Thermal Behavior of Woody Biomass in a Low Oxygen Atmosphere Using Macro-Thermogravimetric Analysis

Huu Linh Nguyen, Duc Dung Le*, Hong Nam Nguyen, and Viet Thieu Trinh

Abstract— *This work focused on investigating the thermal behavior of the coniferous tree (beech) and broadleaf tree (beefwood) that are abundantly available in Vietnam during a low-oxygen combustion condition. Pyrolysis in 100% Nitrogen atmosphere, char oxidation and combustion in 3% Oxygen atmosphere were conducted using a Macro-thermogravimetric analyzer, from room temperature to 900°C. Results showed that, regarding pyrolysis and char oxidation processes, beech biomass has the initial mass loss and the maximum mass loss at higher temperatures compared to beefwood biomass. For the overall combustion process, two stages could be clearly observed in differential thermal analysis curves, which correspond to devolatilization and char oxidation. However, the maximum combustion rate temperature and the char burnout temperature were sharply lower than in the case of pyrolysis and char oxidation that were carried out independently. This is likely due to volatile combustion of gaseous products released in devolatilization that could lead to an increase of the particle temperature and an acceleration of the pyrolysis and char oxidation kinetics. This highlighted the synergistic effects of pyrolysis and char oxidation in the overall combustion process. Results of this study could contribute to the understanding of the combustion profile of these kinds of biomass in a low oxygen atmosphere, in order to better organize the furnace combustion and effectively improve the efficiency of coal/biomass combustion.*

Keywords— **Woody biomass, thermogravimetric analysis, Macro-TGA, low-oxygen combustion.**

1. INTRODUCTION

Biomass is a promising feedstock that could contribute to overcome the major problems associated with the use of fossil fuels. Co-firing of coal with biomass is a friendly approach for mitigating the negative effects of coal burning. In spite of many advantages of biomass, such as advance ignition and burnout, low pollution, there are still several issues in current biomass combustion in furnaces, such as low thermal efficiency, heat load instability, slagging [1, 2]. The difference of fuel properties between biomass and coal might complicate the processes of fuel mixture handling and combustion when co-firing biomass with coal in the existing coal-fired boilers [3]. Thus, a deep knowledge of the thermal behavior of biomass during combustion is critical to assess the feasibility, design and scaling of industrial biomass conversion application [2, 12, 13].

Thermo-gravimetric analyses (TGA) generally involve the preparation of a few milligrams of powdered biomass which heat and mass transfer limitations can be ignored. For co-firing applications at industrial scale, big sizes of the biomass are commonly used, involving internal heat and mass transfer phenomena which are different considerably from thermal decomposition behaviors determined by a typical TGA; however, TGA has been widely used in studying pyrolysis and combustion processes of fuels and evaluating the relative burning properties of fuel samples. Several studies have been carried out to reveal the pyrolysis and combustion characteristic of coal, biomass and coal-biomass blending using TGA. Qing Wang et al [1] investigated the combustion of four different kinds of biomass under different heating rates using TGA and found that the combustion process can be decomposed into three steps: evaporation of water, release and combustion of volatile, char combustion. Wenhan Cao et al [2] reported that the TGA results were unable to identify the impact of particle size on the ignition behavior of biomass, this has also been reported by Jun Li et al [3]. However, also in the study of Jun Li et al [3], it has been seen that larger particle sizes required more time for ignition to start compared to smaller one at the same furnace temperature, according to the testing results in a down-fire reactor. In addition, it was observed that the softwood particles required a longer residence time to be ignited than straw particles. M. L. Contreras et al [4] found that compared with the combustion of solid fuels in conventional air, the temperatures of maximum reaction rate and maximum mass loss were lower under oxy-fuel combustion. The ignition temperature was improved when coal was blended with a biomass. Thermal processes for coal/wood blends can be divided into two reaction regions by temperature corresponding to the combustion behavior of pure fuels [6]. In the lower temperature range, the blend thermal behavior closes to biomass and in the higher temperature region, it is similar to coal. Hoang Anh Tran et al [8] investigated the combustion of Vietnam rice straw, coal and their blends in a macro TG reactor and found that there is a coupling phenomenon between pyrolysis and char oxidation when blending two solid fuels.

