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# Sustainable and Enhanced Hydrogen Production from Biomass through Sulfur Redox Cycle using Georeactor

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## Keywords

Hydrogen production, biomass, sulfur redox cycle, hydrothermal condition, georeactor, geothermal

## ABSTRACT

This study proposes a new method of producing hydrogen which uses organic compounds as raw material and involves sulfur redox cycle, through utilization of georeactor as direct application of geothermal energy. This method consists of two sections of a cycle: (1) hydrogen production from an alkaline aqueous solution at subcritical conditions of water, where sulfide anions,  $\text{HS}^-$  and  $\text{S}^{2-}$  act as reducing agents of water, and (2) sulfide anions regeneration at much lower temperatures, where an organic compounds derived from biomasses act as reducing agents of oxidized sulfur-containing-compounds formed in the first section. Hydrogen production was observed at  $\geq 280$  °C and corresponding saturated vapor pressure in a 60 minutes reaction of sodium sulfide aqueous solution. Sulfide anions were able to be regenerated from the solution after hydrogen production at 300 °C, at  $\geq 60$  °C in a 10 minutes reaction, using glucose as the reducer. A hydrogen production through the sulfur redox cycle was also demonstrated by following procedure: 1<sup>st</sup> hydrogen production - sulfide anions regeneration - 2<sup>nd</sup> hydrogen production, where the hydrogen production and sulfide anions regeneration were conducted at 300 °C and 105 °C, respectively. Considering glucose as the raw material, results indicated that hydrogen production from 1 mol glucose was greater than that by hydrothermal gasification at much higher temperatures up to 500 °C.

## 1. Introduction

Hydrogen is known to be needed in chemical and petroleum industry in a large scale. It is also regarded as a promising clean energy source as well.

At present, many studies have been and being conducted to find effective methods for producing hydrogen by application of renewable resources. One of promising methods to produce hydrogen is through decomposition of organic compounds by utilization of hydrothermal condition,<sup>1-6</sup> which involves the application of water at elevated temperatures and pressures to achieve reaction in an aqueous medium. Hydrothermal reaction has been attracting worldwide attention because of the fascinating characteristics of water as reaction medium.<sup>7</sup>

Geothermal resources, which have been widely developed for many purposes; power generation, providing hot water to green houses, district heating and other facilities, could also constitute an energy source to support advances in hydrogen production technology. Hydrogen production method that is applicable by utilizing the concept of the georeactor<sup>8-11</sup>, which uses a geothermal drill hole as a reactor, is one of possible direct utilizations of geothermal energy.

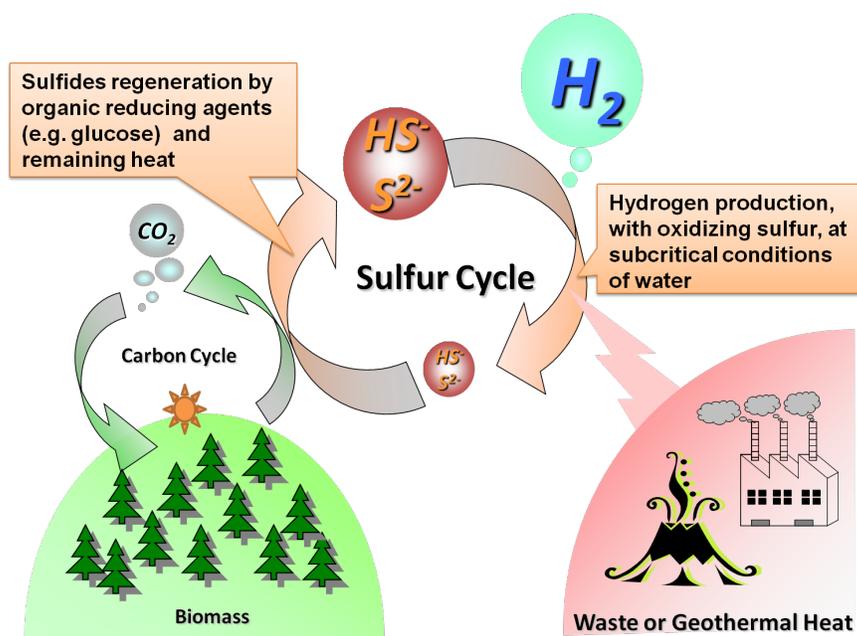


Figure 1. Hydrogen production from biomass through the sulfur redox cycle.

