DELIGNIFICATION OF ALEPPO PINE WOOD (*Pinus halepensis* Mill) BY SODA-ANTHRAQUINONE PROCESS: PULP AND PAPER CHARACTERISTICS

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Aleppo pine, the dominant species of the Algerian forest, grows in sufficient quantity to satisfy its various industrial applications. Papermaking is a possible way for the valorization of the wood products resulting from thinning operations or short rotation logging. The present study observes the delignification of aleppo pine (*Pinus halepensis* Mill) young wood by an alkaline process (soda-anthraquinone), which allows the preparation of a chemical pulp from this type of wood (small wood). The physico-chemical and morphological analysis of the pulp is carried out, along with the study of delignification, to better understand the reactivity of wood in alkaline cooking. The kinetics of delignification shows that a total cooking time of 135 min makes it possible to exceed the defibring point by giving a yield bordering 44% with a kappa number of 29. It is obvious that the results obtained encourage the use of aleppo pine young wood as a raw material for the Algerian paper industry.

Keywords: aleppo pine, soda-AQ, delignification, yield, kappa number, pulp

INTRODUCTION

In Algeria, aleppo pine, *Pinus halepensis* Mill, considered the most important and dominant local forest species, covers a surface estimated[1] at more than 800,000 ha. It is a typically Mediterranean species, easily adaptable to various eco-climatic conditions, which grants it the privilege of being the most often used tree species in the country's reforestation programs. Nevertheless, its industrial utilisation rate remains still low, compared to the available mass of wood.The quantity of mobilized wood is considerable, as part of logging or thinning operations and could satisfy varied industrial uses (timber wood, decking industry, paper industry, etc). The upgrading of small woods may be a possible alternative for paper industry. Thus the wood capital available would contribute certainly to attenuate the deficit of fibre resources.

The search for new resources with necessary qualities constitutes a major concern of the Algerian papermaking branch. In addition, the softwood, known as "conventional", is more demanded in paper industry, if considering the paper quality resulting from the kraft process. However, the problem of olfactory pollution inherent to the kraft process requires an alternative to prevent this harmful effect. The soda-anthraquinone process has already been the subject of many investigations and its application seems more appropriate as an environmentally friendly method, permitting to avoid the malodorous emissions of the sulphur compounds resulting from the kraft

process.[2,3] The beneficial effect of anthraquinone comes from the properties of this quinone, acting as a pseudo-catalyst and allowing an equally fast and complete delignification as that resulted from the kraft process. Indeed, it is well established that the addition of anthraquinone to soda cooking liquors improves the kinetics and selectivity of delignification and increases the pulp yield, as compared to soda alone.[2-4]

In addition, the morphological and chemical characteristics of wood differ greatly among the various species; even within the same species, wood varies with age and origin. Also, the paper qualities differ depending on both the above-mentioned characteristics and the paper treatment applied.[5]

To this end, the pulping of aleppo pine young wood as small wood was performed by the soda-AQ process, to assess its paper potential. This involved the study of the delignification kinetics to understand the behavior and reactivity of wood in the cooking process, along with the analysis of the obtained pulp and paper. Such a study establishes the paper characteristics, allowing a thorough upgrading of this wood species. The present work investigates the soda-AQ pulping of Algerian aleppo pine, under the cooking conditions applied for softwoods.

MATERIALS AND METHOD

Vegetal material

The wood samples used in this study have been collected from a young aleppo pine stand, planted in a natural forest of berbery thuja (*Tetraclinis articulata* Vahl), located in the forest zone of Taount, department of Tlemcen (Algeria). This area, located on the Western littoral, is characterized by:

- a semi-arid bioclimatic layer with wet winter;
- altitude: 240-260 m;
- average annual precipitation: 300-400 mm;
- mean temperature: 18 °C;
- calcareous brown soil type.

The two trees collected, approximately 32 years old, can be considered as young *versus* the maturity age of aleppo pine (80 to 100 years old).

The two harvested trees, between 17 and 20 cm in diameter at breast height, had a total height between 8 and 9 m. The chips were chopped manually to a 5-6 mm width, 5 mm thickness and 25-35 mm length, using pruning-scissors.

