
This is an electronic reprint of the original article.
This reprint may differ from the original in pagination and typographic detail.

Fiskari, Juha; Vihelä, Tuomas; Ruuttunen, Kyösti; Ali-Rekola, Ville; Hautala, Sanna; Sixta, Herbert

Cooking of dry high-lignin Eucalyptus camaldulensis chips followed by TCF bleaching with hydrogen peroxide

Published in:
Cellulose Chemistry and Technology

Published: 01/09/2017

Document Version
Publisher's PDF, also known as Version of record

Published under the following license:
Unspecified

Please cite the original version:
Fiskari, J., Vihelä, T., Ruuttunen, K., Ali-Rekola, V., Hautala, S., & Sixta, H. (2017). Cooking of dry high-lignin Eucalyptus camaldulensis chips followed by TCF bleaching with hydrogen peroxide. *Cellulose Chemistry and Technology*, 51(9-10), 857-861.

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

COOKING OF DRY HIGH-LIGNIN *EUCALYPTUS CAMALDULENSIS* CHIPS FOLLOWED BY TCF BLEACHING WITH HYDROGEN PEROXIDE

JUHA FISKARI,* TUOMAS VIHELÄ,** KYÖSTI RUUTTUNEN,**
VILLE ALI-REKOLA,** SANNA HAUTALA*** and HERBERT SIXTA**

*Laboratory of Organic Chemistry, Department of Chemistry, University of Helsinki,
A. I. Virtasen Aukio 1, 00560 Helsinki, Finland

**Department of Forest Products Technology, School of Chemical Technology, Aalto University,
FIN-02015 Espoo, Finland

***Finnish Forest Research Institute (METLA), P.O. Box 18, FIN-01301 Vantaa, Finland

✉ Corresponding author: Juha Fiskari, juhnis@live.com

To the memory of Acad. Cristofor I. Simionescu,
in acknowledgement of his contributions
to the cellulose science

This paper describes laboratory experiments with *Eucalyptus camaldulensis* grown in South Asia. Pulping of *E. camaldulensis* is known to be challenging because of its high lignin content. Moreover, *E. camaldulensis* chips originating from arid and semi-arid regions of South Asia have often a very low moisture content, which further complicates their pulping. In this research, chips with 5.5% moisture content were screened and the accept fraction underwent a pressurized soaking treatment, which seemingly dissolved carbohydrates, extractives and lignin. The rewetted chips were cooked to a kappa number of 18, oxygen delignified and bleached with hydrogen peroxide. The yield was 45.4% based on unbleached pulp. Pulp viscosities after cooking, oxygen delignification and bleaching were 830, 700, and 600 mL/g, respectively. The high active alkali charge in cooking apparently resulted in low pulp viscosities. In addition to lignin, *E. camaldulensis* probably contained other polyphenolic compounds, which further consumed alkali. The bleached pulp brightness was 85.5% ISO.

Keywords: conventional batch cooking, *Eucalyptus camaldulensis*, dry chips, lignin content, hydrogen peroxide bleaching

INTRODUCTION

E. camaldulensis, also known as red river gum, has proven to be a naturally adaptable species to various soils and climates. It is the most widely planted species in arid and semi-arid regions around the world, mainly in timber plantations.¹ Several reasons have fostered the wide distribution of this species. It can stand cold weather and it survives over the dry season. Moreover, *E. camaldulensis* can grow in saline, commonly flooded soils,² though Benyon *et al.*³ showed that increasing salinity is associated with reduced tree growth. In the Indian subcontinent, *E. camaldulensis* forms a major portion of irrigated plantations in hot arid regions in India.⁴ The species is extensively used for various timber products, furniture, as well as pulp and paper making.

