KINETICS, CATALYSIS, AND REACTION ENGINEERING

Gasification of Organic Waste with Subcritical Steam under the Presence of a Calcium-Based Carbon Dioxide Sorbent

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"HyPr-RING" is a new H_2 production process using carbonaceous fuels in which the fuel is reacted with subcritical steam and a calcium-based CO_2 sorbent. We investigated the applicability of this process to organic matter by examining the performance of the process with fuels of differing volatility. The gasification rate and relative contributions of the volatile and "char" components to H_2 production were investigated by using dried sewage sludge with a high volatile component concentration, coal with an intermediate volatile component concentration, and coal char with a low volatile component concentration. During the initial thermal decomposition, carbon in the fuels rapidly decreased with time and was converted to carbonaceous gas of CH_4 and C_2H_6 in addition to H_2. The amount of the decrease depended on the volatile content in the fuels. Following this initial rapid stage, the residual carbon appeared to become charlike, even for the high volatile content fuel. The gasification rate became slow, and the gasification shifted to favor H_2 production in a molar ratio of H_2 to CH_4 that approximated the equilibrium composition for a char and steam reaction. NaOH catalytically promoted H_2 production even for the sludge.

1. Introduction

From the viewpoint of depletion of fossil fuel resources and 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 production of energy from the organic resources, minimization of CO_2 emissions should be required.

On the other hand, to establish a new social system with clean and efficient energy, such as H_2-based fuel cells, a stable supply of H_2 will be an important issue. Steam gasification of fossil fuel, biomass, or organic wastes is one of the key technologies for H_2 production. However, in conventional steam gasification, a synthesis gas including H_2, CO, and CO_2 is produced.[1−4] As a consequence, some purification steps such as a CO shift and CO_2 separation are required.
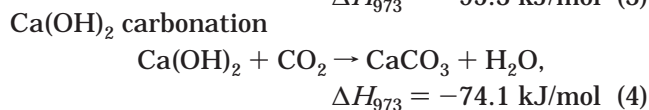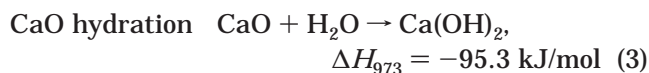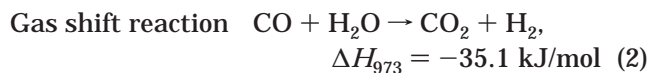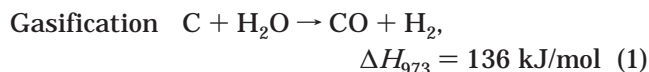
The HyPr-RING (H_2 production by reaction-integrated novel gasification) method, which gasifies organic matter with high-temperature and high-pressure steam under the presence of a calcium-based CO_2 sorbent, has

been proposed.[5−7] It is currently being developed with a continuous bench-scale unit with a fluidized-bed reactor.

Figure 1 shows the concept of the HyPr-RING method. Almost all organic resources such as coal, biomass, plastics, and sewage sludge can be adapted for the HyPr-RING method. Because water is used as a reaction medium and material, there is no requirement for the wet fuels to be dry. H_2 and $CaCO_3$ are the primary final products. There is no admixture of compounds of nitrogen, sulfur, and less toxic metals in the gas product. Such elements are captured by CO_2 sorbent and residual char or remained in ash in the HyPr-RING process.[6] H_2 is used in a fuel cell and/or a H_2 turbine. On the other hand, $CaCO_3$ can be regenerated to CaO by calcinations, while a high-concentration stream of CO_2 is generated.

The reactions in a reactor are as follows:

Gasification $\quad C + H_2O \rightarrow CO + H_2,$
$$\Delta H_{973} = 136 \text{ kJ/mol} \quad (1)$$

Gas shift reaction $\quad CO + H_2O \rightarrow CO_2 + H_2,$
$$\Delta H_{973} = -35.1 \text{ kJ/mol} \quad (2)$$

CaO hydration $\quad CaO + H_2O \rightarrow Ca(OH)_2,$
$$\Delta H_{973} = -95.3 \text{ kJ/mol} \quad (3)$$

Ca(OH)$_2$ carbonation
$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O,$$
$$\Delta H_{973} = -74.1 \text{ kJ/mol} \quad (4)$$

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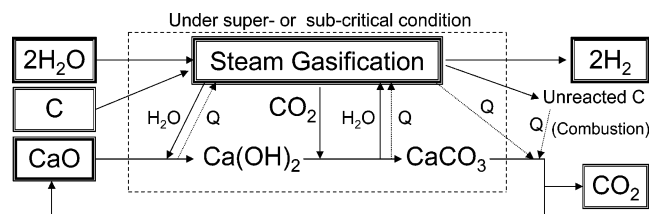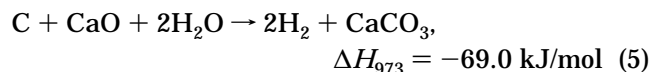**Figure 1.** Concept of the proposed H_2 production method (HyPr-RING method).

