

An environmentally friendly organosolv (ethanol-water) pulping of poplar wood

Mehmet Akgul*¹ and Huseyin Kirci²

¹Department of Forest Products Engineering, Faculty of Forestry, Duzce University, Duzce - 81620, Turkey

²Department of Forest Products Engineering, Faculty of Forestry, Karadeniz Technical University, Trabzon - 61080, Turkey

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Abstract: In this study, pulp production from the fast growing plant, poplar, was examined for organosolv pulping with or without catalysts. In order to find the optimum cooking conditions, 18 different cooking experiments were carried out. The effect of ethanol ratio, cooking time as well as catalyst was studied. It was observed that even at lower temperature (90°C), cooking without catalyst was able to cause sufficient defiberization. It was seen that the increasing proportion of catalyst and cooking temperature resulted in an increased delignification. However in the case of using 0.02% acid catalyst pulp yield and viscosity were lowered to an unacceptable level. The most important cooking factors were found to be the proportion of acid catalyst. Furthermore, the delignification performance was found to be depending on the pH of the black liquor. In a result, the optimum pulp properties were obtained by cooking at 180°C for 90 min with 50% ethanol mixture without catalyst. The pulp yield was noted as 44.49 %, viscosity was 892 cm²g⁻¹ and the kappa number was 67.

Key words: Poplar, Organosolv pulping, Delignification, Ethanol-water cooking, pH
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Introduction

In traditional paper pulp production methods, strong basic or acidic pulping liquor containing mostly sulfur, are used, which is harmful for environment. Paper industry, one of the most polluting industries, is under environmental and legal pressure. (Kordsachia *et al.*, 1992). Minimizing the air and water pollution and continuous control need expensive investments which also effect the paper cost. Although the emission of sulfuric organic compounds that cause bad odor problem is minimized by today's technology, the bleaching of the pulps (mainly produced by craft method) still cause serious water pollution (Patt *et al.*, 1992).

Paper production with chemical methods is also one of the technologies that can not use recycling efficiently. For example during the production of bleached craft pulp, half of the wood raw material is evaluated as product and the other half is either burned during the recycling of inorganic materials used in cooking or is sent to sewers as bleaching liquor without being purified.

One of the most promising solutions for minimizing the existing problems in paper industry is applying new methods named as organosolv or solvent cooking where organic solvents are used in cooking operation. In recent years serious interest is shown in organosolv methods in which the wood is refined. (Johansson *et al.*, 1987). With these methods, it is easy to separate lignocellulosic materials as pulp, lignin and solved wood sugars. As a result, various lateral commercial products will be produced and also environment will be less polluted after cooking. (Sundquist *et al.*, 1998; April *et al.*, 1979).

It was known since the last quarter of 19th century that some organic solvents can extract lignin but using organic solvents for pulp production was not considered until 1930's. The studies were made and the patents were taken about this issue between 1929 and 1939 by Aranovsky and Gortner (1936) and later by Kleinert (1974, 1975), resulted organosolv methods to develop. The most prevalent solvents that are still used, are methanol, ethanol, acetic acid and formic acid. Other organic solvents are phenols, amines, glycols, nitrobenzene, dioxane, dimethylsulphoxide, sulfolene and carbon dioxide (Hergert, 1992). Various organosolv systems using all these solvents are developed. (Aziz and Sarkanen, 1989). It was reported that organosolv process had the following advantages compared to the conventional kraft method (Aziz and Sarkanen, 1989; Stockburger, 1993): Reduced COD and BOD levels, and no AOX in the bleach plant effluents. Minimizing environmental problems caused by waste chemical pollutants such as sulphurous, chlorinated organics *etc.*

The most industrially applicable solvents are ethanol and methanol which can be obtained easily and cheaply. In recent years, various organosolv cooking methods with or without catalyst that consider alcohol as basis, were suggested. In this study, a method which is suitable to non-continuous cooking boiler developed by Kleinert, was selected. This method is principally suitable to low density hardwoods. When cooking the softwoods, the high amount, it is hard to produce a pulp with acceptable strength property, due to higher lignin ratio, structural difference and different local distribution of lignin in cell wall (Paszner and Cho, 1989).

