

THERMOCHEMICAL CYCLES

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Summary

The thermochemical decomposition of water by cyclic reactions can convert thermal energy to hydrogen energy with high efficiency using solar and nuclear heat. The UT-3 and iodine-sulfur (IS) cycles are the most successful thermochemical water decomposition cycles and have reached pilot plant stage.

1. Thermochemical Cycles

The thermochemical decomposition of water by cyclic reactions is considered to be one of the most promising methods to produce hydrogen from thermal energy because of its efficient use of thermal energy. The primary energy source for thermochemical hydrogen production is medium temperature heat from solar and nuclear energy. The thermochemical cycle for water splitting, which consists of multistage closed-cycle series of endothermic and exothermic reactions, can convert thermal energy to hydrogen energy with greater efficiency than the conventional heat engine.

Mark 1		
	$\text{CaBr}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + 2\text{HBr}$	1003 K
	$\text{Hg} + 2\text{HBr} \rightarrow \text{HgBr}_2 + \text{H}_2$	523 K
	$\text{HgBr}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaBr}_2 + \text{HgO} + \text{H}_2\text{O}$	473 K
	$\text{HgO} \rightarrow \text{Hg} + \frac{1}{2}\text{O}_2$	873 K
Mark 15		
	$3\text{FeCl}_2 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$	723-1023 K
	$\text{Fe}_3\text{O}_4 + 8\text{HCl} \rightarrow \text{FeCl}_2 + 2\text{FeCl}_3 + 4\text{H}_2\text{O}$	373-383 K
	$2\text{FeCl}_3 \rightarrow 2\text{FeCl}_2 + \text{Cl}_2$	573 K
	$\text{Cl}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCl} + \frac{1}{2}\text{O}_2$	1073 K

GA cycle (IS cycle)		
	$x\text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{HI}_x + \text{H}_2\text{SO}_4$	366 K
	$2\text{HI}_x \rightarrow \text{H}_2 + x\text{I}_2$	573 K
	$\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2$	1143 K
UT-3 cycle		
	$\text{CaBr}_2 + \text{H}_2\text{O} \rightarrow \text{CaO} + 2\text{HBr}$	1123-1173 K
	$\text{CaO} + \text{Br}_2 \rightarrow \text{CaBr}_2 + \frac{1}{2}\text{O}_2$	800-923 K
	$\text{Fe}_3\text{O}_4 + 8\text{HBr} \rightarrow 3\text{FeBr}_2 + 4\text{H}_2\text{O} + \text{Br}_2$	493-578 K
	$3\text{FeBr}_2 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 6\text{HBr} + \text{H}_2$	923-1123 K

Table 1. Thermochemical cycles for hydrogen production.

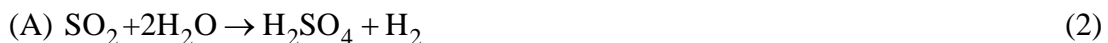
Since the conceptual idea of thermochemical water decomposition by cyclic reactions was presented by Funk, more than 100 thermochemical cycles have been proposed. However, most of them have not been successful because of poor reactivity of the cyclic reaction and/or the difficulty of product separation. Some schemes are at the laboratory stage in conjunction with the evaluation of thermodynamic and kinetic properties of possible cycle reaction steps. Only a few thermochemical processes have reached pilot plant stage. Table 1 summarizes the thermochemical cycles for hydrogen production.

The early research on thermochemical water splitting was focused on the Ispra Mark 1 cycle in this table. This cycle is feasible but was not suited for large-scale application due to the use of mercury. The Iron-Chlorine Mark 15 cycle was also considered to be practically feasible in spite of the poor reactivity of thermal FeCl_3 decomposition and FeCl_2 hydrolysis. However, the economics were not competitive.

The decomposition of sulfuric acid is applicable to thermochemical water splitting, which is an endothermic reaction at high temperature. Thermal energy from primary heat sources can be brought into this reaction step.



