



Chemical characterization and fuel properties of wood and bark of two oaks from Oaxaca, Mexico

Faustino Ruiz-Aquino^{a,c}, Marcos M. González-Peña^{b,*}, Juan I. Valdez-Hernández^c, Ursula S. Revilla^b, Angélica Romero-Manzanares^d

^a Instituto de Estudios Ambientales, Universidad de la Sierra Juárez, Av. Universidad s/n, Ixtlán de Juárez 68725, Oaxaca, Mexico

^b División de Ciencias Forestales, Universidad Autónoma Chapingo, Carretera México-Texcoco km 38.5, Texcoco 56230, Estado de México, Mexico

^c Programa Forestal, Colegio de Postgraduados, Carretera México-Texcoco km 36.5, Texcoco 56230, Estado de México, Mexico

^d Programa de Botánica, Colegio de Postgraduados, Carretera México-Texcoco km 36.5, Texcoco 56230, Estado de México, Mexico

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ABSTRACT

Herein, we describe the chemical composition of sapwood, heartwood and bark of *Quercus laurina* and *Q. crassifolia*, from Ixtlán de Juárez, Oaxaca, Mexico. We also report on the fuel characteristics of wood, bark and charcoal for these species. There was no significant difference in lignin (24.9–25.5%), α -cellulose (47.6–47.9%), and hemicellulose (22.4–23.2%) contents between *Q. crassifolia* and *Q. laurina* wood, while the ash content, hot water solubility, and total extractive content were higher in *Q. crassifolia* wood. The contribution of lignin, α -cellulose, hemicelluloses, suberin, and total extractives in barks, were 25.2–39.6%, 12.2–49.6%, 18.6–23.6%, 1.99–26.6%, and 12.7–31.7%, respectively. Bark had 4–8 times as much ash as the corresponding wood. The wood high heating value (HHV) of both oaks (19.3–19.4 MJ kg⁻¹), was higher compared to other temperate hardwoods; the charcoal HHV varied from 32.0 to 33.3 MJ kg⁻¹. Because of its high polysaccharide (69.7–70.8%) and low extractive (5.29–8.88%) and ash (0.30–0.95%) contents, wood of both species is deemed as suitable for the production of cellulosic pulp, while the content of suberin in the outer bark (20.1–26.6%), suggests its potential as biopolymers source. The fuel properties of wood and charcoal from both species indicate their aptitude as solid fuel.

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1. Introduction

Oaxaca State has the highest oak diversity in Mexico, with 48 species, three of them endemic, which represent about 30% of all oaks in Mexico (Valencia, 2004). In Ixtlán de Juárez, *Quercus laurina* Humb. & Bonpl. and *Q. crassifolia* Humb. & Bonpl. coexist with other 21 species of *Quercus*, and it is the oak's richest region in Oaxaca (Valencia and Nixon, 2004). In Ixtlán de Juárez, oaks are also an abundant resource, with dense stands of 835 trees ha⁻¹ of *Q. laurina* and *Q. crassifolia*, with trees of well-shaped boles with an average height of 14.5 m (Ruiz-Aquino et al., 2014a, 2014b). Local usage of *Q. laurina* and *Q. crassifolia* wood is, however, constrained to the production of firewood and charcoal; for its high density, the timber of these species is also used locally in the manufacture of rustic structural elements (Ruiz-Aquino et al., 2014c).

To visualize new uses of wood for these two oaks, it is required to investigate their chemical constitution, as this is the ordinary starting point to put forward processes for the production of pulp

and paper, biocomposites, and materials with higher added value in the context of a biorefinery (Fengel and Wegener, 1984). The chemical constitution of wood, particularly the amount and type of extractives, is also relevant to the interaction with adhesives, e.g. in the production of veneers, particleboards and laminated beams, or with finishes and coatings in the furniture industry (Pizzi and Salvadó, 2007). The chemical composition of wood also influences its physical properties. For example, a greater amount of cellulose, involves a higher wood basic density, due to the more uniform structure and higher molecular weight of cellulose compared to that of the hemicelluloses (Moya and Arce, 2006); similarly, wood basic density is affected by the extractive content, which indirectly reflects on the mechanical properties of wood.