The aim of this study was to investigate the utilisation possibilities of poplar wood in pulp industry by this new environmentally friendly process.

* Corresponding author: mehmetakgul@duzce.edu.tr



Materials and Methods

Poplar (*Populus euroamericana*) wood chips were selected as raw material in this study. The chips (Tappi T 258 om-89) had the moisture content of 15% (oven dry basis). Wood samples were taken from a poplar plantation in Tokat province in Turkey. Selected trees were 12 years old and had 28-30 cm in diameter.

The chemical analysis of the raw material: Specimens were sampled and prepared according to Tappi T 257 om-85 for chemical tests. Holo cellulose contents was determined by the chlorite method (Wise and Karl, 1962), cellulose content by Kürschner-Hoffner's nitric acid method (Browning, 1967), and α -cellulose content by Tappi T 203 om-71 method (Anonymous, 1992). The following tests were performed to determine the lignin (Tappi T 222 om-98), pentosan indication (Browning 1967) and ash (Tappi T 211 om-93) contents. The solubility properties were also determined based on alcohol-benzene (Tappi T 204 cm-97), cold and hot-water (Tappi T 207 om-93) and 1% NaOH (Tappi T 212 om-98) methods (Anonymous, 1992).

Pulping production: In organosolv (ethanol-water) cooking method, the delignification of the poplar wood was made in a closed autoclave according to the cooking conditions shown in Table 1. In this study, cooking was made with and without catalyst. In cooking without catalyst, the necessary acidic environment for delignification was obtained by the hydrolysis of acetyl groups of lignocellulosic materials at high temperature. As a result, the lignin structure was broken and passed to the solvent phase without decreasing the pH level of the cooking liquor. The purpose of this application is to reach high pulp efficiency and limited degradation carbohydrate part. On the other hand, it is possible to decrease the cooking temperature by using catalyst (Aziz and Sarkanen, 1989).

In the cooking operation, a revolving (at 2 rpm) laboratory rotating digester with a capacity of 15 lt was used. It is resistant to a maximum pressure of 25 kg cm⁻² and has a digital temperature control mechanism. Loadings and discharges were made by hands and 300 g dry poplar wood chip was used in each cooking. Ethanol-water liquor at various ratios were used as cooking liquor, according to the general principles of Kleinert (1975). Also catalyst (H₂SO₄) was added to the liquor to increase delignification. The rising period to maximum temperature is considered constant as 90 minutes and the ratio of liquor to chip was kept as a constant level of 8/1. As mentioned in the previous studies (Kirci and Akgul, 1999), because of the property of organosolv lignin during the discharging of the digester, the lignin passing to liquor phase was treated with basic pulp in order not to be absorbed by the fibers. In this study, the pulp was treated at 95°C for 60 min by 8% alkaline environment. After these operations, the precipitated pulp which is cleaned from organosolv lignin was washed with water. The pH value of the black liquor, taken from the digester at the end of cooking, was measured. After these operations, the pulp was filtered through a Noram type pulp sieve with 0.15 mm mesh. The pulp was then squeezed to 20-25% ratio of solid particle and placed into polyethylene bags. The yield content of the pulps and rejects were determined according to Tappi (T 210) by gravimetric measurements in the laboratory environment. The screened yield was determined from duplicate analyses. Adding the yield of rejects to the screened yield gave total pulp yield. The kappa number (Tappi T236) and viscosity (SCAN cm 15:88) of the pulp samples were also determined by double experiments (Anonymous, 1988).

Results and Discussion

The chemical analysis of the poplar wood: The chemical analysis results applied to poplar wood are given in Table 2.