Chemical analysis of wood

The alleppo pine wood used in the study has been chemically analyzed. Two successive extractions have been carried out, using the traditional Soxhel apparatus, first with water, then with an alcohol/toluene mixture (1/3 2/3), lasting for 7 h each. The following measurements were carried out, by the appropriate methods:

- cellulose content, by the Kurschner-Hoffner method;
- lignin content, by the Klason method;
- furfural yield;
- ash content, by incineration at 800 °C.

Soda-AQ cookings

The soda-anthraquinone process was applied for aleppo pine wood delignication. The addition of about 0.05 to 0.25% anthraquinone (AQ), on dry-mass wood, to the soda cooking liquors leads to the same effect as that of Na_2S in kraft cooking.[3,4] The percentage of anthraquinone used in this study is much higher, for obtaining the maximum effect of the catalyst.

The cookings were carried out in a rotary system composed of 6 “batch system” digesters, having 1.1 L unit capacity “system multi-shells”, electrically heated, available in the Pagora laboratory of Grenoble, France. The rise in temperature is programmed by an automated system, the temperature being measured by thermo-couples.

The cooking reagents have been prepared just before use, to avoid soda carbonation.

After the necessary pulping time, the reaction was stopped as soon as possible, by external watering with cold water for 20 min, then by degasification of the digester before opening, after which the pulp was separated from the black liquor. The soda content not consumed in the black liquor was determined by conductometric analysis, using a titrated hydrochloric acid solution.

Conditions of aleppo pine wood delignification

In line with the data available in the literature on the delignification of the various softwood species by soda-anthraquinone, the following parameters were involved:

- NaOH concentration: 60 g/L;
- Dry wood mass: 120 g;
- Liquor-to-wood ratio (L/W): 5;
- Anthraquinone: 1.5%;
- Cooking temperature: 165 °C;
- Cooking time: variable;
- Rate of temperature rise: 2.3 °C/min.

The liquor-to-wood ratio (L/W) has been intentionally chosen high to prevent a possible high alkali consumption.

For each cooking, the chips have been separated in two fractions, cooked simultaneously, the former, of approximately 100 g, being used to characterize the pulp obtained, the latter, of approximately 20 g, placed in a bag made of stainless cloth (90 µm mesh) and used to determine pulping yield by weighing it before and after the removal from the digester.

Pulp treatments

After each cooking, the resulting pulp was carefully washed with water until neutrality was reached, then disintegrated in a laboratory Sprout Waldron disintegrator. Two passages are necessary, corresponding to disc spacings of 25 hundredths of inch (first step), and then of 15 hundredths of inch (second step). The pulp has been screened using a Weverk apparatus (slit width = 0.15 mm), to separate non-disintegrated elements by collecting the pulp on a sieve of 90 µm mesh. The pulp obtained was beaten using a Lampen mill until reaching a freeness (°SR) equal to 42, and then transformed into paper sheets of 2 g, manufactured on a laboratory Frank Rapid Köthen apparatus. The conditioned sheets were tested for their strength properties.

Analytical methods

To characterize the pulp obtained, the following indices have been measured:

- Kappa number
- Residual lignin rate (Noll method)
- Furfural yield and pentosans content (NF T 12-008)
- Holocellulose content
- Viscosimetric polymerization degree, Vdp (NF T 12-005)

Morphological measurements on fibres have been carried out on a Morphi apparatus. The following paper sheet parameters have been determined:

- Thickness (NF Q 03-016)
- Weight (NF Q 03-019)
- Bulk density, g/cm^3 (relationship between paper mass/m^2 and thickness)
- Breaking length L_B (NF Q 03-004)
- Burst index I_B (NF Q 03-053)
- Tear index I_T (NF Q 03-001)
- Jaw jointed breaking length (LR_0) (m) measured on the dry sheet
- Double-folds

RESULTS AND DISCUSSION

Chemical composition of aleppo pine wood

Aleppo pine wood is a mid-mass wood with an average resin content, being highly similar to pinaster pine wood.[6] Its chemical composition may vary, according to tree age and growth conditions.

Chemical analysis gives the exact composition of the aleppo pine wood used in this work, the results being summarized in Table 1. It seems that the chemical composition of aleppo pine is comparable to that of the pinaster pine, also corresponding to most of the coniferous trees growing in temperate regions. The differences between trees belonging to the same species can be attributed to tree age or to environmental conditions.

