proposed [33] to evaluate three feeding control strategies of the reactor: constant wood feeding rate, variable feeding rate to maintain the reactor temperature at 1200 °C during the day, combination of variable feeding rate plus oxygen injection to operate round the clock. Dynamic simulation during three consecutive typical days was performed, which confirmed the benefit of hybridization for reliable continuous operation, and paved the way to annual simulations for techno-economic assessment.

Solar hybrid methane reforming was patented by Dupassieux and Rodat [23]. In the same way as solar hybrid gasification, it is possible to benefit from the partial oxidation of methane to adjust the thermal power input in the solar reactor, in order to maintain a constant temperature. As depicted in Fig. 9, the reformer can be placed on top of a tower: solar energy provides heat for the reaction when DNI is sufficient, whereas during transients and at night, partial combustion provides the required heat to the process. To our knowledge, such hybrid process has never been experimentally studied.

4. High temperature thermal energy storage and supply for continuous solar processes

In order to provide high temperature heat to solar thermochemical processes at night, thermal storage has been considered. The review of high temperature thermal energy storage systems [35,36] is out of the

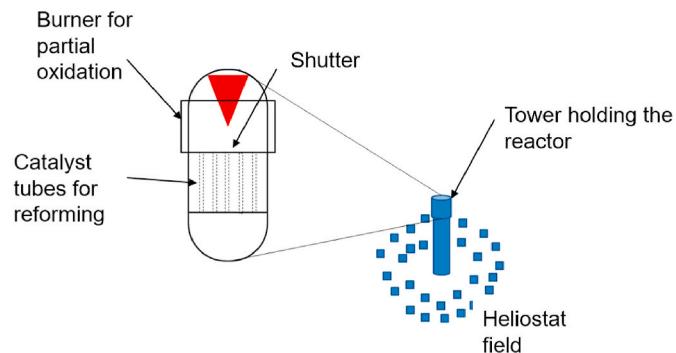


Fig. 9. Hybrid tubular solar reformer with partial combustion [23].

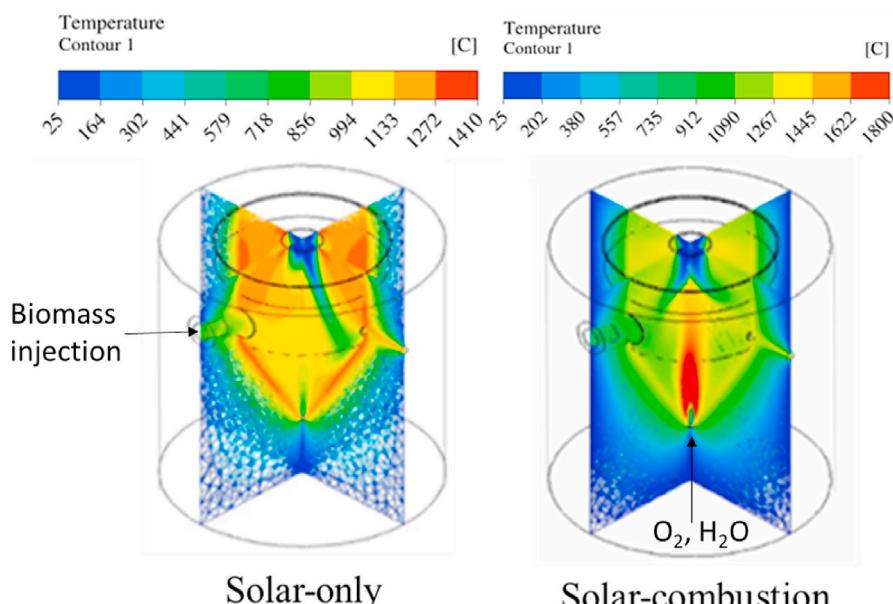


Fig. 8. Temperature distribution in the solar spouted bed reactor in solar only (left, 1.2 g_{wood}/min, 0.2 g_{H2O}/min) and combined solar/combustion (right, 1.2 g_{wood}/min, 0.2 g_{H2O}/min, 0.25 NL_{O2}/min) modes, $Q_{\text{solar}} = 0.88 \text{ kW}$ [34].

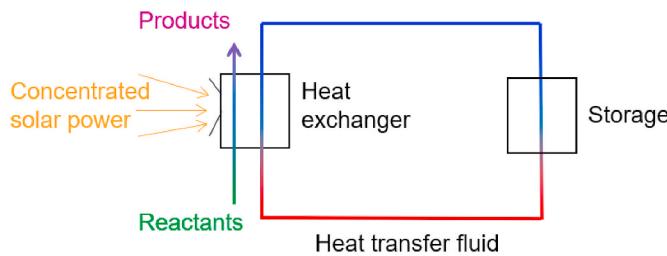


Fig. 10. Indirect heat supply principle.

scope of this work, but the goal is rather to highlight the technological possible connections between solar reactors and thermal storage for continuous operation. Proposed solutions can be divided into two main groups: indirect and direct heat supply. The former uses a heat transfer fluid to indirectly (via a separation wall) bring the heat from the storage to the reactor, whereas the latter proceeds with reaction directly in the heat transfer fluid.

4.1. Indirect heat supply

The principle of indirect heat supply is presented in Fig. 10. It consists of a storage unit and a heat transfer fluid that can transfer excess heat from the receiver to the storage system (either sensible, latent or thermochemical storage) during high solar irradiance period and that can reversely recover energy from the storage to heat the reactor in case of insufficient solar power input. This heat supply mode requires that the solar receiver operates as both a reactor and a heat exchanger (reactor heat exchanger).

This option was retained in the patent of Roeb et al. [37] who proposed a solar reactor heat exchanger with two flow paths (Fig. 11). The reactive mixture flowed through a first flow path while the heat carrier medium passed through a second flow path. Both paths were independent but included in the solar receiver. This way, when solar energy was in excess, the reaction occurred, so a part of solar radiation was converted into chemical energy, while simultaneously the heat carrier medium transferred the energy in surplus toward the storage system. Conversely, when solar radiation was too low, the heat carrier medium transferred heat from the storage to the receiver. At night a shutter was closed at the front to avoid radiative losses from the hot receiver. It was claimed that such a design was capable to compensate temperature fluctuations, but also to maintain a stable products flow rate.