Table - 1: Cooking conditions applied during pulping production from organosolv poplar wood

Pulp code	Ethanol ratio (%)	Pulping time (min.)	Pulping temp. (°C)	Catalyst ratio (H ₂ SO ₄) (%)	Maximum pressure (Mpa)	White liquor pH	Liquor / Wood ratio(w/w)
1	40	90	180	0.00	1.80	8.08	8/1
2	40	90	180	0.01	1.80	8.08	8/1
3	40	90	180	0.02	1.80	8.05	8/1
4	40	120	180	0.00	1.75	8.05	8/1
5	40	120	180	0.01	1.80	8.05	8/1
6	40	120	180	0.02	1.80	8.10	8/1
7	40	150	180	0.00	1.80	8.10	8/1
8	40	150	180	0.01	1.80	8.10	8/1
9	40	150	180	0.02	1.80	8.10	8/1
10	50	90	180	0.00	1.85	7.75	8/1
11	50	90	180	0.01	1.83	7.75	8/1
12	50	90	180	0.02	1.80	7.75	8/1
13	50	120	180	0.00	1.83	7.78	8/1
14	50	120	180	0.01	1.85	7.78	8/1
15	50	120	180	0.02	1.85	7.78	8/1
16	50	150	180	0.00	1.88	7.8	8/1
17	50	150	180	0.01	1.88	7.80	8/1
18	50	150	180	0.02	1.88	7.80	8/1

In all cooking, the maximum cooking temperature was reached at 90 minutes

Table - 2: A Comparison of chemical properties and solubility values of poplar wood (*P. euramericana* L.) and some other hardwoods (% of o.d wood).

Component	<i>Populus euroamericana</i> *	<i>Populus alba</i> **	<i>Carpinus orientalis</i> ***	<i>Salix alba</i> #	<i>Robin opseudoacacia</i> ##
Holocellulose	80.60	—	79.08	78.10	82.03
Cellulose	49.20	49.00	—	53.50	53.10
α -cellulose	42.80	—	—	—	51.63
Lignin	19.30	23.10	18.20	21.60	21.27
Pentosans	28.90	25.60	26.89	21.80	21.93
Ash solubility	0.51	0.20	0.85	—	0.55
Alcohol-benzene	1.85	—	—	3.20	6.23
1% NaOH	20.04	—	20.50	21.50	22.10
Hot water	2.50	—	4.94	7.40	8.06
Cold water	1.88	—	—	—	—

* Mean values are the average of duplicate measurements. **Fengel and Wegener, 1984, ***Tank, 1980, #Eroglu and Usta, 1989, ##Kirci, 1987

Table - 3: The properties of pulping from poplar wood by ethanol-water process

Pulp code	Black liquor pH	Screened yield (%)	Reject (%)	Total yield (%)	Kappa number	Viscosity (cm ² g ⁻¹)
1	3.40	39.17	12.90	52.07	61	844
2	2.97	33.86	5.42	39.38	27	490
3	2.06	20.72	2.89	23.61	17	189
4	3.02	42.06	8.62	50.68	57	755
5	2.90	36.22	2.19	38.41	21	428
6	1.97	16.36	2.01	18.37	15	146
7	3.06	42.47	5.30	47.77	55	701
8	2.86	35.87	1.46	37.33	19	471
9	1.90	14.27	2.28	16.55	14	126
10	4.10	44.49	11.02	55.51	67	892
11	3.15	40.44	3.17	43.61	29	696
12	2.80	22.96	2.80	25.76	16	364
13	3.17	43.01	8.20	51.21	58	889
14	2.80	32.28	2.25	34.53	26	555
15	2.40	15.03	1.42	16.45	16	192
16	3.14	42.82	6.69	49.51	54	825
17	2.76	28.36	1.20	29.56	22	561
18	1.92	12.80	1.90	14.70	13	131

The main components of poplar wood and various solubility values of poplar wood were mentioned as well as other hardwood types. The values of poplar wood (*Populus euramericana*) except pentosan are nearly same in all wood species. However pentosan value is higher in poplar wood.

