Solar-aided Thermochemical Cycle using Sulphur as an Energy Vector

G. Skyfta[1], A. Bakratsa[1], C. Poravou[1], V. Zacharopoulou[1], N. Tsongidis[1], K. Votis[2], G. Karagiannakis[1], D. Dimitrakis[3], C. Agrafiotis[3], D. Thomey[3], M. Roeb[3], C. Sattler[3], S. Sau[4], A. Tizzoni[4], S. Harth[5], D. Trimis[5], C. Kentri[6], S. Boghosian[6], I. Shvets[7], Y.L. Chiew[8], M. Zackrisson[8], J. Vieten[9], P.-F. Mougard-Camacho[10], P. Vespa[10]

[1]ARTEMIS Lab, Centre for Research & Technology Hellas (CERTH), Thermi-Thessaloniki 57001, Greece, [2]Information Technologies Institute (ITI), Centre for Research & Technology Hellas (CERTH), Thermi-Thessaloniki 57001, Greece [3]Institute of Future Fuels, German Aerospace Centre (DLR), Cologne 51147, Germany, [4]Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA), Rome 00123, Italy, [5]Karlsruhe Institute of Technology (KIT), Engler-Bunte-Institute, Karlsruhe 76131, Germany, [6]Department of Chemical Engineering, University of Patras, Patras 26504, Greece, [7]Trinity College, University of Dublin, Dublin D02 PN40, Ireland, [8]RISE Research Institutes of Sweden, 43153 Mölndal, Sweden, [9]ExoMatter GmbH, München 80992, Germany [10]Saint-Gobain Research Provence, 84306 Cavaillon Cedex, France
Keywords: Sulphur, thermochemical cycles, solar thermal, catalytic process.

Presenting author email: gskyfta@certh.gr

Sulphur (S) is a key material for the production of the chemical also called “the most important chemical in the world”; namely Sulphuric Acid (SA). Currently, it is mainly sourced from hydrogen sulfide (H_2S) produced by the hydrodesulphurization of fossil liquid fuels in oil refineries. H_2S is subsequently treated via the known Claus process to produce solid Sulphur. Elemental Sulphur can also be a high-energy density fuel (i.e. 9.3 MJ/kg S), considering its low price and ease of storage and transportation. The path towards green energy and associated energy carriers’ penetration in the economy advocates towards finding alternative ways for Sulphur production and identification of sustainable synergies with the SA industry. The European Commission (EC)-funded SULPHURREAL project aims at investigating materials and key components, in the frame of a thermochemical cycle of reactions originally proposed by the company General Atomics (B. Wong, 2015), to achieve transformation of high temperature solar heat into solid Sulphur which can be combusted on-demand to produce renewable energy (i.e. heat or power when combined with a suitable thermodynamic cycle). Its extensions also involve the exploitation of the cyclic process into SA production when considering an integrated approach adopting essential aspects of circular economy and industrial symbiosis (J.G. Wagenfeld, 2019).

The full 4-step thermochemical cycle investigated, together with the main operational parameters of interest for the reactions involved, is described in Table 1. Reactions 1b), 2) and 4a) require the presence of a catalyst to ensure high conversion rates. Step 1b in particular is highly endothermic and therefore a substantial temperature is necessary to achieve a significant reaction extent. Provision of this high temperature heat matches well the ones achievable by next generation power tower solar thermal plants and especially the ones using solid (ceramic) particle solar receivers (C. Agrafiotis, 2022). It is also noted that reactions 4a) and 4b) are well established chemical processes, already employed commercially for SA production. Naturally, the net sum of the reaction series presented in Table 1 is zero, describing essentially a “closed” cyclic process that stores and releases energy (initially supplied to the process as solar heat) via solid Sulphur production and combustion. However, the cycle can also be operated as an “open” cycle, employing/providing material feedstocks (H_2SO_4, S, SO_2) in combination with SA production or with desulphurization of flue-gas or natural gas. Solid Sulphur and SA can be stored economically and indefinitely using existing industrial technologies already employed routinely in the mature SA industry under ambient conditions and so can, if necessary, SO_2 in liquid form. In either case, all intermediate products such as Sulphur Dioxide and Sulphur Trioxide are recirculated internally without being emitted into the atmosphere with their safe handling based on already mature industrial practices.

The overall concept sets forth the alternative solar-driven use of already industrially produced Sulphur as an additional fuel in our future further diversified portfolio, next to Hydrogen, biofuels and renewable-made hydrocarbons. It lies entirely within the target of transformation of Europe according to the principles of CO_2-free circular economy, and, in contrast to intermittent renewable energy sources (IRES) can provide either baseload or dispatchable electricity. A schematic representation of the concept to facilitate visualization of its main principles and overall approach is provided in Figure 1 (B. Wong, 2015).