The CO_2 sorption by calcium compounds produces enthalpy, which compensates for the enthalpy required for eq 1. The overall stoichiometric reaction can be written by combining eqs 1−4 as follows:

$$C + CaO + 2H_2O \rightarrow 2H_2 + CaCO_3,$$
$$\Delta H_{973} = -69.0 \text{ kJ/mol} \quad (5)$$

According to the thermodynamic analysis, high-pressure conditions will be required to achieve the organic matter gasification with steam and the efficient sorption of CO_2 by $Ca(OH)_2$ simultaneously in a reactor. Lin et al.[5,6] carried out the supercritical steam gasification of various carbonaceous resources as well as coal under a wide range of pressures (>20 MPa) and temperatures (>923 K) using an autoclave with relatively low heating and cooling rates (about 20 K/min). They added an alkaline catalyst (NaOH) as well as $Ca(OH)_2$ to the mixture of organic matter and water and then obtained high carbon conversion (about 90%) with a high yield of H_2 in the product gas (about 80 vol %) and a low yield of CO_2 for raw Taiheiyo coal (Japanese sub-bituminous coal) at 973 K and 60 MPa. Although those results showed a very high performance of the HyPr-RING, it was obtained by using a "slow-heating" autoclave. The particles of organic matter undergo rapid heating in conventional reactors such as a fluidized-bed reactor after they are fed into the reactor.

Therefore, we focused on the initial stage of the HyPr−RING reaction and kinetically studied the characteristics of steam gasification of organic matter with $Ca(OH)_2$. In the present study, pulverized raw Taiheiyo coal, Taiheiyo coal char, and dried sewage sludge were gasified with steam in the presence of $Ca(OH)_2$ at a temperature of 973 K and a high pressure of 20 MPa (subcritical conditions) using a tubing-bomb (TB) reactor. The characteristics of the conversion of the organic matter and the composition of gaseous products formed during the gasification were experimentally investigated.

2. Experimental Section

2.1. Experimental Apparatus. Figure 2 shows the experimental apparatus used in the present study. A TB reactor was used to investigate steam gasification of organic matter with a CO_2 sorbent under high pressure with relatively rapid heating rates. The TB reactor was a seamless tube (100 mm long with an outer diameter of $^1/_2$ in.) made of stainless steel (SUS-316) and sealed at both ends with SUS-316 caps. The reactor had
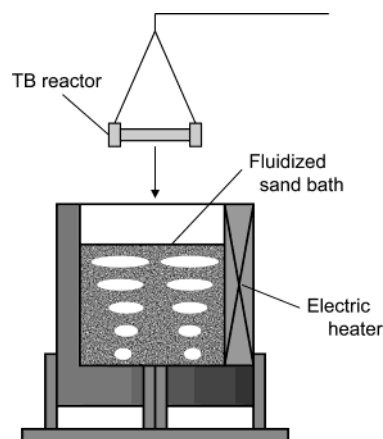

Figure 2. Diagram of the experimental apparatus used in the present study.

a volume of 7.2 cm³. It was externally heated to a given temperature with a fluidized sand-bath heater (inner diameter of 400 mm, bed height of 450 mm, and bed material of silica sand).

