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Torrefaction of some Nigerian lignocellulosic resources and decomposition kinetics

Olumuyiwa A. Lasode[a,*], Ayokunle O. Balogun[b], Armando G. McDonald[b]

[a] Department of Mechanical Engineering, Faculty of Engineering and Technology, University of Ilorin, Ilorin, Nigeria
[b] Department of Forest, Rangeland and Fire Sciences, University of Idaho, Moscow, ID 83844-1132, USA

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ABSTRACT

Torrefaction experiments were carried out on some Nigerian woody (*Albizia pedicellaris* (AP), *Tectona grandis* (TK), *Terminalia ivorensis* (TI)) and non-woody (*Sorghum bicolour* glume (SBG) and stalk (SBS)) biomass resources. The influence of process conditions and consequent change in the elemental configuration of the biomass samples were observed. Biomass type played a dominant role in the solid yield recording 71% for woody and 58% for non-woody samples at 270 °C, while temperature showed the greatest influence with solid yield dropping from an average of 80% (at 240 °C) to 50% (at 300 °C). Both volatile matter and fixed carbon contents experienced significant changes after torrefaction and a decline in O/C ratio from 0.6 to 0.3 was noted. Among the woody biomass, TI experienced the highest increase in higher heating value (HHV) of approximately 38% as compared to AP (32%) and TK (32%), and was subsequently selected for decomposition kinetic study. The decomposition kinetics showed that activation energy ($E(\alpha)$) for the hemicellulose degradation stage ranged between 137 and 197 kJ mol^{-1} for conversion (α) between 0.1 and 0.24 implying that biomass kinetics within this decomposition region is a multi-step reaction. The GC/MS analytical technique revealed that the presence of levoglucosan was highest (7.1%) in woody biomass, while phenolic compounds made up more than one-third of the group of compounds identified.

1. Introduction

The global growing energy consumption, dwindling fossil fuel reserves and increasing environmental concerns relating to the use of petroleum products have inevitably led to an apparent quest for alternative and renewable energy sources. The notable ones include geothermal, wind, solar, biomass and wave energy; however, biomass has assumed a pivotal role because it is the only one that is reported to be carbon neutral and possess infinite sustainability potentials [1]. The wide variety and abundant availability of biomass wastes generated in the processing of raw biomass resources on the one hand, and the concomitant disposal challenges on the other hand, are among the factors that have continued to motivate keen interest in the utilization of lignocellulosic biomass as renewable energy resource.

Torrefaction, a thermochemical conversion process, has gained global attention as a viable pretreatment technology for biomass feedstock in gasification and co-combustion processes [2,3]. The production of high quality char for domestic heating and cooking through the technology of torrefaction has become a subject of scientific research and development [4,5]. Torrefied biomass resource could also be of practical importance in the metallurgical industry [6]. Though similar to pyrolytic conversion process in that it is conducted in an inert atmosphere or in the presence of limited air, other process conditions such as residence time, operating temperature and heating rates differ significantly. Torrefaction experiments are conducted at low heating rates (<100 °C min^{-1}), between 220 and 300 °C and approximately 1 hr residence time resulting in the production of a homogenous carbon-rich char [1]. The characteristic properties of torrefied biomass are substantially influenced by biomass type, particle size and mostly temperature [3,7].

Raw biomass is hydrophilic, heterogeneous in structure, and possesses high moisture content leading to poor combustion characteristics. Furthermore, the high O content of raw biomass has been implicated in smoke emission during combustion [1]. It has been observed that prolonged exposure to smoke emissions from the use of raw woody biomass; as is the case in most rural areas in developing countries, raises some health concerns that manifest in eye-related and respiratory complications [8,9]. Unfortunately, the harvest of woody biomass resources for fuelwood is still common-

* Corresponding author. Tel.: +234 8066778409; fax: +234 8055647409.
E-mail address: oalasode@yahoo.com (O.A. Lasode).

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place in Nigeria in spite of the various land degradation scenarios it also poses. Apparently, biomass residues have been reported to be enormously available in Nigeria. An estimate of 7 million m^3 of forestry wastes is generated annually from logging and sizing operations, while an FAO 2010 data estimated a total of 11.37 million tons of waste from sorghum cultivation [10,11]. Therefore, upgrading of biomass residues through torrefaction has an immense prospect in Nigeria as it could help curb the infamous act of tree felling and also transform the widespread biomass wastes generated to valuable biofuel products.

In the process of torrefaction, moisture and low molar mass organic compounds that are responsible for energy loss due to their endothermic behavior are liberated [12,13]. The hemicellulose fraction is decomposed alongside yielding a hydrophobic and a relatively homogenous product [1,3]. In addition, a change in the elemental configuration is engendered; leading to a reduction in both the O and H components and a significant increase in the C content [14]. Thus, the thermal and structural properties of biomass are enhanced making them suitable for applications such as domestic cooking, residential heating and co-firing options.