Combustion of solid fuels such as coal and biomass in

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low oxygen (O_2) atmosphere exists widely in industrial processes, as O_2 decreases from 21% in fresh air to 3 – 4% at the boiler's furnace outlet. For many advanced swirl burners, the intense recirculation of hot combustion products to the primary reaction zone quickly dilutes the oxygen concentration, and the corresponding ignition and burning processes actually occur in a low O_2 atmosphere. This also even occurs in the new developing combustion technologies such as oxygen-enriched combustion and pure oxygen combustion [5]. In coal-fired power plants, various kinds of woody biomass are blended and co-fired in these days to reduce carbon dioxide (CO_2) emissions in the flue gas. However, there are few data about the combustion characteristics of woody biomass fuels, especially the ignition temperature and combustion characteristics in a low oxygen concentration. The previous studies on biomass combustion behavior by use of TGA reviewed as above were mainly focused on air conditions or high oxygen concentration. Hence, a better expertise and understanding about biomass combustion in this condition is required for any biomass in order to better organize the furnace combustion and effectively improve the combustion efficiency. Therefore, the objective of this work is to study the thermal behavior of the coniferous tree (beefwood) and broadleaf tree (beech) that are abundantly available in Vietnam during a low-oxygen combustion condition by use of non-isothermal thermogravimetry via a macro-thermogravimetric (MTG) system.

2. MATERIAL AND METHOD

2.1 Material preparation

Beefwood and beech, widely planted in the North of Vietnam were selected for this study. The samples were crushed and sieved to collect the particles size of 0.5 – 1.0 mm. This size has been proved to be suitable for co-firing processes in previous studies [9]. The proximate analysis of two materials has been determined in a dry basis, according to the following ASTM standards for woody biomass:

- Volatile matter (VM): E-872,
- Ash content (A): D-1102,
- Fixed carbon (FC): determined by difference,
- Bulk density: E873 – 82.

In addition, higher heating values (HHV) have been determined using the device Parr 6200 Calorimeter. Results are shown in Table 1.

Table 1. Properties of beefwood and beech

Sample	FC (%)	VM (%)	A (%)	HHV (MJ/kg)	Bulk density (kg/m^3)
Beefwood	16.8	82.7	0.5	16.6	230
Beech	17.9	80.8	1.3	16.4	165

In regard to the oxidation of char, char samples have been produced through pyrolyzing raw materials in a muffle furnace Nabertherm. Biomass feedstocks were put into a crucible and placed under an inert atmosphere during seven minutes at 900ºC to release all the volatile matter. Maximum two grams were used for each time to ensure uniformity of the char produced. The latter was then completely cooled down to room temperature, also under N_2 atmosphere, before taking out and being used for the char oxidation experiments.