On the other hand, bark represents 10–35% of the total above-ground biomass of forest species (Young, 1971); unlike wood, bark contains suberin and polyphenols, more extractives, and less polysaccharides (Fengel and Wegener, 1984). The analysis of extractives and monosaccharides in bark, determines its possible use for industrial purposes (Baptista et al., 2013; Feng et al., 2013).

Of the 400 oak species in the world (Aldrich and Cavender-Bares, 2011), we only know the wood chemical composition of 25–30 oak species (Honorato, 2002); our understanding of the oak bark

* Corresponding author. Tel.: +52 17711292864.

E-mail address: m.gonzalez@correo.chapingo.mx (M.M. González-Peña).

chemistry is yet more incomplete. The aim of this study was to determine the chemical composition of sapwood, heartwood and bark of *Q. laurina* and *Q. crassifolia*, in order to propose applications consistent with their chemical makeup. The fuel characteristics of firewood and charcoal from these two species were also investigated.

2. Materials and methods

2.1. Tree selection and specimen preparation

Research material was obtained from three typical, healthy trees per species, in stands dominated by *Quercus* in Ixtlán de Juárez, Oaxaca (17°21'22"N. Lat., 96°27'42"W. Long.), at 2707 MAMSL. The first 2.5 m-long log of each tree was taken, and 2-cm slices were cut at each log end. Each slice was then divided into quadrants, and opposite quadrants were chosen, where sapwood was separated from heartwood. Sapwood of the two slices of each tree was mixed to make a single specimen; the same procedure was followed for heartwood. The material was ground in a Wiley mill 4 (Thomas Scientific, USA), and was then screened between meshes sizes 40 (0.425 mm) and 60 (0.250 mm) in a RX-812 sieve shaker (Tyler, USA). Oak bark was removed from each slice, separated into inner and outer bark, and then ground and sieved as described above. Two-centimeter cubes of sapwood, heartwood and inner bark were cut from the remaining quadrants to determine the density at 50% ± 5% RH at 20 ± 2 °C (normal density, ND).

2.2. Wood chemical characterization

Chemical analyses were performed generally in accordance to ASTM standards for the analysis of wood (ASTM, 2007): extractives in ethanol–toluene (EtOH/Toln, 2:1 v/v) by ASTM D 1107-96; solubility in hot water by ASTM D 1110-84; and total extractives in a Soxhlet with EtOH/Toln (2:1 v/v) for 4 h, followed by EtOH for 6 h, and finally in hot water for 3 h, according to ASTM D 1105-96. Klason Lignin (KL) content was determined in extractive free material following ASTM D 1106-96. Acid soluble lignin (ASL) content was determined according to TAPPI standard UM250 (TAPPI, 1991), by measuring the absorbance of the KL filtrate at 205 nm in a Lambda 25 spectrometer (Perkin Elmer, USA). Holocellulose content was determined by the acidified sodium chlorite method (Fengel and Wegener, 1984), and was corrected by the residual lignin content (KL + ASL). α -Cellulose content was determined by ASTM D 1103-60 (ASTM, 1976); hemicelluloses were determined by difference between holocellulose and α -cellulose. Quantitation of neutral sugars in the KL hydrolysate, as alditol acetates, was performed on a 7890A GC (Agilent, USA) outfitted with a Rtx-225 column (15 m, 0.25 mm i.d., 0.25 μ m film thickness), according to TAPPI standard T249 cm-00 (TAPPI, 1994), but following the miniaturized version of Foster et al. (2010). The GC oven program was: 180 °C for 1 min, 180–220 °C at 40 °C min⁻¹, 220 °C for 3.8 min, and post run at 240 °C for 2 min; the injector and detector were set at 230 °C and 240 °C, respectively. Ash content was obtained with ASTM D 1102-84, the volatile content with ASTM E 872-82 (ASTM, 2006a), and fixed carbon content according to ASTM E 870-82 (ASTM, 2006b). The ash composition was determined by standard procedures.