Properties of organosolv pulps: The screened yield, total yield, reject, black liquor pH, viscosity and kappa number results of organosolv pulps obtained from the poplar wood by different cooking conditions are given in Table 3. As the cooking period increases, while other cooking parameters are kept constant, the total yield decreases and there are losses in screen reject. In cookings made without or with 0.01% acid catalyst, at 40% constant ethanol ratio, when the pulping time was increased from 90 to 150 min, increased the screen yield. When the ethanol ratio is 50% or the acid catalyst ratio is 0.02%, the increase in pulping time, caused loss in screen and total yield.

Maximum screen and total yield were obtained from cookings made without catalyst. Increasing acid concentration in pulping liquor

caused significant losses in screen and total yield. The reasons of these decrease may be the acidity increase of the cooking environment as a result of decreasing black liquor pH values given in Table 2. It is well known that the acidity increase of the cooking environment increases the degradation of carbohydrates and decreases the screened yield relevantly. The increase of acid catalyst ratio, causes the organosolv pulp to cook better and separate into fibers easier which reduces the reject ratio. When acid is used more than a concentration of 0.01%, although a better cooking is achieved and less reject occurs, it causes unacceptable losses in screened yield and paper making capability of the pulp, possibly due to the degradation of carbohydrate composition.

Considering the other pulping parameters constant, when pulping without catalyst, the screen yield measured according to the cooking time is 39-42.5% at an ethanol ratio of 40% while it is 42-44% at an ethanol ratio of 50%. As a result of pulping made without catalyst, pulps cooked with 50% ethanol has a 1.5-3% more yield

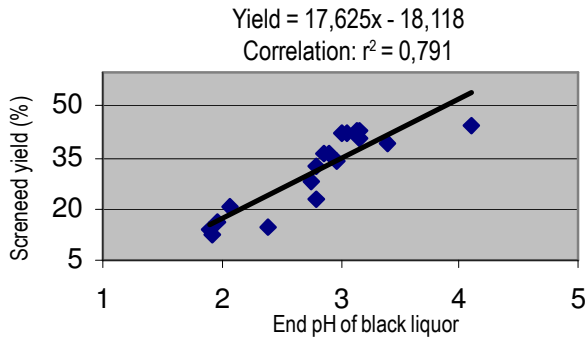


Fig. 1: Correlation between end pH of black liquor and yield

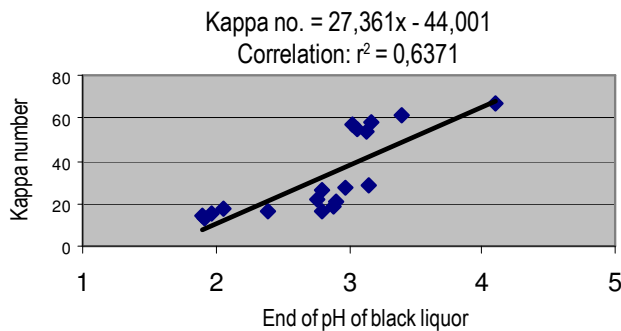


Fig. 2: Correlation between end pH of black liquor and kappa number

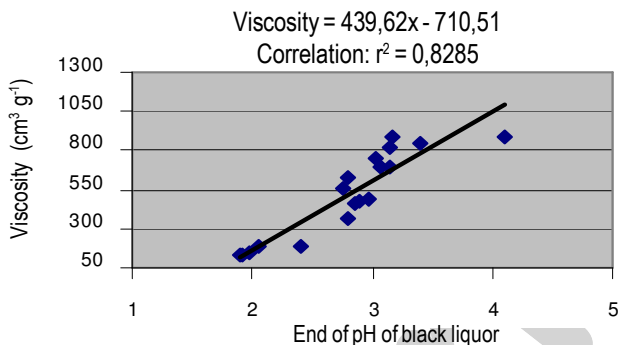


Fig. 3: Correlation between end pH of black liquor and pulp viscosity

compared with pulps cooked with 40% ethanol. The reason is probably the carbohydrates are being protected more effectively against hydrolysis reactions in high alcoholic environment. When acid catalyst is used, the high alcoholic environment can not prevent hydrolysis. As seen in Table 2, in acid concentrations especially higher than 0.01%, yield decreases rapidly.

