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Production of Activated Char and Producer Gas Sewage Sludge

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1. Introduction

According to the depletion of fossil fuel and global warming, energy conversion technology for waste has been considered as value added alternative energy source. Among the potential waste that can be converted into energy, waste sludge continues to be increased due to increased amount of waste water treatment facilities, resulting from industry development and population increase. Most of waste sludge was treated through landfill, incineration, and land spreading (Fullana et al, 2003; Inguanzo et al, 2002; Karayildirim et al, 2006). However, landfill requires the complete isolation between filling site and surrounding area due to leaching of hazardous substance in sludge, and has the limited space for filling site. Utilization of sludge as compost incurs soil contamination by increasing the content of heavy metal in soil, and causes air pollution problem due to spreading of hazardous component to atmosphere. Incineration has the benefits of effective volume reduction of waste sludge and energy recovery, but insufficient mixing of air could discharge hazardous organic pollutant especially in the condition of low oxygen region. In addition, significant amount of ashes with hazardous component will be created after incineration. As alternative technology for the previously described sludge treatment methods, researches on pyrolysis (Domínguez et al, 2006; Fullana et al, 2003; Karayildirim et al, 2006) and gasification treatment (Doğru et al, 2002; Phuphuakrat et al, 2010) have been conducted. Pyrolysis/gasification can produce gas, oil, and char that could be utilized as fuel, adsorber and feedstock for petrochemicals. In addition, heavy metal in sludge (excluding cadmium and mercury) can be safely enclosed. It is treated at the lower temperature than incineration so that amount of contaminant is lower in pyrolysis gasification gas due to no or less usage of air. Moreover, hazardous components, such as dioxin, are not generated. However utilization of producer gas from pyrolysis gasification into engine and gas turbine might cause the condensation of tar. In addition, aerosol and polymerization reaction could cause clogging of cooler, filter element, engine inlet, etc (Devi et al, 2005; Tippayawong & Inthasan, 2010).

As the reduction methods of tar component, in-pyrolysis gasifier technology (IPGT) and technology after pyrolysis gasifier (TAPG) were suggested. Firstly, IPGT does not require the additional post-treatment facility for tar removal, and further development is required for operating condition and design of pyrolysis gasifier. Through these conditions and technical advancement, production of syngas with low tar content can be achievable, but cost and large scaled complex equipments are needed (Bergman et al, 2002; Devi et al, 2003).
Secondly, multi-faceted researches on TAPG, such as thermal cracking (Phuohuakrat et al., 2010; Zhang et al., 2009), catalysis (Pfeifer & Hofbauer, 2008), adsorption (Phuohuakrat et al., 2010), steam reforming (Hosokai et al., 2005; Onozaki et al., 2006; Phuohuakrat et al., 2010), partial oxidation (Onozaki et al., 2006; Phuohuakrat et al., 2010), plasma discharge (Du et al., 2007; Guo et al., 2008; Nair et al., 2003; Nair et al., 2005; Tippayawong & Inthasan, 2010; Yu et al., 2010; Yu et al., 2010), etc have been conducted. For thermal cracking, higher than 800°C is required for the reaction, and its energy consumption surpass the production benefit. Catalyst sensitively reacts with contaminants such as sulfur, chlorine, nitrogen compounds from biomass gasification. Also, catalyst can be de-activated due to cokes formation, and additional energy cost to maintain high temperature is needed. For adsorption, there were several researches utilizing char, commercial activated carbon, wood chip and synthetic porous cordierite for tar adsorption. In case of adsorbers having mesopore, adsorption performance of light PAH tars, such as naphthalene, anthracene, pyrene, etc excluding light aromatic hydrocarbon tar (benzene, toluene, etc) was superior.

Tar reduction in steam reforming, partial oxidation and plasma discharge can produce syngas having major compounds of hydrogen and carbon monoxide through reforming and cracking reaction. The steam reforming has a good characteristic in high hydrogen yield. But it requires high temperature steam which consumes great deal of energy. In addition, longer holding time might require larger facility scale. On the contrary, partial oxidation reforming features less energy consumption, and has the benefit of heat recovery due to exothermic reaction. However, hydrogen yield is relatively small, and large amount of carbon dioxide discharge is the disadvantage. Researches on tar decomposition via plasma discharge were conducted in dielectric barrier discharge (DBD) (Guo et al., 2008), single phase DC gliding arc plasma (Du et al., 2007; Tippayawong & Inthasan, 2010; Yu et al., 2010), and pulsed plasma discharge (Nair et al., 2003). Compared to conventional thermal and catalytic cracking, the plasma discharge shows the higher removal efficiency due to the formation of radicals. However, high cost of preparation of power supply and short life cycle is the key for improvement. A 3-phase arc plasma applied for tar removal is easy to control the reaction, and has high decomposition efficiency along with high energy efficiency. That is to say; all the methods have limitation in the waste sludge treatment for producing products and removing tar in the producer gas. Therefore, the combination of both IPGT and TAPG should be accepted as a new alternative method for with feature of environment-friendliness.

