

ENHANCED SELECTIVITY OF OXYGEN DELIGNIFICATION
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Natural polysaccharide-based gums produced by plants in response to biotic or abiotic factors are used in various industries due to their biodegradability, renewability, biocompatibility, and non-toxic properties. This study examined the use of these gums in a new application, such as adding them to the delignification liquor to decrease the negative effects of radicals formed during the oxygen delignification of stone pine kraft pulps. For this purpose, the effects of sweet cherry gum, both with and without hydrogen peroxide reinforcement, and guar gum on oxygen delignification were examined in this study. The addition of both gums, up to a certain usage level, increased the selectivity of the reaction and protected the viscosity from oxidative damage, while causing only a limited reduction in the kappa number during the delignification process. However, it was determined that cherry gum, in hydrogen peroxide-reinforced oxygen delignification was relatively limited, but increased pulp strength properties and better bleached pulp could be produced.

Keywords: oxygen delignification, cherry gum, guar gum, selectivity, chelating, environmentally friendly bleaching

INTRODUCTION

Due to environmental concerns, the pulp and paper industry is focusing on the development of alternatives to chlorine and chlorinated chemicals in the bleaching process. Oxygen delignification is widely preferred as an extension of the pulping or the first stage of bleaching,¹ with its benefits, such as the compatibility of the wastewater from alkaline oxygen delignification with the recovery process of kraft pulp production, the production of moderately bleached pulp, and its economic and ecological viability.²⁻⁷ The lower lignin content achieved through oxygen delignification allows for a decreased amount of active chemicals needed for bleaching the pulp.⁸ Although it is known to be intensively used industrially after the kraft pulp production process, its potential also extends to other pulping processes, including sulfite, of secondary fibre, and even annual plants.^{6,9-11}

The earliest phases of oxygen delignification exhibit adequate reaction selectivity, which subsequently diminishes because of radical formation, in the presence of transition metals (iron, copper, manganese, *etc.*). This leads to a competition between lignin removal and carbohydrate degradation after 50% delignification.¹² Therefore, commercial delignification should be terminated before the kappa number drops to about 40-50% for unbleached pulps.¹³⁻¹⁵

Several efforts have been performed to enhance the selectivity of oxygen delignification. These include optimizing process parameters, such as those discussed by McDonough,² Cao *et al.*¹⁶ and Heiningen *et al.*¹⁷ Both Samuelson and Otjeg,¹⁸ and Danielewicz¹⁹ investigated the pretreatment of unbleached pulp to improve its selectivity. Additionally, the use of additives to

enhance the efficiency of oxygen delignification has been reported by Suchy and Argyropoulos,²⁰ Gaspar *et al.*,²¹ Peşman *et al.*²² and Gümüşkaya *et al.*²³ The kinetics of oxygen delignification has also been investigated by Heiningen and Violette,²⁴ and Ji.²⁵ Cellulose protectants, such as phenol/MgSO₄,²⁶ or ethoxy-based alcohol surfactants,²⁷ were also studied.

The finding that there is a relationship between the hemicellulose content in the pulp and the selectivity of the reaction in oxygen delignification²⁸ has attracted considerable interest. The study concluded that hemicelluloses, particularly xylan, have the potential to act as protective agents throughout the process of delignification. Based on this research, Heiningen and Violette²⁴ proposed another hypothesis, that polysaccharide-based polymers like guar gum (GG) could produce a similar effect in oxygen delignification. Accordingly, it was concluded that aqueous solutions of homogeneously dispersed additives were unable to react with the radicals. Therefore, it is ideal for the additives to adsorb onto cellulosic surfaces, thereby creating a protective barrier against the radicals. Gümüşkaya *et al.*²³ found that plum gum (PG) applied in oxygen delignification could have similar effects to GG and that increasing its usage improved selectivity. One of the important findings of the study was in the crystallinity of the pulp, which increased with the use of gum. Heiningen and Violette²⁴ outlined the characteristics of an optimal additive for serving as a protective barrier, including the ability to adsorb on cellulose surfaces, forming complexes with transition metals, resisting oxidation by oxygen, adsorption at high pH levels, penetrating fibre pores due to its appropriate size and being compatible with the recovery process with cost-effectiveness.

The sweet cherry tree, known as *Prunus avium* L., is a tree species that has a broad geographic range in Western Asia, including Turkey and the Caucasus, and a major part of Europe.²⁹ According to FAOstat data for 2022, 454644 ha of cherry species were harvested worldwide. The tree is mainly cultivated for its nutritious fruits, but it is also used for landscaping purposes and wood production. Cherry gum is harvested from the trunks and branches of trees. Although cherry gum was initially used in technical applications, it was later replaced by gum arabic obtained from acacia for these purposes. As a result, it is no longer harvested or used for industrial

applications today, and there is no recorded data on the annual global harvest.

