

## **Production of Bio-oil by Oxidative Pyrolysis of Sewage Sludge in Rotating Fixed Bed Reactor**

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**Abstract:** Pyrolysis is an attractive thermal conversion technology used to produce bio-oil and some chemicals. In this study, we investigated the pyrolysis of sewage sludge under N<sub>2</sub> and CO<sub>2</sub> atmosphere at various temperatures (350-750°C) in a rotating fixed bed reactor. For under N<sub>2</sub> atmosphere, thermal gravimetric analysis (TGA) shows two major reaction peaks centered at 300 and 500°C. However, if CO<sub>2</sub> was used instead of N<sub>2</sub>, the reaction rate at 300°C increased by 40%, and the peak at 500°C was significantly shifted to 425°C with the increasing reaction rate of 8-10%. The components in bio-oil obtained from inert and oxidative pyrolysis were identified. The typical characteristics of bio-oil from inert pyrolysis are mainly oxygenated and nitrogenated of aliphatic compounds, and also a little amount of alicyclic and aromatic compounds. If the pyrolysis temperature was increased, more aromatics compounds were obtained. Under CO<sub>2</sub> or oxidative pyrolysis, it was found that the amount of aromatic compounds in the bio-oil was also increased while unsaturated and alicyclic compounds were decreased, which is possibly due to the enhancement of polymerization and cyclization by CO<sub>2</sub>. Moreover, when compared with under N<sub>2</sub> atmosphere, the total bio-oil production was improved by 25% under an oxidative pyrolysis condition.

**Keywords:** Sewage Sludge, Combustion, Oxidative Pyrolysis, Bio-oil, Rotating Fixed Bed Reactor.

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### **Introduction**

Sewage sludge is a by-product from wastewater treatment plants (WWTP's). It contains significant amounts of heavy metals, organic toxins and pathogenic microorganism, which are considered to be harmful to the environment and all living organisms [1]. Agricultural use, land filling and incineration are commonly ways to handle sewage sludge. It was reported that heavy metal from sewage sludge can penetrate to soil causing soil contamination. Advantages and disadvantages of these disposal methods are reported elsewhere [2]. Pyrolysis, a thermochemical process, can be considered as a technique to

obtain valuable chemicals from large hydrocarbon molecules. It is a promising technique to reduce amount of sewage sludge and also obtain high value chemicals [3]. Studies covering kinetic modeling of sewage sludge [2, 4-11], products characterization [3, 9 and 12] and pyrolysis mechanism [10] are also available. Typical pyrolysis utilizes an inert gas e.g. nitrogen or helium. However, we suggest using a mild oxidative gas such as carbon dioxide to perform pyrolysis of the sewage sludge. CO<sub>2</sub> is not only a major component in natural gas but also generated by combustion. The emission of CO<sub>2</sub> to the atmosphere has been considered as a serious cause of the global warming or the green house effects. It is of great interest to use CO<sub>2</sub> the sewage sludge pyrolysis since we can simultaneously reduce the green-house gas in the atmosphere and also obtain the more valuable products from sewage sludge. The aim of the present work was to investigate the sewage sludge pyrolysis under CO<sub>2</sub> atmosphere. The effect of CO<sub>2</sub> concentration and the pyrolysis temperature on the gas and liquid products were studied.

## Material and Methods

### *Sample preparation and characterizations*

In order to obtain a good representative of sewage sludge sample, the sample collection was done according to the ASTM D346-90. The sample was naturally dried for 1-2 days and ground by using a ball mill. To avoid mass transfer complication, the sample's size of 150-250 μm was selected for investigation. The elemental compositions of sludge sample were determined by ASTM D3176-89 (Ultimate Analysis) and the weight percent of C, H, N, S and O (by difference) were obtained. Based on ASTM D3172-89, the proximate compositions (i.e. moisture, volatile, fixed carbon and ash content) of sludge was determined. Finally, the higher heating value (HHV, kJ/kg) of the sludge sample was obtained according to ASTM D2015.