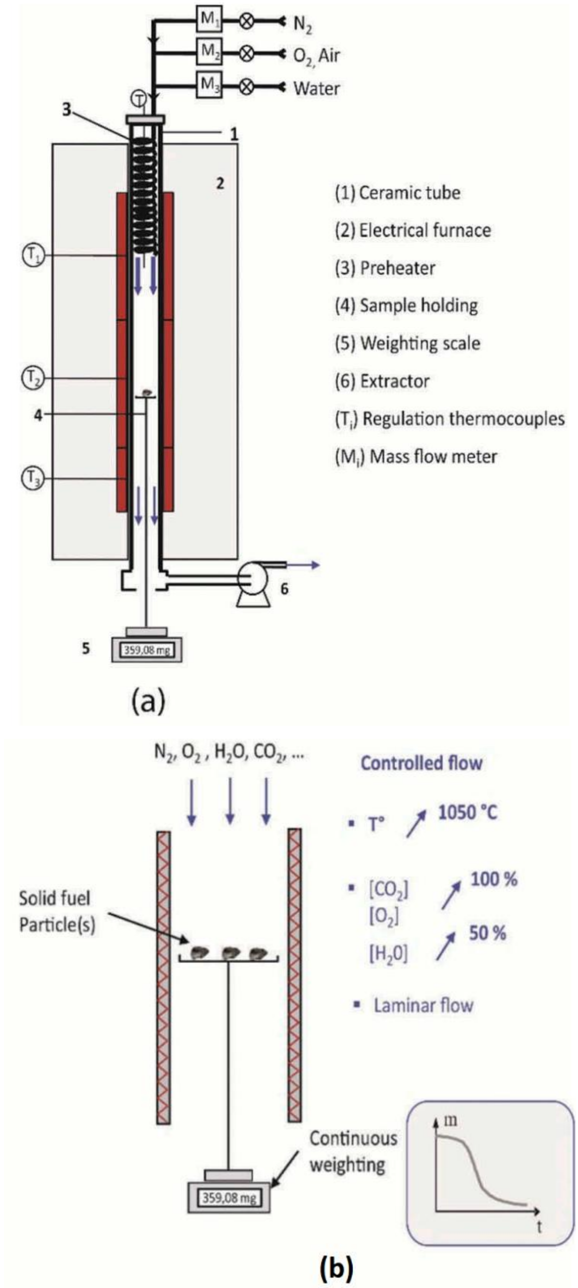


Fig.1. (a) MTG system and (b) its principle [10,11].

2.2 Apparatus and methods

A macro-thermogravimetric (MTG) system, which measures and records mass and temperature changes along the time, was used to determine the pyrolysis and combustion characteristics (Figure 1). The detail of this system has been described in our previous study [6]. In brief, the system consists of a reactor (1), an electrical furnace (2), three thermocouples (Ti) and a microbalance (5). In addition, the system is connected to mass flowmeters (Mi) in the range of 0 – 10 NL/min to control the gas flows (N_2 and O_2) into the reactor, and an extractor (6) to extract the gaseous products out of the reactor. The gas flows were firstly mixed (in the case of mixture) and preheated in a 2-meter-long coiled tube (3) located in the upper part of the reactor before entering the reactor and react with the sample placed on the top of the sample holder (4). The reliability of this system has been proven by a series of previous tests [10, 11].

Three series of experiments were performed independently: pyrolysis, char oxidation and overall combustion. The samples were tested under 100% N_2 for pyrolysis process, and 3% O_2 (in N_2) for char oxidation and overall combustion using a non-isothermal thermogravimetric method, from room temperature to 900 ºC. Instead of using char samples, pyrolysis and overall combustion experiments were carried out with raw biomass. The total gas flow and the heating rate were set to 5 NL/min and 5ºC/min, respectively for all experiments. About 400 ± 10 mg of biomass was used for each test. These conditions have been verified to ensure that the experimental setup is independent of the stoichiometry, as well as the external heat - mass transfer occurred during experiments.

TGA and differential thermogravimetric analysis (DTG) profiles obtained during experiments were used to investigate the thermochemical conversion behavior of the fuel samples. TGA shows a continuous reduction in total weight with increasing temperature, while DTG derived from TGA data gives the rate of reaction with respect to temperature. From the TG-DTG curves, a number of combustion characteristic parameters can be derived, such as fuel starting burning/devolatilization temperature T_{ig}, maximum reaction/combustion rate temperature which corresponds to DTG peak T_{max}, maximum combustion rate at DTG peak R_{max}, and char burnout temperature of the fuel samples T_{bo}, as is illustrated in Figure 2 [6].