Cherry gum (CG), as a by-product of the fruit distribution industry, is typically gathered during the off season.²⁹ Numerous studies have explored its use as an additive for various applications, including emulsifiers, stabilizers, thickening agents and edible coatings in the food industry. The phenolic content of the polymer varies depending on geographical location, meteorological variables, and harvest season.³⁰⁻³³ In a study conducted by Shabani *et al.*,³⁴ the gas chromatography analysis of CG identified the relative molar ratios of mannose (Man), arabinose (Ara), galactose (Gal), and xylose (Xyl) as 1.0:14.7:7.1:2.4, respectively. The concentration of uronic acids was quantified using spectrophotometry and found to be 11%. The molecular weight (Mw) of *Prunus avium* L. was calculated as 2.99 10⁵ g/mol by Amarioarei *et al.*³⁰

Although studies have shown that gums used as additives in oxygen delignification improve selectivity, research on the effects of polysaccharide-based polymers in this process is limited, and there are no studies investigating the use of CG to neutralize radicals during oxygen delignification. This research suggests that CG could have potential to improve mechanical properties of delignified fibers comparably to PG and GG. To explore this, the study separately examined how the addition of CG and GG affects the selectivity and mechanical properties of softwood kraft pulp during oxygen delignification. Additionally, the effects of CG reinforcement in hydrogen peroxide-enhanced oxygen delignification were also studied.

EXPERIMENTAL

Raw materials

Stone pine (*Pinus pinea* L.) was used for pulping. It is an evergreen tree of the *Pinus* genus in the *Pinoidae* subfamily. This species, known as 'stone pine' in English, 'pin pignon' in French, and 'pino domestico' in Italian, typically grows between 10 to 25 meters. Its natural range extends from Portugal and Spain to Anatolia, and from North Africa to Dalmatia. Indigenous to southern Europe and Anatolia,^{35,36} it grows in both pure and mixed forests. The wood features distinct heartwood, variable annual rings, longitudinal tracheid and thin-walled epithelial cells and small transverse resin canals.³⁷

After removing knots and defects, the pine logs were cut into 2-3 cm thick disks, which were then cut into 2-3 cm wide pieces for chipping. These pieces

were further processed into 2-4 mm thick chips using hand tools. The chemical composition of the stone pine used in this study is described in a previous study.³⁸

The dimensions of the wood fibre used in this study were morphologically determined in a previous study by Erişir.³⁹ According to this, the wood fibre has a length of 2.57 mm, a width of 37 μm , a lumen width of 22 μm , and a wall thickness of 6.5 μm . The slenderness ratio was found to be 69.45, the flexibility ratio – 59.45, and the Runkel ratio – 0.59.

Fresh cherry exudate gum was collected from the trunks and branches of the trees in spring in Trabzon, Turkey. The gum was stored under controlled conditions in a refrigerator to preserve its light colour and prevent excessive oxidation until it was used. GG in powder form was commercially obtained. All other chemicals were of analytical grade and were used without further purification.

Pulping process

The kraft pulp method was preferred to produce bleachable pulp (Fig. 1). In the kraft pulping process, the active alkali ratio was 18%, the sulfidity was 25%, the temperature was 170 °C and the solid/liquid ratio was kept at 1:4. The pulping time was 90 min. The cooking process was carried out in a laboratory stainless steel rotary reactor with a capacity of a 15 L capacity, a pressure resistance of 25 kg/cm², automatic temperature control, electric heating and the ability to rotate twice per minute. The reactor was filled and discharged by hand. The resulting pulp mixture was then discharged onto a 200 mesh (0.074 mm) washing screen and thoroughly washed with tap water. The washed pulp was disintegrated in a mechanical stirrer and then screened to determine the screened pulp yield, rejection rate and total yield. The screened pulp was dewatered and stored in polyethylene bags at 4 °C until further processing.

Oxygen delignification process

The optimum conditions for the oxygen delignification (OD) process without any additions were determined by optimization studies. For the gum-reinforced delignification processes (ODC: CG reinforced OD, ODC+P: CG and H₂O₂ reinforced OD and ODG: GG reinforced OD), the gums were initially dissolved in distilled water (10 wt%) being introduced into the delignification liquor. The solution was mixed using a mechanical stirrer to ensure a clear solution. It was then purified by filtering through a 100-mesh metal sieve to remove any impurities.

