ORIGINAL ARTICLE

Analysis of chemical-looping method for production of hydrogen gas from sewage sludge

Toshiyuki Shiraki[1,2] · Satoshi Okumura[3] · Satoshi Uehara[3] · Hiroki Harada[2,3] · Masaki Takaoka[2]

Abstract

The objective of this study is to develop a highly efficient technology for producing hydrogen from sewage sludge using chemical-looping technology. In this study, laboratory-scale gasification experiments were conducted on sewage sludge samples. The effects of CaO as a carrier of oxygen or carbon (C) and as a gasification accelerator were evaluated. Lab-scale tests using a tube-type electric furnace showed that gasification of CaO-mixed dry sludge with steam resulted in substantial absorption of CO_2 by CaO at 600 ℃ and 700 ℃ and the concentration of H_2 in the gas reached 70 vol.%. The gasification was significantly accelerated in CaO-mixed steam gasification compared with pyrolysis gasification and steam gasification of dry sludge in the absence of the CaO mixture. The hydrogen gas (H_2) recovery rate also increased, and tar with a high C weight ratio and high calorific value was recovered. Almost the entire C in the sewage sludge was gasified at 800 ℃. Therefore, this method (pyrolysis with steam and CaO) was shown to be effective as one of the hydrogen production methods from sewage sludge.

Keywords Calcium oxide · Fluidized bed · Chemical-looping gasification · CO_2 recovery · H_2 recovery · Sewage sludge

Introduction

In the context of the recent global social climate for reducing carbon dioxide (CO_2) emissions, ambitious efforts to reduce greenhouse gas emissions are required in the sewage sector.

In 2020, sewage sludge generated in Japan was 77.6 million tons on a concentrated sludge basis, comprising ~20 % of the total industrial waste generated, and 2.26 million tons were generated annually on a dry basis [1–3]. Of this, 80 % is biomass organic material, with a total energy equivalent to ~12 billion kWh, approximately 1.6-fold greater than the annual electricity consumption of sewage treatment plants. Therefore, the recovery of energy from sewage sludge shows high potential for building a climate-neutral society in the region as a renewable energy source [3].

Thus far, technologies to recover energy from sewage sludge have concentrated on converting sewage sludge into solid fuel through incineration waste heat for electricity generation, pyrolysis gasification, biogas utilization, and hydrogen production and supply; however, the percentage of sewage sludge used for energy recovery remains low (~27 %) [3]. Accordingly, to promote energy recovery from sewage sludge, technologies for more efficient energy recovery must be developed [3].

Chemical-looping technology has attracted attention as a technology that can overcome these shortcomings of thermo-chemical conversion approaches for sewage sludge and realize syngas more economically than existing thermo-chemical conversion processes [4]. The

✉ Hiroki Harada
harada.hiroki.3s@kyoto-u.ac.jp

Toshiyuki Shiraki
shiraki_t@hitachizosen.co.jp

Satoshi Okumura
okumura_sa@hitachizosen.co.jp

Satoshi Uehara
uehara_sa@hitachizosen.co.jp

Masaki Takaoka
takaoka.masaki.4w@kyoto-u.ac.jp

1   Hitachi Zosen Corporation, 1-7-89 Nanko-kita, Suminoe-ku, Osaka 559-8559, Japan

2   Department of Environmental Engineering, Graduate School of Engineering, Kyoto University, Kyoto-daigaku-katsura, Nishi-Gyo-ku, Kyoto 615-8540, Japan

3   Business & Product Development Center, Environmental Business Headquarters, Hitachi Zosen Corporation, 1-7-89 Nanko-kita, Suminoe-ku, Osaka 559-8559, Japan
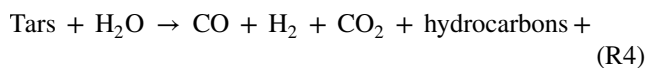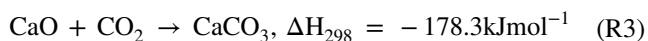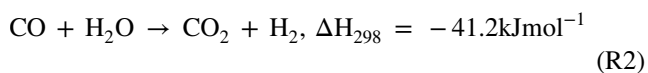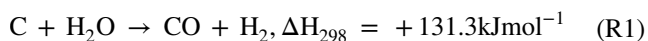
chemical-looping process (CLP) includes chemical-looping combustion (CLC) [5–7]. Chemical-looping Reformation (CLR) [8], Chemical-looping Gasification (CLG) [5, 9], and these processes can be used to produce electricity, syngas, chemicals, and liquid fuels. CLR and CLG are based on the basic principles of CLC, and these technologies were originally developed for fossil fuels; when CLG is adapted for biomass, it is called BCLG.

This study focused on biomass chemical-looping gasification (BCLG) [10], a pyrolysis gasification technology that has recently attracted considerable attention; it offers highly efficient energy recovery along with substantial advantages over conventional biomass gasification processes in terms of circulation, inherent CO_2 recovery, process cyclability, and reduced pollutant emissions [5, 11–14].

In a typical biomass gasification process with steam, there are two challenges: CO_2 production by water–gas shift reactions and tar formation. Therefore, the requirements for CO_2 carriers and biomass conversion catalysts require high CO_2 capture capacity and selectivity, as well as tar decomposition capability [5]. However, calcium oxide (CaO) has been evaluated as a sustainable flow medium system; it can serve as a CO_2 sorbent and alkali catalyst in the biomass gasification process, and it can be recycled by calcination via chemical-looping [5, 15].

Regarding the CLG process that uses Ca compounds as a heat transfer medium, biomass calcium looping gasification (BCaLG) can recover high concentrations of H_2 by gasifying biomass, such as cellulose and sawdust, with added Ca [5]. This system uses CaO as a heat transfer medium and a CO_2 carrier to recover CO_2 from biomass while producing high concentrations of H_2.

Udomsirichakorm et al. [11] conducted research and development on BCaLG using biomass fuels for renewable, sustainable, and environmentally friendly hydrogen production. They outlined some of the key reactions that occur in BCaLG, as follows:

$$C + H_2O \rightarrow CO + H_2, \Delta H_{298} = +131.3 \text{kJmol}^{-1} \quad \text{(R1)}$$

$$CO + H_2O \rightarrow CO_2 + H_2, \Delta H_{298} = -41.2 \text{kJmol}^{-1} \quad \text{(R2)}$$

$$CaO + CO_2 \rightarrow CaCO_3, \Delta H_{298} = -178.3 \text{kJmol}^{-1} \quad \text{(R3)}$$

$$\text{Tars} + H_2O \rightarrow CO + H_2 + CO_2 + \text{hydrocarbons} + \quad \text{(R4)}$$

(R1) is highly endothermic and generally more pronounced at high temperatures (> 1000 ℃), whereas (R2) is exothermic and usually requires a catalyst at lower temperatures (< 400 ℃). (R3) typically operates from 600

to 750 ℃ at atmospheric pressure. During conventional H_2 production, (R1) and (R2) are split into separate reactors because the temperature difference between reactions reduces system efficiency. In BCaLG, (R3) can provide heat to (R1). Furthermore, the in-situ capture of CO_2 by (R3) promotes (R1) and (R2), resulting in increased production of H_2. Additionally, CaO acts as a catalyst for gasification and tar reforming processes, improving the reaction rate and gaseous product formation according to (R4) [11].

Acharya et al. [13] conducted experiments in a batch fluidized bed steam gasifier using CaO as an adsorbent; they found that when sawdust was used as feedstock, the H_2 concentration in the product gas was 71 % and the CO_2 concentration was almost 0 %. In another test using a circulating fluidized bed reactor as a regenerator, they reported 40 % regeneration of CaO at a calcination temperature of 800 ℃.

Wei et al. [15] investigated the characteristics of biomass steam gasification for hydrogen production at atmospheric pressure using CaO as a CO_2 sorbent in a laboratory-scale external circulating concurrent moving bed (ECCMB) system. Their results showed that the addition of a CaO-based CO_2 sorbent increased the hydrogen content in dry gas from the ECCMB process.