This concept was further investigated within the frame of the CONTISOL project. Lapp et al. [38] fabricated and tested the first of this kind prototype at 3 kW scale. The reactor was made of a SiSiC monolith. Because the two channels were not tight (due to material failure issue), it was only tested with inert gas at 850 °C. The authors suggested the use of Inconel to pursue the qualification. Reforming was selected as an

application example but the concept could be generalized to other thermochemical processes. As far as the thermal storage was concerned, Pantoleontos et al. [39] investigated the storage system with dynamic simulations. Thermochemical storage with cobalt oxide redox pair was chosen as this system is able to store and release heat at about 900 °C, which is suitable for the reforming reaction. The impact of cycling on the storage capacity and material stability was neglected. It was assumed that CoO was available regardless of the final conversion of the previous reduction step. The work showed that with an optimized scheme, 24% of the required energy can be provided during night period, the rest has to be provided by an external heat source. One constraint was that the gas flow rate in both channels was fixed in order to maintain a homogeneous temperature distribution. Indeed, the flow rate control was not easy, because there was not only a consideration of power but also a matter of temperature distribution that should be as homogeneous as possible to control the reaction rate and minimize thermal stress on receiver material. In addition, the authors proposed to investigate partial combustion of methane at night to complement thermochemical heat storage.

Furthermore, Synhelion spin off is on the way to develop day and night continuous processes, and a technology for continuous solar thermochemical cycles was proposed [40,41]. The objective was to heat an infrared (IR) absorbing gas (i.e. H₂O or CO₂) in a solar cavity receiver. Receiver solar-to-heat efficiencies beyond 80% were calculated for temperatures up to 1800K [42]. Then, the energy of the heat transfer fluid heated above 1400–1500 °C was used for water or CO₂ splitting thanks to ceria-based thermochemical cycles. The authors claimed possible round the clock operation with integrated heat storage and recovery. Except an existing patent [43] about heat recovery solution based on thermocline storage (sensible heat recovery between the high-temperature reduction and lower-temperature oxidation step), the whole process is not yet described in details.

4.2. Direct heat supply

Direct heat supply is presented in Fig. 12. In this case, the solar-driven reaction proceeds directly in the heat transfer fluid (no use of

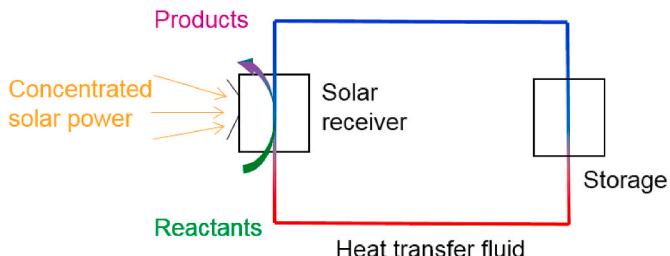


Fig. 12. Direct heat supply principle.

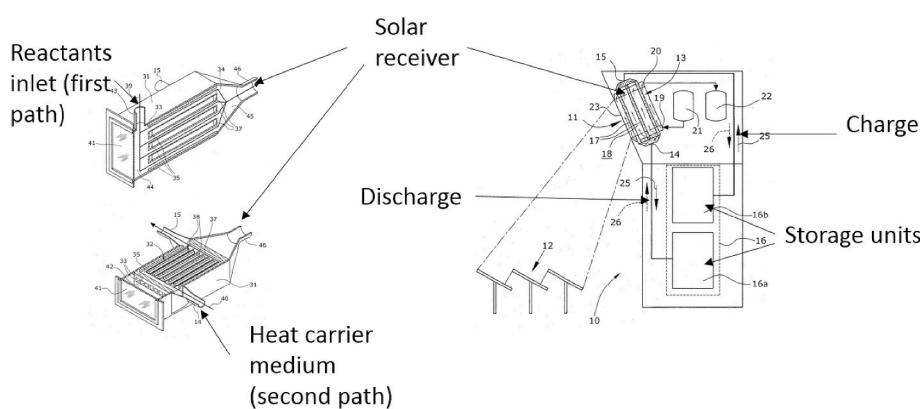


Fig. 11. Reactor heat exchanger (adapted from Ref. [37]).

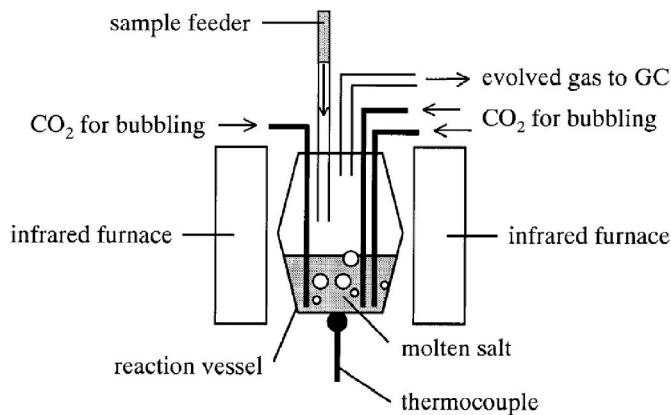


Fig. 13. Experimental apparatus for coal gasification with CO_2 gas bubbling in the molten salt (Reprinted from Ref. [45] with permission from Elsevier).

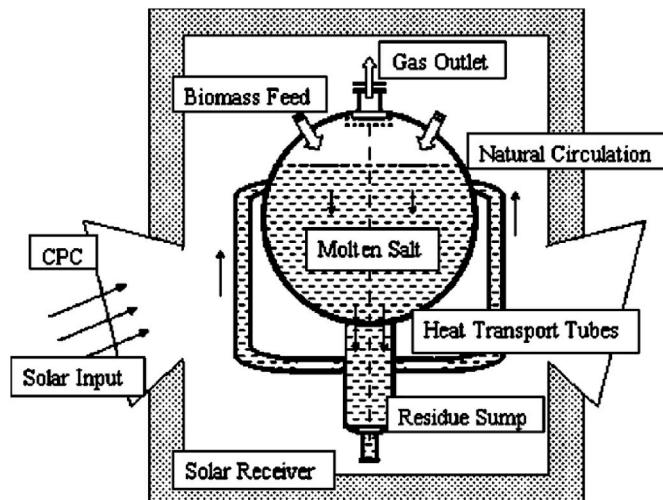


Fig. 14. Solar molten salt pyrolysis reactor (Reprinted from Ref. [46] with permission from ASME).

heat exchanger). By storing directly or indirectly the excess heat of the receiver, it is possible to continuously run the solar process. Indeed, the heat transfer fluid can still provide heat after sunset directly into the reactor. Two heat transfer media have been considered: liquid (molten

salt or liquid metal) or particles.

4.2.1. Liquid heat supply medium

Pioneering work was published by Yoshida et al. [44] in the case of CO_2 coal gasification in molten salts. This first contribution highlighted the potential of the process with reported CO evolution rate being increased by 3.3 times in the presence of molten salt (eutectic mixture of Na_2CO_3 and K_2CO_3). However, coke sedimentation reduced the performance in time because CO_2 was only streamed on the liquid surface inside the tank, thus limiting the contact between CO_2 and coke. Consequently, a CO_2 bubbling reactor was developed ([45], Fig. 13), which showed enhanced performance as the contacting was improved. Nevertheless, the interaction of the salt with ash components of coal was pointed out and required molten salt regeneration.