The chemical composition of *E. camaldulensis* wood differs somewhat from that of other commonly planted eucalyptus species. In previous studies,^{5,6} cellulose and hemicellulose contents of samples representing *E. camaldulensis* of three different ages were measured. The cellulose content varied between 47.1% and 49.9%, while the hemicellulose content varied from 12.9% to 16.6%. According to Lammi,⁵ the lignin content of *E. camaldulensis* was determined to be between 32.2% and 37.0%. In a study by Dutt and Tyagi,⁶ four-year-old *E. camaldulensis* samples grown in India had a lignin content of 33.2%, while Fatehi *et al.*⁷ reported a lignin content of 27.1% for the same species grown in Thailand. The latter two values are also much higher than the lignin contents of

most eucalyptus species grown on plantations. In the kraft process, high lignin content essentially complicates cooking and bleaching. Compared to other eucalyptus species, longer cooking time and higher alkali charges are likely to be needed. Further, high lignin content means the contents of wood polysaccharides (cellulose and hemicelluloses) must be less, which essentially results in lower overall yield in pulping. According to MacLeod,⁸ there is a linear relationship between the lignin content of wood and the predicted yield of bleachable-grade kraft pulp. Over a yield range of 42-55%, it can be expressed as follows:

$$\text{Pulp yield} = -0.69[\text{lignin content, \%}] + 65.8R^2 = 0.95 \quad (1)$$

In addition to its unusually high lignin content, *E. camaldulensis* trees that originate from arid or semi-arid regions tend to have a low moisture content in wood. As a consequence of this, mills have to feed very dry chips to a digester, which is known to cause further complications in cooking. Dry chips tend to absorb cooking liquor rapidly in an uncontrolled and uneven manner, which results in non-uniform cooking and higher reject. In a laboratory cooking study comparing normal and dry hardwood chips (with moisture contents of 38.6% and 0.4%, respectively),⁹ a kappa number difference of 5 units was observed while the penalty in reject was 1.0% (reject contents were of 0.3% and 1.3%, respectively). The problem of low moisture content in chips can be partially compensated by longer impregnation time. According to the observations of Zanuttini *et al.*,¹⁰ air-dry hardwood chips require twice as much impregnation time, when compared to never-dried, water-saturated hardwood. Further, the risk of excessive pH reduction in the digester – and the resulting lignin condensation and precipitation – is much higher than if the chips had a

sufficiently high moisture content. These problems are more pronounced with conventional batch cooking systems, where all cooking liquor must be charged before the actual cooking begins. However, if effective alkali charge is increased, there is a significant penalty in yield. The latter is more pronounced with hardwoods, mainly due to the higher proportion of hemicelluloses and their susceptibility to alkaline attack.⁸ On the other hand, having a high concentration of alkali speeds up the impregnation process in eucalyptus pulping.¹¹

This paper presents laboratory experiments carried out with dry *E. camaldulensis* chips obtained from a South Asian pulp mill. The goal was to gain a better understanding of the behavior of dry *E. camaldulensis* chips in a conventional batch pulping process. Another goal was to observe whether the subsequent bleaching is possible with a simple Totally Chlorine Free (TCF) bleaching sequence with hydrogen peroxide as the sole bleaching agent.

In the laboratory experiments, the chips were first rewetted with water in a pressurized vessel, thereafter cooked and oxygen delignified, and finally bleached with hydrogen peroxide.

EXPERIMENTAL

Materials

Eucalyptus camaldulensis chips were obtained from a South Asian kraft pulp mill. The chips were first screened according to SCAN-CM 40:01 and both accept and reject fractions were characterized for carbohydrates and lignin according to NREL/TP-510-42618. Acetone extractives were quantified by SCAN-CM 49:03. The chemical constituents of the wood are summarized in Table 1. Only the screened accept fraction was used for further cooking and bleaching experiments. The dry matter content of the chips amounted to 94.5%, which was determined by SCAN-C 3:78.

Table 1
Chemical constituents of *E. camaldulensis* chips used in this study

Chemical constituent	Screening accept	Combined screening reject
Acetone extractives, %	1.2	1.3
Acid insoluble lignin, %	34.4	36.9
Acid soluble lignin, %	4.5	5.5
Rhamnose, %	0.4	0.5
Arabinose, %	0.3	0.3
Galactose, %	1.3	2.2
Glucose, %	43.9	39.8
Xylose, %	14.5	12.7
Mannose, %	0.4	0.2

Cooking experiments

In order to avoid major difficulties in cooking, dry chips were soaked with 5 liters of distilled water in a rotating autoclave digester for 3 hours at ambient temperature. The pressure was adjusted to 5.5 bar with oxygen. The cooking of the rewetted chips was carried out in a rotating air-batch digester. The cooking conditions were in accordance with mill practice, when applicable. The alkali charge (active alkali, AA), the white liquor sulfidity, and the liquor-to-wood ratio in cooking were of 22%, 25% and 3.8:1, respectively. The cooking was performed with 40 minutes of heating time (time to bring the digester temperature from 120 °C to 170 °C) and 92 minutes of cooking time at 170 °C, in order to reach the target H factor of 1500.

