African Journal of Biotechnology Vol. 9(11), pp. 1648-1654, 15 March, 2010
Available online at http://www.academicjournals.org/AJB
ISSN 1684–5315 © 2010 Academic Journals

*Full Length Research Paper*

# Pulp and paper production from Spruce wood with kraft and modified kraft methods

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Accepted 26 February, 2010

**In this study, kraft and modified kraft pulping methods were applied for spruce *(Picea orientalis)* wood collected from the Black Sea Region of Turkey. Fiber properties, carbohydrate contents, strength and optical properties of resultant paper were included to determine the properties of these pulp samples. Optimum kraft, kraft-borohydride ($NaBH_4$), kraft-anthraquinone (AQ) and kraft-ethanol pulping conditions were determined. After determining screened yield, kappa number, viscosity, fiber length, fiber coarseness, α-cellulose, holocellulose, lignin and ash content, breaking length, tear indexes and burst indexes of the obtained pulp samples, the differences of SEM image of each pulp sample were captured and evaluated. The results indicated that kraft-AQ pulps from spruce wood exhibited better characteristics than the other pulp samples with lower kappa number, higher paper strength properties and optical properties. However, kraft-$NaBH_4$ method gave pulps with closer characteristics to kraft-AQ and also gave a higher screened yield and α-cellulose ratio than the others.**

**Key words:** Spruce, modified kraft methods, borohydride, AQ, SEM.

## INTRODUCTION

The main aim of producing chemical pulp is to breakdown the structure of the middle lamelle consisting of lignin and thus separates the fibers individually. During this process, since huge amount of lignin and hemicelluloses in the cell wall are being broken down, elasticity of the separated fibers increases. Because mechanical energy is not been used for separating the fibers in chemical pulping methods, mechanical damage are not seen on the fiber surfaces. However, when compared with mechanical and semi-chemical methods, papers made from chemical pulps make stronger bonds between fibers and gives higher paper strength properties (Kırcı, 2006).

Today, most chemical pulps are been produced by kraft method globally. Sulphite method, a most commonly used method for pulp production until 1950’s, accounts for 10% of the total production, while kraft method accounts for 80% (Johansson et al., 1987).

Pulp production using kraft method was developed by a German Chemist, Dahl in 1879 (Casey, 1979; Smook, 2000). Dahl discovered that during alkali consumption, sodium carbonate can exchange with sodium sulphate and sulphate can be reduce to sulphur using the soda method. This method was initially named the sulphate method as it was erroneously thought that sulphate is the active pulping compound when in actual fact the active pulping compounds in the kraft method are $Na_2S$ and NaOH. Kraft pulps (kraft means strength or power in German) are obtained in higher yields and with properties superior to soda pulps (Fengel and Wegener, 1989).

Chemical ratios have been used as 6-10% for semi-chemical kraft pulping and 10-15% for chemical kraft pulping. Additional chemicals such as sodium borohydride ($NaBH_4$) and anthraquinone (AQ) are used for obtaining modified kraft pulps. These chemicals protect the reducing end of carbohydrates against peeling. Thus, pulp yield, brightness and paper strength properties increases. Besides, these additional chemicals serve as

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**Table 1.** Pulping conditions for obtaining kraft and modified kraft pulps from oriental spruce wood.

| Pulping methods | Pulping conditions | | | | | | |
|---|---|---|---|---|---|---|---|
| | Active alkali (%) | Sulfidity (%) | Temp. (°C) | Time (dak) | Ethanol (%) | $NaBH_4$ (%) | AQ (%) |
| L.a. kraft | 20 | 30 | 170 | 90 | - | - | - |
| H.a. kraft | 30 | 20 | 170 | 90 | - | - | - |
| Kraft-$NaBH_4$ | 30 | 20 | 170 | 90 | - | 0.5 | - |
| Kraft-AQ | 30 | 20 | 170 | 90 | - | - | 0.5 |
| Kraft-Ethanol | 15 | 10 | 170 | 90 | 50 | - | - |

Liquor to wood ratio = 4/1 ; L.a. kraft = kraft pulping with lower alkali ratio; H.a. kraft = kraft pulping with higher alkali ratio.

a catalyser during cooking and causes lower cooking time and temperature (Hafızoglu and Deniz, 2007). In industrial application process, variables for kraft pulping are selected as about 165 - 170℃, 1.5 - 2 h cooking time and 3/1 – 5/1 liquor to wood ratio (Ryhdolm, 1965).

