A Study of the Thermochemical Hydrogen Preparation X. Estimation of the Thermal Efficiency of Sulfuric Acid Cycles

Masayuki DOKIYA*, Harumi YOKOKAWA*, Tetsuya KAMEYAMA* and Kenzo FUKUDA*

The thermal efficiency of thermochemical water-splitting cycles which adopt decomposition of sulfuric acid as an oxygen generation step was estimated by analysis of the flow sheets. Mass and heat flow of cycles were assumed based on the experimental results and thermochemical data. The cycles are classified into two types: A) cycles in which an electrochemical reaction is involved; B) cycles in which the methanol synthesis process is involved. It is estimated that more than 500 kcal/mol-H₂ of heat is circulated into cycle, and about 270–460 kcal/mol-H₂ of them should be recovered in the process. The amount of heat that should be circulated in the process will be one of the essential factors which will decide the scale of heat exchanger. Assuming 75–100% of thermal regeneration ratio, higher thermal efficiency (42–74%) can be expected for A type cycles and lower thermal efficiency (30–44%) is expected for B type cycles. However, the scale of plant for A type cycles will be larger than that for B type cycles, because of the dimensional demerit of electrochemical reaction and large amount of heat that should be circulated in the process.

1 Introduction

The thermochemical hydrogen production process produces hydrogen utilizing the nuclear heat from the very high temperature gas-cooled reactor (VHTGR). The thermal efficiency defined by Funk and Reinstrom is adopted in this paper. “Q” is the heat that is supplied from the heat source and “W” is the work which is required to operate the process and “η” is the efficiency of energy conversion from heat to work.

\[ \eta_{\text{HHV}} = \Delta H_{\text{H}_{2}\text{O} (\text{aq})}/(Q + W/\eta) \quad (1) \]

Higher thermal efficiency is expected for the thermochemical hydrogen production process than that by the electrolysis of water utilizing electricity from the nuclear power station. The present thermal efficiency of the electrolysis of water is about 24% and more than 30% of efficiency is expected in future with the improvements in the electrolysis of water.

As previously stated, the sulfuric acid cycles are thought to be promising. Prior to the development of continuous bench-scale experiment, it is necessary to estimate the thermal efficiency of candidate cycles whose chemical feasibility has been experimentally proved. The following sulfuric acid cycles are examined in this paper.

(1) A-1 cycle (SO₂ hybrid cycle) \(^{4-11}\)
\[ \text{SO}_2 + 2\text{H}_2\text{O} \xrightarrow{\text{electrolysis}} \text{H}_2 + \text{H}_2\text{SO}_4 \quad \text{(A-1-1)} \]
\[ \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 1/2\text{O}_2 \quad \text{(A-1-2)} \]

(2) A-2 cycle (SO₂-I₂ cycle) \(^{4-11}\)
\[ \text{SO}_2 + 2\text{H}_2\text{O} + \text{I}_2 \rightarrow \text{H}_2\text{SO}_4 + 2\text{HI} \quad \text{(A-2-1)} \]
\[ \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 1/2\text{O}_2 \quad \text{(A-2-2)} \]
\[ 2\text{HI} \rightarrow \text{H}_2 + \text{I}_2 \quad \text{(A-2-3)} \]

(3) A-3 cycle (SO₂-I₂-Benzene cycle) \(^{14}\)
\[ \text{SO}_2 + 2\text{H}_2\text{O} + \text{I}_2 \rightarrow \text{H}_2\text{SO}_4 + 2\text{HI} \quad \text{(A-3-1)} \]
\[ \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 1/2\text{O}_2 \quad \text{(A-3-2)} \]
\[ 2\text{HI} + 1/3\text{C}_3\text{H}_6 \rightarrow 1/3\text{C}_3\text{H}_4 + \text{I}_2 \quad \text{(A-3-3)} \]
\[ 1/3\text{C}_3\text{H}_6 \rightarrow 1/3\text{C}_3\text{H}_4 + \text{H}_2 \quad \text{(A-3-4)} \]