Oxygen delignification processes were conducted in the same manually controlled reactor used for pulping. Temperature was controlled within the range of 1.00±0.2 °C by a digital processor system, which also featured a pressure control relief valve. The delignification was carried out under consistent conditions: a temperature of 90 °C, oxygen pressure of 7 bar, processing time of 60 minutes, 1% MgSO₄ content and 12% pulp concentration. Each process used 100 g of oven-dried pulp. Once all inputs were mixed in the reactor, oxygen was introduced to the reactor at the room temperature via a hose. Table 1 provides a symbolic representation of the constant and variable parameters used in the experimental systems for oxygen delignification and its variations.

The pH of the black liquor was measured following the delignification process. The delignified pulp was extensively washed with tap water using a 150-mesh screen until all black liquor was removed. The washed pulp was manually squeezed to ensure uniform moisture distribution, and each bleached pulp was placed in a plastic bag. The pulps were sealed and kept closed for 24 hours to allow for moisture equilibration.



Figure 1: Procedure to produce pulp exhibiting high properties

Table 1
Experimental design and conventional denotation of oxygen delignification processes

Process*	Process conditions	Symbolic representation				
ODn series	NaOH (%): 1, 2, 3, 4, 5	OD1	OD2	OD3	OD4	OD5
ODCn series	NaOH (%): 3 CG (%): 1, 2, 3, 4, 5	ODC1	ODC2	ODC3	ODC4	ODC5
ODCn+P series	NaOH (%): 3 CG (%): 2 H ₂ O ₂ (%): 0.5, 1, 2, 3, 4	ODC1+P	ODC2+P	ODC3+P	ODC4+P	ODC5+P
ODGn series	NaOH (%): 3 GG (%): 1, 2, 3, 4, 5	ODG1	ODG2	ODG3	ODG4	ODG5

*ODn: Oxygen delignification without any reinforcements; ODCn: CG reinforced oxygen delignification; ODCn+P: CG reinforced oxygen delignification, and ODGn: GG reinforced oxygen delignification

Pulp characterization

The following equations were used for calculating the yield of pulping and delignification processes:

$$\text{Screened yield of pulp (\%)} = A \cdot B^{-1} \quad (1)$$

$$\text{Total yield of pulp (\%)} = C \cdot B^{-1} \quad (2)$$

$$\text{Rejected yield of pulp (\%)} = (C - A) \cdot B^{-1} \quad (3)$$

$$\text{Process yields of delignification (\%)} = D \cdot E^{-1} \quad (4)$$

where A: the weight of dry pulp passing through the screen after the pulping process (g) – output; B: the weight of the dry chips used in the pulping process (g) – input; C: the weight of total pulp from the reactor after pulping process (g) – input; D: the weight of the dried pulp obtained after oxygen delignification (g) – output; E: the weight of the dried pulp obtained before oxygen delignification (g) – input.

The kappa number and intrinsic viscosity (η) of the pulp were determined by TAPPI T 236 om-99 and SCAN-CM 15:88 standards (Scan Test Methods), respectively. The degree of polymerization (DP) of cellulose in pulp was calculated from intrinsic viscosity by applying the Immergut formula presented below:

$$DP^{0.905} = 0.805 [\eta] \quad (5)$$

The process selectivity (S), delignification ratio (L) and the ratio of viscosity reduction (K) reduction for oxygen delignification were calculated according to the literature:^{22-25,28}

$$L = (K_0 - K_1) \times 100\% \times K_0^{-1} \quad (6)$$

$$V = (V_0 - V_1) \times 100\% \times V_0^{-1} \quad (7)$$

$$S = (K_0 - K_1) \times (1/DP_1 - 1/DP_0)^{-1} \quad (8)$$

where K_0 and V_0 are the kappa number and viscosity of the pulp before oxygen delignification, K_1 and V_1 are

the kappa number and viscosity of oxygen delignified pulp, respectively. DP_0 is the polymerization degree of kraft pulp, while DP_1 is that of delignified pulp.

Preparation and characterization of handsheets

After delignification, handsheets of approximately 60 g/m² of each pulp sample were prepared on a Rapid Köthen Sheet Making Machine according to TAPPI T 205 sp-12 (2018). Before preparing the handsheets, the pulp was initially exposed to a 2-stage beating procedure (TAPPI T 200 om-89 standard) in a Valley type beater for 9 and 12 minutes. The Schopper-Riegler Freeness Tester was used to determine the degree of freeness according to the SCAN-C20:65 standards.