Kraft and modified kraft methods have some advantages. These are: all species can be used as raw material, it offers short cooking time, high strength properties of pulps, poor sensitivity to bark, more insufficient pitch problem, easier recycling of chemicals and waste water as well as production of some secondary products such as turpentine, tall oil and lignin derivatives. However, there are also some disadvantages such as higher establishment costs, higher smelling problem, darker pulps and low beating abilities (Bensend, 1975; Gullichsen and Fogelbolm, 2000).

The objective of this study was to compare different modified kraft pulping methods for processing spruce (*P. orientalis*) wood for the purpose of producing paper-grade pulp. We also focused on the characteristics of the pulp samples and pulp strength properties obtained from the kraft (lower active alkali ratio, denoted as L.a. kraft), kraft (higher active alkali ratio, denoted as H.a. kraft), kraft-borohydride (kraft $NaBH_4$), kraft-anthraquinone (kraft AQ) and kraft-ethanol methods.

## MATERIALS AND METHODS

### Materials

Oriental spruce *(P. orientalis)* has natural spread area on Northern-east cost of the Anatolia with about 135.959 ha. Especially, it spreads on northern braes of the mountains at 1200-2400 m altitudes (Bozkurt and Erdin, 1997). As the raw material for this study, oriental spruce wood was selected from Eastern Black Sea cost of Turkey.

### Chemical composition of spruce

TAPPI T 257 cm-85 and TAPPI T 264 om-88 standard methods were used for the preparation and sampling of oriental spruce wood for chemical analyses. The raw materials were analyzed for holocellulose, α-cellulose, lignin, ash, alcohol–benzene extractable, cold and hot water and 1% soda soluble, in accordance with the TAPPI Standard Methods (Anonymous, 1992): T-203-0S-61, T-222, T-221, T-204, T-257 and T-212, respectively. Five replicates were done for each experiment.

### Pulping and morphological properties of pulp samples

To determine kraft and modified kraft pulping conditions, literature studies were searched and optimum cooking conditions were selected for each kraft (L.a. kraft and H.a. kraft), kraft-AQ, kraft-$NaBH_4$ and kraft-ethanol method. Selected cooking variables are shown in Table 1 for all kraft and modified kraft methods.

The cooking trials were carried out in 15 L electrically heated laboratory cylindrical type rotary digester and governed with digital temperature control system. At the end of pulping, pressure was reduced to atmospheric pressure and then pulps were washed, disintegrated in a laboratory type pulp mixer with 2 L capacity and screened on a Noram type pulp screen with 0.15 mm slotted late. Pulp yield was determined as dry matter obtained on the basis of oven dried raw material. The reactor was loaded with 500 g oven dried wood chips for each trial and cooked with appropriate chemicals needed as shown in Table 1.

Kappa number and viscosity were determined in accordance with T 236 cm-85 and T 230 om-94, respectively. To obtain hand sheets and to determine the strength properties of the paper sheets, TAPPI Standard Methods (Anonymous, 1992) were applied. For obtaining brightness and opacity of the pulp samples, ISO Standard Methods (Anonymous 1997a; Anonymous 1997b) were used. Fiber lengths and fiber coarseness of the pulp samples were determined in Fiber Quality Analyzer (FQA).

### Scanning electron microscope (SEM) measurement of pulp fibers

The fiber surfaces of the kraft, kraft-AQ, kraft-$NaBH_4$ and kraft-ethanol pulp were observed using a scanning electron microscope (SEM). Using a solid-state backscatter, images were acquired at 300×magnification. The acceleration voltage was 5 kV and the working distance was 8 – 10 mm.

