

## 이단계 바이오 수소/메탄 생산공정의 경제성 평가

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## Economic Evaluation of Two-step Biohydrogen/biomethane Production Process

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### ABSTRACT

본 연구에서는 이 단계 연속 바이오 수소/메탄 생산공정의 경제성을 조사하였다. 경제적 관점에서 다양한 수소 및 메탄 발효용 생물반응기를 비교·평가하였다. 이를 바탕으로 포도당으로부터 일 단계 수소발효를 위해 고온 trickling biofilter 반응기 (TBR, 100 m<sup>3</sup> 규모)를, 일 단계 반응의 부산물로 생성된 유기산과 알콜류의 이 단계 메탄전환을 위해 고온 upflow anaerobic sludge 반응기 (UASB; 700 m<sup>3</sup> 규모)를 선정하였다. 본 이 단계 공정의 수소생산 비용은 \$ 0.26/Nm<sup>3</sup>으로 계산되었고, 이는 고온 TBR 반응기만을 이용한 경우보다 약 30 % 낮았다. 이 단계 공정의 낮은 수소생산 비용은 높은 에너지 회수율과 낮은 슬러지 처리비용에 의한 것이었다. 생물학적 수소 생산공정의 경제성은 탄소원의 종류, 생물반응기의 형태 등 여러 인자에 의해 변경될 수 있으나, 본 연구결과는 향후 연구를 위한 유용한 기준으로 고려될 수 있다.

**주요기술용어** : Hydrogen(수소), Biological hydrogen production(생물학적 수소생산), Economic feasibility(경제성), Two-stage fermentation(이단발효), Methane(메탄), Biomass(바이오매스)

### 1. Introduction

Hydrogen is an efficient energy carrier with a high energy content per unit mass. It is considered

to be the cleanest energy carrier because the combustion by-product is only water. It does not produce any green-house gases and neither does it contribute to global warming<sup>1)</sup>. Hydrogen is also an important raw material in various chemical industries, and is gaining increasing attention<sup>2)</sup>.

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Hydrogen can be produced by either chemical or biological methods. The economic feasibility of biological methods mainly depends on the rate and yield of the  $H_2$  production from various substrates. Many researchers have focused on developing efficient processes<sup>3-13</sup>. For example, Kumar and Das<sup>6</sup> immobilized *Enterobacter cloacae* IIT-BT 08 onto lignocellulosic agroresidues and observed a high  $H_2$  production rate of 1,814 mmol  $H_2/l \cdot d$  at a short HRT of 1.08 h. Rachman *et al.*<sup>12</sup> reported that self-flocculating *E. aerogenes* mutant AY-2 exhibits a high  $H_2$  production rate as well as a yield of 1,392 mmol  $H_2/l \cdot d$  and 1.1 mol  $H_2/mol$  glucose at an HRT of 1.49 h. Recently, a thermophilic trickling biofilter reactor (TBR) was studied in detail for fermentative  $H_2$  production<sup>11</sup>. The reactor exhibited a high  $H_2$  production rate of 1,050 mmol  $H_2/l \cdot d$  and, more importantly, could be operated stably for an extended period of 234 d.

Fermentative  $H_2$  production from a biomass produces many organic by-products such as alcohols and organic acids<sup>11,14-16</sup>. These by-products can be utilized for producing more energy: either  $H_2$  in a photo-bioreactor or  $CH_4$  in a second anaerobic reactor. Hydrogen production using a photo-bioreactor is attractive since more  $H_2$  can be obtained<sup>17</sup>, but the problems are that the  $H_2$  production rate is slow and that not all organic by-products are converted into  $H_2$ <sup>18</sup>. In addition, scale-up of the photo-bioreactor is technically difficult and expensive<sup>19</sup>. In comparison, large-scale  $CH_4$  production has been widely practiced in industry for many years<sup>20,21</sup>. Methane fermentation can proceed to completion, whereas most organic compounds generated from dark  $H_2$  fermentation are depleted. Therefore, a two-step biohydrogen/biomethane production

process should be considered as one of the ideal energy production processes at present.

There have been a limited number of reports on the economic feasibility of fermentative  $H_2$  production. Recently, de Vrije and Claassen<sup>17</sup> studied the economics of a relatively small-scale plant (425 Nm<sup>3</sup>  $H_2/h$ ), using lignocellulosic substrate as a raw material. They estimated the production cost to be \$ 0.29/Nm<sup>3</sup>  $H_2$  in a two-stage fermentation that consisted of an extremely thermophilic dark-fermentation as the first stage and a photo-fermentation as the second stage. Tanisho<sup>22</sup> reported on a comparison between fermentative  $H_2$  production and ethanol fermentation, using sugar cane as a raw material. He estimated the  $H_2$  production cost to be \$ 0.48/Nm<sup>3</sup>  $H_2$  and reported that the fermentative  $H_2$  production had a nearly equal feasibility to the fermentative ethanol production. However, none of these studies described the capital investment and plant operation in details.