(4) B-1 cycle (SO₂-I₂-Methanol cycle) \(^{15}\)
\[ \text{SO}_2 + 2\text{CH}_2\text{OH} + \text{I}_2 \rightarrow \text{H}_2\text{SO}_4 + 2\text{CH}_2\text{I} \quad \text{(B-1-1)} \]
\[ \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 1/2\text{O}_2 \quad \text{(B-1-2)} \]
\[ 2\text{CH}_2\text{I} + 2\text{H}_2\text{O} \rightarrow 2\text{CO} + 5\text{H}_2 + \text{I}_2 \quad \text{(B-1-3)} \]
\[ 2\text{CO} + 4\text{H}_2 \rightarrow 2\text{CH}_2\text{OH} \quad \text{(B-1-4)} \]

(5) B-2 cycle (SO₂-I₂-Methanol modified cy-
 cle)\(^\text{15}\)
\[
\begin{align*}
\text{SO}_2 + 2\text{CH}_2\text{OH} + \text{I}_2 & \rightarrow \text{H}_2\text{SO}_4 + 2\text{CH}_3\text{I} \\
\text{H}_2\text{SO}_4 & \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 1/2\text{O}_2 \\
2\text{CH}_2\text{I} + \text{H}_2\text{O} & \rightarrow 7/4\text{CH}_4 + 1/4\text{CO}_2 + \text{I}_2
\end{align*}
\]

(6) B-3 cycle (\text{SO}_2-I_2-Methanol-H_2 cycle)\(^\text{15}\)
\[
\begin{align*}
\text{SO}_2 + 2\text{CH}_2\text{OH} + \text{I}_2 & \rightarrow \text{H}_2\text{SO}_4 + 2\text{CH}_3\text{I} \\
\text{H}_2\text{SO}_4 & \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 1/2\text{O}_2 \\
2\text{CH}_2\text{I} + \text{H}_2\text{O} & \rightarrow \text{CH}_2\text{I} + \text{I}_2 \\
2\text{CO} + 4\text{H}_2 & \rightarrow 2\text{CH}_2\text{OH} \\
\end{align*}
\]

Fig. 1 The flow sheet of A-1 cycle (\text{SO}_2-I_2 hybrid)

Unit: kcal/mol-H_2

Fig. 2 The flow sheet of A-2 cycle (\text{SO}_2-I_2 cycle)

Unit: kcal/mol-H_2

\(\Delta H^\text{non}\) and the decomposition voltage of cell or electrolysis reactions are also shown in the figures.

The concentration of sulfuric acid was assumed to be 40 wt% and 73 wt% for A-1 to A-3 cycles\(^\text{47}\) and B-1 to B-3 cycles\(^\text{13}\), respectively. It was assumed that equilibrium is attained in the decomposition of \text{SO}_2 with 80% of conversion ratio\(^\text{3}\).

The following assumptions were made in the construction of flow sheets.

1. A-1 cycle: R2 designates an electrolysis cell
was assumed to be $-0.12\,\text{V}$. Hydrogen is evolved by the decomposition of hydrogen iodide. The conversion of hydrogen iodide to hydrogen was assumed to be 9.4% under the existence of iodine and this is the equilibrium conversion ratio$^{14}$. 

3. A-3 cycle: R2 designates the same cell reaction as in A-2 cycle. The decomposition voltage was assumed to be $-0.14\,\text{V}$. This value is slightly lower than that of A-2 cycle, because the $I_2/\text{HI}$ ratio was increased from that of A-2 cycle. Hydrogen is evolved by the benzene-cyclohexane cycle. The conversion ratios of reaction A-3-3 and A-3-4 were assumed to be 80%. However, higher conversion ratios can be expected from the experimental results and the equilibrium conversion ratio$^{15}$. 