Pulp washing and screening

After cooking, oxygen delignification and bleaching stages, the pulp was washed with deionized water. After cooking, oxygen delignification and bleaching pulp was screened with a 0.2 mm slotted flat screen, centrifuged and homogenized.

Oxygen delignification

Brownstock pulp was subjected to two-stage oxygen delignification with intermediate washing. The conditions of both stages are summarized in Table 2.

Bleaching

Laboratory bleaching was carried out in a water bath with a chelation stage (Q), followed by a single hydrogen peroxide stage (P). In the chelation stage, the target pH range was 3-5, which was adjusted with sulfuric acid. The pH values of the bleaching filtrate were measured. Residual hydrogen peroxide was determined by iodometric titration. Chemical doses are based on oven dry (OD) pulp, except that of hydrogen peroxide, which is calculated based on air dry (AD) tons. Chemical charges, reaction times and temperatures are presented in Table 2.

Filtrate, liquor and pulp analyses

After the soaking treatment, the filtrate was characterized for dissolved lignin by UV Visible Spectroscopy and dissolved carbohydrates by Gas

Chromatography – Flame Ionization Detector (GC-FID), following acid methanolysis developed by the Finnish Forest Research Institute (METLA). A more detailed description of the acid methanolysis has been presented elsewhere.¹²

Kappa numbers and viscosities of the pulp samples were measured according to SCAN-C 1:00 and SCAN-CM 15:99, respectively. ISO brightness was measured by SCAN-CM 11:95 and SCAN-P 3:93, which describe the methods for the preparation of laboratory sheets and the ISO brightness measurement, respectively. Residual alkali in the black liquor was measured according to SCAN-N 33:94. The dry matter content of the wood and pulp samples was determined by SCAN-C 3:78.

RESULTS AND DISCUSSION

The soaking filtrate was characterized for dissolved lignin and carbohydrates. The results are presented in Table 3.

The color of the soaking filtrate was very dark, and apparently contained polyphenols, which are typical of eucalyptus.¹³ According to the filtrate analyses, the filtrate resulting from the cold water soaking treatment contained some 0.6 g/L of lignin, which means that approximately 3.2 grams of lignin had dissolved in the soaking filtrate. Lammi⁵ observed a similar phenomenon in his experiments with *E. camaldulensis*. The dissolved carbohydrate content in the filtrate was much lower, of 0.3 g/L. In addition, the filtrate contained mostly various acids, such as vanillic acid, benzoic acid, 4-hydrobenzoic acid and citric acid. Their concentration could not be calculated, as the method is more qualitative than quantitative by its nature. The acids probably originated from lignin, because they are typical lignin unit components. Moreover, minor concentrations of C16 and C18 fatty acids were observed.

After cooking, kappa number and viscosity were 18.3 and 830 mL/g, respectively.

Table 2
Conditions and chemical charges in oxygen delignification and bleaching

Parameter	1 st O ₂ stage	2 nd O ₂ stage	Q stage	P stage
Time, min	25	100	30	360
Temperature, °C	90	95	50	90
Consistency, %	10	10	10	10
Pressure, bar	6	5	atmospheric	atmospheric
pH	12.4	12.5	4.9	12.1
NaOH, kg/ODt	24	16	0	20
EDTA, kg/ODt	0	0	0.3	0
H ₂ O ₂ , kg/ADt*	0	0	0	60

*Hydrogen peroxide charge is calculated as ADt to better reflect its consumption under mill conditions

Table 3
Concentrations of chemical constituents in the soaking filtrate of *E. camaldulensis* chips

Chemical constituent	Concentration
Lignin, mg/L	643
Dissolved carbohydrates, mg/L	297
Mannose, mg/L	16
Glucose, mg/L	47
Galactose, mg/L	69
Xylose, mg/L	33
Arabinose, mg/L	60
Rhamnose, mg/L	18
Glucuronic acid, mg/L	0
Galacturonic acid, mg/L	30
Methyl-glucuronic acid, mg/L	24

