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SUBCRITICAL STEAM GASIFICATION OF ORGANIC WASTES UNDER THE PRESENCE OF Ca-BASED CO₂ SORBENTS

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ABSTRACT

To develop a new hydrogen production process of "HyPr-RING" by gasification reaction between steam and coal with calcium based sorbent to capture CO₂ under the high pressure and temperature condition, we have investigated the possibility to apply the concept of HyPr-RING to hydrogen production from high volatile fuels such as biomass and sewage sludge. It would be so important to understand the kinetic mechanism of this gasification reaction with rapid devolatilization. Therefore we focused on the initial stage reaction when using high volatile fuel such as dried sewage sludge and non-volatile fuel as coal char. A mixture of such fuel, water and Ca(OH)₂ was charged into a micro reactor made of SUS-316 with the inside volume of 7.2 cm³. The reactor was put into a fluidized sand bath and rapidly heated to the subcritical steam condition (973 K and 19.8 MPa) to simulate the real heating rate of fuel particles. Gaseous product and solid residue after the gasification were analyzed. In the initial devolatilization within 5 min, some extent of carbon in fuel was rapidly decomposed and converted to gases such as H₂, CH₄ and C₂H₆ and tar. The conversion rate of residual carbon after 5 min was rapidly decreased, which was related to the reaction rate of residual or produced char and steam to produce hydrogen. CH₄ and C₂H₆ in this second stage were gradually produced from tar.

KEYWORDS

Hydrogen, Subcritical steam gasification, Coal, CO₂ sorbent, Sewage sludge

INTRODUCTION

To solve the depletion problem of fossil fuel resources and the global environmental issues, clean utilization of unused carbonaceous resources such as biomass and organic wastes as well as low-rank coal should be promoted. In the energy production from the organic resources and its use, it should be required to minimize CO₂ emissions. On the other hand, to establish a new social system with clean and efficient energy system as hydrogen based fuel cell, stable supply of hydrogen will be an important problem. Steam gasification of fossil fuel is one of the key technologies for hydrogen production.

The HyPr-RING (Hydrogen Production by Reaction Integrated Novel Gasification) method, which gasifies organic matter with high temperature and high pressure steam

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with calcium-based CO₂ sorbents, has been proposed¹⁾.

Figure 1 shows the concept of HyPr-RING method. Almost all organic resources such as coal, biomass, plastics and sewage sludge can be adapted for HyPr-RING method. Water is used as a reaction medium and H₂ and CaCO₃ are mainly obtained as final products. In the gaseous product, basically, no hetero compounds of nitrogen, sulfur and chlorine and toxic heavy metals exist. It might be captured by water and CO₂ sorbent. H₂ as a clean fuel will be used for a fuel cell and a hydrogen turbine. On the other hand, when CaCO₃ is regenerated to CaO by calcinations, CO₂ can be collected in high concentration.

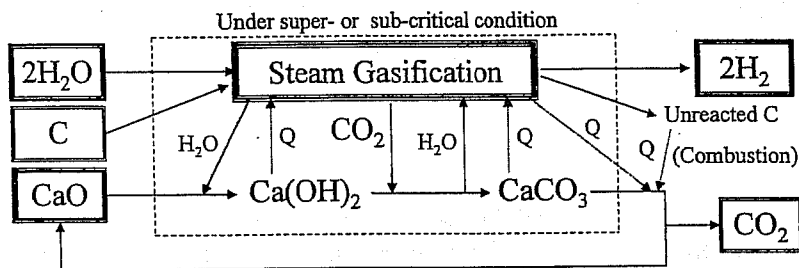
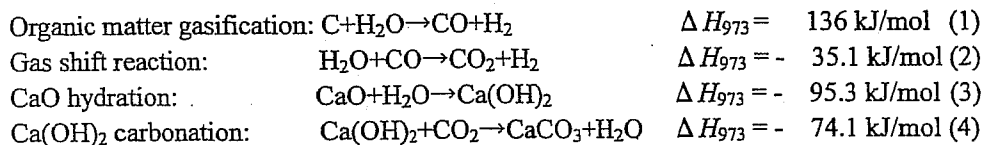


Fig. 1 Concept of HyPr-RING method.

