PYROLYSIS BEHAVIOUR OF SEWAGE SLUDGE PRODUCED AT SUNGAI UDANG CENTRAL SEWAGE TREATMENT PLANT

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Abstract— Sewage sludge management become crucial issue now days as due to its poor managements the environmental as well as human health will be endangered. In order to overcome this issue various solutions were studied and thermochemical conversion is one of the most applicable solution for this problem. Other than large volume reduction, this method also converted the waste into valuable product such as fuel which then can be used to produce energy. Thermochemical conversion can be divided into three main process which are pyrolysis, combustion and gasification. In this study, the effect of temperature and composition of sewage sludge towards the pyrolysis behavior of the sludge were investigated. Proximate and Ultimate analysis were performed to determine the composition of sludge while pyrolysis behaviors were studied by Thermogravimetric Analysis (TGA). Sg. Udang Waste Water Treatment plant was chosen as the location for the sewage sludge collection. The sludge contains 38.6% volatile matter with only 6.14% moisture content after dried in conventional oven for 24hours. The carbon and hydrogen composition in the sludge were 15.2% and 2.57% respectively which make the H/C ratio is 2.1. Other than that, the main decomposition stage (main pyrolysis) of sewage sludge take place in the range temperature of 200^0C – 500^0C. The composition of liquid product produced from the condensation of condensable vapor were determined by GC/MS

Keywords−sewage sludge, pyrolysis, TGA, proximate analysis, ultimate analysis, temperature, GC-MS

INTRODUCTION

Waste now days become a worldwide concern issue as its can be lead to various situation regarding safety and health. There were various types of waste been produce every day from different sources and one of it is sewage sludge. Sewage sludge are by-product that were generated from municipal waste water treatment plant (Syed.Hassan, et al., 2017). As the population keep increasing, the generation of sewage sludge from the wastewater treatment plants was also increase in volume and its handling or treatment process become concern. Sewage sludge that were produced from the waste water treatment plant containing complex blend of organic compound (cellulose, protein, carbohydrates), inorganic compound (sillicates, metals), water and other component such as pathogen and microorganism (Kan, Strezov, & Evans, 2015). As the sludge containing various compound and component which make their disposal become difficult, a proper treatment must be conducted in order to eliminated these harmful substances which can endangered environment as well as health.
There are many conventional treatment for disposal of sewage sludge such as incineration, landfilling, and soil utilization but these treatment methods were limited to certain limitation value (Tang , Zheng, & Zhang, 2018). Due to this concern issues, alternative routes were studied where thermochemical conversion application were considered as one of the most promising method. As generation of sewage sludge keep on increasing, thermochemical conversion not only focus on volume reduction but also an effective in pathogen reduction (Syed. Hassan et al., 2017). Composition of the sewage sludge itself become the constraint of this process, where compared to biomass and coal, sewage sludge were more complex as it contained more percentage of moisture and heavy metals.

Thermochemical conversion process can be categorized into three main process which are pyrolysis, combustion and gasification. As pyrolysis is one of the application of thermochemical conversion, this process can be defined as a process of thermal destruction of organic materials at moderate to high temperature (300^0C-700^0C) in the absence of oxygen (Syed.Hassan, et al., 2017). Pyrolysis can be divided into three types which are slow, fast and flash pyrolysis. All this three sub process were differentiates through their heating rates and residence time. Slow pyrolysis were conducted at slow heating rate with long residence time while fast and flash pyrolysis at high heating rate under short residence time (Syed.Hassan, et al., 2017). Besides, from this conversion process, bio-oil (liquid), bio-char (solid) and non-condensable gases were produced as the pyrolysis product. Bio-oils that were produced from pyrolysis of sewage sludge can be categorized into 3 types which are i) pyrolysis liquid, ii) pyrolysis oil and iii) bio-crude oil (Qiang, Zhi, & Feng, 2009). In order to obtain certain yield of desired product from this process, few main factor that affect this process must be studied. There were various factors that affect the pyrolysis behaviour which then lead to formation of product such as temperature, sewage sludge composition, inert gas flow rate and heating rates. However most studies stated that temperature as well sewage sludge composition were the most influences factors in determining pyrolysis behaviour as well as the final products (Tang , Zheng, & Zhang, 2018), (Gasco, et al., 2004).

