Review of Sulfuric Acid Decomposition Processes for Sulfur-Based Thermochemical Hydrogen Production Cycles

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Abstract: Thermochemical processes based on sulfur compounds are among the most developed systems to produce hydrogen through water splitting. Due to their operating conditions, sulfur cycles are suited to be coupled with either nuclear or solar plants for renewable hydrogen production. A critical review of the most promising sulfur cycles, namely the Hybrid Sulfur, the Sulfur Iodine, the Sulfur Bromine and the Sulfur Ammonia processes, is given, including the work being performed for each cycle and discussing their maturity and performance for nuclear and solar applications. Each sulfur-based process is comprised of a sulfuric acid thermal section, where sulfuric acid is concentrated and decomposed to sulfur dioxide, water and oxygen, which is then separated from the other products and extracted. A critical review of the main solutions adopted for the H₂SO₄ thermal section, including reactor configurations, catalytic formulations, constitutive materials and chemical process configurations, is presented.

Keywords: hydrogen production; thermochemical processes; high temperature sulfuric acid decomposition; reactor concepts; sulfuric acid decomposition catalysts; sulfuric acid concentration

1. Introduction

A large-scale hydrogen economy requires the production of hydrogen, to be used either as an energy carrier producing electric or mechanical work or as a chemical compound employed in chemical plants [1]. Hydrogen production requires external power input to break the bonds of the molecules containing the gas, such as water, fossil fuels and biomass. Adopting water-splitting processes, hydrogen and oxygen are the only products and a closed water cycle can be realized, producing water, again, in a fuel cell or in a combustion engine. However, the direct thermal decomposition of water happens only at high temperatures on the order of 4500 K, making the process impractical for large scale scenarios [2]. Current alternatives to the direct water splitting are electrolysis and indirect thermochemical splitting. Electrochemical water splitting is realized at temperatures close to room temperatures and achieves efficiencies on the order of 70%, requiring electric power inputs of approximately 50 kWh/kgH₂ [3,4]. Recent studies projected H₂ production costs on the order of 4.96–5.78 $/kg for large scale alkaline electrolysis systems installed in South Carolina (USA) [5]. High temperature steam electrolysis processes, in principle, can achieve a higher efficiency than low temperature electrolysis and are currently under investigation as a possible alternative process to be coupled with solar and nuclear power sources [6,7]. Water can also be split through heat-driven chemical reactions with recirculation of intermediate substances in the cycle [8–12]. Such processes, referred to as thermochemical hydrogen production cycles, have been attracting interest since the 1970s. The compounds, recirculating inside the process, are based on many different elements,
such as sulfur, iodine, bromine, iron, manganese, calcium, or chlorine, depending on the specific cycle. These compounds undergo reduction reactions, producing oxygen, and oxidation reactions, producing hydrogen. Comprehensive reviews of the main thermochemical cycles, used for both nuclear and solar applications, can be found in References [13,14]. The screening analyses [13] were carried out, identifying the performance of more than 100 cycles, based on selected characteristics and targets. The performance metric included the following characteristics: number of chemical reactions, number of product separation steps, number and abundance of chemical elements, corrosiveness of the process solutions, presence and flow of solid compounds, maximum temperature, availability of cycle chemistry demonstration data and availability of data demonstrating projected efficiency and costs [13]. Among the screened thermochemical processes, sulfur-based cycles, which see a thermal sulfuric acid decomposition section in common, were among the high-ranking processes [13]. Sulfur-based thermochemical cycles do not include any solid reactant movement and operate at relatively low temperatures (700–900 °C) compared with other competing processes. In addition, the main S-based cycles include two to three main reaction sections, limiting the complexity of the overall process and reducing the product separation sections. The main sulfur-based cycles, currently under investigation, are the Hybrid Sulfur (HyS) process, the Sulfur Iodine (SI) process and the Sulfur Bromine cycle. Two additional cycles have also been examined, namely the General Atomics S-cycle and the Sulfur Ammonia cycle. The General Atomics S-cycle was one of the first cycles proposed by General Atomics in 1970s [15]. However, after initial testing, the research and development work was interrupted mainly due to the presence of five main reactions as well as some critical thermodynamics and kinetics limitations [13,16]. The Sulfur Ammonia cycle, briefly discussed in Section 2, is being studied for solar applications but still requires additional fundamental development to propose a prototype demonstration with production of hydrogen and oxygen [17].

After an initial description and review of the main sulfur-based thermochemical cycles, the paper includes a critical review of the main approaches, configurations and solutions adopted for the \( \text{H}_2\text{SO}_4 \) thermal section, including the \( \text{H}_2\text{SO}_4 \) high temperature decomposition section, the \( \text{H}_2\text{SO}_4 \) concentration section and the \( \text{SO}_2\text{-O}_2 \) separation section. The maturity of each sulfur-based cycle, as well as the techno-economic performance achieved for nuclear and solar applications, is discussed.

2. Sulfur-Based Thermochemical Cycles

Among the thermochemical cycles being currently examined for nuclear and solar hydrogen production, sulfur-based processes are likely the most advanced systems with high potential for low-cost and high-efficiency large scale \( \text{H}_2 \) production. They are characterized by many appealing features, when compared with other thermochemical processes [13,18]. Mainly, sulfur-based cycles operate at relatively low temperatures and do not require any solid material movement. Sulfur-based processes share a high temperature sulfuric acid decomposition section, which will be described in detail in Section 3.

2.1. Main Sulfur-Based Thermochemical Cycles

2.1.1. Hybrid Sulfur Cycle

The Hybrid Sulfur (HyS) cycle was conceived by Los Alamos National Laboratory and Westinghouse [19,20]. Currently, it is one of the main cycles (and the main sulfur-based cycle) under investigation internationally for large-scale hydrogen production. Given the operating conditions, the process can be coupled with both nuclear source and concentrating solar source. The process splits the water molecule through the recirculation of compounds based on sulfur, oxygen and hydrogen within two main chemical sections:

\[
\text{H}_2\text{SO}_4 \rightarrow \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2
\] (1)
The thermal decomposition of H$_2$SO$_4$ to SO$_2$, H$_2$O and O$_2$ (Reaction (1)) is an endothermic process, common to each sulfur-based thermochemical cycle. After the decomposition of the sulfuric acid, sulfur dioxide and oxygen are separated at lower temperatures. Sulfur dioxide is recirculated within the thermochemical process to drive the electrochemical low temperature step (Reaction (2)), while oxygen is extracted from the cycle. Hydrogen is produced in the exothermic process (Reaction (2)), through the electrochemical oxidation of SO$_2$. The sulfuric acid is recirculated and concentrated to drive the H$_2$SO$_4$ thermal decomposition section. The hydrogen is separated from the other products, purified and extracted from the plant.