Unbeaten and beaten pulp samples were used to produce handsheets. Results from each physical test conducted on the handsheets were recorded individually in terms of SR°. Values corresponding to 50 SR° were then computed through interpolation. The grammage and thickness properties of the handsheets were determined according to TAPPI T 410 om-88 and TAPPI T 411 om-89 standards, respectively. The handsheets were conditioned according to TAPPI T 205 sp-12 (2018) at 23±1 °C and maintained in a room with 50±2% relative humidity overnight before testing. The mechanical and optical tests listed in Table 2 were performed on the conditioned handsheets. Each measurement was carried out using ten handsheets.

Table 2
Mechanical and optical tests and standards applied to handsheets

Mechanical and optical properties	Standards
Breaking length (km)	TAPPI T 494 om-88
Burst index (kPa.m ² /g)	TAPPI T 403 om-91
Tearing index (mNm ² /g)	TAPPI T 414 om-88
Opacity (%)	TAPPI 425 om-91
ISO Brightness (%)	TAPPI T 452 om-88

Statistical analysis (one-way ANOVA)

The data was subjected to statistical analysis using the one-way analysis of variance (ANOVA), with IBM SPSS version 11 software. If the simple analysis of variance indicated a statistically significant difference among the groups, the Newman-Keuls test was employed.

RESULTS AND DISCUSSION

Results of the pulping process

To produce pulps intended for oxygen delignification, stone pine wood was chipped according to the standards and the chips were subjected to kraft pulping with 18% active alkali, 25% sulfidity, at a temperature of 170 °C and a solid/liquid ratio of 1:4. The properties of the pulps, such as viscosity, kappa number and yield, were assessed. The kappa number, a crucial parameter for process analysis in industrial settings,⁴⁰ is used to determine the required amount of chemicals for subsequent delignification and bleaching processes.⁴¹ The expected kappa number for a bleachable pulp in pulping ranges between 25% and 55%.^{40,42} After pulping, the kappa number of the pulp was found to be 32.1. On the other hand, the screened yield was determined to be 46.8%. MacLeod⁴³ and Segura *et al.*⁴⁴ have reported similar findings, highlighting the relationship between yield and kappa number in kraft pulping. An increase in kappa number indicates a higher amount of residual lignin in the pulp. This residual lignin also corresponds to additional hemicellulose retention due to the complex interactions between lignin and carbohydrates within the cell wall. Extending the pulping time to achieve a lower kappa number, particularly during the residual delignification phase, can negatively impact both yield and viscosity. The pulp viscosity was found to be 859.40 cm³/g, and previous studies have identified a relationship between pulp strength and viscosity.

Alkali charge optimization of oxygen delignification

Kraft pulps were subjected to oxygen delignification with varying alkaline charge from 1% to 5% to determine the optimum alkaline charge for delignification. The other process parameters were closely aligned with those used in traditional mill scale application, including a pulp consistency of 12%, a reaction temperature of 90 °C, a reaction time of 60 minutes, an oxygen pressure of 7 bar, and the addition of 1%

MgSO₄. Table 3 presents the results of the oxygen delignification process for the pulps treated with different alkali charge.

The alkali charge has a direct impact on pulp characteristics.⁴⁵ The selectivity of the reaction decreases when oxygen delignification is carried out at a high alkali charge,⁴⁶ leading to significant losses in cellulose polymerization due to attacks on the carbohydrate fraction.⁴⁷ As shown in Table 3, as the alkali charge increases during oxygen delignification, both the rates of delignification and of viscosity reduction also increase, as expected.

Jafari *et al.*⁴⁸ and Li *et al.*⁴⁹ created a model to predict variations in the kappa number for different alkali charges. The model, which is based on the calculation of residual lignin and delignification rate, revealed a correlation between the alkaline charge and the experimentally observed delignification rate. Other studies demonstrated that increasing the alkali charge during oxygen delignification enhances lignin removal and increases cellulose degradation, despite the pulp concentration and time remaining constant.⁵⁰ The reason is that higher alkali levels intensify reaction conditions, leading to oxidation, fragmentation, and dissolution of cellulose molecules as smaller fragments, along with lignin.⁵¹

The rate of increase in the delignification decreased from 54.8% to 58.3% after using 3% alkali charge. Using additional alkali had a negligible effect on the amount of lignin removed, while viscosity losses of 8% or more were observed. Zhang *et al.*⁵² reported that raising the alkali charge during the soda-oxygen delignification process led to a reduction kappa number and an increase in pulp brightness.

