

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

Charothon Jindarom¹, Vissanu Meeyoo², Thirasak Rirksomboon¹,
Boonyarach Kitiyanan^{1,*} and Pramoch Rangsunvigit¹

¹The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand. 10330

²Center for Advanced Materials and Environmental Research, Mahanakorn University of Technology, Bangkok, Thailand. 10530

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 N₂ and CO₂ atmosphere at various temperatures (350-750°C) in a rotating fixed bed reactor. For under N₂ atmosphere, thermal gravimetric analysis (TGA) shows two major reaction peaks centered at 300 and 500°C. However, if CO₂ was used instead of N₂, 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 CO₂ 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 CO₂. Moreover, when compared with under N₂ 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.

1. 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. CO₂ is not only a major component in natural gas but also generated by combustion. The emission of CO₂ 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 CO₂ 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 CO₂ atmosphere. The effect of CO₂ concentration and the pyrolysis temperature on the gas and liquid products were studied.

2. MATERIAL AND METHODS

2.1 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.

2.2 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 cm³ min⁻¹ 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⁻¹) was selected to avoid the heat transfer effect.

2.3 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.

2.4 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 N₂ and CO₂ atmosphere. The sludge sample around 50 g was introduced to the basket. The gas flow used was 100 cm³/min. For this flow, the estimated residence time was 25 s. The heating rate used was 20°C min⁻¹ 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.

2.5 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.

3. RESULTS AND DISCUSSION

3.1 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 (C₆H_{11.16}O_{4.44}N_{0.78}S_{0.18})_n for dried sewage sludge compared to (C₆H₁₂O₆)_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.

3.2 Characteristics of sewage sludge mass loss curves and its kinetics

Fig. 1 represents the Thermogravimetric (TG) diagrams of sludge sample treated by different CO₂ concentration. It can be observed that, at the same temperature, the mass loss of the sludge increases with increasing CO₂ concentration. Differential thermogravimetric (DTG) diagram of sludge at different CO₂ 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

(N₂) 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 N₂ and CO₂ 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 N₂ alone. It can be concluded that CO₂ enhances the rate of sludge decomposition. Furthermore, the presence of CO₂ slightly shifts the peak centered at 500°C from the case of only N₂ to 470, 455 and 425°C when CO₂ concentration is 20%, 40% and 100% respectively.

At higher temperature, the decomposition peak at 700°C, observed only in the N₂ 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 CO₂ cannot significantly decompose these compounds, but N₂ at high temperature can. For the second explanation, if the components are not carbonate compounds, CO₂ will oxidize these compounds at much lower temperature, therefore the peak at higher temperature will not be observed.

We can conclude that CO₂ 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, CO₂ does not affect to pyrolytic mechanism but affect to only reaction rate. When the temperature reaches relatively high, CO₂ is likely to promote the oxidation reaction of the solid, thereby oxidation and pyrolysis may coexist.

3.3 Gas evolution profiles

The selected gas evolution profiles from sewage sludge pyrolysis under the N₂ and CO₂ 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, CO₂ promotes the production of H₂ until the temperature reaches ca. 750°C. At temperature of ca. 750°C, the H₂ production is inhibited by presence of CO₂ possibly because H₂ and CO₂ 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 CO₂ and H₂ concentration, the equilibrium of Eq. (1) will shift to the left side; therefore, the H₂ 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 CO₂ 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, CO₂ does not affect the evolution of CH₄ (m/z=15) because CH₄ 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 C₂H₂, C₃H₆ and C₄H₁₀, CO₂ increases the amount of these hydrocarbon productions because CO₂ is more reactive to crack the hydrocarbon molecules of sewage sludge, resulting in generation of more

