Pulp and Paper Production from Bitter Orange (*Citrus aurantium* L.) Woods with Soda-AQ Method

Ahmet TUTUS[1], *Mustafa CICEKLER[1], Nazmiye KUCUKBEY[1]
[1]Kahramanmaras Sütçü Imam University, Faculty of Forestry, Kahramanmaraş
*Corresponding author: mcicekler@ksu.edu.tr

Geliş Tarihi:23.02.2015

Abstract

The objective of this study was to determine the properties of pulp and paper produced from *Citrus aurantium* widely available in The Mediterranean region by applying Soda- Anthraquinon (AQ) method. Chemical compositions of *C. aurantium* in addition to basic properties of papers were evaluated. The results showed that *C. aurantium* had higher holocellulose and alpha-cellulose content values of 81.1% and 48.84%, respectively. According to the chemical components of *C. aurantium*, the raw material has potential for pulp and paper production Then, pulps were produced with a Soda-Anthraquinon (AQ) method. The physical and optical properties of the pulps were determined and the effects of AQ were also investigated. Therefore, 4 different cooking experiments which added AQ in certain proportions were performed to *C. aurantium* woods. The best result in pulp yield was found 42.14% in 4th cooking experiment added 0.5% AQ. The physical and optical properties of the pulps were improved by increasing AQ addition. As a result *C. aurantium* woods can be used for pulp and paper production as a raw material.

Keywords: Pulp, Paper, Anthraquinon, *Citrus aurantium*

Turunç (*C. aurantium*) odunlarından Soda-AQ Yöntemi ile Kağıt Hamuru ve Kağıt Üretimi

Özet

Bu çalışmanın amacı, Akdeniz bölgesinde geniş bir yayılış alanına sahip olan Turunç (*C. aurantium*) odunlarından Soda-Antrakinon (AQ) pişirme yöntemiyle elde edilen kağıt ve kağıt hamurlarının özelliklerini belirlemektir. *C. aurantium*'un kimyasal bileşenlerine ek olarak kağıtların bazı özellikleri de değerlendirilmiştir. Yapılan kimyasal analizler sonucu *C. aurantium* yüksek oranlarda holoselüloz (81.1%) ve alfa-selüloz (44.84%) içeriğine sahip olduğu tespit edilmiştir. Elde edilen bu sonuçlara göre bu hammaddenin kağıt yapımına uygun olduğu düşünülmüştür. Soda-AQ metodu kullanılarak-kağıt hamurları üretilmiştir. Kağıt hamurlarına ait fiziksel ve optik özellikler belirlenmiş ve AQ'nun bu özellikler üzerine etkisi araştırılmıştır. Bu nedenle, farklı oranlarda AQ ilave edilerek 4 farklı pişirme deneyi yapılmıştır. Hamur veriminde en iyi sonuç 0.5% AQ ilave edilen 4 nolu pişirme deneyinde 42.14% olarak bulunmuştur. AQ ilavesindeki artışa paralel olarak fiziksel ve optik özelliklerde iyileşmelerin olduğu gözlemlenmiştir. Sonuç olarak, *C. aurantium* odunu kağıt hamuru ve kağıt üretiminde hammadde olarak kullanılabileceği belirlenmiştir.

Anahtar kelimeler: Kağıt hamuru, Kağıt, Antrakinon, *C. aurantium*

Introduction

Wood makes up about 90% of the conventional raw material used for pulp and paper production. However, depleting forests to obtain the wood has made an impact on the environment. As this issue becomes a crucial one, eco-friendly cooking methods and chemicals will provide a good solution to limiting the destruction of the environment. Many paper industries have applied the kraft process as their main pulping process. The soda cooking method less pollutes the environment (Madakadze et al., 1999; Mohanty et al., 2005).

Bitter orange, seville orange, sour orange, bigarade orange, or marmalade orange refers to a citrus tree (*Citrus aurantium*) and its fruit. It is a hybrid between *Citrus maxima* (pomelo) and *Citrus reticulata* (mandarin) (Needham and Tsien, 1985). Many varieties of bitter orange are used for their essential oil, and are found in perfume, used as a flavoring or as a solvent. The Seville orange variety is used in the production of marmalade.

Bitter orange is also employed in herbal medicine as a stimulant and appetite suppressant, due to its active ingredient, synephrine (Sharpe et al., 2006). Bitter orange supplements have been linked to a number of serious side effects and deaths, and consumer groups advocate that people avoid using the fruit medically.