The electrochemical section, which is the distinguishing section of the HyS process, realizes the SO$_2$ oxidation at an electrolyzer anode to form H$_2$SO$_4$ and hydrogen ions (H$^+$), which recombine with electrons and form the hydrogen molecule at the cathode. The electrolyzer works between room temperatures and about 140 °C, mainly depending on the membrane employed in the component.

The electrochemical component is currently designed either as a liquid-fed or as a vapor-fed electrolyzer. The liquid-fed configuration was developed at the Savannah River National Laboratory (SRNL), during the U.S. Department of Energy (DOE) Nuclear Hydrogen Initiative [21]. The feeding mixture (liquid SO$_2$ and H$_2$O) is oxidized at the anode of the electrolyzer to form H$_2$SO$_4$, which feeds the thermal decomposition section, H$^+$ protons and electrons. Protons pass through the electrolyzer membrane to the cathode and recombine with external electrons to form H$_2$ [22–24]. One of the main issues associated with the use of the liquid fed electrolysis system approach was the sulfur dioxide cross over through the component membrane. Recent experimental data, collected at the SRNL, demonstrated the ability of a novel configuration employing proton exchange membrane (PEM) to prevent sulfur accumulation and sulfur dioxide crossover [25]. The vapor fed electrolysis configuration has recently been developed at University of South Carolina and SRNL [26]. Dry vapor SO$_2$ is fed to the anode of the electrolyzer, while liquid H$_2$O is fed to the cathode of the component. Water diffuses across the membrane to the anode because of the water activity difference and pressure gradients. Water is also transported again to the electrolyzer cathode by electro-osmotic drag. Sulfuric acid and hydrogen protons are produced at the anode. The protons then recombine with electrons to produce hydrogen at the cathode of the component [26].

The reversible cell potential of the electrochemical SO$_2$ oxidation reaction is 0.158 V, i.e., approximately 13% of the water electrolysis potential (1.229 V). The electrolyzer is currently designed adopting a traditional PEM fuel cell approach, allowing a compact design, reduced footprints and lower cost solutions [23,24]. Recent work demonstrated that a PEM electrolyzer, employing sulfonated polybenzimidazole (s-PBI) membranes, has high potential to achieve a practical cell potential of 0.6–0.7 V at current densities on the order of 500 mA/cm$^2$ [27–29]. This cell potential value is equal to approximately one third of the actual water electrolysis potential (i.e., 1.8 V) [20,30]. Platinum material has been adopted as the baseline catalytic formulation to reduce the kinetics overpotential of the SO$_2$ oxidation reaction [31]. However, recent in-situ tests showed that Au nanoparticle catalysts seem to exhibit high current densities and greater stability than Pt nanoparticle catalysts [32].

The electric input, mainly required to operate the electrochemical oxidation of the sulfur dioxide, represents approximately 20% of the thermochemical process input [22]. The thermochemical process efficiency has been assessed to be equal to (realistic) values on the order of 30–40% (based on the hydrogen LHV), depending on the process flowsheet, the layout and on the electric power generation efficiency [30,33–35]. Techno-economic analyses, carried out for both nuclear driven and solar driven HyS processes, identified realistic nuclear H$_2$ production costs on the order of 5.34–6.18 $/kg [36]. Reduced costs could be achieved only with high efficiency HyS process configurations and operating with high temperature nuclear reactors [37]. Solar-driven HyS processes were examined and developed for coupling with concentrating solar power plants. Hydrogen production costs were assessed to be on the order of 2.64–7.58 $/kg depending on the characteristics of the solar plant (e.g., thermochemical efficiency, heliostat cost, solar plant efficiency, location) [22,34,38,39].
HyS plant configurations demonstrated potential to produce hydrogen at costs that can closely approach the DOE target of 2 $/kg. [40].

2.1.2. Sulfur Iodine Cycle

The Sulfur Iodine (SI) cycle was originally developed by General Atomics [13,16,41], mainly focusing on nuclear power applications.

The SI cycle has three main sections, based on compounds of sulfur, iodine, hydrogen and oxygen:

\[ \text{H}_2\text{SO}_4 \rightarrow \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \]  

(3)  

\[ 2 \text{HI} \rightarrow \text{I}_2 + \text{H}_2 \]  

(3)  

\[ \text{I}_2 + \text{SO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2 \text{HI} \]  

(4)  

The thermal decomposition of \( \text{H}_2\text{SO}_4 \) into \( \text{SO}_2 \), \( \text{H}_2\text{O} \), and \( \text{O}_2 \) (Reaction (1)) produces sulfur dioxide and water and oxygen. Sulfur dioxide and oxygen are recycled in an exothermic section (Reaction (4)), referred to as the “Bunsen” section, while oxygen is separated from the other compounds and extracted from the plant as byproduct. Hydrogen is produced in Reaction (3), which is the distinguishing SI plant section, where hydrogen iodide (HI) decomposition to hydrogen and iodine takes place. An aqueous hydrogen iodide mixture, feeding the section at relatively low HI concentrations, requires HI concentration to operate an effective and low energy HI decomposition. The HI section is a critical step in the SI process, due to the homogeneous azeotrope in the system HI-H\(_2\)O making the acid concentration and decomposition highly energy intensive and expensive [42]. Three methods have mainly been examined to concentrate and decompose the hydrogen iodide: the extractive distillation, the membrane-based distillation (i.e., electro-electrodialysis distillation) and the reactive distillation [43–45]. The extractive distillation concept was examined by General Atomics, proposing the I\(_2\) separation by extractive distillation using H\(_3\)PO\(_4\) [41,46]. However, this approach essentially adds another compound (i.e., another section) to the cycle, requiring additional separation units, reactors and electric power input to recycle the phosphoric acid [47]. The electrodialysis distillation approach was proposed by Japan Atomic Energy Agency and Korea Institute of Energy Research [47], but still requires fundamental development for a prototype level demonstration [45,48]. The reactive distillation column approach, proposed by Knoche et al. [49], allows the separation of HI from the other compounds and the decomposition of the hydrogen iodide in a single column. This occurs by utilizing the pressure shift of azeotropic and quasi-azeotropic composition [50]. The reactive distillation approach shows some techno-economic hurdles to be overcome: (1) the column reboiler requires critical high temperature thermal power supply, which is currently provided through a heat pump that increases the plant investment cost and the lifetime costs due to the additional electric input and (2) fundamental research is still required to fully understand the reaction thermodynamics and kinetics [42,44].