### *Thermogravimetric analysis (TGA)*

Thermogravimetric analysis was performed by a Perkin- Elmer Thermo Balance; model TGA7, controlled by a computer with a data acquisition system. The sludge sample was loosely distributed over a sample pan, with initial amount around 10 mg. The nitrogen gas flow rate was set at 20 cm<sup>3</sup> min<sup>-1</sup> in order to provide inert atmosphere. For oxidative atmosphere, carbon dioxide was used instead of nitrogen to study its effects on pyrolytic mechanisms and products. The sample was heated from ambient temperature to 105°C. Then, the sample was held at 105°C for 12 minutes to ensure that the free-water was completely removed. The sample was heated from 105°C to 800°C in order to scan entire decomposition reactions. The heating rate (20°C min<sup>-1</sup>) was selected to avoid the heat transfer effect.

### *Temperature programmed pyrolysis/ Mass spectroscopy (TPPy/MS)*

A Blazers Omnistar™ mass spectrometer (MS) with an ion source of electron impact at 70 eV was employed to analyze gas products from the pyrolysis. Using the same experimental conditions as in the thermogravimetric experiment, the sludge sample of 10 mg was pyrolyzed in a quartz tube cell (TPDRO 1100, ThermoFinnigan) directly connected to the mass spectrometer.

### *Rotating fixed bed reactor (Bio-oil production)*

A rotating fixed bed reactor with internal gas distributor was used. The internal diameter of reactor was 12.5 cm. The reactor was a stainless steel and the sludge sample was introduced inside the stainless steel basket over the gas distributor. The production of bio-oil was performed by pyrolysis of sludge at several pyrolysis temperatures (350-750°C) under both N<sub>2</sub> and CO<sub>2</sub> atmosphere. The sludgesample around 50 g was introduced to the basket. The gas flow used was 100 cm<sup>3</sup>/min. For this flow, the estimated residence time was 25 s. The heating rate used was 20°C min<sup>-1</sup> which was identical to TGA experiments. The pyrolysis products were swept out of the reactor and passed through a liquid quench system (LQS) and the following four impinger bottles were filled with organic solvent. The

last impinger bottle was empty in order to function as a drop separator. 1-Methoxy-2-propanol was chosen as a sampling solvent because of its good solubility for primary and converted tar, secondary

products, and its solubility with water that prevents the problem of ice formation and simplifies the post-treatment of the samples considerably. For the LQS, a glass tube containing an inner and outer tube connects the stainless flexible tube which its temperature was controlled at 150°C and the solvent stock bottle of the LQS. Mode of operations of LQS can be found elsewhere [14]. The solvent stock bottle of LQS and four impingement bottles were kept in ice/acetone bath. After the end of run, the sampling bottle was weighted and the mass of the tar containing solvent was determined and recorded

### ***Gas chromatography/Mass spectroscopy (GC/MS)***

Each liquid pyrolysate obtained at different conditions were analyzed by TraceGC/PolarizQ MS (ThermoFinnigan). The capillary column DB-5 MS was used and the compounds were identified by MS (15-500 a.m.u., 70 eV). The qualitative identification of compounds was performed comparing sample mass spectrum with NIST database reference mass spectrum

## **Results and Discussion**

### ***Sewage sludge characteristics***

Proximate and ultimate analysis and higher heating value of sewage sludge are shown in Table 1. The proximate compositions of sludge are mainly volatile matter and ash content, 43 and 46%, respectively. However, the sludge contains relatively small amount of moisture and fixed carbon content, 6 and 4%, respectively. The ultimate analysis is  $(C_6H_{11.16}O_{4.44}N_{0.78}S_{0.18})_n$  for dried sewage sludge compared to  $(C_6H_{12}O_6)_n$  for pure cellulose. The HHV of sludge in this work (13 MJ/kg) is lower than the HHV of sludge reported in other works [13]. It may be due to the relatively low volatile matter and high ash content of this type sludge.