Adinberg et al. [46] worked on solar pyrolysis of biomass in molten

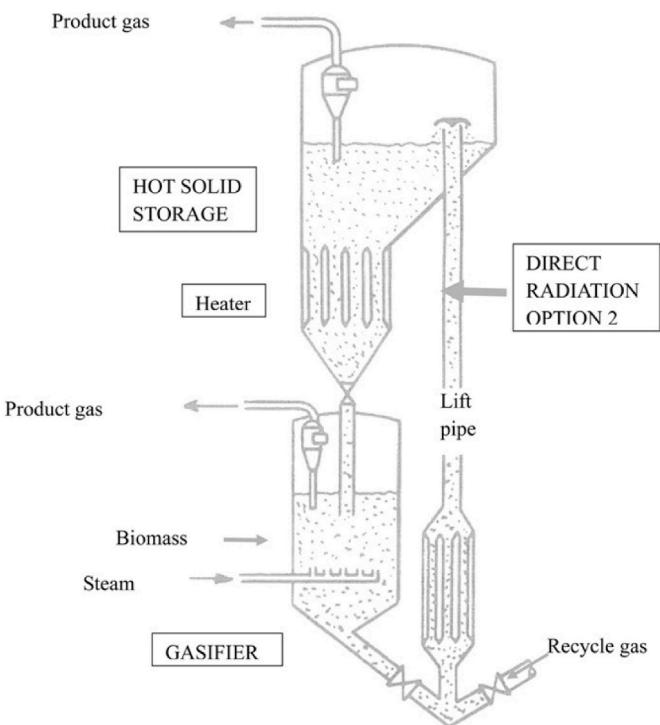


Fig. 16. Possible process configuration for a fluidized bed using an intermediate heating fluid (Reprinted from Ref. [60] with permission from Elsevier).

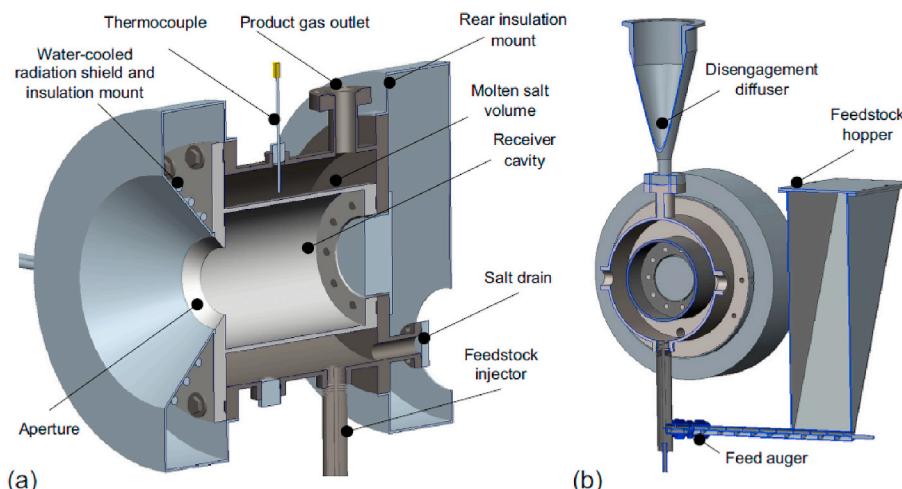


Fig. 15. Solar gasification reactor with molten salt (Reprinted from Ref. [48] with permission from Elsevier).

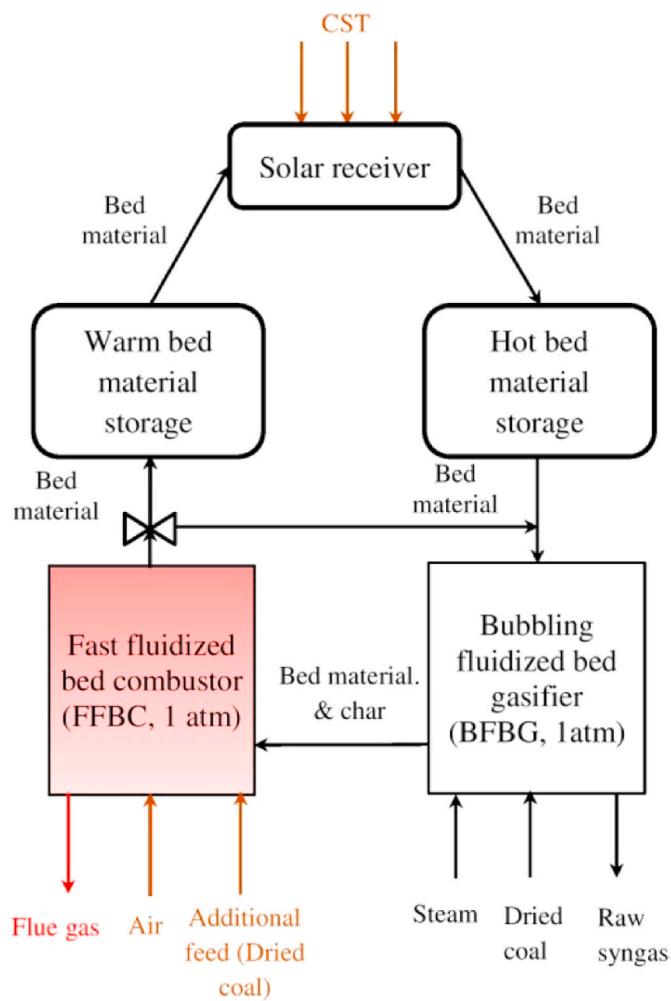


Fig. 17. Flowsheet of the SDFB gasifier with an integrated Solar receiver and sensible heat storages (Reprinted with permission from Ref. [61] Copyright 2015 American Chemical Society).

salt (eutectic mixture of Na_2CO_3 (56 wt%) and K_2CO_3 , melting point: 983 K). The proposed system is depicted in Fig. 14. A molten salt tank was placed into a solar receiver. The tank was surrounded by tubes that connected the bottom of the tank to the top. Biomass was fed at the top of the tank. The subsequent endothermic reaction of pyrolysis tended to decrease the salt temperature at the top of the tank so that cold molten salt dived to the tank bottom creating a thermosiphon. As the tubes absorbed solar irradiation, molten salt was heated up during its ascension back to the top of the tank. This system showed several advantages: high heating rates were obtained by direct contact of biomass with the hot molten salt, and the thermosiphon enabled high heat transfer coefficients within the tubes, offering a good solar to fluid heat exchange. Thus, the use of an intermediate heat transfer fluid enabled a potentially better heat exchange from solar to biomass particles as compared to direct particles/wall heat exchanges. Moreover, alkaline metals catalyzed the pyrolysis reaction. In addition, solar energy could be stored in the molten salt tank for delayed utilization in the form of sensible and even partly in the form of latent heat. Finally, the solid residues (ash, char) could be separated by gravity. The authors evaluated the process at 3 MW scale and calculated that an 80 m³ storage tank (using only 140 °C of sensible heat) would enable round the clock operation for a feed rate of 1 t/h. For the study, they assumed continuous supply (8000 h/year) and stable processing of biomass. During the day (8 h), the 80 m³ storage is charged simultaneously with the biomass processing while excess energy is released during nighttime between 1123 K and 983 K

(16 h). For larger scale, beam down optics is envisioned, associated with a ground molten salt gasifier.