4. B-1 cycle: Methyl iodide and sulfuric acid are produced in R2. The conversion of methanol was optimistically assumed to be 100% under excess $\text{SO}_2$.$^{15}$ The methanol synthesis process is utilized as a methanol recovery process (R4). The conversion ratio was assumed to be 60% (equilibrium) under 300 atm at 600 K. Hydrogen is evolved by the steam reforming reaction of methyl iodide. The experimental results showed that the direct steam reforming reaction of methyl iodide is a difficult process$^{16}$, however it is expected that the further research on the catalyst will realize such
a process. The conversion of methyl iodide was assumed to be 100% with 2 fold excess of steam. The formation of hydrogen iodide was observed experimentally, however, in this flow sheet, it was neglected.

5. B-2 cycle: Except that a two step steam reforming process of methyl iodide was adopted in this cycle (R4 and R5), the other processes are the same processes as in A-1 cycle. The conversions of methyl iodide and methane were also assumed to be 100% with 2 fold excess of steam.
6. B-3 cycle: Except that a hydrogenation process of methyl iodide was adopted in this cycle (R3)\(^{10}\), the other processes are the same processes as in A-1 and A-2 cycles. The formation of hydrogen iodide and its recirculation were assumed in this cycle.

In order to estimate and to compare the thermal efficiency of the cycles, the heat flow in Figs. 1~6 are summarized in Table 1. Definitions of the parameters are given in the foot note. “Q\(_{\text{exch}}\)” implies the amount of heat which should be exchanged within the cycle, between the cycle and the VHTGR, or between the cycle and surroundings. This amount of heats should be adsorbed and exhausted by the endothermic and exothermic steps of the cycle. “Q\(_{\text{lec}}\)” implies the maximum heat which can be recovered within the cycle. It is assumed that this heat is recovered within each reaction step, that is, Q\(_p\) of products is recovered in Q\(_r\) of reactants of the same reaction. This assumption may be reasonable, since the exothermic reactions proceed at low temperatures and the products cannot be used to preheat the reactants of the high temperature endothermic reactions. “Q\(_{\text{H}_2\text{O}}\)” implies the least heat requirement of the cycle, that is, the heat required when 100% thermal regeneration in each reaction step can be realized. Thus, this heat is equal to the sum of the reaction enthalpy at 298 K of the endothermic reaction steps. Q\(_{\text{elec}}\) is also included in Q\(_{\text{min}}\).

Using Q\(_{\text{min}}\) the maximum possible thermal efficiency, “\(\eta_{\text{max}}\)” can be estimated. In actual case, the amount of heat which is required by the cycle will be larger than Q\(_{\text{min}}\). It is possible to estimate the heat requirement of the cycle if the ratio of thermal regeneration “\(R_i\)” can be assumed.

\[
Q_{\text{reg}} = \frac{1}{2} \Delta H_T + Q_r - Q_p \times R_i + Q_{\text{elec}} \\
Q_{\text{min}} = \frac{1}{2} \Delta H_T + Q_r - Q_p + Q_{\text{elec}} \leq 298K + Q_{\text{elec}}
\]

