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Non-isothermal pyrolysis characteristics of giant reed (*Arundo donax* L.) using thermogravimetric analysis

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ABSTRACT

A constructed wetland plant waste, *Arundo donax* L. (AD), was pyrolyzed from room temperature to 1000 °C under a dynamic high-purity nitrogen atmosphere at different heating rates. Results show that three stages occur during thermal degradation of AD. Mass loss rates associated with lignocellulose degradation were not affected by heating rates. Physical and chemical characterization of ADs pyrolyzed under different temperatures indicated that simultaneous pyrolysis occurred during the lignocellulose devolatilization process. The non-isothermal method indicated that the pyrolysis reaction should conform to a single-step reaction model with average E (activation energy) of 163 kJ mol^{-1}, calculated by partial least squares linear regression. The most probable mechanism of thermal degradation of AD, determined by the Malek method with the calculated E as the initial value, is described with the random nucleation and later growth (Johnson–Mehl–Avrami (J–M–A) model). It can be written as $f(\alpha) = 0.28(1-\alpha)[-\ln(1-\alpha)]^{-2.57}$. Finally, E = 163.44 ± 3.50 kJ mol^{-1}, the reaction order n = 0.28 ± 0.031, and the decimal logaritm of pre-exponential factor lg(A) = 13.13 ± 0.096 lg(s^{-1}) were estimated.

1. Introduction

CWs (Constructed wetlands) have great potential for use in wastewater treatment in developing countries owing to their simple operation and low implementation costs. However, rapid accumulation of macrophyte in wetlands due to plant litter recycling can lead to lower pollutant removal efficiency [1]. Biomass harvesting can improve this, particularly in the case of lightly loaded systems [2]. Thus, periodic harvesting can be an effective technique for plant management and for the maintenance of water quality [3]. Plant litter has been reported to accumulate in mature wastelands at productivity rates of 500 g $cm^{-2}y^{-1}$ to 2000 g $cm^{-2}y^{-1}$ [4]. Annually, a large amount of harvested wetland plant waste should be properly treated, but most of them are used for agricultural burning in China. The resulting emission of volatile organic compound, carbon monoxide, and carbon dioxide (CO_2) can account for 0.64%–0.94% of the country's total emissions. An alternative to destroying harvested biomass is putting them to beneficial use, especially in the context of a developing country [1]. In recent years, biomass is being increasingly considered as an alternative energy source because of its renewable nature and its ability to fix CO_2 in the atmosphere through photosynthesis. Thus, as an important renewable energy source, wetland plant litter has significant potential in solving the problem of conventional fossil fuel shortage.

Based on data collected between 1990 and 2010, there are more than 70 types of national optional wetland plant species in CW systems in China. Most regions use pollution-resistant aquatic plants, such as *Arundo donax* L. (AD) [5]. AD is a herbaceous fast-growing perennial grass, native to East Asia and widespread throughout the Mediterranean area [6]. AD is a robust grass that

Abbreviations: CW, constructed wetland; AD, Arundo donax; E, activation energy; n, reaction order; A, pre-exponential factor; ξ, Zeta potential; EC, electrical conductivity; SA, surface area; α, conversion rate; β, heating rate; J-M-A model, Johnson-Mehl-Avrami model; AD-RT, *Arundo donax* biomass at room temperature; AD-200, AD-350, AD-500 and AD-800, Arundo donax biomasses prolized at 200, 350, 500, and 800 °C.

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grows 3 m–10 m tall in many-stemmed cane-like clumps. Individual stems or clumps are tough and hollow, partitioned at their nodes much like bamboo stems, and range from 1 cm to 4 cm in diameter [7]. Lately, bioenergy crops have been the focus of research besides plant wastes. Among several tested energetic plants, AD is a "promising energy plant" and chemical feedstock [8]. Table 1 presents a comparison of the activation energies (E) of AD and other biomass sources.

Despite an abundance of literature on pyrolysis kinetics of many biomass species, only a limited number of studies have reported on the pyrolytic behavior of AD. Most studies have explored the farming, cultivation, productivity, and chemical characterization of AD, or its conversion to activated carbon. For instance, production of biomass from fertilized AD, which is harvested in the autumn, can be a suitable method for reducing ash content by about 20%, thus improving the chemical composition of AD [6]. AD can be a precursor for activated carbon prepared by phosphoric acid activation under a temperature range of 400 °C–550 °C [15,17]. However, only a few papers have reported so far on the thermal degradation characteristics of AD. Jeguirim et al. conducted TGA (Thermogravimetric analysis) and investigated emission characteristics of AD and *Miscanthus giganthus* in atmospheric air. They concluded that thermal degradation rate was higher for *M. giganthus*, and gas emissions followed the same order for both crops [16].