The product of the HI section, after hydrogen separation, is recirculated in the Bunsen section, reacting with the H\(_2\)SO\(_4\) section product, to produce sulfuric acid and hydrogen iodide and close the overall cycle. The Bunsen reaction is exothermic and occurs at temperatures on the order of 100–120 °C [13,51]. Additional work is required to demonstrate the Bunsen reaction, as well as the overall SI cycle, at a prototype level.

Realistic thermochemical efficiencies of 35–38% (based on \( \text{H}_2 \) LHV) were assessed [44,52], also showing high sensitivity to the HI decomposition process configuration [42,47]. The nuclear hydrogen production cost was estimated to be on the order of 3.50–12.0 $/kg depending on the SI cycle and the nuclear reactor configuration [42,52].

2.1.3. Sulfur Bromine Cycle

The Sulfur Bromine cycle was originally developed at the Ispra facilities during the 1970s [43,53].
The cycle has three main sections, based on sulfur, bromine, hydrogen and oxygen compounds:

\[ \text{H}_2\text{SO}_4 \rightarrow \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \]

\[ 2 \text{HBr} \rightarrow \text{Br}_2 + \text{H}_2 \quad (5) \]

\[ \text{Br}_2 + 2 \text{SO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2 \text{HBr} \quad (6) \]

Similarly to the other sulfur cycles, the high temperature decomposition of sulfuric acid (Reaction (1)) produces oxygen and sulfur dioxide. The distinguishing section is the electrochemical decomposition of HBr (Reaction (5)), producing hydrogen, separated from the other compounds and extracted from the process, and bromine. The hydrogen bromide is decomposed to bromine and hydrogen at temperatures in the range of 80–200 °C depending on the electrolyzer characteristics [43]. The electrolysis unit was developed and tested during the 1970s and 1980s, showing voltages on the order of 0.8–1.0 V at current densities of approximately 100–600 mA/cm² [54]. The exothermic recombination of Br and SO₂ (Reaction (6)) occurs at temperatures in the range of 20–100 °C.

The cycle was tested producing hydrogen at 100 LH₂/h for 150 h, with thermochemical process efficiencies on the order of 37% [43]. Currently, the cycle is not under investigation for nuclear or solar applications, mainly due to the high voltage required in the electrolysis unit.

### 2.1.4. Sulfur Ammonia Cycle

The Sulfur Ammonia process was recently conceived by the Florida Solar Energy Center for solar applications [55]. The cycle represents an attempt to use both the thermal and the photonic components of the solar input. The cycle is comprised of five main reactions, based on sulfur, nitrogen, potassium, hydrogen and oxygen compounds, and requires a suitable solar system to collect both the thermal input and the solar light input:

\[ \text{SO}_2 + 2\text{NH}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_3 \quad (7) \]

\[ (\text{NH}_4)_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{H}_2 \quad (8) \]

\[ (\text{NH}_4)_2\text{SO}_4 + \text{K}_2\text{SO}_4 \rightarrow \text{K}_2\text{S}_2\text{O}_7 + 2\text{NH}_3 + \text{H}_2\text{O} \quad (9) \]

\[ \text{K}_2\text{S}_2\text{O}_7 \rightarrow \text{K}_2\text{SO}_4 + \text{SO}_3 \quad (10) \]

\[ \text{SO}_3 \rightarrow \text{SO}_2 + \frac{1}{2} \text{O}_2 \quad (11) \]

The cycle distinguishing reaction (Reaction (8)) is the photocatalytic production of hydrogen and ammonium sulfate from an aqueous ammonium sulfite solution, occurring above room temperature (approximately 80–150 °C) and low pressures [56,57]. A sub-cycle is identified by the Reaction (9) and Reaction (10). Ammonium sulfate product is reacted with potassium sulfate (Reaction (9)), at temperature on the order of 400 °C, to generate potassium pyrosulfate, which is decomposed (Reaction (10)) at temperatures on the order of 550 °C, to K₂SO₄ and SO₃ [57]. K₂SO₄ is recirculated to drive Reaction (9) and close the sub-cycle. SO₃ is catalytically decomposed to SO₂ and O₂ (Reaction (11)), as for the other sulfur-based thermochemical processes, at high temperatures on the order of 800–1000 °C. The separation of sulfur dioxide and oxygen occurs in Reaction (7) with water mixing and production of aqueous ammonium sulfite. Thermodynamic and kinetics tests demonstrated the feasibility of the proposed cycle at laboratory scale [56], but additional work is required to demonstrate the actual performance of a closed cycle at prototype level.

### 3. Sulfuric Acid Thermal Decomposition

Every sulfur-based thermochemical cycle is comprised of a high temperature section, referred to as H₂SO₄ thermal section, where sulfuric acid is decomposed to sulfur dioxide, oxygen and water.
The sulfur dioxide and the water are separated from the oxygen, which is extracted from the cycle as byproduct, and processed in the other sections of the thermochemical cycles. The main processes occurring in the H$_2$SO$_4$ thermal section are: (1) high temperature decomposition of concentrated sulfuric acid, (2) concentration of the inlet sulfuric acid mixture, (3) separation of the oxygen from the sulfur dioxide mixture. The oxygen is then purified, reaching the required purity targets, and extracted from the plant as byproduct.