### ***Characteristics of sewage sludge mass loss curves and its kinetics***

Fig. 1 represents the Thermogravimetric (TG) diagrams of sludge sample treated by different CO<sub>2</sub> concentration. It can be observed that, at the same temperature, the mass loss of the sludge increases with increasing CO<sub>2</sub> concentration. Differential thermogravimetric (DTG) diagram of sludge at different CO<sub>2</sub> concentration are shown in Fig. 2. In this work, DTG is used to determine the characteristic temperatures [16] such as maximum mass loss temperature or peak temperature, and final decomposition temperature which are defined as the temperature at 90% mass loss. Table 2 shows characteristic temperatures from the thermogram. Decomposition under inert (N<sub>2</sub>) atmosphere shows two major peaks centered at ca. 300 and 500°C. However, the two small peaks at ca. 120 and 700°C are also observed, which can be explained as the loss of physical-adsorbed water and the loss of carbonate compounds respectively. When N<sub>2</sub> and CO<sub>2</sub> is presence together, two major DTG peaks are still observed at around 300°C and 500°C, but both peaks have higher magnitude than those from N<sub>2</sub> alone. It can be concluded that CO<sub>2</sub> enhances the rate of sludge decomposition. Furthermore, the presence of CO<sub>2</sub> slightly shifts the peak centered at 500°C from the case of only N<sub>2</sub> to 470, 455 and 425°C when CO<sub>2</sub> concentration is 20%, 40% and 100% respectively.

At higher temperature, the decomposition peak at 700°C, observed only in the N<sub>2</sub> atmosphere, is possibly due to two possible explanations. First, if the major component of the sludge at the peak 700°C is carbonate compounds, then CO<sub>2</sub> cannot significantly decompose these compounds, but N<sub>2</sub> at high temperature can. For the second explanation, if the components are not carbonate compounds, CO<sub>2</sub> will oxidize these compounds at much lower temperature, therefore the peak at higher temperature will not be observed. We can conclude that CO<sub>2</sub> does not affect the low temperature thermal decomposition mechanisms but it enhances the thermal decomposition rate correspond to its oxidizing ability. In another word, the pyrolytic mechanisms involve the devolatilization mechanism when the temperature is low so, CO<sub>2</sub> does not affect to pyrolytic mechanism but affect to only reaction

rate. When the temperature reaches relatively high, CO<sub>2</sub> is likely to promote the oxidation reaction of the solid, thereby oxidation and pyrolysis may coexist.

### Gas evolution profiles

The selected gas evolution profiles from sewage sludge pyrolysis under the N<sub>2</sub> and CO<sub>2</sub> atmosphere are shown in Fig. 3. The possible products are listed in Table 3. The chemical assignments have been done and agreed with other assignments reported in other literatures [6, 10 and 12]. Hydrogen is evolved in the wide range of temperature (400-800°C). As clearly seen, CO<sub>2</sub> promotes the production of H<sub>2</sub> until the temperature reaches ca. 750°C. At temperature of ca. 750°C, the H<sub>2</sub> production is inhibited by presence of CO<sub>2</sub> possibly because H<sub>2</sub> and CO<sub>2</sub> reach the equilibrium of water gas shift reaction with the water and CO which are generated during the process, as shown in Eq. (1). For higher CO<sub>2</sub> and H<sub>2</sub> concentration, the equilibrium of Eq. (1) will shift to the left side; therefore, the H<sub>2</sub> is consumed and then its evolution is lowered. This phenomenon can be confirmed by the fact that, at temperature ca. 750°C, CO evolution is increased while CO<sub>2</sub> is decreased. However, at this temperature, fixed carbon in the sewage sludge sample and char generated from pyrolysis can be gasified to form CO. Therefore, the CO evolution from the fixed carbon and char gasification can also be generated and shown in Eq. (2)