TGA was selected for examining the thermal decomposition process. Kinetic data obtained from TGA are very useful for the understanding of thermal degradation processes and mechanisms [17]. A wide range of kinetic schemes have been used, including parallel reactions, nucleation models, and discrete activation energy models, for the pyrolysis of lignocellulosic materials [17–21]. However, only limited information is available on the pyrolysis kinetics of AD. Jeguirim and Trouvé investigated the pyrolytic characteristics of AD by TGA. They identified two main phases in the thermal process, namely, an active phase for the degradation of hemicellulose and cellulose polymers, and a passive phase for the pyrolysis of lignin polymers [8]. The authors found that global pyrolysis of AD can be satisfactorily described by a global independent reaction model for hemicellulose and cellulose over a temperature range of 200 °C–350 °C. Although the study assumed the single pyrolysis of hemicellulose, cellulose, and lignin for AD, lignocelluloses were found to possess a strong crystalline structure in which lignin closely associated with cellulose and hemicelluloses [22] and simultaneous pyrolysis for above several components was exhibited when pyrolyzed [23]. Thus, other kinetic equations, such as nucleation and nucleus growing phase boundary reactions, diffusion, and power law, can be used to accurately describe the pyrolysis process.

Lignocellulose is the main component of AD straws and a potential source of energy. The main objective of this study was to identify the thermo-chemical characteristics of AD biomass. TGA was conducted to investigate the pyrolysis behavior of AD at different heating rates. Moreover, proximate and ultimate analyses of AD biomass were performed. FTIR (Fourier transform infrared spectroscopy) was employed to identify the chemical functional groups present in the pyrolyzed biomass. The final objectives were to obtain the kinetic parameters of decomposition by adopting the Kissinger, the FWO (Flynn-Wall-Ozawa), and the FRL (Friedman-Reich-Levi) methods, to identify the most probable mechanism function, and to determine the degradation mechanism by performing the Malek and the fitted methods.

2. Materials and methods

2.1. Material

The AD straw used in this study was obtained from CWs in Gaofeng, Chongqing, China [24]. The AD straw was cleaned with distilled water to remove dirt and air-dried at room temperature for 2–3 days. The samples were then crushed and sieved to a desired particle size (180 μm–250 μm) using heavy-duty cutting mill (FW-80, Taisite, China). Finally, the samples were dried in a vacuum oven at 80 °C for 24 h and then stored in a tightly closed screw cap bottle. No physical or chemical treatment was undertaken in this study. The lignocellulosic components present in AD, determined by the method described by Ref. [25], are as follows: cellulose 43.17 ± 0.8wt.%$_{db}$, hemicelluloses 28.97 ± 0.2 wt.%$_{db}$, lignin 15.00 ± 0.3 wt.%$_{db}$, and ash 0.27 ± 0.01 wt.%$_{db}$.

2.2. Method

The experimental setup diagram was shown in Fig. S1 (in the Supplementary Data). The pH, ξ (Zeta potential), EC (electrical conductivity), and SA (surface area) of the feedstock and the pyrolyzed biomass were determined, and proximate and ultimate analyses were conducted. Results were obtained from experiments using triplicate samples and the average values of the triplicate pyrolytic runs are reported. The pH of the sample was estimated in a suspension of 1:20 deionized water using a compound glass electrode (PB-10, Sartorius, Germany). The suspension was shaken for 2 h before measurement [26,27]. ξ and EC were subsequently measured using a zetasizer (NANO ZS90, Malvern, UK). The BET (Brunauer–Emmett–Teller) surface areas were measured based on the N_2 adsorption multi-layer theory using an analyzer (ASAP 2010, Micromeritics, USA).

Proximate analysis of the biomass samlpes was carried out according to ASTM D3173 (moisture), ASTM D3174 (ash), and ASTM D3175 (volatile matters) methods. Fixed carbon content was determined by difference. Ultimate sample analysis was conducted using an elemental analyzer (Vario MACRO, Elementar, Germany). The elemental composition of the biomass including C, H, N, S, and O was determined by dry combustion. These data were used to calculate molar ratios of H/C, O/C, (O + N)/C, and (O + N + S)/C.

Possible chemical functional groups present in the feedstock and in the pyrolyzed samples were determined by FTIR spectrometer (Spectrum 2000, Perkin Elmer, USA) over wavelengths of 400 cm^{-1} to 4000 cm^{-1}, and the results are shown in Fig. S2 (in the Supplementary Data). SEM (Scanning electron microscopy) was applied to characterize the shape and the size of the biomass particle, as well as their porous surface structure (VEGA 2 LMU, Tescan, Czech). Supplemental Fig. S3 (in the Supplementary Data) shows

Table 1
Activation energy of various biomass sources.

Biomass	E (KJ mol^{-1})	Reference	Biomass	E (KJ mol^{-1})	Reference
AD	90–140	[8]	Corn stover	57.95	[9]
Wood chip	28.6	[10]	Corn straw	98–148	[11]
Date palm biomass	12.03–25.85	[12]	Rice husk	50–89	[11]
Flax straw	120	[13]	Shea meal	67	[14]