In this study, thermal treatment system with pyrolysis gasifier, 3-phase gliding arc plasma reformer, and sludge char adsorber was developed for energy and resource utilization of waste sludge. A pyrolysis gasifier was combined as screw pyrolyzer and rotary carbonizer for sequential carbonization and steam activation, and it produced producer gas, sludge char, and tar. For the reduction of tar from the pyrolysis gasifier, a 3-phase gliding arc plasma reformer and a fixed adsorber bed with sludge char were implemented. System analysis in pyrolysis gasification characteristics and tar reduction from the thermal treatment system were achieved.

2. Experimental apparatus and methods

2.1 Sludge thermal treatment system

A pyrolysis gasification system developed in this study was composed of pyrolysis gasifier, 3-phase gliding arc plasma reformer, and fixed bed adsorber, as shown in figure 1.
A pyrolysis gasifier was designed to be a combined rig with a screw carbonizer for pyrolysis of dried sludge and a rotary activator for steam activation of carbonized material. The screw carbonizer was manufactured as feed screw type for carbonization of dried sludge. Feed screw controls the holding time of dried sludge at carbonizer according to motor revolution number. The screw carbonizer features dual pipe, and steam holes were installed at radial direction of external wall, and high pressure steam is discharged to activator radially. The rotary activator is composed of rotary drum with vane and pick-up flight, indirect heating jacket, pyrolysis gas outlet, gas sampling port, char outlet, etc. Retention time of activated sludge is controlled via number of rotation for a rotary drum. A sludge feeding device is for holding of dried sludge in a dried sludge hopper which is installed at inlet of the combined pyrolysis gasifier. A screw feeder is installed at the bottom of the hopper, and controls the input amount of dried sludge via revolution number. The feeder feeds the dried sludge into the screw carbonizer. A hot gas generator is for producing hot gas to heat a heating jacket and supply hot steam into a rotary drum. It was composed of a combustor with burner and a steam generator.

A 3-phase gliding arc plasma reformer was installed at downstream of outlet for the pyrolysis gasifier. The gliding arc plasma reformer utilized a quartz tube (55 mm in diameter, 200 mm in height) for insulation and monitoring purposes, and a ceramic connector (Al$_2$O$_3$, wt 96%) in electrode fixing was adopted for complete insulation between three electrodes. The three conical electrodes in 120° (95 mm in length) were installed, maintaining 3 mm gap. At the inlet of the plasma reformer, a orifice disc with 3 mm hole for injection of producer gas was installed. A 3-phase AC high voltage power supply unit (Unicon Tech., UAP-15K1A, Korea) was used for stable plasma discharge at the inside of the plasma reformer.

A sludge char adsorber was made of a fixed bed cylinder (76 mm in diameter, 160 mm in length), and installed at the rear section of the plasma reformer. To fix the packing material at an adsorber, a porous distributor in stainless steel (25-mesh) was installed at the upper part. The porous distributor was made in a honeycomb ceramic for preventing channeling effect of input producer gas.

Fig. 1. Experimental setup of a pyrolysis gasification
Experiment was conducted at optimal condition for high quality porosity in sludge char and for the largest amount of combustible gas formation. The experimental conditions and each temperature condition were given in table 1. All the data in experiments were taken after stabilizing temperatures at each part, particularly the screw carbonizer and rotary activator. After finishing experiment by setting condition, sludge char in a char outlet is cooled up to room temperature by nitrogen passed the pyrolysis gasifier to protect the oxidation of the sludge char by air. Gas was sampled for 5 minutes in a stainless cylinder at the sampling ports of each pyrolysis gasifier, plasma reformer, and adsorber (Refer a gas sampling line in section 2.3.2). For tar sampling, it was conducted for 20 minutes by tar sampling method (as shown section 2.2), and total amount of gas was measured with a gas-flow meter. For a test, the gas and tar sampling were conducted 3 times during test time of 120 minutes stably, and the taken data were averaged. Adsorption capacity of sludge char was calculated from weight of adsorber before/after experiment divided by test time.