The present study proposes a sustainable hydrogen production from biomasses through a redox cycle of sulfur, which can utilize hydrothermal condition in geothermal field (Figure 1). This method consists of two sections of a cycles: (1) hydrogen production from an alkaline aqueous solution at subcritical conditions of water, where sulfide anions,  $\text{HS}^-$  and  $\text{S}^{2-}$  act as reducing agents of water ( $\text{S}^{2-}$  is used hereafter to represent both anions), and (2) sulfide anions regeneration at much lower temperatures, where an organic compounds derived from biomasses act as reducing agents of oxidized sulfur-containing-compounds formed in the first section. In this study, glucose is used as a model of the reducing agents from biomasses, as it is by far the most common carbohydrate which is classified as a monosaccharide, an aldohexose, and is a reducing sugar. Like other aldehydes, an aldose is easily oxidized to yield the corresponding polyhydroxy carboxylic acid (aldonic acid) or aldonate in alkaline conditions.

This experimental study presents fundamental findings of each section, demonstrates the possibility of the proposed hydrogen production, and evaluates the hydrogen yield in the hydrogen production by comparing it with the values in the hydrothermal gasification of biomasses at supercritical conditions of water.

## 2. Experimental

For the hydrogen production section, 1.2 g  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  was dissolved into 120 ml distilled water, and the solution was loaded into a Hastelloy C-22 autoclave with 200 ml volume. The autoclave equipped with a stirrer, a temperature controller, a pressure gauge and gas and liquid sampling valves. The solution loaded into the autoclave was then bubbled with  $\text{N}_2$  gas for 15 minutes to avoid sulfur oxidation by air. Reaction was started by elevating solution temperature to the predetermined value (250 °C, 280 °C, 300 °C and 320 °C). The solution was reacted for 60 minutes at the predetermined temperature and corresponding saturated vapor pressure, with stirring during entire reaction. For analysis, liquid and gas samples were collected after cooling down the reactor to around the room temperature.

For the sulfide anions regeneration section, D-glucose was used as a model of biomasses. The sulfide anions regeneration section was investigated by reacting 30 ml of the resulting solu-

tion in the hydrogen production at 300 °C, with 90 mg D-glucose, using a beaker glass equipped with a rubber cap. Reactions were conducted at 60 °C, 70 °C and 80 °C, and the atmospheric pressure for 10 min. To conduct reaction at the determined temperature, a hot magnetic stirrer equipped with a thermocouple was used. After 10 minutes reaction at the determined temperature, liquid sample was taken for analysis.

The hydrogen production through the sulfur redox cycle was investigated by coupling the above two experiments, with modified reaction condition for sulfide anions regeneration section as explained in results and discussion part.

Gas samples were analyzed for hydrogen by GC-TCD. Liquid samples were analyzed for sulfide anions ( $\text{S}^{2-}$ ) and sulfur oxyanions ( $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SO}_3^{2-}$ , and  $\text{SO}_4^{2-}$ ) by CE (Capillary Electrophoresis).

