Characterization of Spanish agricultural residues with a view to obtaining cellulose pulp

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ABSTRACT *Spain abounds with annual agricultural residues from felled olive trees, pruned vine shoots, cereal straws, sunflower stalks, and cotton plant stalks. These residues were characterized to gather information about their potential use in paper and paperboard. Tests included water solubility, caustic solubility, alcohol-benzene extractives, ash, holocellulose, α-cellulose, pentosans, and lignin content.*

Sunflower stalks were the most soluble in water and caustic, while olive tree residues were the most soluble in alcohol-benzene. Cotton plant stalks were the least soluble in water, caustic, and alcohol-benzene. Vine shoots had the highest holocellulose contents, followed by wheat straw and cotton plant stalks. Olive tree wood and wheat straw gave the highest α-cellulose and pentosans contents, respectively. Sunflower stalks had high ash contents.

KEYWORDS
Ecology
Natural fibers
Plant residues
Pulping
Raw materials
Straw pulps

Wood was not used as a raw material by the paper industry until a little over a century ago. The typical sources then were cotton, linen, and, to a lesser extent, cereal straw. Between 1965 and 1984, however, the proportion of wood used as a fiber source for producing pulp for paper and paperboard increased from 73.87% to 92.26% (*1*).

This growth, which was more marked in developed countries (*2*), led to extensive tree felling. Today in India, for instance, forests account for only 22% of the land, while its optimum ecological forest area should be at least 33% (*3*).

This extensive forest utilization, despite the advent in the market of paper substitutes, has resulted in an ever-increasing shortage of fiber raw materials. Countries are contending with this problem in a number of ways.

One solution is to import wood and stop the increase in pulp production. This is the policy adopted by Finland, which imports 40% of its pulp wood (*2*). But the increase in paper and paperboard consumption runs parallel to the increase in the *per capita* income of a country, so imports are undesirable, and production cuts are particularly undesirable.

Another solution involves moving pulp production plants to underdeveloped countries with reasonable current and potential wood resources (such as Brazil, Congo, Angola, Venezuela, and Cameroon). The chief problem in these examples arises from the lack of capital needed not only to build the manufacturing facilities but also to create the infrastructure required to facilitate the transport of wood and chemicals and the installation of water connections. Furthermore, there is no certainty about the behavior of indigenous woods in reforestation programs because of their varied nature, hardness, and composition and because of their varied success in reforestations after the first felling.

Another alternative involves the use of deciduous plants. There are some technical difficulties with this option, however. The quality of pulp from husk or wheat straw, for example, is not comparable to that of wood pulp. Nevertheless, deciduous vegetable pulp can satisfy the needs of some areas in the paper industry if the properties are matched to the product requirements. But the chief problem lies in the delivered cost of these bulky vegetable materials. Even if their initial cost is low, their transport and handling costs are usually high.

The problems are made worse by the fact that the raw materials are almost always seasonal. This periodic availability requires that all the materials be collected and stored for a whole year of production in a short period.

Despite these shortcomings, the use of deciduous agricultural waste in areas where they abound may be feasible. Such is the case with Spain and, particularly, with Andalusia, which abounds with various agricultural residues such as those from felled olive trees, cereal straw, sunflower, and cotton plant stalks, and vine shoots. Their harvest times cover the months between January and April (olive trees), June and August (cereal straw), August and October (sunflower stalks), and October and December (vine shoots and cotton plant stalks). If these residues were used successively, then raw materials would be available throughout the year without the need to store them for long periods. **Table I** lists the Spanish and Andalusian productions of these agricultural residues in 1985 (*1*).

Nonwoody and deciduous vegetables have been the subject of much research in various countries (*3-7*). Studies have included research on the raw materials we studied in this work: olive tree residues, wheat straw, sunflower stalks, cotton plant stalks, and vine shoots. It seems that only Jiménez (*8*) and Camacho and Jiménez (*9, 10*) have studied olive tree residues for pulping. On the other hand, there are many papers on wheat straw, including a number of recent publications (*11-21*). Sunflower stalks have been studied by Guha and Bhargava (*22*) and McGovern (*23*), while Lossada (*24*) and Garoglio (*25*) have studied vine shoots. Cotton plant stalks have also been the subject of much research (*26-37*).