Three closures of the cycle were proposed as follows:





The Westinghouse sulfur cycle consists of the thermal decomposition of sulfuric acid (Eq. (1)) and SO₂ electrochemical oxidation (Eq. (2)). The HBr based cycle involving HBr electrolysis (Eq. (4)) and the thermal decomposition of H₂SO₄ (Eq. (1)) was developed by the Commission of the European Communities at ISPRA, Italy. A complete bench-scale continuous plant was built and operated at ISPRA. Since Eqs. (2) and (4) are electrochemical, the cycles with closures (A) and (B) are called thermochemical-electrochemical hybrid processes. General Atomics (GA) proposed and developed the HI–SO₂–H₂SO₄ cycle with closure (C). Eq. (5) is called the Bunsen reaction and produces two kinds of acid, H₂SO₄. A bench-scale system was constructed and used to demonstrate the operation of the GA cycle and the test components. The Japan Atomic Energy Research Institute (JAERI) is continuing to study the HI–SO₂–H₂SO₄ cycle called the iodine-sulfur (IS) process.

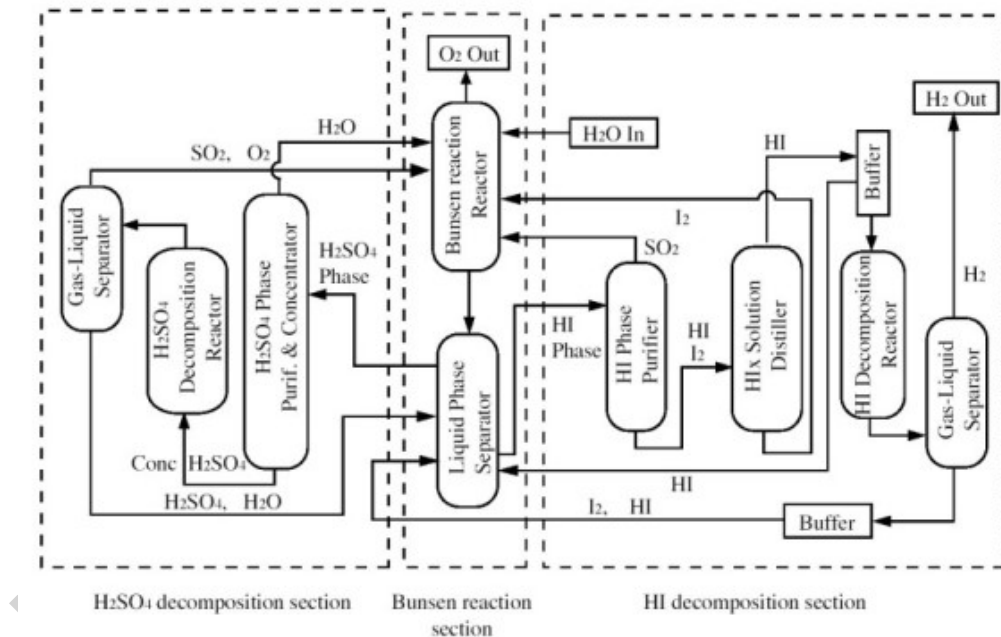


Figure 1. Flow sheet of the IS process

Figure 1 shows the flow sheet of the IS process. The process can be divided into three sections; Bunsen reaction section, H₂SO₄ decomposition section, and HI decomposition section. On the condition of excess iodine concentration, the products of a Bunsen reaction form two phases, one rich in HIx (the heavier phase) and the other rich in H₂SO₄ (the lighter phase). After separation, each of the phases is introduced into the HIx and H₂SO₄ decomposition sections, respectively. It is essential for the steady state operation of the closed cycle to maintain the compositions and for the flow rates of process solutions from the liquid separator to be constant.

The UT-3 cycle is one of the successful thermochemical cycles, which consists of four gas–solid reactions; bromination and hydrolysis reactions of Ca and Fe compounds.

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Biographical Sketch

Atsushi Tsutsumi, born November 2, 1956, in Japan; is an associate professor of Chemical System Engineering at the University of Tokyo. He received his Doctorate of Engineering from the University of Tokyo in 1986. He has been active in research on innovative thermochemical energy technology and nonlinear dynamics and chaos scale-up methodology development for multi-phase reactors for the last ten years. He has over 70 scientific publications and 100 proceedings in international journals and conferences.

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