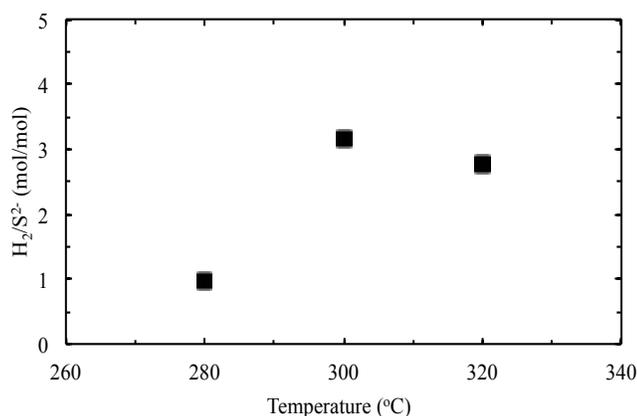
## 3. Results and Discussion

### 3.1 Hydrogen Production

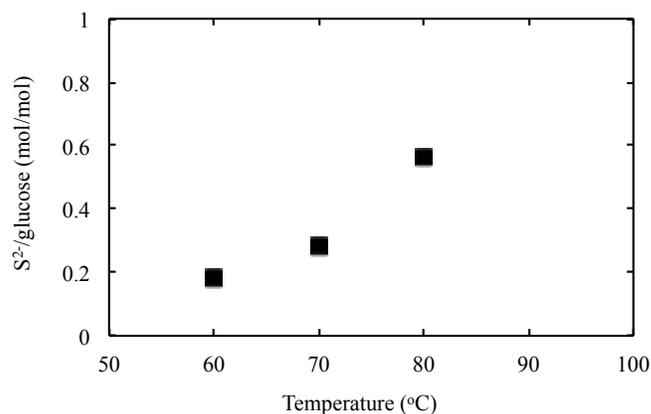
Hydrogen production and sulfide anions consumption increased with increasing reaction temperature. No hydrogen production was observed at 250 °C in the 60 minutes reaction. Produced hydrogen after 60 minutes reaction at 280 °C, 300 °C and 320 °C were 1.2 mmol, 6.3 mmol and 12.1 mmol respectively. Concentration change of sulfide anions after 60 minutes reaction at 280 °C, 300 °C and 320 °C were -10.1 mmol/L, -16.6 mmol/L and -36.5 mmol/L respectively.

Sulfur oxyanions,  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$ , were also formed during the reaction. Formations of  $\text{SO}_3^{2-}$  were observed with concentration of 0.3 mmol/L, 0.7 mmol/L and 1.5 mmol/L for reaction at 280 °C, 300 °C and 320 °C respectively. At 320 °C, presence of  $\text{SO}_4^{2-}$  was also detected with concentration of 0.2 mmol/L. However, sulfur balance could not be confirmed with sulfide anions oxidation only to these detected sulfur oxyanions. This may have been caused due to the limitation of the analysis method which could not detect polysulfide and polythionates.

The ratio of  $\text{H}_2$  production/ $\text{S}^{2-}$  consumption for reaction at 280 °C was approximately 1. While for both reaction at 300 °C and 320 °C, the ratio was about 3, which might indicate that same mechanism occurred, only with different reaction rate (Figure 2).



**Figure 2.** Relationship between the ratio of  $\text{H}_2$  production/  $\text{S}^{2-}$  consumption with the temperature.



**Figure 3.** Relationship between the ratio of regenerated  $\text{S}^{2-}$ /added glucose with the temperature.

### 3.2 Sulfide Anions Regeneration

At every given temperature (60 °C, 70 °C and 80 °C), sulfide anions were able to be regenerated from resulting solution of the 60 minutes hydrogen production experiment at 300 °C, by using glucose as the reducing agent of oxidized sulfur compounds. Increase in concentration of sulfide anions after 10 minutes reaction was 3.0 mmol/L, 4.7 mmol/L and 9.4 mmol/L for reaction at 60 °C, 70 °C and 80 °C respectively. Increase of sulfur oxyanions ( $S_2O_3^{2-}$ ,  $SO_3^{2-}$  and  $SO_4^{2-}$ ) were also detected, although only in small concentration (less than 1 mmol/L) which were significantly smaller than the concentration change of sulfide anions. Regarding the conduction of reaction in a glass beaker, these increments of sulfur oxyanions may have been caused by oxidation by air.

It was found that the ratio of regenerated  $S^{2-}$ /added glucose increased with increasing temperature (Figure 3). Maximum value in the temperature range was approximately 0.6 at 80 °C, while the complete regeneration of sulfide anions obtained if the ratio is 1. Considering trend of the result, complete regeneration was expected when increasing the temperature to around 100 °C.

