

Overview of the Modified SI Cycle to Produce Nuclear Hydrogen Coupled to VHTR

Youngjoon Shin, Taehoon Lee, Kiyong Lee, Minhwan Kim

Korea Atomic Energy Research Institute 150 Dukjin-dong, Yuseong-gu, Daejeon, Republic of Korea 305-600

* Corresponding author: nyjshin@kaeri.re.kr

1. Introduction

The VHTR-based hydrogen production technologies will vary depending on the raw materials, the adopted principles, and the quantity and purity of the hydrogen required. Many researchers are developing a wide range of processes for producing hydrogen economically and in an environmentally friendly way.

The steam reforming of methane is one of hydrogen production processes that rely on cheap fossil feedstocks. Today, nearly all hydrogen production is based on raw fossil materials. Worldwide, 48% of the hydrogen is produced from natural gas, 30% from oil, 18% from coal, and the remaining, 4% via water electrolysis [1]. However the new task presented to us due to the Kyoto Protocol from the UN Framework Convention on Climate Change in December 1997 is how to overcome the carbon dioxide emission problem with this technology. Several CO₂-free alternatives [2,3], which are based on a steam reforming of methane, were introduced conceptually, named the Methane-Methanol-Methanal(3M) cycle and the Methane-Methanol-Iodomethane(MMI) cycle.

Modification of the conventional steam reforming process to incorporate the recycle concept of carbon compounds may offer a number of advantages over the conventional processes in the conservation of energy resources and the global environment.

In our current work, the modified sulfur-iodine (SI) cycle, which is based on the SI chemical process without Bunsen reaction and HI_x handling processes conjugated with the conventional steam reforming of methane, has been introduced and the uncertainties of several chemical reactions revealed in the theoretical evaluation have been discussed.

2. Modified Sulfur-Iodine Cycle

The modified SI cycle is composed of the conventional steam reforming of methane and the sulfuric acid handling part from the original SI cycle to produce iodomethane from methanol.

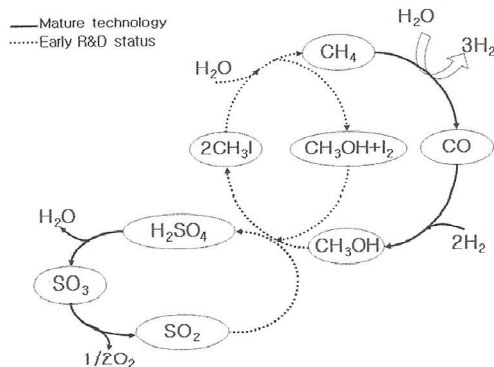


Fig. 1. Modified sulfur-iodine cycle.

Based on the modified SI cycle in Fig. 1, the following 5 chemical reaction steps can be established and the physical properties of the chemical compounds or elements which participate in the chemical reactions are shown in Table 1.

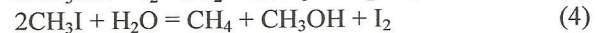
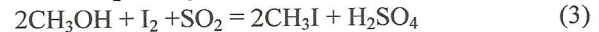


Table 1. Physical properties of chemical compounds in the modified SI cycle

Compounds	ρ (g/ml; ρ_g g/l)	T_{melting} (°C)	T_{boiling} (°C)	Solubility
CH ₄	0.424 ⁴⁰	-182.5	-161.5	3.3ml in 100g H ₂ O 47.1ml in 100g alcohol
CH ₃ OH	0.791 ²⁰	-97.7	64.7	Miscible with H ₂ O
CH ₃ I	2.279 ²⁰	-66.5	42.4	Miscible with alcohole 1.4 part/100 part H ₂ O
I ₂	4.660 ²⁰	113.6	184.2	Soluble in alcohole 0.029 ²⁰ /100partH ₂ O
H ₂ SO ₄	1.832 ²⁰	10.4	280	Very soluble in H ₂ O

When comparing with the original SI cycle, the modified SI cycle has a carbon compound cycle instead of the Bunsen reaction and HI_x handling processes.