One of the product yields after torrefaction is the condensed liquid (bio-oil) from which various chemicals and fuels can be extracted [15]. The chemical composition of the bio-oil is of prime importance because information concerning what refinement process or upgrading technique might be needed can be gathered. Apparently, the composition of bio-oil from pyrolytic conversion of biomass has been investigated extensively [16–18]. Since temperature affects the formation and concentration of the chemical species in the liquid portion produced during thermochemical conversion processes, it becomes imperative to investigate the makeup of the bio-oil from torrefaction experiments. Given that not much effort has been seen in this direction, one of the objectives of this study therefore is to subject the condensed liquid from torrefaction process to GC/MS instrumental analysis.

The thermal decomposition of biomass involves a very complex chemical reaction that often defies a one-step kinetic scheme. It has been noted that multi-step mechanisms provide more accurate descriptions of the reaction processes that follow successive and parallel routes [7,19]. These are frequently encountered in the thermal treatment of biomass. Isoconversional methods also referred to as model-free techniques, have been improved upon to handle multi-step reactions. These evaluate kinetic parameters as a function of degree of conversion (α). They are implemented on the basis of multiple thermogravimetric analysis (TGA) measurements and the elimination of an assumption of any reaction model. Flynn–Wall–Ozawa (FWO) and Starink are two foremost model-free techniques that are commonly used in the calculation of kinetic data [20,21] and these will be used in this study.

The primary objective of this study was to investigate how varied torrefaction process conditions influence the yield distributions on some Nigerian hardwoods and non-woody biomass resources. The consequent chemical changes on the different biomass resources will also be monitored, while thermal decomposition kinetic studies will be performed on the hardwood, *Terminalia ivorensis*.

2. Materials and method

2.1. Materials

2.1.1. Biomass source

Biomass resources categorized into agricultural (non-woody) and forestry (woody) were obtained from a farm site (8°37′ N, 4°46′ E) and a timber processing plant (8°27′ N, 4°35′ E) in the city of Ilorin, Nigeria respectively in December 2012. The non-woody sample was *Sorghum bicolour* (SB, guinea corn), while the woody samples were tropical hardwoods namely: *Albizia pedicellaris* (AP), *Tectona grandis* (TK) and *T. ivorensis* (TI).

2.1.2. Harvesting and handling

The maturity period of the SB plant is six months. After harvesting and threshing, SB panicles and stems were air dried for about one month. The SB glumes (SBG) were handpicked, while the leaves on the SB stems were stripped off and the SB stalk (SBS) cut into a length of 0.305 m. Woodchips from the stem of forestry samples, with age between 40 and 45 years, were also produced and air dried for about one month. These were separately packed in polyethylene bags and transported to the Renewable Materials Laboratory at the University of Idaho.

2.1.3. Sizing, sieving and storage

Biomass resources described in Section 2.1.2 were milled in Thomas Wiley Laboratory Mill Model 4 to pass a 1 mm screen and then sieved into particle sizes ranges <0.25 mm, 0.25–0.5 mm and 0.5–1.0 mm. Thereafter they were all stored in Ziploc bags and kept in a desiccator at room temperature.

2.2. Methods

2.2.1. Proximate and elemental analyses

The method according to the British Standard BS EN 15148:2009 [22] was used for the evaluation of the content of volatile matter (VM). The ash content determination was carried out in a muffle furnace at 580 °C in accordance with the method of ASTM D1102-84 [23], while the moisture content (MC) measurement was performed on a HB 43-S Mettler Toledo moisture analyser. The fixed carbon content (FCC) was calculated by difference. Elemental analysis was conducted using CE 440 elemental analyser to determine C, H and N contents and O was calculated by difference.

2.2.2. Heating value

Higher heating value (HHV) of biomass samples, in triplicate, was determined using a Parr oxygen bomb calorimeter model 1341 according to the ASTM D5865-04 [24]. Biomass sample (1.0 g) was pelletized (6 mm Ø) on a Carver Laboratory hydraulic press to a pressure of 13.8 MPa and dried prior to charging the bomb.

2.2.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (Perkin Elmer TGA-7, Massachusetts, USA) with N_2 purge gas (30 mL min^{-1}) was used for the decomposition tests. Samples (2–5 mg, <0.25 mm) were heated under non-isothermal conditions; temperature was held for 1 min at 323 K and subsequently ramped from 323 to 1173 K at 5, 10 and 20 K min^{-1}. Experiments were done in duplicate and good reproducibility was obtained. duplicate and good reproducibility was obtained.

2.2.4. Gas chromatography–mass spectrometry (GC–MS) analysis

A drop of the condensed liquid (bio-oil) (2–3 mg) released during torrefaction was placed in a 2 mL GC vial and diluted with 1.0 mL of methanol. The mixture was analyzed using a GC–MS_{EI} (FOCUS-ISQ ThermoScientific, San Jose, CA, USA), temperature profile: 50 °C (10 min) at 5 °C min^{-1} to 290 °C; GC capillary column: (ZB-1, 30 m, 0.25 mm Ø, Phenomenex, Torrence, CA, USA). The eluted compounds were identified with authentic standards, NIST 2008 library matching and by their mass spectra [25,26].

2.2.5. Torrefaction

Fig. 1 shows the laboratory scale set-up of the equipment that was used for torrefaction experiments. It consists of a tubular reactor (10 mm Ø × 305 mm, Swagelok cap fittings at both ends),