In the present study, the economics of a two-step, fermentative  $H_2$  and  $CH_4$  production process was investigated. Various processes for  $H_2$  and  $CH_4$  production were reviewed and compared from an economic standpoint. A thermophilic TBR (100 m<sup>3</sup>) for fermenting glucose for  $H_2$  production under darkness was chosen as the first stage, and a thermophilic upflow anaerobic sludge blanket (UASB) reactor (700 m<sup>3</sup>) for conversion of the first-stage by-products to  $CH_4$  was selected as the second stage (Fig. 1). The capital and operating costs of the two-step process were estimated, and the unit cost of  $H_2$  production (\$/Nm<sup>3</sup>) was evaluated. Finally, the cost was compared with that of a single-step thermophilic TBR and with those of other  $H_2$  production processes.

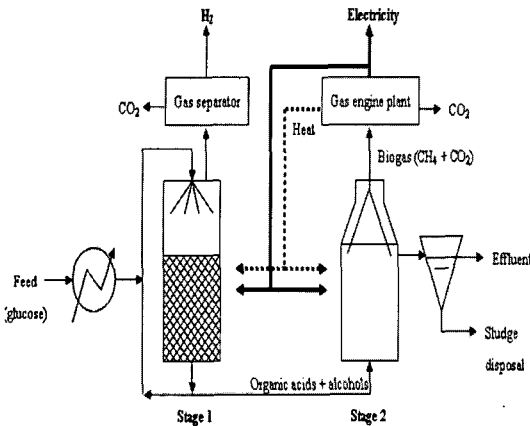


Fig. 1 Schematic diagram of a two-step biohydrogen/biomethane production process

## 2. Selection of bioreactors for two-step biohydrogen/biomethane production process

For the economical production of  $H_2$  and  $CH_4$ , proper bioreactor systems should be selected. Bioreactors can be divided into suspended and immobilized systems. Suspended systems, typically represented by a continuously stirred tank reactor (CSTR), are simple in configuration and easy to operate. However, when operated at a high dilution rate or fed with a toxic substance, the system becomes unstable and often results in the washout of the cells. The immobilized system uses a support matrix onto which biofilms are established. This system yields a higher volumetric production rate than the suspended one. In addition, it is more stable in the event of an abrupt change in operating conditions such as pH, temperature, or organic load, since the cells in the biofilms are generally harder to an external disturbance than planktonic free cells.

Table 1 summarizes selected  $H_2$ -production results from several continuous reactors.

Immobilized systems yield a several-times higher  $H_2$  production rate than suspended ones, although the yields for carbon sources are similar. Among the immobilized systems, the results by Rachman *et al.*<sup>12)</sup>, Chang *et al.*<sup>3)</sup>, and Kumar and Das<sup>6)</sup> on packed bed reactors are interesting since the production rates are very high, in the range of 1,188 to 1,814 mmol  $H_2/l \cdot d$ . However, in the cited studies, the operating period was short, less than 40 d, the reactor volume was small, less than 250 ml, and/or pure culture was used<sup>6,12)</sup>. This information is not sufficient for evaluating the reactor performance for long-term operation and scale-up. In comparison, a thermophilic TBR by Oh *et al.*<sup>11)</sup> and a UASB by Chang and Lin<sup>4)</sup> have been stably operated for long periods of more than 230 d. The TBR also exhibited a high  $H_2$  production rate (1,050 mmol  $H_2/l \cdot d$ ) and yield (1.1 mol  $H_2/mol$  glucose). Therefore, the thermophilic TBR was selected as the first stage for the purposes of further analysis in this study.

