Journal of Analytical and Applied Pyrolysis 124 (2017) 113–121

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

New insights into microwave pyrolysis of biomass: Preparation of carbon-based products from pecan nutshells and their application in wastewater treatment

G. Duran Jimenez [a], T. Monti [b], J.J. Titman [c], V. Hernandez-Montoya [a], S.W. Kingman [b], E.R. Binner [b,*]

[a] Departamento de Ingeniería Química y Bioquímica, Instituto Tecnológico de Aguascalientes, 20256 Aguascalientes, Mexico
[b] Microwave Process Engineering Research Group, Faculty of Engineering, University Park, University of Nottingham, Nottingham NG7 2RD, UK
[c] School of Chemistry, University Park, University of Nottingham, Nottingham NG7 2RD, UK

ARTICLE INFO

Article history:
Received 30 September 2016
Received in revised form 13 February 2017
Accepted 15 February 2017
Available online 17 February 2017

Keywords:
Biomass
Pecan nutshells
Microwave pyrolysis
Lead removal
Ion exchange
Carbon-based product

ABSTRACT

Microwave pyrolysis of pecan nutshell (*Carya illinoinensis*) biomass was used to produce carbon-based solid products with potential application in contaminated water treatment.

A range of analytical techniques were applied to characterize the intermediate products of microwave pyrolysis in order to monitor the physico-chemical effects of the interacting energy on the biomass.

The performance of the carbon-based products was tested through evaluation of lead ion removal capacity from solution. Further analyses demonstrated that ion-exchange by calcium ions on the material surface was the main mechanism involved in lead removal. Calcium compound development was directly correlated to the interaction of the electromagnetic waves with the biomass.

Through monitoring the physico-chemical effects of biomass–microwave interactions during microwave pyrolysis, we have shown for the first time that the intermediate products differ from those of conventional pyrolysis. We hypothesize that selective heating leads to the (hemi)cellulosic and lignin degradation processes occurring simultaneously, whereas they are largely sequential in conventional pyrolysis.

This work provides optimization parameters essential for the large scale design of microwave processes for this application as well as an understanding of how the operating parameters impact on functionality of the resulting carbon-based materials.

1. Introduction

Microwave treatment for biomass pyrolysis has received significant attention in the last three decades because the microwave heating mechanism has the potential to overcome several of the limitations of conventional heating. With appropriate microwave cavity configuration, energy can be transferred directly into the material, overcoming the heat transfer limitations encountered when conventionally heating low thermal conductivity materials such as biomass and leading to more even heating, shorter processing times and the ability to process larger particles [1]. Previous literature has focused upon correlating microwave parameters such as input power and irradiation time to the physico-chemical features of the final products [2]. There have been several attempts to interpret microwave processing steps in light of the dielectric properties of the biomass under treatment [3–9], the relation of the dielectric properties to the chemical and physical properties of the biomass [10] and the specific effects of the microwave interactions with matter [11,12]. In doing this, comparative analysis of the final products of microwave and conventional heating treatments were carried out [13,14]. Some studies focused on a complete understanding of the microwave process in order to control it and enable industrial scale-up. According to these studies, several hypotheses for explaining the physico-chemical transformations underpinning microwave pyrolysis were formulated and correlated to dielectric properties of the material processed. For example, in [3] and [5] the role of the absorbing phases (–OH groups in coal and water phases in ligneous biomass, respectively) were identified as responsible for the initial heating of the material. Intermediate steps, usually related to the volatilization phase [6], are difficult

* Corresponding author.
E-mail address: eleanor.binner@nottingham.ac.uk (E.R. Binner).

http://dx.doi.org/10.1016/j.jaap.2017.02.013
0165-2370/

to interpret because of the separation of the products (gas, liquid, solid), the rapidity of the transformation and the lack of reliable and specific phase related temperature data. Furthermore, the physico-chemical transformation of the biomass during the microwave treatment leads to carbon-based solid products in which the electron mobility increases because of the formation of an increasingly ordered atomic structure [5]. This must be considered in designing appropriate microwave cavities as it has a dramatic effect on the dielectric properties of the material, which affect the electromagnetic field distribution. Selective and preferential decomposition of cellulose and hemicellulose molecules were also hypothesized to allow microwave pyrolysis at temperatures lower than in the conventional case [11,12]. Until now, these hypotheses have not been confirmed, and this paper addresses this data gap by presenting physico-chemical analysis of the intermediate char products and relating them to the pyrolysis process.

While the gaseous and liquid products of the biomass pyrolysis are mainly employed as biofuels [4], bio char produced during microwave pyrolysis can be used in different areas such as in agriculture [15]. Due to high carbon content and its morphology, bio char can be used as asphalt binder modifier [16]. In separation processes, especially in the form of activated carbon, it can be used to remove chemicals like phenol [17] and dyes [18] and for the removal of heavy metals such as Hg, Cr, Ni [7], Cu, Cd, Zn from wastewater [19]. Furthermore, innovative applications such as super-capacitors, batteries, electrodes and hydrogen storage [20] are also possible.

