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Fireproof Paper Production from Turkish Red Pine (*Pinus brutia* Ten.) Using Fire Retardants

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Abstract

Aim of study: It was our aim to produce fireproof papers from Turkish Red Pine (*Pinus brutia* Ten.) using eco-friendly pulping method and fire retardant chemicals (FR).

Area of study: This work was carried out in Kahramanmaraş Sütçü Imam University, Faculty of Forestry, Pulp and Paper Production Laboratory.

Material and Methods: Three different pulping trials were carried out with soda-anthraquinone method (AQ) and the kappa numbers, viscosities, yields, and optical and physical properties of the pulps were determined in order to find out the optimum cooking condition. Borax (BX), boric acid (BA), alpha-x (AX), and ammonium polyphosphate (APP) were used as FR in certain rates (3, 6, 9%). FR applied papers were subjected to combustion test and the fire properties of the papers were determined as combustion rate.

Main results: The results indicated that addition of AQ to cooking liquor increased the pulp yield about 4.6%. Also, the kappa numbers of the pulps were decreased by adding AQ from 120 to 50. AQ addition had significantly effects on the physical properties of the paper. The best results in fire properties were obtained from BX (6%, 9%), BA (6%, 9%), and AX (9%), respectively.

Research highlights: Considering paper is a flammable material, increasing the fire resistance of papers is needed. In addition, production using environmentally friendly methods is required in the world where population and technology are increasing rapidly.

Keywords: Pinus brutia, anthraquinone, fire retardant, pulp and paper.

Kızılçam (*Pinus brutia* Ten.) Odunundan Yanmayı Geciktirici Kimyasallar Kullanarak Yanmaya Karşı Dirençli Kağıt Üretimi

Özet

Çalışmanın amacı: Bu çalışmanın amacı, yanmayı geciktirici kimyasallar ve çevre dostu yöntemler kullanarak kızılçam odunlarından (*Pinus brutia* Ten.) yanmaya karşı dirençli kağıtlar üretmektir.

Çalışmanın alanı: Bu çalışma Kahramanmaraş Sütçü İmam Üniversitesi, Orman Fakültesi, Kağıt Hamuru ve Kağıt Üretim Laboratuvarı'nda yürütülmüştür.

Materyal ve Yöntem: Soda-Antrakinon (AQ) metodu kullanarak 3 farklı pişirme yapılmış ve optimum koşulu belirlemek için elde edilen kağıt hamurlarının fiziksel ve optik özellikleri, kappa numaraları, viskozite ve hamur verimleri tespit edilmiştir. Boraks (BX), borik asit (BA), alfa-x (AX) ve amonyum polifosfat (APP) yanmayı geciktirici kimyasallar üretilen kağıtların alt ve üst yüzeylerine belirli oranlarda (%3, 6, 9) uygulanmıştır. Bu kimyasalların uygulandığı kağıtlar yanma testine tabi tutulmuş ve yanma oranları belirlenmiştir.

Sonuçlar: Elde edilen sonuçlara göre pişirme çözeltisine AQ ilavesi ile kağıt hamuru veriminde yaklaşık %4.6 oranında artış gerçekleşmiştir. Ayrıca, kappa numarası 120'den 50'ye düşmüştür. AQ ilavesi fiziksel özellikleri önemli derecede etkilerken optik özellikler üzerinde etkili olmamıştır. Yanmaya karşı en iyi direnç özelliklerini sırasıyla BX (%6, %9), BA (%6, %9) ve AX (%9) ilaveli kağıtlar vermiştir.

Araştırma Vurguları: Kağıt alev alabilen bir malzeme olduğu için yanmaya karşı direncinin arttırılması gerekmektedir. Buna ek olarak, nüfus ve teknolojinin hızla arttığı dünyada çevre dostu yöntemler kullanarak kağıt hamuru üretimi yapılmasına ihtiyaç duyulmaktadır.

Anahtar kelimeler: Kızılçam, antrakinon, yanmayı geciktirici, kağıt hamuru ve kağıt

Introduction

In the last 40 years pulp and paper industries effort to prevent air and water pollution from bleaching and pulping processes. Fundamental developments were accomplished for recent delignification processes. Furthermore, modified pulping process were developed to manufacture pulps, which are easily bleachable and eco-friendly (Bektas et al., 1999; Khristova, et al., 2006).

