Article

Thermal behavior of woody residues in a reduced-oxygen atmosphere using Macro-thermogravimetric technique

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Abstract

In the context of sustainable development, co-gasification or co-firing of biomass residues and coal is becoming a relevant solution to mitigate the negative impact of fossil fuels. For this reason, it is crucial to understand the characteristics, as well as the thermal behaviors of these residues, especially in a low-oxygen condition that is often found in industrial processes. In this study, woody residues, namely bamboo and rubberwood chips that are abundantly available in Vietnam were characterized. Thermal degradation of these residues in 4 % oxygen was also conducted using a Macro-thermogravimetric analyzer, from room temperature to 700 °C. The results showed that bamboo had a higher volatile matter and a higher hemicellulose content compared to rubberwood chips, hence is easier for ignition in a thermochemical conversion process. Regarding the thermal behaviors of these residues in a reduced-oxygen condition, three stages could be clearly observed in the TGA-DTG curves. Rubberwood chip had a higher ignition temperature and higher temperatures of maximum mass loss rate compared to bamboo chip. Results could contribute to the understanding of the thermal behaviors of these biomass feedstocks in order to improve the efficiency of co-gasification or co-firing processes.

Keywords. Low-oxygen combustion, thermogravimetric analysis, Macro-TGA, woody residues.

1. INTRODUCTION

Biomass is an important source of raw materials for energy production, contributing to minimizing environmental impacts from fossil fuels.^[1-3] Woody residues are abundantly available in many countries, and research activities are being promoted to take advantages of this resource.^[4-6] Amongst available technologies, co-firing or co-gasification of coal with biomass residues is a friendly and promising approach for mitigating the negative effects of coalburning.^[7–9] The blending of fuels in these processes was proven to have important advantages. The ignition temperature could be improved when coal is blended with biomass.^[9] The synergistic effects when blending two solid fuels were also observed.^[10] Air pollution from the system is also mitigated.^[7] Despite these advantages, several issues in current technologies still exist, such as low thermal efficiency, heat load instability, slagging.^[11]

To overcome these barriers, two important problems should be addressed. The first problem comes from the properties of forest residues. The wide variation in compositions and particle sizes of forest residues compared to coal creates a big challenge for the utilization of these fuels in cofiring.^[12-14] Woody biomass often has high volatile matter and low fixed carbon content, in contrary with coal. In addition, the properties of biomass residues depend not only on their intrinsic nature but also on the upstream processing technologies, as well as storage conditions.^[13,15] Indeed, the co-firing or cogasification of different woody biomass gives different results in terms of efficiency and product quality. The second problem comes from the lack in understandings of thermal behaviors of woody residues in a low oxygen (O₂) atmosphere. Thermal degradation of solid fuels in a low O₂ atmosphere exists widely in industrial processes. In combustion, O₂ decreases from 21 % in fresh air to 3-4 % at the boiler's furnace outlet due to the fact that intense recirculation of hot combustion products to the primary reaction zone quickly dilutes the oxygen concentration. In gasification using air/O2 as the reactive gas, a small amount of O₂ was also present in the process. Therefore, the corresponding ignition and conversion processes actually occur in a low O_2 atmosphere. This also occurs in the new developing conversion technologies such as oxygen-enriched combustion and pure oxygen combustion.^[16]

The previous studies on thermal behaviors of woody biomass were mainly focused on high O₂ concentrations.^[16-18] Up to date, only a few studies have focused on the thermal behaviors of woody biomass in a low O₂ atmosphere.^[16,19,20] therefore the information has still been small and fragmented. Moreover, the existing studies generally involved the preparation of a few milligrams of powdered biomass, in which heat and mass transfer limitations were ignored. For co-firing applications at industrial scales, large amounts 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. Thus, a deep knowledge of the thermal behavior of biomass in their original form in a reduced-oxygen is critical to assess the feasibility, design, and scaling of industrial biomass conversion applications.

Therefore, this study aims to (1) characterize woody residues that are abundantly available in Vietnam, namely bamboo chip and rubberwood chip, and (2) study the thermal behavior of during a lowoxygen condition using a Macro-thermogravimetric (MTG) system to take into account the effect of heat and mass transfer within the biomass particle.

