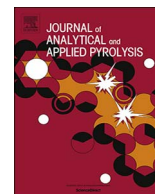




Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Behavior of Stable Carbon and Stable Nitrogen Isotopes during Hydrothermal Carbonization of biomass

M. Toufiq Reza^{a,b}, Simon R. Poulson^c, Silvia Román^{d,*}, Charles J. Coronella^e^a Department of Mechanical Engineering, Ohio University, 1 Ohio University, Athens, OH, 45701, USA^b Institute for Sustainable Energy and the Environment, 350 West State Street, Athens, OH, 45701, USA^c Department of Geological Sciences & Engineering MS-172, University of Nevada, Reno, 1664 North Virginia Street, Reno, NV, 89557, USA^d Department of Applied Physics, University of Extremadura, Avda. Elvas, s/n, 06006, Badajoz, Spain^e Department of Chemical and Materials Engineering, MS 170, University of Nevada Reno, 1664 North Virginia Street, Reno, NV, 89557, USA

ARTICLE INFO

Keywords:

Hydrothermal carbonization
Stable carbon isotope
Stable nitrogen isotope
Hydrochar
Modified van-Krevelen diagram
Elemental analysis

ABSTRACT

This work studied the changes of stable isotope compositions (C and N) of diverse biomass feedstocks (loblolly pine, cow manure, and sewage biosolids) as a result of hydrothermal carbonization (HTC), and provides insight into degradation pathways based on these changes. HTC was conducted at different times (5 and 30 min) and temperatures (180, 220, and 260 °C) and produced hydrochars were characterized in terms of ultimate, proximate, stable carbon isotope ($\delta^{13}\text{C}$), and stable nitrogen isotope ($\delta^{15}\text{N}$) compositions. In addition to reaction conditions, results showed that the differences in feedstock composition, closely related to reactivity, determined in large part isotope behavior. In general, the carbon densification associated with HTC corresponded to a small but consistent decrease of $\delta^{13}\text{C}$ values. In contrast, there were significant increases of $\delta^{15}\text{N}$ values during HTC, with larger shifts associated with increased HTC reaction severity. These trends in isotopic compositions, related to changes of characteristic elemental indices (O/C, H/C, O/N, H/N), allowed for the identification of particular reaction pathways for individual feedstocks.

1. Introduction

The global energy crisis and increased atmospheric carbon dioxide concentration are a result of the imbalance between the rapid consumption of fossil fuels in anthropogenic activities and the very slow formation of fossil fuels. Hydrothermal carbonization (HTC) can provide a purposeful, sustainable, simple, and efficient way for partially counteracting the imbalance of the carbon cycle, by allowing the rapid conversion of waste biomass into fuels and chemicals [1]. HTC is a unique process that takes wet biomass and converts it into a homogenized, friable, hydrophobic, carbon-rich, and stable solid hydrochar (HC) at mild temperature and pressure conditions. As a result of HTC, a solid HC is formed, with higher energy density than the raw feedstock as well as many other promising features such as rich surface functionality [2], incorporation of natural binders that can improve further pelleting [3], and improved mineral composition [4].

Many published works have given evidence about the advantages of HTC as compared to other traditional thermochemical processes and also about the wide range of applications of HCs produced by HTC, e.g., solid biofuel, sorbent, nanostructure carbon material, carbon catalyst, electrode material in energy storage devices, and slow-release fertilizer

[5]. HTC is, therefore, a hot topic of research, and many efforts are being currently devoted to determine the effects of feedstock and process parameters on product distribution between phases and product quality. However, there are still important knowledge gaps, especially in relation to the underlying reaction chemistry. Under HTC conditions, subcritical water has a maximum ionic product, and behaves as a catalyst [6], enhancing the hydrolysis of extractive compounds, hemicellulose, and cellulose, which are degraded into monomers, aldehydes, and intermediates, primarily depending on HTC temperatures [7]. Reactive intermediate species promote other chemical reactions such as decarboxylation, dehydration, aromatization, and condensation-polymerization in a subcritical water medium [7]. As a result of these reactions, many intermediates (re)-polymerize into an amorphous solid and thus enhance the solid-solid reaction. Although the former scheme has been adopted as a general pathway for HTC, there is little information about the detailed reaction mechanisms occurring and how they are affected by processing conditions. Typically, degradation mechanisms are assigned based on elemental analyses of HCs as compared to initial feedstock, and complemented with the use of surface chemistry analyses such as NMR or FTIR analyses [8,9].