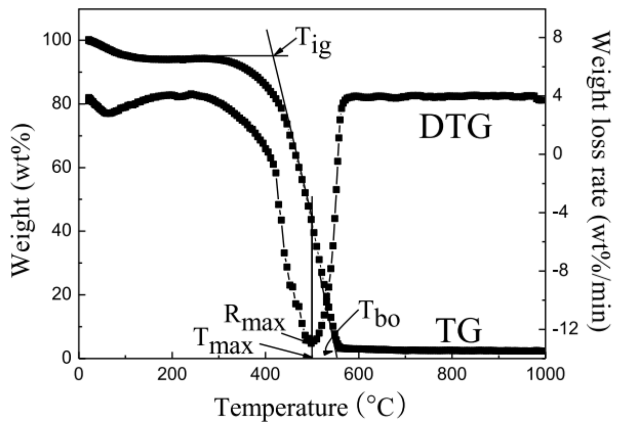


Fig. 2. An example of TG-DTG curves of coal combustion [6].

The thermal behavior has been characterized by calculating the percent weight loss (dry basis), ΔW, for each thermal process (pyrolysis, char oxidation and overall combustion). The weight loss, ΔW, was calculated as following equation:

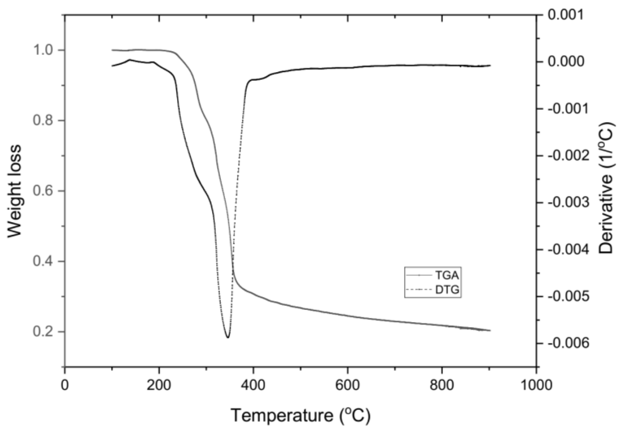
$$\Delta W = 1 - \frac{m_{100} - m_i}{m_{100}} \quad (1)$$

where m_{100} and m_i are respectively the weight of feedstock sample after drying at 100 ºC and the weight of sample at time t.

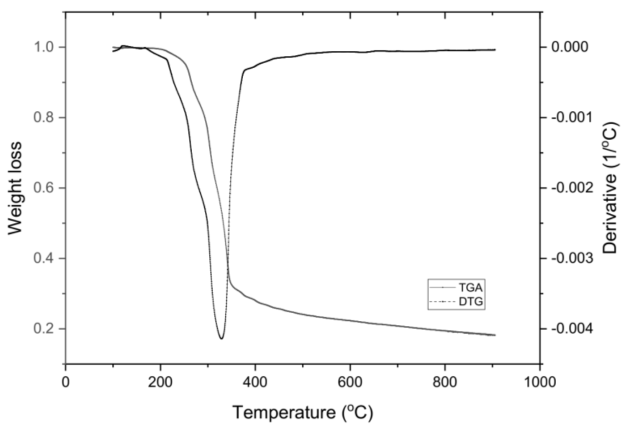
All the obtained results presented below are an average of at least two repeatable tests within an error range of less than 10% in measurements, which is totally acceptable in the case of biomass experiments.

3. RESULTS AND DISCUSSION

Thermogravimetric analysis of samples was recorded by plotting TG and DTG curves in the temperature range of 100-900 ºC at the heating rate of 5 ºC/min (Fig. 3–5).



b) Beefwood



b) Beech

Fig.3. TGA and DTG plots of pyrolysis.