MATERIALS AND METHODOLOGY

Sewage sludge collection and handling

Sewage sludge that were obtained in this study was collected from Sg. Udang Wastewater Treatment Plant where the sludge was produced as the by-product from the water treatments. Sludge that were collected then were dry in a conventional oven at 105^0C for 24 hours to reduce the moisture content in the sewage sludge, where the moisture can highly affect the physical characteristic of the sludge. Then, the dried sludge were crushed by using a pestle and mortar, and sieve up to 500μm size before it being stored in airtight bags.

Proximate and Ultimate Analysis

Physicochemical analysis can be divided into 2 types of analysis which are proximate and ultimate analysis. Proximate analysis was performed to determine the moisture content, volatile matter, fixed carbon and ash. The value of fixed carbon can be calculated by 100 minus the summation of moisture, char and volatile matter content. Next, by ultimate analysis, more comprehensive result than proximate analysis will be produced. Ultimate analysis will determine the content of carbon, hydrogen, nitrogen, oxygen and sulfur in the sludge. Both analysis, proximate and ultimate analysis were conducted by thermogravimetric analyzer and elemental analyzer respectively.

Pyrolysis experiment

The thermal analysis (TG/DTG) for the sewage sludge behaviour was conducted by TGA where approximately 20mg of the sample were used. The sample were heated from ambient temperature to 500^0C. The heating rate and the inert gas flow (nitrogen) were set constantly at 10^0C/min and 10L/min respectively. The same conditions were adopted in a small vertical tube furnace (model: VT-1200-F) with 15g of sewage sludge sample. The residual (solid) and liquid product were collected at the end of the experiment and weight.

Pyrolysis liquid analysis by GC/MS

Pyrolysis of sewage sludge will produce 3 different products which are bio-oil (liquid), char (solid) and non-condensable gases. In this study the evolve gas from the pyrolysis of sewage sludge were feed into series of bottle gas washing dreschells to be condensed. The liquid from the condensation process were collected and sent to be analyze. GC/MS analysis were used to determine the composition of the liquid sample produced.

RESULTS AND DISCUSSION

Characterization of sewage sludge

Table 1: Proximate Analysis of the sludge sample

Characteristic	(%)
Moisture Content	6.14
Volatile Matter	38.60
Ash	41.79
Fixed Carbon	13.46

From physicochemical analysis that were done via proximate and ultimate analysis, various component in the sludge sample were determined. Both proximate and ultimate analysis were conducted with sludge sample that had been dry for 24 hours in a conventional oven at temperature 105^0C. As shown in Table 1 above, the remaining moisture content in the sludge were 6.14% as the sludge sample were dried first before analyse. Previously, the moisture content of the sludge sample was 59.80% which shown that the sample were originally wet thus drying process was essential to reduce the moisture content. Normally the moisture in the sewage sludge sample will end up in the liquid product thus high moisture content of the raw material must be avoided. Besides, higher value of moisture content will reduce the heating value of the sample thus increase the energy requirement (Fonts, et al., 2012)

The volatile matter and ash were 38.60% and 41.79% respectively. Ash in the sewage sludge mainly consist of minerals such as microline, calcite and quartz. These minerals that were formed from Fe, Ca, K and Mg were able to catalyze pyrolysis reactions (Fonts, et al., 2012). Volatile matter content were consist of biomass component except for water which are liberated as gas and vapors at high temperature (Dhyani & Bhaskar, 2017). The value of fixed carbon in the sludge sample were determined by using equation below;

Fixed carbon (%) = 100 - moisture content – volatile matter – ash (equation 1)

The value of fixed carbon in the sample can be related to the high calorific value as it were the non-volatile fraction of biomass while it not the same case for the volatile matter. If the value of the volatile matter were determined to be high it does not guarantee the caloric value will be high as some of the component in the volatile matter itself are formed from non-combustible gases such as CO_2 and H_2O (Ozyuguran & Yaman, 2016).

Table 2: Ultimate Analysis of the sludge sample

Characteristic	Unit	
C	wt%	15.2
H	wt%	2.57
O	wt%	14.62
N	wt%	1.55
S	wt%	0.93
Calorific Value (HHV)	MJ/kg	6.5
H/C		2.1
H/O		2.8
H/N		1.7

Ultimate analysis was conducted to determine the carbon, hydrogen, oxygen, nitrogen and sulfur (CHONS) content in the sludge sample as shown in Table 2 above. It was determined that carbon was the highest element contained in the sewage sludge sample at 15.2%. Higher value in carbon content will increase the calorific value of the sample. The calorific value of the sludge sample was 6.5 MJ/kg which were small in value compare to previous research.