Hathaway et al. [47] further explored the concept of biomass steam gasification in molten salt (mixture of 32% Li_2CO_3 , 33% Na_2CO_3 , 35% K_2CO_3 , melting point: 670 K) into a bubbling tubular reactor. The use of Li_2CO_3 reduces the melting temperature and limits corrosion. Due to reaction of water with the salt, CO_2 gasification was investigated in a 2.2 kW solar reactor [48]. The developed reactor, presented in Fig. 15, was a double-cylindrical wall cavity. Injection of cellulose feedstock was performed at the bottom while gas products recovery was at the top. Injection of the feedstock was performed with an auger that transported the feedstock into an injector. Cellulose was entrained by the CO_2 flow toward the cavity, which required very high flow rate of CO_2 (stoichiometric ratio of 11), resulting in a very low gas residence time, in high heat losses due to gas heating, and in particles entrainment toward the exit. As a result, the reactor achieved a solar-to-fuel efficiency of 30% with 47% of carbon conversion during continuous operation at 1218 K. Efficiency up to 55% was expected, provided that the CO_2 flow rate could be reduced to stoichiometric ratio and that chars remained in the salt until complete conversion. A new biomass injection system (screw feeder) was recently proposed and a reactor thermal efficiency of 40% was reported [49]. Moreover, Xie et al. [50] analyzed the solar pyrolysis of cotton stalk with and without molten salt. The comparison proved that the use of molten salt improves gas yield.

Alkali molten carbonates were also studied for methane pyrolysis; however, side reactions between carbon and salt were reported [51] leading to the production of CO and CO_2 . A special attention has to be paid to the molten salt degradation during the process. In any case, it is participating in the chemical process as a catalyst. In the absence of oxidant, another way consists in using a liquid metal that offers higher density (thus better carbon separation) and conductivity (enhanced heat transfer). Tin was selected by Paxman et al. [52] for its wide temperature stability range (232–2600 °C). Methane was bubbled in a molten tin column. 78% hydrogen yield was reached at 1175 °C. No fouling issue was encountered as the carbon was mainly recovered at the surface of the tin bath. Carbon was in the form of particles (40–100 nm). The authors suggested that the molten metal used for methane cracking process could act as a potential thermal storage medium, and it could thus dampen solar variations due to the higher thermal heat capacitance of metal as compared to gas. For operation during the hours of low solar availability, burning methane is proposed to heat the liquid bath. In another recent work [53], carbon contamination by metal was reported. A molten salt (KBr, NaBr) floating at the surface of the liquid metal (NiBi) was proposed to purify carbon but traces of molten salts remained on the carbon particles. Eventually, solar methane pyrolysis in liquid metal may be interesting to produce hydrogen, provided that carbon can be continuously stripped off at the surface and valorized, which is still challenging.

Kodama et al. [54] published first results about solar methane dry reforming in molten salts ($\text{K}_2\text{CO}_3/\text{NaCO}_3$) to provide stable operation under fluctuating insolation and thermal uniformity in the solar reformer under concentrated solar irradiation. Ni, Fe, Cu and W catalysts were tested. Ni was identified as the most promising. About 70% methane conversion was obtained at 1223 K. A 7 days run was simulated with stops at night, which revealed that methane cracking progressively occurred. A reaction sequence was proposed to explain this phenomenon even if it is not fully understood. Beside these results, the study indicated that in spite of the carbon formation, the catalysts were not deactivated because carbon was only found at the upper side of the molten salt bath.

In summary, various studies have been published about the stabilization of solar processes operation using liquid metals or molten salts. However, these studies mainly focused on either the reaction itself or the general process. Neither transient behavior nor storage integration have been considered to experimentally demonstrate the benefit for day and night continuous operation. Additional investigations are also required on extended experimental runs to check the long-term molten salts/

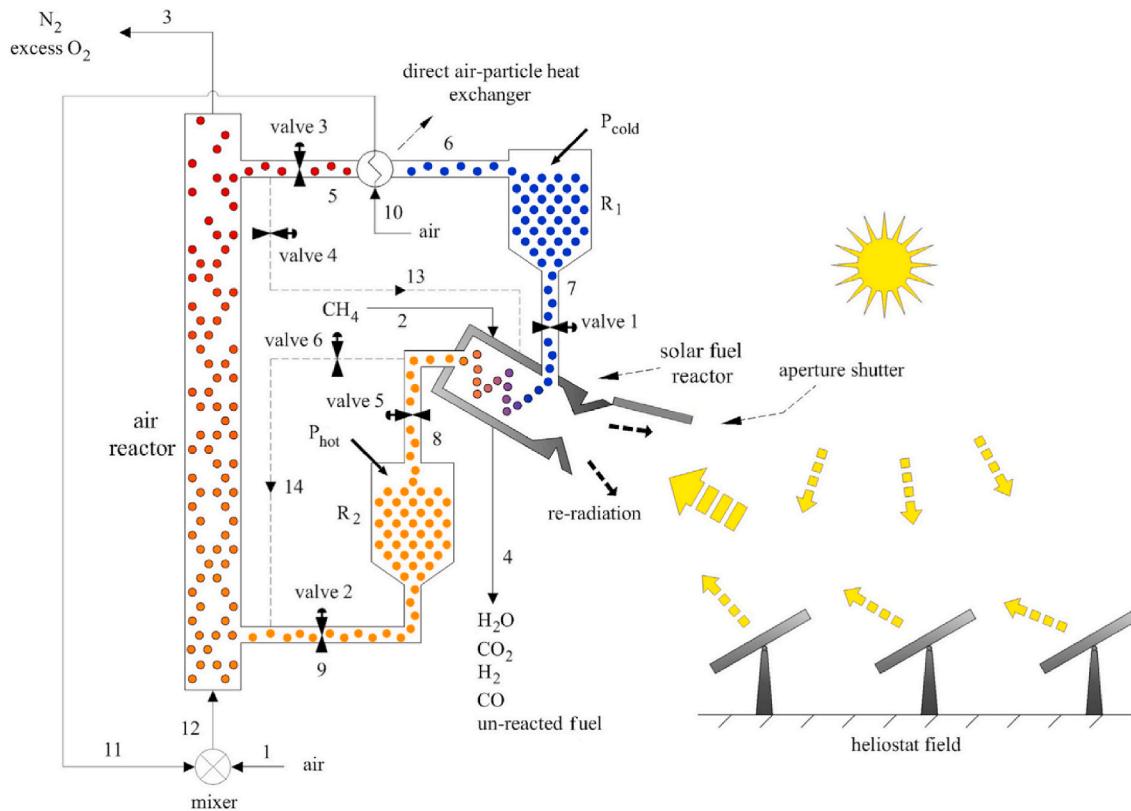


Fig. 18. Solar chemical looping combustion hybrid system (Reprinted from Ref. [64] with permission from Elsevier).

