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Use of X-ray diffraction to obtain the mean microfibrillar angles of three species of the cerrado biome

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ABSTRACT

From the year 2000, several studies were initiated to evaluate the microfibrillar angle, in view of its importance to explain other wood properties. This study aims to estimate the angle of the microfibrils of the woods Tachigali vulgaris, Myracrodruon urundeuva and Amburana cearensis, using the X-ray diffraction (XRD) technique. Microfibrillar angle evaluation is essential to understand the mechanical and performance properties of woods in different applications. The research seeks to contribute with valuable information for the timber sector and for the development of best practices for wood management and treatment, aiming to optimize its physical and mechanical characteristics. For this, basal disks of three upright trees of three species planted in the Cerrado region, between the state of Goiás and the Federal District, were prepared to produce the samples used for measurement of the AMF by the X-ray diffraction method. From the results obtained it was possible to observe that: the average MPA measured was equal to 12.57° for Tachigali vulgaris, and 10.36° for Amburana cearensis and 8.49° for Myracrodruon urundeuva. It was possible to estimate the AMF as a function of the T value, obtained from X-ray diffraction, using the cubic model AMF = – 12.198T^3 + 113.67T2 – 348.4T + 358.09 (R2 = 0.99).

Keywords: Microfibrillar angle, X-ray diffraction, Wood drying.

INTRODUCTION

The Cerrado Biome, known for its rich biodiversity and complex ecosystems, is home to a variety of plant species with distinct anatomical and chemical characteristics. Among these, the woods of Tachigali vulgaris, Myracrodruon urundeuva and Amburana cearensis stand out, whose physical-mechanical and structural properties are essential for various applications, from civil construction to handicrafts.

Wood is mostly composed of cellulose, hemicellulose, and lignin, with lignin being a vital polymer that imparts rigidity and strength to the cell wall structure. The microfibrillar angle, in turn, refers to the orientation of the cellulose fibrils and is crucial for determining the strength and flexibility of the wood.

Cellulose microfibril is the basic structural unit of plant fibers, playing a crucial role in defining the physical and mechanical properties of wood. The angle of the microfibrils, which refers to the orientation of the microfibrils in relation to the axis of the fiber, directly influences the strength, stiffness, and durability of the woody species.

Studying the microfibrillar angle is therefore critical for building materials and engineering applications.

Estimating the angle of wood microfibrils is critical due to the impact this parameter has on the mechanical, physical, and functional properties of wood, such as tensile strength, flexibility, density, and behavior in industrial transformation processes.

Silva (2014) defines the microfibrillar angle (MFA) as the angle formed between the microfibrils present in the S2 layer of the cell wall with the longitudinal axis of the cell, being an essential property, which has a significant effect on the characteristics of strength, elasticity and retractability of the wood.

Despite the importance of these characteristics, there is a knowledge gap on how they vary among different species in the Cerrado and how this variation relates to the physical-mechanical properties of wood.

The present study seeks to fill this gap, exploring the relationship between the microfibrillar angle, the lignin content and the wood properties of Tachigali vulgaris, Myracrodruon urundeuva and Amburana cearensis, contributing to a better understanding of the ecology and sustainable use of Cerrado species.

The woods Tachigali vulgaris, Myracrodruon urundeuva and Amburana cearensis are among the most significant sources of renewable raw material for the production of numerous products around the world. However, the use of sawn wood is still limited in view of, among other factors, the appearance of defects during drying.

The drying of wood is of fundamental importance for most of the purposes for which it is intended. The process consists, in summary, of reducing the moisture of the wood to the desired equilibrium moisture, achieved in the shortest time and with the lowest incidence of defects, under satisfactory economic conditions.

The drying process results in contractions in the wood and, when conducted improperly, causes defects. However, little is known about the effect of drying on the ultrastructure of the cell wall.

The exit of water below the fiber saturation point (PSF) - at which all cell walls are saturated with water - causes changes in the ultrastructure of the cell wall, such as, for example, a decrease in the distance between cellulose microfibrils. Such an approximation is responsible for the contractions of the wood (SKAAR, 1972).