Monitoring the stable isotope composition of materials subjected to

* Corresponding author.

E-mail address: sroman@unex.es (S. Román).<https://doi.org/10.1016/j.jaap.2018.02.006>Received 22 October 2017; Received in revised form 5 February 2018; Accepted 5 February 2018
0165-2370/ © 2018 Elsevier B.V. All rights reserved.

thermal treatments has the potential to provide unique information about specific degradation pathways undergone by biomass, which may not be available from ultimate, proximate, and morphological analyses. Many forensic, environmental and geochemical studies have demonstrated that stable carbon isotope ($\delta^{13}\text{C}$) analysis is particularly useful to trace the origin of organic species and to identify underwent reaction mechanisms [10–12]. For example, Gilbert et al. studied the mechanisms involved in the pyrolysis of various hydrocarbons from position-specific $\delta^{13}\text{C}$ composition analyses and reported that the main variations in alkanes occur between terminal and sub-terminal atom positions; from their results, they concluded that heating these compounds produced a trend of $\delta^{13}\text{C}$ -depletion in the terminal atom position [10]. Meanwhile, Saiz et al. studied the disequilibrium between stable carbon isotopes during burning of savanna wood and grass and related their results to the extent of combustion [12]. Similarly, Wurster et al. [13] studied the reactions involved in the pyrolysis of various biomasses by observing the isotope partitioning. After pyrolysis, they isolated the stable polycyclic aromatic carbon (SPAC) from the semilabile carbon component (SLC). They found that SLC was converted to SPAC during cellulose decomposition (at 400–500 °C) through aromatization and condensation, and the remaining residue exhibited a moderate decrease of $\delta^{13}\text{C}$ values. They also followed lignin decomposition, which mainly happened at higher temperatures (800 °C), with low $\delta^{13}\text{C}$ values in methoxyl-rich ($\text{CH}_3\text{-O}$) lignin moieties preferentially remaining in the SLC.

These studies are useful not only to address the emission of pollutants but also to obtain information about the biomass origin, which can be used to provide paleoclimatic insights. As first discussed by Bergius, HTC can be compared to natural coalification in the subsurface [14]. During both processes, biomass is degraded in the presence of water and loss of heteroatoms gives rise to a carbon densification process. In this way, the knowledge of the fate of stable carbon isotopes during HTC can be used to help interpret stable isotope values and even to understand natural coalification processes.

Despite its relevance, the authors have not found any previous studies of the $\delta^{13}\text{C}$ isotopic changes associated with HTC with respect to the nature of the initial feedstock. Furthermore, the existing studies on thermal treatment of biomass (mainly pyrolysis studies) have shown contradictory results regarding the changes (or not) of $\delta^{13}\text{C}$ values. While some authors have reported that $\delta^{13}\text{C}$ values do not change from the original biomass values [11], others have reported a moderate decrease [12,13] or increase [15,16]. The wide variability of results indicates the complexity of the process, since many factors (carbonization temperature and time, aerobic or anaerobic conditions, pH, and initial biomass composition, etc.) can influence the $\delta^{13}\text{C}$ preservation potential [17]. Understanding the stable carbon isotope systematics is important during thermal treatment of biomass, especially when HCs are applied for soil amendment.

The application of HCs as a soil amendment has recently been suggested [18]; in this context, many studies have been devoted to study the fate of nutrients in order to maximize the plant uptake (and closing of nutrient cycles) and to minimize ecological hazards. For example, in the particular case of nitrogen, it is important to accurately know its fate in soils because of the effects associated with the formation of ammonia, nitrate, nitrite, and nitrogen-containing gases. Although conventional non-isotopic analyses have been extensively used, they only account for the difference between the nitrogen content of the fertilized and unfertilized crops. However, nitrogen stable isotope methodology may allow for the determination of the proportions of nitrogen taken up by a plant from a specific soil amendment or fertilizer. Stable nitrogen isotope analysis has been used to determine the variations of nitrogen source, nitrogen fixation, bioaccumulation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), soil nitrogen balance, type of fertilizer, and to distinguish between urine or feces [19–21].

