Project Briefing – Solar Thermochemical cycles

AIM:

The aim of this document is to briefly present the solar thermochemical cycles and their availability to use CO_2 to produce renewable fuels, as a part of the solution to reach Net zero emission.

THERMOCHEMICAL CYCLES:

A well-known way to produce fuels is using water and/or carbon dioxide as raw materials to split them and obtain hydrogen and/or carbon monoxide respectively. However, these molecules are extraordinarily stable and their decomposition is not thermodynamically favored even at temperatures as high as 3000 °C [1].

Solar thermochemical cycles (TCC) are suggested as a promising alternative that require lower temperatures to perform the water or carbon dioxide split reaction. As shown in Fig.1, TCC follow a redox reaction scheme and involve a metal oxide redox pair:
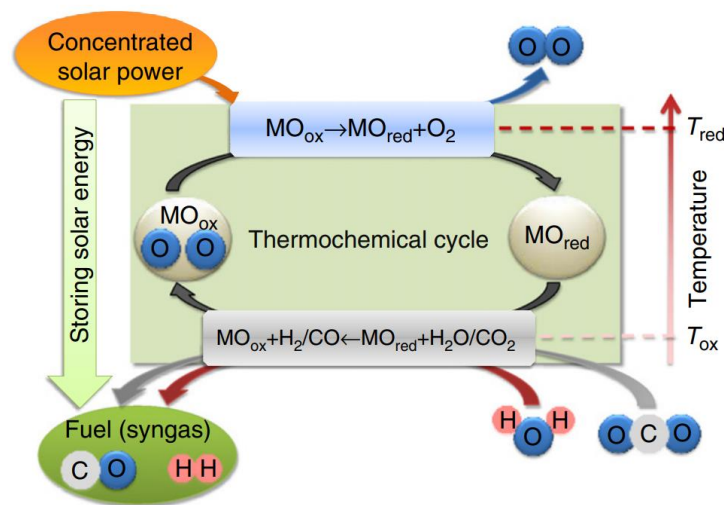

Figure 1: Schematic representation of a TCC, consisting on a redox reaction involving a metal oxide pair (depicted as MO_{ox}/MO_{red}) to produce hydrogen (H_2), carbon monoxide (CO) or both (synthetic gas). Extracted from [2].

The first reaction is an endothermic thermal reduction (TR) carried at a high temperature and which can be driven by concentrated solar power [3], while the second reaction is an exothermic oxidation carried at a lower temperature [2]. It must be also noted that oxygen and hydrogen or carbon monoxide are produced separately, so that no additional separation step is further needed and thus avoiding otherwise potentially dangerous reconversions [1].

Depending on the metal oxide used, TCC may fall in two categories: volatile and non-volatile cycles. In the former, the TR temperature is higher than the melting (or even boiling point) of the oxidized metal, which increases the complexity of the system due to vaporization and recombination issues. Therefore, the latter type has received most of the scientific attention [2]. For non-volatiles cycles, which remain in solid phase through the cycle, four main families of compounds are considered of interest: ferrites ($T_{TR} \approx$ 1300-1400 °C), ceria compounds ($T_{TR} \approx$ 1500 °C), perovskites and hercynites. For most compounds, T_{ox} is between 700 and 1000 °C (slow kinetics are reported at lower temperatures) [2].

Significant efforts are being made on developing and optimizing reactors that can host the aforementioned reactions so that this technology could become commercially available in the future. There are several criteria that must be observed when designing TCC reactors.

Firstly, an optimal arrangement should be found to use the maximum available sun radiation. Depending on the type of cycle, literature suggests designs of solar reactors performing only the TR step (volatile cycles) or hosting the two steps of the cycle (non-volatile cycles). For the latter, solar reactors based on ceramic monolithic honeycombs (HYDROSOL technology [4]) and ceramic foams (SUN-to-LIQUID technology [5]) have shown interesting results and are currently under optimization [6]. Additionally, these designs must be coupled to the available solar concentrating technology (i.e. solar towers or dishes), although indirect approaches have also been suggested [2].

Secondly, TR strongly depends on oxygen partial pressure, with enhanced performance at low values. These values may be achieved with sweep gases other than air (e.g. nitrogen) or vacuum [7]. Remarkable achievements have been recently reported that take advantage of certain metal oxides to remove oxygen from gas mixtures via temperature and pressure swing adsorption. Such processes are claimed to be less energy-intensive than cryogenic distillation [8].

Finally, several studies confirm that adequate heat recovery is also a parameter of major relevance [7,9]. This recovery is mostly focused on heat exchange between oxidized and reduced metal oxide streams and between reactor's inlets and outlets. Research on this topic is currently on-going [10].

Hydrogen produced in solar TCC can be directly used as a fuel, but it is also possible to obtain synthesis gas by one of the three possible pathways [11]: H_2 production followed by reverse water gas shift (RWGS) with CO_2, CO production followed by water gas shift (WGS) with H_2O or by (simultaneous) splitting of H_2O and CO_2. Both hydrogen and synthesis gas can be directly injected at a certain extend on natural gas pipelines without requiring any modification of the grid [3].

Furthermore, synthesis gas can be reformed with mature technology towards methanol [12], dimethylether [1] and other valuable liquid fuels such as gasoline, kerosene or diesel [13] via Fischer-Tropsch synthesis. These options can be fed to currently available vehicles with some minor changes or even directly, hence fostering the transition. The figure below illustrates the integration of Solar TCC to the current energetic needs.
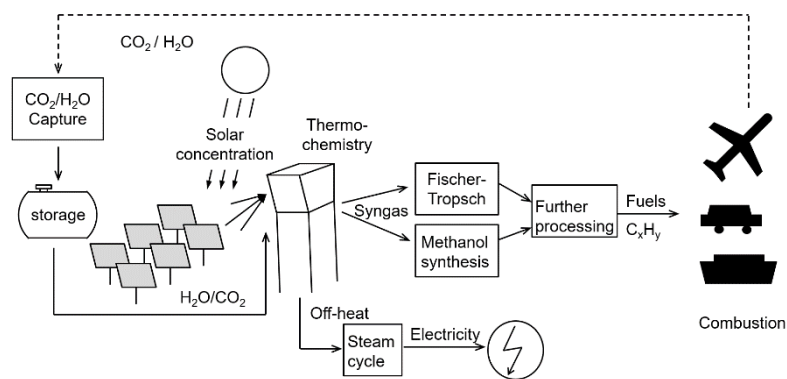

Figure 2: Schematic block diagram showing integration of solar fuels produced by TCC in the energy system. Note the carbon circularity of the process. Extracted from [14].

Several authors have studied the relevance of solar fuels produced by TCC [3,9,15]. Some of the two most critical parameters to determine whether the present approach could become a feasible solution to produce carbon-neutral fuels is the sun-to-fuel efficiency and the levelized cost of fuel (LCOF), which are, in fact, closely related. The former is defined as the higher heating value (HHV) of the produced fuel divided by the solar power input of the cycle [9], while the latter is the production cost of this fuel

considering the facility's initial investment and lifetime, but also other factors such as the financial discount rate or the plant's capacity factor [3].

Sun-to-fuel efficiencies above 10% are considered promising because such plants would require smaller solar fields and, according to several technoeconomic assessments [11,12,16], these sunlight collecting systems account for the highest share of the initial investment. Therefore, higher sun-to-fuel efficiencies, combined with lower manufacturing costs of heliostats and receivers, would lead to lower LCOF. As a consequence, more competitive market selling prices should be possible for solar fuels.

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