

## Thermogravimetric characteristics and pyrolysis kinetics of Giheung Respi sewage sludge

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**Abstract**—Sewage sludge acquired from Giheung Respi treatment facility was characterized and converted into gas, bio-oil and char by pyrolysis. The rate of conversion as a function of temperature was obtained from differential thermogravimetric analysis (DTG) for different heating rates. The activation energy calculated from data selected conversions shows that the activation energy decreased with increasing conversion up to 10%, steadily increased from 10 to 70%, and substantially increased from 70 to 90%. Depending on the level of conversion, the values of activation energies varied between 181 and 659 kJ/mol. The gas product obtained in the experiment at 450 °C, 20 min mainly included CO<sub>2</sub> (30%), CO (23%) and CH<sub>4</sub> (17%). The product yields of gas, oil and char were systematically studied by changing the pyrolysis temperature and residence time.

Key words: Biomass, Pyrolysis, Sewage Sludge, TGA, Conversion

### INTRODUCTION

Sewage sludge is one of the largest constituents in the municipal wastewater effluent. In the Republic of Korea, 2.6 Mtons/year of sewage sludge was generated in 2006 with the number expected to increase in the years to come. The Republic must take a pre-emptive stand to prepare for the most stringent regulation imposed by the international community that prohibits sewage disposal into the sea by 2012, following the London convention, which prompts the Republic to opt for other methods of sewage disposal. Besides land fill, other alternatives such as combustion, incineration, pyrolysis and utilization of sludge as a fertilizer in agriculture land have been considered as probable approaches of sludge disposal methods.

Combustion and incineration of sewage sludge are attractive and, perhaps, inevitable disposal methods for countries with stringent legislation for waste disposal. The amount of sludge being incinerated in the countries such as Japan reached 55% from the sludge produced, followed by 25% in USA, 24% in Denmark, 20% in France, 15% in Belgium and 14% in Germany [1]. These methods of sludge disposal are, however, highly energy intensive and costly to operate, despite their guaranteed success in ensuring complete thermal destruction of toxic organic compounds [2]. Another drawback limiting the attractiveness of combustion/incineration as a means for disposing completely of sewage sludge may derive from the fact that there still remains a considerable amount of solid (approximately 30%) in form of ash at the end of the processes [3].

As opposed to the combustion/incineration process which is highly

exothermic, pyrolysis is rather endothermic, and the energy associated with the process is reported to be on the order of 100 KJkg<sup>-1</sup> [4]. Sewage sludge is generally known to contain polysaccharides, lignins, nitrogen-containing compounds and compounds of unspecific origins that have calorific value similar to that of coal. If the sludge is pyrolyzed in an oxygen-free environment, non-condensable gases, liquid substances and solid residues can be obtained. The gases from the process are mainly hydrogen, methane, carbon monoxide, carbon dioxide, and several other gases in smaller concentrations. The liquids are acetic acid, acetone or methanol, which are derived from the carboxylic and phenolic compounds from the sludge. The solids consist mainly of char manifested in a pure carbon form with small amounts of inert materials. Fluidized bed pyrolysis has been tried for sewage sludge treatment, in which the physical and attrition properties of sewage sludge were changed [5].

The desired product of the pyrolysis is, generally, the liquid oil that has a potential for use as biofuel. It is the remarkable feature of the pyrolysis process to produce biofuel that brings about attractiveness of the method to be used for sludge treatment and disposal, or to accompany other processes during the waste treatment. In this study, the pyrolysis process is selected to convert sewage sludge into solid, liquid and gaseous products. The product yields of gas, oil and char were systematically studied by changing the pyrolysis temperature and residence time.

### EXPERIMENTAL

#### 1. Characterization Methods

The sewage sludge raw sample applied in this study was obtained from Giheung Respi waste treatment plant located in Yongin-si,

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South Korea. The plant used waste water derived from the community for their treatment with the capacity of sewage sludge at 90 tons/day. The sludge sample taken from this plant was first dried before it was pulverized into smaller particles to a size between 600 and 850  $\mu\text{m}$ . The moisture, ash, specific gravity and volatile contents of the solid particles were determined by using ASTM E 1756, ASTM E 1755 [6], ASTM C373-88 [7] and Standard methods (2540 A-G) [8], respectively. The component contents of C, H, O, N and S were determined by the automatic elemental analyzer (Flash EA1112, CE Instruments). The inorganic components of ash fractions were analyzed by energy dispersive X-Ray spectroscopy (EDX, Oxford EDX system). Thermogravimetric analysis of the solid samples was carried out using TGA (TA Instrument, TGA Q50). A sample mass of 30-40 mg was used for the thermogravimetric analysis in each experiment. Nitrogen was used as a carrier gas at 20 mL/min. The heating rate was controlled at 5, 10, 15 and 20  $^{\circ}\text{C}/\text{min}$ , respectively, from 40  $^{\circ}\text{C}$  to 800  $^{\circ}\text{C}$ .