Our study was carried out to add to the data produced by this earlier research. We determined moisture contents, cold water solubles, hot water solubles, 1% caustic solubles, alcohol-benzene extract, ash, lignin, holocellulose, α-cellulose, and pentosans content.

I. Production of various agricultural residues in Spain and Andalusia in 1985

Residue	Production, 1000 tons/year	
	Spain	Andalusia
Olive tree	3547	2071
Wheat straw	6991	1077
Sunflower stalks	2105	1307
Vine shoots	2725	304
Cotton plant stalks	454	380

II. Fiber dimensions of various agricultural residues and some hardwoods

Material	Length, mm	Diameter, μm
Olive branches	0.63	11.0
Olive stems	0.92	14.0
Wheat straw	1.18	13.0
Sunflower stalks	1.37	11.5
Vine shoots	0.80	12.5
Cotton plant stalks	1.03	12.0
Pine	1.05	15.0
Eucalyptus	2.50	36.0

Materials and methods

Materials

The olive tree residues used were stem wood and branches. The stem wood came from trunks with a diameter greater than 5 cm, while branches included thin stems (less than 5 cm in diameter), stems, and leaves.

The cereal straw used was wheat.

The sunflower stalks were leaf-free, as were the vine shoots and cotton plant stalks.

Methods

Each of these residues was air dried at ambient temperature and reduced for analysis by grinding according to the TAPPI Test Method T 11 m-59.

The samples were tested by the following TAPPI Test Methods:

- Moisture: T 11 m-59
- Ash: T 15 m-58
- Water solubles: T 1 m-59
- 1% NaOH solubles: T 4 m-59
- Alcohol-benzene extract: T 6 m-59
- Pentosans: T 19 m-50
- Lignin: T 13 m 59
- α, β-, and γ-cellulose: T 203 os-61.

In addition, holocellulose was determined by the method of Wise (*38*).

Results and discussion

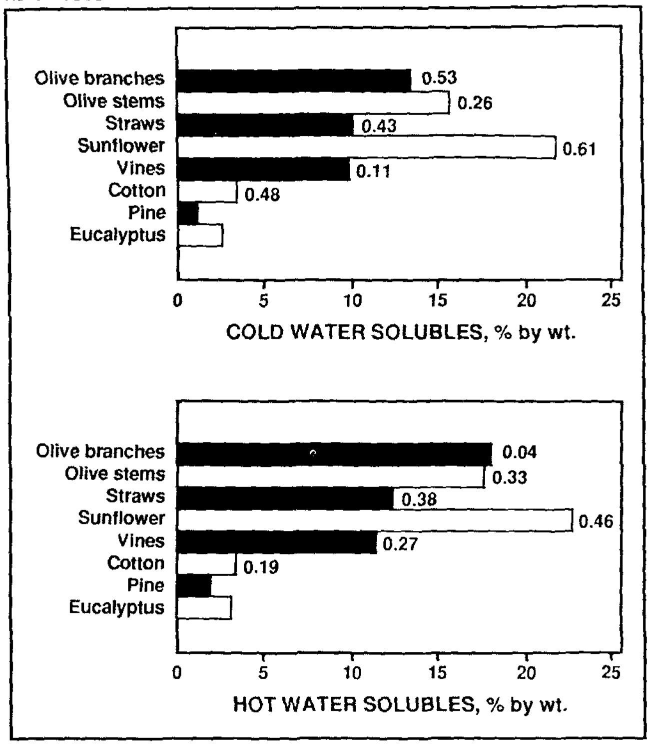
The average values and standard deviations found in the analysis of the four samples of each of the residues assayed are shown in **Figs. 1-5**. These results are compared with some typical hardwoods (eucalyptus) and softwoods (pine) commercially used in Spain (*39*).

Holocellulose consists of three fractions, α-cellulose, β-cellulose, and γ-cellulose. As a rule, the α-cellulose content of a raw material represents the undergraded cellulose of higher molecular weight, while β-cellulose and γ-cellulose consist mainly of hemicellulose (*35*). The α-cellulose contents of agricultural residues studied are between 37.16% and 40.95%, so that the β- and γ-cellulose contents are between 35.37% and 23.95%. These compositions are consistent with the pentosans contents, which are relatively high.

