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Morphological analysis of pulps from orange tree trimmings and its relation to mechanical properties

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ABSTRACT

To optimize the pulping and refining processes of new alternative raw materials for papermaking, researchers generally perform tests that consume considerable time and large amounts of sample. We propose measuring the morphological properties of pulps from orange tree trimmings by image analysis systems, which are fast and user-friendly, to develop models relating key mechanical properties to the dimensions, the deformation and the population of fibers. Data modeling involves multiple linear regression, as used in other studies, and support vector regression, not used before for this purpose, achieving higher R^2 values (up to 0.90). Although tensile, tear and burst tests are still required to obtain accurate values, a quick morphological characterization allows for a rough but satisfactory prediction of paper strength. In this case, chemical pulping and moderate refining are shown to be necessary to obtain pulps of acceptable quality from orange tree trimmings.

1. Introduction

Measuring the morphological properties of cellulosic fibers has been a complicated task in the past, but the development of image analysis techniques provides fast and accurate determinations [1]. It is well-known that the fiber morphology in cellulosic pulps can be correlated to the mechanical performance of the final product. A model to predict paper strength from morphological data is an appealing alternative to mechanical tests, which are destructive and time-consuming. It stands as an approximate but satisfactory way to address the suitability of new raw materials for papermaking.

Seth [2] explained theoretically how fiber length and coarseness affect tensile strength. Adhesion between fibers, which is key for paper strength, depends on the characteristics of their surface [3]. Higher proportions of fines are translated into lower freeness values [4].

Empirical equations relating fiber dimensions to mechanical properties have been developed for hardwood kraft pulps [5], softwood kraft pulps [6], kenaf soda pulps [7], white leadtree soda pulps [8], and soda-anthraquinone pulps of date palm midrids [9], among other lignocellulosic materials. They are usually based on linear regression or multiple linear regression, but non-linear regression techniques may yield better results. Among them, those based in machine learning have gained a considerable attention in the past few years for their versatility and accuracy.

Support vector regression (SVR) aims at building a model to fit a regression function, $y = f(x)$, able to predict with accuracy the outputs (y_i) of a set of new input samples (x_i) never presented to the model before. To account for non-linear relationships, SVR maps the input data into a higher dimensional feature space, F, in which it performs a linear regression of the form:

$$F(x, w) = (w \cdot \Phi(x) + b) \quad (1)$$

Φ is the function that maps the input vectors to the feature space and w is the weight vector of the linear correlation in the feature space ($w \in F$). The large computational effort required to map the data into the feature space is avoided by using kernel functions that perform the dot product of the input vectors without having to transform them [10]. SVR models are adequate to tackle regression problems in which the number of independent variables is high in comparison to the available sample points. This technique has been used to predict some mechanical properties of paper from the density of the raw material [11].

Paper sheets in this study are obtained from the woody part of orange tree trimmings (*Citrus sinensis*). *C. sinensis* is an angiosperm and evergreen tree, generally shorter than 10 m, commonly found in temperate climate zones [12]. At least after the third year, this

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tree needs to be pruned annually, generating large amounts of waste, but farmers have not found a convincing way to manage the trimmings. They often end up being open-burnt, which is hazardous to the soil and to the air [13].

There are powerful reasons to consider papermaking a good way to reuse orange tree trimmings. Their usual moisture content, above 50%, makes burning and pyrolysis expensive. Their lignin content, approximately 20%, is similar to that of *Eucalyptus globulus* wood, the most common raw material for printing paper [14,15]. The convenience of bleached organosolv pulps from orange tree trimmings has been discussed elsewhere [16]. González et al. [17] cooked them with soda and anthraquinone, concluding that the resulting pulps are suitable for papermaking. However, as far as we are concerned, researchers have not previously addressed the fiber characteristics of pulps from this raw material, the influence of the cooking reagent on those characteristics and on paper strength, and the relation between morphological and mechanical properties.

In this work, pulps from *C. sinensis* trimmings are obtained through sulfur-free processes [18,19], under mild conditions, and refined to different degrees. We aim to evaluate the influence of pulping and beating on fiber characteristics and on key mechanical properties of the final product. Besides fitting the data to common first degree equations, we report a non-explicit model, based on support vector regression, with a view to predicting the tensile index, the burst index and the tear index from morphological parameters and pulp freeness.

2. Materials and methods

2.1. Pulping and refining

Orange trees were grown in the Southeast of Spain. The woody part of their trimmings, i.e., branches and stems whose diameter was greater than 1 cm, was separated from the rest, milled to a size of 5 mm or less, and then pulped. A simplified scheme of the process is shown in Fig. 1.

