

Solar-Assisted Hybrid Sulfur Cycle Using CSP and PV for Hydrogen and Oxygen Production in the Chilean Copper industry



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Copper is a critical mineral for power generation, transport, and renewable energy. Chile produces ~25% of global supply, with the sector consuming nearly 37% of national industrial energy. Much of the smelting capacity is located in the north, where exceptionally high solar irradiation enables solar-based decarbonization. The Hybrid Sulfur (HyS) cycle offers a promising pathway, co-producing O₂ and H₂ via sulfuric acid decomposition and SO₂ electrolysis, which has lower electricity demand than conventional PEM electrolysis [1].

Hybrid Sulfur Cycle

The Hybrid Sulfur (HyS) cycle simultaneously produces oxygen and hydrogen. As shown in Fig. 1, it couples high-temperature (>800 °C) catalytic decomposition of sulfuric acid (H₂SO₄) to generate O₂ with low-temperature (80–100 °C) and SO₃-depolarized electrolysis to produce H₂.

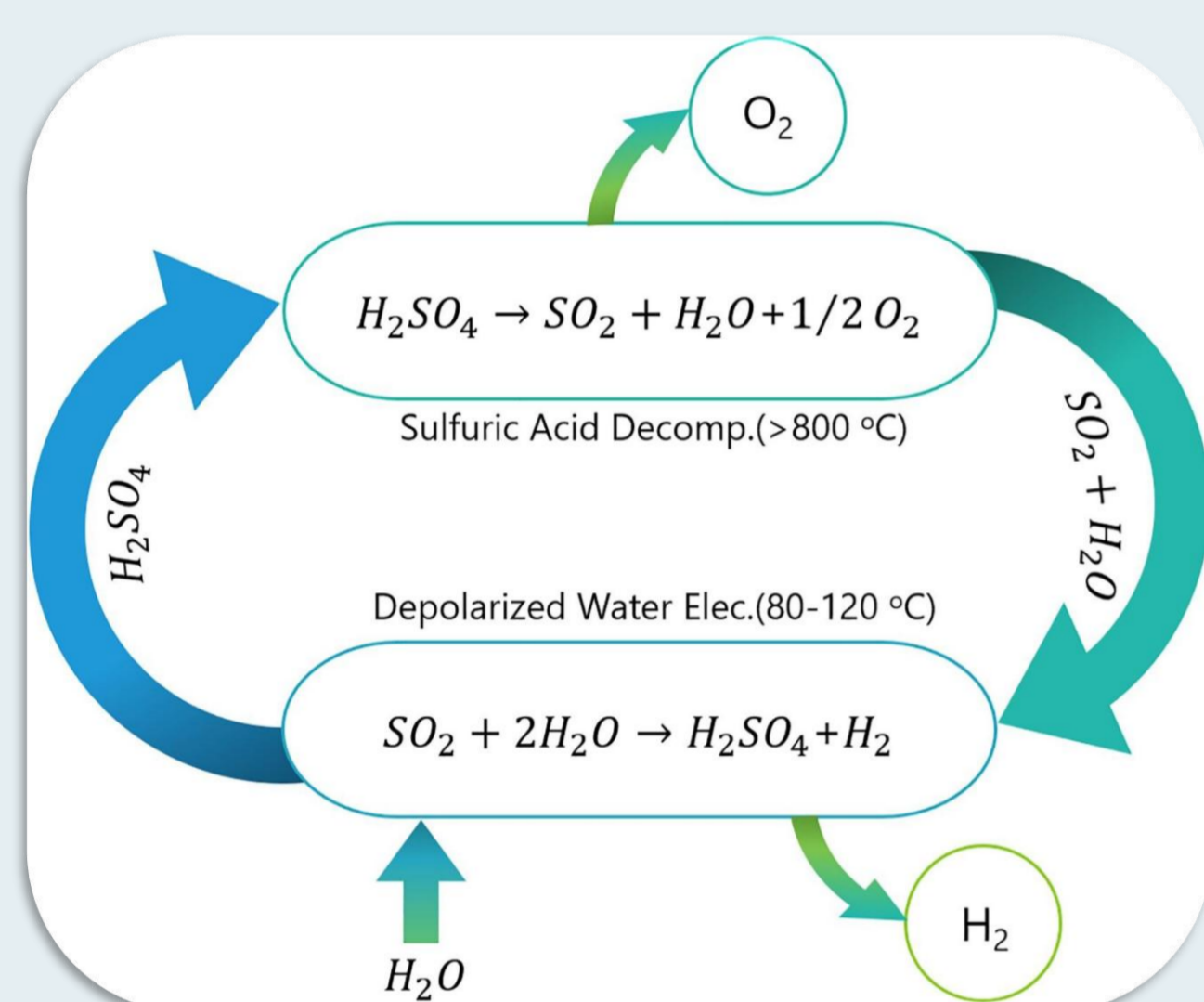
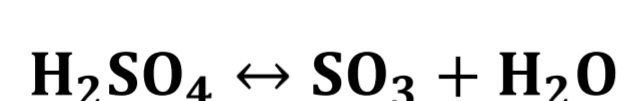