The work will present the overall concept, its practical implementation in the framework of a solar-thermal aided approach, the main challenges associated to each reaction step involved and the potential implications and extensions of the proposed cycle with emphasis on practical interfaces with the supply of solar heat for its implementation on the one hand and the SA industry on the other.

Table 1. Main reactions of the elemental Sulphur thermochemical cycle and main operational parameters

		Reaction	Reaction enthalpy kJ/mol S	Indicative temperature ºC
1a	SA splitting	$3H_2SO_4(aq) \rightarrow 3SO_3(g) + 3H_2O(g)$	-826	450 - 500
1b		$3SO_3(g) \rightarrow 3SO_2(g) + 1.5O_2(g)$		650 - 900
2	Disproportionation	$3SO_2(g) + 2H_2O(l) \rightarrow 2H_2SO_4(aq) + S(s)$	-254	50 - 200
3	Sulphur combustion	$S(l) + O_2(g) \rightarrow SO_2(g)$	-297	500 - 1500
4a	Contact process & Absorption	$SO_2(g) + O_2(g) \rightarrow SO_3(g)$	-99	400
4b		$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$	-176	< 200

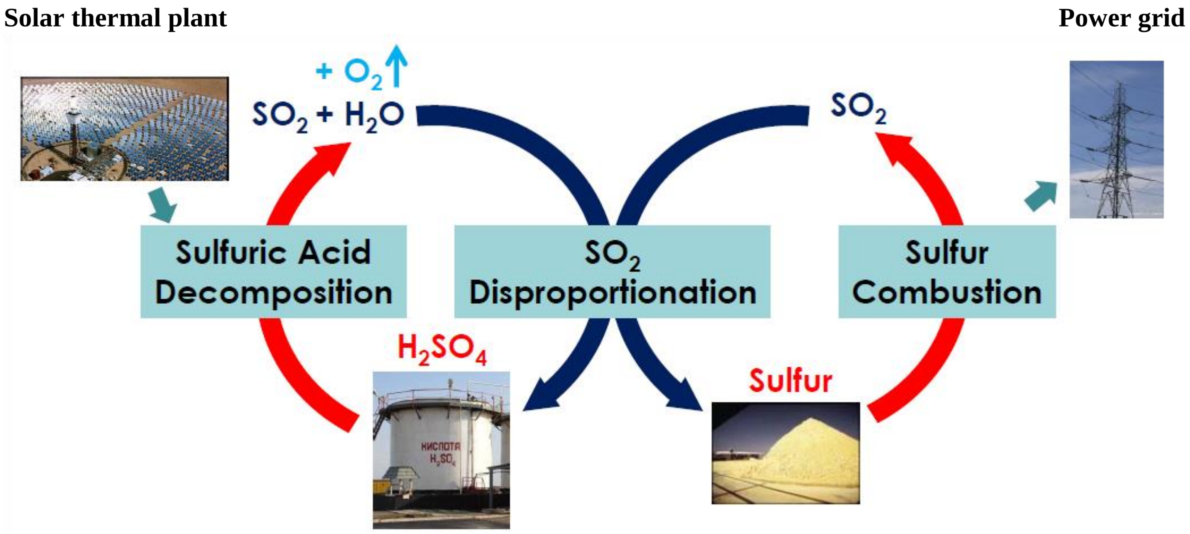

Figure 1: Schematic representation of the concept for utilization of solid Sulphur as an energy vector based on the proposed solar-thermal aided thermochemical cycle (B. Wong, 2015)

Acknowledgements
This work has received funding by the European Commission through the HORIZON EUROPE project "*SULPHURREAL*" under grant agreement number 101115538.

References

B. Wong. L. C. Brown, R. Buckingham, W. Sweet, Solar Energy, 118 (2), 134-144, (2015), https://doi.org/10.1016/j.solener.2015.04.037
J.G. Wagenfeld, K. Al-Ali, S. Almheiri, A. F. Slavens, N. Calvet, Waste Management, 95, 78-89, (2019), https://doi.org/10.1016/j.wasman.2019.06.002
C. Agrafiotis, D. Thomey, L. de Oliveira, M. Ebert, B. Gobereit, J. Pernpeintner, B. Schlogl-Knothe, G. Alkan, M. Roeb, C. Sattler, Solar Energy, 234, 21-38, (2022), https://doi.org/10.1016/j.solener.2022.01.032