| Test conditions | Steam feed amount (mL/min) | Moisture content of dried sludge (%) | Retention time (min) |
|-----------------|---------------------------|-------------------------------------|----------------------|
|                 |                           | 9.8                                 | Activator Carbonizer |
| Temperature (°C) |                           | 100                                 | 30 30                |
| Activator       |                           | 820                                 | 450 450             |
| Steam generator |                           |                                    | 400 35               |
| Plasma reformer |                           | 1,010                               | 450                  |
| Adsorber        |                           | 450                                 |                      |

1) Moisture content of dried sludge is average number

Table 1. Detailed conditions in each section

2.2 Tar sampling and analysis methods
Tar sampling and analysis were used by the method of biomass technology groups (BTGs) (Good et al, 2005; Neeft, 2005; Phuohuakrat et al, 2010; Son et al, 2009; Yamazaki et al, 2005). Wet sampling module was installed with 6 impingers (250 mL) in two separated isothermal baths for adsorption of tar and particles. At the first isothermal bath, 100 mL of isopropanol was filled into 4 impingers, respectively, along with 20°C of water. For the second bath, isopropanol was filled while it was maintained at -20°C using mechanical cooling device (ECS-30SS, Eyela Co., Japan). Among 2 impingers, 1 unit was filled with 100 mL of isopropanol, and the other was left as empty. In the series of impinger bottles, the first impinger bottle acts as a moisture and particle collector, in which water, tar and soot are condensed from the process gas by absorption in isopropanol. Other impinger bottles collect tars, and the empty bottle collects drop. Immediately after completing the sampling, the content of the impinger bottles were filtered through a filter paper (Model F-5B, Advantec Co., Japan). The filtered isopropanol solution was divided into two parts; the first was used to determine the gravimetric tar mass by means of solvent distillation and evaporation by evaporator (Model N-1000-SW, Eyela, Japan) in which temperature and steam pressure were 55~57°C and 230 hPa, respectively. The second was used to determine the concentrations of light tar compounds using GC-FID (Model 14B, Shimadzu, Japan).
Quantitative tar analysis was performed on a GC system, using a RTX-5 (RESTEK) capillary column (30 m - 0.53 mm id, 0.5 μm film thickness) and an isothermal temperature profile at...
45°C for the first 2 min, followed by a 7 °C/min temperature gradient to 320°C and finally an isothermal period at 320°C for 10 min. Helium was used as a carrier gas. The temperature of the detector and injector were maintained at 340 and 250°C, respectively.

Fig. 2. Tar sampling line system

2.3 Sludge char and gas analysis
2.3.1 Pore development in sludge char
The structural characterization of the sewage sludge char was carried out by physical adsorption of N₂ at -196°C. The adsorption isotherms were determined using nanoPOROSITY (Model nanoPOROSITY-XQ, MiraeSl Co. Ltd, Korea). The surface area was calculated using the BET (Brauner-Emmet-Teller) equation. Using BJH (Barret-Joyner-Halenda) equation, incremental pore volume and mean pore size was calculated. To compare pore development in sludge char, SEM (scanning electron microscopy; Model S-4800, Hitachi Co., Japan) was used, and image was taken at 50,000X resolution for morphological analysis. Chemical properties and constituent components were analyzed via EDX (Energy-dispersive X-ray spectroscopy; Model 7593-H, Horiba, UK).

2.3.2 Sampling and analysis producer gas
The produced gas was sampled for 5 minutes in a stainless cylinder as sampling gas flow rate is 1 L/min. As can be seen in figure 2, a set of backup VOC adsorber was installed downstream of the series of impinger bottles to protect the column of the gas chromatography from the residual solvent or VOCs, which may have passed through the impinger train. The set of backup VOC adsorber consists of two cotton filters and an activated carbon filter connected in a series. Gas analysis was conducted with GC-TCD (Model CP-4900 Varian, Netherland). MolSieve 5A PLOT column for H₂, CO, O₂, and N₂ and PoraPLOT Q column for CO₂, CH₄, C₂H₄, and C₂H₆ were used for simultaneous analysis.