The change in ethanol ratio in cookings made with or without acid catalyst have a little effect on kappa number. When cooking period and acid ratio is kept constant, kappa number increases with increasing ethanol ratio. Kappa number increases 1-6 units when ethanol ratio is increased from 40 to 50% without using catalyst. Even when acid catalyst is used, kappa number increases with increasing ethanol ratio.

In 90 min, when ethanol ratio is increased from 40 to 50%, the kappa number of the pulp increases by 6% but in 150 minutes of cooking there is no difference. When acid concentration is

increased, kappa number decreases related with time. Generally increasing the cooking period effects delignification positively. However if the period is too long, delignification reactions slow down and even lignin condensation may occur. The reason of this phenomena, is acidity increase of black liquor due to increase of cooking time and temperature and as a result lignin fragments reacting with radicals to combine again and also the solution's electrolytic balance being destabilized and lignin passing to cooking solutions as colloidal pieces and determined on the fibers again (Paszner and Cho, 1989; Mc Danough, 1993). This phenomenon is especially evident in cookings made without catalyst.

It is clearly seen that in cookings made by the use of catalyst, the kappa numbers are lower than cookings without catalyst. In general, in all the cookings, as acid ratio increases kappa number decreases. Eventhough adding catalyst decreases residual lignin ratio, it has an adverse effect on efficiency and fiber quality.

In cooking environment where there is alcohol, it is possible to see the same effect as acidity increases. In cases where acid is not added as catalyst, environment acidity increases in high temperatures as wood gets away from acetyl groups, thus benefiting delignification. Adding low quantity of inorganic acid to the cooking environment accelerates delignification reactions. (Aziz and Sarkanen, 1989).

In cookings made with and without catalyst, the increase in ethanol ratio has less effect on viscosity. If acid catalyst ratio and cooking time is kept constant and ethanol ratio is increased, the viscosity also increases. In cookings made without catalyst, if ethanol ratio is increased from 40 to 50% and cooking time is increased from 90 to 150 min, the viscosity increases by 50-125 cm³ g⁻¹. Even if acid is used, increasing ethanol ratio has a protective effect on viscosity. Viscosity increase due to ethanol ratio increase in the cooking liquor was also determined in previous studies (Sierra-Alvarez and Tjeerdsma, 1995).

In cooking with 40% of ethanol ratio and without catalyst, if the cooking time is increased, the viscosity decreases. However no change in viscosity is observed if ethanol ratio is 50%. A 67 cm³ g⁻¹ decrease can only be seen when the cooking time is 150 minutes. As a result, the decrease in viscosity can be prevented by increasing ethanol ratio when cooking time is increased without catalyst.

Generally the viscosity values of the cookings without catalyst are higher. When the catalyst ratio is increased, significant viscosity decreases occur in pulp. As acid ratio and cooking time increases, the pH of the cooking environment decreases abnormally and cellulose degradation becomes dominant which causes viscosity to decrease. As in traditional methods, the increase of each two variables affects the viscosity negatively. (Browning, 1967). It is clear that, during the washing of pulp with diluted base after cooking, most of the base is consumed by organosolv lignin. Also cellulose is not effected much in this operation, only hemicelluloses with low polymerization degrees, which can be easily hydrolyzed in base, can be dissolved. It is obvious that, in order to obtain well cooked

pulps with maximum viscosity, cooking should be made without catalyst or with catalyst and at low temperature.