2.2. Experimental Procedure. Under ambient conditions and a nitrogen atmosphere, the TB reactor was loaded with a mixture of the organic sample (raw Taiheiyo coal, Taiheiyo coal char, or dried sludge), distilled water, and reagent-grade $Ca(OH)_2$ prior to being sealed. The TB reactor was then soaked in the fluidized sand bath at a temperature of about 973 K. Table 1 shows the mixing ratios of organic matter, sorbent, and water used. As confirmed in our previous work,[8] which used a similar TB reactor, the TB reactor has a considerably lower heat capacity than that of the conventional autoclaves and thus allows much more rapid heating. The average heating rate is approximately 330 K/min. It takes about 3 min to reach the desired temperature under the present experimental conditions. The temperature in the reactor was confirmed to be almost the same as that of the sand bath in a separate measurement using a type-K thermocouple. The target pressure in the reactor was calculated based on the reactor volume, water quantity, and practical gasification temperature and also confirmed by a separate measurement using a pressure transducer. When a reaction that increases the number of moles of gas, such as $Ca(OH)_2 + H_2O + C \rightarrow CaCO_3 + 2H_2$, takes place, the pressure should continue to rise until the carbon is depleted. However, because the H_2O/C ratio is about 6 in this experiment, the pressure rise due to H_2 production is expected to be relatively small. Thermodynamic equilibrium calculations show the pressure increase is only 10−20%. Consequently, the effect of this pressure change should have relatively little impact on the composition of product gases.

After a desired soaking time, the reactor was rapidly removed from the sand bath and cooled to room temperature with water in order to quench the reaction. After gaseous products were collected through the water substitution method,[8] the volume of collected gaseous products was measured with a graduated cylinder. Then, the concentrations of H_2, O_2, N_2, CH_4, CO, CO_2,

Table 1. Mixing Ratios of Organic Matter, Sorbent, and Water Used

organic matter	$Ca(OH)_2$	water	H_2O/C	Ca/C
Taiheiyo coal char: 0.059 g raw Taiheiyo coal: 0.060 g dried sludge: 0.101 g	0.350 g	0.350 cm³	5.88 mol/mol	1.43 mol/mol

Table 2. Proximate and Ultimate Analyses of Organic Samples Used

	proximate analysis [wt %, dry basis]				ultimate analysis [wt %, dry ash-free basis]		
sample	volatile matter	fixed carbon	ash	moisture	C	H	N
coal char	2.34	76.00	21.66	2.00	86.44	0.60	2.57
raw coal	51.30	40.80	7.90	5.08	71.50	6.10	1.10
dried sludge	68.02	10.61	21.37	5.67	49.66	7.15	3.94

C_2H_4, and C_2H_6 were analyzed using a thermal conductivity detector coupled with a gas chromatograph (TCD-GCs: the AeraM200 Microsensor Gas Analyzer (1) MS-5A and PPQ columns with argon carrier gas and (2) a PPU column with helium carrier gas). The instrument accuracy was within 0.01 vol %. The residual solids collected were subjected to thermogravimetric analysis (TGA) to measure the amounts of residual $Ca(OH)_2$, $CaCO_3$, and carbon.[8] The instrument accuracy was within 0.01 mg.

2.3. Samples. Results of proximate and ultimate analyses of organic samples [raw Taiheiyo coal $(25-73$ μm), Taiheiyo coal char $(<125$ μm), and dried sludge $(53-125$ μm)] are shown in Table 2. Here, Taiheiyo coal char was made through devolatilization of raw Taiheiyo coal at 873 K for 2 h in a N_2 flow. The reagent-grade $Ca(OH)_2$ (Nacalai Tesque, Kyoto, Japan) was used as the CO_2 sorbent.

3. Results and Discussion

3.1. Change of Residual Carbon in the Solid Residue with the Soaking Time. Transient results for the amount of carbon contained in the residue are shown in Figure 3. The percentages of the residual carbon in this figure were evaluated using the carbon content values obtained from the TGA analysis based on the carbon content in fuel in Table 2.

In the case of Taiheiyo coal char, it is found that 17 wt % of carbonaceous material was converted within 1 min and the residual carbon continued to decrease monotonically thereafter. This "1 min" means the period when a TB reactor was soaked in the sand bath including the 1 min of heating period up to about 873 K and the added time required to cool the sample. The soaking time after 3 min in Figure 3 includes the heating period to the desired temperature, the reaction period at equilibrium temperature, and the brief cooling and associated handling time. On the other hand, 39 and 76 wt % of the carbon in the raw Taiheiyo coal and dried sludge, respectively, were consumed during the

Figure 3. Changes of residual carbon in the solid residue after reaction with the soaking time for raw Taiheiyo coal (●), Taiheiyo coal char (▲), and dried sludge (■).

heating period in the first 1 min. As for the repeatability for different samples, experimental errors for Figure 3 were within about 3.5 wt % on the average of several times.