Fig. 1: Hybrid-Sulfur thermochemical cycle. Adapted from Oruc, O., & Dincer, I. (2021) [2].

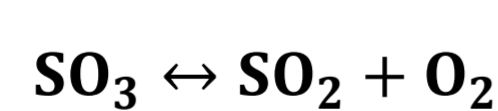
Sulfuric acid (H₂SO₄) thermal decomposition

The thermal decomposition of sulfuric acid follows two reactions:

1. H₂SO₄ dehydration (400–500 °C):



2. Decomposition of sulfur trioxide (>800 °C):



- The thermal decomposition of sulfuric acid is highly endothermic. As shown in Fig. 2, elevated temperatures are crucial to achieve higher SO₃ conversion, while higher pressure shifts the equilibrium toward the reactants, reducing conversion at a given temperature.

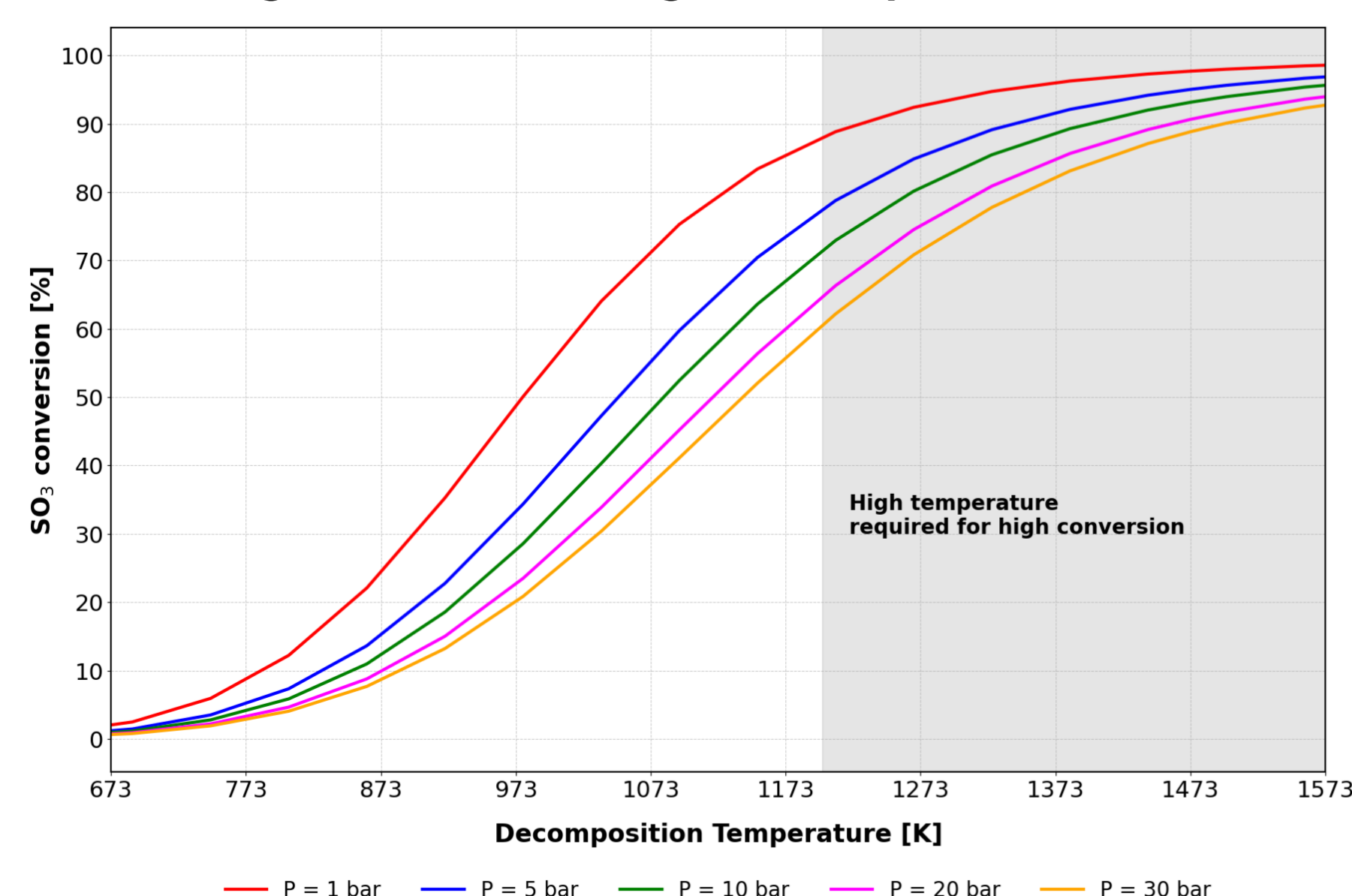


Fig. 2: SO₃ equilibrium conversion as a function of decomposition temperature and pressure.

Hybrid Sulfur Cycle with CSP + PV Integration: Proposed Plant

The proposed HyS plant, shown in Fig. 3, was simulated in Aspen Plus. It integrates a solar tower (modeled with Solstice) and a PV system (simulated with SAM), with grid electricity and fossil fuel as backup sources.

- The design targets a **100 kt_{Cu}/year (~11.4 t/h) copper smelter**, with an oxygen demand of ~1.03 t_{O₂}/t_{Cu} and a fuel demand of ~5,429 MJ/t_{Cu} [3]. The reactors operate at 1 bar to carry out the decomposition reactions.
- The plant is simulated considering Chuquicamata, northern Chile, with a DNI above 3,300 kWh/m²/year.

