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Highly-Efficient Power Generation Utilizing Liquid-Solid Redox Reactions between Inorganic Media and Biomass/Low-Rank Coal

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Highlights

- A novel power generation method utilizing biomass or low-rank coal has been proposed.
- The proposed method utilizes redox reactions of inorganic media.
- Theoretical power generation efficiency of the proposed method is over 80%.
- Rates of reactions between inorganic media and biomass/low-rank coal were measured.

1. Introduction

An efficiency of power generation by biomass or brown coal utilizing a conventional boiler is as low as 10–20 %. This is mainly because chemical energy of biomass or brown coal is converted to thermal energy by combustion, which loses a lot of exergy [1], regardless of their low calorific value compared to natural gas and high-rank coal. Power generation combining gasification with a gas turbine (IGCC) is expected as a highly-efficient power generation technology. However, the gasification process generally requires a high temperature of more than 1000 °C, which limits the efficiency of biomass power generation to only about 30 % [2].

We have recently succeeded in preparing a carbon catalyst with nano-sized metal particles highly dispersed by carbonizing biomass or brown coal after impregnation with metal ions [3]. In the study we found the reduction temperature of metal ions could significantly be lowered by improving the contact situation between biomass or brown coal and metal ions. Such high ability to reduce metal ions of chemically active biomass or brown coal can be expected to be utilized for energy conversion. Then, we have proposed a novel method which can reduce exergy loss by converting biomass or low-rank coal to chemical energy and subsequently converting the chemical energy to electric power as conceptually shown in Figure 1.

In the proposed method, inorganic media in a liquid phase are reduced by biomass or low-rank coal. When the reduced inorganic media are electrochemically oxidized by air, electric power is generated. The oxidized media then recycled to the former reactor to be reduced again. Theoretical power generation efficiency of the proposed method can be estimated to be over 80 % when using redox reductions of VO^{2+} (V(IV)) to V^{3+} (V(III)), or Cu^{2+} to Cu. Even when an actual efficiency of the latter electrochemical oxidation is taken into account, the overall power generation efficiency can be expected to be more than 50 %. In this study we examined if the former reduction reaction of inorganic media by biomass or low-rank coal could proceed at as low as around 250 °C.

2. Methods

A cellulose, a main constituent of biomass, and a brown coal were used in this study. Aqueous solution of $VOSO_4$ or $CuSO_4$ was used as the inorganic medium in a liquid phase. H_2SO_4 was added only to the $VOSO_4$ aqueous solution.

A test tube made of Pyrex glass in

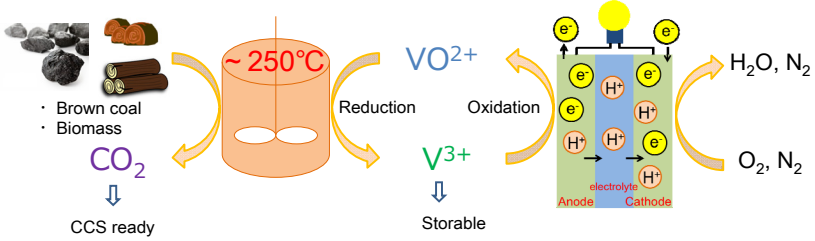

Figure 1. Concept of the proposed method.

which 36 mg of cellulose and 0.7 cm^3 of $VOSO_4$ or $CuSO_4$ solution (0.5–2.0 mol/L) were charged was placed in an autoclave made of stainless steel. After purging the inside of the autoclave with nitrogen gas, the autoclave was heated using a fluidized sand bath kept at 225–300 °C. After 15–60 min, the autoclave was taken out of the fluidized sand bath and immediately immersed into a water bath to terminate the reaction. After cooling down, the evolved gas was collected to a sampling bag and analyzed by gas chromatography. The aqueous phase separated from the solid residue by filtration was analyzed using UV-visible spectrophotometer for determining conversions of the inorganic media. The solid residue was dried at 70 °C for 2 h and characterized by XRD analysis.