Alonso et al. [16] indicated that the BCaLG concept relies on the high reactivity of biomass as a fuel, allowing effective combustion at ~700 ℃ in air at atmospheric pressure.

Under these conditions, CaO particles fed to the fluidized bed combustor react with the CO_2 produced during biomass combustion, allowing effective CO_2 capture. Release of the enriched CO_2 stream requires the regeneration of $CaCO_3$ in an oxygen-fired combustor, which they expected to integrate into a large oxygen-fired power plant and/or large post-combustion calcium loop system.

Zhao et al. [5] call the process Sorption Enhanced Chemical Looping Gasification (SE-BCLG), which aims to simultaneously achieve hydrogen-rich gas recovery and CO_2 capture using CaO as a CO_2 capture (CC) along with oxygen carrier (OC) when biomass fuel is gasified by a chemical loop process and distinguish it from BCaLG.

Yin et al. [17] focused their research efforts on the development of a new calcium loop-based combined cycle biomass-integrated gasification combined cycle process, which increased the energy density of syngas by capturing CO_2 in a carbonation unit.

On the other hand, the following studies have been reported on CLG of sewage sludge. Huang et al. [18] conducted a study on CLG of sewage sludge using hematite as an oxygen carrier. They reported that carbon conversion and gas yield increased almost linearly with temperature from 62.14 % and 0.33 m^3/kg-SS at 800 ℃ to 84.72 % and 0.44 m^3/kg-SS at 950 ℃. Deng et al. [19] conducted experiments using copper slag fired at 1100 ℃ (1100CS)

as an oxygen carrier. First, the calcination temperature of the copper slag was investigated and 1100CS was selected as the OC for the study because it had the highest Fe_2O_3 content. The study results showed that 1100CS not only promoted carbon conversion of SS, but also worked effectively as a catalyst for tar cracking, reporting the carbon conversion rate of 70.2 % and the gas yield of 0.23 m^3/kg. Furthermore, Dong et al. [20] studied the use of new oxygen carrier (Ni_2O-CS OC) modified by impregnating 1100CS with 20 % NiO, and reported the maximum carbon conversion of 87.09 % and the gas yield of 0.39 m^3/kg-SS.

Thus, although research has been conducted on CLG of sewage sludge, there are no examples of studies focusing on hydrogen production using CaO as a CO_2 carrier or biomass conversion accelerating medium. In this background, the present study was performed to obtain basic data for a technology that is capable of efficiently producing highly concentrated H_2 using inorganic Ca as a heat medium and as a CO_2 absorber. This study was conducted to apply BCLG with Ca compounds (CaO) to sewage sludge. Specifically, in addition to examining the basic behavior of CaO addition to sewage sludge, including the production rates of char, tar, and gas during pyrolysis gasification, the effects of CaO on gasification enhancement and H_2 production were investigated.

Materials and methods

Test materials

Properties and pretreatment of dried sludge samples

Table 1 shows the properties of dewatered sewage sludge collected from a sewage treatment plant in a city. And the lower heating value, which is important in the evaluation of energy recovery, was 17–18 MJ/kg-dry solid (DS), which is within the standard range of 14–19 MJ/kg-DS [21].

In this experiment, dewatered sludge was dried at 105 ℃ for 1 day and night, then homogenized by grinding with a vibration mill (CMT, TI-300) for 30 s.

CaO sample

CaO (Yoshizawa Lime Industry Co., Ltd., Tochigi, Japan), which has been studied in the chemical loop process using coal and woody biomass, was used in experiments [22]. The particle size was ≤ 100 μm to confirm the basic characteristics.
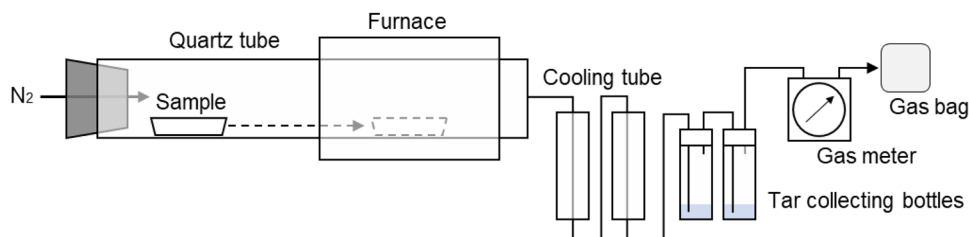
Dried sludge sample mixed with CaO

The dried sludge and CaO samples were placed in a 200 mL glass bottle at the ratio described in Section "Experimental conditions and procedures" and shaken for ~3 min to ensure that the samples were homogeneous.

Experimental apparatus

Figure 1 shows the experimental setup. The system consisted of a gas supply section to supply carrier gas and steam for gasification, a gasification reaction section consisting of a quartz reaction tube (OD55 mmφ × ID45 mmφ × 600 mm), a horizontal tube furnace (KT-1153P; heating length: 230 mm; Toyo Seisakusho Co., Ltd., Japan), and a gas cooling section to condense and recover tar components and water in the generated gas. The gas cooling section consisted of two sets of Graham-type coolers and two sets of wash bottles containing cooling water. $CaCl_2$ for moisture removal, a tar collection trap, an integrated flowmeter, and a gas bag

Table 1 Properties of dewatered sewage sludge (wt.%-dry)

Combustibles		
	C	44.0
	H	6.8
	N	5.3
	O	34.4
	S	0.6
Ash		8.9
Total		100.0

Fig. 1 Outline of Test Equipment

Table 2 Test conditions

Parameter		Unit	Conditions	Note
Sample	Sewage sludge	g	5	
	CaO	g	0, 10, 20	CaO/C = 0, 1, 2
Supplied gas	Carrier gas (N₂)	mL/min	200	
	Steam	g/min	0, 0.12	ST/C = 0, 2.2
Temperature		℃	500—800	
Time		min	60	

Table 3 Measurement and analysis items of gasification products

Part	Analysis items
Gas	Volume and composition
Tar	Concentration of tar*
	Total weight**
	Concentration of C, H, N, S
	Moisture, ash, volatiles
	Fixed carbon
	HHV
	LHV
Char	Total weight
	Concentration of C, H, O, N
	Moisture, ash, volatiles
	LHV
	Amount of fixed CO_2

*An acetone solution sample (solution) was distilled and concentrated with a rotary evaporator at 60 °C, and further concentrated with a dryer set at 80 °C to a constant weight to remove the contained acetone and water by volatilization to obtain a concentrated tar. The weight of this concentrated tar was measured

**The weight of recovered tar was obtained by adding to the weight of concentrated tar the increase or decrease in each of the weights of the cleaning bottle in the gas cooling section, $CaCl_2$ for removing water, and cylindrical filter paper for collecting tar before and after the test

for gas sampling were installed in the backstream of the gas cooling section.

Experimental conditions and procedures

Table 2 shows the experimental conditions. The prepared CaO mixed dry sludge sample was placed in an alumina boat (width: 25 mm; length: 120 mm) and set at the end of a quartz reaction tube. The reaction tube was heated to the target temperature of 500–800 ℃ while a predetermined flow rate of carrier gas N₂ and steam (ST) was supplied. After the reaction tube reached the target temperature, the alumina boat was inserted from the end of the reaction tube into the central part (inside the tube furnace); simultaneously, the emitted gas was sampled into a gas bag. During the experiments, the flow rate and temperature readings of the integrated flowmeter were recorded at regular intervals to determine the gas emission behavior and total volume generated. At 60 min after insertion, the alumina boat was pulled from the center of the reaction tube to the end; concurrently, gas sampling and the experiment were terminated. After the reaction tube had cooled, the pyrolysis residue remaining in the alumina boat was weighed for recovery and used as char for analysis, as described below.

The condensed components that collected in the gas cooling section were washed and collected with acetone, then analyzed for concentrated tar. The change in weight of the cleaning bottle in the gas cooling section and the $CaCl_2$ for water removal were measured before and after the experiment. The weight change plus the concentrated tar content was used as the amount of tar component recovered. The tar component, along with the hydrocarbon component, was recovered as a mixture of unreacted feed water vapor and moisture generated by thermal decomposition of the feed. Concerning gas collection in the gas bag, the amount of gas recovered was calculated from integrated flow rate values before and after the start of the reaction; the quantity obtained by subtracting the carrier gas flow rate from this value was regarded as the volume of gas produced. The gas composition was analyzed using a gas chromatograph (thermal conductivity/flame ionization detectors, GC7100; J-Science Lab Co., Kyoto, Japan).