There are various cellulosic raw materials in paper production. However, the wood raw material is the most important of these. If the raw material insufficiency is considered as today's and the future's biggest problem, the route must be directed to fast growing tree species that can be used in paper pulp.

Improvement works on performance and resistance properties were made by putting various chemicals with a previously prepared solution to boiling tub. Some of these chemicals are not preferred due to the environmental aspects, so alternative methods are searched. Due to sodium sulfide's unpleasant smell and detrimental effect to the environment used in craft method, negatively affects human health.

Anthraquinone (AQ) is used as a digester additive in the production of pulp by alkaline processes, like the Kraft, the alkaline sulfite or the Soda-AQ processes. The anthraquinone is a redox catalyst. The reaction mechanism may involve a single electron transfer. AQ is oxidizing the reducing end of polysaccharides in the pulp, i.e., cellulose and hemicellulose, and thereby protecting it from alkaline degradation (peeling) (Samp, 2008).

In this study, the chemical compositions of *C. aurantium* were determined and pulps and papers were produced by using Soda-AQ as eco-friendly chemical. Then, the pulp yields, physical and optical properties of the pulps and papers were investigated.

Material and Method

Material

This study was conducted at Kahramanmaras Sutcu Imam University Faculty of Forestry, Pulp and Paper Production Laboratory.

The raw material used for this study was Bitter Orange (*Citrus aurantium* L.). Chemical analyses, raw material preparation, physical and optical tests of handsheets were made according to the standard methods.

Chemical compositions of *C. aurantium*

Air-dried *C. aurantium* chips were ground to 60 mesh fractions in willey mill and selected in order to determine its chemical composition, which is in accordance with relevant TAPPI Standard Methods. Determination of humidity, α-cellulose, lignin, ashes were performed following standards Tappi T 264 om-88, Tappi T 203 os-71, Tappi T 222 om-88, Tappi T 211 om-85, respectively. Ethanol-toluene solubility, water solubility and NaOH 1% solubility were determined using ASTM D1107-96 (2013), Tappi T 207 om-88 and Tappi T 212 om98, respectively. The holocellulose content of the raw material was determined according to Wise's chlorite method (Wise and Karl, 1962); Kurschner and Hoffer, (1993); Anon., 1998; Tutus et al., 2010)

Pulp and paper production from *C. aurantium*

4 cooking experiments were performed to *C. aurantium* chips by Soda-AQ process to determine optimum pulping condition (Table 1).

Table 1. Cooking conditions of *C. aurantium*

Cooking Number	NaOH (%)	AQ (%)	Temp (°C)	Time (Sec.)
1	26	-	155	110
2	26	0.1	155	110
3	26	0.3	155	110
4	26	0.5	155	110

C. aurantium were chipped. Cooking experiments were made in an electrically heated laboratory rotary digester of 15 liters capacity and maximum pressure of 25 kg/cm^2. All pulps were washed and screened on a 0,15 mm slotted screen. Screened pulps were beaten in a hollander beater to 50±5 °SR freeness levels according to Tappi T 200 sp-96 and five handsheets per tested sequence with grammage of 70 g/m^2 were prepared using a Rapid-Kothen sheet former according to ISO 5269/2. Physical and optical properties of handsheets were measured according to TAPPI T 220 sp-96, ISO 2469 (brightness), Tappi T 425 om-96 (opacity) standard test methods, respectively. The viscosities and kappa numbers of the pulps were determined according to TAPPI standards T230 om-08 (2008) and T236 om-13 (2013), respectively (Anon., 1992; Anon., 2004; Anon., 2014).

Results and Discussions

Chemical compositions of *C. aurantium*

The chemical compositions of *C. aurantium* used in this study were given in Table 2.

Table 2. Chemical compositions of *C. aurantium*

Chemical Comp	(%)	SW (Kirci, 2006)	HW (Kirci, 2006)
Holocellulose	81.18	63-73	72-82
Alpha Cellulose	48.84	-	-
Lignin	19.73	25-32	18-26
Ash	2.69	0.2-0.5	0.2-0.7
Extractives	7.94	1-6	1-6
% 1 NaOH sol.	14.92	8-10	12-25
Hot water sol.	7.94	1-5	1-8
Cold water sol.	5.66	0.5-4	0.2-4

*SW: Softwoods, HW: Hardwoods

The holocellulose content *of C. aurantium* (81.18%) is approximately equal to that of hardwood and higher than that of softwood. Holocellulose is a combination of cellulose and hemicellulose content. Within increases in holocellulose content of raw material, quality of papers will be increased.

The high NaOH solubility is due to the presence of low molecular weight carbohydrates and other alkali soluble matters. Also, NaOH solubility indicates the extent of fiber degradation during the pulping process.