The microfibrillary angle (MFA) is a significant property of the cell wall, it is related to the angle formed between the fiber axis and the orientation of the cellulose microfibrils in the S2 layer of the secondary cell wall. MFA is related to other wood properties, such as the modulus of elasticity, which, according to Barnett and Bonham (2004), is higher in woods with lower MFA.

There are several methods for measuring MPA, including iodine precipitation, Raman microspectroscopy, polarized light microscopy, and X-ray diffraction (DONALDSON, 2008).

X-ray diffraction is a non-destructive technique that allows measuring MFA from a set of cells, reducing the time and costs of analyses, in addition to the possibility of measuring the microfibrillar angle in both green and dry wood. Although it has several advantages and is one of the most widely used techniques in the world for measuring MPA, no reports were found on the use of this technique in Brazil.

With the approximation of cellulosic microfibrils after drying, it is expected that there will also be a decrease in MPA. However, no information on this relationship was found for the woods under study and, therefore, studies that allow understanding it are important and necessary.

Woods from species such as Tachigali vulgaris, Myracrodruon urundeuva and Amburana cearensis are widely used in the timber industry due to their desirable characteristics, including strength and aesthetics. The X-ray diffraction (XRD) technique presents itself as an effective tool for the analysis of the microfibrillar angle, allowing a non-destructive and high-precision approach.

THEORETICAL FRAMEWORK

ANGLE OF CELLULOSIC MICROFIBRILS OF THE CELL WALL

Cellulosic microfibrils are fundamental structures in the cell wall of plants, playing a crucial role in determining the mechanical and structural properties of plant tissues. In the case of the species Tachigali vulgaris, Myracrodruon urundeuva and Amburana cearensis, each one has specific characteristics in relation to the arrangement and angle of these microfibrils.

1. Tachigali vulgaris: This species, common in tropical forests, has microfibrils arranged at angles that provide rigidity and resistance to elongation. The arrangement of the microfibrils in this plant is designed to withstand the mechanical stresses of the environment, giving robustness to the trunk and branches.
2. Myracrodruon urundeuva: Popularly known as mastic, this plant has microfibrils that are organized in order to maximize shear and compression resistance. The angle of the microfibrils can be oriented in a way that allows flexibility, allowing the plant to adapt to external forces such as wind and growth.
3. Amburana cearensis: This species, also typical of semi-arid regions, has microfibrils whose angles are adapted to optimize both the strength and lightness of the tissue. The arrangement of microfibrils in this plant can vary depending on environmental conditions, reflecting an adaptation to a habitat where resistance to water loss and mechanical strength are crucial.

The study of the angle of cellulosic microfibrils is important to understand how these plants adapt to their respective environments and how their morphological properties influence the sustainable use of forest resources.

More detailed analyses, such as scanning electron microscopy and X-ray diffraction techniques, can offer additional insights into the structure and organization of these microfibrils, contributing to a deeper understanding of the biology and ecology of these species.

In the S1 and S3 layers, the microfibrils show transversely with respect to the fiber axis. In the intermediate layer, S2, the microfibrils are axially oriented (Wardrop and Preston, 1947).

The S2 layer is thicker than the others, so it has a greater contribution to the physical, chemical (Cave, 1968) and mechanical properties of the wood (CAVE and WALKER, 1994).

The microfibrillar angle (MFA) corresponds to that formed between the cellulose microfibril and the longitudinal axis of the fiber (CAVE, 1968).

According to Donaldson (2008), variations in MFA play a functional role in tree growth and, among other factors, are age-dependent. Also according to this author, in the longitudinal axis, the MPA is greater at the base and decreases towards the top.

On the radial axis, Vainio et al. (2001) and Lima et al. (2014) detected a decrease in the AMF angle in the medulla-bark direction. Analyzing the AMF, the authors found that there was a decrease in the AMF in the rings formed more recently in relation to the older ones.

The orientation of microfibrils plays an important role in determining wood properties. According to Barnett and Bonham (2004), AMF influences, among other properties, the dimensional stability, rigidity and mechanical resistance of wood.

ESTIMATION OF AMF BY X-RAY DIFFRACTION

According to Donaldson (2008), the methods of measuring MPA are divided into two types: those measuring individual fibers or tracheids, through microscopy, and those measuring a set of cells using near-infrared spectroscopy or X-ray diffraction techniques, both techniques are based on the principle of cellulose crystallinity.