However, CO<sub>2</sub> does not affect the evolution of CH<sub>4</sub> (m/z=15) because CH<sub>4</sub> can be formed by termination of methyl and hydrogen radicals, which are generated from thermal decomposition of the sludge [10]. For small molecular weight hydrocarbon such as C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>6</sub> and C<sub>4</sub>H<sub>10</sub>, CO<sub>2</sub> increases the amount of these hydrocarbon productions because CO<sub>2</sub> is more reactive to crack the hydrocarbon molecules of sewage sludge, resulting in generation of more quantity of small hydrocarbon molecules at higher evolution rate, as shown in the TGA results. The production of acetic acid (m/z=60) is started at temperature ca. 600°C cannot be explained by the thermally decomposition of the sludge sample at the high temperature since mass loss at the high temperature was not observed in the TG and DTG results. In addition, sludge cannot directly

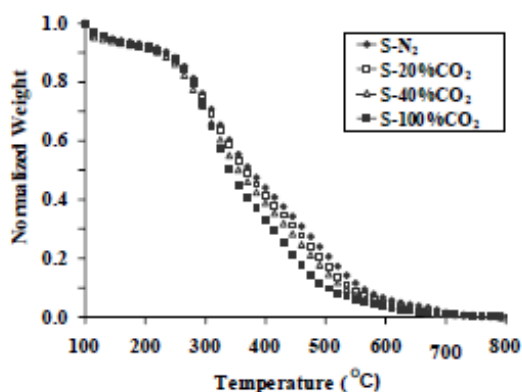
**Table 1** Proximate and ultimate analysis

Proximate analysis				
	Moisture content (wt%)	Volatile matter* (wt%)	Fixed carbon* (wt%)	Ash* (wt%)
	6.16	43.26	4.52	46.06
Ultimate analysis				
	C (wt%)	H (wt%)	N (wt%)	S (wt%)
	19.49	3.01	2.87	1.52

\*dry basis

**Table 2** Characteristic temperatures of sewage sludge pyrolysis

Sample	Atmosphere	T <sub>m1</sub> (°C)	T <sub>m2</sub> (°C)	T <sub>90%</sub> (°C)
S-N <sub>2</sub>	N <sub>2</sub>	305	500	540
S-20%CO <sub>2</sub>	20%CO <sub>2</sub> + 80%N <sub>2</sub>	305	470	520
S-40%CO <sub>2</sub>	40%CO <sub>2</sub> + 60%N <sub>2</sub>	305	455	515
S-100%CO <sub>2</sub>	CO <sub>2</sub>	305	425	510



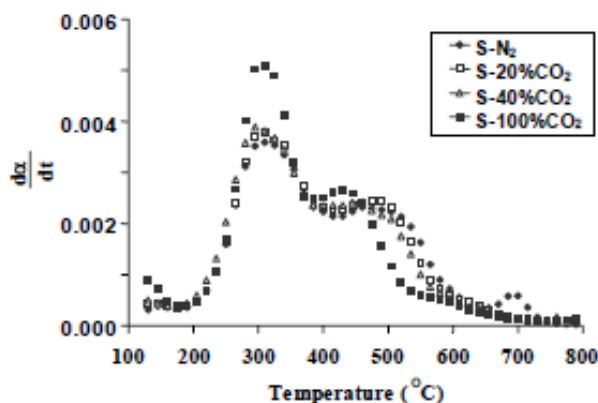
**Fig. 1** TG profiles of sewage sludge pyrolysis under (◆) N<sub>2</sub> atmosphere, (□) 20%CO<sub>2</sub> balance with N<sub>2</sub> (Δ) 40%CO<sub>2</sub> balance with N<sub>2</sub> and (◻) CO<sub>2</sub> atmosphere.