Table 4
Pulp characterization results after cooking, oxygen delignification and bleaching

Parameter	Cooking	O ₂ delignification	QP bleaching
Kappa number	18.3	9.6	6.2
Viscosity, mL/g	830	700	520
Brightness, % ISO	-	-	85.4
Yield, %	45.4	97.3	97.0

The South Asian mill normally cooks to a kappa number of 20. The cooking yield and the reject content were 45.4% and 0.3%, respectively. These values are in relatively good agreement with similar laboratory experiments reported by Fatehi *et al.*⁷ On the other hand, Equation 1 predicted a bleachable-grade pulp yield of 39% for this *Eucalyptus camaldulensis* chips sample, as its total lignin content was 38.9%. Generally speaking, the yield is of course quite low for hardwood and can be explained by the high lignin content in wood and high alkali charge in cooking. However, yields of over 50% with *E. camaldulensis* have been reported elsewhere.⁶ Nevertheless, in this study, the cooking of dry *E. camaldulensis* was relatively uniform, as the reject content was reasonable, when compared to a similar laboratory study with very dry chips and a different hardwood species.⁹ It is obvious that anatomical and chemical differences between different hardwood species often have a significant influence on the behavior of wood chips during pulping.¹⁴ Table 4 summarizes the pulp characterization results after cooking, oxygen delignification and bleaching.

The residual alkali in the cooking liquor was 0.6 g/L (effective alkali, EA) only, while 5-15 g/L is considered normal.¹⁵ Colodette *et al.*¹⁶ observed that low residual alkali in cooking is beneficial for eucalyptus pulp yield, however, the suggested range was 3-4 g/L. In this research, significant

lignin condensation has possibly occurred during the latter part of cooking, which in turn may have resulted in precipitation of condensed lignin on the fibers.^{15,17}

After the oxygen delignification, kappa number and viscosity were 9.6 and 700 mL/g, respectively. The kappa number reduction was 47.5%, and the viscosity loss over the oxygen delignification was 130 mL/g. The yield over oxygen delignification was 97.3%. The overall performance of oxygen delignification was in good agreement with mill practice.

Bleaching was carried out with a QP sequence and the bleached pulp was subjected to analyses. The final kappa number was 6.2 and the kappa number reduction was 35.4%. The viscosity was 520 mL/g and the viscosity loss over bleaching was 180 mL/g. In a mill-scale trial with similar bleaching,¹⁸ hardwood pulp viscosities varied between 505 mL/g and 615 mL/g. Fatehi *et al.*⁷ reported viscosities of 520-580 mL/g for *E. camaldulensis* pulp that had been bleached with an ECF bleaching sequence. In this research, the bleached pulp reached an ISO brightness value of 85.4% ISO. The residual hydrogen peroxide concentration in the bleaching filtrate was insignificant (0.003%). The brightness vs. hydrogen peroxide consumption relationship is in good agreement with the findings of other similar studies.^{19,20} In a TCF bleaching sequence that has only one long P stage with high reaction

temperature and no added magnesium sulfate, all hydrogen peroxide is likely to be consumed, though there are usually significant opportunities for process optimization. Apparently, a small magnesium salt addition could have had a slight positive impact on both viscosity and brightness gain. However, overdosing magnesium salt in the P stage could have suppressed peroxide brightening reactions, resulting in lower brightness and high hydrogen peroxide residuals.^{18,21}

CONCLUSION

Batch cooking with subsequent oxygen delignification and hydrogen peroxide bleaching of very dry *E. camaldulensis* wood chips was found as possible, and achieved reasonably high brightness and low reject. The low initial moisture content of the chips was adjusted with a soaking treatment. In addition, the anatomical properties of *E. camaldulensis* were apparently in favor of sufficient impregnation of the cooking liquor. Challenges in cooking liquor impregnation were also compensated with a high alkali charge in cooking. The residual alkali concentration in the cooking liquor was very low, which may have resulted in lignin condensation and precipitation. However, the fact that relatively high brightness was reached with oxygen delignification and bleaching with hydrogen peroxide only suggests little or no lignin precipitation on fibers. Nevertheless, the hydrogen peroxide consumption in bleaching was very high. This proves that further optimization of the process is essential.