Results show that this raw material has a high potential for use as fibers for pulp and paper production. Also, the lignin content is lower than that of hardwoods and softwoods. Lignin functions as an adhesive to bind cellulose together in the fiber. Lower lignin content makes the fiber strength greater and harder to break (Tran, 2006).

Pulp and paper properties of *C. aurantium*

Pulps yields, physical and optical properties of the pulps were given Table 3 and 4.

Akgul and Tozluoglu (2009) reported that the total pulp yield was increased by using AQ in soda cooking method. The best result in total yield was found 37.98%. In control cooking, the pulp yield was found 35.80%. According to these results, the pulp yield increased about 6.1% with AQ.

Table 3. The pulps yields of *C. aurantium* L.

	AQ (%)	Screened yield (%)	Screen reject (%)	Total yield (%)
1	0	33.27	5.14	38.41
2	0.1	38.82	1.97	40.79
3	0.3	40.07	1.47	41.54
4	0.5	40.78	1.36	42.14

The best result in the total pulp yield was found 42.14% in 4th cooking (0.5% AQ). When compared with the control cooking (1st cooking) the total pulp yield was increased by AQ about 9.71% and the screen rejects, not able to use for paper making, was decreased about 73.54%. In Fig. 1, the effects of AQ on the total and screened pulp yields was given.

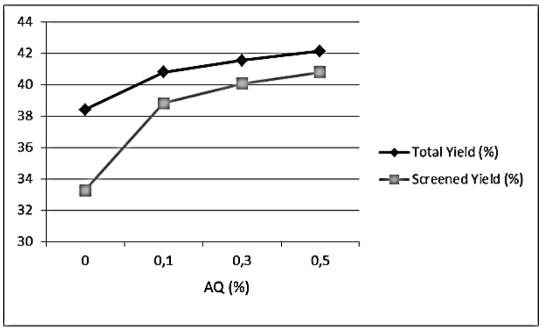

Figure 1. Effects of AQ on pulp yields

In Table 4, kappa numbers and viscosities of the pulps were given. Within increases in AQ addition of 0% to 0.5%, kappa numbers were decreased from 49.2 to 44.6, viscosities were increased from 1052 to 1169.

Table 4. Effects of AQ on kappa number and viscosity of the pulps

	AQ (%)	Kappa No	Viskozite
1	0	49.2	1052
2	0.1	47.4	1078
3	0.3	45.8	1150
4	0.5	44.6	1169

In Table 5, the best result in breaking length and burst index were found 3576 m and 2.59 $kPa.m^2.g^{-1}$, respectively. It is obvious that AQ has improvements on physical and optical properties of the pulps as additive. The breaking length, burst index, and brightness of the pulps were increased by using AQ about 37.9%, 23.9%, and 12.4%, respectively.

Table 5. Physical and optical properties of *C. aurantium*

	Opacity (ISO)	Brightness (ISO)	Breaking Length (m)	Burst index ($kPa.m^2.g^{-1}$)
1	99.7	28.3	2594	2.09
2	99.7	28.1	3260	2.29
3	99.8	30.9	3512	2.47
4	99.6	31.8	3576	2.59

Tamminen et al. (2013) reported that using AQ in pulping has improvements on physical properties. Effects of AQ on the breaking length and burst index were given in Fig. 2.

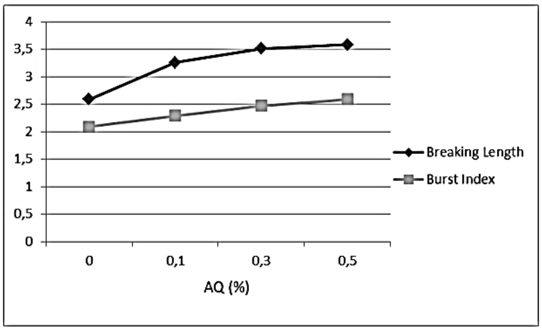

Figure 2. Effects of AQ on physical properties of *C. aurantium* pulps

Kamthai (2007) reported that due to the 0.1% AQ addition in AS pulping had an advantage such as higher brightness and easier to bleach.

Conclusions

C. aurantium can pulped by different pulping processes. The results of this study presented the modification of soda pulping by AQ adding in cooking liquor is accelerated lignin degradation, increased the physical and optical properties and maintained high pulped yield. Soda-AQ (0.5%) screened yield was approximately about 22.5% higher than soda screened yield. One reason of these increases is that AQ is oxidizing the reducing end of polysaccharides in pulp, i.e., cellulose and hemicellulose, and thereby protecting it from alkaline degradation (peeling).

