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THE INFLUENCE OF PRE-HYDROLYSIS KRAFT (PHK) CONDITIONS ON PULP FOCK REACTIVITY

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SUMMARY

Regenerated cellulose is a sustainable material made from renewable sources such as wood pulp, cotton linters, and other lignocellulosic materials. Its properties, like biodegradability, versatility, absorbance, and softness make its fibers a natural alternative to synthetic materials from non-renewable sources.

Alternative methods such as pre-hydrolysis kraft cooking are increasingly becoming the primary means of producing dissolving pulp from wood due to the unsustainable nature of cotton linters. While cotton linters are indeed an excellent source of cellulose, their high-water requirement and reliance on insecticides make them environmentally unfriendly. In contrast, pre-hydrolysis kraft cooking offers several advantages, including its adaptability to various raw materials and greater efficiency in recovering chemicals used during the process.

This study aimed to investigate dissolving pulps with different compositions and analyze their properties, focusing on correlations between hemicellulose content, viscosity, and Fock reactivity. The study examined Pre-hydrolysis Kraft (PHK) pulp in two variants: one with less than 2.5% hemicellulose and a viscosity of 549 cm^3/g, and another with 5% hemicellulose content and a viscosity of 874 cm^3/g. The results showed that the PHK pulp with reduced hemicellulose content exhibited superior Fock reactivity (65%) compared to the pulp with 5% hemicellulose content (52%).

Additionally, the study explored the feasibility of using recycled pulp as a source for dissolving pulp fiber. The recycled pulp underwent a chemical treatment to enhance its Fock reactivity. The findings demonstrated a notable 40% increase in reactivity following the treatment, highlighting the potential of recycled materials as a valuable and sustainable source for dissolving pulps production.

Keywords: Dissolving pulp, Fock test, Pre-hydrolysis Kraft, Recycled pulp

INTRODUCTION

Dissolving pulp

Dissolving pulp is a particular type of pulp used primarily in the production of rayon, viscose, and other cellulose-based products. It is derived from wood or other plant-based materials and has unique characteristics that make it suitable for these applications. The choice of raw source for dissolving pulp production plays a significant role in adopting greener and more sustainable producing methods(1).

Choosing a renewable raw source, such as sustainably managed forests or agricultural residues, ensures that the production of dissolving pulp is not depleting finite resources. Sustainable forestry practices, including reforestation and responsible harvesting, help maintain the long-term viability of the raw material supply(2). By prioritizing sustainable raw sources for dissolving pulp production, manufacturers can contribute to greener production methods, reduce environmental impacts, and promote the transition to a more sustainable and circular economy.

Given the above-mentioned objective, wood is increasingly utilized as the primary source to produce dissolving pulp. The wood species used impacts the amount of chemicals needed and the energy efficiency of the process. The denser and hemicellulose/lignin-rich the wood used, the harsher conditions must be applied to obtain high-quality dissolving pulp. By this means, fast-growing

hardwoods (e.g., *Eucalyptus globulus*), have a lower environmental impact compared to slow-growing softwoods(3).

The production of dissolving pulp involves specific methods and processes to obtain the desired qualities, that is:

High Purity: Dissolving pulp has a high cellulose content (typically above 90%) and low levels of impurities, such as lignin and hemicelluloses(1).

High Alpha-Cellulose Content: Dissolving pulp contains a significant proportion of alpha-cellulose, allowing a homogenous regeneration in the final stage of the process. This characteristic makes it suitable for chemical processing and conversion into various cellulose derivatives.

Low Degree of Polymerization: Dissolving pulp has a relatively low degree of polymerization (DP), which refers to the number of glucose units in a cellulose chain. The low DP enhances the solubility of dissolving pulp in certain solvents, facilitating its conversion into viscose and other products. However, it is important to note that there exists a limit for this parameter, as an excessively low degree of polymerization can lead to the production of regenerated fibers that are weak in strength(4).

Consistent and Uniform Fiber Properties: Dissolving pulp is produced with emphasis on achieving consistent and uniform fiber parameters, such as fiber length, width, and flexibility. These properties contribute to the quality and performance of the final products made from dissolving pulp(2).

Pre-hydrolysis kraft (PHK)

Pre-hydrolysis kraft (PHK) cooking is a method commonly used in the production of high-quality dissolving pulp. It involves an additional hydrolysis step before the main kraft pulping process. PHK cooking offers several advantages in terms of producing dissolving pulp with desired properties(5).