It is important to know the content of extractives characteristic of pine wood, as it may have a negative effect on the chemical cooking process. In the sample under analysis, it does not exceed a total content of 5%. The resin amount measured by the quantity extracted by an alcohol/toluene mixture represents about 32% of the total extracts.

The pentosans content obtained according to the furfural yield, which is higher in young than in old wood, provides information on the amount of hemicelluloses.[7] The pulp yield was lower, whereas the quantity of hemicelluloses is more significant.[5]

Delignification study

The delignification kinetics has been obtained by varying the duration of the stage (20, 40, 60, 90 and 120 min) after a rise in identical temperatures with 2.3 °C/min for each cooking. The delignification results obtained are listed in Table 2.

The kinetic study shows that the delignification, illustrated by the graphic ln (Y.K) = f(t) in Figure 1, can be assimilated, after the temperature rise phase, to the succession of two first-order reactions: bulk and final.[8-10] The transition point located between bulk and final delignification corresponds to the optimum conditions at which the pulp shows concomitantly the best possible mechanical characteristics and a good bleaching capacity. In the case of aleppo pine pulp, the transition point is identified at 135 min, for a temperature level of 165 °C, which corresponds[11] to an H factor equal to 920 and to a delignification degree of 92%.

Table 1
Wood chemical composition (% to dry wood)

Component, %	Aleppo pine	Pinaster pine[5]
Water extract	3.2	1.3
Alcohol/toluene extract	1.5	2-4
Cellulose	46.3	47.1
Lignin	26.9	25.6
Furfural yield	8.4	-
Pentosans*	14.3	12.3
Ash rate	0.31	0.30

* based on the furfural yield

Table 2
Aleppo pine wood delignification

Cooking	Total time (min)	Time to max. temperature (min)	Raw yield (%)	Kappa number	Remaining lignin content (%)
1	78.8	20	53.74	66.78	10.19
2	99.5	40	49.81	42.41	6.70
3	118.5	60	47.71	34.13	4.87
4	149.3	90	41.62	25.53	4.26
5	178	120	39.25	23.27	4.11

The yield and kappa number evolution according to the cooking time is presented in Figure 2. The relation correlating these two parameters, for kappa numbers ranging between 20 and 70, can be expressed by a linear equation as:

$y = 35.1 + 0.293 \times K$, where

y: yield (%), K: kappa number.

Figure 3 and Table 3 illustrate the evolution of the main wood components during cooking (soda + AQ). Mention should be made of the subsequent reduction in the amount of pentosans (proportional to the amount of hemicelluloses) as the cooking time increases, which consequently leads to a significant drop in pulp yield. The elimination of hemicelluloses is largely due to the nature of this type of polymers (polymeric, with branched structure, low molecular mass and a high number of reaction sites, as compared to cellulose). The loss of hemicelluloses appeared in the initial phase and continued especially during the bulk phase, resulting in a loss of pentosans higher than 70% (Fig. 3). Initially, the holocellulose loss is related mainly to the dissolution of hemicelluloses, due to the primary peeling effect.

The holocellulose content will undergo a second drop during the bulk phase, *i.e*. between 120 and 135 min, which obviously corresponds well to polysaccharides degradation under the action of alkaline hydrolysis and secondary peeling. At the level of the final phase, the holocellulose quantity continues to decrease, although only slightly, by the loss of – especially – pentosans, while the delignification degree is slightly improved in this phase by only 2%, compared to the value obtained in the transition point.

Wood delignification is also accompanied by modifications in the pulp morphology.[12] The results provided by the Morphi apparatus for each cooking are listed in Table 4.

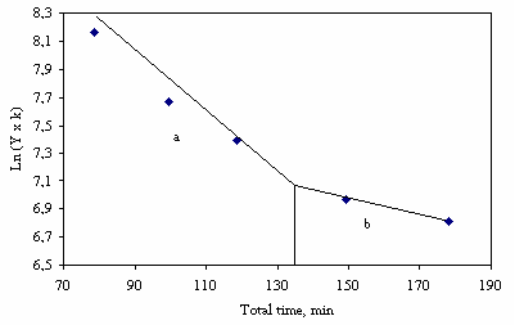

Figure 1: Determination of the transition point: a – bulk delignification; b – final delignification