In this study, it was understood that delignification is related with the pH of the black liquor. When Table 3 is examined, it will be seen that reactions are more moderate when pH of the black liquor is around 4, as acetyl groups can not be liberated sufficiently in high pH values. Whereas, in cookings with acid catalyst, if pH is lower than 3, the lignin passing to the pulping liquor tends to precipitate again on the fibers. In studies made about this subject, a complex mechanism was considered such as dissolved lignin fragments recondensating at low pH value, as well as hemicelluloses dissolving hydrolytically and carbohydrate degradation occurring (Mc Danough, 1993; Kirci and Akgul, 1999).

During the cooking of hardwoods by ethanol – water method without catalyst, acetyl groups within the structure of o-acetyl-4-o-methyl glucuronoxylan chipping off at high temperature contribute to decrease of pulping liquor pH value (Pasznar and Cho, 1989). As seen in Table 3, especially if pH is below 3.5, a good fiber separating occurs with help of acetic acid as catalyst. At maximum temperature, an increase in pulping time results with a decrease in pH value and kappa number of the pulping liquor. Although catalyst addition to pulping liquor accelerates the delignification reaction, if excess mineral acids are added to pulping liquor, degradation reactions of polysaccharides at low pH values are accelerated which may cause serious viscosity and yield losses. Especially the hydrolytic degradation reactions of carbohydrates accelerate seriously if more than 0,01% mineral acid is added to pulping liquor.

The yield of ethanol–water pulps obtained from poplar wood, kappa number and viscosity values are closely related with the last pH value of the black liquor (Fig. 1-3).

As seen in Fig. 1, there is a statistically linear relation between black solution pH and pulp efficiency. ($R^2=0.791$) Hydrolytic and separating reactions are dominant. In low pH's the most important problem is the unacceptable decreases in pulp yield.

In Fig. 2, the effect of last pH to kappa number can be seen. As seen in Fig. 2, there is a statistically linear relation between black liquor pH and pulp yield ($R^2=0.6371$). As a result of increasing the reaction period and catalyst ratio, a rapid pH decrease can be observed in pulping liquor related with the acceleration of the carbohydrate decay in delignification process. Besides it was found that there is a statistically important relation with last pH value with pulp viscosity. As seen in Fig. 3, the R^2 value that reflects the degree of the relation is calculated as 0.8285. In acidic environment, cellulose chains may possibly be broken with acid hydrolysis. Similar results were obtained by Kirci and Akgul (1999).

According to above evaluations, cooking number 10 was selected as the most suitable cooking. In these conditions, regarding the organosolv pulps obtained from poplar wood, the screened yield was measured as 44,49%, viscosity as $892 \text{ cm}^3 \text{ g}^{-1}$ and kappa number as 67.

In order to produce a pulp with high yield, acid catalyst should not be used. Cooking with acid addition, increases delignification, decreases the reject ratio and causes serious yield losses in screened pulp. If acid concentration is more than 0.01% the yield decrease becomes more significant. Besides, carbohydrate degradation reactions decrease the DP of the cellulose and the strength of pulp relevantly.

Maximum pulp screened yield is obtained at 50% ethanol usage and without acid. If the purpose is to produce bleachable pulp with short fibers, a cooking period of 120-150 minutes may be enough. However the pulp screened yield will be lower than basic pulp producing methods. Maximum delignification was obtained from cookings made with 0.01 and 0.02% acid catalyst. However due to increasing hydrolysis reactions in acidic environment and also thermic hydrolysis reactions occurring, serious decreases take place in pulp viscosity and relevantly in cellulose DP which will abnormally decrease the resistance properties of the pulp.