The conditions and codes of the different treatments are shown in Table 1. The yield was determined as the relation between the mass of pulp obtained and the mass of raw materials introduced, both on a dry basis.

For chemical pulping (ETN40, ETN60, SAQ15, SAQ30), cooking was carried out in a stainless steel digester with heating jacket and PID controller to keep temperature constant. Liquid-to-solid ratio was 6. Two different reagents were used: commercial monoethanolamine and sodium hydroxide (in pellets). In the soda pulping processes, anthraquinone powder was added to the batch reactor with the white liquor, in order to increase selectivity to lignin. Mechanical pulping (MP) was carried out by beating three times in a 12″ Sprout-Waldron equipment. Thermomechanical pulping (TMP) consisted of cooking with water in the aforementioned reactor, liquid-to-solid ratio being 6 again, and then beating twice in the Sprout-Waldron.

The pulp obtained was washed, crumbled, screened and stored at temperatures below 10 °C. Before refining, the kappa number of each of the chemical pulps (samples 1, 7, 13, 19) was determined according to ISO 302.

Pulp samples were disintegrated by stirring at 3000 rpm (ISO 5263). They were refined in a Maskin's Mark VI PFI mill (0.37 kW) to various levels of refining (Table 1), following ISO 5264/2. The change in drainability was measured by means of a Canadian Standard Freeness (*CSF*) tester (TAPPI T227).

2.2. Morphological analysis

MorFi, the fiber analyzer from Techpap (France), was the device used to measure the dimensions of fibers, their shape and their population. This analyzer, based on an image analysis system, is probably the fastest way known to determine a large number of morphological properties. The suspensions for this analysis were prepared by diluting 1 g of each pulp in 600 mL of water. Imaging was performed with a spatial resolution of 3 μm, until the device had counted 5000 fibers. The system software (V. 7.9.13E) processed the images, reporting the distribution of each property and the average value. Each measurement was made three times. This method is described in more detail elsewhere [20].

Photographs were taken from a scanning electron microscope (SEM), JEOL, model JM-6400. Each sample was placed on a cylindrical slide and, afterwards, in a vacuum oven at 45 °C and 200 mbar for 24 h. Once dried, the sample was coated with gold. Then, it was visualized with a magnification of 100 and 1000 times.

2.3. Mechanical tests

Up to ten handsheets were obtained from each of the pulps, following the ISO standard 5269-1, save that water was not recirculated. Agitation was performed by hand, using a perforated steel plate with vanes as the stirrer. The nominal aperture size of the screen was 125 μm and the press worked at 4 kg/cm^2. The basis weight of the handsheets was approximately 60 g/m^2.

We measured the strength of the paper sheets by means of three mechanical testers: one from Tinius Olsen for the tensile index (ISO 1924-2), another one from Messmer for the tear index (UNE-EN 21974), and a last one from Metrotec for the burst index (ISO 2758).

2.4. Data modeling

First, a correlation matrix was built with *CSF* and the properties measured by MorFi, in order to analyze the dependence among them. The selected set of fiber characteristics (independent variables) were related to the pulpsheet properties by using multiple linear regression (MLR) in Origin Pro 8.5. The coefficients whose p-value was higher than 0.05 were discarded. For each of the dependent variables, we chose the equation which, as long as the null hypothesis could be safely rejected for all parameters, had the highest R^2.

Alternatively, we carried out a support vector regression (SVR) in Python programming language, using the libraries developed by Pedregosa et al. [21], to predict sheet properties from morphological parameters and *CSF*. In order to achieve an acceptable accuracy and a high generalization capacity (to avoid overfitting), it is necessary to tune the SVR hyperparameters, namely the kernel function, the threshold (ε), the trade-off between accuracy and model complexity (C), and the gamma parameter of the kernel function (γ). The selection was carried out by means of an algorithm based on a simulated annealing procedure [22]. Each of the SVR models was 5-fold cross validated. This means that the models were fitted with exclusive random subsets of the input data and the goodness of each fitting was the correlation between estimated and measured output values of the corresponding test subset. The final correlation coefficient R^2 given corresponds therefore to the average of the five ones calculated for each fold.

The fiber characteristics taken into account are the ones considered in other studies [7], plus the percentage of microfibrils (in area), the percentage of kinked fibers and the percentage of fibers with broken ends. While there is a correlation between the kappa number and paper strength [6], it is reasonable to think that the properties measured by MorFi already show the influence of the delignification.