3. Results and discussion
3.1 Dried sludge characteristics
Sludge from a local wastewater treatment plant was dewatered by a centrifuging. And then the dewatered sludge was dried to less than 10% of moisture content using a rotary kiln type dryer developed by the corresponding researcher. The pyrolysis gasification is a
process of which heat is applied by external source or partial oxidation. Vaporization temperature of moisture is lower than thermal decomposition temperature for organic compound in sludge. Therefore, high moisture content in sewage sludge will show significant energy loss due to preemptive utilization of the heat for drying. In addition, delayed pyrolysis gasification will affect the producer via reaction with moisture and reactant. Therefore, less than 10% of moisture content in the dried sludge was taken for this study.

Table 2 shows proximate analysis and ultimate analysis on the dried sludge.

| Proximate analysis (%) | Moisture | Volatile matter | Fixed carbon | Ash |
|------------------------|----------|-----------------|--------------|-----|
| 9.7                    | 51.7     | 6.1             | 32.5         |

| Ultimate analysis (%) | C | H | O | N | S |
|-----------------------|---|---|---|---|---|
| 52.3                  | 8.2 | 32.2 | 7.92 | 0.01 |

Table 2. Properties of the dried sludge

3.2 Thermal behavior analysis

To determine pyrolysis temperature, TGA (thermo gravimetric analysis) and DTG (derived thermo-gravimetric) analysis was shown in figure 3. According to TGA and DTG results, the maximum weight loss temperature and final decomposition temperature, etc can be derived (Karayildirim et al, 2006).

![Fig. 3. TGA and DTG for pyrolysis of the dried sewage sludge](image)

Thermal decomposition of the dried sludge showed weight loss after evaporation of small moisture content at 100~150°C as shown in DTG curve. This could be elucidated by two steps. First step (primary pyrolysis) is discharging of volatile component at 200~500°C, and the second step is decomposition of inorganic compound at over 500°C. First step for volatile component discharge displayed two peaks, and it can be explained as follows. The first peak might be due to decomposition and devolatilization of less complex organic
structures which is a small fraction. The second peak was caused by decomposition of more complex organic structures corresponding to a larger fraction. Second step (secondary pyrolysis) is related to decomposition of inorganic compound as described before. In first step, TGA displayed 57\% at 500°C, and 900°C for the second step was 46.2\%. That is, 43\% of moisture content and volatile component was discharged during the first step, and in second step 10.8\% reduction (from first step) was corresponded to decomposing ash which is an inorganic component in dried sludge. Therefore, for the pyrolysis gasification experiment in purpose of improved yield of producer gas and higher adsorption rate, pyrolysis carbonization were maintained at 450°C which discharges the largest amount of volatile component, and steam activation was set to 850°C for increasing the porosity in the sludge char.

3.3 Characteristics of a pyrolysis gasifier

Figure 4 shows mass yield for char, tar, and gas from a pyrolysis gasifier. The product amount ordered was producer gas of 43.6\%, sludge char of 35.4\% and tar of 21\%. As described before, the corresponding experiment setup was made to primary pyrolysis carbonization at screw carbonizer which is set to 450°C and post-activation at rotary kiln activator along with steam injection, which is set to 820°C. Producer gas was formed by decomposition and volatilization of organic compound in a screw carbonizer (refer first step description of DTG in figure 3), and gas formation was increased due to steam reforming of tar and char in a rotary kiln activator. Sludge char in mass was reduced by vaporization of volatile component during the passing of the carbonizer, and steam gasification and inorganic decomposition in the activator. Heavy tar was formed and then it was converted into producer gas and light tar at the activator.

![Fig. 4. Mass yield of the products](image)