Using Table 1, the summary of heat flow and the expected thermal efficiency of cycles.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>(Q_{\text{exch}}) kcal</th>
<th>(Q_{\text{lec}}) kcal</th>
<th>(Q_{\text{H}_2\text{O}}) kcal</th>
<th>Q(_{\text{elec}}) kcal</th>
<th>Q(_{\text{H}_2\text{O}}) kcal</th>
<th>Q(_{\text{min}}) kcal</th>
<th>(\eta_{\text{max}}) %</th>
<th>(\eta_{R_i=0.75}) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>297</td>
<td>227</td>
<td>0</td>
<td>55</td>
<td>199</td>
<td>125</td>
<td>55</td>
<td>76</td>
</tr>
<tr>
<td>A-2</td>
<td>2759</td>
<td>2672</td>
<td>0</td>
<td>2</td>
<td>2005</td>
<td>90</td>
<td>74</td>
<td>44</td>
</tr>
<tr>
<td>A-3</td>
<td>547</td>
<td>464</td>
<td>0</td>
<td>0</td>
<td>357</td>
<td>92</td>
<td>40</td>
<td>37</td>
</tr>
<tr>
<td>B-1</td>
<td>516</td>
<td>272</td>
<td>88</td>
<td>0</td>
<td>66</td>
<td>156</td>
<td>42</td>
<td>9</td>
</tr>
<tr>
<td>B-2</td>
<td>547</td>
<td>272</td>
<td>101</td>
<td>0</td>
<td>66</td>
<td>170</td>
<td>48</td>
<td>33</td>
</tr>
<tr>
<td>B-3</td>
<td>592</td>
<td>292</td>
<td>116</td>
<td>0</td>
<td>66</td>
<td>185</td>
<td>34</td>
<td>30</td>
</tr>
</tbody>
</table>

\(\Delta H_T\); reaction enthalpy at TK. \(\Delta H_{298}\); reaction enthalpy at 298 K.

\(Q_p = \text{reactant} (H_T - H_{298})\).

\(Q_r = \text{product} (H_T - H_{298})\).

\(Q_{\text{H}_2\text{O}}\); \(Q_r\) and \(Q_p\) of water.

\(Q_{\text{elec}} = \text{Decomposition Voltage} A-1 or A-2 - (\text{Decomposition Voltage} A-1)\) / 0.4

\(\eta_{\text{max}} = 0.83 \times Q_{\text{min}}\).

\(\eta_{R_i=0.75} = 0.83 \times [\text{Decomposition Voltage} A-1 or A-2 - (\text{Decomposition Voltage} A-1)] / 0.4\).
the hydrated water of sulfuric acid and hydriodic acid. As can be seen from Table 1, very large portion of the $Q_b$ and $Q_c$ is the $Q_{H_2O}$, especially in A cycles.

3 Discussion

From the estimated values of $Q_{exch}$, it becomes clear that a large amount of heat should be circulated in the thermochemical hydrogen production process. The amount of heat should be circulated in a cycle will decide the scale of heat exchanger and then will be one of the essential factors to determine the cost of hydrogen. The estimated value of $Q_{rec}$ for A-2 cycle is too large to be accepted from this standpoint. A-2 cycle can be improved by introducing a two step benzene-cyclohexane cycle instead of the direct decomposition of hydrogen iodide. It is concluded from these A-2 and A-3 cycles that it is essential to replace a reaction whose conversion is low by other two step reactions whose conversions are high enough. A-3 cycle will still need larger heat exchanger than B cycles. This is mainly due to the large $Q_{H_2O}$, as can be seen from Table 1. In order to reduce the $Q_{rec}$ of A-3 cycle further, it is desirable to produce concentrated sulfuric acid and hydriodic acid. This will be possible by adding external electricity and by the improvement of the electrolysis cell. The amount of $Q_{H_2O}$ will be also related to the thermal regeneration ratio $R_t$, since more than half of $Q_{H_2O}$ is the heat of evaporation (condensation) of water, thus, in order to realize higher thermal regeneration ratio for a such a low temperature heat, larger heat exchanger will be required. The estimated values of $Q_{rec}$ and $Q_{H_2O}$ indicate that smaller scale of heat exchanger and higher thermal regeneration ratio than those for A-3 cycle are expected for B cycles, although almost the same amount of heat should be circulated in A-3 and B cycles.

A very high thermal efficiency can be expected in A-3 cycle, if 100% thermal regeneration is realized. However, when the thermal regeneration ratio is 75%, the expected thermal efficiency will decrease to 48%. The expected maximum thermal efficiency for A-1 and B cycles are 55% and about 40%, respectively.