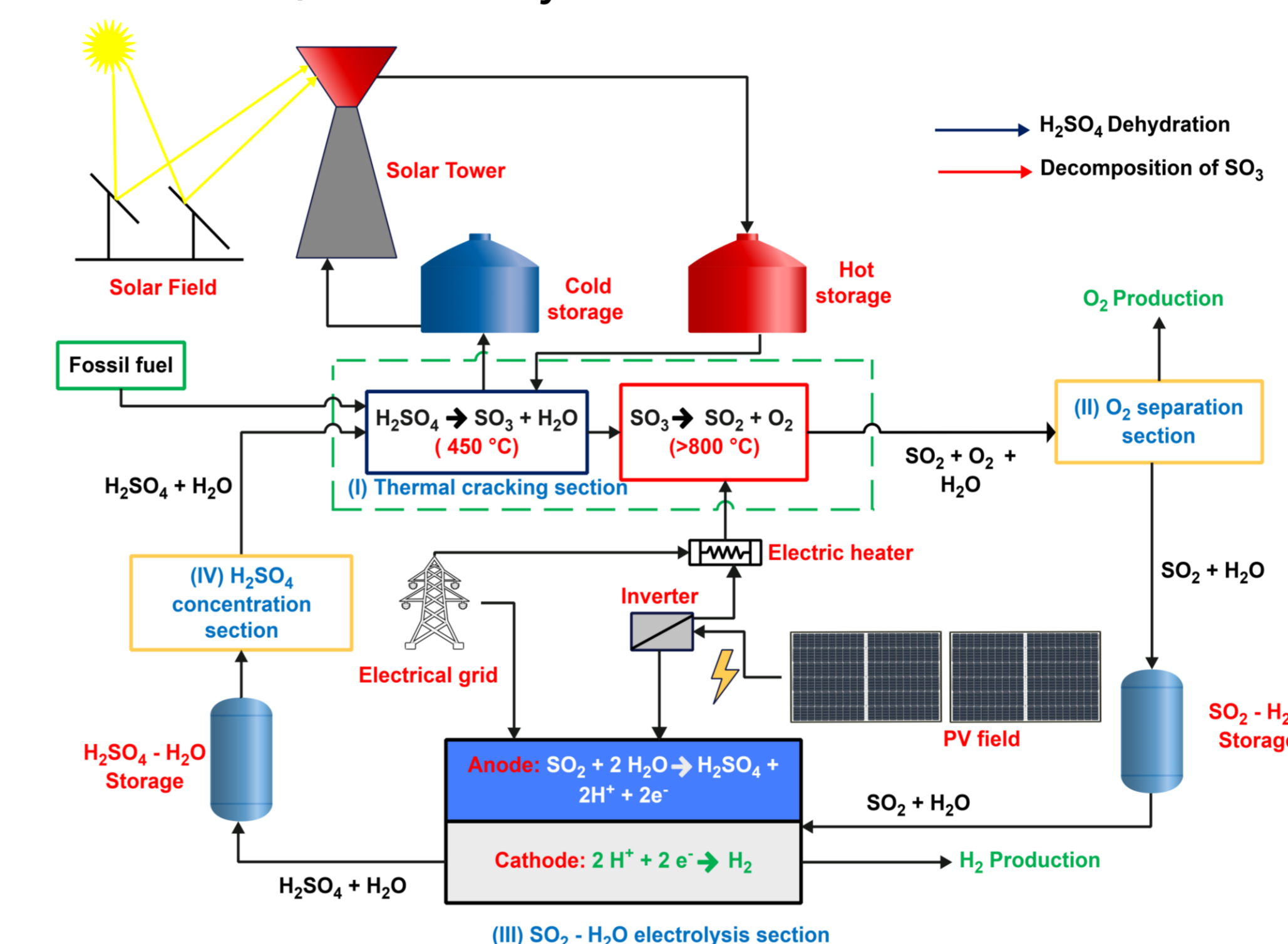


Fig. 3: Integration of solar tower and PV systems in the HyS cycle.

(I) Thermal Cracking Section:

– Medium-temperature reaction (~450 °C):

The reaction heat is supplied by a solar tower with solar salt as the heat-transfer fluid, with TES for continuous operation and fossil fuel as backup.

– High-temperature reaction (>800 °C):

The reaction heat is provided by an electric heater powered by a PV field, with grid electricity as backup.

(II) O₂ separation Section:

In this section, oxygen is separated from the SO₂ + O₂ + H₂O stream, yielding high-purity O₂.

(III) SO₂–H₂O Electrolysis Section:

The electrical demand is supplied by the PV field with grid backup, enabling hydrogen production while regenerating H₂SO₄.

(IV) H₂SO₄ Concentration Section:

The sulfuric acid is concentrated (~65–75 wt%) by removing excess water.

H₂SO₄ Decomposition:

Two reactor concepts for the decomposition of sulfuric acid considered in the literature are:

- Bayonet-type reactor (Sandia National Laboratories):** Uses coaxial SiC tubes, with heat recovery between incoming acid and hot products, SO₃ decomposition is conducted isothermally [4].
- Solar receiver reactor (SOL2HY2 project):** Consists of a rapid heat-up zone an adiabatic catalytic section for SO₃ decomposition [5].

Both approaches isothermal and adiabatic are considered in the simulations.

Technical results

Overall, as shown in Fig. 4, higher acid concentrations reduce energy demand due to lower water content, even though dilute acids achieve slightly higher conversions.