In this research, the overall yield was relatively low for hardwood. However, this is not surprising as the *E. camaldulensis* chips had a lignin content of about 39%. Moreover, the extractives content was also relatively high. For a modern kraft mill, these create good opportunities for partial recovery of lignin and/or extractives for more value-added products.

ACKNOWLEDGMENTS: The authors thank Markus Paananen for the carbohydrate and lignin analyses of the *E. camaldulensis* chips used in this research.

REFERENCES

- ¹ K. G. Eldridge, J. Davidson, C. E. Harwood and G. van Wyk, in "Eucalypt Domestication and Breeding", Clarendon Press, 1993, 312 p.
- ² D. R. Donaldson, J. K. Hasey and W. P. Davis, *Calif. Agr.*, **37**, 20 (1983).

- ³ R. G. Benyon, N. E. Marcar, D. F. Crawford and A. T. Nicholson, *Agr. Water Manage.*, **39**, 229 (1999).
- ⁴ V. P. Tewari, A. Verma and V. S. Kishan Kumar, *Bioresour. Technol.*, **85**, 137 (2002).
- ⁵ L. Lammi, MSc Thesis (in Finnish), Forest Products Technology, Helsinki University of Technology, 1996.
- ⁶ D. Dutt and C. H. Tyagi, *Indian J. Chem. Techn.*, **18**, 145 (2011).
- ⁷ P. Fatehi, S. Arabshahi, Z. Ziaee, R. O. Malinen and Y. Ni, *Can. J. Chem. Eng.*, **88**, 455 (2010).
- ⁸ M. MacLeod, *Pap. Puu*, **89**, 1 (2007).
- ⁹ A. Geffert, J. Geffertova and B. Seman, *Key Eng. Mater.*, **688**, 3 (2016).
- ¹⁰ M. Zanuttini, M. Citroni, V. Marzocchi and C. Inalbon, *Tappi J.*, **4**, 28 (2005).
- ¹¹ M. C. Inalbon, M. C. Mussati and M. A. Zanuttini, *Ind. Eng. Chem. Res.*, **48**, 4791 (2009).
- ¹² P. Kilpeläinen, K. Leppänen, P. Spetz, V. Kitunen, H. Ilvesniemi *et al.*, *Nord. Pulp Pap. Res. J.*, **27**, 68 (2012).
- ¹³ W. E. Hillis and M. Sumimoto, in "Natural Products of Woody Plants", edited by J. W. Rowe, Springer, 1989, pp. 880-920.
- ¹⁴ E. Sjöström, in "Wood Chemistry. Fundamentals and Applications", Academic Press Inc., 1981, pp. 1-20.
- ¹⁵ J. Gullichsen, in "Chemical Pulping", edited by J. Gullichsen and C.-J. Fogelholm, Fapet Oy, 2000, pp. A17-A243.
- ¹⁶ J. L. Colodette, J. L. Gomide, R. Girard, A.-S. Jääskeläinen and D. S. Argyropoulos, in *Procs. 2000 International Pulp Bleaching Conference, Oral Presentations*, Halifax, June 27-30, 2000, pp. 41-48.
- ¹⁷ J. Fiskari, O. Derkacheva, T. Kulomaa and D. Sukhov, *Cellulose Chem. Technol.*, **50**, 213 (2016).
- ¹⁸ J. Fiskari, J. Gullichsen, V. Jokela and K. Ruohoniemi, in *Procs. TAPPI Pulping Conference*, San Francisco, October 19-23, 1997, pp. 1069-1073.
- ¹⁹ H. U. Süss, N. F. Nimmerfroeh and O. Mambrim Filho, *J. Pulp Pap. Sci.*, **23**, J517 (1997).
- ²⁰ J. Fiskari, M. Savela, K. Ruuttunen, V. Ali-Rekola, P. Kilpeläinen *et al.*, *Cellulose Chem. Technol.*, **48**, 713 (2014).
- ²¹ J. Devenyns, F. Desprez and N. Troughton, in *Procs. TAPPI Pulping Conference*, San Diego, November 6-10, 1994, pp. 381-389.