The expected thermal efficiency will decrease to 42% and 30–34% for A-1 cycle and B cycles, respectively, when the thermal regeneration ratio is 75%. Comparing A and B cycles, it becomes clear that the maximum thermal efficiency largely depends on the exhaust heat ($Q_{rec}$) from the cycles by the exothermic reactions. If this waste heat can be recovered, for example as electricity, the total efficiency of the VHTGR can be improved.

The thermochemical water-splitting cycle includes the separation and the transportation processes in addition to the reaction processes. In these flow sheets, it is assumed that the products of different phases can be separated spontaneously and that the additional work or heat to purify the separated products will be negligible.

In the cycles studied here, no solid materials are used except for iodine. In the actual case, the iodine can be treated in a dissolved state in hydriodic acid. Thus, the work for the transportation of materials can be assumed to be negligible. However, in B cycles, an additional work to compress CO and hydrogen up to 300 atm is required in the methanol synthesis process. The theoretical work to compress $n$-mol of ideal gas from 1 atm to 300 atm at 298 K is calculated by eq. 4 and 10.2 kcal/mol-methanol is required.

$$W_{com} = nRT\ln\frac{P_f}{P_i} = 3 \times 2 \times 298 \times 10^{-3} \times \ln 300 = 10.2$$

In the industrial methanol synthesis plant including the steam reforming process to produce hydrogen and CO from natural gas, the waste heat from the process is recovered for the turbo-compressor and the amount of waste heat is estimated to be 40–70 kcal/mol-methanol from the published unit consumption figures\(^{17,22}\). From these considerations, it is concluded that the steam reforming and the methanol synthesis steps in B cycles will require large energy consumption. Moreover, in B cycles, hydrogen should be separated from CO. From the published data\(^{11}\) on the industrial pressure swing adsorption (PSA) and the cryogenic separation processes, it is estimated that about 2.7 kcal/(mol-gas mixture) of electricity is required to separate hydrogen from CO, CH\(_4\), etc. Using this data, it is estimated that B-1 and B-2
cycles will consume about 14 kcal of electricity to separate hydrogen from CO (3.68H₂/1.34CO in S₁ and S₂) and that B-3 cycle will consume 23 kcal of electricity to separate hydrogen and hydrogen iodide from CO and CH₄ (0.25H₂, 1.5 HI/2CH₄ in S₁ and 3.68 H₂/1.34 CO in S₂). Thus, in order to obtain higher thermal efficiency, an effective utilization of \( Q_{\text{rec}}^\text{II} \) is desired for B cycles. This \( Q_{\text{rec}}^\text{II} \) is low temperature heat (400–600K). It will be difficult to utilize such a low temperature heat effectively in the compression of CO and hydrogen and in the separation of hydrogen from the other gas.

The separation of SO₂ from O₂ is a common process in A and B cycles. This process will require not so much energy, since SO₂ can be liquified easily (bp. -10°C). The published data on the separation of acidic gas (CO₃, COS, H₂S) from hydrogen, CO, etc by Rectisol process indicate that about 0.7 kcal of electricity and 1.2 kcal of steam per one mol of acidic gas are required. If the application of the Rectisol process for the separation of SO₂ is possible, the energy consumption for the purification of O₂ will be small compared to the other steps.

From the standpoint of the separation process, A cycles are better than B cycles. However, the demerit of A-2 and A-3 cycles also originates from the separation problem in A-2-1 reaction. In order to produce the hydriodic acid from sulfuric acid separately, the cell reaction is adopted, thus, it is inevitable that the large scale plant is required compared to B cycles because of dimensional demerit of electrolysis cell. The same is true for A-1 cycle. The addition of external electricity will be a method to increase the current density and then to reduce the scale of plant. Moreover, by this method it is possible to increase the concentration of acids and to reduce \( Q_{\text{H₂O}} \) and then, to reduce the scale of heat exchanger. On the other hand, \( T_{\text{max}} \) will decrease, for example by addition of 0.3V of external electricity, \( T_{\text{max}} \) of A-1, A-2, and A-3 cycles will decrease to 43, 54, and 54%, respectively.