The pyrolyzing gas product was quantitatively characterized by GC with FID and TCD detector. (a) The GC - FID (M600D - Younglin Co.), equipped with capillary column of HP-Plot/Al<sub>2</sub>O<sub>3</sub> (50 m  $\times$  0.53 mm  $\times$  15 mm), was applied for analyzing the hydrocarbon fraction. To quantify the hydrocarbon composition from C<sub>1</sub>-C<sub>6</sub> in gas product, the peak areas of these components were calibrated using a standard gas mixture (Supelco - Scotty 14). (b) The GC - TCD (ACME 6000GC - Younglin Co.), with packed column Carbosphere (80/100 mesh, 6ft  $\times$  1/8 inch  $\times$  0.85 inch, Alltech) was used for determining the content of CO, CO<sub>2</sub> and H<sub>2</sub>. The pure gases of CO, CO<sub>2</sub> and H<sub>2</sub> were used as standard gases for determining the content of gas product.

## 2. Pyrolysis in a Tubular Micro-reactor

A tubular bomb micro-reactor was employed in the pyrolysis of the sludge samples [9]. The tubular micro-reactor reserved 40 mL volume to accommodate sample mass of approximately 5 g during the experimental runs. Eutectic salt containing KNO<sub>3</sub> (59 wt%) and Ca(NO<sub>3</sub>)<sub>2</sub> (41 wt%) was chosen, prepared and used in the study due to its excellent heat transfer properties and involatility. The temperature of the molten salt bath was maintained at 350, 400 and 450  $^{\circ}\text{C}$  within  $\pm 1$   $^{\circ}\text{C}$ . The above pyrolysis temperatures were employed with inference from the maximum peak of DTG (differential thermogravimetric) curves obtained at different heating rates of 5, 10, 15 and 20  $^{\circ}\text{C}/\text{min}$ . The reaction products were analyzed for the amount of gases formed, oil formed and char formed. The tubular micro-reactor was opened after cooling to room temperature to allow gas to release gently. Gas yield was obtained by weighing the tubular micro-reactor before and after venting off the gases. Other pyrolyzed products were separated into oil and coke/char by hexane extraction technique in which char was separated from the oil by dissolving the oil in hexane and insoluble char was filtered by using 0.45  $\mu\text{m}$  micro filter paper. The yields of gas, oil and char were determined by the ratio of each product weight to feed weight [9].

## 3. Calculating Kinetic Parameters Based on Thermogravimetric Analysis

Results from the thermogravimetric experiments were expressed as a function of conversion X, which is defined as,

$$X = (W_0 - W)/(W_0 - W_{\infty}) \quad (1)$$

where W<sub>0</sub> is the initial mass of sample; W is the mass of pyrolyzed

sample; W<sub>∞</sub> is the final residual mass. The differential method was used to determine the pyrolysis kinetic parameters from the thermogravimetric data following the literature [9] as follows:

$$\ln(dX/dt) = \ln(AX^n) - E/RT \quad (2)$$

The apparent order of reaction, n, and the pre-exponential factor, A, can be obtained from the intercept of the semi-log plot at a predetermined level of conversion.

## RESULTS AND DISCUSSION

### 1. Characteristics of Sewage Sludge

The characteristics of the dried sludge sample taken from Giheung Respiia sewage sludge treatment plant using ASTM standard procedures for determining moisture, ash and volatile solid are presented in Table 1. The moisture, ash and volatile solid contents of the sample were 7.3%, 25.6%, and 67.1%, respectively. The carbon (C), hydrogen (H) and oxygen (O) contents of the sludge were 30.0, 5.0 and 27.5%, respectively, rather lower than those of lignocellulosic material which consisted of 43.8%, 6.4% and 49.8% of the respective elements as reported in the previous work [10]. Especially, the sludge obtained from the location contained unexpectedly high ash and sulfur elements. This high sulfur content possibly came from hydrogen sulfide that was formed by the degradation of bacteria in the sludge, or perhaps, from the degradation of organic sulfur compounds such as mercaptanes and thiophenes [11]. Based on this composition analysis, the general formula of sewage sludge was drawn as in form of CH<sub>2</sub>O<sub>0.69</sub>N<sub>0.34</sub>S<sub>0.33</sub>. In addition, the higher heating value (HHV) applying Demirbas method [12] was also attained using the data from this analysis.

