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An investigation of raw and torrefied lignocellulosic biomasses with CaO during combustion

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ABSTRACT

The thermal degradation of three categories of raw and torrefied biomass [agri-residue: wheat straw, forest residue: sawdust, energy crop: miscanthus] was studied in a TGA-FTIR system with or without catalyst (CaO). The thermal degradation of biomass was carried out in the temperature range of 25–900 °C at a heating rate of 20 °C/min. The air flow rate was controlled based on the stoichiometric air requirement for complete combustion. The non-linear regression (NLREG) model was adopted to determine the kinetic parameters. The weight loss, heat flow, maximum weight loss temperature, and activation energy were observed to be dependent on the types of biomass and the process parameters. The maximum weight loss temperature was higher for torrefied biomass compared with raw biomass. The activation energy was higher in the case of torrefied biomass compared with raw biomass, and CaO helped to shrink the activation energy. The maximum weight loss temperature and activation energy were varied from 310 to 509 °C and 15–85 kJ/mol, respectively. The CaO supplement seems to have a positive impact on the thermal degradation process; thus, it may help in improving the thermal degradation process of torrefied biomass.

1. Introduction

The growing energy demand due to the increase in industrial development and population growth resulted in an increase in greenhouse gas (GHG) emissions, one of the serious problems that humankind faces today. Consequently, renewable bioenergy has been identified as an alternative to fossil fuels. Lignocellulosic biomass (hereafter referred as biomass) has huge potential to be a renewable source of energy (solid, gaseous and liquid). Recently, the co-utilization (co-gasification or co-combustion) of treated or untreated biomass with fossil fuel (i.e., coal) has gained attention to abate GHG emissions and reduce fossil fuel consumption [1], which will likely have technical, economic and environmental advantages [2,3].

Although biomass is a widely recognized alternative to fossil fuels, raw biomass cannot be combusted/gasified in conventional combustors/gasifiers efficiently. Torrefied biomass has the potential with improved thermal characteristics, which is a more stable, denser, hydrophobic material with higher energy values; thus, it reduces the biomass handling cost, can easily be transported and fed to the gasifier [4]. However, it is important to know the kinetics and degradation of feedstocks because the thermal degradation and energy production process depends on feedstock quality and process parameters [5,6]. Thermogravimetry is a method in which weight loss and heat flow are determined throughout the imposed thermal cycle [7]. Several researchers have studied the thermal degradation of biomass, mostly centered on types of biomass, degradation temperature and pretreatment [8–10]. Most of the studies were conducted based on raw biomass except for a few examples [10–12]. For example, Kuo et al. [10] studied the biomass steam gasification of raw and torrefied biomass with different steam ratios and found higher syngas yield compared with raw biomass. Torrefied biomass were reported to be suitable for co-utilization with coal [13–15]. The activation energy and maximum weight loss temperature of pyrolyzed biomass is found to be dependent on the components of biomass [16]. However, torrefied biomass required greater activation energy [12,17] compared to raw biomass. As

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far as the authors are concerned, there is no study reported in the literature that has attempted to reduce the required activation energy for torrefied biomass during combustion.

Several researchers have studied the effect of catalysts in gasification, combustion and co-pyrolysis processes [18–21]. Biomass steam gasification with the addition of CaO captures CO_2 producing $CaCO_3$ and releasing heat, thus reducing the energy requirement in the decomposition process [18,19]. Catalysts were also used in the combustion process of biomass to determine their impact on particulate matter emissions and found that the application of catalysts reduces emissions [21]. The catalytic co-pyrolysis of municipal solid waste (MSW) and paper sludge (PS) reduced the initial reaction temperature and activation energy which are also dependent on the ratio of MSW and PS, and the catalyst. Hence, the use of catalyst may help in reducing activation energy for torrefied biomass during combustion. Therefore, thermal degradation of biomass (raw and torrefied) with and without CaO was studied to understand the thermal degradation characteristics and determine if the activation energy can be reduced.

2. Materials and methods

2.1. Materials

In Canada, the main sources of biomass are agri-residues, forest residues and energy crops. Therefore, three feedstock were selected, i.e., one from each group (agri-residues: wheat straw, forest residues: sawdust (pine) and energy crop: miscanthus) to determine the thermal decomposition characteristics of raw and torrefied biomass with or without CaO. The feedstock was sun-dried to about 14% moisture content and the ground feedstock (250 μm) has been used in this study. The feedstock and CaO were mixed on an aluminum cup encompassing 50% feedstock and 50% CaO (i.e., the ratio of biomass and CaO was controlled to one) in the case of catalytic conversion.

2.2. Proximate analysis

The proximate analysis was conducted by using the ASTM standards (Moisture: ASTM-E871; Ash: ASTM-E1755; Volatile matter: ASTM-E872). A certain amount of each feedstock was placed in the furnace (Thermo Scientific – F48055-60, Waltham, MA). The samples were dried at 105 °C (furnace temperature was controlled at 103 ± 2 °C) for 16 h. The dried samples were then placed in the furnace at 575 °C for 5 h to determine the ash content. The volatile matter was measured by firing the samples at 950 °C for 7 min.

2.3. Ultimate analysis

The biomass samples were analyzed with CHNS-O analyzer (Flash 200 CHNS-O, Organic Elemental Analyzer, Thermo Fisher Scientific, The Netherlands) based on ASTM D5373-08. The samples were dried at 105 °C for 24 h prior to ultimate analysis. Then the samples were combusted at 925 °C in Helium atmosphere, while reduction was carried out at 650 °C.

2.4. Heating value

The oven dried feedstock were used to determine the higher heating values (HHV) of feedstock. The HHV was measured with a bomb calorimeter (IKA-C200, Wilmington, NC). Pure oxygen was used to pressurize the vessel to 30 bar before being ignited with a cotton thread, and the calorific value of the sample was recorded.

2.5. Torrefaction

The torrefaction process is a mild heat treatment given to the biomass, typically from 200 to 300 °C in an inert atmosphere that improves the thermochemical properties of biomass. Torrefied biomass were produced with a Quartz Wool Matrix (QWM) reactor at 275 °C for 45 min in an inert condition [22]. The reactor consists of a stainless steel tube, a perforated stainless steel basket acting as the sample holder, four electric heaters (1.25 kW each) and a balance (Fig. 1).

2.6. Thermal degradation

The thermal degradation experiments were carried out in a micro reactor (TGA-FTIR; TGA: SDT-Q600, TA Instruments-Waters LLC, New Castle, USA; FTIR: Thermo Scientific Nicolet 6700, TA Instruments-Waters LLC, New Castle, USA) setup at the University of Guelph. The air flow rate was controlled based on the stoichiometric air requirement for complete combustion. The samples were heated from 25 °C (room temperature) to 900 °C with a heating rate of 20 °C/min [23]. The weight loss and heat flow were recorded in a computer for the analysis of thermal degradation properties.

2.7. Kinetics analysis

The weight loss of feedstock during the thermal degradation process was measured as a function of temperature. The power law model has been used to analyze the reaction kinetics of biomass (Eq. (1)). The reaction rate constant was calculated by using the Arrhenius equation (Eq. (2)). The degradation rate, dx_A/dt, is the function of the temperature dependent reaction rate constant (k), the conversion function $(1-x_A)$, and the reaction order (n). The conversion factor (x_A) can be calculated from the third equation (Eq. (3)). The non-linear regression (NLREG) model has been used to determine the pre-exponential factor, activation energy and the reaction order.

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