The hydrolysis process entails subjecting wood chips to elevated temperatures and a low concentration of water/acid. The acidic pH aids in selectively removing hemicelluloses, as their amorphous structure renders them less stable compared to cellulose(6). Meanwhile, under these conditions, lignin tends to precipitate, with only a small portion remaining soluble in the solution.

By previously removing hemicelluloses before kraft cooking, the delignification process is improved. The degradation and removal of hemicellulose give a more efficient diffusion of the pulping liquor, and soften the fiber, helping in reducing shives and knots that can affect future fiber applications.

Additionally, the pre-hydrolysis process results in a sugar-rich solution that can be further valorized by the conversion of the hemicelluloses removed (mainly xylans) into xylooligosaccharides with proven benefits as prebiotics(7).

Fock reactivity

The Fock test is a widely used method for assessing the reactivity of dissolving pulp, which is used in the production of viscose rayon. The test measures the pulp reactivity as the amount of cellulose that reacts with carbon disulfide, expressed as a percentage(8). The Fock test is used to determine the suitability of dissolving pulp for viscose rayon production and to optimize the production process.

The conditions that can impact the xanthation process between cellulose and carbon disulfide are crucial in this procedure. Additionally, it is essential to consider that the measurement can be influenced by the composition of the pulp outside the designated reaction conditions. A study found that the pulp reactivity increased with decreasing kappa number, and the highest reactivity was obtained after total lignin removal(9).

However, the effect of hemicellulose in this process is relatively controverse, where some studies show the negative effect of higher hemicellulose content(10) and others show the enhance reactivity of pulps with higher hemicellulose content(11).

Although, the principles underlying Fock reactivity and cellulose dissolution are distinct (Fock reactivity

gauges the number of free hydroxyl groups available for chemical reactions and cellulose dissolution evaluates the pulp's capacity to dissolve in a specific solvent), under conventional circumstances, the higher the Fock reactivity, the greater the pulp's propensity to undergo chemical modification, including dissolution(8).

Recycled pulp

Recycled pulp, which is obtained from recovered paper products, contains cellulose fibers that can be processed and converted into dissolving pulp. The recycling process typically involves the collection, sorting, and processing of wastepaper, including mechanical treatment to liberate the fibers in the paper(12). In addition to paper production, these fibers can gain new life in the production of dissolving pulp, after adequate chemical treatment. However, the high content of impurities and the heterogeneity of the source rise particular difficulties. Recycled pulps often contain impurities such as ink and coatings, metals, fillers, and binder materials, as well as unwanted natural compounds like lignin and hemicellulose(13). One notable challenge related to these impurities is the detrimental impact of metals on the pulp's reactivity when exposed to dissolution solvents(14), showing the need to take them into consideration.

To minimize these impurities, different processes must be applied, such as screening, cleaning, deinking, and bleaching. These steps aim to remove contaminants, ink particles, and other unwanted substances, improving the quality of the recycled pulp and making it more suitable for dissolving pulp production.

The aim of this study was to evaluate the impact of pulp composition on Fock reactivity and to assess the feasibility of chemical treatment in utilizing recycled pulp as a viable cellulose fiber source for dissolving pulp production.

EXPERIMENTAL

Raw Material and chemical treatment conditions

E. globulus wood chips (3−4 mm thickness) supplied by Biotek S.A. (Vila Velha de Rodão, Portugal) were used to produce pre-hydrolysis kraft pulp (PHK pulp). The pre-hydrolysis kraft cooking comprises the following three steps: pre-hydrolysis, kraft cooking, and bleaching.

The pre-hydrolysis was carried out using the following two approaches: using a batch reactor under auto-hydrolysis conditions and a flow-through reactor (FTR) using a dilute acid solution as a feed.

Batch auto-hydrolysis and the kraft cooking were conducted in stainless steel reactors with a 150 mL total volume attached to a mechanical rotating shaft, enabling the vessel to be immersed in an oil bath with temperature control.

A different setup was used to produce dissolving pulp with the flow-through reactor as shown in figure 1.