3.3.1 Characteristics of the sludge char

Figure 5 compares incremental pore volume and SEM photos of the dried sludge and sludge char. The pore size classification in this study follows the IUPAC classification (IUPAC, 1982; Lu, 1995) i.e. micropores (<20 Å), mesopores (20∼500 Å) and macropores (>500 Å). Pore
of sludge char after carbonization activation showed significant increase compared to the dried sludge, and pore distribution was less than 500 Å, which is comprised of micropores and mesopores. The pyrolysis gasifier in this study had been designed as continuously combined type for carbonization of dried sludge at a screw carbonizer and steam activation at a rotary activator. The dried sludge experienced evaporating of moisture and decomposing of organic component for pore development through passing the screw carbonizer (Lu, 1995). And then carbonized material was exposed to steam at the rotary activator for the formation and development of micropores and mesopores. For steam activation in developing micropores, steam should deeply penetrate into pores of the carbonized material for surface reaction. High temperature activation had the benefit of diffusion and penetration of the steam to develop micropore. On the other hand, it was blocked by tar in the carbonized material, resulted as well-developed mesopore. This is the reason that the sludge char from the carbonization activation had well-developed micropores and mesopores. Sludge drying was made with a parallel flow rotary kiln drier with direct-hot gas application. Hot gas inflow in turbulent flow was directly contacted with the dewatered sludge in the dryer. Inside of the dryer was set to 255°C in average value. For dried sludge, small portion of micropore and mesopore was formed. It is considered to be formed due to discharging of volatile organic material and dehydroxlation of inorganic material from the dried sludge. Bagreev et al. proved that water released by the dehydroxylation of inorganic material could aid pore formation and moreover could act as an agent for creating micropores (Bagreev et al., 2001). In addition, Inguanzo et al. proposed that carbonization increases the porosity through unblocking many of the pores obscured by volatile matter (Inguanzo et al., 2001). Surface of the dried sludge from SEM photograph in 50,000 times of magnification shows smooth surface with less pores, but the sludge char presents overall formation of pores.

![Incremental pore volume and SEM images of the dried sludge and sludge char](image)

**Fig. 5.** Incremental pore volume and SEM images of the dried sludge and sludge char

Table 3 compares the results of the sludge char made from this study and 3 types adsorbent from the study of Thana Phuphuakrat etc (Phuphuakrat et al, 2010). For the sludge char,
specific surface area and pore volume were smaller than commercial activated carbon, and mean pore size was larger. The sludge char displayed mesopore similar to wood chip and synthetic porous cordierite, but the activated carbon featured micropore. Adsorption capability of the sludge char was less than the one with wood chip, but larger than the one of activated carbon and synthetic porous cordierite. The adsorption experiment in this study was conducted by using benzene only. So the comparison in the adsorption capacity has difficulty because the study of Thana Phuphuakrat etc was achieved in a continuous test rig using Japanese cedar which produced pyrolysis gas including all tars and water. However, it might be considered that the wood chip adsorbed large amount of steam when compared to the sludge char, because of hydrophilic surface and mesoporous material favoring water adsorption. Although the test in non-condensable light aromatic hydrocarbon (e.g. benzene) was conducted in this study, it should be expected for the sludge char to adsorb well for the condensable light PAH (e.g. naphthalene, anthracene, pyrene) due to having mesopores as proved in the other study.

| Adsorbent                  | Specific surface area (m²/g) | Mean pore size (Å) | Pore volume (cm³/g) | Adsorption capacity (mg/g) |
|----------------------------|------------------------------|--------------------|---------------------|---------------------------|
| Sludge char¹)              | 98.1                         | 63.49              | 0.2354              | 120.6                     |
| Activated carbon           | 987.1                        | 11.28              | 0.5569              | 97.5                      |
| Wood chip                  | 1.072                        | 100.77             | 0.0058              | 155.7                     |
| Synthetic porous cordierite| 6.045                        | 27.43              | 0.0083              | 12.8                      |

¹) Sludge char from this study

Table 3. Porous characteristics and adsorption capacity of the adsorbents from this study and other results (Phuohuakrat et al, 2010)

A semi quantitative chemical analysis of dried sludge and sludge char, figure 6 and table 4, was obtained from the EDX analyzer coupled to SEM measurements. The results indicate that both samples present relatively high carbon content in addition to mineral components. The relative amount of carbon decreased after carbonization and activation, as expected considering the decomposition of the organic components. These atoms might be considered as the potential catalysts for pyrolysis reaction. For example, with Al, if existing in the form of Al₂O₃, it would be an acid catalyst for cracking reaction (Sinfelt & Rohrer, 1962); or with K, and Ca atoms, they were already reported as the catalyst for biomass pyrolysis in literature (Yaman, 2004). Figure 7 shows the N₂ adsorption-desorption isotherm for the dried sludge and sludge char. According to the isothermal adsorption graphs, the dried sludge exhibited only a small amount of adsorption, but the sludge char displayed a larger amount of adsorption at lower nitrogen concentrations. As shown in figure 5, the sludge char exhibited well-developed micro- and meso-pore structures. The analysis on the adsorption isotherm provides an assessment for the pore size distribution. According to the IUPAC classification, the curve of the sludge char corresponds to Type V isotherm. A characteristic of the Type V isotherm is the hysteresis loop, which is associated with the capillary condensation in mesopores and limiting uptake at high relative pressure (Khalili et al, 2000).
Fig. 6. EDX spectrums of dried sludge and sludge char