3. Evaluation of Thermodynamic Properties

Thermodynamic properties of the heat of the chemical reaction (ΔH) and the Gibbs free energy (ΔG) on Eq. (1) to (5) have been calculated.

By analyzing the Gibbs free energy change, it has been intimated in Fig. 2 that most reactions are available within the temperature range of 298 K – 1,373 K.

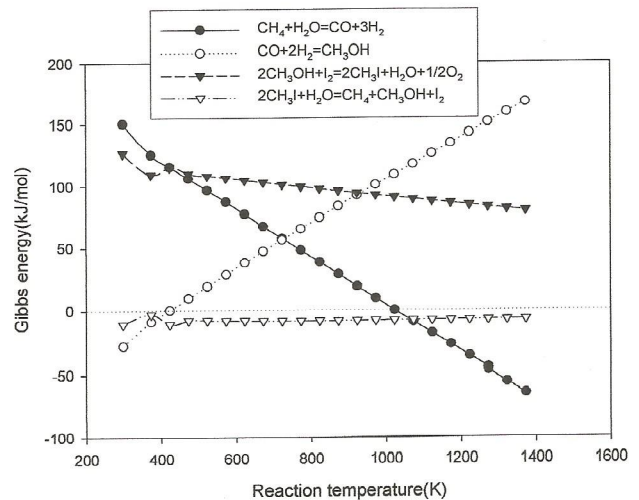


Fig. 2. Gibbs free energy as a function of the reaction temperature in the modified SI cycle.

As shown in Fig. 2, a steam reforming of methane has a negative value of ΔG above 1,023 K, however the syngas reaction to obtain methanol maintains a negative value of ΔG below 423 K.

The hydrolysis of methyl iodide, Eq. (4) always has a negative value for the Gibbs free energy regardless of the reaction temperature. In Fig. 3 showing the enthalpy changes as a function of the reaction temperature, we can easily observe that the chemical reaction of Eq. (1) is endothermic reaction but that reactions Eq. (2) and (4) are exothermic reactions. The sensitivity of the reaction temperature on the heat of the reaction is very mild above 473 K.

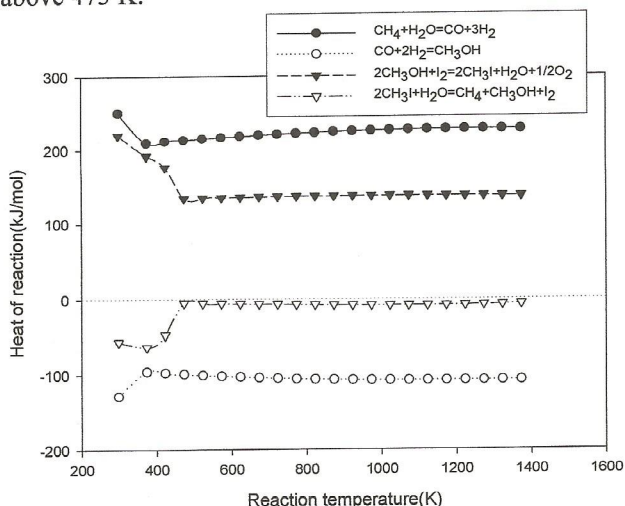


Fig. 3. Heat of the chemical reaction as a function of the reaction temperature in the modified SI cycle.

Even if there is no problem in each chemical reaction step, some catalysts and a modification of the reaction condition such as the temperature and pressure are required to increase the chemical reaction rates and conversion yields.

In the case of chemical reactions Eq. (3) and (5), we have to find a chemical reaction pathway which could maintain a negative Gibbs energy. As a precondition of this, the chemical reaction pathway ought to satisfy a closed loop by a recycling of the reactants perfectly. One of the considerable pathways is a dissociation and recombination of sulfuric acid in series; as follows,



Figs. 4 and 5 show the Gibbs free energies and enthalpies of chemical reactions Eq. (3), (6), and (7).