Bioreactors for  $CH_4$  production are summarized in Table 2. The UASB reactor with a conventional or expanded bed generally has been accepted as the most effective, and is the most widely used, in treating high-strength wastewater<sup>21,23,24)</sup>. This system employs sludge granules that contain spatially self-organized, microbial consortia of various acidogens and methanogens. For  $CH_4$  production, the granules can utilize not only sugars such as glucose, fructose, sucrose, starch, among others, but also  $H_2$  fermentation by-products such as ethanol, formate, acetate, propionate, succinate and other small organic acids<sup>25)</sup>. The UASB process can be operated at either thermophilic (45 - 65°C) or mesophilic (30 - 40°C) temperatures. The thermophilic UASB has a much higher metabolic rate than the mesophilic, allowing a higher COD

## 이단계 바이오 수소/메탄 생산공정의 경제성 평가

Table 1 Comparison of some selected continuous bioreactors for fermentative H<sub>2</sub> production

| System      | Reactor type<br>(Working vol., l)        | Microorganism                         | Support matrix               | Operating period (d) | HRT (h) | Carbon substrate | Volumetric H <sub>2</sub> production rate (mmol H <sub>2</sub> /l · d) | H <sub>2</sub> yield (mol H <sub>2</sub> /mol substrate) | Ref. |
|-------------|--|---------------------------------------|------------------------------|----------------------|---------|------------------|--|--|------|
| Immobilized | TBR (2)                                  | Mixed culture                         | Synthetic polymer            | 234                  | 2       | Glucose          | 1,050  | 1.1  | 11   |
|             | Packed-bed (3)                           | Mixed culture                         | Activated carbon             | 13                   | 1       | Sucrose          | 1,188 <sup>a</sup>   | 1.1 <sup>a</sup>   | 3    |
|             | Packed-bed (0.25)                        | <i>Enterobacter cloacae</i> IIT-BT 08 | Lignocellulosic agroresidues | > 40                 | 1.08    | Glucose          | 1,814  | nr   | 6    |
|             | Packed-bed (0.09)                        | <i>E. aerogenes</i> mutant AY-2       | None                         | 18                   | 1.49    | Glucose          | 1,392  | 1.1  | 12   |
|             | Packed-bed (0.075)                       | <i>E. aerogenes</i> strain HO-39      | Porous glass bead            | 8                    | 1       | Glucose          | 803 <sup>a</sup>   | 0.73   | 13   |
| Suspended   | UASB (3)                                 | Mixed culture                         | None                         | 230                  | 8       | Sucrose          | 271  | 1.5  | 4    |
|             | CSTR (4)                                 | Mixed culture                         | None                         | 100                  | 13.3    | Glucose          | 184 <sup>a</sup>   | 1.63   | 5    |
|             | CSTR (2.3)                               | Mixed culture                         | None                         | 62                   | 8.5     | Glucose          | 119 <sup>a</sup><br>(189) <sup>ab</sup>                                | 0.85<br>(1.43) <sup>b</sup>                              | 9    |
|             | Chemostat-type digester (4) <sup>c</sup> | Mixed culture                         | None                         | nr                   | 6       | Glucose          | 711  | 1.7  | 7    |
|             | Chemostat-type digester (1) <sup>d</sup> | Mixed culture                         | None                         | nr                   | 2       | Glucose          | 47 <sup>a</sup>  | nr   | 10   |
|             | Anaerobic sequential batch reactor (5)   | Mixed culture                         | None                         | nr                   | 4       | Sucrose          | 470  | 1.4  | 8    |

nr: Not reported.

<sup>a</sup> Estimated from experimental data of the reference.

<sup>b</sup> N<sub>2</sub> was continuously sparged at a flow rate of 110 ml/min.

<sup>c</sup> Completely mixed with produced biogas.

<sup>d</sup> Completely mixed by a liquid circulation pump.

Table 2 Comparison of some selected continuous bioreactors for fermentative CH<sub>4</sub> production

| System      | Reactor type        | Microorganism | Requirement for support matrix | HRT (h) | Input COD (kg COD/m <sup>3</sup> ) | Organic loading rate (kg COD/m <sup>3</sup> · d) | COD removal (%) | Ref. |
|-------------|---------------------|---------------|--------------------------------|---------|------------------------------------|--|-----------------|------|
| Immobilized | UASB (Mesophilic)   | Mixed culture | no                             | 4 - 12  | 5 - 15                             | 4 - 12   | 75 - 85         | 29   |
|             | UASB (Thermophilic) | Mixed culture | no                             | 1 - 12  | 3 - 30                             | 10 - 100   | 75 - 95         | 24   |
|             | Fixed bed           | Mixed culture | yes                            | 24 - 48 | 10 - 20                            | 1 - 5  | 75 - 85         | 29   |
|             | Expanded bed        | Mixed culture | yes                            | 5 - 10  | 5 - 10                             | 5 - 10   | 80 - 85         | 29   |
| Suspended   | CSTR                | Mixed culture | no                             | > 10 d  | 0.25 - 3                           | 0.25 - 3   |                 | 30   |
|             | Contact             | Mixed culture | no                             | 2 - 10  | 1.5 - 5                            | 0.5 - 2.5  | 75 - 90         | 29   |

