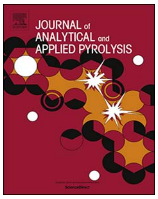
Journal of Analytical and Applied Pyrolysis 126 (2017) 39–49

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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



Potential applications of biochar and terpene-enriched bio-oil produced from a semi-arid native Asteraceae

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ARTICLE INFO

Keywords:
Flourensia oolepis
Pyrolysis
Bio-oil
Terpenes
Biochar
Germination

ABSTRACT

Biomass of *Flourensia oolepis*, a native shrub of the semi-arid central region of Argentina, was treated by vacuum pyrolysis to investigate the potential of this species to be used as a source of energy and chemicals. In this study we determined the influence of temperature on the product yields in different plant organs (leaves and stems), characterized the bio-oil, and assessed the bioactivity of biochar aqueous extracts through germination and growth bioassays with *Lactuca sativa*. The pyrolysis oils showed a predominance of long chain, cyclic and aromatic hydrocarbons in the leaves pyrolysate. The sesquiterpene spathulenol was the major compound in these reactions. Pyrolysis of stems produced mainly phenolic compounds. The effect of phosphoric acid pretreatment on leaves and stems was also evaluated in order to improve bio-oil yield and selectivity to any interesting compound. The results showed that acid treatment enhanced the liquid formation in pyrolysis of leaves giving a high amount of long chain hydrocarbons compared with the untreated organ. The biochar water extracts from leaves exhibited a hormetic type of response, with a promoting growth effect on roots and shoots up to 225%, and only a transient inhibition of germination at higher doses ($\geq 7.5\%$ w/v). Biochar water extracts from stems did not affect seed germination and showed a remarkable promoting effect, stimulating growth at all concentrations tested up to 330%. Although additional testing is required, overall results show *F. oolepis* as a promissory species for the production of bio-oil and biochar with a wide range of applications, including the potential use as growth regulator.

1. Introduction

Bio-fuels and biomass-based energy have the potential to become major contributors to the global primary energy supply in both developed and developing nations [1]. So far, market demands on bio-fuels have been largely met by traditional crop species that are also used for food [2] posing the question as whether this could be in any way sustainable [3–5]. In the last decade, many countries have invested in programs aimed at developing new bioenergy crops, and new or more efficient processing technologies that would allow plant biomass or alternative feedstocks to be converted into bio-fuels, gas, biochar and other valuable sub-products that are used in different industries. However, prospection has rarely been focused on species from arid environments, which host the largest pool of marginal lands that could be used for energy purposes without competing for food crops. In this sense, research aimed at evaluating the potential energy uses of native species from arid and semi-arid areas is mandatory.

The Asteraceae are among the largest families of flowering plants [6] and many species are well known for their use in traditional and western medicine [7]. The genus *Flourensia* (Family Asteraceae; Subfamily Asteroideae; Tribe Heliantheae; Subtribe Enceliinae) comprises 25 species of resinous shrubs distributed throughout America, twelve of them native to Argentina [7,8]. *Flourensia oolepis* (chilca), hereinafter referred to as FO, is an endemic species of the semi-arid central region of Argentina [7,9] and is found growing at high densities in almost pure stands [10]. FO is a long-lived shrub, with a woody perenneting structure (xylopodium) from which it sprouts profusely after fires [11], and traditionally used as fuel in rural areas [12]. Our ecophysiological studies on species of the genus, including FO, show an array of adaptations to xerophytic environments [11], as the production of high

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http://dx.doi.org/10.1016/j.jaap.2017.06.026
Received 31 January 2017; Received in revised form 12 June 2017; Accepted 29 June 2017

levels of compatible solutes [13] and a diversity of secondary compounds produced in glandular hairs and resin ducts [11,14] that serve as defense against biotic stressors (microbes and insects), or play a role in allelopathic interactions [15]. Altogether, the fact that FO naturally exhibits most of the traits recognized as desirable for bioenergy production and sustainable yield in perennial species [2] and the feasibility of obtaining plants derived from seeds [11], makes this species an interesting target for its development as energy crop.

Among the different technologies available for biomass conversion, pyrolysis is receiving worldwide attention [16] as a promising pathway to sustainability, as it allows for the complete utilization of the biomass yielding bio-oil, bio-syngas and biochar. In this process, where organic material undergoes rapid thermal decomposition in the absence of oxygen, the relative contribution of each product is influenced by feedstock properties and operation parameters [17]. The obtained bio-oil can be directly used in diesel engines, turbine and furnace with some modification of equipment [18,19] or as transportation fuel after an upgrading process [20]. The gas and char products can be burnt for heating, reducing the additional production cost for heating the system. In addition, the bio-oil, being a rich mixture of organic compounds, may be the source of some pure chemicals such as anhydrosugars [21] and furans among others [22].

Prior to pyrolysis, pretreatment of lignocellulosic feedstocks has been carried out in order to increase the efficiency of the process and the production of high-valued compounds. Within the chemical methods, the use phosphoric acid has proved to be effective in dissolving the crystalline structure of cellulose [23] facilitating its hydrolysis into fermentable sugars and other bio-based products that could be used as chemical intermediates or platform chemicals.

On the other hand, biochar has been the focus of increased research due to its major potential benefits in relation to carbon sequestration, bioenergy, enhanced soil fertility, and waste management owing to their low cost [24–32]. Biederman and Harpole [33], in a comprehensive meta-analysis on the effects of biochar on multiple ecosystem functions, including plant productivity and nutrient cycling, conclude that biochar indeed may be regarded as a promissory solution to energy, carbon sequestration and ecosystem function; although caution should be taken in considering biochar impacts on yet unexplored, non-target environments [29,33,34]. Negative effects may derive from VOCs and other adsorbed compounds that may be released to the environment [32–35], which may interfere with biological signaling within the rhizosphere [36] affect the soil biota [37] and produce phytotoxic effects [38].