Possible reactions related to Fig.1 are as follows:



CO₂ sorption by calcium compound produces reaction heat, which compensates for the reaction heat required for Eq. (1). The overall stoichiometric reaction can be written by combining Eqs. (1) to (4) as follows:



EXPERIMENTAL

In the present study, pulverized Taiheiy-coal char, raw Taiheiy-coal and dried sludge were gasified with steam in the presence of Ca(OH)₂ under the temperature of 973 K and the relatively high pressure of 20 MPa (subcritical condition) using a tubing-bomb micro-reactor (TB reactor). Then, the characteristics of the transient conversion of each organic matter and the composition of gaseous products during the reaction were experimentally examined.

Experimental Apparatus

Figure 2 shows experimental apparatus used in the present study.

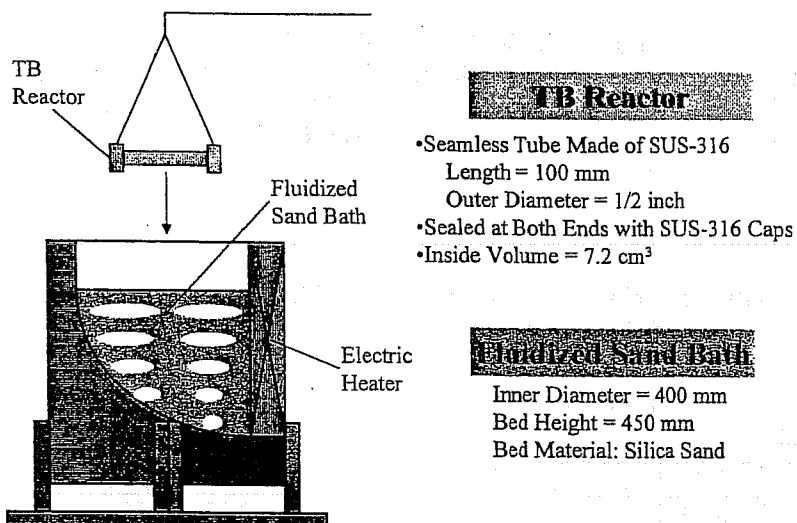


Fig. 2 Diagram of experimental apparatus.

A TB reactor was used to investigate steam gasification of organic matters with a CO₂ sorbent under high pressure with relatively rapid heating rates. The TB reactor was a seamless tube of 100 mm long and with an outer diameter of 1/2 inch, which was made of SUS-316 stainless steel and sealed at both ends with SUS-316 caps. This tube, which has a volume of 7.2 cm³, was used as an airtight micro reactor. The TB reactor was externally heated to the desired temperatures with a fluidized sand-bath heater (Inner diameter is 400 mm, bed height is 450 mm, and bed material is silica sand).

Experimental Procedure

A mixture of fuel of Taiheiyo-coal char, raw Taiheiyo-coal or dried sludge and distilled water together with reagent grade Ca(OH)₂ was charged with nitrogen into the TB reactor. The TB reactor was put into the fluidized sand bath at 973 K and was heated. Mixing ratio of organic samples, sorbent and water are shown in Table 1.

Table 1 Mixing ratio of organic samples, sorbent and water.

	Organic matter	Ca(OH) ₂	Water	H ₂ O/C	Ca/C
Taiheiyo-coal char	0.059 g	0.350 g	0.350 cm ³	5.88 mol/mol	1.43 mol/mol
Raw Taiheiyo-coal	0.060 g				
Dried sludge	0.101 g				

It was already confirmed in our previous work²⁾ that the heating rate was approximately 330 K/min when using the TB reactor of lower heat capacity, and it took about 2 min to reach the desired temperature. It was also confirmed that the measurement values of temperature and pressure in the reactor agrees well with the calculation values by the sand bath temperature and the water amount in the reactor. After a desired soaking time, the reactor was rapidly picked up from the sand bath, and it was rapidly cooled down to room temperature with water to quench the reaction. Gaseous product was collected through the water substitution method²⁾ and the volume of collected gas was measured with a

measuring cylinder. Concentrations of H₂, O₂, N₂, CH₄, CO, CO₂, C₂H₄ and C₂H₆ were analyzed with TCD-GCs (the Aera M200 Microsensor Gas Analyzer (1) MS-5A and PPQ columns with Ar carrier gas, (2) a PPU column with He carrier gas). Residual solids collected were subjected to thermogravimetric analysis (TGA) to measure the amounts of residual Ca(OH)₂, CaCO₃ and carbon²⁾.