### 3.1. High Temperature Sulfuric Acid Decomposition

The sulfuric acid decomposition section is the highest temperature section of each sulfur-based thermochemical process, where the endothermic decomposition of H$_2$SO$_4$ to SO$_2$, H$_2$O and O$_2$ occurs. The H$_2$SO$_4$ decomposition takes place in two separate steps. The first reaction sees the vaporization and the instantaneous (i.e., equilibrium) decomposition of the H$_2$SO$_4$ mixture, feeding the section, to SO$_3$ and H$_2$O, as shown in Reaction (12), at temperatures in the range of 300–450 °C:

$$\text{H}_2\text{SO}_4 \rightarrow \text{SO}_3 + \text{H}_2\text{O}$$

(12)

The second reaction sees the decomposition of the products of Equation (12) to SO$_2$ and O$_2$, as shown in Equation (13):

$$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2$$

(13)

The endothermic reaction of Equation (13) is thermodynamically favored at high temperatures and low pressures. For a reasonable conversion, this reaction should take place at temperatures usually on the order of 750–900 °C. The feeding sulfuric acid mixture is at temperatures of approximately 200–300 °C and concentrations on the order of 70–90 wt %, depending on the plant configuration and the operating conditions. Figure 1 shows the equilibrium SO$_2$ conversion of a sulfuric acid solution at 90 wt % at temperatures between 500 °C and 900 °C and pressures between 1 bar and 50 bar.

![Figure 1](image-url)  
**Figure 1.** H$_2$SO$_4$ fractional conversion to SO$_2$ at equilibrium for the 500–900°C temperature and 1–50-bar pressure ranges (calculated by Gibbs free energy minimization using the symmetric Electrolyte Non-Random Two Liquid (eNRTL) model [58] for a 90-wt % H$_2$SO$_4$ solution vaporized, heated, and pressurized to the indicated conditions).
The reacted mixture is condensed and cooled to achieve the required conditions to separate oxygen. The undecomposed SO$_3$ reacts with water to produce H$_2$SO$_4$ again, following the reaction in Equation (12). The thermal power available from the cooling, condensation and exothermic formation of H$_2$SO$_4$ can be internally recovered to drive the H$_2$SO$_4$ decomposition reaction.

The main challenges faced with the development of an effective sulfuric acid decomposition process are mainly related to: (1) identification of suitable constitutive materials, being able to withstand aggressive and high temperature environments, (2) identification of high performance catalytic materials, to achieve high activity, reduced degradation and suitable costs for large scale hydrogen production and (3) identification of effective heat transfer configurations, allowing both an effective external source heat exchange and a proper internal heat recovery.

3.1.1. Constitutive Materials

Several comprehensive tests were carried out during the DOE Nuclear Hydrogen Initiative, examining the behavior of different (i.e., ceramic and metallic) constitutive materials. The performance was measured under selected conditions and configurations, including different sulfuric acid concentrations, temperatures and structural configurations [59,60]. Ceramic materials, namely SiC, were found to be the most (and likely only) suitable materials for the high temperature sulfuric acid vaporization and decomposition, given the operating temperatures and the aggressive environment [59,60]. Table 1 [59] summarizes the corrosion test results obtained for concentrated sulfuric acid vaporization and decomposition at 1 bar under different temperature ranges.
Table 1. Summary of material options for the sulfuric acid decomposition process [59]. (Reproduced with permission from General Atomics).

| Process                  | Conditions               | Candidate Materials                                      | Compatibility–Corrosion Results | Comments                                                                                      |
|--------------------------|--------------------------|----------------------------------------------------------|--------------------------------|---------------------------------------------------------------------------------------------|
| H₂SO₄ vaporization       | 350–550 °C, H₂O + SO₃,   | Structural: Incoloy 800 H, AL610, high Si steel, SiC,     | 800 H, 800 HT. High Si steel  | Coated materials (Pt) cost issue. Ceramics promising, but fabrication and joining issues.   |
|                          | other contaminants       | Si₃N₄, Hastelloy G, C-276                                 | (SiO₂) < 5 mm/year. SiC ≈ no | Dry wall boiler with ceramics may be an option.                                              |
| H₂SO₄ decomposition      | 550–950 °C, H₂O, H₂SO₄,  | Structural: Incoloy 800 HT, Incoloy 800 H (with         | Intergranular corrosion        |                                                                                             |
|                          | SO₃, SO₂, O₂             | aluminide coatings), AL610, Ceramics, Pt or Au coatings   | observed for 800 H. Noble      |                                                                                             |
|                          |                          | on superalloy structural materials                        | metal coatings may provide    |                                                                                             |
|                          |                          |                                                          | corrosion protection.          |                                                                                             |
|                          |                          |                                                          | Pt coatings may serve the     |                                                                                             |
|                          |                          |                                                          | function of catalyst and      |                                                                                             |
|                          |                          |                                                          | reduce corrosion. C-SiC        |                                                                                             |
|                          |                          |                                                          | composites should be         |                                                                                             |
|                          |                          |                                                          | examined. Corrosion benefits  |                                                                                             |
|                          |                          |                                                          | of noble metal coatings must  |                                                                                             |
|                          |                          |                                                          | be demonstrated.              |                                                                                             |
A more recent work, carried out in Japan, also examined the performance of constitutive materials in high temperature sulfuric acid mixtures for thermochemical hydrogen production cycles [61]. The authors examined similar candidate materials as those shown in Table 1. For lower temperature operations (i.e., vaporization) the main candidates were: SiC, Si₃N₄, FeSi (i.e., high silicon iron materials) and Au, while for the high temperature gas decomposition the main candidates were: Incoloy 800, Hastelloy C276, Inconel 625 and SiC. Corrosion tests were conducted at H₂SO₄ concentrations of 75 wt %, 85 wt % and 95 wt %, temperatures of 320 °C, 380 °C and 460 °C, pressures up to 20 bar and exposures up to 1000 h. The corrosion rates, measured for all SiC, Si-SiC (SiC at 80 wt % and Si at 20 wt %) and Si₃N₄ specimens, showed excellent resistance with absence of weight changes [61]. FeSi materials with silicon content of 20 wt % showed evidence of crack formation [61].

Recent work, carried out as part of the European Union funded HycycleS project, examined the behavior of several materials, i.e., alumina, tantalum-coated steel and materials from the SiC-family, analyzing their stability in concentrated sulfuric acid vaporization and decomposition processes by carrying out long-term corrosion tests [62,63]. Post-characterization of the materials revealed that Siliconized SiC (Si-SiC) was the most suitable material for sulfuric acid vaporization and decomposition [62].