2. MATERIALS AND METHODS

2.1. Feedstock collection and preparation

Two types of residues, namely bamboo chip and rubberwood chip were collected in processing factories in different regions of Vietnam. The moisture content of these feedstocks was firstly determined following the ASTM E1756–08 standard. Biomass feedstocks were then cleaned with distilled water to remove dust and impurities, and dried in a oven (Memmert Model 800 Class B) at 105 °C for 24 hours to remove their moisture content. Bulk density was determined following the ASTM E873–82 standard. The biomass samples were then stored in air-tight boxes at room temperature for further analyses.

2.2. Feedstock characterization

Proximate (volatile matter, fixed carbon and ash contents), ultimate (Carbon (C), Hydrogen (H),

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Nitrogen (N), Sulfur (S) and Oxygen (O) contents) and biochemical analyses (cellulose, hemicellulose, and lignin contents), and calorific values were conducted to characterize biomass feedstocks. The volatile matter of biomass samples was determined the ASTM D 3175-07 standard. The ash content was determined following the ASTM D 3174-04 standard. The fixed carbon content was calculated by difference. The higher heating value of biomass feedstocks was evaluated using the Parr 6200 Calorimeter, following the procedure described in the NREL protocol. The Carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O) contents of biomass samples were determined using the PerkinElmer 2400 Series II Elemental Analyzer. The cellulose, hemicellulose and lignin contents were determined following the Forage Fiber Analysis method.^[21]

2.3. Experimental setup

A new macro-thermogravimetric reactor (Macro-TGA) was designed and set up to experiment char gasification kinetics (Fig. 1). The reactor consisted of a ceramic tube, 111 cm in length, with an internal diameter of 7.5 cm (1), placed in an electrical furnace (2). Heating was ensured by three independently controlled heating zones, ensuring the temperature was uniform throughout the reactor. The reaction atmosphere was generated by a mixture of N₂ and O₂. Each gas was controlled by mass flowmeters. The gas mixture was preheated in a 2-m long coiled tube (3) located in the upper heated part of the reactor. The reliability of this system was proven by a series of previous tests.^[22,23]

The samples were tested under 4 % O₂ (in N₂) for using a non-isothermal thermogravimetric method, from room temperature to 700 °C. The total gas flow and heating rate were set to 5 Nlmin⁻¹ and 5 °Cmin⁻¹, respectively for all experiments. About 2 g \pm 0.1 g of biomass was used for each test.

Thermal gravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) profiles obtained during experiments were used to investigate the thermochemical behavior of these residues. From the TGA-DTG curves, a number of combustion characteristic parameters can be derived, such as ignition temperature T_{ig} , maximum reaction 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 illustrated in Fig. 2. All the obtained results presented below are an average of at least two repeatable tests within an error range of less than 5 %

in measurements, which is totally acceptable in the case of biomass experiments.



Figure 1: The Macro-TGA system



Figure 2: A typical TGA and DTG curves provided by thermal analysis

3. RESULTS AND DISCUSSION

3.1. Characteristics of woody residues

The moisture content in biomass varies depending on

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the type, growing conditions, and harvesting time. Regarding agricultural and forest residues, moisture content also greatly depends on upstream processing steps, as well as storage conditions. The moisture content of these biomass samples was high, from 16.19 to 19.11 % (table 1).

Table 1:	Proximate	analysis	results
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Biomass	M (%wt)	BD (kg/m ³)	Pr a (% V	oxima nalys 6 wt, 0 A	ate is db) FC	HHV (MJ/kg, db)
Bamboo	19.11	280.5	80.61	2.71	16.68	15.47
Rubber	16.19	460.8	71.21	1.91	26.88	16.77

The high moisture content of the feedstock strongly affects thermal conversion processes. It reduces the temperature in the system, resulting in the incomplete conversion of biomass feedstock and/or other operational problems. Moisture above 10 % is usually not preferred in the thermochemical conversion process.^[24–26] Therefore, these wood chips are highly recommended to be dried before using feedstocks for any energy conversion process.