This result may vary due to the origin of the sewage sludge which effects its composition. The treatments process such as waste water purification and stabilization process were not standardized in the waste water treatment plant. This situation can lead to the possibility that even same treatments were adopted, the composition of the sewage sludge sample collected from different treatment plant may vary significantly.

The nitrogen value in the sample was determined at 1.55%. This nitrogen element mainly comes from the protein fraction in the sample and its origin in the microorganism used in water purification.

Pyrolysis of Sewage Sludge

The pyrolysis of sewage sludge produced 3 main products which are bio-oil (liquid), bio-char (solid) and condensable gas. Pyrolysis condition such as temperature can affect the yield distribution of the products. Table 3 below shows the yield of all three sewage sludge pyrolysis product that was calculated by weight difference;

Table 3: Product distribution of sewage sludge pyrolysis at temperature 500°C

Product	**Liquid**	**Gas**	**Bio-char**
Yield (%)	9.53	25.07	65.4

It shows that the yield of bio-char was the major product produced with a yield of 65.4%. This result (yield) may due to the high ash content in the sewage sludge sample as well as slow heating rate that were used in the experiment. The other two products which were liquid and gas yield were 9.53% and 25.07% respectively.

TGA was chosen as one of the analysis as it can measures the decrease of mass in the substrate that caused by the release of volatiles (devolatilization) during thermal decomposition (White, Catallo, & Legendre, 2011). This analysis provides information regarding the initial and final temperature for thermal degradation of sewage sludge. The TG/DTG curves that were obtained from the analysis were shown below;

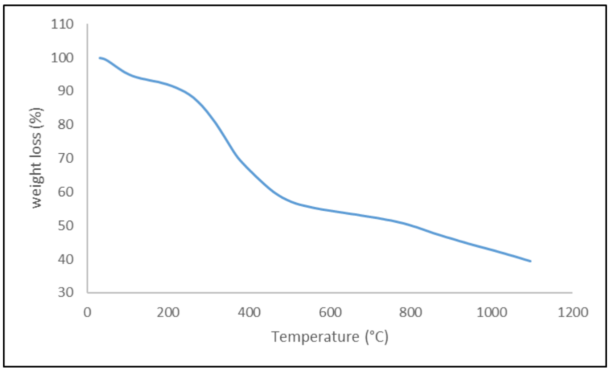

Figure 1: TG curve of sewage sludge

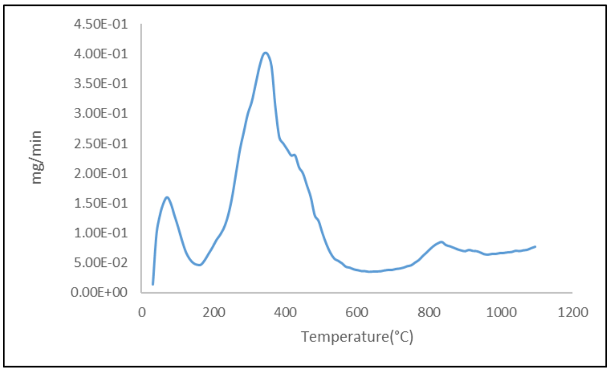

Figure 2: DTG curve of sewage sludge

Thermal degradation of biomass can be divided into 3 stages which are i) moisture drying, ii) main devolatilisation and iii) continuous slight devolatilisation. Based on Figure 1 and 2 the thermal decomposition of sludge sample take place in 3 stages correspond to the previous research. The first stage was considered as drying stage where the remaining moisture content in the sludge were removed. The highest peak during this moisture drying stage were detected at 67.20^{0}C and this stage take place at temperature range (32°C-136°C). The next stage was main decomposition stage (main pyrolysis) which organic compound decomposed at this stage. The third stage was continuous slight devolatilisation stage where the formation of char as one of the pyrolysis product take place.

