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Pyrolysis, combustion and gasification characteristics of miscanthus and sewage sludge

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ABSTRACT

The energetic conversion of biomass into syngas is considered as reliable energy source. In this context, biomass (miscanthus) and sewage sludge have been investigated. A simultaneous thermal analyzer and mass spectrometer was used for the characterization of samples and identified the volatiles evolved during the heating of the sample up to 1100 °C under combustion and gasification conditions. The TG and DTA results were discussed in argon, oxygen, steam and steam blended gas atmospheres. Different stages of pyrolysis, combustion and gasification of the samples have been examined. It was shown that the combustion and gasification of char were occurred in two different temperature zones. The DTA–MS profile of the sample gives information on combustion and gasification process of the samples (ignition, peak combustion and burnout temperatures) and gases released (H_2, O_2, CO and CO_2). The results showed that the different processes were mainly dependent on temperature. The evolution of the gas species was consistent with the weight loss of the samples during pyrolysis, combustion and gasification process. The effect of the ambiences during pyrolysis, combustion and gasification of the samples were reported. The appropriate temperature range to the sludge and miscanthus gasification was evaluated. The kinetic parameters of the biomass and sewage sludge were estimated for TGA using two models based on first-order reactions with distributed activation energies. The presence of ash in the biomass char was more influential during the gasification process.

1. Introduction

Biomass gasification represents one of a number of renewable technologies that intend to alleviate an overdependence on fossil-derived hydrocarbons. Biomass sources exhibit higher hydrogen and oxygen content, but a lower carbon content when compared with coal, hence low level of CO_2 emissions. The disposal of sewage sludge in an economic and environmentally compatible manner was a common problem to all communities which has municipal waste water treatment facilities. Research and information are required to change public opinion on sewage sludge and to support the most suitable technological choice in each case. Pyrolysis is a process of producing gas or oil from carbonaceous materials using high temperature thermal cracking via an external heat source without the supply of air or steam. The conventional gasification technology makes use of partial combustion by controlling the amount of air to convert hydrocarbons into carbon monoxide, carbon dioxide, and hydrogen. Due to the high thermochemical reactivity of biomass char, the evolution of biomass gasification technology has been an area of increasing interest over the past few decades [1–4]. Traditionally, biomass is used in combustion for energy related applications. The main application is the use of biomass in utility boilers alone or co-fired with coal. In the recent times, alternative solutions are encouraged to increase the biomass conversion efficiency. Several researchers [5–8] have indicated that co-firing of biomass with coal does not only reduce the emissions of greenhouse gases (CO_2, CH_4, etc.) per unit of energy produced but may have a positive impact on the emission of other pollutants, such as SO_2 and NO*x*. Biomass can be pyrolyzed or gasified for producing liquid fuel or gaseous fuel such as methane, hydrogen and carbon monoxide. Numerous researchers have pointed out that pyrolysis is one of the suitable technologies with industrial perspectives for biomass valorization, since the process conditions can be optimized to maximize the yields of gas, liquid and char [3,9–12]. Some studies have demonstrated the burning characteristic and gaseous emissions in biomass/coal co-combustion during oxidation process [13,14,8,15]. Thermogravimetry coupled with mass spectrometry (TG–MS) is a well-recognized and suitable technique in the pyrolysis research of solid fuels,

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particularly coal and biomass for its simultaneous and elaborate information about the weight loss and gas formation behaviors as a function of time and temperature [16–20]. In this regard, most studies have been focused on pyrolysis and combustion processes. However, gasification studies have been less reported in literature, being most of them focused on the study of coals [20,21]. TGA–MS is an excellent tool for determining the kinetics of process. Hence, the kinetics of gasification is essential for modeling gasification processes at an industrial scale. Besides, a knowledge of the process kinetics has great importance for a correct design and product yield control. Magdziarz et al. [17] have examined the combustion products of biomass wood/oats, sewage sludge and coal using thermogravimetric analysis (TGA) coupled with mass spectrometer (MS) methods. The effects of co-combustion of biomass or sewage sludge with coal were assessed and found it to be beneficial.

Karampinis et al. [22] have described the combustion properties of miscanthus and poplar. They have concluded that the miscanthus and poplar as reactive fuels with high volatile matter with low ash contents. Özgür et al. [23] have implemented the combustion experiments on miscanthus and poplar, also they have found that the combustion of biomass fuels is highly exothermic and suitable as an appropriate fuel feedstock. Kok and Özgür [24] have characterized the miscanthus, poplar, and rice husk samples using differential scanning calorimeter (DSC) and thermogravimetry (TG–DTG) tests and found that the biomass samples have two-stage of combustion and the energy release; due to the combustion of fixed carbon in the later stage. Michel et al. [25] have investigated the miscanthus gasification characteristics in steam ambience to produce syngas using GC/MS method. Recently, Mimmo et al. [26] have examined the effect of pyrolysis temperature on miscanthus char.