Pinus brutia is intrinsic to the eastern Mediterranean region. It mostly has a distribution area in Turkey, but it also spreads to other eastern Mediterranean countries such as Iran, Georgia, Cyprus, Israel etc. It is usually grown at 600 - 1.200 meters. Besides, it is rapidly growing species. It constitutes 15% of the forest areas of Turkey (Yorgun et al., 1990).

Various chemicals are added to cooking boilers to improve performance and durability properties. Some of these chemicals are not preferred due to the harmful to human health and the environment, and alternate methods are sought. The sodium sulfide used in the Kraft method adversely affects human health due to the bad odor and harmful effects on human health. (Tutus et al., 2016).

Anthraquinone (AQ) is used in alkaline pulping processes such as Kraft and Soda methods as an additive to increase yield. It is a redox catalyst and during pulping process AQ is oxidizing the reducing end groups of carbohydrates such as cellulose and hemicellulose. This prevents the carbohydrates from deteriorating (Samp, 2008).

As known, the paper products are quickly flammable and this makes them less interest for fire safety in buildings. To overcome this drawback, it can be treated with fire retardant chemicals.

Fire retardants (FR) are used in paper used in some applications such as laminating paper boards, honeycomb inserts for doors and wall, shopping papers in malls, markets, etc.

In 1820, Joseph Louis Gay-Lussac suggested some treatments with borax and ammonium phosphates in order to increase resistance to fire. Today, similar processes are using and many organic chemicals have also been applied as FR. Tin, phosphates, borates, silicates, zinc, and calcium based formulations were used for wood (Mclntyre et al., 2004). Boron compounds are used in wood impregnation processes (Ayrilmis et al., 2007; Winandy et al., 2008), and these compounds are used to increase the physical and optical properties of some papers and boards. (Tutus et al., 2016). The most common fire retardant chemicals are ammonium phosphates, boric acid, zinc chloride, sodium borate, borax, ammonium sulfate, antimony oxide, and phosphoric acid (Kozlowski et al., 1995; Ozdemir and Tutus, 2016).

In this study, some fire retardant chemicals were applied to paper obtained from *Pinus Brutia* with more environmentally friendly pulping process i.e. soda-AQ pulping, compared to kraft pulping. Combustion rates of the papers were reported. In addition, the physical and optical properties of the treated papers were also determined.

Material and Method

Material

This work was carried out in Kahramanmaras Sutcu Imam University Faculty of Forestry, Pulp and Paper Production Laboratory.

In this study, Turkish Red Pine (*Pinus brutia* Ten) was used as the raw material. The chemical analysis, raw material preparation, physical and optical properties and combustion tests of papers were determined according to the relevant methods. Chemicals used in this study were borax (BX), boric acid (BA), alpha-x (AX) and ammonium polyphosphate (APP) as fire retardant.

Determining Chemical Composition of *P. brutia*

Air-dried *P. brutia* chips were floured to 60 mesh fractions using mill and chosen to determine the chemical components in accordance with relevant TAPPI Standard Methods. The humidity, lignin, α-cellulose, ashes were determined following standards Tappi T 264 om-88, Tappi T 222 om-88, Tappi T 203 os-71, Tappi T 211 om-85, respectively. NaOH 1%, Ethanol-toluene and water solubilities were determined using Tappi T 212 om-98, ASTM D1107-96 (2013) and, Tappi T 207 om-88 respectively. The cellulose and holocellulose contents were determined according to Kurschner-Hoffer nitric acid and Wise's chlorite methods, respectively (Wise and Karl, 1962; Browning, 1967; Kurschner and Hoffer, 1993; Tutus et al., 2010).

Pulp and Paper Production

Air dried samples were chipped and cleaned from impurities. Three cooking experiments were performed on *P. brutia*, using soda-AQ process to determine optimum pulping condition (Table 1). Cooking experiments were done with a rotary digester. Obtained pulps were subjected to washing and screening on a 0.15 mm slotted screen in order to separate screen rejects. The pulps were beaten with hollander beater to 50±3 °SR (Schopper Riegler) freeness level. Then, ten papers with grammages of 70 g•m^{-2} per tested sequence were prepared using a sheet former (Rapid-Kothen) according to ISO 5269/2. The opacity (TAPPI T 425 om-96), brightness (ISO 2469), tear index (TAPPI T 414 om-12), breaking length (TAPPI T 494 om-01), burst index (TAPPI T 403 om-2), of papers were also investigated (Anon., 1992).