| Item                      | C     | O     | Mg    | Al    | Si    | P     | S     | Cl    | K     | Ca    | Ti    | Fe    | Zn    | Ba    |
|---------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Dried sludge (wt %)      | 53.65 | 44.62 | 0.06  | 0.23  | 0.45  | 0.55  | 0.03  | 0.01  | 0.06  | 0.07  | 0.01  | 0.24  | 0.02  | 0     |
| Sludge char (wt %)        | 47.65 | 44.83 | 0.14  | 1.21  | 5.34  | 0.46  | 0.03  | 0.02  | 0.09  | 0.11  | 0     | 0.21  | 0     | 0.01  |

Table 4. Elements content of dried sludge and sludge char

Fig. 7. Isothermal adsorption-desorption linear plot
3.3.2 Tar characteristics for the pyrolysis gasification

Results produced from the pyrolysis gasifier were shown in Table 5. Representative tars for the corresponding benzene ring were selected to benzene (1 ring), naphthalene (2 ring), anthracene (3 ring) and pyrene (4 ring). And the representative tars with nitrogen for the sewage sludge (Fullana et al., 2003) were taken as benzonitrile and benzeneacetonitrile. Gravimetric tar was 26.3 g/Nm$^3$. Total concentration of light tar was 10.9 g/Nm$^3$, and its amount order was benzene, naphthalene, benzonitrile, benzeneacetonitrile, anthracene, and pyrene. Dried sludge formed sludge char, tar, and gas during pyrolysis at screw carbonizer, and then steam activation was achieved in rotary activator. The gravimetric tar is total amount of tar after passing carbonization and activation process. Benzene and naphthalene among light tar are products produced during secondary pyrolysis at carbonizer, and some part of both tars converts to gas during steam activation at activator. In addition, anthracene and pyrene were directly formed by primary pyrolysis from dried sludge at carbonizer. Both tars should be known as not affecting by carbonization-activation temperature and steam amount (Umeki, 2009).

| Gravimetric tar | Benzene | Naphthalene | Anthracene | Pyrene | Benzonitrile | Benzeneacetonitrile |
|-----------------|---------|-------------|------------|--------|--------------|---------------------|
| 26.3            | 6.31    | 2.97        | 0.87       | 0.12   | 0.61         | 0.11                |

Table 5. Tar concentrations from a pyrolysis gasifier (unit: g/Nm$^3$)

3.3.3 Producer gas characteristics

Table 6 shows producer gas concentration and higher heating value from a pyrolysis gasifier. Major components in gas were analyzed to be hydrogen, carbon monoxide, methane, and carbon dioxide along with trace amount of nitrogen and oxygen. The higher heating value was 13,400 kJ/Nm$^3$ having half value of natural gas.

| H$_2$ | CO  | CH$_4$ | CO$_2$ | C$_2$H$_4$ | C$_2$H$_6$ | O$_2$ | N$_2$ | Higher heating value |
|-------|-----|--------|--------|------------|------------|-------|-------|----------------------|
| 41.2  | 17.3| 9.5    | 15.4   | 0          | 0          | 0.5   | 3.3   | 13,400               |

Table 6. Concentration of producer gas (dry vol. %) and higher heating value (kJ/Nm$^3$)

Hydrogen was produced by the cracking of the volatile matter generated by the pyrolysis gasification. Methane resulted from cracking and depolymerization reactions, while carbon monoxide and carbon dioxide were produced from decarboxylation and depolymerization or the secondary oxidation of carbon (Xiao et al., 2010). In addition, the presence of steam at high temperatures gave rise to in situ steam reforming of the volatile matters and partial gasification of the solid carbonaceous residue, as shown in the reactions of Eqs. (1) and (2). Non-condensable products may also undergo gas phase reactions with each other. For example, the CO and CH$_4$ contents may be affected by the methane gasification and water gas shift reactions, as shown in Eqs. (3) and (4) (Domínguez et al., 2006).