removal rate at a shorter wastewater retention time<sup>26</sup>. For example, Uemura and Harada<sup>27</sup> have reported that, in a lab-scale (5.5 l) thermophilic UASB, the COD (chemical oxygen demand) removal efficiency was 96% at an organic loading rate of 87 kg COD/m<sup>3</sup> · d, using a sucrose-acetate mixture as a substrate. Ohtsuki *et al.*<sup>28</sup> reported that, for beer brewing wastewater, which usually

contains many recalcitrant compounds for biological degradation, a large-scale (1,400 l) two-stage UASB system showed a COD removal efficiency of 90 % at 30 kg COD/m<sup>3</sup> · d. Continuous operation of a thermophilic UASB reactor with the effluent of H<sub>2</sub> fermentation broth has yet to be reported, but the literature indicates that this system is the most appropriate for CH<sub>4</sub>

production. As a consequence, the thermophilic UASB reactor was selected as the second stage in this study.

### 3. Cost estimation of two-step biohydrogen/biomethane production process

Performance-efficiency and operating- cost estimations of the selected two-step biohydrogen/biomethane production process are shown in Tables 3 and 4. Glucose was selected as the model substrate in this study. Pure glucose is expensive and not usually used for energy production on a commercial scale. However, most of a biomass is converted into glucose before being utilized in many biological processes and some food wastewater such as those from coffee processing, palm oil mills or cannery distilleries<sup>31)</sup> can be used for this purpose. In the case of using wastewater, the cost of pretreating the biomass varies greatly depending on the source of the wastewater and pre-treatment methods, and thus is difficult to estimate. In this study, the cost of glucose and pre-treatment was not taken into account. This is not unreasonable, however, since the cost of wastewater treatment or the gate fee could compensate for the cost of the pre-treatment of a carbonaceous biomass in many circumstances<sup>32)</sup>.

The basis for the estimation, considering a relatively small-scale system that is to be fed by a locally available biomass, was 100 Nm<sup>3</sup> H<sub>2</sub>/h. The TBR was assumed to treat the wastewater at a rate of 1,200 m<sup>3</sup>/d for a glucose concentration of 21 kg/m<sup>3</sup><sup>11)</sup>. The operating conditions, H<sub>2</sub> production yield, and glucose removal efficiency of the large-scale TBR were assumed to be the same as those of the bench-scale TBR. Hydrogen from the TBR was assumed to be purified to

satisfy the specifications for fuel cell application using pressure swing adsorption. The capital costs of the thermo-bioreactor and H<sub>2</sub> recovery/purification were estimated based on the analyses by de Vrije and Claassen of a two-step process of hyper-thermophilic dark/photo biohydrogen production<sup>17)</sup>. The energy requirement necessary for operating the thermo-bioreactor and H<sub>2</sub> recovery/purification system was also estimated according to de Vrije and Claassen<sup>17)</sup>, even though it could be fully supplied from the second-stage CH<sub>4</sub> in the present two-stage process. Most H<sub>2</sub> fermentation processes generate microbial sludges, the disposal of which incurs cost. In the present process, however, the biomass generated in the first stage can be continuously treated in the subsequent CH<sub>4</sub> reactor, and thereby its disposal cost is nullified. This might also improve the performance of the UASB reactor by accelerating the acidogenesis of carbon sources transferred from the first stage without treatment<sup>33)</sup>. The cost for nutrients and other chemicals required for the H<sub>2</sub> fermentation was estimated according to Kaylen *et al.*<sup>34)</sup> The labor cost was assumed, according to Luccio *et al.*<sup>35)</sup>, to be 20 % of the total operating cost.

Maintenance and annualized capital requirements were estimated based on the analyses of a two-stage indirect biophotolysis process by Beneman<sup>36)</sup>. Insurance, taxes, and other indirect costs were included in the overall maintenance costs as 6 % of the capital cost. The annualized capital costs were assumed to be 19 % of the actual capital cost, which included actual capital charges (averaging returns on investments and interest payments on debt) and depreciation.