X-rays comprise electromagnetic radiation with a wavelength shorter than that of ultraviolet radiation, and which is found in the region between 10 and $^{10-2}$ nm. X-ray diffraction (XRD) occurs when there is constructive interference, which happens when the Bragg equation (equation 1) is satisfied between the X-ray beam and the atoms present in the material.

$$n\lambda = 2d\,\mathrm{sen}\,\theta \quad \text{(Equation 1)}$$

Where:

n = order of reflection (integer)

λ = wavelength

d = distance between two atomic planes

θ = is the Bragg angle

The use of X-ray diffraction for MPA measurement was established by Cave (1966), when he developed the theoretical relationship between MPA and the diffraction profile.

From this relationship, Cave (1966) deduced the equation AMF= 0.6 T, where T is half the distance between the intersections of the tangents at the inflection points of the profile curve with the baseline.

The equation developed by Cave was experimentally proven by Meylan (1966), through the comparison between the T value and the AMF, for *Pinus radiata wood*, obtained by the iodine precipitation technique.

The iodine precipitation technique consists, in short, of the deposition and precipitation of iodine crystals in the cell wall. Such crystals are oriented in the direction of the cellulosic microfibrils and their visualization is done with the aid of a microscope (DONALDSON, 2008).

Yamamoto et al (1993), when using the aforementioned equation to estimate the MFA in wood of *Camaecyparis obtusa*, *Cryptomeria japonica*, *Liriodendron tulipfera* and *Magnolia obovata*, at different heights, including normal wood and reaction wood, and comparing the MPA obtained through the iodine precipitation technique, found that the Cave method is inaccurate in regions where the MPA is less than 10° and greater than 25°.

The relationship between the T value and the MFA, according to Yamamoto et al. (1993), is described by an inverse S-type curve and given by the following equation: $MFA = 1.575x103T^3 - 1.431x10-1T^2 + 4.693T - 36.19$, regardless of the species and position studied.

Among the advantages of XRD, the speed in collecting information and the possibility of measuring the AMF in several fibers simultaneously stand out. However, the interpretation of diffraction patterns is the main disadvantage of using this technique.

The XRD measurements of the samples of the plants in question were carried out in the X-ray diffractometer of the analytical center of IQSC – Faculdade São Carlos, more specifically, the D8 Advance of Bruker. With this equipment, it was possible to analyze the types of samples prepared for this. To perform the diffraction measurements, the samples were prepared in the most convenient way possible and then the data were collected, identifying the phases of materials.

MATERIAL AND METHODS

COLLECTION OF MATERIAL AND PREPARATION OF SPECIMENS

The basal discs extracted from trees of the species Tachigali vulgaris, Myracrodruon urundeuva and Amburana cearensis, approximately 15, 22 and 20 years old, respectively from the Cerrado biome, were used to prepare the specimens.

The trees had a diameter at a height of 1.30 m (D1.30) of 29.48 cm, 33.90 cm and 34.5 m, respectively.

The central fillet was removed from each disc and the wood on one side of the marrow was used to make two blocks. One of the blocks was used to calibrate the X-ray diffraction technique.

From the block used for calibration, 200 x 100 x 100 mm samples were prepared for XRD analyses. From these samples, 10 x 10 x 2 mm blocks were removed and dried in air to estimate MPA via X-ray diffraction.

The second block, used to evaluate the variation of MFA with drying, was divided into 200 x 100 x 100 mm samples, which then had their dimensions reduced to 10 x 10 x 2 mm and were stored in water.