The most suitable cooking parameters were determined according to the screened yields and strength of cooking parameters pulps by adding AQ to pulping. The optimum condition was 26% NaOH, 0.5% AQ with 110 minutes and 155 ºC. Screened yield, total yield and strength properties were observed to be at an optimum level when compared to other conditions.

The event which did the most to spark the enthusiasm for quinone additives was the disclosure by Holton in 1978 that AQ itself is an effective additive in alkaline pulping. In fact, he claimed that a modified soda process employing AQ surpasses an unmodified kraft process in rate and yield in pulping hardwoods and softwoods.

As a result, together with high level of cellulose and holocellulose content and low level of lignin content, *C. aurantium* that is suitable for paper production, showed a high yield results in cookings when AQ charge was increased. If some changes are made in cooking conditions, (chemical addition, decreasing temperature, increases time, etc.) *C. aurantium's* suitability for paper production will be better proved.

References

Akgul, M., Tozluoglu, A., 2009. A comparison of soda and soda-AQ pulps from cotton stalks, African Journal of Biotechnology 8 (22), 6127-6133.

Anonymous, 1992. TAPPI test methods, standard methods for pulp and paper, technical association of pulp and paper industry. Tappi Press, Atlanta.

Anonymous, 1998. ASTM D 1107-96 1998. Standard test method for ethanol-toluene solubility of wood, Philadelphia, PA., USA.

Anonymous, 2004. ISO 5269/2, 2004. Pulp – Preparation of laboratory sheets for physical testing, Part 2: RapidKöthen method.

Anonymous, 2014. ISO 2469:2014. Paper, board and pulps, Measurement of diffuse radiance factor (diffuse reflectance factor).

Holton, H. H., 1978. Better cooking with anthraquinone, Pulp and Paper Internat, 20 (9), 49-52.

Kamthai, S., 2007. Comparison of AS-AQ pulping of Sweet Bamboo (*Dendrocalamus asper* Backer) and pulping by conventional kraft process, Chiang Maai. J. Sci., 34 (1), 97-107.

Kirci, H., 2006. Pulp Industry Lecture Notes. Karadeniz Technical University, Forest Faculty Publication, Trabzon-Turkey.

Kurschner, K., and Hoffer, A., 1993. Cellulose and cellulose derivative, Fresenius Journal of Analytical Chemistry. 92(3), 145-154.

Madakadze, I.C., Radiotis, T., Li, J., Goel, K., and Smith, D.L., 1999. Kraft pulping characteristics and pulp properties of warm season grasses, Bioresource Technology, 69(1), 75-85.

Mohanty, A.K., Misra, M., and Drzal, L.T., 2005. Natural Fibers, Biopolymers and Biocomposites, ISBN 978-0849-31-7415, 896 pages, CRC Press, Boca Raton.

Needham, J., Tsien, T., 1985. Science and Civilisation in China, Volume 5, Chemistry and Chemical Technology, Part 1. Paper and Printing, Cambridge University Press, 504 pages.

Samp, J.C., 2008. A comprehensive mechanism for anthraquinone mass transfer in alkaline pulping, Ph.D., Georgia Institute of Technology, 120 pages, Atlanta.

Sharpe, P.A., Granner, M.L., Conway, J.M., Ainsworth, B.E., Dobre, M. 2006. Availability of weight-loss supplements: Results of an audit of retail outlets in a southeastern city, Journal of the American Dietetic Association, 106 (12), 2045-2051.

Tamminen, T., Milanez, A., Andreotti, J., Gomes, F., Colodette, J., Barth, D., Liitia, T., 2013. Soda-O_2, Soda-AQ and organosolv pulping as pretreatments of Eucalyptus for bioethanol production, 6th International Colloquium on Eucalyptus Pulp (24-27 November 2013), 1-8, Colonia, Uruguay.

Tran, A.V., 2006. Chemical analysis and pulping study of pineapple crown leaves, Industrial Crops and Products, 24(1), 66-74.

Tutus, A., Ezici, A.C., Ates, S., 2010. Chemical, morphological and anatomical properties and evaluation of cotton stalks (*Gossypium hirsutum* L.) in pulp industry, Scientific Research and Essays, 5 (12), 1553-1560.

Wise. E.L., Karl, H.L., 1962. Cellulose and Hemicelluloses in Pulp and Paper Science and Technology, Vol. 1. Pulp, Edited by C. Earl Libby, McGraw Hill-Book Co., New york.