Sewage sludge conversion via hydrothermal liquefaction (HTL) – A preliminary study

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Abstract. Sewage sludge is regarded as a residue produced from municipal waste water treatment system. This waste is often used in low-value applications such as composting and incineration or disposed in landfills. Such practices posed many potential environmental hazards due to high levels of pollutants in the sludge. Sewage sludge is also a potential energy and currently received renewed attention for potential recovery of bio-oils and biochemicals through thermochemical conversion route. Hydrothermal liquefaction is a promising green method for conversion of sewage sludge. Hydrothermal liquefaction of sewage sludge were investigated at different temperatures (250°C, 300°C, 350°C and 400°C) and 1 hour reaction time. Experiments were carried out in a 10 ml stainless steel bomb reactor. The initial calorific value of sewage sludge was 12.36 MJ/kg. It was found that significant bio-oil yield of 52.23% and 48.25% were obtained at 350°C and 400°C respectively. Overall, the bio-oil yield increases with temperature up to critical temperature of water. It was clear that synergetic effect on the yield of liquid and solid were observed due to extended biomass fragmentations and depolymerization when reaction temperature was raised. The bio-oils produced from liquefaction of sewage sludge at 350°C contained an abundant number of ester based compounds, highlighting its potential as biofuel.

1. Introduction

Sewage sludge is a by-product from the urban wastewater treatment plant. The productions of sewage sludge in Malaysia are mostly from municipal and industrial wastewater plant and the volume has been on the rise each year. Sewage sludge poses a potential risk to human and the environment as it contains many types of contaminant such as pathogens, micro pollutants, heavy metals and others hazardous substances [1]. Heavy metal is one of the main concerns in treated sludge because of its high density and poisonous at low concentration. Examples of heavy metals are Mercury, Cadmium, Arsenic, Chromium, and Lead. Heavy metal is dangerous to human as it can accumulate biologically and can increase over time in a biological organism. Lead (Pb) for example can cause serious health problem such as nervous system damage, damaging kidney, liver, reproductive system, basic cellular processes and brain function [2].

According to Zakaria et al. [3], the production of sewage sludge in Malaysia increase drastically with a yearly production of 4.9 million tonnes and the value is expected to increase twofold in the next six years. In current trends, landfililing, ocean disposal, land application and agriculture are the methods used for the disposal of sewage sludge. The current disposal methods will cause environmental issues such as air, water and land pollution. Thermochemical conversion of sewage
sludge into energy has been an attractive growth in technology around the globe [4]. Hydrothermal liquefaction (HTL), also known as direct liquefaction is the thermochemical conversion of biomass into liquid fuels by processing in hot, pressurized water with enough time to breakdown solid biopolymeric structure into mainly liquid components [5].

HTL process has its own advantages when being compared to pyrolysis process. HTL process differs from pyrolysis as it can utilize wet biomass, thus produce a bio-oil that contains about twice density of pyrolysis oil. Although the yield obtained from pyrolysis is relatively high, bio oil from HTL process is more favorable in terms of its oxygen and water contents. This characteristic makes HTL as a good method in treating waste into valuable products (bio-oil). Based on research conducted by Anastasakis and Ross [6], HTL with brown micro-alga Laminaria Saccharina. The maximum bio-oil obtained was 29.5% with 1:10 biomass: water ratio at 350°C and 15 minutes residence time. Meanwhile, by using another type of algae (raw Scenedesmus), the bio-oil obtained is 45% as referred to Vardon et al. [7]. This shows that bio-oil could be obtained by using the HTL method with an interesting value of product.

Among several possibilities, sewage sludge is considered to be an excellent source of bio-oil because of their advantages such as high photosynthetic efficiency, maximum biomass production, fast growth rate and lack of arable soil requirements. Sludge is regarded as a potential source to achieve valorization via strategies such as resource recovery, sludge based adsorbents preparation and thermal valorization. A very little attention on HTL of sewage sludge process is available as for now and very few attempts of pilot plants globally, for instance, Pittsburgh Energy Research center of U.S Bureau of Mines took place in the 1990s but stopped later due to economic crisis [8]. Hence, an attempt has been made to bridge the gap in the literature and create a possibility to take the research on HTL of sewage sludge to next level by selecting the best available feedstock and the operating conditions. Further research on tuning of the critical operating parameter such as temperature and pressure for better yield is still under progress.