Concerning the gasification of CaO-mixed dried sludge in a steam atmosphere, the reaction is assumed to proceed based on the elementary reactions of (R1)–(R3) described earlier. Therefore, the conditions for the amount of CaO added (Ca/C) in this experiment were determined using these reaction equations. The total amount of steam supplied during the reaction time of 60 min was set at a molar ratio of 2.2 (hereinafter referred to as ST/C, where C is the amount of carbon in the sludge).

As a preliminary analysis, pyrolysis experiments were conducted twice on two types of sewage sludge, A and B, and CaO with the compositions shown in Table 1S using the experimental apparatus and procedures described in this paper (see Supplementary Materials). The experimental conditions and the results are shown in Table 2S and Fig. 1S respectively. Although the sludge type, ST/C, temperature, and holding time differed between A and B, the sample reproducibility was generally observed when comparing the results from the first and second experiments (A1, A2 and B1, B2). Therefore, we concluded that our experimental approach was reproducible and proceeded with a single experiment for each condition.

Analysis items and evaluation methods

Product measurement and analysis items

Table 3 summarizes the measurement and analysis items related to the gasification products (gasification gas, tar, and char) obtained in this experiment. Inorganic C (as CO_2) and organic C were separately determined for C in char to evaluate the effect of CO_2 separation based on (R3) above. Ash was included in the char component.

Gas

Gas composition was analyzed by gas chromatography (thermal conductivity/flame ionization detectors, GC7100; J-Science Co.). The composition of the gasification gas was evaluated on a dry basis. All N_2 compositions were excluded because they were derived from the carrier gas. The gas recovery on a weight basis was evaluated using the assumed gasification gas composition and the amount of gas produced. Although 5 wt. % N content is present in dry sludge, this experiment was performed with the assumption that almost all of the gasified N content condensed in the gas cooling section as NH_3, HCN, etc. and was recovered as tar content [23, 24]. Gas chromatography–mass spectrometry (GC-MS; GC6890N/5973 inert MSD, Agilent Technologies, Santa Clara, CA, USA) was used for qualitative analysis of the tar.

Char and tar

Table 3 summarizes the methods used to analyze the tar weight and char in the gasification experiments of CaO mixed dry sludge. Inorganic C (as CO_2) was presumably present in the char in the form of $CaCO_3$. Therefore, C in the char was determined by separating inorganic C from organic C. After the inorganic C was volatilized as CO_2 by acid treatment of the char samples, the amount of C measured by an elemental analyzer (Vario EL cube; Elementar, Langenselbold, Germany) was regarded as organic C; the difference from the amount of C contained in the sample before acid treatment was regarded as inorganic C.

Results and discussion

Gasification behavior of sewage sludge in a N_2 atmosphere

To confirm the validity of this experimental method and apparatus, and to obtain basic data necessary for evaluating H_2 production from sewage sludge, gasification (pyrolysis) experiments were conducted on dried sludge samples in a

N_2 atmosphere to determine the material balance of gas, tar, and char.

Using N_2 at 500–800 ℃ under ambient conditions, along with gas, tar, and moisture, led to the formation of char components; however, the total recovery of these components was in the range of 68–86 wt.%, with unrecovered components in the range of 14–32 wt.%. This was presumably because of the portion adhering to the reaction tube walls and pipe inner walls, volatilization of low-boiling tar components during the volatilization of acetone from the tar recovery solution, and other factors [20, 25, 26]. Additionally, because the dried sludge feedstock contains several wt.% of internal water that does not volatilize at 100 ℃ and because some amounts of moisture are generated in the gasification of dried sludge [13], it was assumed that the moisture volatilized during the concentrated tar analysis and was unrecovered; however, no method is available to confirm this assumption. Thus, the unrecovered portion was excluded from analysis. Figure 2 shows the ratio of gas, tar, moisture, and char. In this figure, as the gasification temperature increased, the recovery rate of char decreased and the transfer rate to the gas side (including tar) increased. Furthermore, as the gasification temperature increased, recovery of the tar component decreased, and recovery of gas increased.

Lin et al. [27] reported the following effects of temperature on the gas phase (Gas-C) and char phase (Cha-C) with respect to C distribution during pyrolysis under an argon atmosphere. When the temperature increased from 800 to 900 ℃, the Gas-C content increased from 57.9 to 79.7 % and the Char-C content decreased from 14.9 to 3.2 %. Thus, the total C content (gas-C + char − C) increased from 72.8 to 82.9 % with increasing temperature, indicating that the amount of C (tar-C) distributed in the tar decreases. Overall,
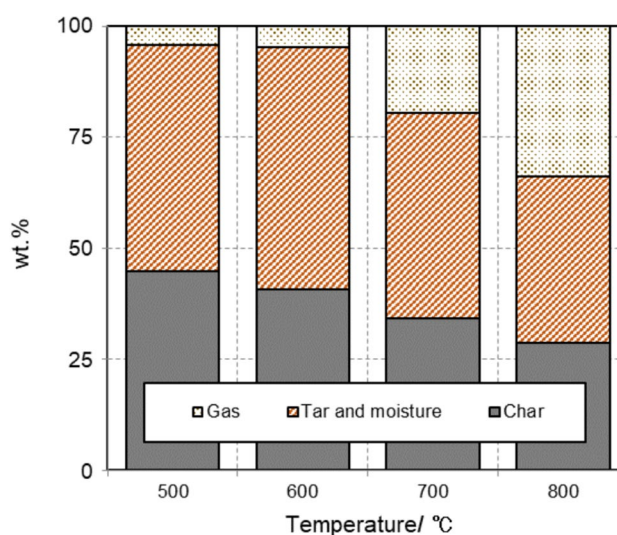
Fig. 2 Recovery Rate of Pyrolysis Gas (after correction of unrecovered parts)
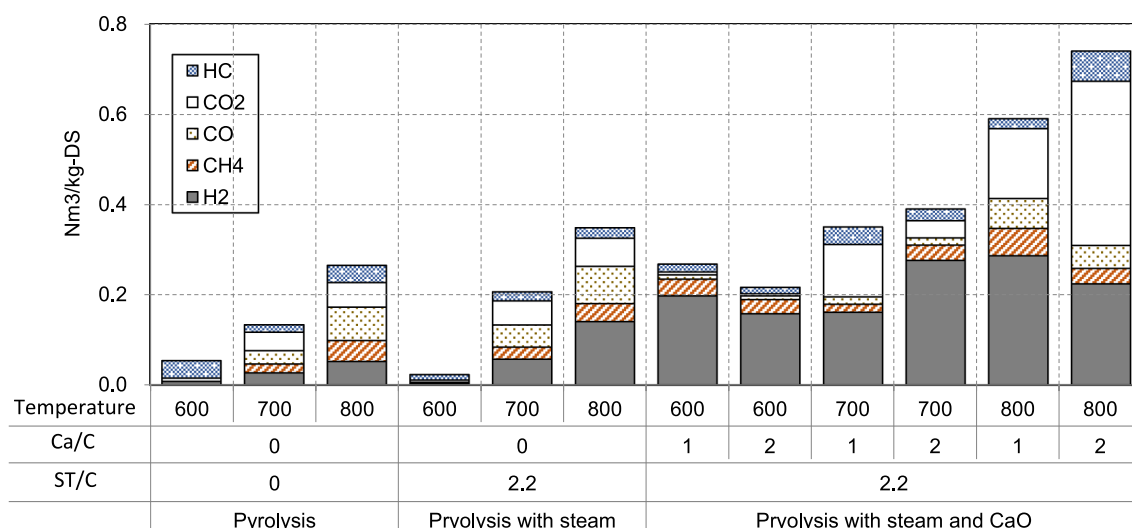
Fig. 3 Volume and Composition of Gas Components Generated by Three Types of Gasification Methods

the study showed that an increase in pyrolysis temperature is beneficial for the formation of Gas-C and plays a role in reducing the formation of Tar-C and Char-C; these results are similar to trends observed in the current study.