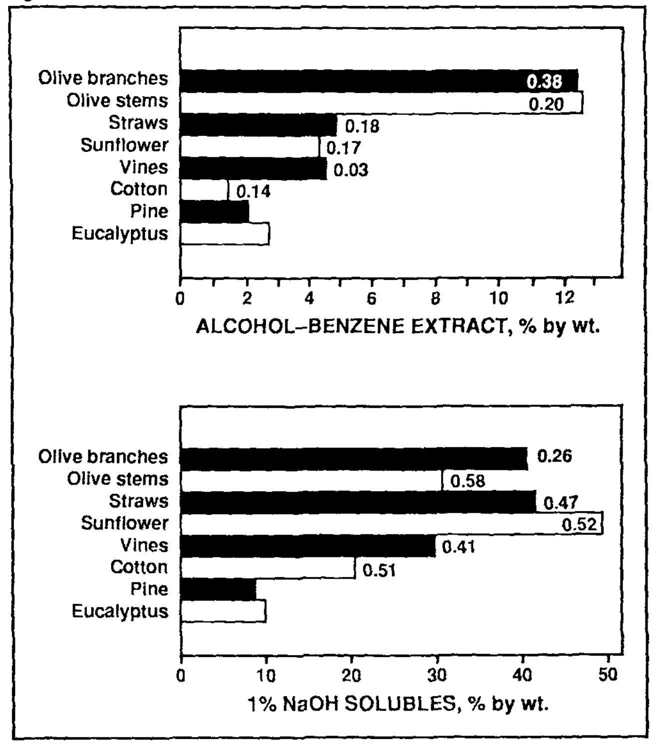
A comparison of our results with those reported by others for olive tree wood (*8, 40*), wheat straw (*3, 11, 15, 16, 20, 41, 42*), sunflower stalks (*43, 44*), vine shoots (*24, 25*), and cotton plant stalks (*3, 20, 27, 31, 32, 35, 36*) shows significant differences, in some cases. These differences show the influences of the nature, source, and composition of the different raw materials and the influence of the analytical procedures employed.

Wheat straw has relatively high ash and pentosans contents, while sunflower stalks have high water solubles, caustic solubles, and ash contents. Cotton plant stalks have the lowest water solubles, caustic solu-

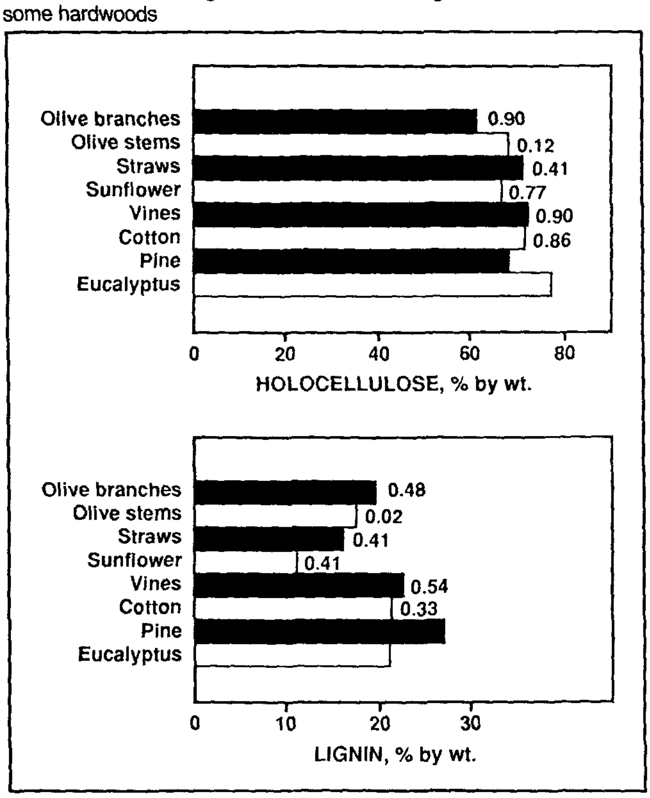
1. Cold and hot water solubles of various agricultural residues and some hardwoods