Thus, this article attempts to investigate the effect of temperature on the conversion of sewage sludge into bio-oils suitable for upgrading as valuable biochemicals product.

2. Experimental

2.1. Materials

The raw sewage sludge used in this process was collected from Indah Water Konsortium treatment plant. The sludge was treated by using biological treatment technology. The collected sludge sample was first dewatered and dried in an oven at 105°C for 2 hours to ensure complete removal of water content in the sample. Ultra-pure water was used as the solvent for all experiments in the stainless steel bomb reactor. Dichloromethane (QReC; Grade Ar) was used as a solvent.

2.2. Proximate and ultimate analysis

Proximate analysis sludge sample were performed according to the standard D7582-12 and D3172-07a of the American Society for Testing and Materials (ASTM). Thermogravimetric analysis (TGA) were carried out by using a Perkin Elmer, TGA 8000 with a nitrogen flow rate of 20 ml/min, and weight (approximately 10 mg) was heated to 900°C at a rate of 10°C/min. Ultimate analysis were carried out by using a Perkin Elmer 2400 II CHNS/O elemental analyser.

2.3. Hydrothermal liquefaction

HTL experiments were carried out in a 10 ml stainless steel (SS316) batch reactor at reaction temperature 250°C, 300°C, 350°C and 400°C. For each experiment 5 ml ultra-pure water was poured into the bomb reactor. The assembled bomb reactor was placed in the carbolite furnace and heated at the desired temperature for 1 hour. The assembled bomb reactor was then cooled down in cold water bath. The content of the reaction mixture was subjected to further analysis. In this work,
the gaseous product was not collected and analysed but safely discharged. Figure 1 shows overall experiment scheme for sewage sludge HTL.

![Diagram](image)

**Figure 1.** Sewage sludge HTL experiment scheme

2.4. Separation procedure
Dichloromethane was used as washing solvent for recovery of the liquid and solid products of HTL experiments. Liquid product was separated from the solid using the filtration apparatus. The solid product collected on the whatman filter was dried at 105°C in an oven to remove moisture before it was cooled in a dessicator and weighed. The liquid product collected in separator funnel which contained aqueous and organic phase was readily separated due to immiscibility between dichloromethane and water. Finally, the organic fraction was evaporated in a rotary evaporator to remove dichloromethane from the bio-oils product. The products that were obtained from HTL were bio-oils, water soluble products, solid residue and. The HTL product yield was calculated on dry ash-free basis which can be calculated by using the following equations

Bio-oil yield (%): \[
\frac{\text{Weight of Bio-oil}}{\text{Weight of Sewage Sludge}} \times 100
\]

Liquefaction char yield (%): \[
\frac{\text{Weight of char}}{\text{Weight of Sewage Sludge}} \times 100
\]

Gas + Water yield (%): \[
\frac{1 - \text{Weight of Bio-oil} - \text{Weight of char}}{\text{Weight of sewage sludge}} \times 100
\]

2.5. Product characterization
Bio-oil compositions was analysed by using CHNS/O elemental analyser (Perkin Elmer, 2400 Series II). The calorific value was calculated by using Dulong formula:

\[
\text{CV} = 0.3383C + 1.442 \times (H - \frac{O}{8}) \times 100
\%
\]

where, C, H, N, O and S were carbon, hydrogen, nitrogen, oxygen and Sulphur respectively. Mass percentage of oxygen was calculated by difference. GC-MS (gas chromatography-mass spectroscopy) analysis was used to identify the chemical compositions of bio oil. Helium carrier with flowrate set at 1.2 mL/min was used. The specific column temperatures of GC used in this experiment were as follow: initial temperature 40°C (hold for 3 min), ramped to 190°C at 12°C/min, (hold for 1 min) and finally increased to 290°C at 8°C/min (hold for 20 min). The temperature of the ion source, transfer line, and temperature injection chamber were set to 230°C, 280°C and 270°C respectively. In addition,
functional chemical groups present in the bio-oils were identified from the FTIR spectra obtained using Bruker Vertex 70.