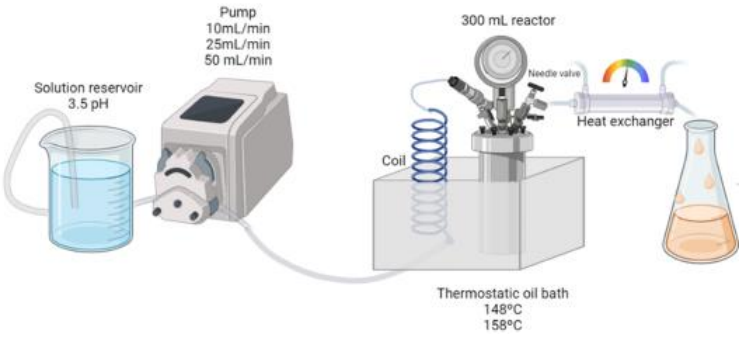

Figure 1 – Schematic diagram of the flow-through reactor(15).

A standard ECF bleaching sequence, $D_0E_1D_1E_2D_2$, was employed with chlorine dioxide (D) and NaOH (E), where the dioxide and alkali charge is dependent on the kappa number of each pulp.

The recycled pulp, provided by Papeleira CoreBoard, Portugal, underwent a three-step treatment to improve Fock reactivity. An auto-hydrolysis was carried out for 210 minutes at 148ºC, followed by an alkali treatment stage with 24% active alkali (as NaOH) with 30% sulfidity at different temperatures and a bleaching sequence.

Pulp composition and characterization

The TAPPI standard method T222 om-02 was employed to quantify acid-insoluble and soluble lignins in the lignocellulosic materials. This involved a two-step acid hydrolysis process using 72% (w/w) and 4% (w/w) sulfuric acid. The final hydrolysis step was conducted by autoclaving the sample at 121 °C for 60 minutes, following the NREL/TP-510 standard, using a 2540 mL vapor autoclave manufactured by Tuttnauer (Netherlands). The resulting solution was utilized for determining the carbohydrate compositions of the lignocellulosic materials through High-Pressure Liquid Chromatography (HPLC). To identify and measure the pulp composition, a Rezex ROA-Organic Acid H+ column was employed, operated at 70ºC. The compounds used for identification included xylose, glucose, galactose, furfural, and hydroxymethylfurfural. Each HPLC run employed 0.005N sulfuric acid solution as the mobile phase, with a flow rate of 300 µL/min.

Intrinsic pulp viscosity was measured according to the ISO standard (ISO 5351:2010).

Fock reactivity

The procedure optimized by Tian (8) was followed. 0.50 grams of pulp (on an oven-dry basis) was carefully transferred into a 50 mL reactor; 50 mL of a 10% NaOH solution was added, and the suspension was stirred thoroughly; following this, 1.3 mL of CS_2 was introduced into the reactor, and the reactor was sealed tightly. The stirring process was maintained at a rate of 300 rpm for a period of 3 hours at a temperature of 15°C.

Following the reaction time, distilled water was added to the mixture to attain a total weight of 100 g. The resulting solution underwent centrifugation at 5000 rpm (3600 G) for 15 minutes, after which a 10 mL portion of the supernatant was combined with 3 mL of 20% w/w sulfuric acid solution for neutralization. Subsequently, the sample was subjected to degasification by stirring it in a fume hood for 15-20 hours to facilitate the release of any unreacted carbon disulfide.

Subsequently, the solution was subjected to stirring while adding a 20 mL sulfuric acid solution (68% w/w) and mixed for an hour. Following this, a 10 mL $K_2Cr_2O_7$ solution (0.16 M) was introduced, and the solution was refluxed for an additional hour.

In the end, the solution is diluted to 100 mL, and an aliquot of 40 mL is used for titration with sodium thiosulfate (0.1 M) solution. The cellulose dissolved in the CS_2 is measured by the following equation:

$$Dissolved\ cellulose\ (\%) = \frac{\left(v1\ c1 - \left(v2\ c2 * \frac{100}{40}\right) * \frac{1}{6}\right) * M * \frac{1}{4} * \frac{100}{10.4}}{m} * 100 \qquad (1)$$

Where the following values are used:

v_1 is the volume of the $K_2Cr_2O_7$ solution; c_1 is the concentration of the $K_2Cr_2O_7$ solution; v_2 is the volume of $Na_2S_2O_3$ consumed; c_2 represents the concentration of $Na_2S_2O_3$; 100/40 is the dilution of the 40 mL sample to 100 mL; 1/6 corresponds to each dichromate ion that consumes six thiosulfate ions; M is the molecular weight of glucose (162 g/mol); ¼ means each glucose united consumed by four dichromate ions; 100/10.4 represents the 10 mL aliquot taken from the 100 g viscose liquid m is the oven-dry

weight of the pulp tested (g).