ESTIMATION OF THE MICROFIBRILLAR ANGLE VIA X-RAY DIFFRACTION

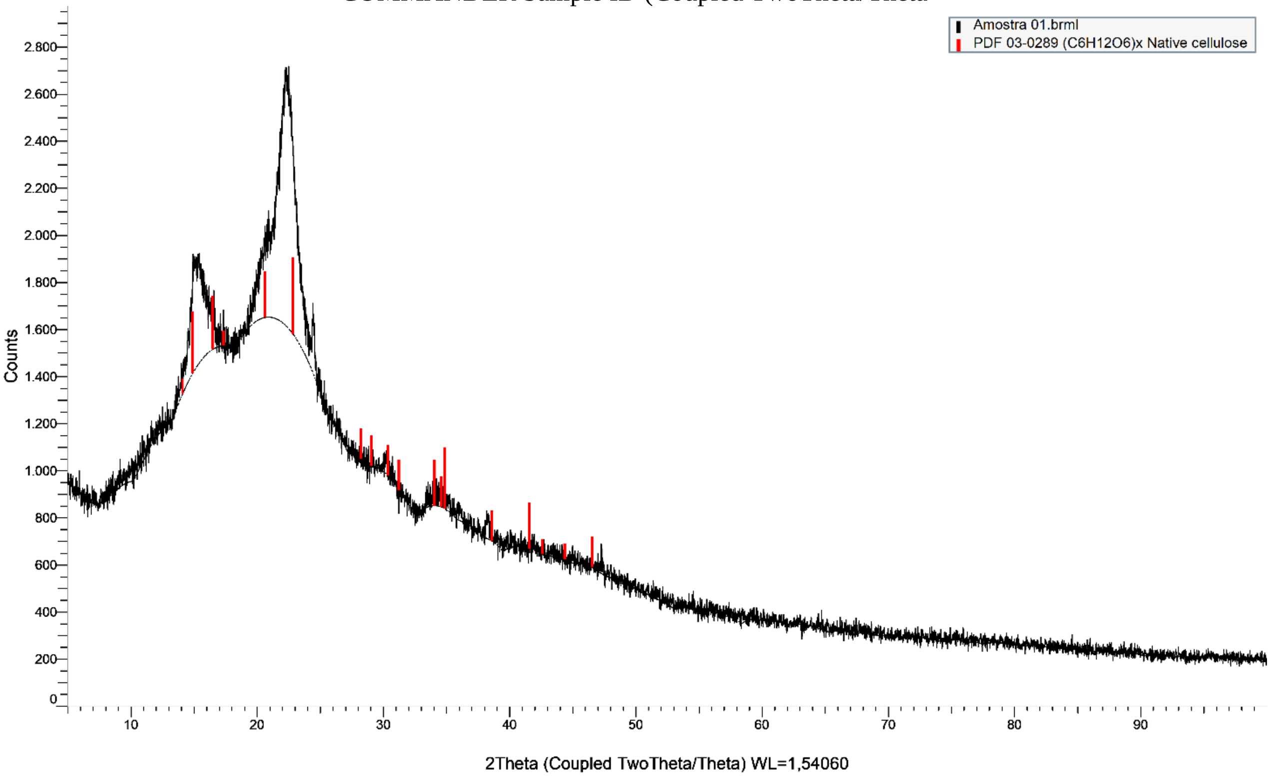
The AMF measurements were carried out at the Chemistry Laboratory of the Center for Instrumental Chemical Analysis of the Institute of Chemistry of the University of São Carlos - USP, where routine analysis services were performed with identification of phases, as well as analysis of refinement and determination of structures, using the D8 Discover diffractometer, Bruker.

The geometry used in the equipment is θ/2□. The data were collected in step-by-step mode, with a step of 0.05º, counting time of 3s per point, CuK□ radiation, 1.543 nm, voltage of 40 kV and current of 30 mA were used.

The specimens were placed in a horizontal position in the center of the sample holder. The X-rays hit the surface of the sample and the diffracted beam, the detector.