In the CH<sub>4</sub> plant, the CH<sub>4</sub> production yield was assumed as 0.35 Nm<sup>3</sup> CH<sub>4</sub>/kg COD<sup>37)</sup>. The COD

## 이단계 바이오 수소/메탄 생산공정의 경제성 평가

Table 3 Performance of two-step biohydrogen/ biomethane production process

| Item   | Unit                                    | Value               | Basis   |
|--|---|---------------------|---|
| <i>Feed</i>  |   |                     |   |
| · Flowrate   | m <sup>3</sup> /d                       | 1.2×10 <sup>3</sup> |   |
| · Glucose concentration                                      | kg/m <sup>3</sup>                       | 21                  |   |
| · Ambient temperature  | °C                                      | 20                  |   |
| <i>Performance of first-stage TBR<sup>a</sup></i>            |   |                     |   |
| · Glucose loading rate                                       | kg/m <sup>3</sup> · d                   | 250                 |   |
| · Hydraulic retention time                                   | h                                       | 2.0                 |   |
| · Reactor volume (V1)  | m <sup>3</sup>                          | 100                 |   |
| · Reactor temperature  | °C                                      | 60                  |   |
| · Glucose removal efficiency                                 | %                                       | 70                  |   |
| · Sludge production (annually)                               | kg VSS/yr                               | 0 <sup>b</sup>      |   |
| · H <sub>2</sub> production yield                            | mol H <sub>2</sub> /mol glucose         | 1.1                 |   |
| · H <sub>2</sub> production rate (daily)                     | Nm <sup>3</sup> /d                      | 2.4×10 <sup>3</sup> |   |
| · H <sub>2</sub> production rate (hourly, Q <sub>h</sub> )   | Nm <sup>3</sup> /h                      | 100                 |   |
| · H <sub>2</sub> production rate (annually, Q <sub>a</sub> ) | Nm <sup>3</sup> /yr                     | 8.8×10 <sup>5</sup> |   |
| <i>Performance of second-stage UASB</i>                      |   |                     |   |
| · Flowrate   | m <sup>3</sup> /d                       | 1.2×10 <sup>3</sup> |   |
| · Inlet COD concentration                                    | kg COD/m <sup>3</sup>                   | 18 <sup>c</sup>     |   |
| · Inlet COD loading rate                                     | kg COD/m <sup>3</sup> · d               | 31                  |   |
| · Hydraulic retention time                                   | h                                       | 14                  |   |
| · Reactor volume (V2)  | m <sup>3</sup>                          | 700                 |   |
| · Reactor temperature  | °C                                      | 55                  |   |
| · COD removal efficiency                                     | %                                       | 90                  |   |
| · COD, converted   | kg COD/d                                | 1.9104              |   |
| · Sludge production (annually)                               | kg VSS/yr                               | 1.0×10 <sup>6</sup> | 0.1 kg VSS/kg COD <sup>d</sup>  |
| · CH <sub>4</sub> production yield                           | Nm <sup>3</sup> CH <sub>4</sub> /kg COD | 0.35 <sup>e</sup>   |   |
| · CH <sub>4</sub> production rate                            | Nm <sup>3</sup> /d                      | 6.8×10 <sup>3</sup> |   |
| · CH <sub>4</sub> content                                    | %                                       | 60                  |   |
| · Biogas production rate                                     | Nm <sup>3</sup> /d                      | 1.1×10 <sup>4</sup> |   |
| · Biogas energy production (annually)                        | GJ/yr                                   | 1.0×10 <sup>5</sup> | 1 Nm <sup>3</sup> biogas = 0.026 GJ (lower heating value) <sup>f</sup>    |
| · Energy conversion efficiency of gas engine                 | %                                       | 35                  | 35%, electricity generation; 50%, heat generation; 15%, loss <sup>f</sup> |
| · Electricity generated by gas engine (annually)             | kWh/yr                                  | 1.0×10 <sup>7</sup> | GJ = 277.8 kWh  |
| · Electricity generated by gas engine (hourly, AH)           | kWh                                     | 1.2×10 <sup>3</sup> |   |

<sup>a</sup> Adopted from bench-scale experiments by Oh *et al.*<sup>11</sup>

<sup>b</sup> Under the assumption that the biomass, generated in the first stage, is continuously fed into the UASB reactor.

<sup>c</sup> Composed of biomass, residual glucose, and by-products from the first-stage TBR.

<sup>d</sup> From Oh *et al.*<sup>40</sup>

<sup>e</sup> From Speece<sup>37</sup>.