Amount and composition of pyrolysis gases

Figure 3 shows the amount and composition of gas produced by gasification of dried sludge or CaO-mixed dried sludge samples. With respect to the pyrolysis gasification test, the recoveries of each gas component at a gasification temperature of 700 ℃ were H_2:0.03 Nm^3/kg-DS, CH_4:0.02 Nm^3/kg-DS, CO: 0.03 Nm^3/kg-DS, and CO_2:0.04 Nm^3/kg-DS. These results are approximately consistent with those reported by Oshita et al. [28], and it is considered that the test apparatus and method are valid. For pyrolysis gasification, gasification in the presence of water vapor (steam gasification), and gasification of CaO-mixed dry sludge in the presence of water vapor (CaO-mixed steam gasification), the amount of gas generated increased with the gasification temperature in all cases. Upon comparison of gas generation volumes at the same temperature for each gasification method, the gas generation volume in CaO-mixed steam gasification significantly increased compared with pyrolysis gasification and steam gasification. In particular, at a gasification temperature of 600 ℃, the amount of gas produced by pyrolysis gasification and steam gasification was < 0.05 Nm^3/kg-DS, whereas the amount produced by CaO-mixed steam gasification was > 0.2 Nm^3/kg-DS. The amount of gas produced increased by more than four-fold with the CaO mixture.

Concerning the concentrations of H_2 and CO_2 in the gas, during pyrolysis gasification, the concentrations of both H_2

and CO_2 were ~20 vol.% at any temperature. In steam gasification, the H_2 concentration increased to 40 vol.% at 800 ℃. In contrast, during CaO-mixed steam gasification, the H_2 concentration increased to > 70 vol.% at temperatures of 600 ℃ and 700 ℃ (Ca/C = 2), whereas the CO_2 concentration significantly decreased. However, at a temperature of 800 ℃, the H_2 concentration decreased to < 50 vol.% compared with the 700 ℃ case; concurrently, the CO_2 concentration increased to 26 vol.% (Ca/C = 1) and 49 vol.% (Ca/C = 2). However, no specific trend was observed when comparing Ca/C = 1 and 2 for CaO-mixed steam gasification. This result suggests that the addition of excess Ca does not have a pronounced effect.

Taken together, our results indicate that the gasification of sludge samples is significantly accelerated with CaO-mixed steam gasification, compared with pyrolysis gasification or steam gasification. The reason for this acceleration is that CaO exerts a catalytic effect in the gasification reaction in (R1), and tar reforming reaction in (R4), thereby accelerating gasification and reforming. The mechanism of catalytic effect of CaO on gasification and reforming for tar is reported as follows [29–31]: first, tar molecules (C_nH_m) and H_2O/CO_2 adsorb onto the CaO active site. Here, the basic sites of CaO promote dehydrogenation (C–H cleavage), dealkylation (alkyl C–C cleavage), and ring opening (aromatic C=C cleavage) of the tar molecules to form active carbon deposits and gas species (C_xH_y and H_2). The activated carbon deposits are further condensed to form coke, which reacts with H_2O/CO_2 to form gas and is converted to CO/CO_2 and H_2. The same mechanism is considered to be responsible in this study.

Additionally, higher concentrations of H_2 and lower concentrations of CO_2 were possible at temperatures of 600 ℃

and 700 ℃. These concentrations may be possible because CO_2 is removed from the gas reaction field by the CO_2 absorption reaction to CaO, as described in (R3), and the (R1) and (R2) reactions are accelerated [11].

Jakkapong et al. [32] reported that in a steam gasification test of sawdust using silica sand and CaO as a flow medium, the hydrogen concentration in the product gas at a gasification temperature of 650 ℃ was 48 vol.% for silica sand, while it was as high as 78 vol. % for CaO. The same trend was observed in the present study.

On the other hand, it has been reported that repeated use of CaO results in a decrease in CO_2 absorption performance to removal, the extent of which varies greatly depending on the generation method of CaO, the type of loaded material, and other factors [33]. Therefore, for the practical application of BCLG, it is necessary to study the generation method of CaO, the type of supported materials, the amount of CaO replenishment in the total system, thermal balance, economics, and other factors.

Finally, at 800 ℃, the pyrolysis of $CaCO_3$ becomes dominant [21]; (R3) shifts to the left and CO_2 increases. In this case, the reaction in (R2) does not proceed, and the higher concentration of H_2 does not occur.

Tar properties

Qualitative analysis by gas chromatography–mass spectrometry

Table 4 summarizes the compound species among the top 10 peaks with the strongest peak intensities detected in the GC–MS analysis of concentrated tar recovered in each gasification experiment, for which a library search of the National Institute of Standards and Technology (Gaithersburg, MD, USA) yielded a match rate of ≥ 85 %. In this table, linear hydrocarbons with C numbers ranging from 15 to 19 and aromatic hydrocarbons, such as phenol and cresol, were detected by gasification of dried sludge. The results of this analysis are similar to the results of the analysis of tar components generated by gasification of woody biomass [35–37].

According to Kambara et al. [38], when biomass compounds are pyrolyzed at ambient pressure, primary vapors, mainly oxygen-containing compounds, are first produced as primary products, and the gas phase reaction of the primary products progresses to secondary products (lower hydrocarbons, aromatic hydrocarbons, olefins) and finally to the formation of tertiary products (CO, H_2, CO_2, and H_2O). Therefore, regarding Table 4, it is conceivable that in the pyrolysis reaction of sewage sludge, after the formation of acid-containing linear hydrocarbons (C15–C19) as primary products, aromatic compounds, such as phenol, cresol, and naphthalene, were formed as secondary products.

This tar component must be separated and removed in the gas purification process for utilization of the produced gas in hydrogen and other products.

Indole was detected as an aromatic compound containing N-H groups as a component specific to dried sludge. Other components (triacetoneamine, diacetone alcohol, and isopropylideneacetone) were presumably formed by the reaction between acetone (used as a solvent for tar recovery during the experiment) and gasification reaction products [39]. In particular, the peak intensity of triacetoneamine tends to be large, suggesting that it is a component formed by the reaction of acetone with ammonia gas derived from the gasification of N content in sludge. Therefore, these components were excluded from the evaluation of tar components in the following sections.

Assumption of average molecular weight

The recovered weight of the tar component was used to estimate its average molecular weight, which enabled determination of the gas volume of tar content in the gasification gas. In the estimation, the average molecular weight was calculated assuming that the tar components solely consisted of components identified in the previous section and that the content ratio was proportional to the peak area ratio of each component in the GC–MS analysis.
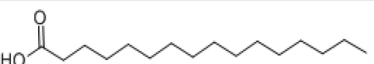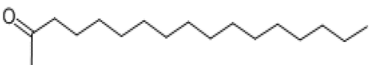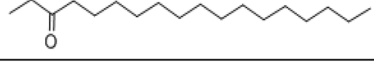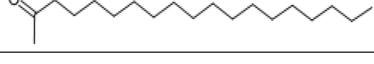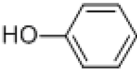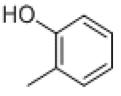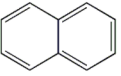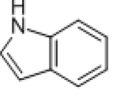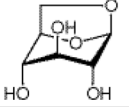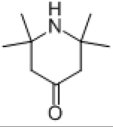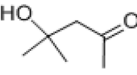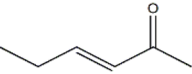
Figure 4 summarizes the relationship between gasification temperature and the estimated average molecular weight of tar. The average molecular weight decreased as the gasification temperature increased. Combined with the results shown in Table 4, it is clear that in the temperature range of 600–700 ℃, the proportion of C15–C19 linear hydrocarbons with molecular weights in the range of approximately 220–290 g/mol was high; in the temperature range of 700–800 ℃, aromatic hydrocarbons, such as cresol, phenol, naphthalene, and indole (with molecular weights of 90–130 g/mol) increased. In the high temperature range, the tendency for naphthalene to occur was similar to the tendency reported in the literature [36, 37].