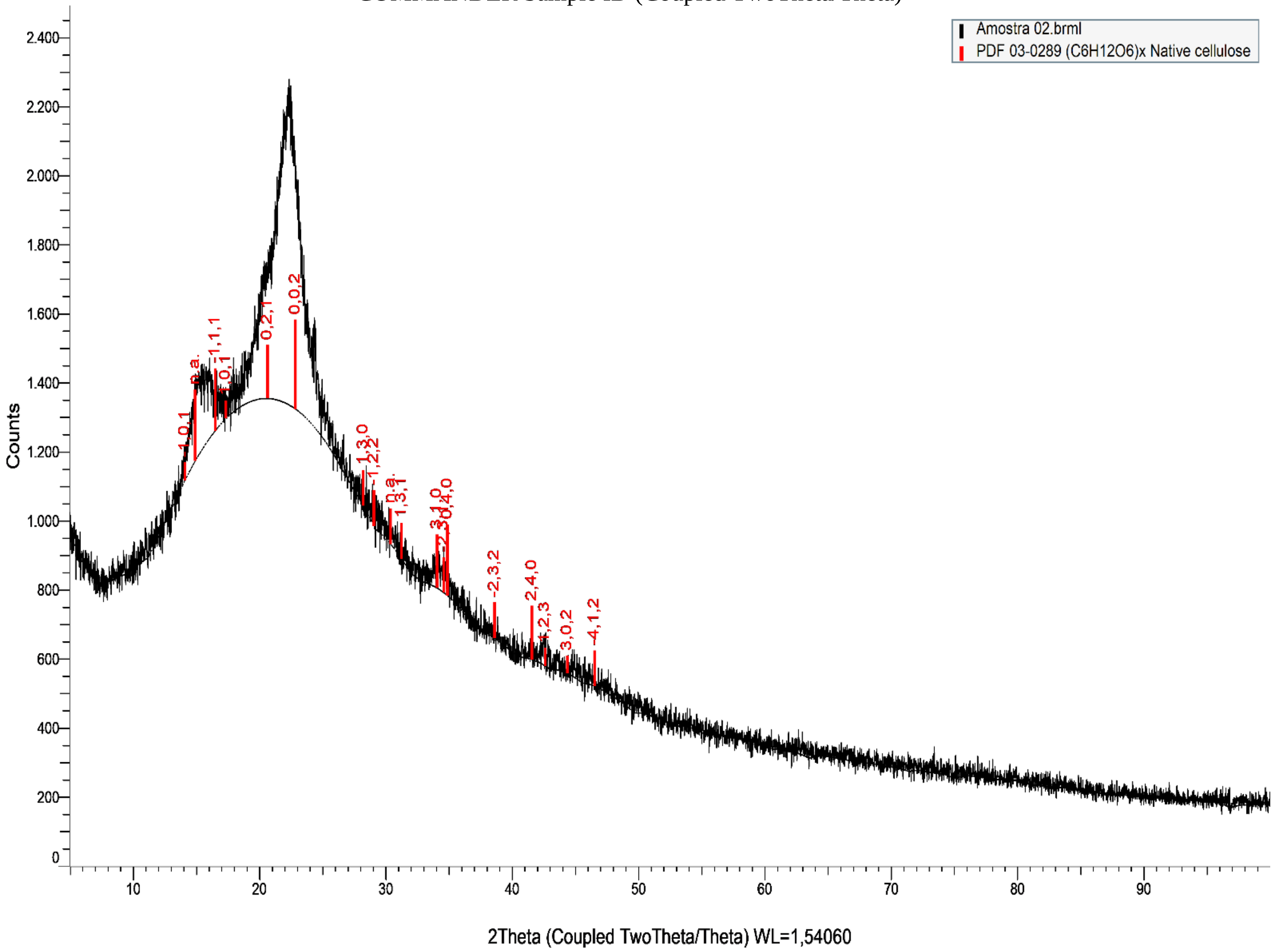
The diffractograms obtained were submitted to corrections to obtain the T value and, subsequently, the MFA. (Figures 1, 2 and 3)

Figura 1 - Amostra 1 - Myracrodruon urundeuva
COMMANDER Sample ID (Coupled TwoTheta/Theta