This higher heating value was calculated as follows:

$$\text{HHV (MJ/kg)} = \{33.5[\text{C}] + 142.3[\text{H}] - 15.4[\text{O}] - 14.5[\text{N}]\} \times 10^{-2} \quad (3)$$

where [C], [H], [O], and [N] were the contents (wt%) of carbon,

**Table 1. Characteristics of Giheung Respiia sewage sludge**

Moisture (%) <sup>a</sup>	7.3
Ash (%) <sup>b</sup>	25.6
Specific gravity <sup>c</sup>	0.73
Volatile solid <sup>d</sup>	67.1
Ultimate analysis (%)	
C	30.0
H	5.0
O	27.5
N	11.7
S	26.3
General formula	CH <sub>2</sub> O <sub>0.69</sub> N <sub>0.34</sub> S <sub>0.33</sub>
HHV (MJ/kg) <sup>e</sup>	11.2

<sup>a</sup>ASTM E1756, Standard test method for determination of total solid in biomass

<sup>b</sup>ASTM E1755, Standard test method for ash in biomass

<sup>c</sup>ASTM C373-88, Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Whiteware Products

<sup>d</sup>Standard Methods, 2540 A-G

<sup>e</sup>Demirbas, 1997 [12]

**Table 2. Elements and compositions in the ash determined by EDX**

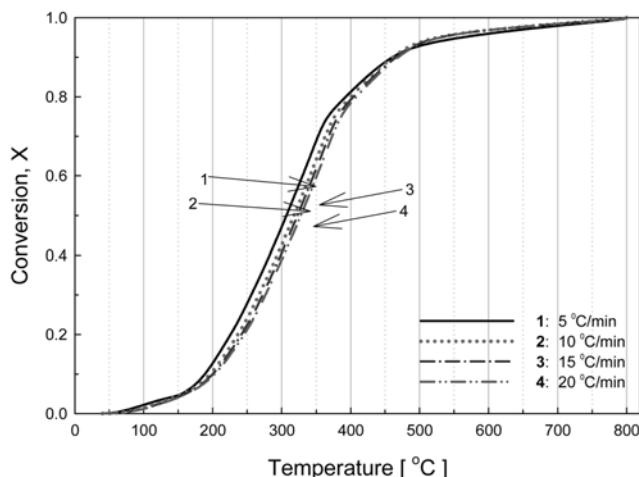
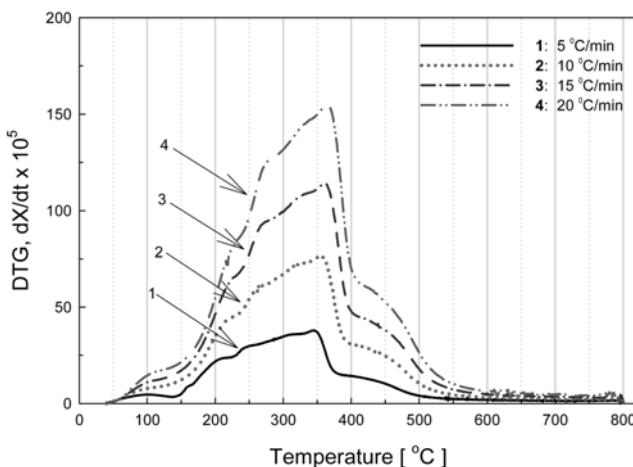
Element	Weight%
C	10.26
O	53.36
Na	0.58
Mg	0.98
Al	9.13
Si	9.40
P	6.68
S	0.84
K	1.75
Ca	3.98
Fe	3.05
Total	100.00

hydrogen, oxygen and nitrogen, respectively. The result of the higher heating value of the sludge sample was obtained at 11.2 MJ/kg, close to that of biomass samples from other works [13,14].

Table 2 shows the elements and compositions in the ash determined by EDX. Except carbon and oxygen content, the major components in the ash are Si (9.4 wt%), Al (9.13 wt%), P (6.68 wt%), Ca (3.98 wt%), Fe (3.05 wt%), K (1.75 wt%), Mg (0.98 wt%), S (0.84 wt%) and Na (0.58 wt%). From this result, it can be seen that Al, P, Ca, Fe and K constituted with a considerable amount. These atoms might be considered as the potential catalysts for pyrolysis reaction. For example, with Al, if existing in the form of  $\text{Al}_2\text{O}_3$ , it would be an acid catalyst for cracking reaction [15]; or with K, and Ca atoms, they were already reported as the catalyst for biomass pyrolysis in literature [16].