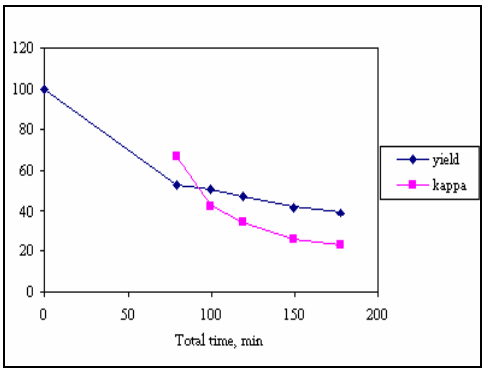

Figure 2: Yield and kappa number evolution *versus* time

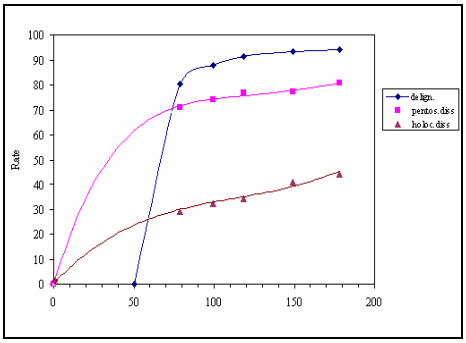

Figure 3: Delignification and polysaccharides dissolution *versus* time

Table 3
Delignification rate of pentosans and holocellulose (%/wood) *versus* time

Cooking time (min)	Delignification rate	Pentosans (%)	Holocelluloses %
78.8	80.2	4.14	48.31
99.5	87.7	3.7	46.10
118.5	91.4	3.31	44.82
149.3	93.4	3.26	40.07
178	94.2	2.76	37.42

Table 4
Morphological characteristics of the pulp measured on the Morphi apparatus

Cookings	Number (mil/g)	Fines (%/surface)	Mean length	Width (µm)	Coarseness (mg/m)
1	1.51	1.03	1.76	34.4	0.42
2	1.56	0.8	1.71	34.2	0.40
3	1.76	0.48	1.63	32.2	0.38
4	2.07	0.32	1.61	32.7	0.31
5	2.14	0.27	1.63	31.8	0.30

Table 4 shows that the reduction in pulp yield led to an increase in the number of fibres per gram and, consequently, to low coarseness, without significant modifications in the fibre size (length and width). A significant reduction of the fine elements in the pulps was also observed. The fine elements ratio depends especially on the refining intensity, being related to fibre rigidity.

Unbleached pulp characteristics

a. Physical, chemical and morphological characteristics

The pulp produced at a total cooking time of 135 min (corresponding to the transition point between bulk and final delignification) shows the physico-chemical and morphological characteristics summarized in Tables 5a and 5b.

Table 5a shows that aleppo pine wood can be easily delignified by the soda-AQ process, an important yield, comparable to that found for other pine species, Radiata pine particularly,[13] being recorded at the same delignification degree. The kappa number obtained, equal to 29.3, is a normal value, corresponding in practice to the conventional value found for softwood. At such a level, the delignification rate reached is of 92% *versus* the initial lignin rate registered in wood. The uncooked wood chips rate is also weak, expressing the delignification quality *versus* the net yield.

The measurement of the viscosimetric polymerization degree (Vpd = 1470) indicates[5] a good quality of the produced pulp (a good pulp should have a Vpd higher than 1100).

The furfural yield is very low, expressing the decreased pulp content of the hemicelluloses. The remaining pentosans content was equal to 3.3%, while the dissolution rate of this fraction amounted to 77%.

Fibres with a length below 2 mm represent 60% in the pulp, of which 47% range between 0.1 and 0.5 mm, so that the arithmetic mean length reaches only 1.6 mm and average width = 23 μm. The other characteristics are presented in Table 5b.

In addition, the soda remaining in the black liquor indicates that the consumed soda content is of 12.7% (to the dry wood), which permits to specify that the initial soda amount necessary for cooking the pine wood was between 18 and 20%, at a liquor-to-wood ratio (L/W) from 3 to 3.5.