<sup>f</sup> From de Mes *et al.*<sup>20</sup>

Table 4 Cost estimation for two-step biohydrogen/ biomethane production process

| Item  | Unit                              | Value                | Basis  |
|---|-----------------------------------|----------------------|--|
| <i>Operating factor</i>                                 |                                   |                      |  |
| · Annual operating days                                 | d                                 | 365                  |  |
| <i>Capital and operating costs of first-stage TBR</i>   |                                   |                      |  |
| <i>Capital cost</i>                                     |                                   |                      |  |
| · Thermo-bioreactor with pumps                          | \$                                | 3.8×10 <sup>5</sup>  | \$1.5×10 <sup>6</sup> (V1/400 m <sup>3</sup> ) <sup>g</sup>                                |
| · H <sub>2</sub> recovery/purification                  | \$                                | 1.6×10 <sup>5</sup>  | \$7.0×10 <sup>5</sup> (Q <sub>h</sub> /430 Nm <sup>3</sup> H <sub>2</sub> /h) <sup>g</sup> |
| · 'Saran-Lock' packing                                  | \$                                | 2.0×10 <sup>4</sup>  | \$200/m <sup>3</sup> <sup>b</sup>  |
| · Total capital cost                                    | \$                                | 5.6×10 <sup>5</sup>  |  |
| <i>Annual operating costs</i>                           |                                   |                      |  |
| · Pre-treatment cost                                    | \$/yr                             | - <sup>c</sup>       |  |
| · Energy  | \$/yr                             | 0 <sup>d</sup>       |  |
| · Sludge disposal                                       | \$/yr                             | 0 <sup>e</sup>       |  |
| · Chemicals   | \$/yr                             | 4.8×10 <sup>4</sup>  | <sup>f</sup>   |
| · Labor   | \$/yr                             | 4.7×10 <sup>4</sup>  | 20% of total operating cost (I) <sup>g</sup>   |
| · Overall maintenance                                   | \$/yr                             | 3.4×10 <sup>4</sup>  | 6% of total capital cost <sup>h</sup>  |
| · Annualized capital costs                              | \$/yr                             | 1.1×10 <sup>5</sup>  | 19% of total capital cost <sup>h</sup>   |
| · Total operating costs (I)                             | \$/yr                             | 2.4×10 <sup>5</sup>  |  |
| · Unit cost of H <sub>2</sub> production                | \$/Nm <sup>3</sup> H <sub>2</sub> | 0.27                 | 1/Q <sub>a</sub>   |
| <i>Capital and operating costs of second-stage UASB</i> |                                   |                      |  |
| <i>Capital cost</i>                                     |                                   |                      |  |
| · Bioreactor unit                                       | \$                                | 2.3×10 <sup>5</sup>  | \$330/m <sup>3</sup> <sup>i</sup>  |
| · Gas engine plant                                      | \$                                | 8.4×10 <sup>5</sup>  | AH×\$700/kWh <sup>l</sup>  |
| · Total capital cost                                    | \$                                | 1.1×10 <sup>6</sup>  |  |
| <i>Annual operation costs</i>                           |                                   |                      |  |
| · Energy  | \$/yr                             | 0 <sup>d</sup>       |  |
| · Chemicals   | \$/yr                             | 4.5×10 <sup>4</sup>  | <sup>k</sup>   |
| · Labor   | \$/yr                             | 8.8×10 <sup>4</sup>  | 20% of total operating cost (III) <sup>g</sup>   |
| · Sludge disposal                                       | \$/yr                             | 4.0×10 <sup>4</sup>  | \$40/1,000 kg TSS <sup>l</sup>   |
| · Overall maintenance                                   | \$/yr                             | 6.4×10 <sup>4</sup>  | 6% of total capital cost <sup>h</sup>  |
| · Annualized capital costs                              | \$/yr                             | 2.0×10 <sup>5</sup>  | 19% of total capital cost <sup>h</sup>   |
| · Income from electricity sales (II)                    | \$/yr                             | -4.5×10 <sup>5</sup> | <sup>m</sup> -, Profit   |
| · Total operating costs (III)                           | \$/yr                             | 4.4×10 <sup>5</sup>  |  |
| · Total operating costs (IV) <sup>n</sup>               | \$/yr                             | -8.6×10 <sup>3</sup> | -, Profit: III - II  |
| <i>Operating costs of two-stage TBR/UASB system</i>     |                                   |                      |  |
| · Total operating costs (V)                             | \$/yr                             | 2.3×10 <sup>5</sup>  | I + IV   |
| · Unit cost of H <sub>2</sub> production                | \$/Nm <sup>3</sup> H <sub>2</sub> | 0.26                 | V/Q <sub>a</sub>   |

Nomenclature: V1, volume of first-stage TBR; Q<sub>h</sub>, H<sub>2</sub> production rate (hourly); and, AH, electricity (hourly) generated by gas engine.

<sup>a</sup> From de Vrije and Claassen<sup>17</sup> based on 1 EURO = \$1.16.

<sup>b</sup> Provided by Dokil Felt Industry, Ltd., Seoul, South Korea.

<sup>c</sup> Assumed zero. See the text.

<sup>d</sup> Supplied by energy (electricity and heat) from gas engine of second-stage CH<sub>4</sub> plant.

<sup>e</sup> Assumed that the biomass, generated in the first-stage, is continuously fed to the UASB bioreactor without treatment.