As volatile matter consisted of biomass components, there were 3 main components that exist in the sludge which were cellulose, hemicellulose and lignin. The decomposition of organic matter at main devolatilisation stage were due to decomposition of cellulose and hemicellulose contained in the sludge sample. Hemicellulose can be decomposed at low temperature with most decomposition take place in temperature range of 180^{0}C – 340^{0}C with very less solid residue remained after 400^{0}C. Cellulose were decomposed at much higher temperature range 230^{0}C-450^{0}C while lignin can only decompose at temperature above 500^{0}C (Mishra & Mohanty, 2017). Among these 3 component of biomass, lignin was the most difficult to be decomposed and also have the highest solid residue left after the pyrolysis (Dhyani & Bhaskar, 2017).

Based on the TG/DTG curve the maximum decomposition occur between 170^{0}C-600^{0}C which correspond to the previous research where cellulose and hemicellulose were decomposed at this stage. Cellulose were decomposed by the bonds split into monomers at low temperature which then produced CO, CO2 and carbonaceous gas as the product of pyrolysis (White, Catallo, & Legendre, 2011). Other than that, based on the DTG curve it shows that the peak temperature for the main pyrolysis stage occurred at 347.07^{0}C. At this temperature the decomposition of cellulose and hemicellulose were done rapidly which then result in the large mass loss of the sample. The mass loss in the low temperature region (<400°C) may due to decomposition of easily degradable compounds in the sludge such as carbohydrates, amino acid and simple lipids while, at much higher temperature range it may due to decomposition of compound with higher molecular weight like aromatic compounds (Ko, Wang, & Xu, 2018).

GC-MS Analysis

As the pyrolysis of sewage sludge produced non-condensable gas, these gas component may also react with each other and char residue. The reaction of these gas components lead to shifting reaction as well as tar cracking reaction which then contribute to much more product gases. The GC-MS analysis was conducted to determine the composition of liquid product produced from the condensation of pyrolytic gas.

Based on the retention time, the characteristic of the compounds were indicated by chromatogram which then define the chemical compound in the sludge sample. The chemical compound which were defined in the analysis were tabulated in the table as shown below;

Table 4: Summary of chemical compound found in the sludge sample

Retention time (min)	Chemical compound	Amount (%)
3.1870	2-Oxazolidinethione	0.408
3.2125	Allyl(methoxy)dimethylsilane	0.645
4.2079	Diethoxydimethyl-silane	0.690
4.7809	Hexamethyl- cyclotrisiloxane	1.11
7.9738	Octamethyl-cyclotetrasiloxane	0.421

The chemical compound tabulated in the table above were the main compound detected by the GC-MS library at pyrolysis temperature 500°C.

Liquid product that were produced from pyrolysis of sewage sludge were complex mixtures which made up of hundreds organic compound from wide variety of chemical groups. This product consist of water and organic compound. The water produced is the result of dehydration and degradation of high molecular compound containing oxygen. As shown in table above, the chemical compound found in the liquid samples mostly are aromatic compound. As shown in Table 3 above, the highest chemical compound detected in the liquid sample was Hexamethyl-cyclotrisiloxane which is at 1.11%. This Hexamethyl-cyclotrisiloxane were categorized as the organosilicon compound that contained of carbon-silicon bond. The boiling point of this chemical compound is at 134°C which make this compound become gas at stage 1 (drying) of sewage sludge pyrolysis. The evolve gas that contained this chemical compound then undergo condensation to produce liquid product thus make cyclotrisiloxane become the highest compound detected.

Another chemical compound that was detected by GC-MS library is Diethoxydimethyl-silane (0.6455%) and octamethyl-cyclotetrasiloxane (0.421%).

CONCLUSION

In this study, pyrolysis behaviour of sewage sludge were observed and analyze through TGA/DTG curve. The effect of pyrolysis temperature as well as sewage sludge composition towards the product produced were observed. Pyrolysis of sewage sludge take place in 3 phase correspond to the previous research which are drying stage, main decomposition stage and continuous slight devolatilisation stage. As the sewage were dried first, the moisture content in the sludge were small make the drying stage take place in small temperature range. The main decomposition stage which decomposed most of the organic component in the sludge such as cellulose and hemicellulose take place at 200°C-500°C. In order to ensure all the organic compound in the sludge undergo decomposition, 500°C was chosen as pyrolysis temperature as most organic compound decomposed at temperature range 450°C-500°C.

The composition of liquid pyrolysis of sewage sludge were determined by GC-MS where most of the compound detected were aromatic compound. The liquid sample collected contained water and organic compound make the analysis become harder.

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