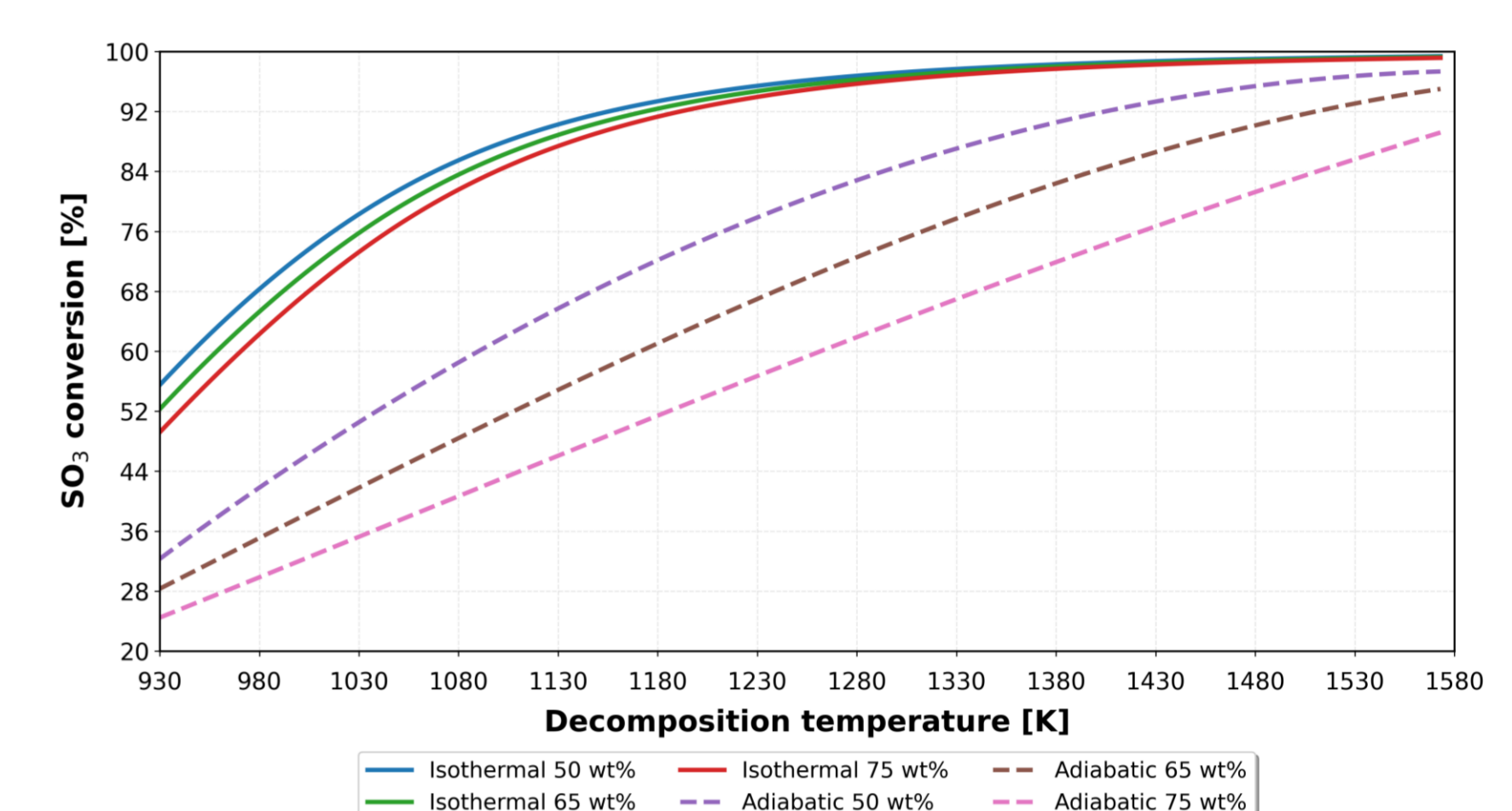


Fig. 4: Effect of acid concentration and reactor type on SO₃ conversion.

As shown in Fig. 5, at medium temperature (MT) the heat demand gap between isothermal and adiabatic reactors is larger, since the isothermal case benefits from higher energy recovery (pinch analysis). At high temperature (HT), differences remain small up to ~1130 K, after which the demand increases as more energy is used for sensible heating of products rather than driving the chemical reaction. Generally, despite the larger ΔT, MT energy demand exceeds HT, mainly due to the decreasing of the specific heat capacity of the reacting mixture as decomposition progresses.