Elemental composition (CHONS) and lower heating value

Figure 5 shows the results of elemental composition analysis of tar components and the lower heating value of tar components. The tar components obtained by CaO-mixed steam gasification tended to have a higher C content ratio and a higher heating value than the components obtained by pyrolysis gasification and steam gasification. The reason for this difference is unknown, but the mechanisms of the reforming reaction of sludge by pyrolysis or steam are distinct.

The N content ranged from 7 to 10 wt.% under all conditions, and the content tended to slightly increase with the gasification temperature. Most of the N content was

**Table 4** Concentrated tar component identified by GC–MS

Category		structure	Molecular formula	Molecular weight
Straight chain (C15)			$C_{15}H_{30}O$	226
Straight chain (C16)			$C_{16}H_{32}O_2$	256
Straight chain (C17)			$C_{17}H_{34}O$	254
Straight chain (C18)			$C_{18}H_{34}O_2$	282
Straight chain (C19)			$C_{19}H_{38}O$	282
Phenol			C_6H_6O	94
Cresol			C_7H_8O	108
Naphthalene			$C_{10}H_8$	128
Indole			C_8H_7N	117
Glucopyranose			$C_6H_{10}O_5$	162
Others	Triacetone amine		$C_9H_{17}NO$	155
	Diacetone alcohol		$C_6H_{12}O_2$	116
	Isopropylideneacetone		$C_6H_{10}O$	98

attributed to the N content in the sludge sample volatilized as NH_3 and HCN gas through gasification, then condensed and recovered at the same time as the water and tar content of gas in the gas cooling section. The increase in N content with increasing gasification temperature was likely related to the increased generation of N-containing tar such as indole, as mentioned above.

Material balance of carbon

Figure 6 summarizes the mass balance related to the C content of the dried sludge samples. In pyrolysis gasification, the percentage contained in solid residue as char was generally around 30 wt.% at gasification temperatures of 600–800 ℃, although this percentage slightly decreased with
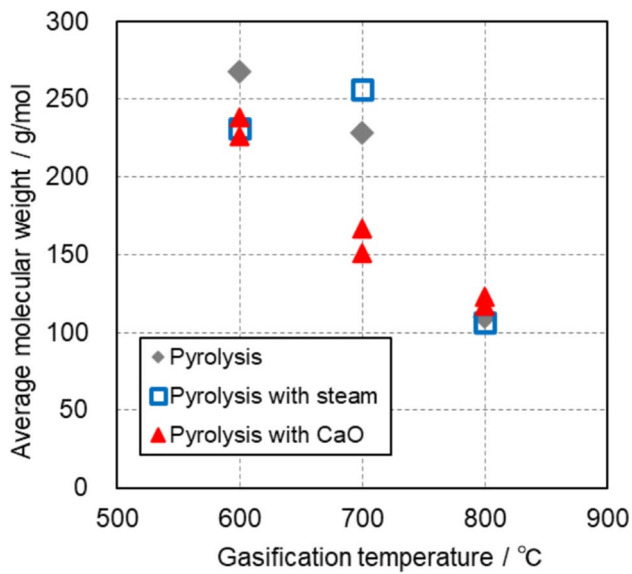
Fig. 4 Estimated Gasification Temperature and Tar Average Molecular Weight

increasing temperature. The percentage transferred to the gas side including tar was 70 wt.%.

During steam gasification, gasification was accelerated at a temperature of 800 ℃, with a gas-to-tar ratio of ~85 wt.%. In contrast, during CaO-mixed steam gasification, the amount of organic C in the char significantly decreased compared with pyrolysis gasification and steam gasification at all temperatures. Notably, at the gasification temperature of 800 ℃, almost all of the C was transferred to the gas/tar side.

As shown in Figure 6, the results of the CaO-mixed steam gasification experiment indicate that the inorganic C in char exists as $CaCO_3$ after the C in the sludge sample

is absorbed by CaO following gasification. At gasification temperatures of 600 ℃ and 700 ℃, ~30 wt.% of the C in the raw sludge sample was converted to $CaCO_3$. At a gasification temperature of 800 ℃, the amount of inorganic C in the char was negligible, indicating that no CO_2 absorption reaction had occurred. This result supports the behavior of a high H_2 concentration and a reduction in the CO_2 concentration according to the analysis of generated gas production and composition shown in Fig. 3.

During CLG, the organic C remaining in the char from the gasification process and the inorganic C fixed as $CaCO_3$ are circulated to the CaO regeneration process, whereas the organic C content is used as a heat source for CaO regeneration. Therefore, the absence of organic C content in the char at a gasification temperature of 800 ℃ is concerning because it would significantly increase the auxiliary heat source required in the CaO regeneration process.

The gasification temperature is a very important parameter for future efforts to achieve efficient design of the entire system. Below we discuss some findings from the literature with respect to the appropriate gasification temperature.

Biomass as a fuel is highly reactive and burns effectively at ~700 ℃ in air at atmospheric pressure [16]. With respect to the temperature of the fuel reactor during CLG, the following two reactions should be considered:

$$\text{Carbonation}: \ CaO + CO_2 \rightarrow CaCO_3 \tag{R5}$$

$$\text{Calcination}: \ CaCO_3 \rightarrow CaO + CO_2 \tag{R6}$$
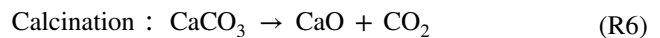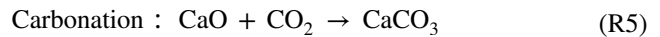
(R5) is a carbonation reaction; because it is an endothermic reaction and favors low temperatures, relatively
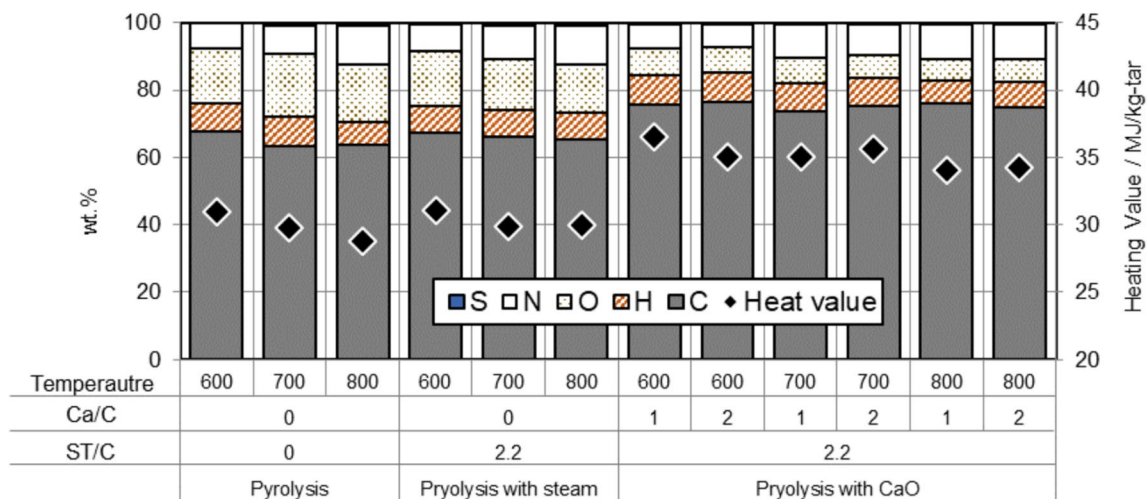
Fig. 5 Results of Elemental Composition Analysis of Tar Components