Bamboo had a lower bulk density, haft than that of rubberwood (table 1). The low bulk density not only causes difficulties in storage, transportation or loading of the feedstock to the system. This also causes difficulties during the energy conversion processes. Therefore, pretreatment techniques such as pelletization or densification of bamboo are recommended.

Volatile matter of bamboo (80.61 %) was higher than rubberwood (72.21 %). High volatile matter in biomass could be an advantage for thermal chemical conversion processes: during the decomposition, it is evolved as gas instantaneously, leaving behind only a small amount of char, chemical energy is stored mainly in the form of fixed carbon and volatile matter, which can be released via direct or indirect combustion. The ash content of these biomass samples was not significant, indicating that they are particularly well suited for thermochemical conversion processes.

The higher heating value of biomass samples ranged from 15.47 to 16.77 MJ/kg, comparable to half of the coal generally.^[27] This heating value of woody residues could be an input in the calculation of heat balance and simulations, therefore help determine the capacity and dimensions of the energy conversion systems.

Regarding the ultimate analysis results (table 2), the different biomass samples possessed slightly different contents of C, H, and O. A small amount of N and S were trapped into biomass during the growth. These contents in all biomass feedstocks were very low, less than 0.17 %, therefore the potential for NO_x and SO_x emissions from biomass feedstocks is also negligible.

Table 2: Ultimate analysis results

Biomass	Ultimate analysis (% wt, daf)			Atomic ratios			
	С	Η	0	N	S	H/C	O/C
Bamboo	51.11	6.22	42.52	2 0.09	0.06	1.46	0.62
Rubberwood	51.44	6.32	41.99	0.17	0.08	1.47	0.61
Table 3: Biochemical analysis results							
Biomass	Hemio (% rec	celluo wt, a ceiveo	olose as 1)	Celllu (% wt receiv	iose t, as ved)	Lig (% w recei	nin t, as ved)
Bamboo	1	8.11		47.	01	18.	.12
Rubberwood	1	2.12		49.:	53	21.	.17

The contents of cellulose and lignin in biomass (table 3) strongly affect the yields of thermochemical conversion products. The biochemical constituents of biomass have different levels of thermal stability, hemicellulose reacts first at 370 °C, followed by cellulose at 405 °C then lignin at 410 °C.^[28] Therefore, bamboo with higher hemicellulose contents is also easier for ignition, with more smoky flame released.

3.2. Thermal behaviors of woody residues

The TGA-DTG curves presenting the thermal behaviors of bamboo chip and rubberwood chip in 4 % O₂ (in N₂) were given in Fig. 3.

The thermal degradation of bamboo chip and rubberwood in their original form can be divided into three distinct phases: drying, char formation, and char combustion.

The peak in phase I (< 200 °C) corresponded to the remaining moisture released from biomass feedstocks. The decomposition of biomass at phase I was not significant.

Phase II is considered as the active pyrolytic zone. Thermal degradation of hemicellulose and cellulose gradually occurs between 200 °C and 400 °C. The ignition temperature (T_i) of biomass, which corresponded to the starting point of the devolatilization of volatile matter, was 210 °C for bamboo chip and 225 °C for rubberwood chip. This means the initial weight loss of rubberwood chip

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occurred more slowly, resulting in a harder ignition and a later start of pyrolysis reactions than that of the bamboo chip. Bamboo chip had a peak with the lower temperature $T_{max1} = 305$ °C, corresponding to a maximum weight loss rate of $R_{max1} = 0.61$ % °C⁻¹. Meanwhile, rubberwood chip had a peak with the temperature $T_{max1} = 320$ °C, corresponding to a maximum weight loss rate of $R_{max1} = 0.52$ % °C⁻¹.



Figure 3: TGA-DTG curves of bamboo chip and rubberwood chip in 4 % O₂ (in N₂)

Phase III corresponded to the combustion of chars produced at the pyrolysis process, which happened between 400 and 550 °C. The thermal degradation of chars occurred with a lower weight loss rate compared to the degradation of volatile matter. Bamboo chip had a peak with the lower temperature $(T_{max2} = 450 \text{ °C} \text{ and } R_{max2} = 0.28 \% \text{ °C}^{-1})$ compared to that of rubberwood chip $(T_{max2} = 465 \text{ °C} \text{ and } R_{max2} = 0.29 \% \text{ °C}^{-1})$. The char was finally burned out slowly at the end of the process.