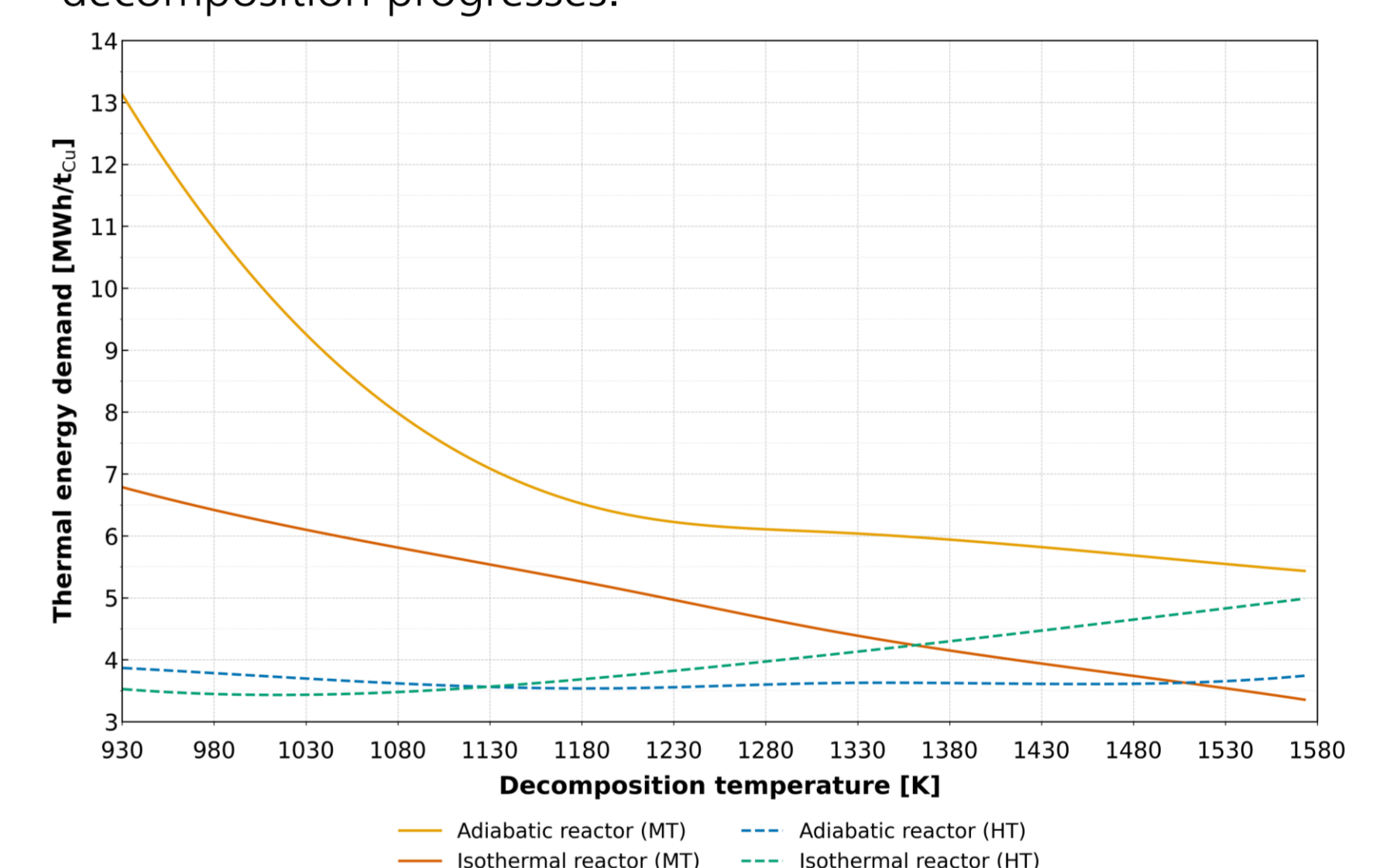


Fig. 5: MT and HT thermal energy demand for adiabatic and isothermal reactors vs. decomposition temperature.