Assuming that no carbon conversions took place during sample cooling, the rates of carbon consumption averaged over the initial 5 min of the soaking time are about 5.8, 12, and 16 wt %/min for the char, the coal, and the sludge, respectively. The rates after the initial 5-min period were found to have decreased to about 0.76, 0.93 and 0.47 wt %/min for the char, the coal, and the sludge, respectively. Because after the first 5 min the rates for the coal and the sludge are similar to the rate for the char which has little volatile content, the residual carbonaceous compounds of the coal and the sludge would appear to have become char. The gasification rate of the produced char is slower than the rate of initial thermal decomposition.

3.2. Changes of Gases Produced from Organic Samples with the Soaking Time. Using the results of the gas analysis, the yields of the gaseous products for each fuel are plotted as a function of the soaking time in Figure 4. For the Taiheiyo coal char, H_2 and CH_4 were the dominant products and the yields increased with time. The experimental error on gas yields was within about 0.03 mol/mol$_{carbon}$. The rate of H_2 production for the coal char is higher than that of CH_4, and the molar ratio of H_2 to CH_4 at 30 min is about 4, which approximately equals the equilibrium composition of H_2 and CH_4 for the present experimental condition. In addition, no CO_2 was observed in the gaseous products at any soaking time, which suggests that calcium-based sorbent completely captured CO_2 during the gasification. The CH_4 yield was slowly increased with time even after the initial thermal decomposition, which suggests the possibility of the following reaction:[9]

$$2C + Ca(OH)_2 + H_2O \rightarrow CH_4 + CaCO_3,$$
$$\Delta H_{973} = -31.2 \text{ kJ/mol} \quad (6)$$
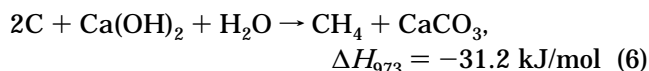
The CH_4 production rate was low, but the yield of CH_4 produced in the initial stage was not decreased, so that the conversion rate of CH_4 to H_2 by eq 7 is suggested to be low.

$$CH_4 + Ca(OH)_2 + H_2O \rightarrow 4H_2 + CaCO_3,$$
$$\Delta H_{973} = 115 \text{ kJ/mol} \quad (7)$$
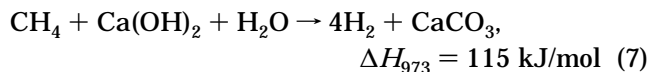
In the first 5 min for the coal, the amount of H_2 produced was as much as that from the char. For instance, the H_2 yields for the char and the coal at 5 min are about 0.27 and 0.31 mol/mol$_{carbon}$, respectively. However, the CH_4 yield for the coal is much higher than that for the char. In addition, a small amount of C_2H_6 was produced. All of this suggests that CH_4 and C_2H_6 are produced in the initial stage and H_2 is mainly produced in the reaction between char and steam. After the first 5 min, the amount of additional CH_4 produced from the coal becomes comparable to that from the char.
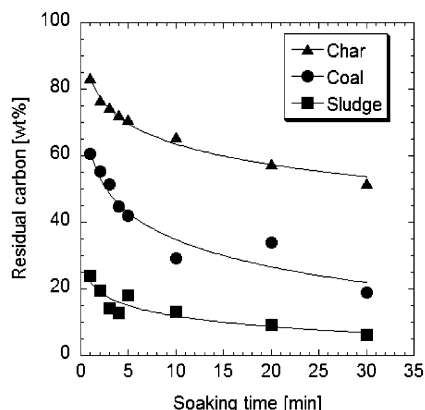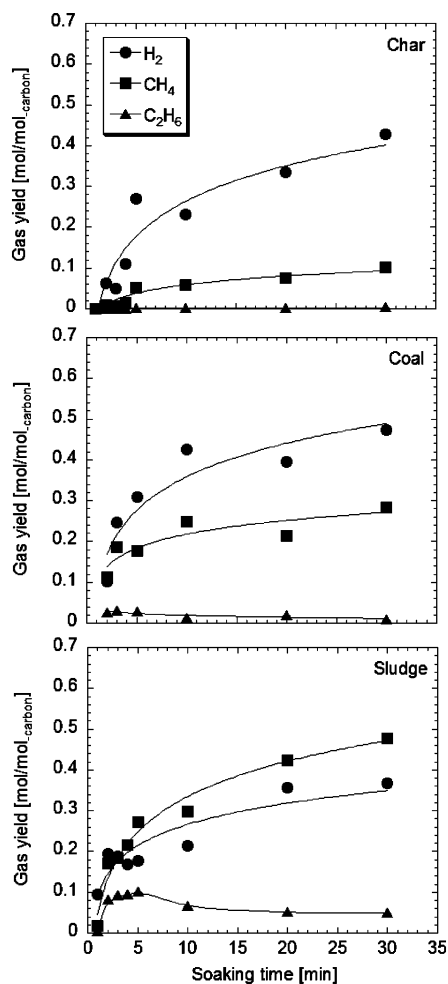
Figure 4. Changes of gases such as H_2 (●), CH_4 (■), and C_2H_6 (▲) produced from raw Taiheiyo coal, Taiheiyo coal char, and dried sludge with the soaking time.