The Gibbs energies related to the dissociation of sulfuric acid and sulfur trioxides are decreased by increasing the reaction temperature. The negative values of the Gibbs energies are above 423 K in reaction Eq. (6) and above 1,073 K in reaction Eq. (7), respectively. However reaction Eq. (3) has a negative value for the Gibbs energy below 373 K. Furthermore the conversion yield is too small because of the lower absolute value of

its Gibbs energy. If we maintain a lower temperature to increase the equilibrium value, a long reaction time to obtain a high yield is required because the forward reaction rate is too low. Therefore, we not only need a proper catalyst but also a high pressure system for this reaction.

Taking into account the enthalpy information, the chemical reactor related to chemical reaction Eq. (3) requires a cooling system because of its exothermic reaction scheme. On the other hand, chemical reactions Eq. (6) and (7) require a heating system due to their endothermic reactions. In the case of chemical reaction Eq. (3), a side reaction to form HI has to be prevented. From the aspects of the Gibbs energy changing values as a function of the reaction temperature in the sequential decomposition of sulfuric acid, the primary decomposition of sulfuric acid to sulfur trioxide and water can be achieved easily. However the secondary decomposition of sulfur trioxide to sulfur dioxide and oxygen requires a catalyst to increase its reaction kinetics.

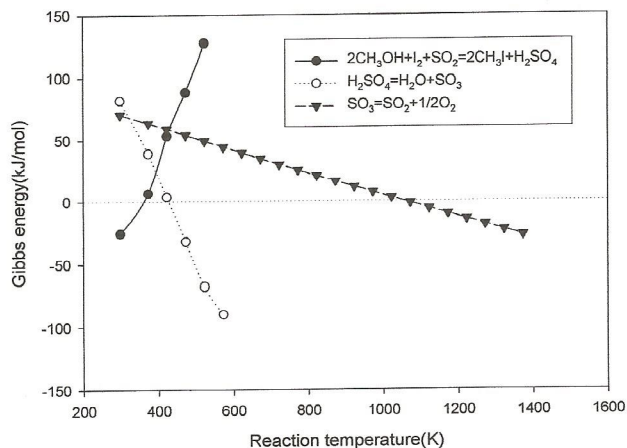


Fig. 4. Gibbs free energies of the iodization of methanol and dissociation of sulfuric acid.

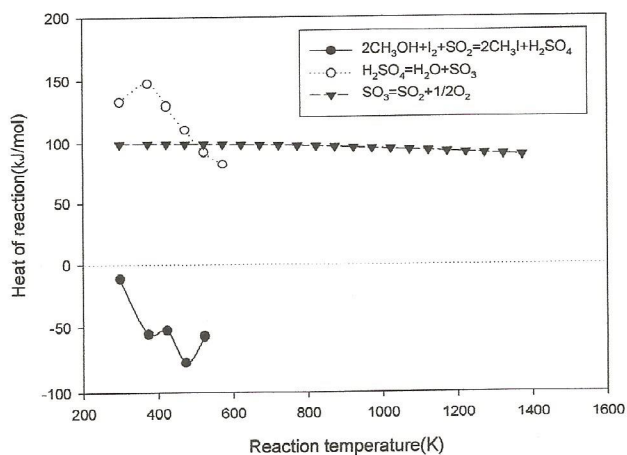


Fig. 5. Enthalpies of the iodization of methanol and dissociation of sulfuric acid.

4. Conclusions

An overview of the VHTR-based nuclear hydrogen production process with the modified SI cycle has been carried out to establish whether it can be adopted as a feasible technology to produce nuclear hydrogen.

By analyzing the Gibbs free energy change, it has been found that most reactions are available within the temperature range of 298 K – 1,298 K. In order to obtain methyl iodide from methanol to satisfy the modified SI cycle, a SO₂-catalytic chemical reaction pathway during the step of an iodization of methanol is possible.

Acknowledgments

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