### 3.1.2. Catalysts

A comprehensive list of catalytic materials, used for the H₂SO₄ decomposition process during the initial development of sulfur-based thermochemical hydrogen production cycles, can be found in the studies carried out in the USA (by General Atomics and Westinghouse) and in Japan (by Yokohama National University) in the late 1970s and 1980s [16,20,51,64,65]. Table 2 summarizes the test results carried out at General Atomics [51].

**Table 2.** Studies of various catalysts for H₂SO₄ decomposition (≈0.5 s residence time) [51] (Reproduced with permission from General Atomics).

| Catalyst        | Onset of Failure Temperature (K) | Failure Mode                      |
|-----------------|----------------------------------|-----------------------------------|
| 0.5% Pt/Al₂O₃  | 890                              | Al₂(SO₄)₃ poisoning                |
| Fe₂O₃/Al₂O₃     | 1000                             | Sulfate formation                 |
| V₂O₅/Al₂O₃      | 910                              | Sulfate formation, volatile       |
| Cr₂O₃/Al₂O₃     | 1070                             | Sulfate formation, volatile       |
| CuO/Al₂O₃       | 950                              | Sulfate formation                 |
| 0.1% Pd/Al₂O₃  | 970                              | Al₂(SO₄)₃ poisoning                |
| MnO₂/Al₂O₃      | 1120                             | Sulfate formation                 |
| CoO/Al₂O₃       | 1140                             | Sulfate formation                 |
| NiO/Al₂O₃       | 1160                             | Sulfate formation                 |
| 0.1% Pt/Al₂O₃  | 950                              | Al₂(SO₄)₃ poisoning                |
| Al₂O₃           | 1250                             | Poor catalyst                     |
| CuO/SiO₂        | 1010                             | CuSiO₃ formation?                 |
| 0.5% Pt/SiO₂    | 850                              | Gradual temperature cut-off       |
| CeO₂            | 1180                             | Poor catalyst                     |
| 0.08% Pt/TiO₂ (surface) | 800 | Gradual temperature cut-off       |
| 0.1% Pt/TiO₂    | 900                              | Gradual temperature cut-off       |
| Pd/TiO₂         | 1090                             | Initially better, sulfation?      |
| Fe₂O₃/TiO₂      | 1090                             | Unknown                            |
| CuO/TiO₂        | 1000                             | Sulfate formation                 |
| 0.08% Pt/TiO₂  | 790                              | Gradual temperature cut-off       |
| TiO₂            | 1140                             | Poor catalyst                     |
| Pt/ZrO₂ (surface) | 830 | Substrate sulfation               |
| Fe₂O₃/ZrO₂      | 1020                             | Sulfate formation                 |
| CuO/ZrO₂        | 970                              | Sulfate formation                 |
| ZrO₂            | 1130                             | Poor catalyst                     |
The main conclusions of the study described in ref. [51] are indicated here below. Some metals, such as chromium, nickel, manganese, cerium and uranium, failed to achieve acceptable catalytic activity, mainly due to formation of stable sulfates at relatively high temperatures. Results relative to the substrates showed that Al₂O₃ is a poor substrate for platinum group metals, probably due to the platinum catalysts poisoning by Al₂(SO₄)₃. Catalyst vaporization was also demonstrated to be another reason of poor performance. A few catalysts (e.g., V₂O₅, Cr₂O₃) seemed to move downstream and coat colder walls, acting as a reverse catalyst [51]. For systems operating at high temperatures and low pressures, oxide materials (e.g., Fe₂O₃ and CuO) seemed to show good performance. The authors concluded that the following catalysts: Pt/BaSO₄-TiO₂, Pt/TiO₂, Pt/ZrO₂, and Pt/SiO₂ were found to be suitable systems at a large range of temperatures [51].

Following the outcomes from the initial catalytic material work, more recent activities (in the 2000s), funded by the DOE as part of the Nuclear Hydrogen Initiative [66], focused on identifying the performance of Pt catalysts on different supports. Idaho National Laboratory was the leading institution for H₂SO₄ decomposition catalyst development in the Nuclear Hydrogen Initiative, examining activity and degradation of Pt catalysts with different supports [67,68]. Results showed the feasibility of selected Pt formulations on TiO₂ support with reduced deactivation after an initial activity decrease. In the studies carried out by Idaho National Laboratory [68], samples of 1 wt % Pt/TiO₂ (rutile) catalysts were exposed to sulfuric acid mixtures flowing at 1123 K and 1 bar for times on stream between 0 and 548 h (Figure 2).

| Catalyst               | Onset of Failure Temperature (K) | Failure Mode          |
|------------------------|----------------------------------|-----------------------|
| Nb₂O₅/BaSO₄            | 1140                             | Poor catalyst         |
| CuO/BaSO₄              | 1050                             | Sulfate formation     |
| Fe₂O₃/BaSO₄            | 980                              | Sulfate formation     |
| U₃O₈/BaSO₄             | 1070                             | Sulfate formation     |
| BaSO₄                  | 1250                             | Poor catalyst         |
| 0.07% Pt/BaSO₄-TiO₂    | 780                              | Gradual temperature cut-off |

Table 2. Cont.

Figure 2. SO₂ and O₂ production rates as a function of time on stream (H₂SO₄ concentration 95.7 wt %, pressure 1 bar, measured temperature 1113 ± 10 K) [68]. (Reproduced with permission from Ginosar D, Applied Catalysis A: General, 2008).
Pt sintering and oxidation were likely the main issues observed under the adopted conditions and some Pt was lost by volatilization. Results showed an initial catalyst activity reduction (about 66 h), with a subsequent recovery (up to approximately 102 h). A slow deactivation period, between 102 h and the end of the testing time on stream, was observed. Catalyst sulfation did not seem to be detrimental to catalyst activity and the activity profile seems to highlight a complex dynamical situation, including platinum sintering, oxidation, and sublimation, along with TiO2 morphological changes, that affected the catalyst activity [68]. The sulfation of the Pt catalyst did not seem to be the reason for the performance reduction.