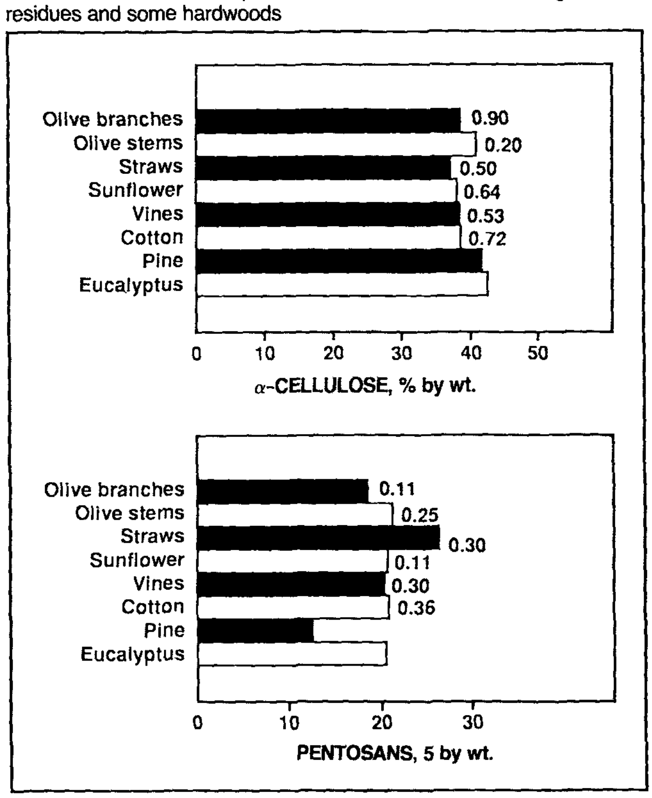
2. Alcohol-benzene extract and 1% NaOH solubles of various agricultural residues and some hardwoods



3. Holocellulose and lignin contents of various agricultural residues and some hardwoods



4. The α-cellulose and pentosans contents of various agricultural residues and some hardwoods



bles, and alcohol-benzene extract contents. Vine shoots have the highest holocellulose content of all six types of residue, followed by wheat straw and cotton plant stalks. Finally, olive tree residues feature the highest α-cellulose content.

By microscopy work, we determined the average cell length and diameter of the agricultural residue fibers. In **Table II**, these are shown with values for some eucalyptus and pine (*45*). The differences between our results and those reported by others (*3, 7, 11, 24, 46-48*) may arise from natural variability due to differences in fiber source, growing conditions, and methods.

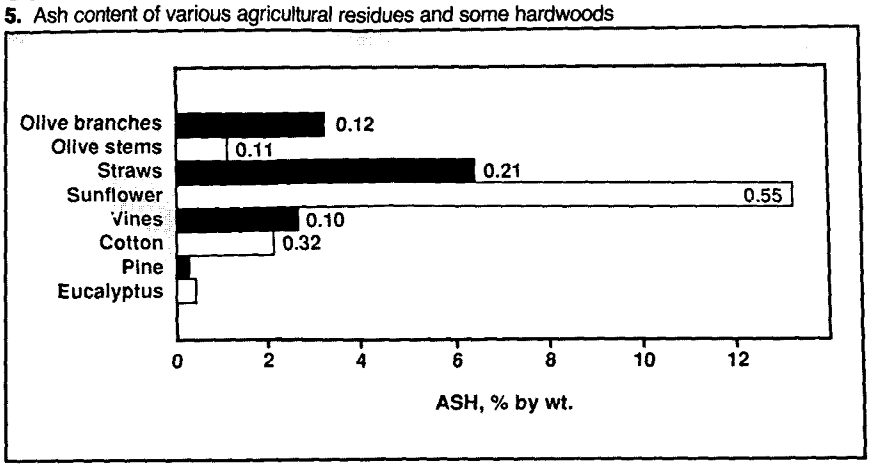
Conclusions

The acceptable holocellulose and α-cellulose contents in the agricultural residues studied makes them a possible raw material for the production of pulp for paper and paperboard.

The characterization of raw materials is important research that gives us needed information. In fact, once the fundamental fiber properties of a particular fiber raw material are known, it is easy to determine (a) whether it is suitable for the production of pulp, (b) which manufacturing process will be the best, and (c) the type of pulp that can be produced.