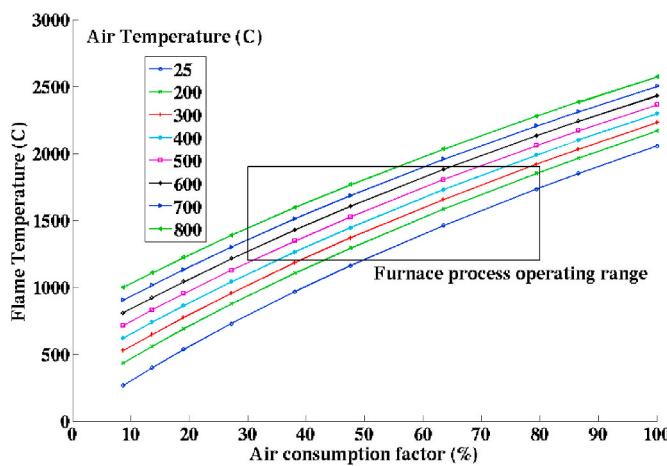


Fig. 19. Flame temperature as a function of the air consumption factor for various air preheating temperatures.

catalysts chemical stability.

4.2.2. Particle heat supply medium

In the field of high temperature continuous solar processes, particle receivers represent a new technological solution [55] aiming to reach temperatures beyond 1000 °C. Many patents were filed in the past 10 years [56–59]. The application mainly concerns electricity production via high temperature pressurized gas cycles, but this technology could even be more performant for continuous thermochemical processes. Indeed, in this case, the absorbed heat by the particles can be directly used in the solid-gas processes (no need for a particle/gas heat exchanger as it is the case to run a gas cycle). A concept for continuous solar biomass gasification was briefly introduced by Nzihou et al. [60],

according to Fig. 16. In this case, the inert particles circulating inside a tube were heated by concentrated solar radiation. The hot particles could be stored or directed toward the gasifier to provide the reaction enthalpy (solid-solid and solid-gas heat transfers). A continuous solar process could be obtained. Electric hybridization was also envisioned to complete the power supply when required. Also, Guo et al. [61] performed annual simulations of a solar hybrid dual fluidized bed in which particles acted as both heat transfer fluid and storage medium (Fig. 17). The concept offered a sensible thermal storage of bed material, the use of inert particles in the solar receiver to avoid the need for sealing, and a process that delivered a constant production rate and quality of syngas despite solar variability. For a solar multiple of 3 and bed material storage capacity of 16 h, the annual solar share was 21.8% (assuming 100% char conversion in the gasifier). During off-sun hours, coal was burnt in the fluidized bed combustor to provide the required heat.

Reactive metallic particles could also add chemical storage to sensible heat storage thanks to metal oxy-combustion. A hybrid solar chemical looping combustion system has been patented [62] and reported by Hong et al. [63] and by Jafarian et al. [64], the latter including diurnal storage (Fig. 18) to increase the solar share up to 60% during daytime (night time not included). The original objective of chemical looping combustion was to avoid the direct contact of air with the fuel to obtain enriched CO₂ streams. By using oxygen carrier particles, it is possible to run oxy-combustion without any air separation units. In one reactor (fuel reactor), the oxygen carrier particles are reduced by the fuel (endothermic reaction), while the exothermic re-oxidation of the particles with air generates the process heat in a second reactor (air reactor). By introducing solar energy into the system, it is possible to reduce both CO₂ emissions and fuel consumption while providing continuous high temperature process heat.

5. The “solar flame” concept

In general, high temperature processes are heated with fossil fuel

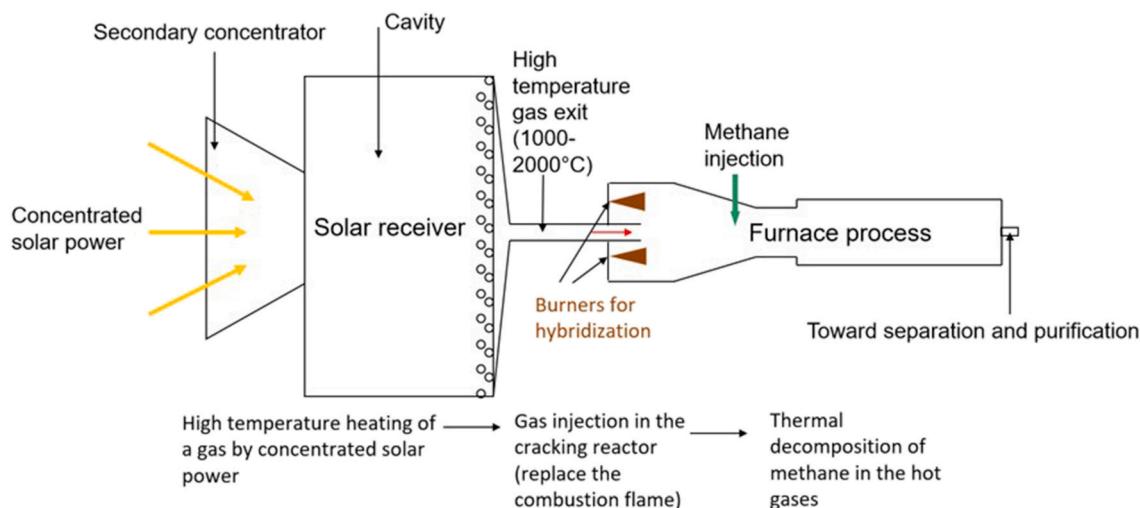


Fig. 20. Principle of the solar flame concept.

burners. A flame is nothing else than a gas mixture at high temperature. The flame temperature mainly depends on the excess oxygen and the air preheating temperature, as depicted in Fig. 19. Typical flame temperatures range from 1200 to 2000 °C. It has to be noted that for low air consumption factors, the remaining oxygen can react with the feedstock to provide additional heat at the expense of the solid carbon production. Consequently, it is possible to replace the combustion flame by the “solar flame” that consists in heating a gas (inert gas such as N₂ or Ar, or IR absorbing gas such as H₂O or CO₂) at the desired temperature to run an endothermic process. Rodat et al. [65] patented this technology that particularly suits the furnace black process since it requires a volumetric reaction (i.e. not a surface reaction over a heated wall or particles). The furnace black process features a closed reactor in which the feedstock to be decomposed (oil or methane) is injected into a hot flue gas coming from a fossil fuel burner. Thus, the dissociation reaction occurs in the gas volume to form mainly carbon black nanoparticles and hydrogen.