From the standpoint of thermal efficiency, A-3 cycle seems to be the most promising cycle compared to the other cycles. B cycles are attractive because of smaller scale of reactors and heat exchanger, however, the separation and shaft works will reduce the thermal efficiency to a lower level. There is a more essential method to improve the B cycles than the effective utilization of \( Q_{\text{rec}}^\text{II} \), if CH₄ can be produced directly by the following reaction 1, instead of reaction B-1-1, the whole cycle can be simplified and the expected thermal efficiency will be improved.

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 + \text{CH}_4
\]

The preliminary experimental results indicate that the reaction 1 is difficult to be carried out without side reactions, however, further research is still desirable in order to establish suitable thermochemical cycle.

References:

第9回 高温化学研究懇談会
本協会衆議院議員会議長並びに在日・在仏関係学者会合催の「第9回化学研究懇談会」が昭和53年5月23日（水）13時30分より大阪大学工学部で開催された。講演は以下の2件が行われた。

1. X線透過法による高温化学反応の直接観察
   大阪大学産業化学研究所 小泉光栄
   無機物質の合成についての基礎研究は、今日までに多くの研究者によって行われているが、その中でもX線透過法による直接観察が注目されている。本講演では、試料の種類別にX線透過法の応用例を紹介した。

2. 高温下における無機合成反応
   大阪大学産業化学研究所 小泉光栄
   無機物質の合成についての基礎研究は、今日までに多くの研究者によって行われているが、その中でもX線透過法による直接観察が注目されている。本講演では、試料の種類別にX線透過法の応用例を紹介した。

協会レポート

第10回 高温化学研究懇談会
昭和53年10月20日（金）午前9時より、本協会秋季大会を開催する「高温化学研究懇談会」が開催された。講演は以下の6件が行われた。

1. プラズマによる高温安定化合物の合成
   （青山学院大学）松本修
   プラズマによる高温安定化合物の合成についての基礎研究は、今日までに多くの研究者によって行われているが、その中でもX線透過法による直接観察が注目されている。本講演では、試料の種類別にX線透過法の応用例を紹介した。

2. 高周波波磁場結合型アークプラズマを用いた高温化学反応
   （東大）西村秀博
   高周波波磁場結合型アークプラズマを用いた高温化学反応についての基礎研究は、今日までに多くの研究者によって行われているが、その中でもX線透過法による直接観察が注目されている。本講演では、試料の種類別にX線透過法の応用例を紹介した。

3. 高周波波磁場結合型アークプラズマを用いた高温化学反応
   （青山学院大学）松本修
   高周波波磁場結合型アークプラズマを用いた高温化学反応についての基礎研究は、今日までに多くの研究者によって行われているが、その中でもX線透過法による直接観察が注目されている。本講演では、試料の種類別にX線透過法の応用例を紹介した。

4. 高周波波磁場結合型アークプラズマを用いた高温化学反応
   （青山学院大学）松本修
   高周波波磁場結合型アークプラズマを用いた高温化学反応についての基礎研究は、今日までに多くの研究者によって行われているが、その中でもX線透過法による直接観察が注目されている。本講演では、試料の種類別にX線透過法の応用例を紹介した。

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6. 高周波波磁場結合型アークプラズマを用いた高温化学反応
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7. 高周波波磁場結合型アークプラズマを用いた高温化学反応
   （青山学院大学）松本修
   高周波波磁場結合型アークプラズマを用いた高温化学反応についての基礎研究は、今日までに多くの研究者によって行われているが、その中でもX線透過法による直接観察が注目されている。本講演では、試料の種類別にX線透過法の応用例を紹介した。