**Table 3** selected molecular ions from mass spectrometer

m/z ratio	Molecular ions	Mainly due to
2	H <sub>2</sub> <sup>+</sup>	Hydrogen
15	CH <sub>3</sub> <sup>+</sup>	Methane
26	C <sub>2</sub> H <sub>2</sub> <sup>+</sup>	Ethylene
28	CO <sup>+</sup>	Carbon monoxide
39	C <sub>3</sub> H <sub>3</sub> <sup>+</sup>	Propylene
44	CO <sub>2</sub> <sup>+</sup>	Carbon dioxide
55	C <sub>4</sub> H <sub>7</sub> <sup>+</sup>	Butane
60	CH <sub>3</sub> COOH <sup>+</sup>	Acetic acid

**The liquid pyrolysate**

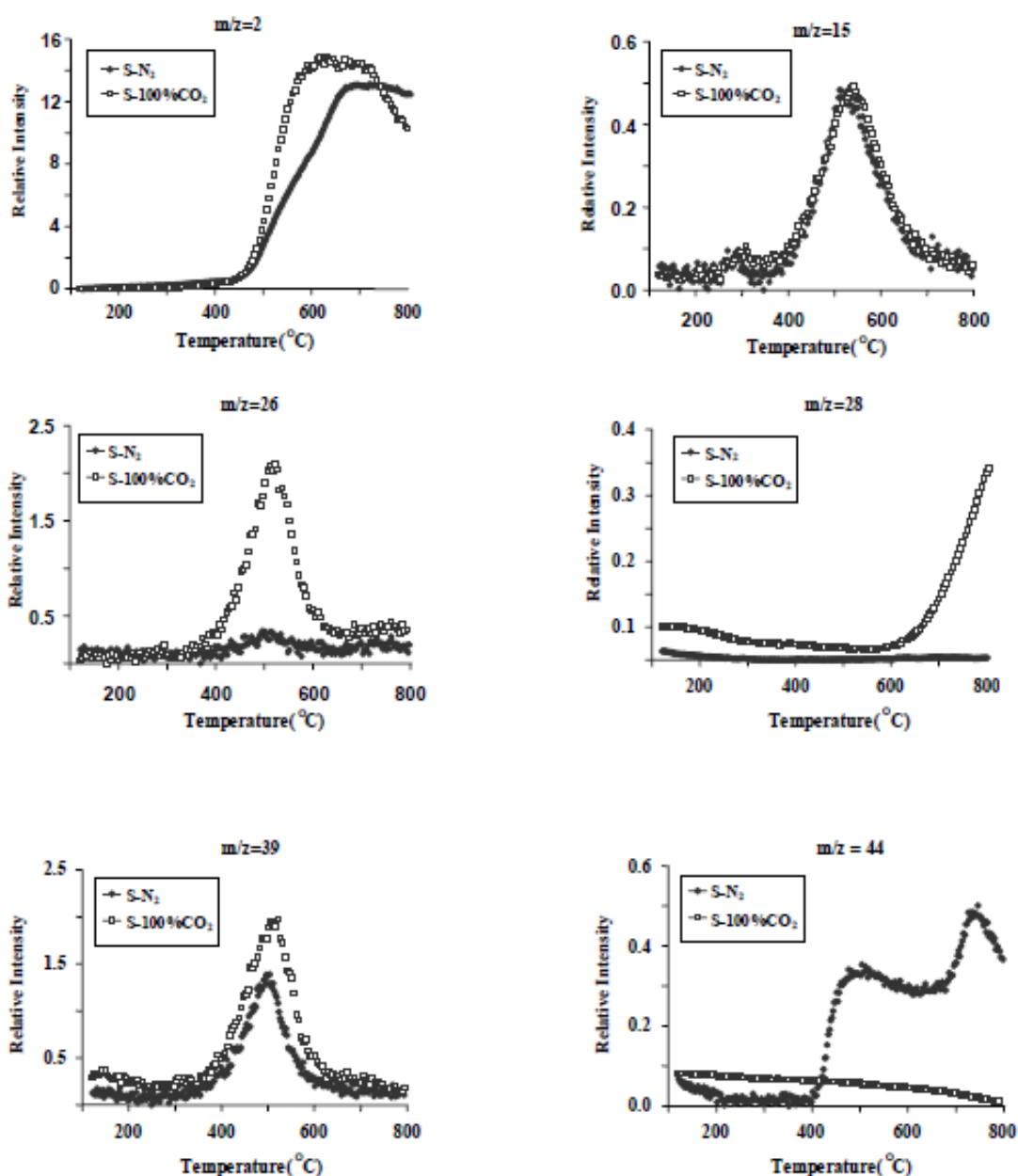
The liquid fraction is obtained from the condensed vapor of pyrolysis products at temperature around -20 °C. To identify the components in these products, GC/MS is utilized to analyze these samples. Table 4 summarizes the compounds in the liquid fraction from the pyrolysis of the sewage sludge. The liquid pyrolysate is composed of several types of decompose to acetic acid by itself. There are two possible reasons to explain the formation of acetic acid. First, CO<sub>2</sub> reacts with active volatile produced in the gas phase then form acetic acid. Second, CO<sub>2</sub> reacts with solid residue (or sludge itself) and accept proton then form acetic acid.