**Fig. 6** Mass Balance of Carbon in Gasification Tests
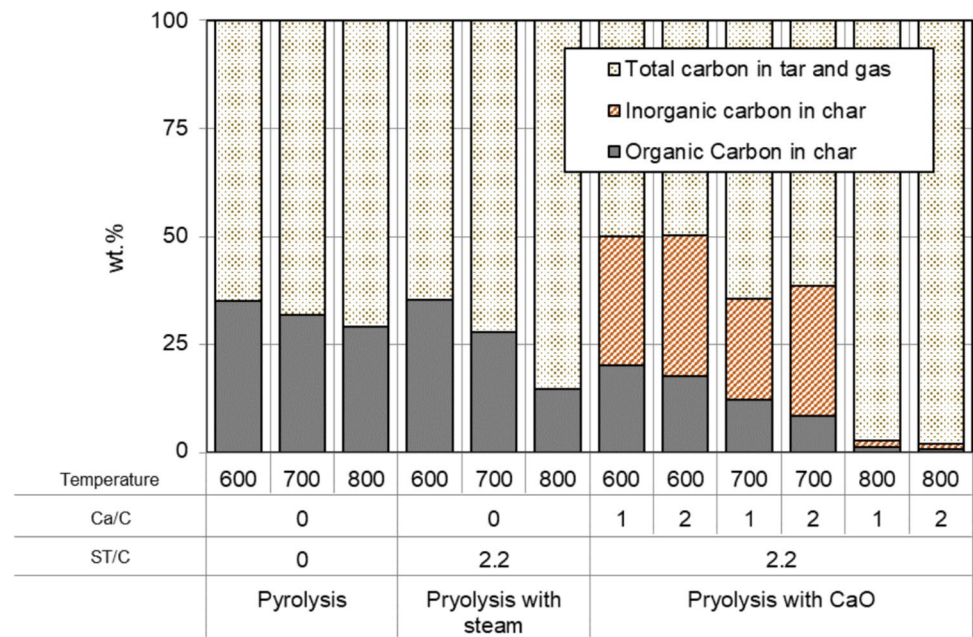
low temperatures (< 700 ℃) are preferred [34]. Conversely, $CaCO_3$ is calcined (R6) at high temperatures (≥ 800 ℃) and converted to CaO [34].

In experiments evaluating the effects of various process parameters, Avishek et al. [4] found that the H_2 concentration produced in the fuel reactor decreases at temperatures above 750–800 ℃. Thus, they concluded that the gasification temperature of the fuel reactor should be 700–800 ℃. In contrast, Niu et al. [40] reported an increase in C conversion (enhanced char gasification) with sewage sludge as the gasification temperature increased from 700 to 900 ℃.

Thus, previous studies have not yielded a consensus regarding the optimal gasification temperature for the fuel reactor. The present results suggest that 700 ℃ is the appropriate gasification temperature; however, the thermal efficiency of the entire system should be considered before reaching a conclusion.

Estimation of hydrogen production

The steam gasification reaction of C in sludge and the CaO-mixed steam gasification reaction in this process are expressed by the following equation. Assuming that all C can be gasified and reformed, 2 mol of H_2 can theoretically be produced from 1 mol of C. Therefore, using Eq. (1) below, we estimated the final amount of H_2 production that can be produced through the reforming (and shifting) process, based on the transfer rate of the C content in the raw sludge to the gas side (discussed in Section "Material balance of carbon" Material balance of Carbon).
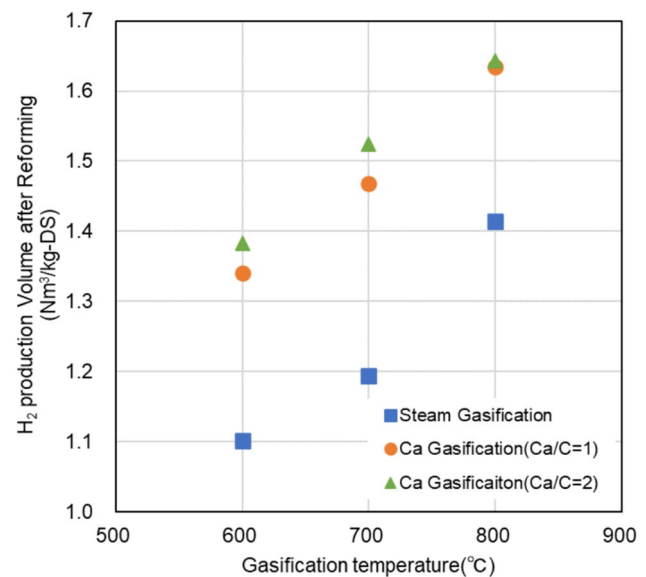
Fig. 7 Estimated H_2 Production Volume based on Carbon Mass Balance assessment

$$V = W_c/M_c \times 22.4 \times X \times 2 \tag{1}$$

V: H_2 production volume [Nm^3/kg-DS]

W_c: carbon in dry sewage sludge [g/kg-DS]

M_c: molecular weight of carbon [g/mol]

X: conversion rate of carbon to gas and tar due to gasification reaction[−]

Figure 7 shows an estimate of the expected amount of H_2 production after reforming. First, it is clear that the amount of H_2 production is greater in CaO-mixed steam gasification

than in steam gasification. Next, the amount of H_2 obtained by Ca-mixed steam gasification was estimated to be ~1.52 Nm^3-H_2/kg-DS at 700 ℃ and ~1.63 Nm^3-H_2/kg-DS at 800 ℃ with Ca/C = 2. This estimate suggests that 91–98 % of the energy of the input sewage sludge can be recovered as H_2 gas when the BCLG process is used to recover energy from sewage sludge. Considering the current status of methane gas recovery by anaerobic fermentation, where only ~40 % of methane gas is recovered as energy [3, 41], H_2 gas recovery from sewage sludge via CLG is expected to significantly improve energy recovery efficiency. However, with respect to the overall process, it is important to consider energy circulation and the power consumption of equipment in the system. Thus, additional detailed studies using scale-up experiments and process calculations are needed.
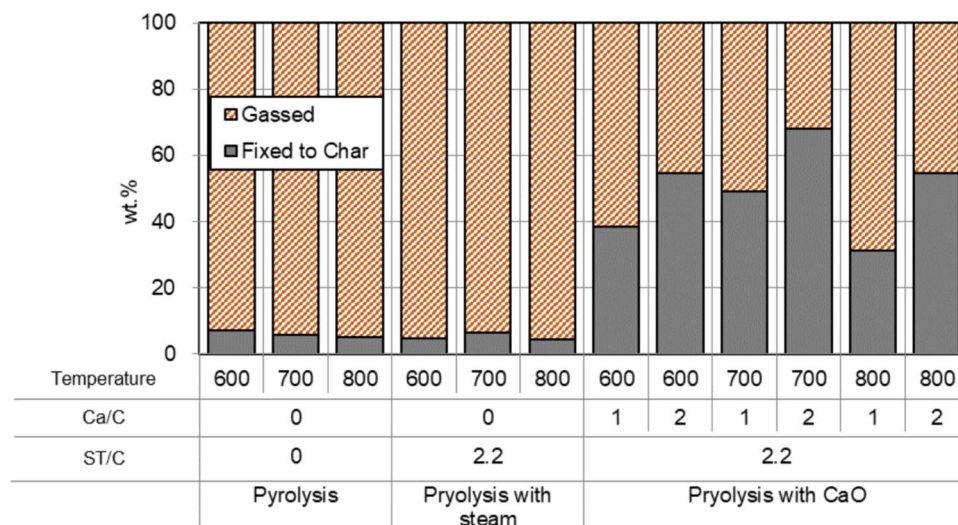
Material balance of nitrogen

Figure 8 summarizes the mass balance of N content in raw sludge, where "char fixation" in the legend indicates the weight ratio of N content in char to total N content in raw sludge, and "gasification" is the value obtained by subtracting "char fixation" from 1. This figure indicates that > 90 % of the N content in the sludge is volatilized and transferred to the gas side, including tar. In Ca-mixed steam gasification, the transfer rate to the gas side is larger than in pyrolysis gasification and steam gasification, where volatile N content is in the form of NH_3 and HCN gas [23, 24], most of which is assumed to comprise NH_3. Based on these results, the interaction between N-containing gas and CaO should be considered in future studies of the reforming process.

