Potential of C. citriodora *wood species for kraft pulp production*

TIAGO E. S. SEGURA AND FRANCIDES G. DA SILVA, JR.

ABSTRACT: This work characterizes the wood from *Corymbia citriodora* for pulp production. We evaluated wood chip samples from an 8-year-old *C. citriodora* plantation. A sample of *Eucalyptus grandis x Eucalyptus urophylla* chips from a 7-year-old plantation was used as reference material. Wood fiber morphology and chemical composition were analyzed. A modified kraft pulping was carried out to achieve kappa 18 on brownstock pulps. After that, pulps were oxygen delignified, and then underwent elemental chlorine free (ECF) bleaching to achieve the target brightness of 90±0.5% ISO. The bleached pulps were refined in a PFI mill at 0, 750, 1500, and 3000 revolutions, and their physical-mechanical properties were analyzed. *C. citriodora* wood had a relatively high wood basic density (0.568 g/cm^3), low lignin content (22.3%), and high holocellulose content (73.1%) compared with *E. grandis x E. urophylla*. The fibers of this species had 1.07 mm length, 16.1 μm width, and 66% wall fraction, which reflect its high basic density. For the same kappa number, *C. citriodora* and *E. grandis x E. urophylla* yields were similar – the main pulping highlight for this wood species is the low specific wood consumption – 2.93 m^3/a.d. ton. *C. citriodora* pulp had a relatively lower kappa number after oxygen delignification and lower bleaching chemical demand than *Eucalyptus* pulp. *C. citriodora* pulp had a high specific volume and capillarity, and low water retention value. The physical properties of *C. citriodora* suggest that it might be suitable for use in tissue paper manufacturing.

Application: *C. citriodora* is a dense hardwood species that is easier to pulp than *Eucalyptus* and might be useful in tissue paper manufacturing.

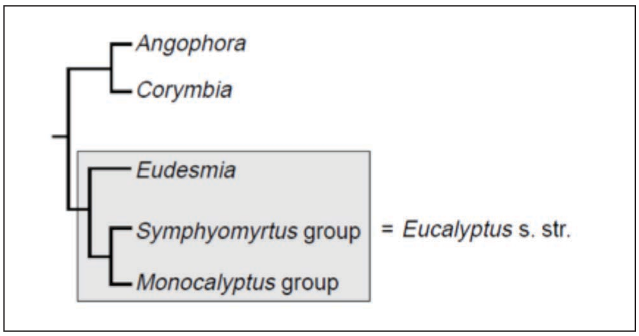
Brazil is the fourth largest pulp producer in the world. Its production is primarily based on hardwood pulp from *Eucalyptus* species. The Brazilian soil and climate are suitable for growing *Eucalyptus*, and breeding programs have resulted in high forest productivity.

Some studies from the 1970s indicated that the original *Eucalyptus* genus was not a natural taxonomic group [1]. Later studies indicated the existence of two main lineages: the first included the *Angophora* and *Corymbia* subgenus, and the second included the *Eucalyptus* subgenus (**Fig. 1**) [1]. In 1990s, the *Eucalyptus* genus was regrouped and *Corymbia* and *Angophora* were created as separate genus groups [2].

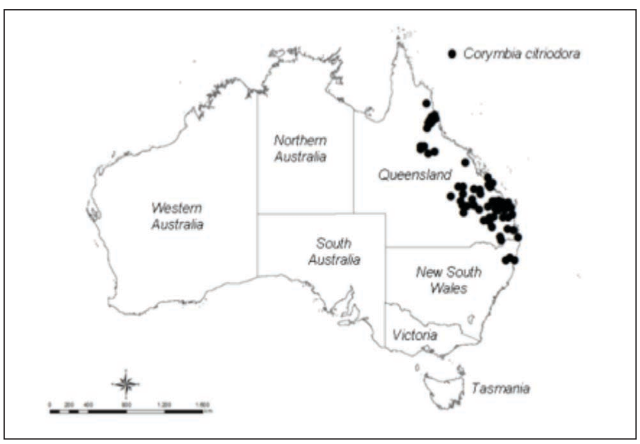
Corymbia consists of 113 known species [3,4], with high basic density, extractives, carbohydrate ratio, and low lignin content. Some of these species have commercial importance for oil extraction from the leaves. The wood is used in construction, charcoal production, and energy generation. *C. citriodora* species is native to Queensland, Australia (**Fig. 2**) [5], from which it was introduced to many regions of the world (**Fig. 3**) [6].

C. citriodora's high basic density results in less wood use per unit of pulp production. Some studies report that the high basic density of the wood negatively affects pulping processes, increases alkali consumption, increases pulp rejects, and decreases the pulp screened yield [7-9].