RESULTS AND DISCUSSION

Wood and recycled pulp composition

Wood consists predominantly of cellulose fibers, lignin, hemicellulose, and a diverse array of other organic compounds. The cellulose fibers are responsible for conferring strength and establishing the structural integrity of the wood, whereas lignin plays a crucial role as a binding agent. Hemicellulose, on the other hand, acts as a complex carbohydrate that aids in the cohesion of the cellulose fibers.

The production of wood pulp for dissolving passes by the removal of the different compounds and the isolation of cellulose fibers. In figure 2, the overall composition of the different pulps tested can be followed.

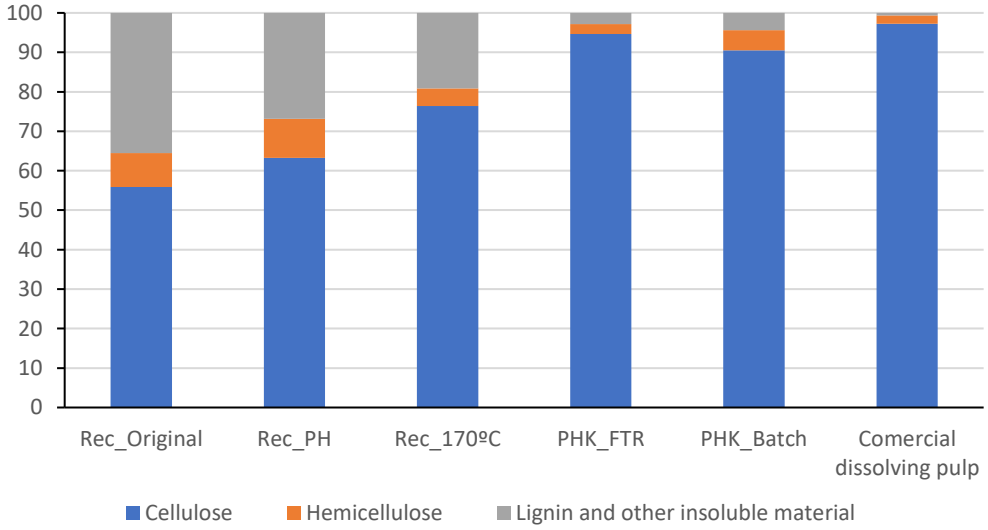

Figure 2 – Pulp composition, % of each component.

Comparing the recycled pulp samples (Rec_Original, Rec_PH, and Rec_170ºC), it can be observed that as the hydrolysis and chemical treatment are applied, the impurities are removed (43% to 24%). Despite the composition being far from the dissolving pulp commercial pulp, the cellulose proportion of this pulp improved from 55% to 74% of the biomass. However, the autohydrolysis process applied on the recycling pulp didn't enhance hemicellulose removal as anticipated; this process is mostly used in wood to remove most of the hemicelluloses, where the mild acid pH results from the release of acetic acid during hemicellulose degradation(5). For the recycled paper, the autohydrolysis was not so efficient and a dilute acid hydrolysis may be recommended. Nevertheless, the alkaline conditions and high temperatures used in the cooking stage enabled the removal of both lignin and hemicellulose in higher extent.

The composition of PHK pulps obtained using different pre-hydrolysis operating modes (batch vs flow through) shows a prominent distinction. The flow-through mode resulted in a pulp containing 94.7% cellulose, 2.5% hemicellulose, and 2.8% lignin. On the other hand, the batch system produced a pulp with lower cellulose content (90%) and higher hemicellulose (5%) and lignin (4.4%) proportions, approximately double the amount of hemicellulose and lignin compared to the flow-through reactor.

Intrinsic pulp Viscosity

Intrinsic pulp viscosity gives an estimation of the average degree of polymerization of the cellulose. Dissolving pulp requires a reduced viscosity compared to paper pulp to provide better reactivity and a homogenous solution of the dope after dissolution. In figure 3, the intrinsic viscosity of the pulps studied can be followed.