Alternatives to the Pt/TiO2 catalyst are currently being investigated to find a catalytic formulation with long stability and reduced deactivation. One of the options is to use metal oxides in different configurations. Idaho National Laboratory also examined the behavior of complex metal oxides analyzing the performance for accelerated stability testing (about 160 h) at 850 °C and atmospheric pressure [69]. The following metal oxides were analyzed: FeTiO3, MnTiO3, NiFe2O4, CuFe2O4, NiCr2O4, 2CuO·Cr2O3, CuO, Fe2O3. The authors stated that every material examined in the study displayed shortcomings including material sintering, phase changes, low activity at moderated temperatures due to sulfate formation and decomposition to their individual oxides. The final statement from the authors on metal oxide catalysts was that more effort would be needed to discover metal oxide materials that are less expensive, more active and more stable than platinum catalysts [69]. A more recent work, carried out by a European consortium (HycycleS), also investigated the possibility of using metal oxides in different configuration and recto structures [62,70,71]. The authors carried out a comparative assessment of Fe2O3, CuO, Cu–Fe, Fe–Cr, Cu–Al and Cu–Fe–Al mixed oxides coated as catalysts on silicon carbide monolithic honeycomb structures, with respect to sulfuric acid decomposition reaction conditions for 100 h at 850 °C and ambient pressure [62]. The study concluded that Fe2O3, CuO and Fe–Cr mixed oxide retained their chemical and structural stability after exposure to reaction conditions, while the other three mixed oxides studied suffered from significant phase decomposition phenomena [62]. In general, every study about metal oxides concluded that selected formulations may be considered as a promising alternative to Pt-based catalytic formulations with potential for high catalytic activity and high stability. However, additional investigation is required for a commercial use of metal oxide catalysts, especially to avoid sintering phenomena and catalytic activity reduction experienced at temperatures lower than 800 °C, as shown in Figure 3 [69].

![Figure 3. Temperature dependent SO2 yields over metal oxide materials: (a) complex metal oxides; (b) copper and iron simple and complex metal oxides) between 725 and 900 °C at 1 bar and a weight hour space velocity (WHSV) of approximately 50 g acid/g catalyst/h [69]. (Reproduced with permission from Ginosar D, Int J Hydrogen Energy, 2009).](image)

Another catalytic formulation, alternative to the single metal Pt/TiO2 catalyst, sees the use of bimetallic catalytic materials on different supports. This is a novel concept for the H2SO4 decomposition reaction and recent research and development activities have been carried out by Idaho National Laboratory, the University of South Carolina and Greenway Energy, as part of the DOE Hydrogen
and Fuel cells Technology Office (HFTO) HydroGEN consortium [72]. Initial results demonstrated
the ability of the a Pt/Ir formulation on boron nitrite (BN) support (namely 1wt %Pt/7.5wt %Ir/BN)
to achieve high activities and essentially absence of degradation for about 75 h under a 91 wt % H₂SO₄
concentrated flow at 800 °C and 1 bar [72]. Additional testing will be required for longer duration
performance assessment.

3.1.3. Reactor Concepts

Two main approaches are currently being investigated to identify effective high temperature
H₂SO₄ decomposition reactor configurations. The first reactor concept, which sees a direct coupling of
the H₂SO₄ decomposition process with the external thermal source, is referred to as a direct cavity
reactor, and is especially suited for solar applications. The second concept is referred to as an indirect
solar tubular reactor and is based on an indirect coupling with the external source. In the first
configuration, the thermal power is provided directly by the primary source without the presence of
intermediate heat exchanger loops. The second concept includes an intermediate heat transfer fluid,
transferring the required thermal input and exchanging it with the H₂SO₄ mixture.

The German Aerospace Center (DLR) has been developing one of the main direct cavity reactor
configurations (currently under development) with two solar absorbers in series, where the vaporization
reaction and the catalytic decomposition reaction take place in separate units, as shown in Figure 4 [73,74].
This allows specific and different designs for the two separate reactions to be used.

Figure 4. Two-unit direct H₂SO₄ vaporization and decomposition reactor: (a) conceptual design;
(b) experimental solar driven reactor at German Aerospace Center (DLR) with foam absorber in
evaporator (left) and honeycomb decomposer (right) [74]. (Reproduced with permission from Roeb M,
Int J Hydrogen Energy, 2012).
A laboratory scale concept was tested at the DLR facilities. The feeding acid vaporized in a ceramic foam absorber (left side reactor in Figure 4b), which collects to the concentrated solar power through a quartz window. The intermediate products (SO$_3$, H$_2$O) flowed through the second absorber (honeycomb structure, right side reactor in Figure 4b), where the decomposition of SO$_3$ to SO$_2$ took place. The SO$_3$ decomposition reactor tests were carried out at atmospheric pressure and temperatures of approximately 850 °C, with peak values of 1200 °C. The reactor was also tested, examining the behavior under different H$_2$SO$_4$ concentrations and different catalytic formulations. SO$_3$ reaction yield close to the equilibrium values was demonstrated using Pt catalyst and operating at temperatures of 1000–1200 °C [73]. The use of metal oxide catalysts based on Fe or Cu was also successful, showing conversions of SO$_3$ to SO$_2$ of more than 80% at temperatures of approximately 850 °C [74].

The proposed direct reactor concept shows some barriers to achieve an effective internal heat recovery. Since the H$_2$SO$_4$ decomposition takes place in two separate units, a separate heat transfer unit is required to internally recover the heat available from the high temperature reacted mixture. The concept proposed by DLR also requires further development for a prototype level demonstration at pressures higher than 1 bar.

The main indirect reactor concept proposed recently for the H$_2$SO$_4$ decomposition, either using a nuclear source or a solar source, is based on a reactive bayonet heat exchanger concept. The concept was originally developed as part of the DOE Nuclear Hydrogen Initiative [75] and demonstrated at SNL at laboratory scale SO$_2$ productions (i.e., H$_2$ productions) of approximately 100 L/h [76]. A schematic is shown in Figure 5.

![Figure 5. Indirect H$_2$SO$_4$ vaporization and decomposition bayonet heat exchanger-based reactor.](image)

The inlet mixture (H$_2$SO$_4$ in) feeds the component at temperatures on the order of 200–300 °C through an annular region, from the inlet to the dome of the component. The concentrated H$_2$SO$_4$ is
vaporized and decomposed to SO₃ in the bottom part of the annular region, reaching temperatures of approximately 450 °C.

The SO₃ mixture is then superheated (up to 600–700 °C) before the catalytic decomposition to SO₂ in the upper region of the component occurs.

The reacted SO₂ mixture flows through the cylindrical inner region of the reactor down to the base at low temperatures. The heat required to decompose the acid is provided by an external heat transfer fluid (the “High-Temperature Heat” region in Figure 5) and the internal heat recovery from the reacted mixture flowing through the inner region.