Fig. 8 Mass Balance of N Components in Raw Sludge
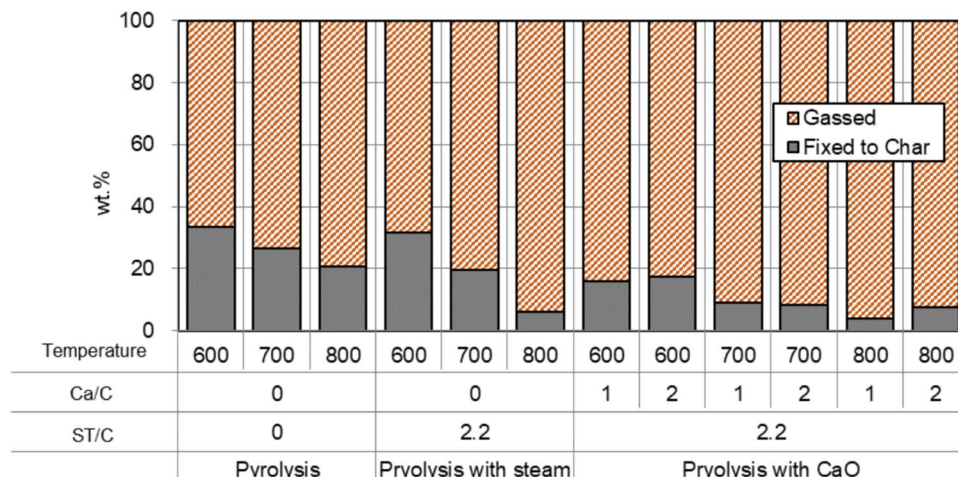
**Fig. 9** Mass balance of S Components in Raw Sludge

Material balance of sulfur

Gas sulfur compounds in the syngas produced by CLG can react with oxygen carriers to cause various adverse effects, including deactivation of the circulating flow media and corrosion of back-flow equipment [42]. Therefore, it is important to understand the behavior of sulfur content in the chemical-looping process.

Figure 9 shows the mass balance of S content in raw sludge. The findings in this figure indicate that the amount of S content fixed in the char is high in CaO-mixed steam gasification. Thus, in CaO-mixed steam gasification, H_2S generated by gasification presumably reacts with CaO and is immobilized as CaS, as shown in (R7) [28].

$$H_2S + CaO \rightarrow CaS + H_2O \qquad (R7)$$
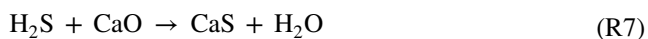
Conclusions

Lab-scale gasification experiments were conducted on dried sludge samples at gasification temperatures of 600–800 ℃. The following points (1–4) summarize our findings.

1) Regarding the generated gas, gasification was significantly accelerated in CaO-mixed steam gasification compared with pyrolysis gasification and steam gasification. At temperatures of 600 ℃ and 700 ℃, the absorption of CO_2 by CaO was substantial, and the concentration of H_2 in the gas approached 70 vol.%.

2) Analysis of tar components showed that the sludge contained C15–C19 linear hydrocarbons and aromatic hydrocarbons, such as cresol, phenol, and naphthalene. Indole was also detected as a component unique to sludge. The average molecular weight of tar was estimated to be in the range of 100–280, with a trend toward lower molecular weight at higher gasification temperatures, suggesting a greater proportion of aromatic hydrocarbons than linear hydrocarbons. In CaO-mixed gasification, tar with a higher C-to-weight ratio and higher calorific value was recovered compared with the results of pyrolysis gasification and steam gasification.

3) The results of the mass balance evaluation of C showed that in CaO-mixed steam gasification, the rate of transfer to the gas side was higher than in pyrolysis gasification and steam gasification, and almost all C was gasified at a temperature of 800 ℃. Additionally, at temperatures of 600 ℃ and 700 ℃, the char contained inorganic C, suggesting that the organic C in the sludge material was immobilized as $CaCO_3$ after gasification to CO_2. For example, at 600 ℃, 50 wt.% (20 wt.% organic C + 30 wt.% inorganic C) of the sludge material was immobilized in the char. These results indicate that 50 wt.% of the C in the sludge can be separated and recovered in the chemical loop regeneration process.

4) Assuming that all hydrocarbon components in the gasification gas were reformed and converted to H_2 and CO_2 in the reforming process, the amount of H_2 production obtained after reforming was estimated from the transfer rate of C contained in the sludge material to the gas side, which was 1.52 Nm^3-H_2/kg-DS at 700 ℃ and 1.63 Nm^3-H_2/kg-DS at 800 ℃.

To confirm the superiority of CLG over the conventional energy recovery system for sewage sludge, it is necessary not only to consider the cost of pretreatment system and flue gas treatment system (i.e. gas purification system to separate and remove tar, NH_3, HCN, H_2S, etc. for utilization of the product gas), but also to evaluate the system energy circulation and equipment power consumption for the entire system. Thus, further detailed studies using scale-up experiments and process calculations are needed. It is also necessary to study the performance and durability of CaO when used repeatedly or cyclically.

References

1. Home page; Ministry of Environment, Government of Japan (2021) Annual report on the environment in Japan 2021. https://www.env.go.jp/policy/hakusyo/r03/html/hj21020301.html

2. Home page; Ministry of Environment, Government of Japan (2022) (in Japanese) https://www.env.go.jp/press/110813.html

3. Home page; Ministry of Land, Infrastructure. Transport, Tourism ; Government of Japan (2018) (in Japanese) https://www.mlit.go.jp/mizukokudo/sewerage/mizukokudo_sewerage_tk_000364.html

4. Nhut MN, Falah A, Paul D, Bernd E (2021) Biomass-based chemical looping gasification: overview and recent developments. Appl Sci 11:7069. https://doi.org/10.3390/app11157069

5. Zhao X, Zhou H, Sikarwar V, Zhao M, Park A, Fennell P, Shen L, Fan L (2017) Biomass based chemical looping technologies: the good, the bad and the future. Energy Environ Sci 10:1885–1910. https://doi.org/10.1039/C6EE03718F

6. Adanez J, Abad A, García-Labiano F, Gayan P, de Diego LF (2012) Progress in chemical-looping combustion and reforming technologies. Prog Energy Combust Sci 38:215–282. https://doi.org/10.1016/j.pecs.2011.09.001

7. Nandya A, Lohaa C, Gub S, Sarkarc P, Karmakara MK, Chatterjeea PK (2016) Present status and overview of chemical looping combustion technology. Renew Sustain Energy Rev 59:597–619. https://doi.org/10.1016/j.rser.2016.01.003

8. Luo M, Yi Y, Wang S, Wang Z, Du M, Pan J, Wang Q (2018) Review of hydrogen production using chemical-looping technology. Renew Sustain Energy Rev 81:3186–3214. https://doi.org/10.1016/j.rser.2017.07.007

9. Lin Y, Wang H, Wang Y, Huo R, Huang Z, Liu M, Wei G, Zhao Z, LiFang HY (2020) Review of biomass chemical looping gasification in China. Energy Fuels 34:7847–7862. https://doi.org/10.1021/acs.energyfuels.0c01022

10. Avishek G, Elyas M, Wen L, Chao H, Jukka K (2022) Biomass chemical looping gasification for high-quality syngas; A critical review and technological outlooks. Energy Convers Manage 268:116020. https://doi.org/10.1016/j.enconman.2022.116020

11. Udomsirichakorn J, Salam P (2014) Review of hydrogen-enriched gas production from Steam gasification of biomass: the prospect of CaO-based chemical looping gasification. Renew Sustain Energy Rev 30:565–579. https://doi.org/10.1016/j.rser.2013.10.013

12. Moghtaderi B, Zanganeh J, Shah K, Wu H (2012) Application of concrete and demolition waste as CO_2 sorbent in chemical looping gasification of biomass. Energy Fuels 26:2046–2057. https://doi.org/10.1021/ef300145t

13. Acharya B, Dutta A, Basu P (2009) Chemical looping gasification of biomass for hydrogen enriched gas production with in-process carbon-dioxide capture. Energy Fuels 23:5077–5083. https://doi.org/10.1021/ef9003889

14. Zhu J, Wang W, Lian S, Hua X, Xi Z (2017) Stepwise reduction kinetics of iron-based oxygen carriers by CO/CO_2 mixture gases for chemical looping hydrogen generation. J Mater Cycles Waste Manag 19:453–462. https://doi.org/10.1007/s10163-015-0443-2