Table 1. Pulping conditions of *P. brutia*

Pulping Condition	Unit	Values
NaOH rate	%	25
AQ rate	%	0, 0.1, 0.3
Temperature	°C	165
Time to max. temp.	Min	40
Time at max. temp.	Min	120
Liquor/material	L/kg	5/1

Viscosity measurement of pulp plays an important role in identifying the characteristics of the pulp such as polymerization degree or cellulose chain length (Yasar et al., 2016), while the kappa number is an indication of the residual lignin content or bleachability of pulp. Viscosity and kappa number of the pulp were measured according to TAPPI T 230 om-08 and TAPPI T 236 om-13, respectively (Anon., 1992).

BX, BA, AX, and APP were impregnated to the paper surfaces in certain rates (3, 6, 9%). The impregnation was applied by using a roller brush and impregnated papers were dried overnight at room temperature. Then, the papers were exposed to flame for one second. The burnt areas were measured and combustion rates were determined.

Result and Discussions

Chemical Compositions of *P. brutia*

The chemical components of *P. brutia* were presented in Table 2 with those of some wood species and annual plants. The holocellulose, cellulose, and alpha cellulose content of *P. brutia* were found to be higher than that of softwood.

After extractives, lignin, and the ash-forming elements removed, holocellulose remains in wood. Holocellulose contains cellulose, hemicellulose and fibrous residue (Wise, 1946). Due to high holocellulose content, in softwood species, *P. brutia* is the most suitable species for pulp and paper ındustry.

When compared to previous studies, values of determined chemical analysis results for *P. brutia* were found to match with literature (Table 2). Extractives of *P. brutia* were higher than softwoods and hardwoods. Most of the extractives were fatty and resin acids. The extractives were found to be high because *P. brutia* contains high-grade resin.

Table 2. The chemical compositions and solubility of *P. brutia* with some annual plants and wood species

Annual plants and wood species	Chemical Compositions: Holocellulose (%)	Cellulose (%)	Alfa cellulose (%)	Lignin (%)	Ash (%)	Solubility: Extractives (%)	%'1 NaOH	Hot water (%)	Cold water (%)	Literature
P. brutia	77.6	54.1	36.9	24	1.93	7.7	14.5	2.13	1.14	Current Study
A. membranaceus	76.7	36.7	49.8	23.6	5.45		29.4	8.4	7.20	Tutus et al., 2014
P. somniferum	79.8	40.9	51.7	19.2	4.66	-	30.3	10.4	5.10	Tutus et al., 2011
Cotton straw	75.6	45.5	39.9	18.2	2.52	6.1	30.9	14.2	11.7	Tutus et al., 2010
Cotton straw	72.2	-	41.6	19.3	2.40	6.1	42.9	17.8	16.7	Akgul, 2007
P. brutia	78.6	54.24	48.6	27.6	0.48	7.7	14.5	2.19	1.14	Tutus et al., 2012
Wheat straw	77.1	52.3	39.6	18.3	7.12	5.5	40.9	12.2	7.65	Tutus, 2003
Semen secalis	74.1	51.5	44.4	15.4	3.20	9.2	39.2	13.0	10.2	Usta and Eroglu, 1987
Corn straw	64.8	45.6	35.6	17.4	7.50	9.5	47.1	14.8	-	Eroglu et al., 1992
N. tabacum	67.6	-	37.5	19.5	7.30	6.5	42.9	19.1	15.8	Tank et al., 1985
Lake cane	77.9	50.3	47.5	18.7	3.90	4.0	28.3	3.8	3.30	Kirci, 1996
H. Cannabinus	81.2	54.4	37.4	14.5	4.10	5.0	34.9	12.8	11.7	Dogan, 1994
Softwoods	63-74	55-61	-	25-32	0.2-0.5	1-6	8-10	1-5	0.5-4	Kirci, 2006
Hardwoods	72-82	38-55	-	18-26	0.2-0.7	1-6	12-25	1-8	0.2-4	Kirci, 2006

The Chemical, Physical and Optical Properties of *P. brutia* Pulps

The chemical, pulps optical and physical properties were given in Table 3 and 4. AQ addition had significant effect on the physical properties. The breaking length and burst index were increased about 17.5% and 17.1, respectively by using AQ probably due the better delignification of pulps with this additive. The pulp yield increased with adding 0.1% of AQ, but it decreased after using 0.3% of AQ. Screened yield increased about 4.6% using AQ (0.1%) compared with control cooking.