3. Results and Discussion

3.1. Proximate and ultimate analysis
Proximate and ultimate analyses of sewage sludge sample are listed in Table 1. The volatile organic matter content (dry basis) of sewage sludge was 60.8 wt% and ash 39.2 wt% which contrary with result from Thipkhunthod et al. [9] where volatile matter 42.6 wt% and ash 52.8 wt%. The HHV (high heating value) of the dried sample was determined to be 12.36 MJ/kg slightly higher compared to Peng et al. [10] 10.97 MJ/kg.

| Proximate analysis (wt.%)* | Ultimate analysis (wt.%)* | HHV* (MJ/kg) |
|---------------------------|--------------------------|--------------|
| Volatile Organic matters  | Ash                      | C   | H   | N   | S   | O*  |               |
| 60.8                      | 39.2                     | 35.21| 3.12| 2.93| 0   | 22.47| 12.36         |

*Dry basis SS, *O% = 100% - C% - H% - S%

3.2. Bio-oils Yield
Reaction products distribution obtained at different hydrothermal liquefaction temperature of sewage sludge is presented in Table 2. Hydrothermal liquefaction of sewage sludge resulted in the formation of gases, bio-oil, water soluble substance and solid. As shown, in Table 2, the yield of bio-oil increases from 21.45 wt% to 52.23 wt% as reaction temperature was raised from 250°C to 350°C respectively. On contrary, the char yield decreased from 61.53 wt% to 11.13 wt% with an increase in the reaction temperature. As the reaction temperature increases, it adds synergetic effect on the yield of liquid and solid due to extended biomass fragmentations and depolymerization when temperature is relatively larger than activation energies for bond cessation [11]. As can be seen from the table, the maximum bio-oil yield of 52% was obtained at 350°C. Similar finding was observed by Peng et al. [10]. Higher reaction temperature of 400°C resulted in the slight drop of oil yield to 48.25 wt% whereas solid char yield continue to decrease to 1.76 wt%. At higher temperature (above critical point 373°C) bio-oils tend to undergo secondary decompositions and Bourdard gas reaction become active which lead to formation of more gases [11].

| Temperature (°C) | Liquid (wt%) | Solid (Char) (wt%) | Gas + Water (wt%) |
|------------------|-------------|--------------------|-------------------|
| 250              | 21.45       | 61.53              | 17.62             |
| 300              | 37.38       | 48.05              | 14.57             |
| 350              | 52.23       | 11.18              | 36.59             |
| 400              | 48.25       | 1.76               | 49.99             |

3.3. Functional group in bio-oil
The FTIR spectra of raw sewage sludge and bio oil samples obtained at different liquefaction temperatures are shown in Figure 2. Information relating to the relative changes of certain chemical functional groups of compounds as a function of the process temperature was observed. Based on the identification peaks assigned in Figure 2, several observations can be deduced;
The two peaks at 3000 cm\(^{-1}\) and 2800 cm\(^{-1}\) present the aliphatic C-H stretching vibration in methyl and methylene groups [12]. There is no prominent fluctuation shown based on the stretching vibration.

The broad band at 1650-1550 cm\(^{-1}\) ascribed to –C=O stretching vibration in amides and ketones group due to the effect of decarboxylation of sewage sludge components. The presence of O-H functional group at 1440-1395 also indicates that there is a presence of carboxylic acid and their derivatives.

Transmittance peaks between 1124-1087 and 1205-1124 indicate the presence of C-O stretching vibrations of secondary and tertiary alcohol [13]. These functional groups can only be seen at temperature 300°C and 400°C only, in which the former only have secondary alcohol to be detected in its spectra and the latter to have both secondary and tertiary alcohol detected in its spectra.

Band at 1200 cm\(^{-1}\) corresponds mainly to ether, was detected to be either present or totally absent at a low in density in the bio-oil. Alkyl aryl ether absent in the raw sewage sludge spectrum.

The peak at 700 cm\(^{-1}\) is AL/Si-O bending, which highly suggested the presence of Al\(_2\)O\(_3\) or SiO\(_2\) in the sewage sludge. Mineral compounds were also retained in the HTL process as shown by the ash content [10].