## RESULTS AND DISCUSSION

Main chemical composition and some solubility values of the oriental spruce wood were determined and shown in Table 2. As shown in Table 2, lignin content of spruce wood was found as 25.20%, which is comparable to all softwoods (25 - 32%), it is however, substantially higher than all annual plants and hardwoods (17-26%). The average holocellulose content of spruce wood was found as 74.46%; most annual plant and coniferous were 68-

**Table 2.** Some chemical analyses results of oriental spruce wood.

| Chemical Composition | Mean (%) | S.d. | Coniferous |
|---|---|---|---|
| Holocellulose | 74.46 | 0.24 | 68 - 74 |
| α-Cellulose | 44.31 | 0.31 | 40 - 45 |
| Lignin | 25.20 | 0.27 | 25 - 32 |
| Ash | 0.32 | 0.19 | < 1 |
| Alcohol-benzene solubility | 3.40 | 0.23 | - |
| 1% NaOH solubility | 10.26 | 0.33 | - |
| Hot water solubility | 2.81 | 0.22 | 2 - 6 |
| Cold water solubility | 1.47 | 0.25 | 2 - 5 |

S.d. = Standart deviation.

**Table 3.** Some chemical, strength and optical properties of oriental spruce wood pulp samples obtained wit kraft and modified kraft methods. (45 ± 5 SR$^o$).

| Pulping methods | Screened Yield (%) | Screen Reject (%) | Total yield (%) | Kappa Number | Viscosity (cp) | Holocellulose (%) | α-Cellulose (%) | Lignin (%) | Ash (%) | Tear Index (mN.m$^2$/g) | Breaking Length (km) | Burst Index (kPa.m$^2$/g | ISO Brightness (%) | ISO Opacity (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| L.a. kraft | 43.60 | 4.1 | 47.70 | 49.90 | 23 | 92.4 | 87.1 | 7.58 | 0.27 | 8.51 | 5.15 | 3.64 | 15.10 | 97.58 |
| H.a. kraft | 42.10 | 0.3 | 42.40 | 19.33 | 15 | 95.3 | 85.6 | 2.94 | 0.21 | 7.62 | 4.65 | 3.09 | 27.45 | 98.23 |
| Kraft-$NaBH_4$ | 44.50 | 0 | 44.50 | 18.60 | 12 | 97.0 | 87.6 | 2.83 | 0.19 | 8.06 | 4.86 | 3.21 | 25.75 | 96.56 |
| Kraft-AQ | 43.50 | 0 | 43.50 | 14.70 | 14 | 97.5 | 86.2 | 2.23 | 0.20 | 8.24 | 5.02 | 3.45 | 29.98 | 97.98 |
| Kraft-Ethanol | 40.60 | 3.91 | 44.51 | 52.00 | 24 | 90.7 | 85.2 | 7.94 | 0.23 | 7.85 | 4.95 | 3.30 | 18.63 | 97.74 |

L.a. kraft = **K**raft pulping with lower alkali ratio; H.a. kraft = kraft pulping with higher alkali ratio.

**Table 4.** Morphological properties of the pulp samples in FQA.

| Pulping methods | Morphological properties | | |
|---|---|---|---|
| | Sample numbers | Fiber lengths (mm) | Coarseness (mg/m) |
| L.a. kraft | 4514 | 2.21 | 0.230 |
| H.a. kraft | 4210 | 1.64 | 0.184 |
| Kraft-$NaBH_4$ | 4342 | 1.85 | 0.193 |
| Kraft-AQ | 6156 | 2.13 | 0.223 |
| Kraft-ethanol | 3538 | 1.95 | 0.207 |

L.a. kraft = Kraft pulping with lower alkali ratio; H.a. kraft = kraft pulping with higher alkali ratio; FQA= fiber quality analyzer.

74%. The α-cellulose in spruce wood (44.31%) is higher than some annual plants and hardwoods (32-43%). Spruce wood also showed similar solubility with some hardwood (eucalyptus and quercus) and softwoods (abies and *Pinus sylvestris*). As can be seen from Table 2 all main chemical composition and some solubility values are in normal range (Ates et al., 2008).