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References

- Anonymous: Poplar cultivation in Turkey, T.C. Ministry of Forest, Research Department for Rapid Growing Forest Trees Like Poplar, Izmit (1994).
- Anonymous: Tappi Test Methods 1992-1993. Tappi Press Atlanta, GA, USA (1992).
- Anonymous: Pulps-Viscosity in Cupri-ethylenediamine Solution, SCAN-CM 15:88, Scandinavian Pulp, Paper and Board Testing Committee, Sweden (1988).
- April, G.C., M.M. Kamal, J.A. Reddy, G.S. Bowers and M. Hansen: Delignification with Aqueous-Organic Solvents. *Tappi Journal*, **62**, 83-85 (1979).
- Aranovsky, S.I. and R.A. Gortner: U.S. Patent No. 2037-001 (1936).
- Aziz, S. and K. V. Sarkanen: Organosolv pulping-A review. *Tappi Journal*, **72**, 169-175 (1989).
- Browning, B.L.: Methods of Wood Chemistry. Vol. 1-2, Interscience Publishers, N.Y., USA (1967).
- Eroglu, H. and M. Usta: Investigations on utilisation possibilities of white willow (*Salix alba* L.) wood in pulp and paper industry. *J. Agric. Forestry of Tubitak*, **13**, 235-245 (1989).
- Fengel, D. and G. Wegener: Wood: Chemistry, Ultrastructure, Reactions. Walter de Gruyter, 613 s. Berlin (1984).
- Hergert, H.L.: Tappy 1992 Solvent Pulping Symposium Notes, Tappi Press, Atlanta. p. 1 (1992).
- Johansson, A., O. Aaltonen and P. Ylinen: Organosolv pulping methods and pulping properties. *Biomass*, **13**, 45-65 (1987).
- Kleinert, T.N.: Organosolv pulping with aqueous alcohol. *Tappi Journal*, **57**, 99-102 (1974).
- Kleinert, T.N.: Ethanol-water delignification of wood-rate constants and activation energy. *Tappi Journal*, **58**, 170-172 (1975).

- Kirci, H.: Investigations on the utilisations possibilities of locust wood (*Robinia pseudoacacia* L.) in the pulp and paper industry. *J. For. Faculty KTU*, **10**, 64-90 (1987).
- Kirci, H. and M. Akgul: Autocatalyzed ethanol-water pulping of wheat (*Triticum aestivum* L.) straw, Turkish. *J. Agric. Forestry*, **23**, 1283-1290 (1999).
- Kordsachia, O., B. Wandering and R. Patt: Some investigations an ASAM pulping and chlorine free bleaching of Eucalyptus from Spain. *Holz als Roh und Werkstof*, **50**, 85-91 (1992).
- Mc Danough, T.J.: Solvent pulping. The chemistry of organosolv delignification. *Tappi Journal*, **76**, 186-193 (1993).
- Paszner L. and H. J. Cho: Organosolv pulping: Acidic catalysis options and their effect on fiber quality and delignification. *Tappi J.*, **72**, 135-142 (1989).
- Patt, R., O. Kordsachia and H.L. Schubert: Laboratory and Pilot Plant Scale ASAM Pulping of Soft and Hardwoods and Chlorine Free Bleaching of The resulting Pulps, Proc. Braz. Symp. Chem. Lignins Other Wood Compan. 2nd, 3, 56-71 (1992).
- Sierra-Alvarez, R. and B.F. Tjeerdma: Organosolv pulping of poplar wood from short-rotation intensive culture plantations. *Wood and Fiber Science*, **27**, 395-401 (1995).
- Stockburger, P.: An overview of near-commercial solvent-based pulping process. *Tappi Journal*, **76**, 71-74 (1993).
- Sundquist, J., L. Laamanen and K. Poppius: Problem of non-conventional pulping processes in the peroxyformic acid cooking experiments. *Paperi Ja Puu.*, **70**,143-148 (1988).
- Tank, T.: NSSC Pulping Characteristics of Beech and Hornbeam Woods, Istanbul University Press, Book No. 2779-231, Istanbul (1980).
- Wise, E.L. and H.L. Karl: Cellulose and hemiselulose. *In: Pulp and paper science and technology* (Ed.: C. Earl Libby). Vol.: I, Pulp. Mc Graw Book Co., New York (1962).