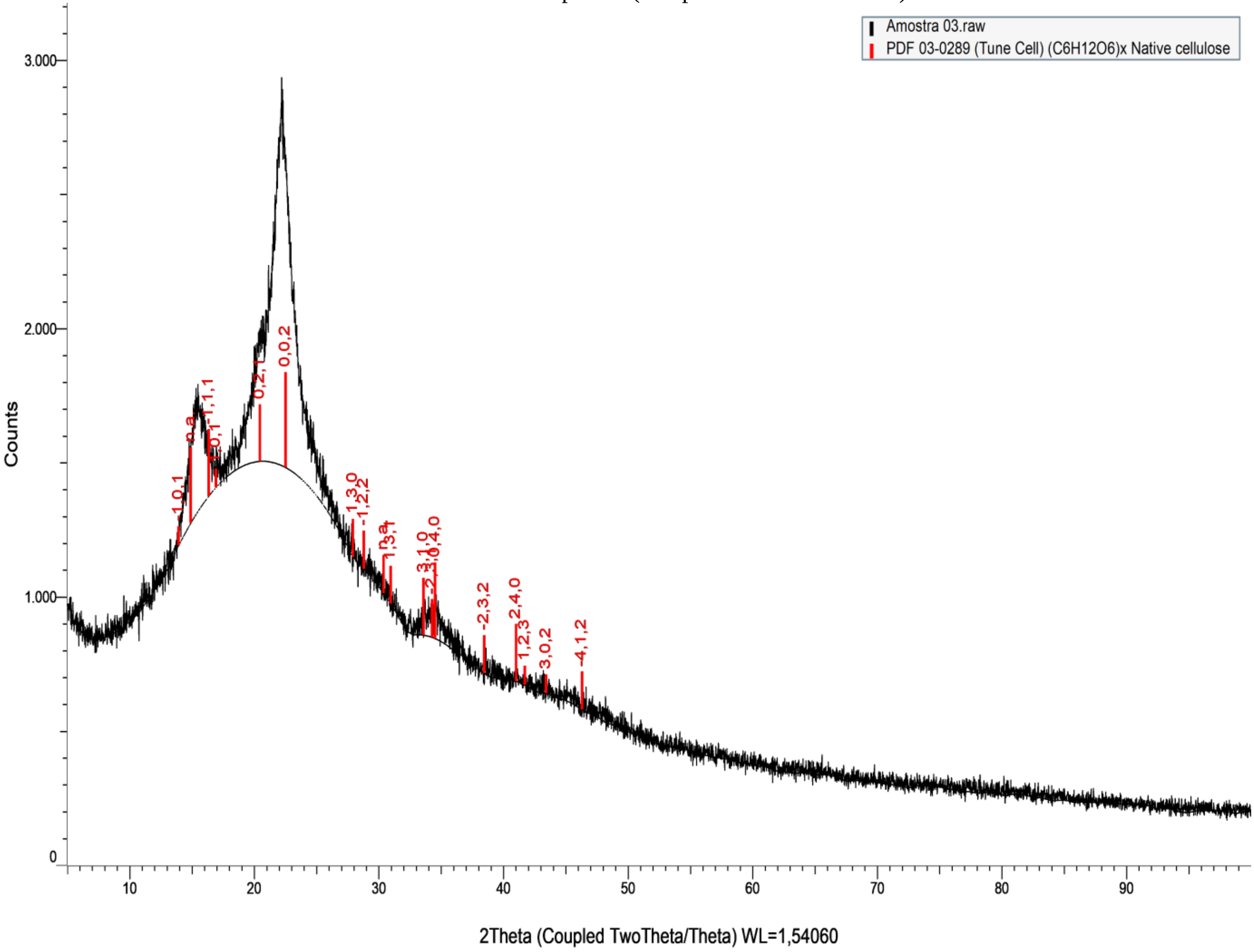
Source: Institute of Chemistry of the University of São Carlos.

Figure 2 - Sample 2 – Amburana cearensis
COMMANDER Sample ID (Coupled TwoTheta/Theta)



Source: Institute of Chemistry of the University of São Carlos.

Figure 3 - Aexhibition 3 – Tachygali Vulgaris
COMMANDER Sample ID (Coupled TwoTheta/Theta)



Source: Institute of Chemistry of the University of São Carlos.

DATA ANALYSIS

Descriptive statistics were performed, considering that the cubic equation developed by Yamamoto et al (1993) is not adequate to estimate the MFA from the data obtained in X-ray diffraction. Thus, the transmission method was used and with the reflection technique, the regression analysis of the data obtained in the calibration stage was performed.

RESULTS AND DISCUSSION

As for the results obtained, all materials presented structures typical of ligno-cellulosic materials with different crystallinities. The PDF files showed the phases discovered.

MICROFIBRILLAR ANGLE BY X-RAY DIFFRACTION

Equation 2, below, obtained in the aforementioned analysis was, therefore, adequate to estimate the MFA obtained from XRD.

MFA = -12.198T3 + 113.67T2 – 348.4T + 358.09 (Equation 2).

