Suppression effect of various alkaline additives on hydrogen sulfide generated through hydrothermal reaction

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Abstract:
Development of new fuels, such as hydrogen is highly desirable. Our research group has reported that highly-pure hydrogen can be formed from various biowastes by decomposing them in the hydrothermal reaction field. However, when the biowastes containing heteroatoms, such as sulfur, nitrogen, halogens, are subjected to hydrothermal processes, a series of heteroatom compounds are formed that cause damage to the environment. A process to suppress the generation of hydrogen sulfide in hydrothermal reaction has been investigated with the addition of Na₂CO₃. The results indicate that addition of Na₂CO₃ did not suppress the release of CO₂ in the gas phase. However, addition of Ca(OH)₂ decreased the release of CO₂ in the gas phase as well as the generated hydrogen. Furthermore, the release of generated hydrogen sulfide to the gas phase was also suppressed.

Keywords: Hydrogen sulfide generation, Biomass, GC-MS, Hydrothermal reaction

1. INTRODUCTION
Development of alternative fuels to replace the fossil fuels is highly desirable since the depletion of fossil fuels is well insight. Hydrogen fuel is expected to be most promising alternative fuel because of its wide applications in a variety of energy systems, including fuel cells. Therefore, there has been increasing interest in developing highly effective process to generate hydrogen.

Previous efforts by our research group have shown that highly-pure hydrogen fuel can be formed from various biowastes by decomposing them in the hydrothermal reaction field [1]. However, when the biowastes containing heteroatoms, such as sulfur, nitrogen, halogens, etc., are subjected to hydrothermal processes, a series of heteroatom compounds are formed that can cause damage to the environment.

Our research has shown that the release of hydrogen sulfide in the gas phase was effectively suppressed by adding Na₂CO₃ through dissolution of hydrogen sulfide in the liquid phase and also via adsorption on the solid residue. But it appears that the amount of dissolution of hydrogen sulfide in liquid phase is more than that of adsorption of hydrogen sulfide on solid residue. The former was the major process for H₂S trapping.

In this work, heteroatom compounds formed through the hydrothermal reaction of biowastes has been analyzed with specific focus on hydrogen sulfide. Furthermore, the effect of addition of various alkaline on the formation of heteroatom compounds has been studied in detail.

2. EXPERIMENT
An amino acid L-cysteine, containing sulfur was used as a surrogate biomass sample (Fig.1). The hydrothermal reaction was performed in a stainless steel reactor (about 10 ml). About 80 mg of L-cysteine was placed in to the reactor with 5 ml of water and additives, Na₂CO₃ or Ca(OH)₂ (about 300mg). The reactor was introduced into the GC oven after the remaining air was purged by a N₂ flow (Fig.2).

The oven temperature was programmed up to 400 ℃ (@30 ℃/min), and then maintained at this temperature for about 50 min. The pressure was kept at about 26MPa throughout the reaction. After cooling down to a room temperature, the evolved gas and the liquid phase were analyzed with GC-MS, while the gas samples were analyzed with GC-TCD. The amount of hydrogen sulfide was determined from the peak area observed on the selected ion chromatograms for m/z 34, which corresponds to the molecular weight of hydrogen sulfide.
3. RESULT AND DISCUSSION

Fig. 3 Gases generated through the hydrothermal reaction without additive

Fig. 4 Gases generated through the hydrothermal reaction with Na$_2$CO$_3$

Fig. 5 Gases generated through the hydrothermal reaction with Ca(OH)$_2$

Figures 3, 4, and 5 show the gases generated through the hydrothermal reaction without additives, with Na$_2$CO$_3$ and with Ca(OH)$_2$, respectively. The results show larger amount of hydrogen was produced under conditions used in Fig. 4 than that in Fig. 3. This is because the equilibrium of the following reaction proceeds to the right by the trapping of CO$_2$ in the water.

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]

From our previous study, release of CO$_2$ to the gas phase could be suppressed with the addition of Na$_2$CO$_3$ (300mg). This was not the case from the results obtained in the present experiments. The dissolution of H$_2$S into water likely suppressed that of CO$_2$.

Figure 5 shows that the amount of H$_2$ gas generated decreases, and the release to gas phase of CO$_2$ decreases. This is because it is probably thought that CO$_2$ generated through hydrothermal reaction was changed to CaCO$_3$ from the reaction with Ca(OH)$_2$. So it is thought that in this case, the addition of Ca(OH)$_2$ is the better way than that of Na$_2$CO$_3$.

Fig. 6 Effect of additive on suppression of hydrogen sulfide in the gas phase

Figure 6 shows the amount of hydrogen sulfide obtained in gas phase in the presence of Na$_2$CO$_3$ and Ca(OH)$_2$ and without additives. In this figure, the amount of hydrogen sulfide in the gas phase decreased drastically by the addition of Na$_2$CO$_3$ and Ca(OH)$_2$. Thus, Ca(OH)$_2$ and Na$_2$CO$_3$ have almost the same ability for suppressing the release of hydrogen sulfide.

From this result, it is considered that the hydrogen sulfide will be dissolved into liquid phase and also trapped on solid residue.

Fig. 7 Hydrogen sulfide in the liquid phase

Figure 7 shows the amount of hydrogen sulfide trapped in the liquid phase in the presence of Na$_2$CO$_3$ and Ca(OH)$_2$ and without additives. As expected, the amount of hydrogen sulfide in the liquid phase increased with the addition of alkaline reagent. This figure suggests that the amount of hydrogen sulfide in the liquid phase with Na$_2$CO$_3$ is more than that with Ca(OH)$_2$ effectively suppressed by adsorption to solid residue, it is probably thought that hydrogen sulfide generated through the hydrothermal reaction was changed to CaS from the reaction with Ca(OH)$_2$.

4. CONCLUSIONS

By the addition of Ca(OH)$_2$, it was found that releases of CO$_2$ and hydrogen sulfide to the gas phase were decreased dramatically and that the amount of hydrogen sulfide in the liquid phase was also decreased.

REFERENCES

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