The concept, presented in Fig. 20, involved a gas heated by concentrated solar energy at temperatures suitable for an industrial process. The example of the furnace black process was proposed. Hydrocarbons (methane) were injected directly in the hot gas to undergo thermal dissociation in the hot volume in the same way as the standard process. At night, it was possible to use burners to supply heat (from fossil or renewable fuel). During period of low solar radiation, solar energy could be used to preheat combustion air. As compared to the methane cracking into liquid metal, this solution eliminates the need for carbon black purification, while the recovery of the carbon black makes use of conventional technologies. Moreover, the reaction occurs in the gas phase, so that carbon blacks are expected to better match industrial standards of the well-established commercial-grade carbon black production. Deposits on reactor wall surface should also be avoided as in conventional process. The influence of the gas flame composition on the carbon black properties remains an aspect to be addressed. However, methane dissociation in hot argon has already been considered by Javadi et al. [66] in the furnace process. Overall, almost all conventional processes using fossil fuel combustion can be supplied by the “solar flame”. The current challenges remain in the high temperature heating of a gas, but some innovative and promising solutions are being explored [42].

6. Conclusion

This review paper reports for the first time the different investigated options for day and night continuous high temperature solar thermochemical processes. External heating (fossil, electric) is the first mean to maintain a constant heat supply to the reactor whatever the solar

resource. Internal combustion in the case of gasification or reforming (hybrid solar/autothermal operation) appears to be another solution to regulate the solar receiver temperature, at the expense of variations in the output gas composition and partial feedstock consumption for supplying process heat. The third option is thermal energy storage either via indirect heat supply to the solar receiver thanks to a reactor/heat exchanger or direct heat supply thanks to heat transfer fluids (such as molten salts, liquid metals or particles). Finally, the hybridized solar flame could also be a relevant option for continuous high temperature heat supply to conventional processes. In order to reach the objective of continuous round the clock operation, it is of importance to tackle both sharp and smooth transients. Sharp transients are related to cloud passages, while smooth ones are linked to day and night cycles. Tackling rapid disturbances is probably the most challenging task. Sharp transients can be tackled with systems providing high thermal inertia such as the direct heat supply with molten salts or metals. Internal combustion could also enable a quick response to stiff transients thanks to direct oxygen injection in the reactor. Conversely, external combustion would require burner starting with some response delay but, in case the solar share is low, the rapid modulation of the burner (without stops) seems feasible. The same applies for indirect heat supply (with heat transfer fluid) that requires operating pumps. Anyway, if progresses are achieved in the field of DNI forecast, then it should be possible to use model predictive control to manage the different technologies in the best way. A combination of external heating and high thermal inertia processes could also offer the opportunity to limit the molten media quantity while still permitting round the clock operation. Indeed, in this case, the heat transfer fluid with high heat capacity would dampen short transients while a burner or external heat supply would enable nighttime operation. State of the art shows that research on this topic is at its infancy and more work is required for developing scalable and robust processes. High temperature resistant materials, energy storage materials, design, control and dynamic simulation of the hybrid systems have to be considered in future work. It is expected that the development of continuous solar processes will enable to improve economics, durability and credibility of the only-existing sustainable high temperature heat source represented by concentrated solar energy.

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.

Acknowledgements

The authors thank Elsevier, ASME (American Society of Mechanical Engineers) and ACS (American Chemical Society) for reprint permission of figures. The financial support of ADEME (French Environment and Energy Management Agency) is gratefully acknowledged.