Some chemical, strength and optical properties of oriental spruce wood pulp samples obtained with kraft and modified kraft methods are given in Table 3. Fiber quality analyzer (FQA) results are also shown in Table 4.

Though used most commonly globally pulping method based on polysaccharide breakdown reaction in strong alkaline media kraft method has high yield lost. However, when compared with sulphite pulp, kraft pulps produced with the same residual lignin content using the same chemical amount, always produces higher yield. The addition of some chemicals to kraft white liquor such as sodium borohydride, anthraquinone and ethanol leads to the protection of the reducing group of the carbohydrates

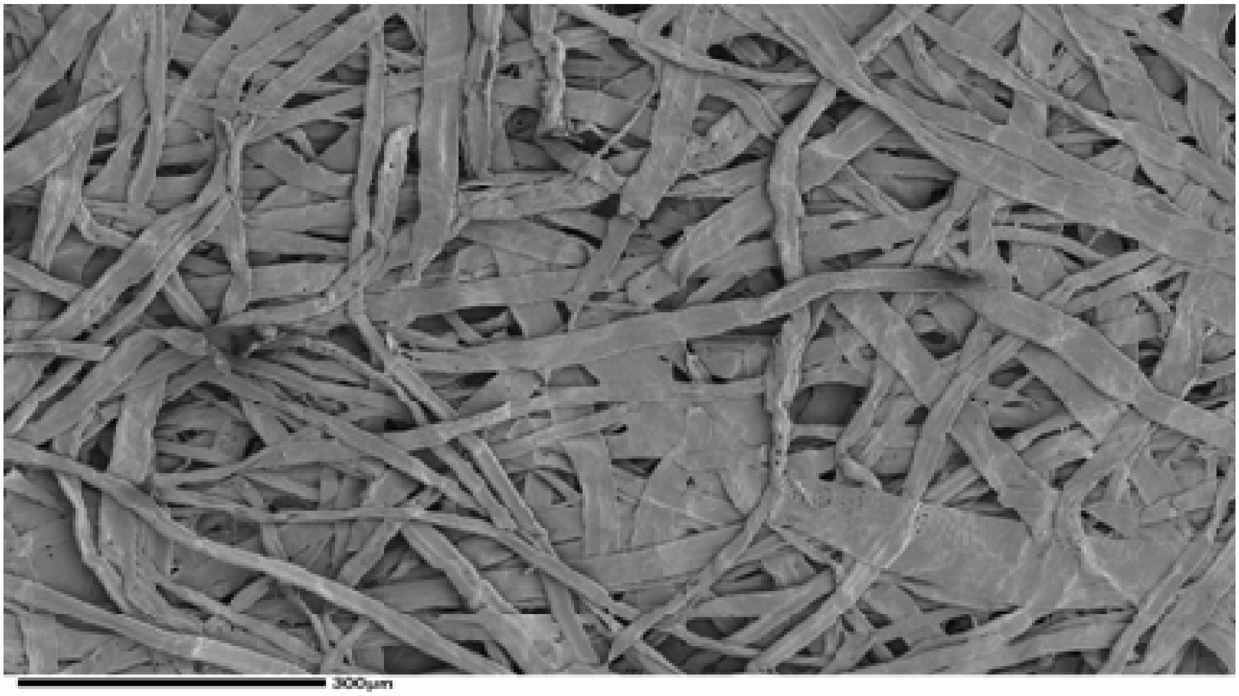

**Figure 1.** Scanning electron microscope (SEM) observation of L.a. kraft (lower active alkali) pulp fibers.

against peeling reaction and thus, obtained papers show higher strength and optical properties.

For La-kraft pulping method (with 20% active alkali and 30% sulphidity charge) screened yield, kappa number and pulp viscosity were obtained as 43.60%, 49.90 and 23 cp, respectively, whereas, Ha-kraft pulping method (with 30% active alkali and 20% sulphidity charge) gave 42.10%, 19.33 and 15 cp, respectively. Using higher alkali condition caused kappa number, viscosity and yield decrease. Although, these decreases were not much in screened yield, reduction in kappa number and viscosities of pulp samples were significant. Holocellulose content of the Ha-kraft pulps and α-cellulose content of the La-kraft pulps were higher when compared with another 3.04 and 1.72% respectively.