Increased hydroxyl ion concentration typically plays a more significant role in promoting the depolymerization of cellulose rather than delignification during chemical processes.⁵³⁻⁵⁴ In accordance with the literature, increasing the alkali charge up to 3% led to the removal of more than half of the residual lignin in the kraft pulp, while maintaining an acceptable reduction in viscosity. After evaluating the effect of alkali charge on both total yield and selectivity, the OD3 method was selected as baseline for applying gum and peroxide additions in this study.

Table 3
Alkali charge optimization in oxygen delignification
(viscosity and kappa number of stone pine kraft pulp were 859.4 cm³/g and 32.1, respectively)

Method	[η]	Kappa number	Yield (%)	Delignification ratio (L, %)	Viscosity reduction (K, %)	Process selectivity (S) (Sx10 ⁻⁴)
OD1	871	24.6	96.2	23.4	-1.3	-64.8
OD2	833	17.5	96.2	45.5	3.1	52.9
OD3	807	14.5	95.7	54.8	6.1	31.1
OD4	792	13.6	94.5	57.6	7.8	24.9
OD5	790	13.4	93.7	58.3	8.1	24.4

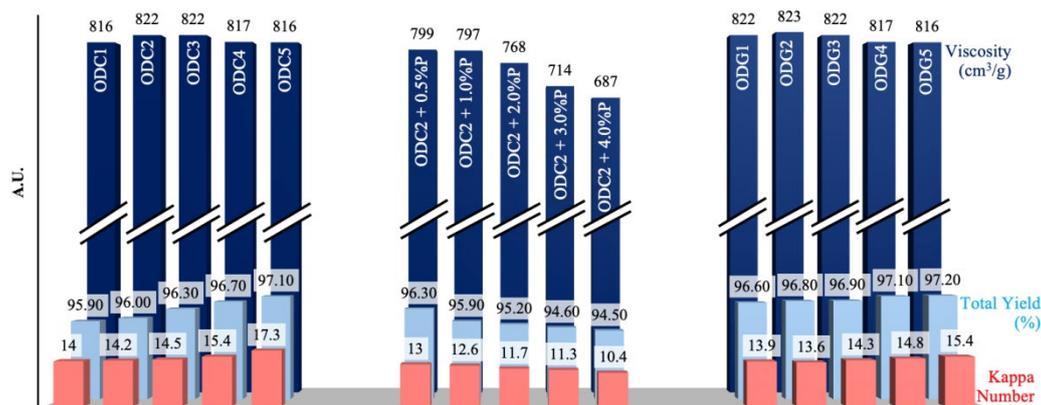


Figure 2: Effect of additives on some properties of stone pine kraft pulps during oxygen delignification (the viscosity of stone pine kraft and OD3 pulps was 859.4 and 807 cm³/g, and kappa numbers were 32.1 and 14.5, respectively)

Reinforced oxygen delignification – effects of additives on chemical properties of pulps

The main research objective of the study was to investigate the effects of adding CG (1-5%) on oxygen delignification of kraft pulp, both with and without hydrogen peroxide reinforcement (0.5-4%). Additionally, the impact of adding GG was also assessed under the same conditions as CG, but without any additional reinforcement. The results of these processes are shown in Figure 2. It was observed that all treatments resulted in at least a 50% reduction in lignin content compared to the kraft pulp (with a kappa number of 32.1).

Initially, the addition of gums, which are water-soluble hemicellulosic substances with a low degree of polymerization, to the oxygen delignification process led to a decrease in the resulted kappa number, while viscosity and total yield exhibited only a slight increase. The kappa number, which was 14.5 for OD3, initially decreased with the addition of both gums, but then increased, particularly when the addition exceeded 3%. Numerous studies have indicated a correlation between pulp yield and kappa number, possibly due to the presence of covalent linkages between polysaccharides and lignin in the pulp.⁵⁵

It is believed that, at high concentrations, the gums form a denser layer on the fibre surfaces. The molecular size of polysaccharide-based polymers, which allows them to penetrate the fibres, may explain the phenomenon. Consequently, they help preserve the benzyl ester linkages between polysaccharides and lignin, especially in the inner layers of the cell wall. Gümüşkaya *et al.*²³ investigated the effects of PG during oxygen delignification and found that when the gum concentration reached 3% or higher, the kappa number increased. This was attributed to the gum's barrier effect, which hinders oxygen diffusion to the fibre wall.

Zou *et al.*²⁸ observed that pulps with xylan content are more resistant to delignification, but demonstrate greater selectivity compared to pulps with a low xylan level. The researchers attributed this effect to the reduced accessibility of lignin during oxygen delignification due to the higher xylan concentration. Additionally, the improved delignification ratio with gum additions may be explained by the reduced degradation of the linkages between polysaccharides and lignin. They are also responsible for the observed

improvement in delignification yield when both gums are utilized.