To the best of the authors' knowledge, all research conducted on

HTC has investigated the behavior of N and C in the HC using elemental analysis, or studied the surface functionality of the carbon using techniques such as FTIR, Raman, and NMR [9,18]. This study represents the first effort to study the behavior stable C and N isotopes in HCs and their evolution during various HTC processing conditions. Different biomass precursors (cow manure, digested biosolids, loblolly pine) were subjected to HTC processes under varying conditions of temperature (180–260 °C) and reaction time (5–30 min). In addition to stable isotope analyses, concomitant changes in elemental and thermogravimetric compositions were also quantified and related to stable isotope analyses. The results allow for the inference of the influence of HTC conditions on stable C and N isotope behavior in conjunction with the changes of elemental compositions, and the chemistry associated with these trends is discussed.

2. Materials and Methods

2.1. Materials

Loblolly pine (LP, *Pinus taeda*), cow manure (CM) and digested biosolids (DB) were used as raw materials for HTC experiments. Mature LP was harvested in Marengo County, AL in May 2011. Wood stems were debarked and comminuted into wood chips. The material was dried in a warehouse by free air circulation for four weeks and further chopped into particles < 15 mm by Bliss hammermill model 4460 (Ponca City, OK), and stored in a plastic container in dry storage until further use. To promote a more homogeneous biomass, a commercial household blender was used to reduce the raw biomass size. Samples were sieved to $-1.18\text{ mm} + 0.60\text{ mm}$, air dried, and stored in a sealed ziploc bag until used in the thermochemical treatments. Meanwhile, fresh CM was collected from the University of Nevada, Reno (UNR) Main Station Farm (Reno, NV), with the freshest manure pile in the steer pen being selected in the morning of collection. During collection, care was taken to prevent bedding from being collected with the manure. The manure sample was frozen immediately to minimize biological activities. The dried manure was sieved and the 0.2–0.8 mm fraction was separated and stored in a ziploc bag prior to thermal treatments.

DB was collected from a local water treatment plant (Truckee Meadows Water Reclamation Facilities) in Reno, NV. Samples were taken after centrifuging the outlet of anaerobic digesters, and had a moisture content of 86%. The sample was oven dried at 105 °C for 5 h to minimize biological activity. The dried digested biosolids was stored in a ziploc bag prior to HTC treatment.

2.2. Hydrothermal Carbonization (HTC)

In a typical HTC experiment, approximately 8 g of dry feedstock was weighed and transferred into a 100 ml Parr stirred reactor (reactor series 4524, Moline, IL). Approximately 40 ml of de-ionized water was measured (1:5 biomass-to-water-ratio) and poured into the reactor. Experiments at three different temperatures (180, 220, and 260 °C) were performed in this study, with a 5–30 min reaction time. The reaction temperature was controlled by a PID temperature controller (4520 series, Moline, IL, USA) with an accuracy of ± 2 °C. The reactor pressure was not fixed but was monitored during HTC reactions, and corresponded quite closely to the vapor pressure of pure water at the temperature of reaction. At the end of the reaction period, the heater was turned off and the reactor was cooled rapidly in an ice-water bath. It took 5–10 min to cool from 260 °C to 25 °C (about 1 min from 260 °C to 180 °C), during which time the pressure dropped from 4–4.5 MPa to 0.2–0.5 MPa. The gaseous product was vented in a fume hood. Hydrochar was collected by vacuum filtration with a Whatman 3 filter paper for 5 min. Solid hydrochar was dried at 105 °C overnight, and subsequently placed into a zip-lock bag and stored for further analyses. Each individual experiment was performed at least three times.

Download English Version:

<https://daneshyari.com/en/article/7606346>

Download Persian Version:

<https://daneshyari.com/article/7606346>

[Daneshyari.com](https://daneshyari.com)