<sup>f</sup> Estimated based on the unit cost and amounts of nutrients and other chemicals required for production of ethanol from lignocellulosic

feedstocks (Kaylen *et al.*<sup>34</sup>).

<sup>a</sup> From Luccio *et al.*<sup>35</sup>

<sup>b</sup> From Benemann<sup>36</sup>.

<sup>c</sup> From van Haandel and Lettinga<sup>25</sup>.

<sup>d</sup> From 2002 brochure, Jenbacher AG, Jenbach, Austria (<http://www.jenbacher.com>).

<sup>e</sup> For pH neutralization only; based on the costanalysis for pH neutralization of anaerobic digester by Trout *et al.*<sup>39</sup>

<sup>f</sup> From Yoon *et al.*<sup>41</sup>

<sup>m</sup> (Electricity for sales) = (annual electricity generated by gas engine) (electricity consumption for the first stage and the second stage). It was assumed that the methanogenic plant consumes 31% of the electricity generated by gas engine (de Mes *et al.*<sup>20</sup>).

<sup>n</sup> Income from electricity sales was considered.

loading rate of 31 kg COD/m<sup>3</sup> · d was assumed to be treated by the second-stage UASB<sup>27,28</sup> because most CODs transferred from the first stage were easily biodegradable. Biogas produced in the UASB can be directly fed to a gas engine and used to generate electricity without further purification. It was assumed that the electricity produced would be partially used for operating the two-stage TBR/UASB plant, and the remainder was supplied to a public grid for sales without loss. The electricity charges for commercial and industrial uses are \$ 0.070/kWh and \$ 0.045/kWh, respectively<sup>38</sup>. In this study, the commercial charge was assumed for sales. The construction cost of a UASB reactor is dependent on volume, depth, type of separator, construction materials, and other factors. The capital cost for the UASB was estimated according to van Haandel and Lettinga<sup>25</sup>. The cost for the gas engine plant was estimated according to Jenbacher AG, Jenbach, Austria (<http://www.jenbacher.com>). It was assumed that no chemical except for pH neutralization was needed for CH<sub>4</sub> fermentation. The chemical cost (e.g. lime) was estimated based on the cost for pH neutralization of an anaerobic digester, as suggested by Trout *et al.*<sup>39</sup>. Other operating costs were estimated similarly to the case of the first-stage H<sub>2</sub> production plant.

The data summarized in Tables 3 and 4 show that the cost by the two-step process was estimated to be \$ 0.26/Nm<sup>3</sup> H<sub>2</sub>, which is equivalent to \$ 20/GJ (based on the upper combustion value). If biohydrogen were produced by a single-step thermophilic TBR process without the subsequent CH<sub>4</sub> fermentation, the cost would increase to \$ 0.37/Nm<sup>3</sup> H<sub>2</sub> (data not shown). Without the second-stage CH<sub>4</sub> reactor, savings in capital and operational costs are significant. However, less energy is recovered, and additional costs for treating the sludge and COD from the first-stage are incurred. The difference of \$ 0.11/Nm<sup>3</sup> H<sub>2</sub> indicates that the presence of the second stage is advantageous.

#### 4. Comparison of various H<sub>2</sub> production process

In Table 5, some data from the literature are summarized and compared with the present data according to H<sub>2</sub> production cost and net CO<sub>2</sub> emission. It was not easy to compare the current result with the others, since the economics are dependent on not only many direct factors (H<sub>2</sub> conversion efficiency, the H<sub>2</sub> production scale, the configuration and long-term stability of a system, and the utility of related facilities) but also indirect factors (labor cost, annualization of capital costs, overhead, licenses, civil works, etc.) that are site- and project-specific. Nonetheless, we noticed that the H<sub>2</sub> production cost by the present two-step or single-step process is comparable to that reported for most other H<sub>2</sub> production technologies except for the biophotolysis of water. In the latter case, the conversion efficiency of sunlight was assumed to be 10 %. This is far