Sample

The chemical properties of Taiheiyo-coal char less than 125 μm, raw Taiheiyo-coal between 25 and 73 μm and dried sludge between 53 and 125 μm are shown in Table 2.

Table 2 Proximate and ultimate analyses of organic samples.

	Proximate analysis (dry) [wt%]				Ultimate analysis (daf) [wt%]			
	VM	FC	Ash	Moist.	C	H	N	O, S (dif.)
Char	2.34	76.00	21.66	2.00	86.44	0.60	2.57	10.39
Coal	51.30	40.80	7.90	5.08	71.50	6.10	1.10	18.50
Sludge	68.02	10.61	21.37	5.67	49.66	7.15	3.94	39.25

Taiheiyo-coal char in this table was made by pyrolyzed raw Taiheiyo-coal at 873K for 2 hours in N₂ flow. The reagent grade Ca(OH)₂ (Nacalai tesque, Kyoto, Japan) was used as CO₂ sorbent.

RESULTS AND DISCUSSION

Change of Residual Carbon in Solid Residue with Soaking Time

Changes of residual carbon in three kinds of fuel with soaking time are shown in Fig. 3. This carbon balance was obtained from TGA of solid residues.

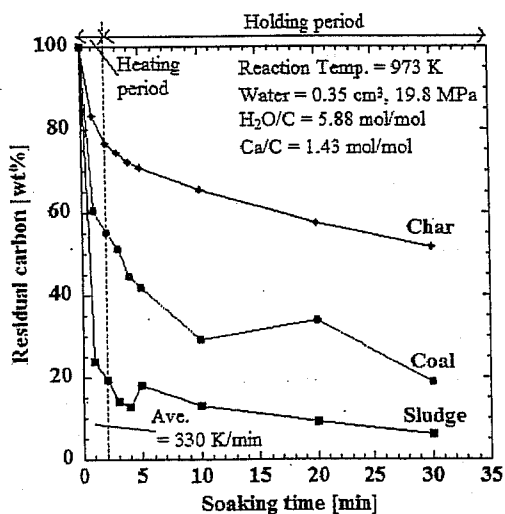


Fig. 3 Change of residual carbon in solid residue with soaking time.

In the case of Taiheiyo-coal char, 17 wt% of carbon was converted to gas or tar within 1 min, and then carbon was monotonously decreased with time.

On the other hand, 39 and 76 wt% of carbon for raw Taiheiyo-coal and dried sludge was respectively consumed during the heating period within 1 min, which might be due to the devolatilization. These rapid decreases were continued for the next 4 minutes. Then, slow consumptions of carbon are seen after 5 min. The rates of carbon consumption are similar to the rate for the char of coal. Thus, also in the subcritical steam condition, there is two reaction stage of thermal decomposition of volatile matter and char gasification. The gasification rate of char by steam is slower than the pyrolysis rate of volatile matter.

Change of Gases Produced from Organic Samples with Soaking Time

From the results of gas analysis, it was found that the amounts of gaseous products for each fuel of Taiheiyo-coal char, raw Taiheiyo-coal and dried sludge are plotted as a function of soaking time in Fig. 4.