3.1 Pyrolysis process of beefwood and beech

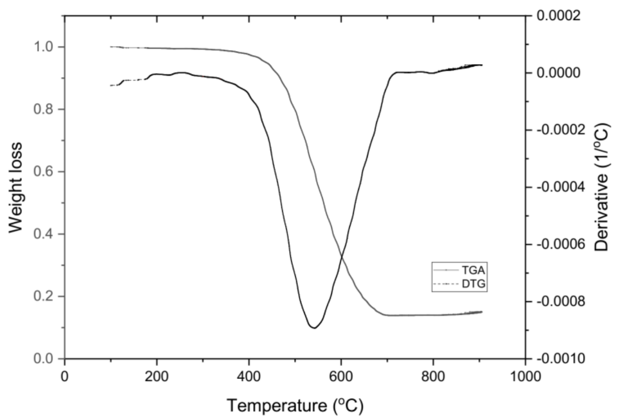
Fig. 3 shows TG-DTG curves of the two biomass samples as a function of temperature in an inert atmosphere. These curves show notably similar changes for both samples. The major mass loss was recorded in the temperature range of 300-400 ºC represented by the peaks in the DTG curves, which is the result of thermal decomposition and loss of volatile gases. The DTG curve for beefwood pyrolysis has a peak with higher temperature (T_{max} = 345 ºC) and maximum rate of weight loss (R_{max} = 5.8 x 10^{-3} %/ºC) compared to those of beech (T_{max} = 330 ºC, R_{max} = 4.2 x 10^{-3} %/ºC). Additional, it can be seen from the TG curves that, the beefwood has higher T_{ig} of 265 ºC compared with the beech (T_{ig} = 255 ºC). This means the initial mass loss of beefwood occurred slower resulting in a harder ignition and later start of combustion reaction than that of beech.

3.2 Char oxidation process of beefwood and beech

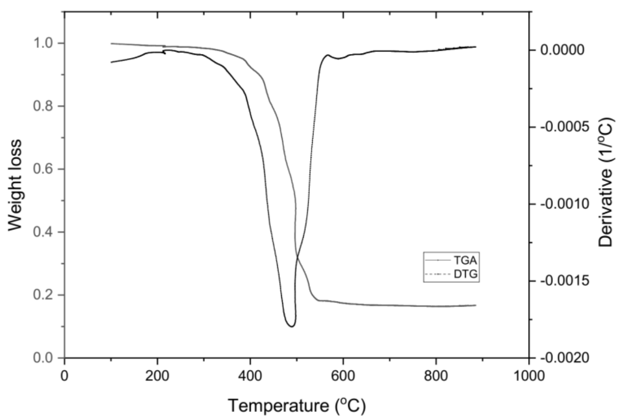
Fig. 4 presents the TG-DTG curves of char oxidation process of beefwood and beech in a low O_2 concentration (3%) in N_2. The DTG curve for char of beefwood has a peak with higher temperature (T_{max} = 540 ºC) and lower maximum mass loss rate (R_{max} = 0,9 x 10^{-3} %/ºC) compared with beech char, which has a sharp peak with lower temperature of maximum mass loss rate (T_{max} = 495 ºC) and higher maximum loss rate (R_{max} = 1.75 x 10^{-3} %/ºC). In addition, TG curves show that the temperatures of ignition and burn-out of beefwood char was recorded at higher temperature (T_{ig} = 490 ºC, T_{bo} = 630 ºC) than that of beech char (T_{ig} = 430 ºC, T_{bo} = 600 ºC). The lower they are, the higher the combustion reactivity is. This can improve the combustion reaction effectively.

3.3 Overall combustion process of beefwood and beech

Fig. 5 illustrates the TG-DTG curves of overall combustion process of the two raw materials of beefwood and beech in 3% O_2 (in N_2). The total mass loss at 900 ºC for both samples are higher than two separate processes due to combination of devolatilization and char oxidation. Two stages were obviously shown in the DTG curves for both samples. In the first stage, the main mass loss occurs within the temperature range of 250-350 ºC for both samples with a well-defined peaks corresponding to the devolatilization and volatile oxidation. This stage occurs similarly to that seen in N_2. However, the maximum mass losses were observed at lower temperatures. This is likely due to the partial combustion of volatiles generated during the process. The second stage associated with char combustion happened between 350 ºC and 550 ºC. Passing through a maximum combustion rate, at last the char was burned out at the end of the combustion process [6]. There is a significant reduction in the T_{max}, and T_b compared to in the case of the only char oxidation. This could be explained by the oxidation of volatiles released in the devolatization process, resulted in an increase of particle temperature and an acceleration of the char oxidation at lower temperature [6,8]. There was nearly no change of mass yield in the temperature range of 550-900 °C for both samples.