Table 5a
Physical and chemical characteristics of unbleached pulp

Raw yield (%)	43.8
Net yield (%)	43.0
Kappa number	28.6
Viscosimetric polymerisation degree *DPv*	1470
Furfural yield	1.93
Pentosans content (%)	3.28
Residual lignin (%)	4.61
Consumed soda (%)	12.7

(%: on dry wood)

Table 5b
Morphological characteristics of fibres

Fiber number (mil/g)	Fines (%/surface)	Mean length (mm)	Width (μm)	Coarseness (mg/m)
2.11	0.35	1.636	32.4	0.336

Table 6
Mechanical characteristics of unbleached pulp

Freeness (°SR)	42
Weight (g/m²)	68.1
Thickness (μm)	95.3
Bulk (cm^3/g)	1.4
Tear index ($mN \cdot m^2/g$)	8.62
Burst index ($kpa \cdot m^2/g$)	5.13
Breaking length (m)	7300
Jaw jointed breaking length (LR_0 dry) (m)	14270
Double-folds (under mass 600 g)	658

b. Mechanical characteristics

Paper quality depends not only on the wood type used for pulping, but also on the process applied for pulp preparation.[5,13] The physical properties of the pulp beaten at 42 °SR are summarized in Table 6.

All these characteristics are related to the chemical aspect of the obtained pulp, which contains only a small amount of hemicelluloses, with prevailingly short fibres. The paper characteristics reflect the nature of the vegetal material used – young wood –, being fully integrated in the interval of values expected for the physical properties of softwood pulp, in particular those related to pines.

CONCLUSIONS

Aleppo pine, *Pinus halepensis* Mill, largely widespread in Algeria, presents a paper potential that should be taken into account for a complete upgrading strategy of this species. The delignification of aleppo pine young wood by the soda-anthraquinone process permits to establish the optimum conditions of delignification, *i.e*. the "transition point between bulk (fast) and the final (slow) delignification", which corresponds to a necessary cooking time of 135 min, at a temperature of 165 °C; the pulp yield exceeds 43.8% and the Kappa index is 29. Such a yield value is normal, if taking into account the lignin content in wood. Compared to the initial lignin content in wood (27%), the deligni-fication degree now reached is equal to 92%.

Delignification, following "the deligni-fication kinetics", shows that the prolongation of the cooking beyond 135 min leads to an approximately 1% loss of yield by point of kappa gained, which corresponds to a strong degradation of the carbohydrates fraction.

As to the morphological aspect, yield reduction possibly results in reduced coarseness, a significant reduction of the fine elements for the well-delignified pulp being noticed.

The characteristics of the paper refined at 45 °SR are relatively good – considering the raw material used – comparable with those obtained for softwood pine species, especially.

The main physical tests performed indicate that the breaking length, burst index and tear index take values of 7300 m, 5.1 $kpa \cdot m^2/g$ and 8.6 $mN \cdot m^2/g$, respectively.

The results obtained are encouraging as to considering aleppo pine as a possible fibrous source for the Algerian papermaking industry and as a means for a rational upgrading of the wood resources available by aleppo pine reforestation.

REFERENCES

[1] B. Kadik, "Contribution à l'étude du pin d'alep (*Pinus halepensis Mill*) en Algérie. Ecologie, dendrométrie, morphologie", Office des Publications Universitaires, Alger, 1986, 581 pp.
[2] L. Olm, L. Hakansdotter and T. Jönsson, *Zellcheming Annual Meeting*, Sweden, 2001, pp. 41-45.
[3] H. H. Holton and F. L. Chapman, *Tappi J*., **60**, 121 (1977).
[4] A. Robert, *ISWPC*, Paris, April 27-30, 1987, Vol. 1, p. 415.
[5] D. Vallette and C. De Choudens, "Le bois, la pâte et les papiers", Centre technique du papier, 2ème Ed., 1989, 192 pp.
[6] A. Dilem, *Thèse de Doctorat*, INP de Lorraine, France, 1992, 173 pp.
[7] A. Haddad, D. Lachenal, A. Marechal, M. Kaid-Harche and G. Janin, *Ann. Forest Sci*., **63**, 493 (2006).

[8] J. Gierer, *Wood Sci*. *Technol*., **19**, 289 (1985).
[9] K. E. Vroom, *Pulp Paper Can*., **88**, 228 (1957).
[10] M. Petit-Conil, *ATIP*, **53**, 95 (1999).
[11] A. Rahme, *Thèse de Docteur-Ingénieur*, Université de Nancy, 1972, 219 pp.
[12] A. W. McKenzie, *Appita J*., **38**, 428 (1985).
[13] G. Janin*, Thèse de Docteur-Ingénieur*, Université de Grenoble, 1983, 238 pp.