![Figure 2. Comparison of FTIR Spectra between raw sewage sludge and the resulting bio-oils produced at different hydrothermal liquefaction temperatures](image)

FT-IR analysis of bio-oils produced from HTL of sewage sludge at various temperatures shows that there are significant differences in each spectrum generated. For instance, functional group such as C=O stretching, that is assigned to unsaturated ester is only present at temperature 400°C. Carbonyl group, C=O is also considered to be one of the important functional group in bio-oil as it responsible for bio-oil property changes upon storage and during upgrading. Bio-oil obtained at 350°C has a higher percentage of carbon and a lower percentage of oxygen compared to others, proving that this temperature is the optimum condition to produce bio-oil by hydrothermal liquefaction [14].

3.4. Chemical composition in bio-oil
Bio-oils obtained from hydrothermal liquefaction of sewage sludge was characterized by GC-MS to identify its chemical compositions. The bio-oils resulted from different reaction temperatures (250°C, 300°C, 350°C and 400°C) were analysed and compounds detected and identified were tabulated in Table 3. Bio-oils are known to be composed of large number of chemical species in different
concentrations. For identification purposes, only compounds with peak area higher than 1.0% are listed. The bio-oils produced at 350 °C contained abundant number of oxygenated compounds such as ester based compounds (2- butenedioic acid, 2-ethyl-3-methyl-, dimethyl ester, 14.2%; tetrahydropyran Z-10-dodecenoate, 12.1%; oxalic acid, butyl cyclohexylmethyl ester, 9.9%; oxalic acid, cyclobutyl tridecyl ester, 8.0%; Methyl 4-nitrohexanoate, 6.6%). There are series of complex reaction occur during the conversion process which includes the decomposition and repolymerization of the compounds in sewage sludge (e.g., lipids, carbohydrates and protein). In normal cases, fatty acid esters are produced from transesterification of lipids and esterification process of fatty acid with alcohol.

Table 3. GC-MS analysis for bio-oils obtained from sewage sludge hydrothermal liquefaction