Thermochemical methods are seen as promising alternatives for sewage sludge disposal when compared to traditional routes, due to its inherent improvement in the reduction of waste volume level and energy production. There are several technologies available, both in the market and under different stage of development, for thermal processing of dried sewage sludge. Typically, these can be grouped into three categories, i.e. mono-incineration, co-combustion, and other thermal processes [27]. Thermogravimetric analysis and mass spectrometry (TGA–MS) have been used to describe the sewage sludge thermal decomposition [28], and estimate the reaction kinetics and also to detect the composition of the non-condensable gases. Some researchers have reported that the composition of the non-condensable gases from thermogravimetric experiments of sewage sludge pyrolysis using gas chromatography–mass-spectrometry (GC–MS) systems [17,29,30]. They have found that the weight loss occurs principally in three stages, centered around the temperature at 250, 350 and 550 °C, producing high quantities of gases such as H_2, water, hydrocarbons (C1 ± C4, both saturated and unsaturated), methanol, carbon dioxide and acetic acid. Fonseca et al. [31] have described the kinetics of thermally induced reaction such as the combustion of carbonaceous materials. Liu et al. [32] have found that the sewage sludge released the volatiles around 550 °C and above, char combustion occurred under oxygen-enriched air conditions and also estimated kinetic parameters. Otero et al. [33–35] have investigated the combustion of coal–sludge blends using DTG, DSC and MS analysis and determined the kinetic parameters of the process. Hanmin et al. [36] and Folgueras et al. [37] also studied the co-combustion of coal and sewage sludge using thermo gravimetric analysis. Ischia et al. [38] used clay in a TG–MS study to evaluate the possible advantages of co-pyrolysis of clay and sewage sludge. Su et al. [39] have established the using of TG–FTIR analysis of sewage sludge, in which the released HCl and SO_2 decreased with the optimum condition, and also satisfying the environmental requirement. Werther and Ogada [27] have conducted the detailed study of sewage sludge combustion incorporating various issues. They have stated that the sewage sludge combustion releases low net emissions of NO*x* along with the conversion ratio of fuel N to NO*x* being less than 5%. Fonts et al. [40] reviewed the liquid production from sewage sludge pyrolysis, in which recent thermogravimetric pyrolysis mechanism was also discussed. Shao et al. [41] have demonstrated the different stages of pyrolysis and kinetics of sewage sludge using thermogravimetry and FTIR analyzers. Singh et al. [42] have reported the pyrolysis characteristics of waste materials, biomass wood waste, scrap tyre, refuse derived fuel (RDF) and waste plastic materials using TGA–MS and TGA–FTIR analyzers. Soria-Verdugo et al. [43] have reported the biomass and sewage sludge devolatilzation and estimated the kinetic parameters using distributed activation energy model.

Since, most of the papers were examined the pyrolysis characteristics of miscanthus and sewage sludge. There is limited research on combustion and gasification characteristics of these materials, this work dealt the gasification of miscanthus and sewage sludge that were selected according to their potential usage in thermochemical conversion processes. This study was performed to understand process along with various factors which influences the combustion and gasification process. Also, it is necessary to understand the pyrolysis mechanism of miscanthus and sewage sludge in order to increase conversion of solids to oil and gases, especially to increase H_2 during the gasification. This paper aims at a better understanding of the basic phenomena associated with thermogravimetric analysis of miscanthus and sewage sludge. Particularly, volatile matter evolution and burning characteristics of biomass char during combustion have been estimated. The pyrolysis of biomass samples was carried out to obtain a solid fuel (char), subsequently it was combusted with oxygen and in another test which was gasified using steam/steam mixtures. The gases released during the gasification process were analyzed by MS. Moreover, kinetics of combustion and gasification of miscanthus and sewage sludge have not been documented so well under oxy-fuel atmospheres and steam/steam mixtures, hence the need for the present research. Hence, a preliminary kinetic analysis of the thermo chemical conversion process was performed in order to obtain the apparent reaction rates by using two kinetic models: Friedman method and Coats and Redfern method.

2. Experimental

2.1. Materials and thermogravimetric analysis

Miscanthus and sewage sludge samples were originated from France. The size of the miscanthus sample was in the range from 2 to 4 mm, whereas the sewage sludge samples were finer particles, which comprises from few microns to 1 mm size ranges. The dried sewage sludge composition is almost comparable with miscanthus. So, dried sludge is opted for the present study. The ultimate and proximate analyses of the miscanthus and sewage sludge sample are given in Table 1. Thermogravimetric analysis study was performed using a NETZSCH STA 429 thermal analyser at inert and reactive atmospheres containing argon and steam at STP conditions up to 1100 °C. The experimental setup used for the gasification experiments was described in a previous study [20]. A separate steam (water vapor – WV) generator was connected with the STA, in which steam generator and transfer line were maintained at the temperature of 180 °C and 150 °C respectively. During the experiment, about 80 mg of sample was placed in a ceramic crucible and heated up to 1150 °C with a heating rate of 40 °C/min and isothermal sections retained at 950 and 1000 °C in some cases. Argon was used as protective gas with the flow rate of 20 ml/min in pyrolysis and combustion process. In gasification