## 2. Thermal Decomposition Analysis of Sewage Sludge

The conversion level as a function of temperature at different heating rates is shown in Fig. 1. The small change of conversion in the samples, initially, is attributed to vaporization of moisture and volatile components that were attached to the surface of the samples. The samples started to decompose at 230 °C as more of the volatile organic elements were liberated from the samples. The TGA graphs

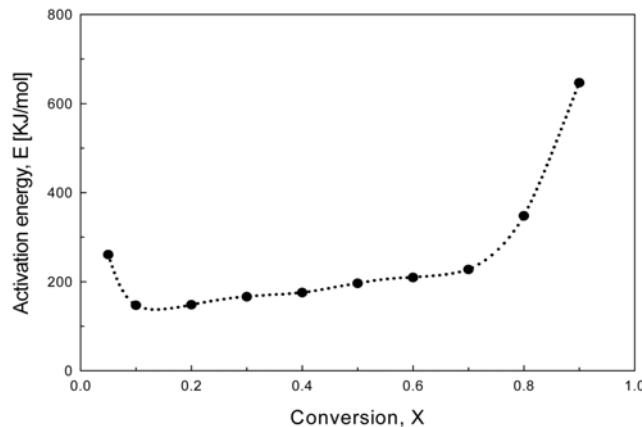
**Fig. 1. The effect of pyrolysis rate on conversion as a function of temperature.****Fig. 2. The effect of pyrolysis rate on DTG as a function of temperature.**

at different heating rates of 5, 10, 15, 20 °C/min indicated similar conversion level in the beginning (<200 °C) and ending (>450 °C) process. In between the extremity of the two temperatures, lower heating rate resulted in slightly better conversion possibly due to the higher heat energy that was gained by the samples. At higher heating rate, less heat energy was transferred to the samples, prompting more heat to be supplied (represented by the increase in temperature) in order to achieve the same conversion level as that of the sample heated at lower heating rate. The TGA curves of the sludge sample show one weight loss step (not shown), and major decomposition (demonstrated by the steepest slope of the curves) was observed to occur between 200 °C and 400 °C, hence the basis used for the lower end of the pyrolysis temperature (350 °C) in this work. At this temperature range, the decomposition was attributed to organic materials such as cellulose, hemicellulose, and lignin [17]. The decomposition of sludge sample at 450 °C or higher progressed slowly because of the residual, hard-to-burn lignin or possibly char.

The rate of conversion as a function of temperature was obtained from differential thermogravimetric analysis (DTG) for different heating rates. The analysis is shown in Fig. 2. The DTG curve for each heating rate exhibited an exclusive peak, in the band between 150 °C and 500 °C, increased in intensity with increase in the heating rate. The increase of heating rate caused the peak of the curve to shift rightward to slightly higher temperature. The maximum peak of conversion occurred at 350, 359, 363 and 368 °C for heating rate of 5, 10, 15 and 20 °C/min, respectively. As the heating rate increased, the DTG curves showing maximum rate of  $dX/dt$  also increased. The maximum rate of decomposition tends to increase at higher heating rate because it provided higher thermal energy to facilitate better heat transfer between the surrounding and inside of the samples.

## 3. Kinetic Parameters of Pyrolysis Using TGA

Fig. 3 shows the activation energy calculated at different conversion following the procedure in the literature [9]. It was observed that the activation energy decreased first with increasing conversion up to 10% and then steadily increased from 10 to 70%, before it increased sharply thereafter. The sharply increasing activation energy values at higher conversions were known to be a consequence of further de-volatilization reaction of char after the primary reaction.



**Fig. 3. Calculated activation energy of pyrolysis as a function of conversion.**

The values of activation energies vary between 181 and 659 kJ/mol depending on the level of conversion. This implies that the decomposition of organic materials such as cellulose, that has the maximum activation energy of 285 kJ/mol [18], requires that a conversion level of at least 70% be attained.