At the same pulping temperature and time level, reduction in lignin content viscosity and increase in screened yield for kraft-$NaBH_4$ and kraft-AQ pulp were observed. Using lower sulphidity charge in the mentioned modified kraft methods will make positive contribution to water and air pollution. Also, since $Na_2S$ is about five times more expensive than NaOH, modified kraft pulping methods significantly provides lower pulping cost. However, the highest holocellulose and α-cellulose ratio and the lowest lignin content were obtained for kraft-$NaBH_4$ and kraft-AQ pulps.

In a previous study, obtained screened yield, holocellulose content, α-cellulose content and residual lignin ratio was 41.9, 80.9, 65.9 and 18.1%, respectively for olive wood kraft pulp (Lopez et al., 2000). However, in the present study, screened yield, holocellulose content, α-cellulose content, residual lignin ratio and ash content were obtained as 44.50, 97.0, 87.6 and 2.83%, respectively, for Kraft-$NaBH_4$ pulp sample. Also, modified kraft methods gave more bleachable pulps. In another study, lower screened yield and higher kappa number were obtained (Deniz et al., 2004).

Due to its higher content of fines and shorter average fiber length, the soda-AQ pulp had lower breaking length and tear index than the ethanol pulp. The reason is probably because the carbohydrates are being protected more effectively against hydrolysis in a high alcoholic environment (Akgul and Kirci, 2002) coupled with the effect of the alkali in white liquor. Kraft-AQ pulp showed similar characteristics with soda-AQ pulp. There is no significant difference between the two alkaline pulps.

The fibres of the pulp of SEM observations (Figures 1, 2, 3, 4 and 5) are smooth, clean and samples show no fibrillation, but are of different thickness and the fine ratio is lower. As can be seen on Figures 2 and 5, cooking chemicals were well penetrated in cell wall and lignin in the structure was well degraded. Precipitation of lignin on fibers and maximum kappa number was obtained for kraft-ethanol pulp. Figures 1, 3 and 4 gave higher thickness and lower flexibility but fibers of pulp from H.a. kraft, kraft-AQ and kraft-$NaBH_4$ were softer and thinner than L.a. kraft and kraft-ethanol. This can be explaned with low degradation of holocellulose.