The increase in the amount of H_2 generated after the first 5 min also becomes comparable for the coal and the char. These similarities between the char and the coal suggest that the coal after 5 min becomes char.

C_2H_6 seems to be slowly decreasing after the initial 3 min, which might be due to the following reaction:

$$2C_2H_6 + Ca(OH)_2 + H_2O \rightarrow 2H_2 + 3CH_4 + CaCO_3,$$
$$\Delta H_{973} = -14.5 \text{ kJ/mol} \quad (8)$$
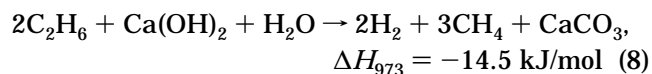
For the sludge, the amount of H_2 produced is less, while the amounts of CH_4 and C_2H_6 are more than that from the coal. The molar ratio of H_2 to CH_4 at 30 min is about 0.77 and lower in comparison to 1.7 in the case of the coal. In the initial 5 min, the CH_4 and C_2H_6 yields are higher than those for the coal. The carbonaceous gases for the sludge with higher volatile content might be produced from the carbon material consumed in the initial stage as shown in Figure 3. However, the H_2 production rate after 5 min becomes very similar to that from the other fuels. This also suggests that even the sludge with a high initial volatile content becomes char after 5 min.

3.3. Distribution of Carbon to Gases and Char.
Figure 5 shows distributions of the carbon recovery as gases (such as CH_4, CO, and CO_2 contained in $CaCO_3$, C_2H_4, and C_2H_6) and char for the three fuels of raw Taiheiyo coal, Taiheiyo coal char, and dried sludge with the soaking time, based on the analyses of the gas
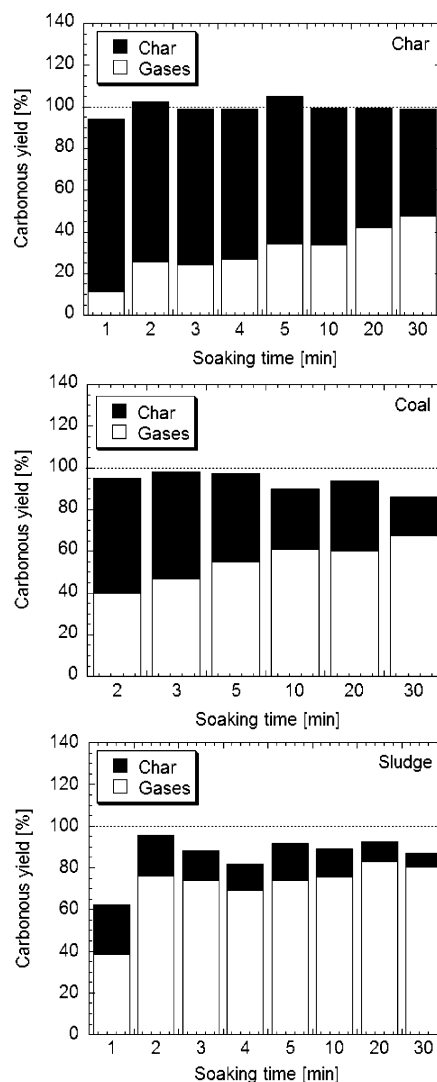

Figure 5. Distributions of carbon to gases (□) and char (■) for three fuels of raw Taiheiyo coal, Taiheiyo coal char, and dried sludge with the soaking time.

products and solid residues. For the char, the conversion of carbon to gases increases monotonically during the soaking time. This suggests that the production rate of the carbonaceous gas from the char is relatively low. When the total of carbon yields for the three fuels is compared, the carbon balance for the char is almost 100%, which means that the product gases and the residues were completely collected. On the other hand, incomplete accounting of the carbon is found for both the coal and char, suggesting that the missing yields are dependent on the volatile contents of the fuels. The missing yield is quite high at 1 min for the sludge. A likely explanation for the missing carbon can be found in our previous paper[8] on gas and tar production by the thermal decomposition of the coal. A deposition of a tar on the wall of the reactor during the heating period that was not subsequently collected could explain the missing carbon. In this experiment, the sludge with its high volatile content would be especially prone to this problem.