**Fig. 2** DTG profiles of sewage sludge pyrolysis under (◆) N<sub>2</sub> atmosphere, (□) 20% CO<sub>2</sub> balance with N<sub>2</sub> (Δ) 40%CO<sub>2</sub> balance with N<sub>2</sub> and (◻) CO<sub>2</sub> atmosphere.

hydrocarbons. However, based on the GC/MS chromatogram, the result can be divided into three zones or three major groups of hydrocarbon compounds, according to the elution time, related to the molecular weight and polarity of the compounds. First zone is contributed to oxygenated and nitrogenated compounds. Second zone is due to the aliphatic and alicyclic compounds. Third zone is involved with aromatic compounds were found due to the significant amount of oxygen and nitrogen contents in original sludge. Because of its high oxygenated and nitrogenated compounds content, this pyrolysate is highly reactive.

For the pyrolysis at lower temperature (350°C), the chromatogram of liquid pyrolysate mainly consists of the oxygenated and nitrogenated compounds, aliphatic and alicyclic compounds, and small amount of aromatic compounds. Since the temperature is relatively low, the aromatic compounds are probably come from the devolatilization mechanism. When the CO<sub>2</sub> is present, the liquid pyrolysate from oxidative conditions give very similar chromatogram.



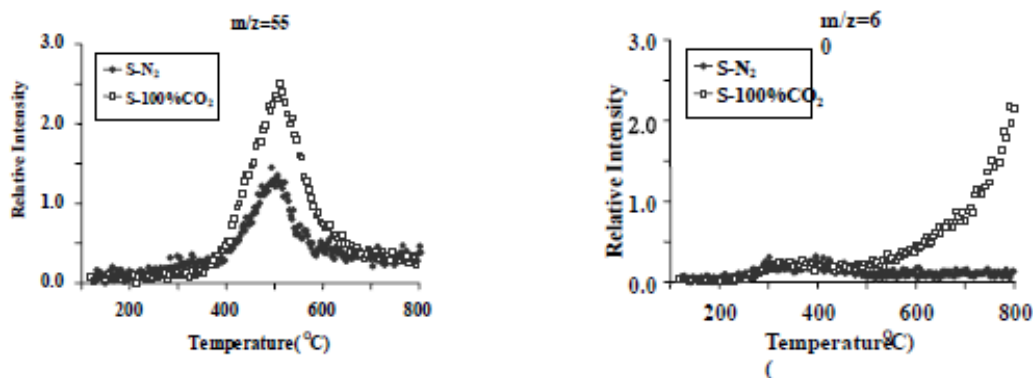


Fig. 3 selected evolution profiles of gas products from sewage sludge pyrolysis in different atmosphere. (◆) N<sub>2</sub> atmosphere, (■) CO<sub>2</sub> atmosphere.