### 3.3 Hydrogen Production Cycle

Previous result showed that temperature of above 80 °C was indicated to provide optimum condition for sulfide anions regeneration reaction. However, the decomposition (e.g. dehydration reaction) of glucose may start to occur at >90 °C.<sup>12</sup> Hence, it was important to employ a reaction condition that enabled increase in the ratio of regenerated  $S^{2-}$ /added glucose with minimized decomposition of glucose. In the attempt to fulfill such requirements, a hydrogen production from glucose through the sulfur redox cycle was examined as follows. The hydrogen production experiment was performed at 300 °C for 60 min (first hydrogen production). After that, considering the glucose decomposition at such temperature, reaction was performed by increasing the temperature up to 105 °C, then immediately cooled down. Finally, the hydrogen production at 300 °C for 60 min was performed using the solution which contained regenerated sulfide anions and organic compounds (second hydrogen production).

The  $H_2/S^{2-}$  ratio in the first hydrogen production was 2.8. Detected compounds in the resulting solution of first hydrogen production are as shown in Figure 4a. In the sulfide anions regeneration with the modified procedure, the ratio of regenerated  $S^{2-}$ /added glucose was approximately 0.9. This result showed that almost 1 mol sulfide anions could be regenerated by 1 mol glucose. Incomplete sulfide anions regeneration explained by the remaining sulfite and unknown compound in resulting solution after sulfide anions regeneration (Figure 4b).

In the second hydrogen production, the  $H_2/S^{2-}$  ratio was 2.5, only slightly different from the first hydrogen production. Detected compounds in the resulting solution of second hydrogen production (Figure 4c) also correspond to the compounds in the

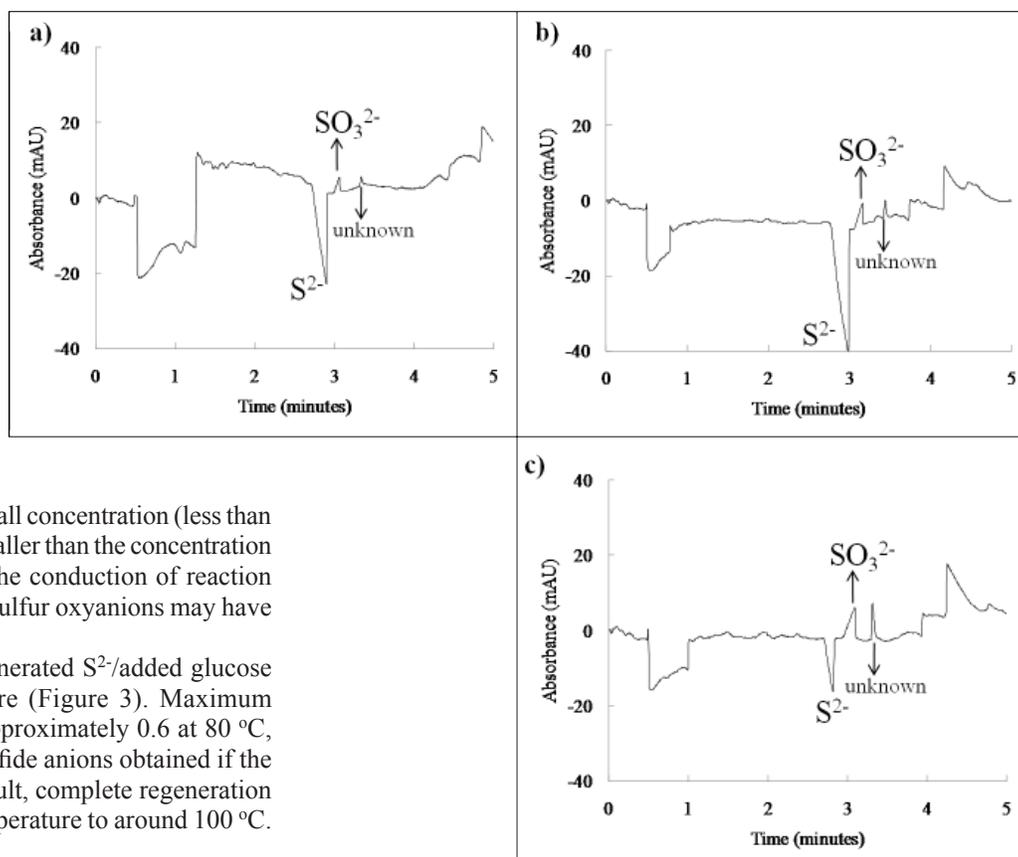
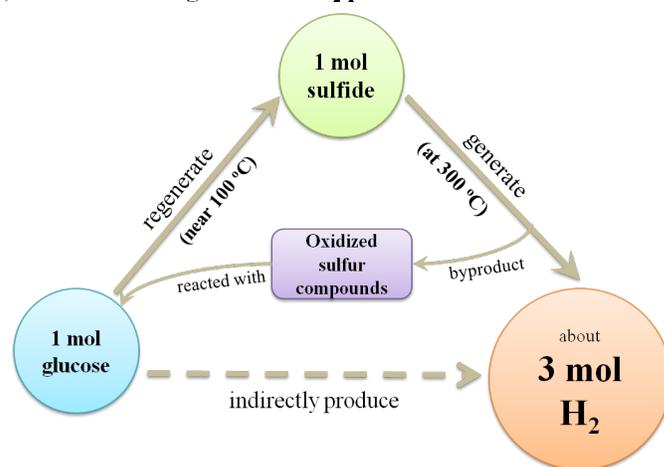