## 이단계 바이오 수소/메탄 생산공정의 경제성 평가

Table 5 Comparison of H<sub>2</sub> production costs and net CO<sub>2</sub> emissions in small-scale production plants with capacity in the range of 20 - 1,500 Nm<sup>3</sup> H<sub>2</sub>/h<sup>a</sup>

| Production   | Assumed conversion efficiency       | Production cost (\$/Nm <sup>3</sup> H <sub>2</sub> ) | Net CO <sub>2</sub> -emission (kg/Nm <sup>3</sup> H <sub>2</sub> ) | Ref.          |
|--|-------------------------------------|--|--|---------------|
| Two-step biohydrogen/biomethane production process from glucose              | 1.1 mol H <sub>2</sub> /mol glucose | 0.26   | 0  | Present study |
| Single-step biohydrogen production process from glucose                      | 1.1 mol H <sub>2</sub> /mol glucose | 0.37   | 0  | Present study |
| Two-step dark/photo biohydrogen production process from biomass <sup>b</sup> | 3.2 mol H <sub>2</sub> /mol glucose | 0.29 <sup>f</sup>                                    | 0  | 17            |
| Single-step biohydrogen production process from sugar cane                   |                                     | 0.48 <sup>d</sup>                                    | 0  | 22            |
| Biophotolysis of water   | 10% <sup>e</sup>                    | 0.13 <sup>f</sup>                                    | 0  | 36            |
| Steam-reforming of natural gas   |                                     | 0.37 <sup>e</sup>                                    | 0.8  | 17            |
|  |                                     | 0.35-0.38  | nr   | 38            |
| Partial oxidation of oil   |                                     | 0.42   | nr   | 43            |
| Steam-reforming of biomethane  |                                     | 0.37 <sup>e</sup>                                    | 0  | 17            |
| Gasification of biomass  |                                     | 0.17   | 0  | 44            |
| Pyrolysis of biomass   |                                     | 0.17   | 0  | 44            |
| Electrolysis with conventional electricity                                   |                                     | 0.27 <sup>d</sup>                                    | 1.8  | 17            |
| Electrolysis with CO <sub>2</sub> -lean electricity                          |                                     | 0.31-0.42 <sup>e,g</sup>                             | 0  | 17            |
| Electrolysis with electricity from wind turbines                             |                                     | 0.29 <sup>e</sup>                                    | 0  | 17            |
| Electrolysis with electricity from photovoltaic cells                        |                                     | 3.42 <sup>e</sup>                                    | 0  | 17            |

nr: not reported.

<sup>a</sup> For large-scale H<sub>2</sub> production, >40,000 Nm<sup>3</sup> H<sub>2</sub>/h for biophotolysis of water and >30,000 Nm<sup>3</sup> H<sub>2</sub>/h for gasification of biomass.

<sup>b</sup> Based on zero substrate cost (acquisition of biomass and hydrolysis) and without personnel costs.

<sup>c</sup> Assumed 1 EURO = \$1.16.

<sup>d</sup> Assumed \$1 = 108¥ and 1 Nm<sup>3</sup> H<sub>2</sub> = 12.77×10<sup>3</sup> GJ (high heating value).

<sup>e</sup> Assumed that solar conversion efficiency of CO<sub>2</sub> fixation into storage products (glycogen or starch) is 10% and that the storage products are stoichiometrically converted to H<sub>2</sub> gas (e.g. 12 H<sub>2</sub>/mole of glucose).

<sup>f</sup> Assumed 1 Nm<sup>3</sup> H<sub>2</sub> = 12.77×10<sup>3</sup> GJ (high heating value).

<sup>g</sup> CO<sub>2</sub> is sequestered, rendering the process CO<sub>2</sub>-neutral.

more optimistic, considering that the current value in most experiments falls below 1 %<sup>42</sup>). For the small-scale H<sub>2</sub> production of 100 Nm<sup>3</sup> H<sub>2</sub>/h, the thermophilic TBR process combined with the auxiliary UASB reactor can be considered to be a potentially economical process in its present state.

The emission of CO<sub>2</sub> in H<sub>2</sub> production

processes is an important concern, since it is responsible for global warming<sup>2</sup>). As distinguished from the physicochemical methods in which natural gas or conventional electricity is used, biological methods yield no net CO<sub>2</sub> emission. Biological H<sub>2</sub> production also proceeds along with the production of CO<sub>2</sub>; however, this CO<sub>2</sub> has been previously immobilized from atmospheric CO<sub>2</sub> into the biomass<sup>17</sup>). As a consequence, the biological process is considered to be CO<sub>2</sub>-neutral.

The present analyses are based on the many data from the literature as well as our own assumptions. For more reliable analyses, extensive experiments on the proposed two-step biohydrogen/biomethane production process are required. First of all, a scale-up of the thermophilic TBR process should be conducted. Second, many assumptions on the performance of the combined H<sub>2</sub> and CH<sub>4</sub> production process should be verified. Especially, the rate and yield of biogas production along with the operational stability of the two-stage system should be confirmed. Third, depending on local legislation concerning standards of effluent quality, post-treatment might be required for removal of organics and other nutrients including nitrogen and phosphorus. In this case, the cost for such post-treatment facilities should be included in the economic analysis of the two-step process.

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