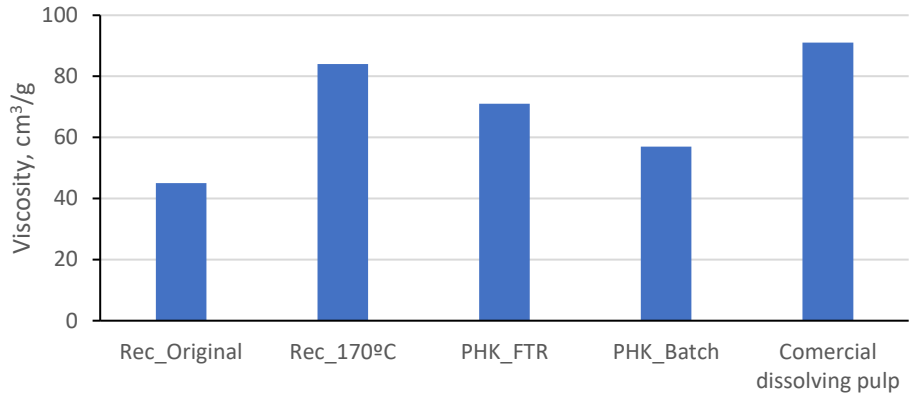

Figure 3 – Viscosity of the different pulps assessed.

The viscosity of cellulose fibers is influenced by reactions conditions to which it was submitted. As anticipated, the viscosity decreases when recycled paper undergoes chemical treatment (669 to 413 cm^3/g). The original recycled pulp already possesses a relatively low viscosity due to previous treatments it has undertaken. However, the chemical treatment employed, additionally reduced the value to the expected range for dissolving pulps (400-600 cm^3/g) (1) .

Regarding the virgin pulp, the enhanced removal of hemicelluloses in the flow-through pre-hydrolysis increases the exposure of fibers to the white liquor employed in the kraft stage. As a result, the cellulose fibers experience a higher reduction in viscosity compared to the pulp obtained from the batch reactor, in accordance with results achieved by other studies(16, 17).

The enhanced pre-hydrolysis resulted in a pulp with similar characteristics with the market dissolving pulp.

Reactivity

Reactivity is a measure of how easily a substance undergoes a chemical reaction. The relation between the pulps characteristics and the reactivity is resumed in the table 1.

Table 1- Reactivity, hemicellulose content, and viscosity of the different pulps.

	Reactivity, %	*Hemicellulose content, %*	*Intrinsic viscosity, cm^3/g*
Rec_original	45	8.70	669
Rec_170ºC	84	4.40	413
PHK_FTR	71	2.50	549
PHK_Batch	57	5.10	874
Commercial Dissolving pulp	91	2.10	474

Pulp reactivity can be dependent on a wide variety of factors; in this case, the hemicellulose content and viscosity values were analysed. There are two pulps that don't follow the behaviour of the others.

The Rec_170ºC pulp despite having a high hemicellulose content, it's the second pulp with higher reactivity. Regardless of displaying different relationships between the two parameters compared to the other pulps, it is evident that the low viscosity has a greater impact than the hemicellulose content. The same result can be observed in the PHK_Batch pulp; in this pulp, despite having a similar hemicellulose content with the Rec_170ºC (5.1% and 4.4%), the reactivity is lower (57% and 84% respectively), highlighting the effect of the viscosity value of the pulps on the reactivity. PHK_Batch pulps have almost 2-folded the viscosity value of the Rec_170ºC pulp.

The results go in concordance with other studies(9, 17), where the lower viscosity pulps allowed better penetration and diffusion of the solvents into the crystalline structure of cellulose, leading to improved chemical reactions. However, viscosity is not the sole determinant of reactivity and additional studies must be conducted.

CONCLUSION

This study aimed to evaluate the effect of pre-hydrolysis conditions on dissolving pulps characteristics, using a flow-through reactor and a batch reactor to carry out the pre-hydrolysis. The utilization of a flow-through reactor led to enhanced hydrolysis, resulting in pulps with reduced hemicellulose content and viscosity in comparison to the batch reactor. Furthermore, the Fock reactivity was significantly affected, with the PHK flow-through pulp achieving a reactivity of 71%, whereas the batch pulp exhibited a lower reactivity of 57%.

The parallel study with recycled pulp allowed us to evaluate the effect of chemical treatment on the Fock reactivity. The low-viscosity fibers present in the recycled pulp seem to enhance the reactivity towards the method evaluated. Throughout the chemical treatment, the impurities and hemicellulose content also dropped while the Fock reactivity increased from 45% to 84%, showing the benefits of using this method for potentializing the use of recycled pulp to produce dissolving pulp.

Nevertheless, additional research is required, particularly to examine the fiber characteristics that exert the most influence on pulp reactivity. In this initial investigation, viscosity appears to be the more prominent parameter. However, comprehensive studies are necessary to gain a deeper understanding of other fiber attributes and their impact on pulp reactivity.

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