Where:

MPA = microfibrillar angle (°)

T = value T (°).

The mean microfibrillar angles calculated from Equation 2 for trees 1 - Tachigali vulgaris, tree 2 - Myracrodruon urundeuva and tree 3 - Amburana cearensis, were 12.57°, 8.49° and 10.36°, respectively, as can be seen in Table 1.

Table 1 – Microfibrillar angle of Tachigali vulgaris, Myracrodruon urundeuva and Amburana cearensis woods, obtained by X-ray diffraction (minimum, mean, maximum values and coefficient of variation).

Species	Min.(°)	Medium (°)	Max(°)	CV(%)
Tachigali vulgaris, e	10,48	12,57	14,91	18,61
Myracrodruo Urundeuva	8,13	8,49	9,19	8,24
Amburana cearensis,	9,33	10,36	11,81	13,99

Source: the author

The analysis of mean microfibrillar angles (AMM) for different tree species, such as those mentioned (Tachigali vulgaris, Myracrodruon urundeuva and Amburana cearensis), can provide important information about the characteristics of the wood and its potential applications in functional bioproducts.

Variation of Microfibrillary Angles

The mean microfibrillar angles vary between species: 12.57° for Tachigali vulgaris, 8.44° for Myracrodruon urundeuva and 10.36° for Amburana cearensis. This difference influences the mechanical and physical properties of the wood, such as tensile strength, bending, and compression.

Impact on Wood Properties

Tachigali vulgaris: it has a greater angle, which results in greater flexibility, but also less resistance. This characteristic makes it suitable for uses where malleability is desired.

Myracrodruon urundeuva: with the lower AMM, it has a stiffer and stronger wood, which makes it an ideal choice for structural applications and products that require high durability.

Amburana cearensis: has an intermediate AMM, suggesting a balance between strength and flexibility, potentially suitable for a variety of applications in the furniture and construction industry.

Functional Bioproducts

The choice of species for the production of functional bioproducts (such as bioactive compounds, medicines, or perfumery products) can be influenced by the mean microfibrillary angles. Species with lower microfibrillar angles have a higher density and possibly higher concentration of desirable chemicals.

The specific properties of the wood influence the treatment and extraction of functional compounds, affecting both the efficiency and the quality of the bioproducts.

Sustainability and Forest Management

Understanding microfibrillar characteristics can help in the sustainable management of forests, allowing the selection of species that are more suitable for certain economic and functional purposes, promoting the conservation and responsible use of forest resources.

CONCLUSIONS

In the case of the mean microfibrillar angles for trees 1,2 and 3 are 12.57°, 8.44° and 10,36°, respectively for the trees Tachigali vulgaris, Myracrodruon urundeuva and Amburana cearensis, the following considerations are considered:

1. Mechanical Properties: A smaller microfibrillar angle indicates a more aligned orientation of the microfibrils, resulting in a stronger and more rigid wood. Comparing the values, the tree Myracrodruon urundeuva (8.49°) has superior mechanical properties in relation to the others, although the difference is not very large.
2. Growth and Adaptation: Differences in angle are a result of the adaptations of the trees to the environmental conditions where they grew. A smaller angle indicates a growth in conditions where the competition of light was intense, which leads to a more robust structure as in response.
3. Industrial Applications: The choice of wood for different applications is influenced by these angles. Woods with smaller microfibrillar angles are preferred for structures that require greater strength and durability, while those with larger angles are used in applications where flexibility is more valued.
4. Functional Bioproducts: The choice of species for the production of functional bioproducts (such as bioactive compounds, medicines, or perfumery products) is influenced by the mean microfibrillary angles. Species with lower microfibrillar angles have a higher density and, consequently, a higher concentration of desirable chemicals. Thus, the specific properties of the wood influence the treatment and extraction of functional compounds, affecting both the efficiency and the quality of the bioproducts.
5. Process Performance: The angle of the microfibrils can also affect the behavior of the wood in

drying and processing processes. Wood with smaller angles has less tendency to deformation during drying.

Therefore, the evaluation of the angle of microfibrils is a useful tool to understand the properties of wood and assist in the selection of raw material for different uses. The difference between the angles of the species in question indicates that they have distinct characteristics, which must be considered in practical applications.

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