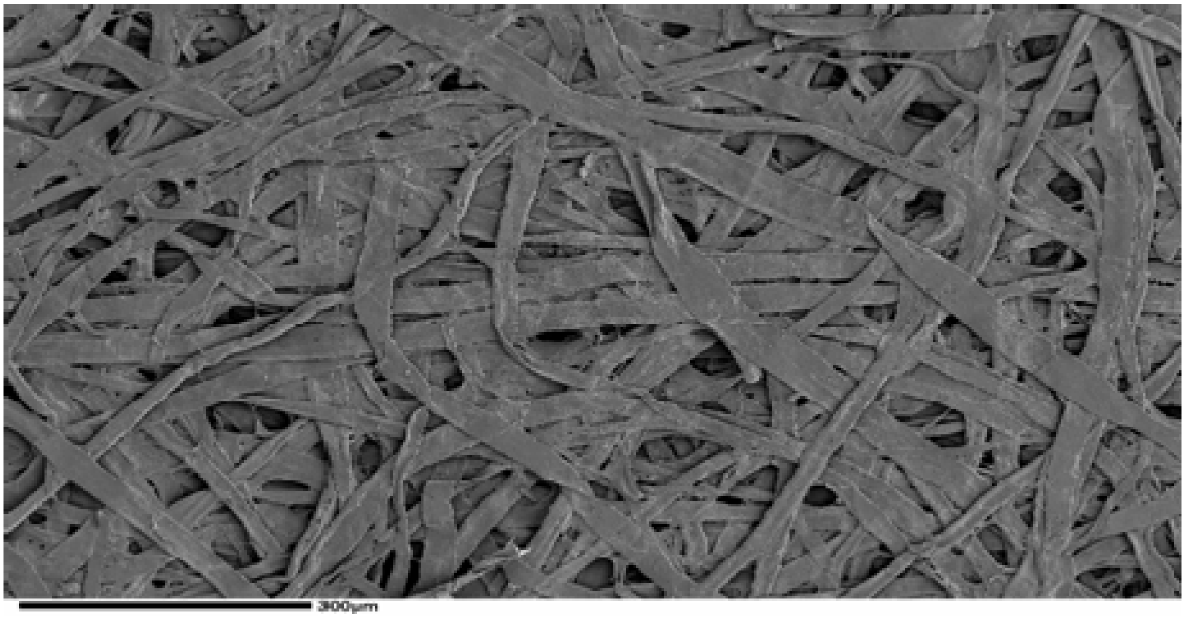

**Figure 2.** Scanning electron microscope (SEM) observation of L.a. kraft (higher active alkali) pulp fibers.

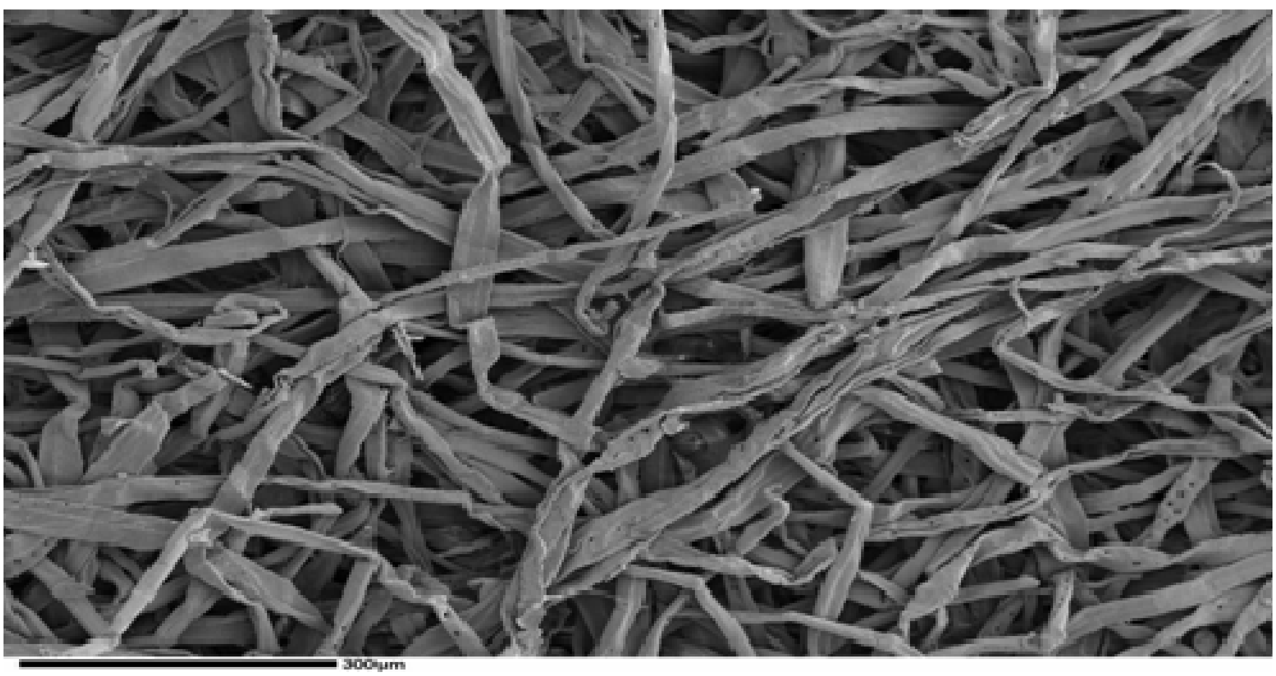

**Figure 3.** Scanning electron microscope (SEM) observation of kraft-$NaBH_4$ fibers.

## Conclusion

Kraft (H.a. kraft and L.a. kraft) and modified kraft methods were compared and kraft-AQ, kraft-$NaBH_4$ and kraft-ethanol were determined as an optimal pulping method for yield and chemical properties of pulp samples. It is worth noting that when this method is used, chemicals with lower sulphur content is preferable. This method tends to partially prevent water and air pollution and thus, pulp production is more environmentally suitable. In addition, production costs is reduced when using lower sulphidity rate and higher alkali charge. Finally, high yield, quality and easy bleachable pulps can be produced with kraft-AQ and kraft-$NaBH_4$ methods.