In principle, the bayonet reactor has two main advantages over other possible configurations: (1) the heat, available from the exothermic reactions, can be internally recovered in a single unit, and (2) the reactor ceramic structure and the plant interfaced metal equipment can be connected at low temperatures (200–250 °C), avoiding any metal–ceramic material connection issues.

The reactor, initially developed for nuclear applications, was suitably adapted to be coupled with concentrating solar power plants, using helium as the intermediate heat transfer fluid [22,77].

Figure 6 shows the results of a pinch analysis applied to model the fluid vaporization and decomposition as well as the cooling and condensation with internal heat recovery in the bayonet reactor. The approach used to simulate the component is detailed in References [30,78], but modified to use the symmetric eNRTL model developed by Kaur et al. [58] for thermodynamic properties. The specific case was simulated assuming a maximum temperature of 875 °C, pressure equal to 35 bar and inlet H₂SO₄ concentration equal to 82 wt % and examining the equilibrium conditions, without including any kinetics effect. The reactive mixture (dashed line in Figure 6) goes through the following processes: (1) initial heating process (up to temperatures of approximately 400 °C), (2) vaporization and decomposition of H₂SO₄ to SO₃ (up to temperatures on the order of 500 °C), (3) superheating of the reacted mixture (up to 650 °C) and (4) high temperature decomposition of SO₃ to SO₂ (up to 875 °C). The reacted mixture (solid line in Figure 6) is cooled, reaching approximately 500 °C, with following condensation and reassociation of SO₃ to H₂SO₄ achieving a final temperature of approximately 245 °C. The heat duty from the external source (Figure 6) is 347.3 kJ/molH₂ under the operating conditions described above [72].

Additional sensitivity pinch analyses, carried out at different pressures, temperatures and acid concentrations, can be found in References [30,78].

Results obtained from CFD simulations also showed the technical feasibility of a solar driven bayonet reactor, with He as the intermediate heat transfer fluid. Temperature and concentration profiles showed the ability of the proposed concept to closely approach the equilibrium yield at temperatures of 850 °C, employing a Pt-based catalyst [79]. The adoption of a bayonet reactor in solar power applications requires the presence of an intermediate heat exchanger (i.e., using He as heat transfer fluid), resulting in additional capital costs and reduced performance of the overall plant [22].

Recently, a novel reactor concept has been proposed within the DOE HydroGEN program [80], which allows the direct external source heating and the internal heat recovery to be realized in a single unit, without any intermediate heat transfer fluid. A single unit conceptual design, driven by solar radiation, is shown in Figure 7 [80].

Results of CFD simulations carried out for the unit shown in Figure 7, with a feeding H₂SO₄ mixture of 0.28 kg/s, showed the effectiveness of the proposed concept for maximum temperatures on the order of 875 °C, inlet pressure equal to 14 bar and inlet concentration of 82 wt %. Results highlighted an effective internal heat recovery, maintaining temperature differences of less than 100 °C between the inlet (reactive) and the outlet (reacted) mixtures, and a proper SO₃ decomposition [80]. Additional optimization of the proposed concept should be carried out, to design and demonstrate a commercial-scale reactor configuration.
3.2. Sulfuric Acid Concentration

Sulfuric acid mixtures, produced internally in sulfur processes, need concentrating to achieve suitable H$_2$SO$_4$ concentrations to feed the high temperature decomposer. Two main, traditional approaches are used to concentrate sulfuric acid, using either low temperature and low (sub-atmospheric) pressures or higher temperatures and pressures on the order of 1–10 bar.

The first acid concentration concept uses low pressure (vacuum) distillation columns, usually operating at pressures on the order of 0.1 bar, with column reboiler temperatures on the order of 120–160 °C, depending on the required H$_2$SO$_4$ concentration, and column condenser temperatures of about 40 °C [30,35]. A single distillation column is generally adequate for typical operating conditions.
of sulfur thermochemical cycles, where an H$_2$SO$_4$ concentration in the range of 75–90 wt % is required to achieve suitable efficiencies in the high temperature H$_2$SO$_4$ decomposition reaction [30,72,77]. Different flowsheet layouts have been developed, with essentially two main configurations. The first approach sees the vacuum column product (i.e., concentrated H$_2$SO$_4$) pumped and fed directly to the high temperature decomposition unit with recirculation of the undecomposed sulfuric acid in the other sections of the plant [30]. The second approach sees the concentrated sulfuric acid pumped and fed to a quench column, where it contacts the effluent (recirculated, undecomposed sulfuric acid) from the decomposition reactor. The quench column is designed with a minimum number of equilibrium stages (e.g., two stages), one of which is the partial condenser [35,72]. The main advantage of the vacuum distillation concept resides in the relatively low operating temperatures, allowing effective internal heat recovery in the thermochemical plant and, therefore, resulting in increased process efficiencies. The main drawback is the low operating pressures (i.e., low volumetric flow rates), posing techno-economic challenges associated with the design of the components (distillation column, reboiler, condenser) that require large volumes [72,77].

The second acid concentration concept uses a series of flashes operating at pressures on the order of 1–10 bar and temperatures up to values on the order of 300–400 °C, depending on the required concentration level. Selected plant layouts and chemical flowsheets based on this approach can be found in References [13,42,44]. One configuration [13] proposes four pressure flash units, connected in series with a vacuum distillation column operating at 0.07 bar. The inlet sulfuric acid mixture, along with internally recycled sulfuric acid, is concentrated to 40 mole % in the high pressure four-stage isobaric concentrator operating at constant pressure of 35.5 bar and increasing temperatures from 299 °C up to 371 °C in the fourth flash unit [13]. The product of the isobaric concentration unit is concentrated in three flashes in series operating at 8 bar, 2 bar and 50 Torr before feeding the vacuum distillation unit. The bottom product of the distillation column is azeotropic sulfuric acid at approximately 90 mole % H$_2$SO$_4$ at 212°C [13]. Another flowsheet configuration [42,44] uses three pressure flash units, operating at different pressures and different temperatures. The sulfuric acid mixture feeds the three-stage concentrator at 57 wt %. The mixture is concentrated up to 87 wt % by the three-flash distillation process at different pressures (0.08 bar, 5.7 bar and 7 bar) reaching a final temperature (in the third flash) of 300 °C. The main drawback of the pressure multiple flash concentrator approach is the requirement of heating power at relatively high temperatures, provided either through internal heat recovery or an external source, resulting, in general, in a reduction in the overall cycle efficiency [13,42]. Lower sulfuric acid concentrations (i.e., on the order of 62.5 wt %) can be achieved at lower temperatures (144 °C) and lower pressures (1 bar), but this results in a reduced efficiency of the high temperature decomposition reactor [33].