2.3. Bark chemical characterization

Bark chemical characterization was similar to the one for wood, except for the extractive determinations. For total extractive content, bark was Soxhlet extracted with dichloromethane (CH₂Cl₂, 4 h), followed by EtOH (6 h), and finally in hot water under reflux (3 h) (Pereira, 2013). The solubility in CH₂Cl₂ and EtOH was determined by solvent evaporation, while the final hot water solubility

was determined by weight difference to the unextracted material discounting CH₂Cl₂ and EtOH solubility. The solubility in hot water was obtained according to ASTM D 1110-84, and the solubility in 1% NaOH was obtained from unextracted material following ASTM D 1109-84. Suberin was quantified as the free fatty acids and long-chain alcohol monomers content, and was determined by methanolysis of extractive-free material, following the method of Miranda et al. (2012, 2013). Holocellulose was determined from extractive free material, without correction for residual lignin, while Klason lignin was determined from extracted, desuberinized bark (Pereira, 1988).

2.4. Charcoal manufacture and characterization

Sapwood and heartwood cubes of 0.8 cm per side were placed in porcelain crucibles before being introduced into a modified muffle, and then pyrolyzed in N₂ atmosphere, with the following program at a heating rate of 20 °C min⁻¹: 20 min at 150 °C, 20 min at 250 °C, 30 min at 350 °C, 45 min at 400 °C, and 45 min at 450 °C (Tello et al., 2014). The furnace was allowed to cool down to 105 °C under N₂ before removing the specimens; charcoal specimens were then cooled down over silica gel, and weighed to compute charcoal yield. Charcoal equilibrium moisture content at 50% ± 5% RH at 20 ± 2 °C, and volatile and ash contents were determined according to ASTM D 1762-84; fixed carbon (FC, %) was computed by difference to the original oven-dry charcoal weight with: FC = 100 – (volatiles + ash).

2.5. Fuel characteristics of wood, charcoal and inner bark

The high heating value (HHV, MJ kg⁻¹) was determined in inner bark specimens, and in wood and charcoal specimens of sapwood and heartwood, according to ASTM D 5865-13 (ASTM, 2013), using a 6200 isoperibolic calorimeter (Parr, USA), equipped with a water handling system Parr 6510. Energy density (ED, GJ m⁻³) was obtained with: ED = HHV × ND, where ND (g cm⁻³) is the normal density at 50% ± 5% RH at 20 ± 2 °C. The fuel value index (FVI) was computed with: FVI = (HHV × ND)/(AC × EMC), where AC is the ash content (w/w), and EMC is the equilibrium moisture content (w/w) at 50% ± 5% RH at 20 ± 2 °C.

2.6. Statistical analysis

An analysis of variance for the parameters of the chemical composition and for HHV of wood was run in SPSS package ver. 22.0.0.0. A factorial design was used, where species and type of wood were the factors. When it was determined that a variation factor produced a significant effect on the parameter of interest, means were compared with a Tukey HSD test (α = 0.05).

3. Results and discussion

3.1. Wood chemical characterization

No significant differences were found in the chemical composition of sapwood and heartwood within each species, except for the ash content, which was higher in the heartwood in both oaks (Table 1). The wood chemical makeup was very similar in the two species, especially so regarding wood polymers; we only found higher contents in ash, total extractives and hot water solubility in *Q. crassifolia* wood, in both sapwood and heartwood, compared to the sapwood and heartwood of *Q. laurina* wood (Table 1).

In wood of the two oaks, the solubility in hot water (4.66–8.62%) was very similar to the content of total extractives (5.29–8.88%), which highlights the polar nature of the bulk of the wood extractives in both species, typically phenols and polyphenols; this is consistent with previous characterizations (Bárcenas et al., 2008).

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