#### 4. The Composition of Gas Product

The gas product of the experiment at the condition of 450 °C, 20 min was used for GC analysis with FID and TCD detector. The GC-TCD result shows that the content of CO<sub>2</sub> and CO gas, the common products of usual burning process, was respectively 30 and 23% of gas product, contributing considerably (53%) to the gas product of pyrolysis process. In contrast, the hydrocarbon-rich pyrolyzing gas analyzed by GC-FID demonstrates that the fraction of C<sub>1</sub>-C<sub>4</sub> comprised a small amount, namely CH<sub>4</sub> (17%), C<sub>2</sub>H<sub>6</sub>, (10%) and C<sub>3</sub>H<sub>8</sub> (7%). It can be seen that the total content of all the above components was not 100%, which means there was some other unknown gas which could derive from the decomposition of nitrogen or sulfur-containing compounds. In comparison with other researches, this gas composition was different. For instance, as reported by Meier and Chen [19,20], the gas product from lignocellulosic pyrolysis consisted of a major amount of CO, CO<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub>. This can be firstly explained by the difference in the chemical composition between sewage sludge and lignocellulosic materials. In fact, the sewage sludge contained a relatively large quantity of nitrogen and sulfur-containing compounds (as presented in Table 1). Once these compounds are decomposed at high temperature, there might occur the formation of free nitrogen dioxide or sulfur dioxide, which could play the role of strong oxidation reactants or probable catalysts of gas phase reactions. Additionally, with the presence of potassium and calcium in the feed of pyrolysis, two metals already known as potential catalysts for biomass decomposition as reported by Yaman [16], the gas composition was therefore changed completely.

#### 5. Pyrolysis Kinetics of Sewage Sludge

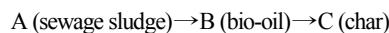
Pyrolysis of the sludge by the tubular bomb micro-reactor produced different yields of gas, oil and char. The distribution of gas, oil and char formation from the pyrolysis of the sludge sample as a function of pyrolysis temperature is shown in Table 3. The yield of gas, oil and char was in the range of 6.1-14.5 wt%, 11.2-32.4 wt%, and 53.1-82.7 wt%, respectively. The yield of oil, in particular, in-

**Table 3. Product yields of gas, oil and char after pyrolysis (wt%)**

	Reaction time (min)					
	3	5	7	10	15	20
<b>Pyrolysis at 350 °C</b>						
Gas (wt%)	6.1	7.9	8.2	9.3	10.1	11.1
Oil (wt%)	11.2	15.6	18.6	19.1	19.6	23.0
Char (wt%)	82.7	76.5	73.2	71.6	70.3	65.9
<b>Pyrolysis at 400 °C</b>						
Gas (wt%)	8.7	9.3	11.4	12.8	12.0	13.5
Oil (wt%)	15.0	18.9	20.1	19.5	25.9	24.3
Char (wt%)	76.3	71.8	68.5	67.7	62.1	62.2
<b>Pyrolysis at 450 °C</b>						
Gas (wt%)	7.5	12.2	13.6	14.4	14.8	14.5
Oil (wt%)	18.8	21.3	24.0	29.2	31.2	32.4
Char (wt%)	73.7	66.5	62.4	56.4	54.0	53.1

creased with increase in the pyrolysis temperature and residence time. The highest yield of oil (32.4 wt%) from the process was attained at a pyrolysis temperature of 450 °C and residence time of 20 minutes.

The pyrolysis mechanism assumed for the kinetic model development in this study is shown as follows:



The relevant reactions during the pyrolysis of the sludge sample were perceived to follow a consecutive order from sewage sludge (solid) to the formation of bio-oil (liquid), followed by the production of char (semi-solid to solid, upon cooling) in an irreversible manner. Of particular interest was the insight and identification of the primary mechanism of the transformation from the solid sludge sample into either pyrolyzed liquid oil or char. The primary pyrolysis reaction proceeded directly via an initial step from the partial or complete depletion of A (sludge) to the formation of B (oil) and subsequently to the formation of C (char). The consistent increase in the yield of gas and oil, and decrease in the yield of char at increasing temperature and residence time, as observed from the table imply that a consecutive reaction had transpired, conforming to the earlier assumption on the proposed kinetic model.

## CONCLUSIONS

The sewage sludge from Giheung Resgia was pyrolyzed at various conditions. The values of activation energies for decomposition of the sludge sample were relatively high, in the range of 181-659 kJ/mol depending on the level of conversion. Successful decomposition of hard-to-burn cellulose materials was achievable provided that a conversion level of at least 70% was attained. At higher than 80% conversion, further de-volatilization of residual char was observed. The main gas products were CO<sub>2</sub>, CO and CH<sub>4</sub> with the amount up to 70% of gas product. The yield of gas, oil and char during pyrolysis was in the range of 6.1-14.5 wt%, 11.2-32.4 wt%, and 53.1-82.7 wt%, respectively. The yield of oil increased with increase in the pyrolysis temperature and residence time. The highest yield of oil (32.4 wt%) was attained at 450 °C with a residence time of 20 min.

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