Table 4 Chemical compounds found in liquid pyrolysate

Compounds name	Formula	Molecular weight	Compounds name	Formula	Molecular weight
<u>Acids</u>			<u>Aliphatic and alicyclic compounds</u>		
Acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	60	Hexane	C <sub>6</sub> H <sub>14</sub>	86
Propanoic acid	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	74	3,3-Dimethyl-1,6-heptadiene	C <sub>9</sub> H <sub>16</sub>	124
Butanoic acid	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88	6-Methyl 1 octane	C <sub>9</sub> H <sub>18</sub>	126
Pentanoic acid	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	102	1,2,3-Trimethyl cyclohexane	C <sub>9</sub> H <sub>18</sub>	126
Hexanoic acid	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	116	1-Decyne	C <sub>10</sub> H <sub>18</sub>	138
<u>Aldehydes and ketones</u>			7-Methyl-1-octane	C <sub>10</sub> H <sub>18</sub>	140
Acetaldehyde	CH <sub>4</sub> O	32	2,5,5-Trimethyl heptane	C <sub>10</sub> H <sub>20</sub>	142
Butanedial	C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	86	Decane	C <sub>10</sub> H <sub>22</sub>	142
3-Hydroxyl butanal	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	89	Undecane	C <sub>11</sub> H <sub>22</sub>	156
3-Methyl butanal	C <sub>5</sub> H <sub>10</sub> O	86	2,4,6-Trimethyl octane	C <sub>11</sub> H <sub>24</sub>	156
Pentanedial	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	100	1-Dodecane-3-yne	C <sub>11</sub> H <sub>24</sub>	164
4-Octan-3-one	C <sub>8</sub> H <sub>14</sub> O	126	4-Dodecane	C <sub>12</sub> H <sub>20</sub>	168
<u>Alcohols and ethers</u>			5-Dodecane	C <sub>12</sub> H <sub>24</sub>	168
Oxirane	C <sub>2</sub> H <sub>4</sub> O	44	3-Methyl-3-undecane	C <sub>12</sub> H <sub>24</sub>	168
Ethyl alcohol	C <sub>2</sub> H <sub>6</sub> O	46	2-Propyl-1,3,3-trimethyl cyclohexane	C <sub>12</sub> H <sub>24</sub>	168
Cyclobutanol	C <sub>4</sub> H <sub>8</sub> O	70	1-Tridecyne	C <sub>13</sub> H <sub>24</sub>	180
Cyclopropyl carbinol	C <sub>4</sub> H <sub>8</sub> O	72	6-Tridecane	C <sub>13</sub> H <sub>26</sub>	182
2-Pentene-1-ol	C <sub>5</sub> H <sub>10</sub> O	86	6-Ethyl-2-methyl decane	C <sub>13</sub> H <sub>28</sub>	184
5-Hexen-2-ol	C <sub>6</sub> H <sub>12</sub> O	99	3,7-Dimethyl undecane	C <sub>13</sub> H <sub>28</sub>	184
2,4-Hexadiene-1-ol	C <sub>6</sub> H <sub>10</sub> O	103	1-Tetradecyne	C <sub>14</sub> H <sub>26</sub>	194
Benzyl alcohol	C <sub>7</sub> H <sub>8</sub> O	108	3-Tetra decane	C <sub>14</sub> H <sub>28</sub>	196
3-Heptyne-1-ol	C <sub>7</sub> H <sub>12</sub> O	112	4-Tetra decane	C <sub>14</sub> H <sub>28</sub>	196
<u>Furans</u>			Pentadecane	C <sub>15</sub> H <sub>32</sub>	212
Furan (Furfural)	C <sub>4</sub> H <sub>4</sub> O	68	Hexadecane	C <sub>16</sub> H <sub>34</sub>	226
2,3-Dihydro-furan	C <sub>4</sub> H <sub>6</sub> O	70	<u>Nitrogenated compounds</u>		
Furfural(2-Furaldehyde)	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	96	Hydrogencyanide	HCN	27
Furfural alcohol	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	98	1H-Pyrrole-1-methyl	C <sub>4</sub> H <sub>4</sub> N	66
<u>Phenols and cresols</u>			4-Pyridinamine	C <sub>6</sub> H <sub>5</sub> N <sub>2</sub>	94
Phenol	C <sub>6</sub> H <sub>6</sub> O	90	2-Methyl pyridine	C <sub>6</sub> H <sub>7</sub> N	93
o,m,p-Cresol	C <sub>7</sub> H <sub>8</sub> O	108	3-Methyl pyridine	C <sub>6</sub> H <sub>7</sub> N	93
2,3-Dimethyl phenol	C <sub>8</sub> H <sub>10</sub> O	122	2-Ethyl pyridine	C <sub>7</sub> H <sub>9</sub> N	107
<u>PLAS</u>			o-Tolyl pyridine	C <sub>7</sub> H <sub>9</sub> N	107
Benzene	C <sub>6</sub> H <sub>6</sub>	78	Indole	C <sub>8</sub> H <sub>7</sub> N	117
Toluene	C <sub>7</sub> H <sub>8</sub>	92	Benzyl nitrile	C <sub>8</sub> H <sub>7</sub> N	117
Styrene	C <sub>8</sub> H <sub>8</sub>	104	1-Isocyno-4-methyl-benzene	C <sub>8</sub> H <sub>8</sub> N	118
o,m,p-Xylene	C <sub>8</sub> H <sub>10</sub>	106	α-Ethylbenzene acetonitrile	C <sub>10</sub> H <sub>11</sub> N	145
Ethyl benzene	C <sub>8</sub> H <sub>10</sub>	106			