- **Steam reforming reaction:**

  \[ \text{Organics (g)} + H_2O(g) \leftrightarrow CO + H_2 \quad (1) \]

- **Steam gasification reaction:**

  \[ C(s) + H_2O(g) \leftrightarrow CO + H_2, \quad \Delta H_{298k} = 132 kJ \text{ mol}^{-1} \quad (2) \]
CH₄ gasification reaction:

\[ CH_4 + H_2O \leftrightarrow CO + 3H_2, \quad \Delta H_{298K} = 206.1kJ mol^{-1} \]  (3)

CO shift reaction:

\[ CO + H_2O \leftrightarrow CO_2 + H_2, \quad \Delta H_{298K} = -41.5kJ mol^{-1} \]  (4)

High temperatures were also responsible for the reduction of C₃H₄, C₃H₆, and C₃H₈. Some of the typical reactions are as follows (Zhang et al., 2010):

\[ C_H_4 \rightarrow C_H_4 + H_2 \]  (5)

\[ C_H_4 \rightarrow CH_4 + C \]  (6)

However, it should be noted that the gas composition may not exclusively be the result of tar cracking and the partial gasification of char due to the complicated interactions of the intermediate products, which would probably affect the final gas composition.

3.4 Plasma reformer and adsorber characteristics

The plasma reformer was installed for converting produced tar from the pyrolysis gasifier into syngas via decomposition and steam reforming. In addition, the fixed bed adsorber was implemented for adsorption of by-passed tar from the plasma reformer.

3.4.1 Tar destruction performance

Fig. 8 shows the results of tar sampling at the rear section of the pyrolysis gasifier, plasma reformer, and fixed bed adsorber. Gravimetric tar concentration at the outlet of carbonization activator was 26.3 g/Nm³, and it was reduced to 4.4 g/Nm³ at the reformer outlet. Decomposition efficiency of the corresponding gravimetric tar was 83.2%. For light tar, total amount of carbonization activator outlet was 10.9 g/Nm³. The concentration was reduced to 1.3 g/Nm³ at the outlet of reformer, and the destruction efficiency of the light tar was 87.9%. Each concentration of the light tars was found to be 0.62 g/Nm³ for benzene, 0.45 g/Nm³ for naphthalene, 0.14 g/Nm³ for anthracene, 0.021 g/Nm³ for pyrene, 0.08 g/Nm³ for benzonitrile, and 0.015 g/Nm³ for benzeneacetonitrile.

Decomposition of heavy tar was happened due to plasma cracking and carbon formation in Eqs. (7) and (8) (Tippayawong & Inthasan, 2010). In addition, steam in producer gas from the pyrolysis gasifier formed excitation species as shown in Eq. (9), and the radicals reduced light tar and carbon black which produce by the reactions of plasma cracking and carbon formation (Guo et al., 2008). It is remarkable that the tars from the pyrolysis gasification should be decomposed significantly by the plasma reformer.

- Plasma cracking:

\[ pC_xH_y \rightarrow qC_aH_{2a} + rH_2 \]  (7)

- Carbon formation:

\[ C_xH_y \rightarrow nC + (x/2)H_2 \]  (8)
- Water excitation:

\[
H_2O \rightarrow H_\bullet, e^{-}, OH, H_2, O_2, H_3O^+, Oh
\]

In Eq. (9), C\textsubscript{n}H\textsubscript{x} represents tar, such as the large molecular compounds, and C\textsubscript{m}H\textsubscript{y} represents a hydrocarbon with a smaller carbon number compared to that of C\textsubscript{n}H\textsubscript{x}. Discharged residual tar from the plasma reformer was removed by the fixed bed adsorber filled with sludge char. Gravimetric tar at the adsorber outlet displayed 0.5 g/Nm\textsuperscript{3}, which is 88.6% of removal efficiency. Total amount of light tar was 0.39 g/Nm\textsuperscript{3}, which is corresponded to 40.5% of removal efficiency. The relevant concentration was 0.28 g/Nm\textsuperscript{3} for benzene, 0.09 g/Nm\textsuperscript{3} for naphthalene, 0.14 g/Nm\textsuperscript{3} for anthracene, 0.01 g/Nm\textsuperscript{3} for benzonitrile, and 0.003 g/Nm\textsuperscript{3} for benzeneacetonitrile. Among residual tar, heavy tar was mostly removed at adsorber, and non-condensed light tar that was not adsorbed was considered to be passed through the adsorber. For satisfactory IC engine operation, an acceptable particle content <50 mg/Nm\textsuperscript{3} and a tar content <100 mg/Nm\textsuperscript{3} is postulated (Milne et al, 1998). Therefore, 0.5 g/Nm\textsuperscript{3} of tar concentration in producer gas is sufficient for utilization. In addition, sampling analysis on particulate matter was not conducted in this study, but the carbon black was not formed due to steam reforming at the plasma reformer. Therefore, it is not considered to be problematic in the operation.