References

- [1] Herrmann U, Kelly B, Price H. Two-tank molten salt storage for parabolic trough solar power plants. *Energy* 2004. [https://doi.org/10.1016/S0360-5442\(03\)00193-2](https://doi.org/10.1016/S0360-5442(03)00193-2).
- [2] Bruch A, Fournigué JF, Couturier R. Experimental and numerical investigation of a pilot-scale thermal oil packed bed thermal storage system for CSP power plant. *Sol Energy* 2014. <https://doi.org/10.1016/j.solener.2014.03.019>.
- [3] Alva G, Liu L, Huang X, Fang G. Thermal energy storage materials and systems for solar energy applications. *Renew Sustain Energy Rev* 2017. <https://doi.org/10.1016/j.rser.2016.10.021>.
- [4] Burgaleta JI, Arias S, Ramírez D. Gemasolar, the first tower thermosolar commercial plant with molten salt storage. *Solarpaces* 2011.
- [5] Powell KM, Rashid K, Ellingwood K, Tuttle J, Iverson BD. Hybrid concentrated solar thermal power systems: a review. *Renew Sustain Energy Rev* 2017. <https://doi.org/10.1016/j.rser.2017.05.067>.
- [6] Steinfeld A, Meier A. Solar fuels and materials. *Encycl. Energy*; 2004. <https://doi.org/10.1016/b0-12-176480-x/00322-3>.
- [7] Meier A, Bonaldi E, Cella GM, Lipinski W, Wuillemin D, Palumbo R. Design and experimental investigation of a horizontal rotary reactor for the solar thermal production of lime. *Energy* 2004. [https://doi.org/10.1016/S0360-5442\(03\)00187-7](https://doi.org/10.1016/S0360-5442(03)00187-7).
- [8] Chuayboon S, Abanades S. Clean magnesium production using concentrated solar heat in a high-temperature cavity-type thermochemical reactor. *J Clean Prod* 2019. <https://doi.org/10.1016/j.jclepro.2019.05.371>.
- [9] Steinfeld A. Solar thermochemical production of hydrogen - a review. *Sol Energy* 2005. <https://doi.org/10.1016/j.solener.2003.12.012>.
- [10] Yadav D, Banerjee R. A review of solar thermochemical processes. *Renew Sustain Energy Rev* 2016. <https://doi.org/10.1016/j.rser.2015.10.026>.
- [11] Petrasch J, Osch P, Steinfeld A. Dynamics and control of solar thermochemical reactors. *Chem Eng J* 2009. <https://doi.org/10.1016/j.cej.2008.07.051>.
- [12] Saade E, Clough DE, Weimer AW. Use of image-based direct normal irradiance forecasts in the model predictive control of a solar-thermal reactor. *J Sol Energy Eng* 2014. <https://doi.org/10.1115/1.4025825>.
- [13] IRENA. Concentrating solar power". *Renew Energy Technol: Cost Anal Ser* 2012;1. Power Sector Issue 2/5.
- [14] Ophoff C, Ozalp N. A novel Iris mechanism for solar thermal receivers. *J Sol Energy Eng Trans ASME* 2017. <https://doi.org/10.1115/1.4037745>.
- [15] Roca L, de la Calle A, Yebra LJ. Heliostat-field gain-scheduling control applied to a two-step solar hydrogen production plant. *Appl Energy* 2013. <https://doi.org/10.1016/j.apenergy.2012.09.047>.
- [16] Gokon N, Nakamura S, Hatamachi T, Kodama T. Steam reforming of methane using double-walled reformer tubes containing high-temperature thermal storage Na₂CO₃/MgO composites for solar fuel production. *Energy* 2014. <https://doi.org/10.1016/j.energy.2014.01.107>.
- [17] Sudiro M, Bertucca A. Synthetic fuels by a limited CO₂ emission process which uses both fossil and solar energy. *Energy Fuels* 2007. <https://doi.org/10.1021/ef7003255>.
- [18] Chinnici A, Nathan GJ, Daily BB. Experimental demonstration of the hybrid solar receiver combustor. *Appl Energy* 2018. <https://doi.org/10.1016/j.apenergy.2018.05.021>.
- [19] Nathan GJ, Battye DL, Ashman PJ. Economic evaluation of a novel fuel-saver hybrid combining a solar receiver with a combustor for a solar power tower. *Appl Energy* 2014. <https://doi.org/10.1016/j.apenergy.2013.08.079>.
- [20] Simakov DSA, Wright MM, Ahmed S, Mokheimer EMA, Román-Leshkov Y. Solar thermal catalytic reforming of natural gas: a review on chemistry, catalysis and system design. *Catal Sci Technol* 2015. <https://doi.org/10.1039/c4cy01333f>.
- [21] Nathan GJ, Daily B, Ashman P, Steinfeld A. A hybrid receiver-combustor. *WO2013142911A1*; 2013.
- [22] Lim JH, Hu E, Nathan GJ. Impact of start-up and shut-down losses on the economic benefit of an integrated hybrid solar cavity receiver and combustor. *Appl Energy* 2016. <https://doi.org/10.1016/j.apenergy.2015.11.028>.
- [23] Dupassieux N, Rodat S. Method for thermochemical conversion of a carbon-containing feedstock, performed continuously in a reactor at least partially using the energy from solar radiation. *WO2016169865A1*; 2016.
- [24] Segal A, Epstein M. Solar ground reformer. *Sol Energy* 2003. <https://doi.org/10.1016/j.solener.2003.09.005>.
- [25] Rowe SC, Hischier I, Palumbo AW, Chubukov BA, Wallace MA, Viger R, et al. Nowcasting, predictive control, and feedback control for temperature regulation in a novel hybrid solar-electric reactor for continuous solar-thermal chemical processing. *Sol Energy* 2018. <https://doi.org/10.1016/j.solener.2018.09.005>.
- [26] Baykara SZ, Bilgen E. Synthesis gas and H₂ production from solar gasification of albertan coal. *Energy Convers Manag* 1985. [https://doi.org/10.1016/0196-8904\(85\)90002-0](https://doi.org/10.1016/0196-8904(85)90002-0).
- [27] Kaniyal AA, Van Eyk PJ, Nathan GJ, Ashman PJ, Pincus JJ. Polygeneration of liquid fuels and electricity by the atmospheric pressure hybrid solar gasification of coal. *Energy Fuels* 2013. <https://doi.org/10.1021/ef400198v>.
- [28] Li X, Shen Y, Kan X, Hardiman TK, Dai Y, Wang CH. Thermodynamic assessment of a solar/autothermal hybrid gasification CCHP system with an indirectly radiative reactor. *Energy* 2018;142:201–14. <https://doi.org/10.1016/j.energy.2017.09.149>.
- [29] Muroyama A, Shinn T, Fales R, Loutzenhiser PG. Modeling of a dynamically-controlled hybrid solar/autothermal steam gasification reactor. *Energy Fuels* 2014; 28:6520–30. <https://doi.org/10.1021/ef501535r>.
- [30] Muroyama AP, Gussetti I, Schieber GL, Haussener S, Loutzenhiser PG. Design and demonstration of a prototype 1.5 kWth hybrid solar/autothermal steam gasifier. *Fuel* 2018;211:331–40. <https://doi.org/10.1016/j.fuel.2017.09.059>.
- [31] Boujjat H, Rodat S, Chuayboon S, Abanades S. Experimental and numerical study of a directly irradiated hybrid solar/combustion spouted bed reactor for continuous steam gasification of biomass. *Energy* 2019. <https://doi.org/10.1016/j.energy.2019.116118>.
- [32] Gomaa MR, Mustafa RJ, Al-Dmour N. Solar thermochemical conversion of carbonaceous materials into syngas by Co-Gasification. *J Clean Prod* 2020. <https://doi.org/10.1016/j.jclepro.2019.119185>.
- [33] Boujjat H, Mitsuhashi Yukio Junio G, Rodat S, Abanades S. Dynamic simulation and control of solar biomass gasification for hydrogen-rich syngas production during allothermal and hybrid solar/autothermal operation. *Int. J. Hydrogen Energy* 2020. <https://doi.org/10.1016/j.ijhydene.2020.01.072>. In Press.
- [34] Boujjat H, Rodat S, Chuayboon S, Abanades S. Combustion-assisted solar gasification of biomass particles in a high temperature conical jet spouted bed reactor. *Daegu (South Korea): SOLARPACES*; 2019. 2019.
- [35] Liu M, Steven Tay NH, Bell S, Belusko M, Jacob R, Will G, et al. Review on concentrating solar power plants and new developments in high temperature thermal energy storage technologies. *Renew Sustain Energy Rev* 2016. <https://doi.org/10.1016/j.rser.2015.09.026>.
- [36] Dutta P. High temperature solar receiver and thermal storage systems. *Appl Therm Eng* 2017. <https://doi.org/10.1016/j.applthermaleng.2017.06.028>.
- [37] Roeb M, Sattler C, Schöllgen D, Thomey D. DE102010053902A1 Method for continuously performing solar-heated chemical reactions in solar-chemical reactor, involves discharging accumulator into receiver for maintenance of reaction at times in which radiation for performing reactions does not suffice. 2010.
- [38] Lapp JL, Lange M, Rieping R, de Oliveira L, Roeb M, Sattler C. Fabrication and testing of CONTISOL: a new receiver-reactor for day and night solar thermochemistry. *Appl Therm Eng* 2017. <https://doi.org/10.1016/j.applthermaleng.2017.08.001>.
- [39] Pantaleontos G, Koutsikopoulos D, Lorentzou S, Karagiannakis G, Lekkos CP, Konstandopoulos AG. Dynamic simulation and optimal heat management policy of a coupled solar reforming–heat storage process. *Chem Eng Res Des* 2018. <https://doi.org/10.1016/j.cherd.2017.05.024>.
- [40] Ambrosetti G, Good P, Furler P, Ackermann S, Geissbühler L. The synhelion absorbing gas solar receiver: a route towards 1'500 °C process heat. *Daegu (South Korea): SOLARPACES*; 2019. 2019.
- [41] Furler P, Ambrosetti G, Good P, Ackermann S, Geissbühler L. *Synhelion solar fuels technology*. Daegu (South Korea): SOLARPACES; 2019. 2019.
- [42] Ambrosetti G, Good P. A novel approach to high temperature solar receivers with an absorbing gas as heat transfer fluid and reduced radiative losses. *Sol Energy* 2019. <https://doi.org/10.1016/j.solener.2019.03.004>.
- [43] Pedretti-Rodi A. WO2017197536A1, Process system for recovering heat, and a method for operating same. 2017.
- [44] Yoshida S, Matsunami J, Hosokawa Y, Yokota O, Tamaura Y, Kitamura M. Coal/CO₂ gasification system using molten carbonate salt for solar/fossil energy hybridization. *Energy Fuels* 1999. <https://doi.org/10.1021/ef980144n>.
- [45] Matsunami J, Yoshida S, Oku Y, Yokota O, Tamaura Y, Kitamura M. Coal gasification by CO₂ gas bubbling in molten salt for solar/fossil energy hybridization. *Sol Energy* 2000. [https://doi.org/10.1016/S0038-092X\(99\)00074-2](https://doi.org/10.1016/S0038-092X(99)00074-2).
- [46] Adinberg R, Epstein M, Karni J. Solar gasification of biomass: a molten salt pyrolysis study. *J Sol Energy Eng Trans ASME* 2004. <https://doi.org/10.1115/1.1753577>.
- [47] Hathaway BJ, Honda M, Kittelson DB, Davidson JH. Steam gasification of plant biomass using molten carbonate salts. *Energy* 2013. <https://doi.org/10.1016/j.energy.2012.11.006>.
- [48] Hathaway BJ, Davidson JH. Demonstration of a prototype molten salt solar gasification reactor. *Sol Energy* 2017. <https://doi.org/10.1016/j.solener.2016.12.032>.
- [49] Hathaway BJ, Davidson JH. Solar steam gasification of cellulose in a molten alkali salt: salt chemistry and reactor performance. *Energy and Fuels*; 2020. <https://doi.org/10.1021/acs.energyfuels.9b03488>.
- [50] Xie Y, Zeng K, Flament G, Yang H, Liu N, He X, et al. Solar pyrolysis of cotton stalk in molten salt for bio-fuel production. *Energy* 2019. <https://doi.org/10.1016/j.energy.2019.05.055>.
- [51] Ao XQ, Wang H, Wei YG, Li KZ, Liu MC. Reduction behavior of methane in alkali molten carbonates. *J Fuel Chem Technol* 2008. [https://doi.org/10.1016/S1872-5813\(08\)60028-6](https://doi.org/10.1016/S1872-5813(08)60028-6).
- [52] Paxman D, Trottier S, Nikoo M, Secanell M, Ordorica-Garcia G. Initial experimental and theoretical investigation of solar molten media methane cracking for hydrogen production. *Energy Procedia* 2014. <https://doi.org/10.1016/j.egypro.2014.03.215>.
- [53] Rahimi N, Kang D, Gelinas J, Menon A, Gordon MJ, Metiu H, et al. Solid carbon production and recovery from high temperature methane pyrolysis in bubble