This is because there is no effect of CO<sub>2</sub> on the pyrolysis at this low temperature, which is also observed in TG results. If the pyrolysis temperature is increased to 450°C, the higher amount of three groups of hydrocarbon compounds is generated. The amount of oxygenated and nitrogenated compounds, aliphatic and alicyclic compounds are reach the maximum at temperature of 550°C while the amount of aromatic compounds are still increasing. If CO<sub>2</sub> is introduced, the higher amount of

oxygenated and nitrogenated compounds, aliphatic and alicyclic compounds were generated because of CO<sub>2</sub> oxidizing ability. Further increasing temperature, the aromatic compounds are the major products instead. It is due to the polymerization and cyclization reactions at high temperature [2]. When CO<sub>2</sub> is present, it enhances the extent of those reactions causing more production of the aromatic compounds. Quantitative analysis of liquid pyrolysate are need to be done in order to have a better understanding of the CO<sub>2</sub> effects on the pyrolytic mechanisms.

## Conclusion

In this study, when the pyrolysis temperature of the sewage sludge is increased, the higher amount of gas and liquid is produced while the solid is less. Under CO<sub>2</sub> or oxidative atmosphere, the rate of thermal decomposition is significantly increased. If the temperature is relatively high (>550°C), CO<sub>2</sub> significantly changes the decomposition behavior of the sewage sludge, and also more amount of gas and liquid is obtained, due to the CO<sub>2</sub> oxidizing ability.

The major compounds in bio-oil obtained from inert pyrolysis are oxygenated and nitrogenated of aliphatic compounds. Furthermore, a small amount of alicyclic and aromatic compounds are also found in the bio-oil. Moreover, if the pyrolysis temperature is increased and CO<sub>2</sub> is used, the aromatic compounds will be more in the liquid products.

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