Figure 2 revealed another important finding regarding pulp viscosity. The addition of gum to the oxygen delignification process increased the viscosity of OD3 pulp ($807 \text{ cm}^3/\text{g}$), leading to an improvement of approximately 1-2%. When gums were added during oxygen delignification, viscosity increased by about 1-2% in OD3 pulp ($807 \text{ cm}^3/\text{g}$). For both gums, it is important to maintain or slightly increase pulp viscosity, while reducing the kappa number when used at low concentrations up to 3%. Zou *et al.*²⁸ reported that hemicellulose-based polymers, particularly xylan, act as viscosity protectors for cellulose. In other words, they demonstrated that a high hemicellulose content in pulp minimizes cellulose degradation, thereby increasing viscosity. Heiningen and Violette²⁴ investigated the impact of GG on oxygen delignification and determined that higher intrinsic viscosities were obtained as the gum loading increased. They stated that using GG at a 2% level resulted in an approximately 30% increase in lignin-cellulose selectivity, regardless of the alkali charge. Similarly, Gümüřkaya *et al.*²³ revealed that adding PG to oxygen delignification liquor significantly stabilized carbohydrates. The phenomenon is very

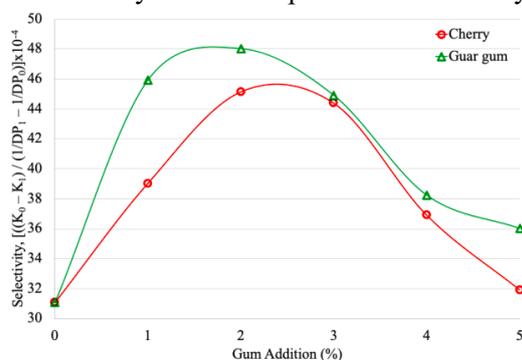


Figure 3: Effects of gum additions on selectivity parameters of oxygen delignification

The studies indicate that oxygen is more reactive towards scavenging agents than they are towards the carbohydrates in cell walls.^{22,56-58} Various substances, including alcohols, poly-alcohols, aldehydes, organic acids, and polymers have previously been employed as scavenging agents.

The selectivity of the GG yields better results compared to that of the CG. The main reason for this difference between gums may be their molecular structure. GG is mainly composed of hemicellulosic components based on

similar to the one that leads to a rise in the kappa number. During delignification, radicals effectively degrade fibres, especially at their surfaces. The reduced permeability of the fibre surfaces limits both oxygen and radical diffusion. The main similarity between these studies is the improved selectivity in oxygen delignification achieved using gums. With the CG and GG used in this study, it was observed that selectivity increases up to a certain additive ratio and then decreases (Fig. 3).

The impact of gum additives on the selectivity parameters of oxygen delignification, as demonstrated by the addition of 2% CG (as shown in Fig. 3), led to further exploration of how hydrogen peroxide influences 2% CG reinforced OD3. The reaction variables of the ODC2 process were chosen as constant due to the low kappa number and similar viscosity, and the effects of hydrogen peroxide in the range of 0.5-4.0% were studied under these conditions. Figure 4 clearly demonstrates that the addition of H_2O_2 produces a negative impact on selectivity, even at a concentration as low as 0.5%. Initially, the viscosity of ODC2 pulp ($822 \text{ cm}^3/\text{g}$) did not have much effect, but it decreased dramatically by 16.5% as the amount of peroxide added increased.

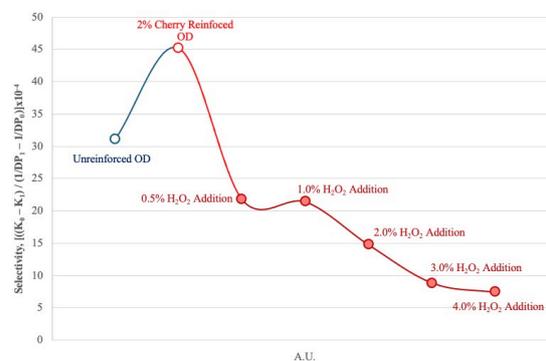


Figure 4: Effects of hydrogen peroxide additions on selectivity parameters of 2% CG reinforced OD3

galactomannan (75.0-85.0%).⁵⁹ Galactomannan is also present in the CG structure, but most of the structure (65%) consists of pentosan-rich monomeric sugars, such as arabinose and xylose.⁶⁰ The sorption of mannan is believed to be greater than that of arabinose-dominated CG, due to the comparable structure of the backbones in mannan and cellulose.⁶¹ These results led to the hypothesis that hexosan-type hemicellulosic structures would have a somewhat greater efficacy in scavenging radicals.