The thermal characteristics determined from these curves for rubberwood chips and bamboo chip are summarized in table 4.

Parameter		Thermal behavior		
	T _{ig} (°C)	210)	
Bamboo	T _{max} (°C)	305	450	
	R_{max} (%/ ^{o}C)	0.61	0.28	
	T_{bo} (°C)	485	;	
Rubberwood	T _{ig} (°C)	225		
	T _{max} (°C)	320	465	
	R _{max} (%/°C)	0.52	0.29	
	T _{bo} (°C)	530)	

Table 4: Thermal degradation characteristics

4. CONCLUSION

The characteristics of woody residues, namely bamboo and rubberwood chips, were characterized in this study. Bamboo chip had a higher volatile matter and a higher hemicellulose content compared to rubberwood chip, hence is easier for ignition in thermochemical conversion processes. Their higher heating value ranged was comparable to half of the coal generally. Moreover, their thermal behaviors in a reduced-oxygen atmosphere were determined using a Macro-TGA system to take into account the effect of heat and mass transfer within the biomass particle. Rubberwood chips had a higher ignition temperature and the maximum mass loss rate at higher temperatures compared to that of bamboo chip. Results of this study could contribute to the understanding of the profiles of these kinds of biomass in a low oxygen atmosphere, in order to improve the efficiency of coal/biomass cogasification or co-firing.

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REFERENCES

- 1. A. O. Abdulrahman, D. Huisingh. The role of biomass as a cleaner energy source in Egypt's energy mix, *J. Clean. Prod.*, **2018**, *172*, 3918-3930.
- X. Chen. Economic potential of biomass supply from crop residues in China. *Appl. Energy*, 2016, 166, 141-149.
- 3. P. T. Mai Thao, K. H. Kurisu, K. Hanaki. Greenhouse gas emission mitigation potential of Rice Husks for An Giang Province, Vietnam, *Biomass Bioenergy*, **2011**, *35*, 3656-3666.

- 4. O. Varela Milla, E. B. Rivera, W. -J. Huang, C. Chien, Y. -M. Wang. Agronomic properties and characterization of rice husk and wood biochars and their effect on the growth of water spinach in a field test, J. Soil Sci. Plant Nutr., **2013**, *13*, 251-266.
- C. S. Goh, M. Junginger, M. Cocchi, D. Marchal, D. Thrän, C. Hennig, J. Heinimö, L. Nikolaisen, P.-P. Schouwenberg, D. Bradley, R. Hess, J. Jacobson, L. Ovard, M. Deutmeyer. Wood pellet market and trade: A global perspective, *Biofuels Bioprod. Biorefining*, 2013, 7, 24-42.
- 6. A. Favero, E. Massetti. Trade of woody biomass for electricity generation under climate mitigation policy. *Resour. Energy Econ.*, **2014**, *36*, 166-190.
- E. Agbor, X. Zhang, A. Kumar. A review of biomass co-firing in North America, *Renew. Sustain. Energy Rev.*, 2014, 40, 930-943.
- D. Mallick, P. Mahanta, V. S. Moholkar. Cogasification of coal/biomass blends in 50 KWe circulating fluidized bed gasifier, *J. Energy Inst.*, 2019, (printing).
- S. K Thengane, A. Gupta, S. M. Mahajani. Cogasification of high ash biomass and high ash coal in downdraft gasifier, *Bioresour. Technol.*, 2019, 273, 159-168.
- Tran H.A., L. V. de Steene, Le D. D. Pyrolysis and char oxidation of biomass and coal blends: Kinetic study Using Thermogravimetric Analysis, *IOP Conf. Ser. Earth Environ. Sci.*, **2018**, *159*, 012035.
- 11. Q. Wang, W. Zhao, H. Liu, C. Jia, H. Xu. Reactivity and kinetic analysis of biomass during combustion, *Energy Procedia*, **2012**, *17*, 869-875.
- 12. A. Skreiberg, Ø. Skreiberg, J. Sandquist, L. Sørum, TGA and macro-TGA characterisation of biomass fuels and fuel mixtures, *Fuel*, **2011**, *90*, 2182-2197.
- M. V. Gil, M. P. González-Vázquez, R. García, F. Rubiera, C. Pevida. Assessing the influence of biomass properties on the gasification process using multivariate data analysis, *Energy Convers. Manag.*, 2019, 184, 649-660.
- 14. G. Teixeira, L. Van de Steene, E. Martin, F. Gelix, S. Salvador. Gasification of char from wood pellets and from wood chips: Textural properties and thermochemical conversion along a continuous fixed bed, *Fuel*, **2012**, *102*, 514-524.
- 15. G. Tao, T. A. Lestander, P. Geladi, S. Xiong. Biomass properties in association with plant species and assortments I: A synthesis based on literature data of energy properties, *Renew. Sustain. Energy Rev.*, **2012**, *16*, 3481-3506.
- 16. Y. Liu, C. Wang, D. Che. Ignition and kinetics analysis of coal combustion in low oxygen concentration, *Energy Sources Part Recovery Util. Environ. Eff.*, **2012**, *34*, 810-819.