The objectives of the present study were: (i) to determine product yields in the vacuum pyrolysis of leaves and stems (untreated and phosphoric acid-treated) of *Fluorensia oolepis* (FO), (ii) characterize the liquid product obtained under optimum pyrolysis conditions to explore its possible uses as fuel and/or chemical feedstock and (iii) characterize the solid product (biochar) and evaluate its potential to be used as soil amendment through studying the effects of biochar water leachates on germination and growth bioassays in *Lactuca sativa*.

2. Materials and methods

2.1. Plant materials

Plant material was collected in a natural area corresponding to the Punilla Valley, Córdoba province, Argentina, in a typical shrub community (total plant cover 70- 90%), dominated by the evergreen shrub *Flourensia oolepis* S.F. Blake (FO). Aerial shoots from 15 specimens of FO were collected in “Dique El Cajón” Capilla del Monte (S 30°51′43″ W 64°33′39.2″, 900-1000 MASL) in early summer (January) of 2015. Harvested shoots were air dried, separated in two fractions: leaves and stems, and stored at ca. 20 °C. A voucher specimen (BAA 26.498) was deposited at the Herbario “Gaspar Xuárez” of the Facultad de Agronomía, Universidad de Buenos Aires, Argentina.

2.2. Sample preparation and characterization

Elemental analysis for carbon (C), hydrogen (H) and nitrogen (N) was carried out using a Perkin Elmer 2400 Series II analyzer. Carbon, hydrogen and nitrogen content (wt% on dry basis) were analyzed in duplicate and average values taken. Oxygen (O) was calculated by difference.

The higher heating values (HHV) of feedstocks and biochars, expressed in MJ/kg, were calculated using the Eqs. (1) and (2) described by Friedl et al. [39] and an average taken from these two values:

$$\mathrm{HHV}_{(\mathrm{OLSmodel})} = 1.87\mathrm{C}^2 - 144\mathrm{C} - 2820\mathrm{H} + 63.8\mathrm{C} \times \mathrm{H} + 129\mathrm{N} + 20147 \quad (1)$$

$$\mathrm{HHV}_{(\mathrm{PLSmodel})} = 5.22\mathrm{C}^2 - 319\mathrm{C} - 1647\mathrm{H} + 38.6\mathrm{C} \times \mathrm{H} + 133\mathrm{N} + 21028 \quad (2)$$

The lignin, hemicellulose and cellulose content were determined by the Laboratorio de Servicios de Nutrición Animal (Faculty of Agronomy, University of Buenos Aires) using an ANKOM 200 fiber analyzer (ANKOM Technologies, USA), following the original method described by Goering and Van Soest [40] and its modifications (Van Soest et al. [41]) as adapted by ANKOM ® 2005 [42]. Oven dried samples (40 °C for 72 h) ground to 1–3 mm particle size, were used to determine neutral detergent fiber [NDF], acid detergent fiber (ADF), and acid detergent lignin (ADL). NDF accounts for all cell wall constituents (hemicellulose + cellulose + lignin), ADF yields cellulose + lignin, and ADL accounts for lignin content (gravimetrically measured). Thus, the concentrations of cellulose and hemicellulose were calculated as: cellulose = ADF − ADL; hemicellulose = NDF − ADF. NDF and ADF are expressed ash free. Other organic fractions, including non-fiber carbohydrates, organic acids, fats, waxes, resins, essential oils, glycosides, and proteins are not determined by this method.

2.3. Pyrolysis experiments

The vacuum pyrolysis reactions were conducted in a tubular reactor under inert atmosphere. The quartz reactor with a length of 25.00 cm and an inner diameter of 2.50 cm was heated externally by using a tube furnace with a temperature-controller device. The reactor was connected to a high vacuum pump where pressures were in the range of 0.05–0.1 Torr. Crashed leaves and chopped stems samples of FO (1.00 g) were placed in a sliding ceramic boat, which was fed into the pyrolysis furnace when temperature (200–300 °C) and vacuum conditions of the system were reached. The sample was subjected to pyrolysis conditions for 20 min, and due to the vacuum system, contact times of the generated products were very short (< 0.5 s). Oxygen-free dry nitrogen, at a flow rate of 0.1 mL s^{-1}, was used as inert carrier gas to improve the transportation of the volatile products to the condensation region. Liquid products were trapped at liquid air temperature (−196 °C) immediately after they escape the hot zone, while gaseous products were not trapped. The liquid pyrolysate was extracted with acetone and subjected to different analyses. After the experiment was finished, the system was led at atmospheric pressure (in an inert medium) and the condensation trap was removed. In order to recover all bio-oil from this trap, acetone was added at room temperature and the solution was subjected to different analyses. After evaporation of acetone, the liquid phase consisting of oil was weighed. The solid char was removed from the ceramic boat and also weighed, and the gas yield was calculated by difference. All yields are expressed as the average of at least three experiments to confirm the reproducibility of the reported results.

The first set of pyrolysis experiments were performed with FO leaves at 200, 250, 280 and 300 °C. FO stems were only tested at the temperature at which bio-oil yield was maximized (i.e., 280 °C). To compare the effect of acid-treatment of starting material on the bio-oil composition, leaves and stems were impregnated with phosphoric acid