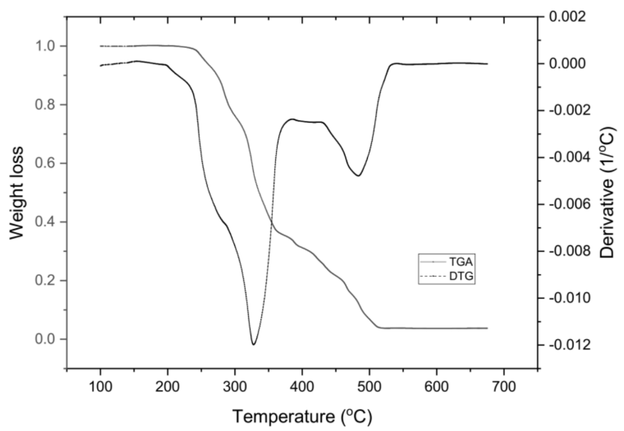


a) Beefwood

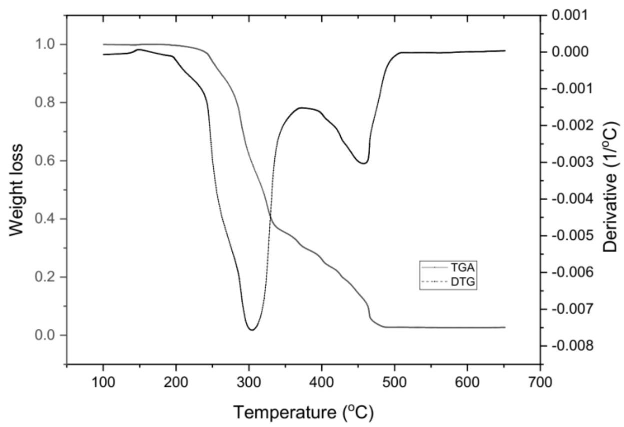


b) Beech

Fig. 4. TGA and DTG plots of char combustion.



a) Beefwood



b) Beech

Fig.5. TGA and DTG plots of raw biomass combustion.

The pyrolysis/combustion characteristics determined from these curves for fuel samples are summarized in Table 2.

Table 2. Parameter characteristics of beefwood and beech

	Parameter	Pyrolysis	Char oxidation	Overall combustion	
Beefwood	T_{ig} (°C)	265	490	270	
	T_{max} (°C)	345	540	330	480
	R_{max} (%/°C)	5.8e-3	9e-4	1.2e-2	5e-3
	T_{bo} (°C)	-	630	510	
Beech	T_{ig} (°C)	255	430	250	
	T_{max} (°C)	330	495	305	460
	R_{max} (%/°C)	4.2e-3	1.75e-3	7.5e-3	3e-3
	T_{bo} (°C)	-	600	480	

4. CONCLUSION

Pyrolysis, char oxidation and overall combustion processes of beefwood and beech and their char products were conducted separately using a Macro-TG. The beefwood has the initial mass loss and the maximum mass loss at higher temperatures compared to that of beech in all experiments. In the terms of overall combustion process, the T_{max}, T_{bo} values recorded were sharply lower than in the case of pyrolysis and char oxidation that were carried out independently. This clearly showed the synergistic effects of pyrolysis and char oxidation in the whole process. Further research is recommended to find out the common combustion characteristics of the coniferous trees and broadleaf trees. Results of this study could contribute to the understanding of the combustion profiles of these kinds of biomass in a low oxygen atmosphere, in order to better organize the furnace combustion and effectively improve the efficiency of coal/biomass combustion.

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