3.3. Separation of Oxygen and Sulfur Dioxide

An important section in each sulfur based thermochemical process is relative to the O$_2$/SO$_2$ separation. Many approaches have been proposed lately to accomplish the SO$_2$/O$_2$ gas separation effectively [22,30,33,35]. One of the very few comprehensive SO$_2$/O$_2$ separation flowsheets available in the literature proposes the adoption of an O$_2$ stripper and an SO$_2$ stripper integrated with an SO$_2$ absorber and an oxygen dryer [35].

The SO$_2$ absorber, which separates oxygen from SO$_2$ based on the different water solubility, is an equilibrium column with multiple stages, without the presence of reboiler nor condenser. The chemical plant flowsheet includes an SO$_2$ absorber operating at a pressure of about 12 bar. The SO$_2$ feeding the absorber exits with the water in the bottoms of the units, almost entirely, while 99.7% of the oxygen exits with the overhead flow.

The SO$_2$ stripper, as proposed and simulated in Ref [35], has seven equilibrium stages operating at atmospheric pressure, including a partial vapor condenser and reboiler. SO$_2$ is stripped from the water solvent, allowing the water to be recycled and reused in the absorber.
The overhead from the SO$_2$ absorber contains less than 1 ppm SO$_2$, but it is saturated with water vapor at 11.8 bar and 40 °C [35]. It is passed through an O$_2$ dryer that removes the moisture, which is recycled in the plant. In the arrangement proposed in [35], pure oxygen is produced at 11 bar and 40 °C.

4. Conclusions

Sulfur based thermochemical processes are viable alternatives to electrolysis to produce hydrogen through water splitting. By using this approach, hydrogen can be produced without carbon-based emissions, with potential to achieve high efficiencies and low H$_2$ costs. These cycles can be coupled with either nuclear or solar plants, to produce hydrogen using a renewable source.

A review of the main sulfur processes was carried out and discussed. The Hybrid Sulfur process is likely the most advanced process, being able to be coupled with nuclear and solar power sources. The distinguishing section is comprised of an electrochemical system where sulfur dioxide is oxidized to produce sulfuric acid and hydrogen. Recent experimental tests demonstrated the ability of the electrochemical component, equipped with s-PBI membranes and Pt-based catalyst, to operate at 0.6–0.7 V and current densities of approximately 500 mA/cm$^2$. Realistic thermochemical cycle efficiencies on the order of 30–40% were documented in the literature, with H$_2$ production costs in the range of 2.64–7.58 $/kg. The Sulfur Iodine cycle is, in principle, a pure thermal process. The distinguishing section is the hydrogen iodide decomposition process. The cycle was extensively developed mainly for nuclear applications. Realistic thermochemical efficiencies on the order of 35–38% were reported, with high sensitivity to the adopted process configurations and approaches. Nuclear driven hydrogen production costs were estimated to be in the range of 3.50–12.0 $/kg. Another two sulfur-based processes were reviewed and compared, namely the Sulfur Bromine process and the Sulfur Ammonia process. The Sulfur Bromine cycle was extensively studied and developed at the end of 1970s for nuclear applications. The distinguishing section is the electrochemical decomposition of hydrobromic acid. The cycle was demonstrated experimentally for 100 L H$_2$/h. However, the high electric input required for the electrochemical reaction resulted in reduced interest in recent years. The Sulfur Ammonia process was developed by Florida Solar Energy Center for concentrated solar applications and represents an attempt to exploit both the thermal and the photonic components of the solar input. The cycle is more complicated than the other sulfur-based cycles, adding additional compounds and chemical sections. In addition, the cycle still requires fundamental research, both on thermodynamics and kinetics aspect, to achieve a prototype level demonstration.

Each sulfur-based thermochemical cycle sees the presence of a high temperature H$_2$SO$_4$ thermal section, where sulfuric acid is concentrated and decomposed, and oxygen is separated from the other compounds. Critical reviews were carried out for each process, analyzing and discussing the main process configurations and layouts proposed since the initial development. A specific review was carried out for the high temperature sulfuric acid decomposition section, discussing constitutive material options, catalytic formulations and decomposition reactor concepts. The referenced documents showed that ceramic materials (i.e., SiC materials) seem to be the most suitable option to withstand the high temperature aggressive environment. Currently, Pt-based catalysts represent the baseline formulation adopted to decompose sulfuric acid to sulfur dioxide, oxygen and water. Novel Pt-based bi-metallic formulations showed encouraging results, with preliminary tests highlighting high activity and minimal degradation. Metal oxide materials may have potential for high activity and high stability but still require additional fundamental work to avoid sintering and activity reduction at lower operating temperatures. Two main reactor concepts were discussed and compared. The first reactor, usually adopted for solar driven processes, is based on a direct cavity reactor concept, with the sulfuric acid decomposition occurring in two separate reactor units. The second concept, mostly employed in nuclear driven configurations, sees the presence of an intermediate heat transfer fluid exchanging the required thermal power. The indirect reactor concept seems to offer some advantages over the
direct cavity reactor, allowing the external heat transfer and the internal heat recovery to occur in a single unit.

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**Nomenclature**

| Abbreviation | Description |
|--------------|-------------|
| HyS          | Hybrid Sulfur |
| SI           | Sulfur Iodine |
| SRNL         | Savannah River National Laboratory |
| SNL          | Sandia National Laboratory |
| PEM          | Proton exchange membrane |
| LHV          | Low heating value (120 MJ/kg H₂) |
| DOE          | U.S. Department of Energy |
| HFTO         | DOE Hydrogen Fuel Cell Technology Office |
| DLR          | German Aerospace Center |
| eNRTL        | Electrolyte Non-Random Two Liquids |
| CFD          | Computational Fluid Dynamic |
| s-PBI        | Sulfonated polybenzimidazole |

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