15. Wei L, Xu S, Liu J, Liu C, Liu S (2008) Hydrogen production in steam gasification of biomass with CaO as a CO_2 absorbent. Energy Fuels 22:1997–2004. https://doi.org/10.1021/ef700744a

16. Alonso M, Diego M, Pérez CC, Chamberlain J, Abanades J (2014) Biomass combustion with in-situ CO_2 capture by CaO in a 300 kWth circulating fluidized bed facility. Int J Greenhouse Gas Control 29:142–152. https://doi.org/10.1016/j.ijggc.2014.08.002

17. Yin F, Shah K, Zhou C, Tremain P, Yu J, Doroodchi E, Moghtaderi B (2016) Novel calcium-looping-based biomass-integrated gasification combined cycle. Thermodynamic modeling and experimental study. Energy Fuels 30:1730–1740. https://doi.org/10.1021/acs.energyfuels.5b02266

18. Huang Z, Xu G, Deng Z, Zhao K, He F, Chen D, Wei G, Zheng A, Zhao Z, Li H (2017) Investigation on gasification performance of sewage sludge using chemical looping gasification with iron ore oxygen carrier. Int J Hydrogen Energy 42(2017):25474–25491. https://doi.org/10.1016/j.ijhydene.2017.08.133

19. Deng Z, Huang Z, He F, Zheng A, Wei G, Meng J, Zhao Z, Li H (2019) Evaluation of calcined copper slag as an oxygen carrier for chemical looping gasification of sewage sludge. Int J Hydrogen Energy 44:17823–17834. https://doi.org/10.1016/j.ijhydene.2019.05.039

20. Dong N, Huo R, Liu M, Deng L, Deng Z, Chang G, Huang Z, Huang H (2021) Chemical looping gasification of sewage sludge using copper slag modified by NiO as an oxygen carrier. Chin J Chem Eng 29:335–343. https://doi.org/10.1016/j.cjche.2020.09.007

21. Mahzoun Y, Oshita K, Takaoka M, Fujimori T (2017) National survey of dewatered sewage sludge composition in Japan: trend of organic elements and prediction of higher heating value. J Sewage Works Association 659:86–95. https://doi.org/10.24748/jswa.54.659_86

22. New Energy and Industrial Technology Development Organization (NEDO) Government of Japan. Report for FY2012 - 2013 Period: Research and Development of Biomass Energy Technologies; Development of Strategic, Next-Generation Technologies for Biomass Energy Use (next-generation technology development); and Development of Advanced Biomass Co-gasification (ABC), a Next-Generation Technology for Biomass Liquid Fuel Production Systems. https://seika.nedo.go.jp/pmg/PMG01C/PMG01CG02 key word: 20150000000769

23. Fang S, Deng Z, Lin Y, Huang Z, Ding L, Deng L, Huang H (2021) Nitrogen migration in sewage sludge chemical looping gasification using copper slag modified by NiO as an oxygen carrier. Energy 288:120448. https://doi.org/10.1016/j.energy.2021.120448

24. Fang S, Deng Z, Lin Y, Huang Z, DingDeng LL, Huang H (2021) Investigation of the nitrogen migration characteristics in sewage sludge during chemical looping gasification. Energy 216:119247r. https://doi.org/10.1016/j.energy.2020.119247

25. Kessas H, Esteves T, Hemati M (2021) Products distribution during sewage sludge pyrolysis in a sand and olivine fluidized bed reactor: comparison with woody waste. Waste Biomass Valorization 12:3459–3484. https://doi.org/10.1007/s12649-020-01209-9

26. Gao N, Li A, Quan C, Qu Y, Mao L (2012) Characteristics of hydrogen-rich gas production of biomass gasification with porous ceramic reforming. Int J Hydrogen Energy 37:9610–9618. https://doi.org/10.1016/j.ijhydene.2012.03.069

27. Lin Y, Mo Y, Fang S, Huang Z, Weid G, Zhao Z, Huang H (2022) A study on the chemical looping combustion of sewage sludge, the emission of NOx and its precursors. Fuel Process Technol 231:107260. https://doi.org/10.1016/j.ijhydene.2012.03.069

28. Oshita K, Mori A, Takaoka M, Takeda N, Matsumoto T, Kitayama A (2008) Fundamental study on the composition and heating value of char tar and gas from sewage sludge pyrolysis. JSCE 64(3):221–230. https://doi.org/10.2208/jscejg.64.221

29. Islam MW (2020) A review of dolomite catalyst for biomass gasification tar removal. Fuel 2020(267):117095. https://doi.org/10.1016/j.fuel.2020.117095

30. Rigo VA, Metin CO, Nguyen QP, Miranda CR (2012) Hydrocarbon adsorption on carbonate mineral surfaces: a first-principles study with van der waals interactions. J Phys Chem C 116:24538–24548. https://doi.org/10.1021/jp306040n

31. Hervy M, Olcese R, Bettahar MM, Mallet M, Renard A, Maldonado L, Remy D, Mauviel G, Dufour A (2019) Evolution of dolomite composition and reactivity during biomass gasification.

Appl Catal Gen 572:97–106. https://doi.org/10.1016/j.apcata.2018.12.014

32. Udomsirichakorn J, Basu P, Salam PA, Acharya B (2014) CaO-based chemical looping gasification of biomass for hydrogen-enriched gas production with in situ CO_2 capture and tar reduction. Fuel Processing Tech 127(2014):7–12. https://doi.org/10.1016/j.fuproc.2014.06.007

33. Lopez JM, Navarro MV, Murillo R, Grasa GS (2017) Development of synthetic Ca-based CO_2 sorbents for sorption enhanced reforming coupled to Ca/Cu chemical loop. Energy Procedia 114(22017):230–241

34. Arias B, Alonso M, Abanades C (2011) CO_2 capture by calcium looping at relevant conditions for cement plants: experimental testing in a 30 kW_{th} pilot plant. Ind Eng 50:6972–6981. https://doi.org/10.1021/acs.iecr.6b04617

35. Dufour A, Girods P, Masson E, Rogaume Y, Zoulalian A (2009) Synthesis gas production by biomass pyrolysis: effect of reactor temperature on product distribution. Int J Hydrogen Energy 34:1726–1734. https://doi.org/10.1016/j.ijhydene.2008.11.075

36. Dufour A, Masson E, Girods P, Rogaume Y, Zoulalian A (2011) Evolution of aromatic tar composition in relation to methane and ethylene from biomass pyrolysis-gasification. Energy Fuels 25:4182–4189. https://doi.org/10.1021/ef200846g

37. Shen Y, Yoshikawa K (2013) Recent progresses in catalytic tar elimination during biomass gasification or pyrolysis-a review. Renew Sustain Energy Rev 21:371–392. https://doi.org/10.1016/j.rser.2012.12.062

38. Kambara S and Moritomi H (2009) Behavior of tar in pyrolysis and gasification reactions of biomass, Chemical engineering 54(3),231–235 https://kambara.main.jp/3publication/Reviews/R14.pdf

39. Bradbury R, Hancox N, Hatt H (1947) The reaction between acetone and ammonia : the formation of pyrimidine compounds analogous to the aldoxans of sp a th. J Chem Soc. https://doi.org/10.1039/JR9470001394

40. Niu X, Shen L, Gu H, Song T, Xiao J (2015) Sewage sludge combustion in a CLC process using nickel-based oxygen carrier. Chem Eng J 260:631–641. https://doi.org/10.1016/j.cej.2014.09.005

41. Japan Science and Technology Agency - JST, Department of R&D for future creation. Methane production from biomass wastes by anaerobic fermentation (First step) Strategy for Technology Development Proposal Paper for Policy Making and Governmental Action toward Low Carbon Societies. https://www.jst.go.jp/lcs/proposals/fy2013-pp-05.html

42. Adánez J, Abad A (2019) Chemical-looping combustion: status and research needs. Proc Combust Inst 37:4303–4317. https://doi.org/10.1016/j.proci.2018.09.002

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.