Reinforced oxygen delignification – effects of additives on physical, optical and mechanical properties of pulps

To evaluate the effects of different additives on oxygen delignification, physical, mechanical and optical tests were applied to handsheets produced from Kraft, OD3*, ODC2*, ODG2* and ODC2+1.0P* pulps. The pulps marked with * are the ones with the highest chemical properties

within their series. The pulps were beaten to 50 SR° for producing handsheets. The physical and optical test results are listed in Table 4. Figure 5 shows the results of mechanical tests of the pulps. The Newman-Keuls test was also applied when significant differences occurred according to a fundamental analysis of variance.

Table 4
Effects of additives on the physical and optical properties of oxygen delignified unbleached pine kraft pulp

Sample code	Paper weight (g.m ⁻²)	Thickness (µm)	Density (kg.m ⁻³)	Opacity (%)	Brightness (%)
Kraft pulp	64.83 (2.48)	74.93 (3.65)	865	92.76 (0.91)	30.04 (0.46)
OD3	64.60 (1.90)	78.00 (2.73)	828	83.84 (0.75)	49.69 (0.47)
ODC2	59.90 (5.20)	77.82 (5.05)	769	84.27 (1.68)	49.71 (0.56)
ODC2+1.0%P	65.70 (2.70)	79.12 (3.63)	830	80.41 (1.26)	54.59 (0.31)
ODG2	67.10 (1.20)	81.30 (2.40)	825	85.20 (0.69)	48.88 (0.27)

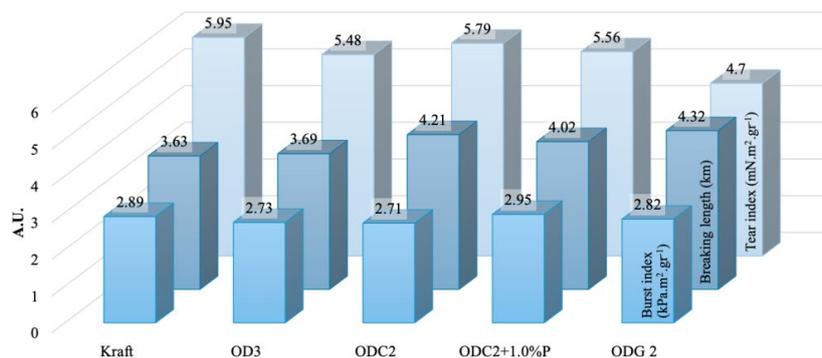


Figure 5: Effects of additives on the mechanical properties of oxygen delignified unbleached pine kraft pulps

The main objective of oxygen delignification is to reduce the residual lignin concentration to obtain an easily bleached pulp, with low chemical consumption in the bleaching process. This process is essentially like the continuous soda-oxygen pulping. The degree of improvement in optical brightness (by 15-20% ISO) depends on factors such as the type of raw material, pulping method, and amount of residual lignin in the pulp.⁴⁷

The Kappa number of the pulps shown in Figure 2 confirms that the selected pulps exhibit the most significant lignin reduction when compared to the other pulps. In this study, an improvement of 24.55% in brightness was

achieved for ODC2+1.0 P (Table 4). It is known that pulp brightness is most affected by the chromophoric groups in the residual lignin.⁶² Chromophores are highly light-absorbing groups, and for the pulp to achieve acceptable brightness levels, it must be entirely free of these groups.⁶³ Chromophore degradation can be provided by perhydroxyl groups (HOO).⁶⁴ The presence of peroxide and perhydroxyl groups in the oxygen delignification liquor served as a reinforcement with their oxidizing ability, leading to a brighter pulp. Koç *et al.*¹¹ reported that comparing peroxide reinforced oxygen delignification with unreinforced process showed an approximate 20% improvement in brightness. The ODC and

OD3 pulps exhibited similar brightness results, both showing an improvement of approximately 20%. Surprisingly, ODG2 pulp, despite having the lowest kappa number, deviated significantly from the expected level, showing a brightness of 48.99%. The results demonstrated the flexibility usage of gums in oxygen delignification and their beneficial impact on the optical properties of pulp. This method offers a promising and effective option for the paper and pulp industry, while also being environmentally sustainable.