Figure 4. Electropherogram from liquid sample analysis a) after first hydrogen production b) after sulfide anions regeneration and c) after second hydrogen production.

#### a) Indirect use of glucose for $H_2$ production



#### b) Direct use of glucose for $H_2$ production

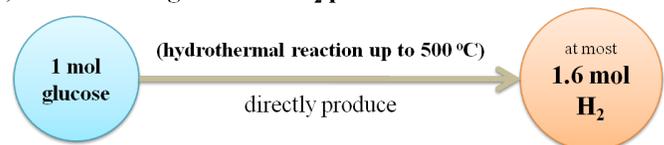


Figure 5. Hydrogen production through a) indirect use of glucose (proposed method in this study) and b) direct use of glucose.

first hydrogen production (Figure 4a), indicating the essentially same mechanism in both the first and second hydrogen production. This finding is significantly important since the solution containing organic compounds can be repeatedly used for the hydrogen production.

Based on the results of the present study, about 3 mol hydrogen is expected to be produced by consuming 1 mol sulfide anions at around 300 °C, and approximately 1 mol sulfide anions is expected to be regenerated by consuming 1 mol glucose at around 100 °C. The hydrogen yield in this hydrogen production is therefore about 3 mol hydrogen per 1 mol glucose at around 300 °C. A comparison of the hydrogen yields by some hydrothermal gasification methods was made in the literature,<sup>13</sup> and provided at most 1.6 mol hydrogen per 1 mol glucose at much higher temperatures up to 500 °C (Figure 5).

Although some details have not been clear, this result reveals that the proposed method produce significantly higher amount of hydrogen in much lower temperature, by the application of hydrothermal condition that can be obtained in geothermal field. Utilization of a closed-type georeactor is expected to be appropriate for this system. In a closed-type georeactor, there is no contact or mixture of substances inside georeactor with subsurface water, so that concentration of reacted compounds during reaction in the georeactor can be controlled. By using a georeactor, this hydrogen production method can be an environmentally friendly system. By the direct use of geothermal resource, the cost of energy for chemical reaction and material processing is expected to be low regarding the high efficiency for heat supply.

## Conclusions

Present results reveal that hydrogen can be produced at subcritical condition of water  $\geq 280$  °C, which is possible to be conducted in a georeactor as a direct use of geothermal energy. Sulfide anions were able to be regenerated from the solution after hydrothermal experiment, by reaction with glucose as reducing agent at 60-80 °C, in which the ratio of regenerated  $S^{2-}$ /added glucose increases with higher reaction temperature. On performing the sulfur redox cycle, sulfide anions regeneration reaction conducted by increasing temperature up to 105 °C then immediately cooled down, to ensure optimum reaction temperature and minimize glucose decomposition. Ratio of regenerated  $S^{2-}$ /added glucose by such procedure was almost 0.9. Present result demonstrated that hydrogen production from glucose through sulfur redox cycle was able to be carried out, with similar mechanism indicated for 1<sup>st</sup> and 2<sup>nd</sup> hydrogen production, and obtained higher hydrogen production than that by hydrothermal gasification of glucose at much higher temperatures up to 500 °C.

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