The pulp yield obtained from agricultural residues is quite variable (25% to 95%), depending on the process used (*3-37*). Assuming a yield of 50%, we would expect the quantity of pulp obtained with the Spanish and Andalusian agricultural residues studied to be approximately 7.9 and 2.6 million tons/year, respectively. These figures represent approximately 2/3 the production of paper in Spain and twice Spain's production of paperboard. This much available raw material warrants further study on harvesting and pulping.□

5. Ash content of various agricultural residues and some hardwoods



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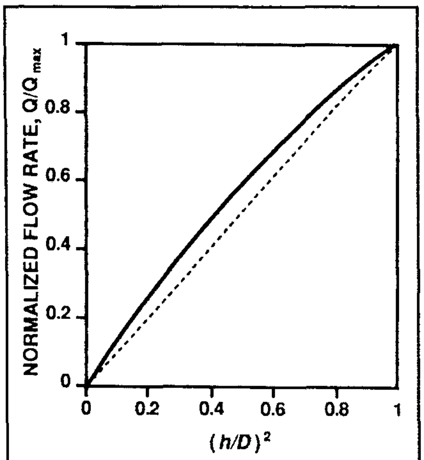
2. Representation of (Q/Q_{max}) vs. $(h/D)^2$, for circular weirs



tility. Thus, denoting by x the normalized liquid level (h/D for circular weirs) and by y the normalized flow rate (Q/Q_{max}) and with the definitions given in Eqs. 9 and 10, we would expect the ratio of Y/X to exhibit a constant value.

$$X \equiv x^2/(1 - x^2) \quad (9)$$

$$Y \equiv y/(1 - y) \quad (10)$$

Following vapor-liquid equilibria convention, we will denote this ratio Y/X by α. An analysis of the curve in Fig. 2 led to the result that this ratio is indeed quite constant, with an average value of 1.406, for the range of $0 < x^2 < 0.5$. This upper limit corresponds to a liquid crest of about 70% of the circular diameter. Thus, a constant value of α is admissible for most problems of open-channel flow. Above this upper limit, α increases slowly up to values around 1.5 as the ratio x approaches 1 (at which point the circular channel is completely full). In this connection, Stevens observes that, at about 70% of the diameter, the reported experimental flow rates begin to increase beyond that given by Eq. 6, indicating a transition from weir flow to orifice flow as the weir becomes surcharged.

Accepting a constant value of α, we can write:

$$Y = \alpha X \quad (11)$$

Further pursuing the analogy with vapor-liquid equilibria, we have:

$$y = \alpha x^2/ [1 + (\alpha - 1)x^2] \quad (12)$$

Inserting the definitions of x and y then yields:

$$Q/Q_{max} = \alpha(h/D)^2/ [1 + (\alpha - 1)(h/D)^2] \quad (13)$$

Finally, using a value of 1.406 for α and invoking Eq. 7, we have:

$$Q = 3.549\, h^2D^{1/2}/ [1 + 0.406\, (h/D)^2] \quad (14)$$

Equation 14 can thus be recommended as an excellent approximation for estimating liquid flow rates through partially filled circular openings. Please recall that all of these formulas for the actual flow rate across a circular weir are based on a constant discharge coefficient of 0.59.

Example

A large vertical cylindrical tank containing liquor stock has a circular opening in its side wall for a short pipe with an inside diameter of 12 in. At some steady-state operating condition, this tank is filled to a liquor level of 4.8 in. above the bottom of this circular opening. We want to determine the liquor discharge rate from this tank through this opening.

Let us perform the more rigorous calculations first. The normalized liquor level above the bottom of the weir (x) is 0.4. Thus, the modulus (k) of the elliptic integrals is 0.632. From Spiegel (*12*), the values of the first and second kinds of complete elliptic integrals for this modulus are K = 1.7772 and E = 1.3997. Inserting these values of D, k, E and K into Eq. 6 yields a value of 0.532 ft³/s for the discharge rate Q. [Stevens tabulates a value of 0.530 ft³/s for the same conditions (*9*).]

For the same values of h and D, which are 0.4 ft and 1.0 ft, the approximate correlating Eq. 14 gives

$$Q = [3.549\,(0.4)^2(1.0)^{1/2}]/ [1 + 0.406\,(0.4/1.0)^2]$$

$$= 0.568/1.065$$

$$= 0.533 \text{ ft}^3/\text{s}$$

Thus, the equation is accurate within 1%.

Conclusions

The equation for flow through circular weirs can be applied to determine overflow rates from a liquor stock tank with a circular discharge in its side. This rigorous equation involves elliptic integrals, but it can be approximated by a simpler expression analogous to the constant relative volatility equation from binary vapor-liquid equilibria.□

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