![Graph showing gravimetric tar and light tar concentrations](Fig. 8. Gravimetric tar and light tar concentrations)

### 3.4.2 Gas formation characteristics

Figure 9 shows the producer gas analysis sampled from the pyrolysis gasifier, plasma reformer, and fixed bed adsorber, respectively. At the outlet of plasma reformer, gas concentration was found to be 50.9% for H\textsubscript{2}, 22.3% for CO, 11% for CH\textsubscript{4}, 8.7% for CO\textsubscript{2}, 0.4% for C\textsubscript{2}H\textsubscript{2}, and 0.2% for C\textsubscript{2}H\textsubscript{4}. Concentration of hydrogen, carbon monoxide, and light hydrocarbon (methane, ethylene, and ethane) were increased compared to the outlet concentration of pyrolysis gasifier. For hydrogen and carbon monoxide, it was increased.
due to Eqs. (1) and (3), steam reforming and methane gasification reaction, respectively. Light hydrocarbon was converted from light tar using tar plasma cracking reaction (7) in portion and from chain reactions of Eqs. (5) and (6). In addition, decrease in carbon dioxide was considered to be dry reforming as shown in Eq. (10) (Devi et al, 2005).

$$C_xH_y + nCO_2 \rightarrow (x/2)H_2 + 2nCO$$  \hspace{1cm} (10)

According to gas analysis results at adsorber outlet, 50.5% of H$_2$, 21.9% of CO, 10.5% of CH$_4$, 7.7% of CO$_2$, and 0.1% of C$_2$H$_2$ were displayed. Compared to the results at plasma reformer outlet, the corresponding concentration was slightly decreased within measurement tolerance, but it was not almost adsorbed. Higher heating value calculated using the gases from each outlet. It was found to be 11,200 kJ/Nm$^3$ for producer gas from the pyrolysis gasifier, 13,992 kJ/Nm$^3$ for the plasma reformer and 13,482 kJ/Nm$^3$ for the adsorber. The increase at the plasma reformer outlet is due to increased amount of combustible gases, particularly methane having high calorific value.

![Gas concentration chart](chart.png)

Fig. 9. Producer gas concentrations at exit of each part

4. Conclusions

To utilize dried sewage sludge as energy and resource, pyrolysis gasifier, plasma reformer, and fixed bed adsorber system were established. From the pyrolysis gasifier, sludge char and pyrolysis gases were produced along with small amount of tar. To improve tar adsorption capability of sludge char, an integrated pyrolysis gasifier was developed for achieving in sequential carbonization and activation. In addition, for higher producer gas yield and tar reduction, a plasma reformer was installed at the rear section of the pyrolysis gasifier, and a fixed bed adsorber, which contains sludge char from the pyrolysis gasifier,
was implemented for adsorption of residual tars. Sludge char from the pyrolysis gasifier displayed 98.1 m$^2$/g of specific surface area and 63.49 Å of mean pore size, showing the distribution of mesopore and micropore with superior adsorption capability. Producer gas was mostly comprised of hydrogen, carbon monoxide, methane, and carbon dioxide, and the corresponding higher heating value was 13,400 kJ/Nm$^3$. Gravimetric tar was 26.3 g/Nm$^3$, and total amount of light tar was 10.9 g/Nm$^3$, which showed benzene, naphthalene, benzonitrile, and benzeneacetonitrile according to the concentration level. Plasma reformer featured tar cracking and steam reformation, and decomposition efficiency of gravimetric tar was 83.2%, which is corresponded to 4.4 g/Nm$^3$. For light tar, total amount was 1.3 g/Nm$^3$, which is 87.9% of decomposition efficiency. Hydrogen, carbon monoxide, and methane among the components of reforming gas were increased, having 13,992 kJ/Nm$^3$ of higher heating value. Gravimetric tar at the adsorber outlet was 0.5 g/Nm$^3$, which is 88.6% of decomposition efficiency. Total amount of light tar was 0.39 g/Nm$^3$, and it was 40.5% of decomposition efficiency. According to gas analysis results, 50.5% of H$_2$, 21.9% of CO, 10.5% of CH$_4$, 7.7% of CO$_2$, and 0.1% of C$_2$H$_2$ were displayed, and the corresponding higher heating value was 13,482 kJ/Nm$^3$. Therefore, carbonization-activation of sludge can form sludge char that could be utilized for tar adsorption, and the relevant clean producer gas is proved to be applicable for heat engine.

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