- columns containing molten metals and molten salts. Carbon N Y 2019. <https://doi.org/10.1016/j.carbon.2019.05.041>.
- [54] Kodama T, Koyanagi T, Shimizu T, Kitayama Y. CO₂ reforming of methane in a molten carbonate salt bath for use in solar thermochemical processes. Energy Fuels 2001. <https://doi.org/10.1021/ef000130t>.
- [55] Ho CK, Iverson BD. Review of high-temperature central receiver designs for concentrating solar power. Renew Sustain Energy Rev 2014. <https://doi.org/10.1016/j.rser.2013.08.099>.
- [56] Maryamchik M, Flynn TJ, Hu S, Kraft DL, Marshall JM, Sakadjian BB. WO2016057283A1 Solids-based concentrated solar power receiver. 2018.
- [57] Al-Ansary H, El-Leathy A, Al-Suhailani Z, Al-Zahrani S, Jeter S, Abdel-Khalik S, et al. US20130068217A1 Solid particle receiver with porous structure for flow regulation and enhancement of heat transfer. 2013.
- [58] Flamant G, Hemati M. US9267709B2 Device for collecting solar energy. 2016.
- [59] Amsbeck L, Reiner D, Gobereit B, Marc RWW. DE102010063116A1 Solar radiation receiver device for use in solar thermal power plant for transmission of energy of falling solar radiation into solid particles, has actuator actuating heat carrier medium during rotation of container against direction. 2010.
- [60] Nzihou A, Flamant G, Stanmore B. Synthetic fuels from biomass using concentrated solar energy - a review. Energy 2012. <https://doi.org/10.1016/j.energy.2012.03.077>.
- [61] Guo P, Van Eyk PJ, Saw WL, Ashman PJ, Nathan GJ, Stechel EB. Performance assessment of Fischer-Tropsch liquid fuels production by solar hybridized dual fluidized bed gasification of lignite. Energy Fuels 2015. <https://doi.org/10.1021/acs.energyfuels.5b00007>.
- [62] Jafarian M, Arjomandi M, Nathan AWO. Al A hybrid solar and chemical looping combustion system. n: d; 2015. 048845.
- [63] Hong H, Jin H. A novel solar thermal cycle with chemical looping combustion. Int J Green Energy 2005. <https://doi.org/10.1080/01971520500288022>.
- [64] Jafarian M, Arjomandi M, Nathan GJ. A hybrid solar chemical looping combustion system with a high solar share. Appl Energy 2014. <https://doi.org/10.1016/j.apenergy.2014.03.071>.
- [65] Rodat S, Abanades S, Flamant G. US9784473B2 Solar system for reproducing the effect of a combustion flame. 2017.
- [66] Javadi M, Moghimian M, Pishbin I. The effect of H₂S on hydrogen and carbon black production from thermal decomposition of sour natural gas. Nat Gas IntechOpen 2010.