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- 17. N. Vhathvarothai, J. Ness, Q. J. Yu. An Investigation of thermal behaviour of biomass and coal during copyrolysis using thermogravimetric analysis, *Int. J. Energy Res.*, **2014**, *38*, 1145-1154.
- M. L. Contreras, F. J. García-Frutos, A. Bahillo. Study of the thermal behaviour of coal/biomass blends during oxy-fuel combustion by thermogravimetric analysis, *J. Therm. Anal. Calorim.*, 2015, *123*, 1643-1655.
- 19. Y. Wei, M. Chen, S. Niu, F. Xue. Experimental investigation on the oxy-fuel co-combustion behavior of Anthracite coal and spent coffee grounds, *J. Therm. Anal. Calorim.*, **2016**, *124*, 1651-1660.
- L. F. de Moura, J. O. Brito, F. G. da Silva Júnior. Effect of thermal treatment on the chemical characteristics of wood from eucalyptus grandis W. Hill Ex Maiden under different atmospheric conditions, *CERNE*, **2012**, *18*, 449-455.
- H. K. Goering. Forage Fiber Analyses: (Apparatus, Reagents, Procedures, and Some Applications); Agricultural Research Service, U.S. Dept. of Agriculture: Washington, D.C, 1970.
- 22. Nguyen H. N., L. V. de Steene, Le D. D. Kinetics of Rice Husk Char Gasification in an H₂O or a CO₂ Atmosphere. *Energy Sources Part Recovery Util.*

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Environ. Eff., 2018, 40, 1701-1713.

- Nguyen H. N., Steene L. V. D., Le T. T. H., Le D. D., Ha-Duong, M. Rice Husk Gasification: From Industry to Laboratory, *IOP Conf. Ser. Earth Environ. Sci.*, 2018, 159, 012033.
- 24. J. S. Tumuluru, J. R. Hess, R. D. Boardman, C. T. Wright, T. L. Westover. Formulation, pretreatment, and densification options to improve biomass specifications for co-firing high percentages with coal, *Ind. Biotechnol.*, **2012**, *8*, 113-132.
- 25. A. Demirbas. Combustion characteristics of different Biomass Fuels. *Prog. Energy Combust. Sci.*, **2004**, *30*, 219-230.
- B. M. Jenkins, L. L. Baxter, T. R. Miles, T.R. Jr., T. R. Miles. Combustion properties of biomass, *Fuel Process. Technol.*, **1998**, *54*, 17-46.
- 27. P. Tan, C. Zhang, J. Xia, Q.-Y. Fang, G. Chen. Estimation of higher heating value of coal based on proximate analysis using support vector regression, *Fuel Process. Technol.*, **2015**, *138*, 298-304.
- W. Cao, J. Li, T. Martí-Rosselló, X. Zhang. Experimental study on the ignition characteristics of cellulose, hemicellulose, lignin and their mixtures, *J. Energy Inst.*, **2019**, *92*(5), 1303-1312.

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