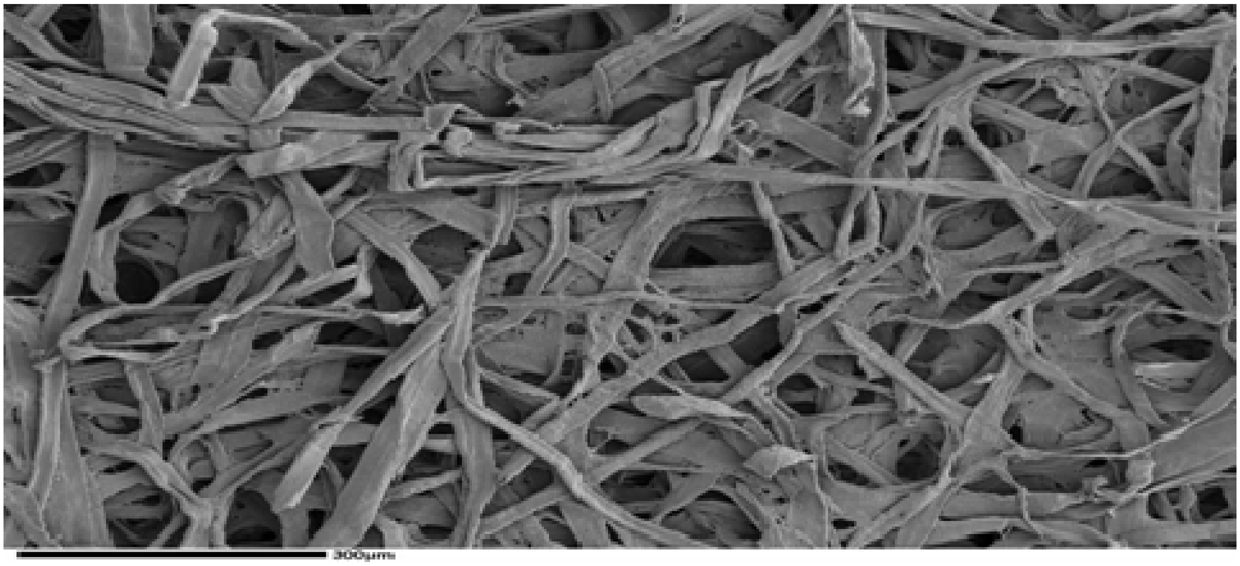


**Figure 4.** Scanning electron microscope (SEM) observation of kraft-AQ fibers.

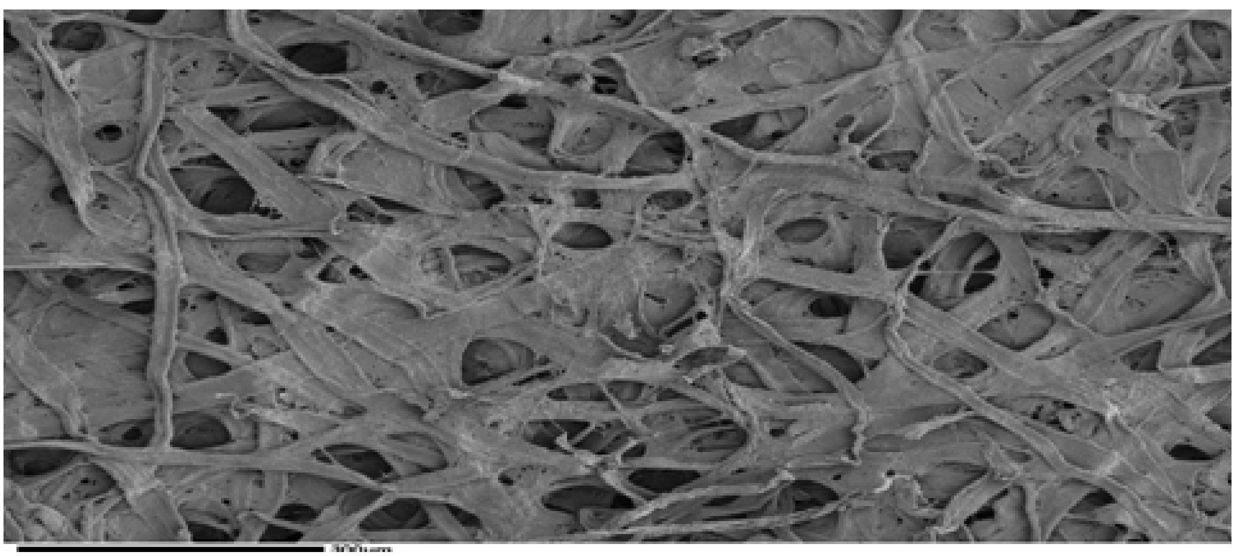

**Figure 5.** Scanning electron microscope (SEM) observation of kraft-ethanol fibers.

## ACKNOWLEDGEMENTS

Authors are also thankful to Dr. Huining Xiao, Department of Chemical Engineering and Limerick Pulp and Paper Centre, University of New Brunswick, Fredericton, Canada for SEM microphotographs.

## REFERENCES

Akgul A, Kırcı H (2002). Production of dissolving grade pulp from poplar wood by ethanol-water process. Turk. J. Agric. For. 26: 239-245.

Anonymous (1992). Tappi Test Methods, Tappi Press, Atlanta, Georgia.

Anonymous (1997a). ISO/DIS, 2470; Paper, board and pulp-measurement of blue reflection factor (ISO brightness) Beuth-Verlag, 10772, Berlin.

Anonymous (1997b). ISO/DIS, 2471; Paper and board determination of opacity (paper backing) diffuse reflectance Method.

Ates S, Ni Y, Akgul M, Tozluoglu A (2008). Characterization and evaluation of Paulownia elongota as a raw material for paper production. Afr. J. Biotechnol. 7(22): 4153-4158.

Bensend DW (1975). Wood Technology Forestry 380, Department of Forestry Iowa State University, Ames, Iowa.