The tar initially produced has two possibilities for its final state, either to become a heavy tar that is converted into char or to become a light tar, which is subsequently converted into gases. According to the results for the first 5 min of Figures 3−5, fuels with
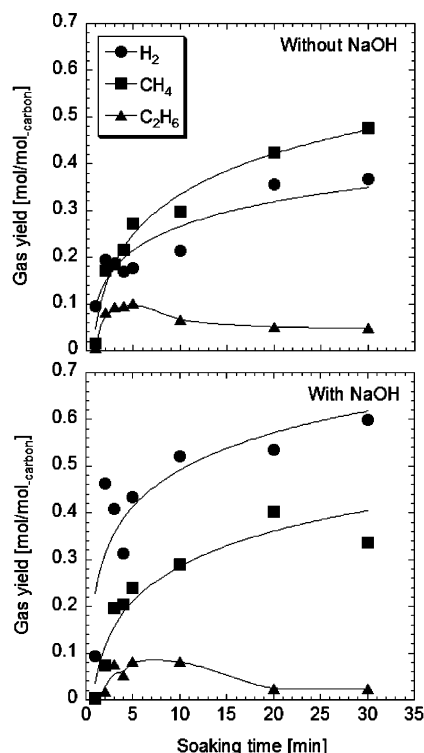
Figure 6. Changes of gases such as H_2 (●), CH_4 (■), and C_2H_6 (▲) produced from dried sludge without and with NaOH as a function of the soaking time.

high volatile content provide rapid conversion of carbonaceous materials (Figure 3), high carbonaceous gas yields such as CH_4 and C_2H_6 (Figure 4), and high missing values in carbon balance (Figure 5). Because the accuracy of the measurement of both the residual carbon and the product gases are high, the unknown or missing carbon material is likely to be tar or tar products deposited on the walls that are not accounted for. Indeed direct visual observation showed tar being produced in the initial stage. Therefore, it is reasonable that the residual tar on the wall that was not converted into carbonaceous gases could be converted into a char deposit on the walls that was not recovered.

3.4. Catalytic Effect of NaOH on H_2 Production. The amounts of gas products for dried sludge without and with NaOH as an alkali, which was of reagent grade (Nacalai Tesque, Kyoto, Japan), are plotted as a function of the soaking time in Figure 6. The amount of H_2 produced with NaOH is higher than that without NaOH, while the amounts of CH_4 and C_2H_6 produced with NaOH are lower than those without NaOH. The molar ratio of H_2 to CH_4 at 30 min increased to 1.8 from 0.77 without NaOH. This suggests that NaOH should have a catalytic effect on CH_4 and H_2 production from the CH_4 and C_2H_6 produced in the initial stage even for the sludge with high volatile content.

4. Conclusions

To understand the kinetic mechanism of the HyPr-RING process for organic waste, the contribution of

volatile contents and char on H_2 production was investigated by using dried sewage sludge with high volatile content, Taiheiyo coal char with little volatile content, and raw Taiheiyo coal with intermediate volatile content. The following conclusions were drawn:

(1) Carbon in the original organic matter rapidly decreases with time by thermal decomposition in the initial stage, and the amount of the decrease strongly depends on the volatile matter content in the fuel. In the second stage after thermal decomposition, the gasification reaction between char and steam is predominant, and the reaction rate is low.

(2) Carbon material consumed in the initial stage becomes carbonaceous gases such as CH_4 and C_2H_6 for the fuels with high volatile content.

(3) In the second stage following the predominant and rapid production of carbonaceous gases of the initial stage, the residual carbon appears to have become char even for the high volatile content fuels.

(4) In subcritical steam gasification of such char, H_2 is predominantly produced, and the molar ratio of H_2 to CH_4 at 30 min approximately corresponds to the equilibrium composition of H_2 and CH_4 for the present experimental condition.

(5) NaOH catalytically promotes H_2 production.

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