The breaking length of stone pine kraft pulp showed a limited increase, of approximately 1.65%, after oxygen delignification (OD3) without reinforcements. The impact steadily increased with reinforcements, reaching a peak of 19.00% for ODG2. The addition of CG resulted in an increase in the breaking length of kraft pine pulp from 3.63 (± 0.62) km to 4.21 (± 0.65) km and 4.02 (± 0.48) km, respectively.

Oxygen delignification is mostly conducted under alkaline reaction conditions,¹ resulting in major lateral swelling of fibres, leading to changes in their bonding properties and strength.⁶⁵⁻⁶⁶ Moreover, incorporating polysaccharide-based gums into the multilamellar structure of the fibre cell wall can improve fibre flexibility by disrupting the hydrogen bonding network between microfibrils and inducing additional swelling of the cell wall. The increased cellulose crystallinity by oxygen delignification,²³ along with these effects, is believed to significantly influence breaking length.

On the other hand, no significant difference was observed between the pulp samples in terms of the burst index. It was determined that there was a loss of approximately 5.5-6% for OD3 and ODC2 pulps, compared to the kraft pulp. It was observed that the amount of loss in burst index with GG decreased to around 2.5%. Notably, there was a 2.08% rise in burst index seen for ODC2 when reinforced with peroxide.

The tear index is significantly impacted by decreases in pulp viscosity⁶⁷⁻⁶⁸ and fibre length. Unbleached kraft pulp exhibited the highest tear index (5.95 mN.m².g⁻¹), as well as the greatest viscosity, compared to all the other pulps. Studies indicate that radicals, particularly HO⁻, target not only lignin, but also carbohydrates, leading to reduced strength, viscosity and yield of pulp.^{24,69-70} Furthermore, Yang *et al.*⁴ observed that after oxygen delignification of softwood kraft pulp fibers with a kappa number of 30, there was a general reduction in average fibre length and an

increase in fines content of up to 98.3%. It was found that the addition of CG can reduce some of the negative effects on tear index of the pulp during oxygen delignification, while the addition of GG can cause losses of up to 21%. Erişir *et al.*⁷¹ and Spönlä *et al.*⁷² reported that an increase in the hemicellulose content in fibres has an adverse impact on strength properties.

As a result, the mechanical test results of the oxygen delignified pulps reveal complex effects on pulp strength when additives are used in the oxygen delignification of kraft pulp. A thorough understanding of the complex relationship between delignification, fibre properties, and additive usage can be attained by optimizing process parameters, conducting detailed analyses of fibre morphology and chemistry, and performing long-term aging studies. It is also important for future research to determine the environmental impact assessments.

CONCLUSION

Kraft pulping of stone pine wood chips was performed using 18% active alkali, 25% sulfidity, at 170 °C, and a 1:4 solid/liquid ratio, yielding pulps with a kappa value of 32.1 and a screened yield of 46.8%. Oxygen delignification with 1%-5% alkaline charge was applied, with the OD3 process (3% alkaline charge) chosen as the standard due to cellulose degradation at higher alkaline levels.

To assess the effects of gums on pulps, gum loading varied from 1% to 5%. The study also explored the impact of CG on oxygen delignification with hydrogen peroxide (H₂O₂) concentrations from 0.5% to 4%. Initially, gum addition reduced the kappa number, but delignification slowed beyond 3% gum due to the barrier effect on fibrils. Gums also improved pulp viscosity by 1-2%. The results showed that oxygen delignification with GG was more selective than with CG, likely due to GG's smaller molecular size and higher radical-scavenging efficiency. In oxygen delignification, the addition of only 1% peroxide to the reaction medium reduced the process selectivity from 45% to 5%, although the kappa number decreased by 1.9 units.

Physical, mechanical, and optical tests on handsheets made from the selected pulps (Kraft, OD3, ODC2, ODG2, and ODC2+1.0P) were conducted to assess the effects of additives on fibres. The pulp strength was found to be enhanced by the addition of both gums. The OD3

pulp exhibited a 1.65% greater breaking length than the stone pine kraft pulp, whereas the breaking length of the oxygen delignified pulp reinforced by both gums showed even greater increases. By using H₂O₂ reinforcement, the ODC2+1.0P pulp demonstrated a significant 24.55% increase in brightness, as expected. Additionally, it exhibited a smaller gain in the breaking length, reaching just 10.7%. GG addition led to a 26% decrease in the tear index and a slight drop in the burst index.

The study shows that plant-based additives, like wood gum, enhance the selectivity of oxygen delignification, offering benefits for sustainability and product quality. Adapting and optimizing this process can lead to a more efficient and eco-friendly solution for the pulp and paper industry. To fully understand process value, a life cycle assessment (LCA) is recommended.

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