Economic results

- LCOE and LCOH_{fuel} are crucial for HyS plant viability when compared to conventional PEM electrolysis (See Fig. 6). At high PEM efficiency (~80%), competitiveness requires either CAPEX reductions or lower HyS energy demand, expected with further technological maturity [6].

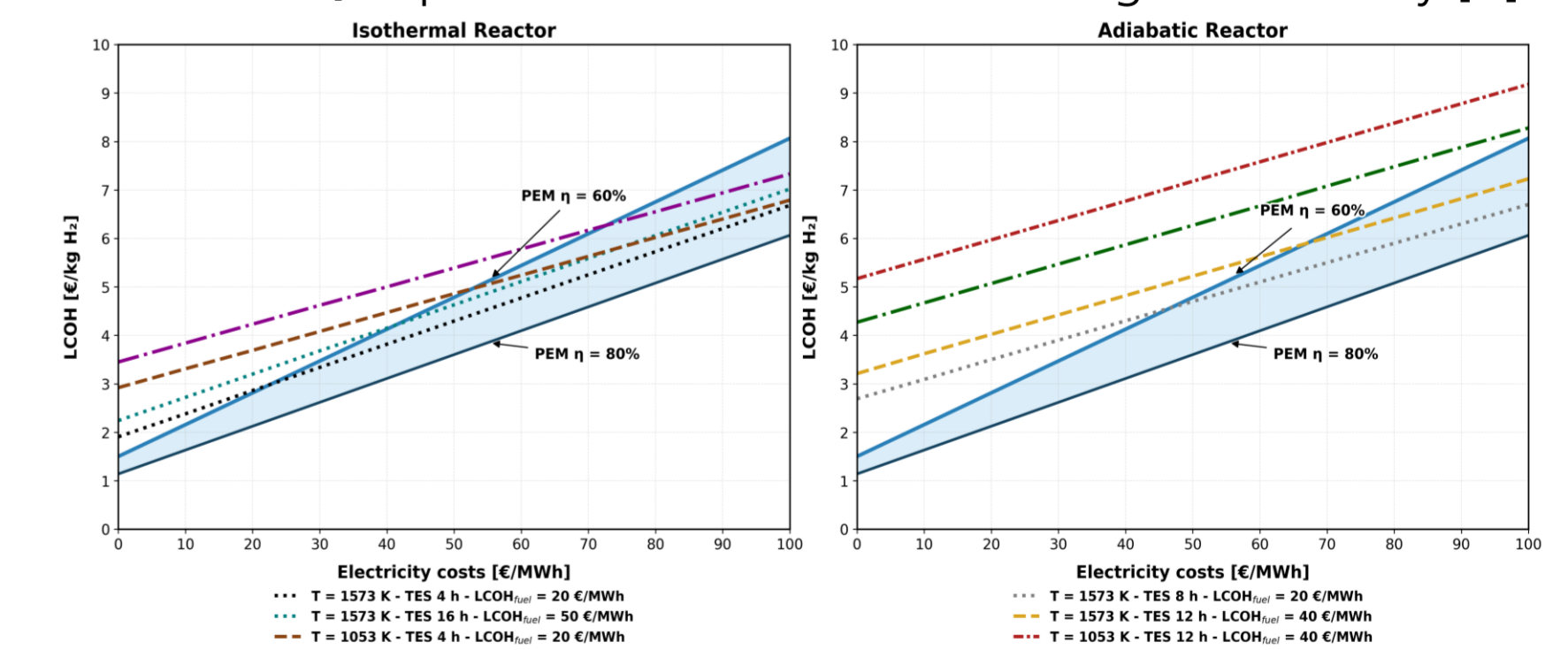


Fig. 6: Economic viability of HyS plants under different electricity and fuel costs compared to PEM electrolysis.

Conclusion and outlook

The HyS cycle shows strong potential for carbon-free hydrogen production in copper smelting. Key challenges remain in high-temperature materials, efficient heat integration, acid corrosion at elevated temperatures, and cost reduction at scale. With further technological maturity, significant reductions in both costs and energy demand are expected, supporting a viable pathway for sustainable copper production in Chile.

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