The reason for the increase is due to the influence of AQ. As mentioned in the introduction section, AQ is oxidizing the reducing end of polysaccharides such as hemicellulose and cellulose, and thereby protecting it from alkaline degradation (Tutus et al., 2016). The kappa number was significantly reduced with AQ addition. It is important to reduce the residual lignin content in pulp production without adversely affecting pulps. It reduces bleaching cost and also provides environmental protection (Vu et al., 2004). At the same time, the viscosities of the pulps were decreased by using AQ. The viscosity value gives an estimation of degree of polymerization and this shows cellulose degradation during pulping (TAPPI, 2013).

Table 3. The chemical properties and pulp yields of *P. brutia*

No	AQ (%)	Screened pulp yield (%)	Screen reject (%)	Total pulp yield (%)	Kappa Number	Viscosity ($cm^3 g^{-1}$)
1	0	49.2	3.6	52.8	120	859
2	0.1	51.4	2.3	53.7	85	806
3	0.3	47.5	0.1	47.5	51	701

Table 4. The physical and optical properties of *P. brutia*

No	Breaking length (km)	Burst index ($kPa.m^2/g$)	Tear index ($mN.m^2/g$)	Brightness (%ISO)	Opacity (% ISO)
1	2.559	1.93	4.08	25.64	97.44
2	2.949	2.26	4.08	26.02	97.74
3	3.007	2.26	4.08	26.96	97.99

Adding AQ, the structural and mechanical properties increased, but had no significant effects on the optical properties of the papers.

Effects of FR on Combustion Rates of the Papers

The combustion rates of the papers impregnated with FR were presented in Table 5. According to the table, FR chemicals had significantly enhanced the fire retardant properties of the papers.

Table 5. The combustion rates of the papers impregnated with fire retardants

Fire Retardants	Combustion areas (cm^2)	Combustion rates (%)
Check Sample	200	100
BX (3%)	104	52
BX (6%)	Combustion was not observed	0
BX (9%)	Combustion was not observed	0
BA (3%)	110	55
BA (6%)	Combustion was not observed	0
BA (9%)	Combustion was not observed	0
AX (3%)	102	51
AX (6%)	100	50
AX (9%)	Combustion was not observed	0
APP (3%)	119	59.5
APP (6%)	75	37.5
APP (9%)	28	14

When combustion rates were examined, BX was the most effective in combustion test. BA and AX also showed an effective resistance against burning. In relation to the increase FR rates, a reduction in combustion area resulted. FR chemicals raise carbonization at relatively low temperatures and advance thermal isolation (Kollman and Cote, 1968; Ozdemir and Tutus, 2013).

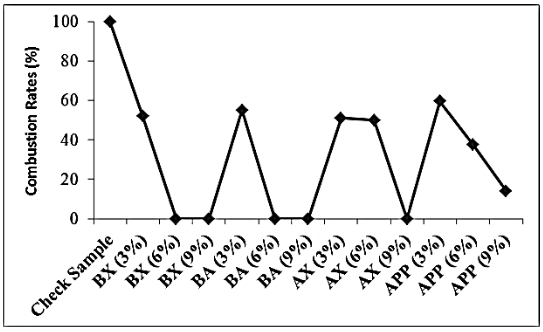

Figure 1. The combustion rates of the papers

In addition to the usual char-forming catalytic effect, when exposed to high temperatures in fires, FR have a rather low melting point and form glassy films (Nussbaum, 1988; Baysal et al., 2007). APP did not perform as well as others (Fig. 1).

Conclusions

1. In Kraft methods, sodium sulfide is using as a delignification chemical and it has unpleasant odor and destructive effect to the environment. For this reason, soda method and its modification must be used in terms of environmental awareness.
2. The results of this study presented the modification of soda pulping by AQ adding in cooking liquor is accelerated lignin degradation. Besides, it increased the physical properties, decreased the kappa number and maintained high pulped yield.
3. Combustion rates of paper specimens using FR chemicals (BA, BX, AX, APP) were studied. These treatments were targeted to benefit from fire retardancy. The papers impregnated with AX, BX, and BA showed the highest fire resistance. APP could not provide sufficient protection when compared to other chemicals.
4. In conclusion, considering paper is a flammable material, increasing the fire resistance of papers is needed. In addition, production using environmentally friendly methods is required in the world where population and technology are increasing rapidly.

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