Although activated carbon can be prepared from a wide range of carbon-based materials (*e.g.* coal and lignite), several biomass residues have been studied in order to obtain valuable products from the treatment: this is useful in recycling waste biomass that, in some cases, represent a potential environmental concern [21]. To this end, a wide range of investigations in which biomasses were used as a precursor for preparing activated carbons by employing microwave heating [22,23] can be found in the literature.

According to the Environmental Protection Agency (EPA), lead is classified as a "priority pollutant" because it is one of the most hazardous substances, with high toxicity and adverse human effects [24]. Cost-effective and selective adsorbents for toxic metals remain in high demand, especially in developing countries where ground water is commonly used for consumption [25].

The aim of the work presented in this paper was to elucidate the intermediate steps of microwave pyrolysis in order to provide optimization data that could be used in the selection and design of microwave processes and also understand how the operating parameters impact upon the functionality of the resulting carbon-based materials. This was carried out through a case study using the conversion of a waste biomass (pecan nutshells) for the treatment of lead-contaminated water. The following objectives were set:

1. Understand and compare the physico-chemical transformations during microwave pyrolysis with conventional pyrolysis.
2. Understand the mechanism of lead adsorption onto microwave-pyrolyzed material.
3. Optimize microwave pyrolysis of pecan nutshells in a 2 kW single mode microwave applicator for the production of carbon-based materials for lead removal from water, using energy requirements and adsorbent performance as optimization parameters.

2. Experimental

In order to meet these objectives, a single-mode microwave applicator was used to prepare activated carbon from pecan nutshell biomass. This technique is based on the high electric field intensity configuration that provides a fast transformation of the biomass sample onto carbon materials without the need for microwave susceptors [4]. The influence of microwave parameters such as input power, absorbed energy and processing time were studied.

The different physico-chemical mechanisms involved in the pyrolytic process were investigated by analysing the products of the treatments by several characterization techniques and correlating them to the measured dielectric properties. ^{13}C NMR and dielectric measurements were employed for understanding the evolution of the polysaccharides in the biomass during the treatment. Results were compared with carbon-based materials prepared via conventional heating.

A hypothetical description of the microwave treatment evolution was formulated and related to the previous literature outcomes. Understanding the evolution of the biomass under microwave processing is necessary in order to control the process, optimize it in terms of input power, treatment time, field intensity and spatial configuration.

In the second part of the paper the microwave bio char was tested for lead removal from contaminated water. The performances of the samples produced with different microwave conditions were related to absorbed energy. X-ray diffraction (XRD) was performed in order to understand the evolution of the inorganic inclusions during treatment, and textural parameters were measured, and these were correlated with lead adsorption performance. Using these methods, the adsorption mechanism mainly responsible for the lead removal by the samples was identified, and a correlation between microwave energy and lead removal was established. This further understanding is a key element for a future optimization of the microwave process for lead removal applications.

2.1. Sample preparation

Pecan nutshells (NS) were collected from an agrifood company in Mexico. The material was washed with deionized water until constant pH then dried at 70 °C for 24 h, and finally milled ground and sieved to obtain a particle size of less than 1 mm.

2.2. Biomass pyrolysis systems

2.2.1. Microwave single mode high-field system

The microwave treatment system was operated at frequency of 2450 ± 25 MHz and included: a Sairem microwave generator with 2 kW maximum output power; two power sensors (Agilent U2001a) connected to the system by a bidirectional coupler (Sairem CMX50WR340) for measuring the input and reflected power; a cylindrical single mode TE010 cavity connected to the generator by a WR430 waveguide, terminated by a sliding short, and a manual 3-stub tuner to improve the impedance or power matching of the system with the generator (Fig. 1). Alumina reactors of 35 mm diameter were used to accommodate the nutshell sample within the cavity, and mullite bricks were used to support the sample. A NS sample of 30 g was weighed and placed in the reactor within the single-mode cavity. The cylindrical chimney was left open on top for accessing the sample inside the applicator and it was terminated by a sub-wavelength choking section. Nitrogen, at a flow rate of 5 L min^{-1}, was used as a sweep gas to aid the removal of volatiles and to maintain an oxygen-free atmosphere within the system. The reflected microwave power was minimized by the manual 3-stub tuner and the sliding short positioning, in order to maximize the power absorbed by the sample. A schematic diagram of the installation is shown in Fig. 1.

For the preparation of the carbon-based samples, a systematic study was carried out by varying input power and time of exposure, in order to understand the influence of these parameters on