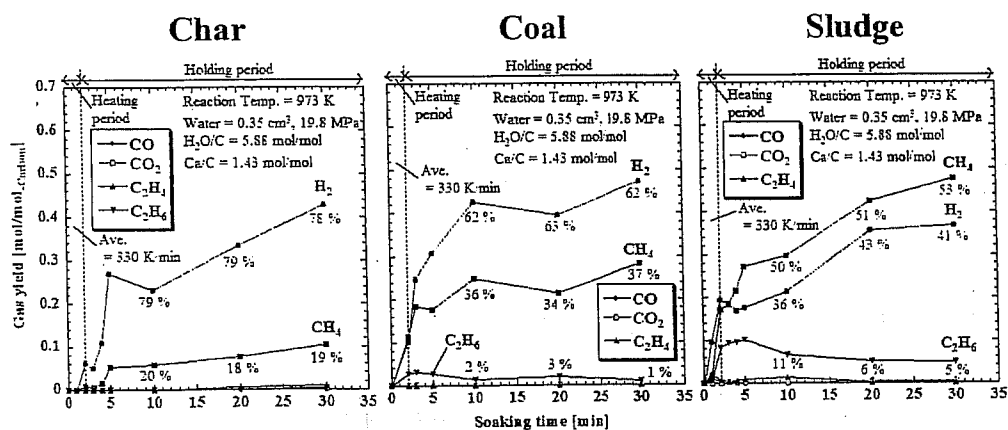


Fig. 4 Changes of gaseous products from each fuel with soaking time.

For the char, H₂ and CH₄ are mainly produced, and the yields are increased with time. The rate of CH₄ production is lower than that of H₂. The molar ratio of H₂ to CH₄ at 30 min is about 4.1, which mostly equals to the equilibrium composition of H₂ and CH₄ for the present experimental condition. In addition, CO₂ yield is significantly low, which suggests that Ca-based sorbent completely captured CO₂ during the gasification. CH₄ yields seem to be slowly increased even in the char gasification stage after 5 min, which suggests a possibility of the following reaction³⁾:



For the raw coal including volatile content, a little C₂H₆ in addition to H₂ and CH₄ is produced. In the initial stage of pyrolysis within 5 min, H₂ yield is similar to that for the char and CH₄ yield is considerably higher than that for the char. This suggests that CH₄ and C₂H₆ are produced mainly in the initial stage and that H₂ is produced in the reaction of subcritical steam gasification with char. Focusing on the second stage of char gasification after 5 min, the formation rates of H₂ and CH₄ from the coal are almost same to those from the char. This means that the higher yield of CH₄ from the coal can be determined by the

CH₄ yield in the initial stage. C₂H₆ seems to be slowly decreased after 3 min.

For the sludge with high volatile content and low char content, H₂ yield should be low comparing with the other fuels and CH₄ and C₂H₆ should be high. The reality of the above prediction can be clear from the result for the sludge in Fig. 6. Since C₂H₆ is decreased with time in the beginning of the second stage, tar produced in the initial stage is thermally decomposed or gasified gradually to CH₄. It results in that a higher formation rate of CH₄ as well as H₂ for the sludge is kept in the second stage. However, the initial stage including heating period is important to decide which of H₂ and CH₄ is predominant. The contribution is a third to a half in comparison of yields of the initial stage at 5 min and the second stage at 30 min. If both formation rates in the second stage could be unchanged, the formation rates in the initial stage would be improved even when applying to low volatile fuel. Another reason is why conversion of the produced CH₄ into H₂ is difficult in the present condition. If the above data are correct, CH₄ formation in the second stage could be controlled and H₂ formation would be promoted.

CONCLUSIONS

In order to understand the kinetic mechanism of the initial stage of pyrolysis and the second stage of char gasification for the HyPr-RING process, we investigated the contribution of volatile contents and char on hydrogen production by using raw coal, coal char and dried sludge with high volatiles. Consequently, we obtained the following conclusions:

- (1) Carbon in organic matter is decreased with time by devolatilization and tar production even during rapid heating, and the amount decreased depends on the volatile matter content in organic matter. The rate in the initial stage is high. In the second stage after pyrolysis, the gasification reaction between char and subcritical steam is predominant and the rate is low.
- (2) In the initial stage of pyrolysis, yields of CH₄ and tar produced depend to the volatile matter content in organic matter. Tar produced in the devolatilization is thermally decomposed or gasified gradually to CH₄.
- (3) In subcritical steam gasification of char, H₂ is mainly produced and the molar ratio of H₂ to CH₄ at 30 min mostly equals to the equilibrium composition of H₂ and CH₄ for the present experimental condition.

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