Bozkurt AY, Ve Erdin N (1997). Odun Teknolojisi, IU Yayınları, Yayın No: 3998, İstanbul.

Casey JP (1979). Pulp and Paper Chemistry and Chemical Technology, John Wiley and Sons, Vol. 1, New York, USA.

Deniz I, Kırcı H, Ates S (2004). Optimization of Wheat Straw *Triticum drum* Kraft Pulping, Ind. Crops Prod. 19: 237-243.

Fengel D, Wegener G (1989). Wood Chemistry, Ultrastructure, Reactions, Walter de Gruyter, Berlin-New York.

Gullichsen J, Fogelbolm CJ (2000). Chemical Pulping, Papermaking

Science and Technology Series, Gummerus Printing, Jyvaskyla, Finland.
Hafızoglu H, Deniz I (2007). Wood Chemistry, KTU Faculty of Forestry Progress, Trabzon.
Johansson A, Altonen O, Ylinen P (1987). Organasolv Pulping Methods and Pulping Properties, Biomass, 13(15): 45-52.
Kırcı H (2006). Kağıt Hamuru Endüstrisi Ders Notları, KTU. Orman Fakültesi Yayınları, Yayın No: 86, Trabzon.
Lopez F, Ariza J, Perez I, Jimenez L (2000). Comparative study of paper sheets from olive tree wood pulp obtained by soda, sulphide or kraft pulping, Bioresour. Technol. 71: 83 86.
Ryhdolm RA (1965). Pulping Processes, Interscience Publishers, London, UK.
Smook GA (2000). Handbook for Pulp and Paper Technologists, Angulus Wilde Publications, Vancouver, Bellingham.