3. Results and discussion

Figure 2 compares gas yields on carbon basis for the experiments at 225–300 °C with or without VO^{2+} (V(IV)). More CO_2 and CO were formed in the presence of VO^{2+} than in the absence of VO^{2+}, suggesting oxidation of cellulose proceeded in the presence of VO^{2+}. Figure 3 shows photos of solutions in test tubes before and after the reaction. The color of the solutions clearly changed from blue, the color of VO^{2+}, to green, the color of V^{3+} (V(III)), by the reaction. The reduction of V(IV) to V(III) was also confirmed by UV-visible spectra of the solution before and after the reaction as shown in Figure 4. Intensity of the peak at 780 nm attributed to VO^{2+} significantly decreased through the experiment while a peak at 390 nm attributed to V^{3+} appeared. These results suggest that cellulose could reduce V(IV) to V(III) at 225–300 °C while the cellulose was oxidized to CO_2. Although part of V^{3+} can precipitate as solid ($VOHSO_4$), which is unfavorable from the viewpoint of recycling of V^{3+} solution, it was shown that precipitation of the solid could be reduced to less than 0.6 mol% by properly selecting an initial concentration of each substance based on the solution theory. Similarly, the progress of reactions between Cu^{2+} and cellulose was also confirmed at around 250 °C.

Kinetic study showed reaction rates at 250 °C for the cellulose and the brown coal with VO^{2+} were respectively 20 times and 5 times greater than that for a bituminous coal, suggesting that such highly-reactive low-grade carbonaceous resources are more suitable for the proposed process.

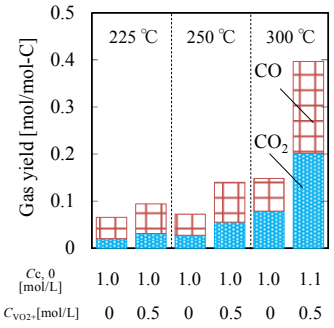

Figure 2. Gas yields.

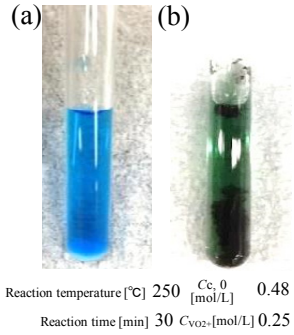

Figure 3. Photos of solutions.

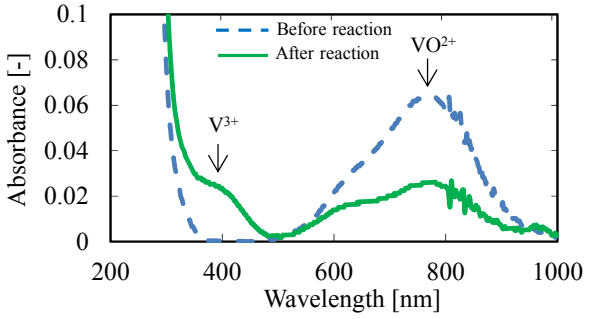

Figure 4. UV-visible spectra of solutions.

4. Conclusions

We have proposed a novel method of highly-efficient power generation by biomass or low-rank coal utilizing redox reactions of liquid phase inorganic media. It was confirmed that the reduction of candidate inorganic media, VO^{2+} and Cu^{2+}, by biomass or low-rank coal well proceeded at as low as around 250 °C, suggesting the possibility of utilizing these media in the proposed method.

References

[1] A.Tsutsumi, Kagakukougaku 77(3), (2013) 19–24.
[2] K. Ichikawa, *et al.*, CRIEPI Research Report (2011) M10022.
[3] K. Fukuoka, *et al.*, The 26th International Symposium on Chemical Engineering (26th ISChE) (2013) OE-28.

Keywords
highly-efficient power generation; redox reactions; biomass; low-rank coal