| No | RT (min) | Peak Area (%) | Compound Name |
|----|---------|---------------|---------------|
| 250°C | 300°C | 350°C | 400°C |
| 1 | 3.04 | - | 1.2 | 1.4 | Difluorophosphoric acid |
| 2 | 3.10 | - | - | 12.1 | - | Tetrahydropyran Z-10-dodecenoate |
| 3 | 3.19 | - | - | - | Methylphenidate |
| 4 | 3.23 | - | - | - | 4.2 | 2-Butanone-4,4,5,5-tetramethyl-oxazoline |
| 5 | 4.29 | - | - | - | 1.2 | 4,6-Octadiyn-3-one, 2-methyl |
| 6 | 4.83 | - | - | 4.5 | 1.1 | 2-Cyclopenten-1-one, 2-methyl |
| 7 | 6.50 | 1.0 | - | 7.7 | - | Benzene, 1-ethyl-2-methyl |
| 8 | 6.51 | - | 5.0 | 2.7 | - | Benzene, (1-methylethyl) |
| 9 | 6.79 | - | - | 1.9 | - | N-Ethyl-2-isopropoxy carbonyl azetidine |
| 10 | 9.23 | - | 3.2 | - | 2.7 | Cyclopentasiloxane, decamethyl |
| 11 | 13.82 | 1.3 | - | 1.8 | 1.3 | Cyclohexasiloxane, dodecamethyl |
| 12 | 18.89 | 3.0 | - | 2.6 | - | Cycloheptasiloxane, tetradecamethyl |
| 13 | 20.21 | - | - | 1.5 | - | Cyclopentane, 1,1,3-trimethyl |
| 14 | 22.36 | - | 1.1 | 4.4 | - | Cyclooctasiloxane, hexadecamethyl |
| 15 | 24.29 | - | 2.7 | - | 4.0 | 2-Nonanone, 9-hydroxy |
| 16 | 26.53 | - | 10.7 | - | 3.3 | 1,1,5,7,7,7-Heptamethyl-3,3-bis(trimethylsiloxy)tetrasiloxane |
| 17 | 29.55 | - | - | - | 6.5 | 1,1,5,7,7,7-Heptamethyl-3,3,5-tris(trimethylsiloxy)tetrasiloxane |
| 18 | 29.56 | 1.3 | - | 7.8 | - | Trimethylamine |
| 19 | 29.77 | 1.6 | 1.3 | 9.6 | - | 1-Tridecanol |
| 20 | 30.50 | - | - | 1.0 | - | Cyclopentane, 1,1,3-trimethyl |
| 21 | 32.68 | - | 6.1 | - | 1.5 | Hydantoin, 1-butyl |
| 22 | 33.46 | - | - | 6.4 | 3.8 | 3,6-Diisopropylpiperazin-2,5-dione |
| 23 | 33.51 | 2.1 | - | 14.2 | - | 2-Butenedioic acid, 2-ethyl-3-methyl-, dimethyl ester |
| 24 | 33.95 | 3.8 | 8.1 | 9.9 | - | Oxalic acid, butyl cyclohexylmethyl ester |
| 25 | 33.99 | 4.5 | - | - | - | 5-Decene, 1-bromo |
| 26 | 34.45 | - | 9.0 | 2.6 | - | Nickel tetracarbonyl |
| 27 | 34.47 | - | 1.9 | 7.1 | 8.9 | Diphenylamine |
| 28 | 34.48 | - | 4.8 | - | - | 2-Nonadecanone |
| 29 | 34.56 | 1.2 | 5.5 | 3.5 | - | Azelaic dihydrazide |
| 30 | 35.28 | 2.7 | - | 9.6 | - | Benzene, 1,2,3-trimethyl |
| 31 | 35.29 | 3.3 | - | 2.3 | 6.0 | Hexadecanoic acid, methyl ester |
| 32 | 35.30 | 4.1 | 2.1 | 8.0 | 3.7 | Oxalic acid, cyclobutyl tridecyl ester |
| 33 | 35.31 | 5.2 | 1.3 | - | - | Ethanimidamide, 2-chloro-N-(1,2-dichloroethenyl) |
| 34 | 35.31 | - | - | - | 2.4 | Cyclopentane, (2-methylbutyl) |
| 35 | 36.13 | - | - | 3.7 | 6.8 | 2-Pentanamine, N-(1-methylbutyl) |
| 36 | 36.67 | - | 2.4 | - | - | 2,5-Piperazinedione, 3,6-bis(2-methylpropyl) |
| 37 | 36.69 | 2.3 | 6.2 | - | - | Heptasiloxane, hexadecamethyl |
| 38 | 36.96 | 1.1 | - | 8.3 | 9.8 | Methanamine, N-hydroxy-N-methyl- |
| 39 | 37.06 | - | - | 6.6 | - | Methyl 4-nitrohexanoate |
| 40 | 37.07 | - | - | 1.4 | 2.0 | Pentadecanoic acid |
Another point of interest is that the organic acids from the decomposition of carbohydrates and protein will help undergo esterification and substitution reactions to form their corresponding ester and derivatives. On the other hand, the reaction of fatty acids and amines go through further dehydration of acid amide to generate nitrile compounds. The reaction of amino acid and acetone may also result to the N-containing ketone that were identified in the sewage sludge [15]. Other oxygenated compounds such as carboxylic acids were also observed.

In summary, temperature has marked influence on the compositions of bio-oil produced. The composition of bio oil obtained at temperature of 350°C is much similar to biodiesel. Hence, the bio-oil could be further processed to produce biofuels and ester based bio chemicals.

4. Conclusion
The results demonstrated that raw sewage sludge possess high volatile organic content and favorable heating value for conversion into fuels and biochemicals. Temperature plays significant influence on the course of hydrothermal liquefaction of sewage sludge. Significant bio-oils yield of around 52% was obtained using ultra-pure water as a solvent at temperature of 350°C and one hour reaction time. It was found that bio oils produced at this temperature was dominated with ester based compounds compared to bio-oils obtained at 250°C, 300°C and 400°C. GCMS analyses results matched with that from FTIR study confirms that the bio-oils was made up of aliphatic hydrogen as well as ester, carboxylic and amide groups

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