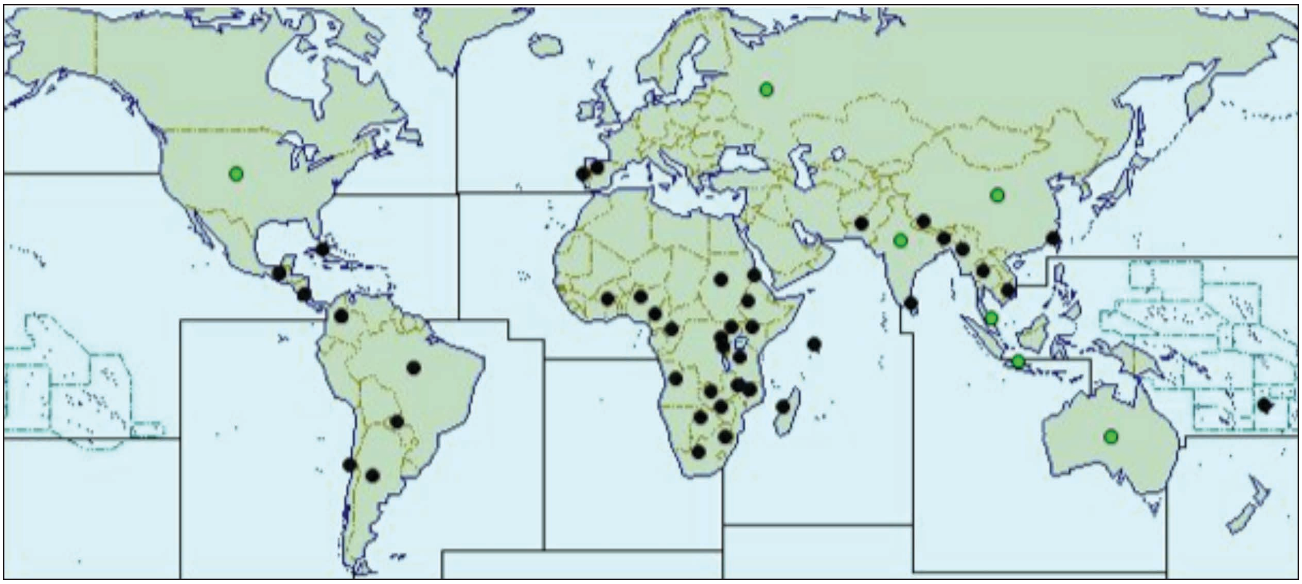
Many studies on the potential of *C. citriodora* for pulp production were published from 1970s to 1990s [10-13]. How-



1. Phylogenetic relationships between **Eucalyptus** ***[1].***



2. Natural occurrence of **C. citriodora** ***[5].***



3. **C. citriodora** *occurrence in different regions [6].*

ever, there has been an absence of breeding programs for *Corymbia* species; it has lower forestry productivity compared to *Eucalyptus*, which has reduced the interest of these species for the paper industry.

A study evaluated the *E. cloeziana*, *C. citriodora*, *E. urophylla*, and *E. urophylla x E. grandis* species for dissolved pulp production [10]. The author noted that *C. citriodora* resulted in pulp with high brightness and good viscosity.

The purpose of our study was to evaluate the *C. citriodora* wood for pulp production by analyzing its characteristics and its performance during the kraft pulping process.

MATERIAL AND METHODS

Wood

Ten 8-year-old trees of *C. citriodora* and ten 6-year-old trees of *Eucalyptus grandis x Eucalyptus urophylla*, which were both planted in Brazil, were collected. Using a laboratory chipper, wood chips from both species were prepared. Chips were screened to obtain those with a thickness between 4 mm and 6 mm. *E. grandis x E. urophylla* wood was used as a baseline to evaluate the *C. citriodora* wood.

Wood characterization

Wood characteristics were measured according to published standards. These included wood basic density [14] and fiber dimensions (as identified by the International Association of Wood Anatomy) [15]. We also considered length, width, and lumen diameter parameters. We followed TAPPI Standard Test Methods to measure total extractive content (TAPPI T 204 "Solvent extractives of wood and pulp"), total lignin (TAPPI T 222 "Acid insoluble lignin in wood and pulp"), and inorganic ash (TAPPI T 211 "Ash in wood, pulp, paper, and paperboard: combustion at 525°C"). Wall thickness was calculated by Eq. (1) and wall fraction by Eq. (2):

$$WT = \frac{FW - LD}{2} \tag{1}$$

and

$$WF(\%) = \frac{2 \cdot WT}{FW} x100 \tag{2}$$

where:
WT = wall thickness, μm
FW = fiber width, μm
LD = lumen diameter, μm
WF = wall fraction, %

Holocellulose content was calculated by Eq. (3):

$$Holo(\%) = 100\text{-}(TE(\%) + LT(\%)) \tag{3}$$

where:
Holo = holocellulose content, %
TE = total extractive content, %
LT = total lignin content, %

Pulping

The modified pulping was performed in a forced circulation digester with a capacity of 10 L and heat exchangers for heating. Pulping conditions were adjusted to obtain a pulp of kappa 18.0 ± 0.9. Trials were made in triplicate. In all trials, sulfidity was 32% and the liquor-to-wood ratio was 4 L/kg. **Table I** lists pulping conditions used in this study.

After pulping, pulp yields were calculated. Kappa number, viscosity, and hexenuronic acids measurements were made on the brownstocks according to TAPPI Standard Test Methods (T 236 om-13 "Kappa number of pulp"; T 230 om-13 "Viscosity of pulp [capillary viscometer method]"; and T 282 om-13 "Hexeneuronic acid content of chemical pulp"). Specific wood consumption was determined using Eq. (4):

$$WSC = \left(\frac{1}{BD \cdot SY}\right) \tag{4}$$

where:
WSC = specific wood consumption, m^3/ton
BD = basic density, g/cm^3
SY = screened yield (as a fraction)

Dry solids formed during the modified pulping were calculated using the following Eq. (5):

$$solids = \frac{(1 - \mathrm{T}Y) + \mathrm{AA}}{\mathrm{SY}} \times 0.9 \tag{5}$$

where:
TY = total yield (as a fraction)
AA = active alkali (as a fraction)
SY = screened yield (as a fraction)

Oxygen delignification followed by elemental chlorine free (ECF) bleaching was performed on brownstock pulps. The purpose of the bleaching was to achieve a brightness of 90±0.5% ISO on bleached pulps. **Table II** shows oxygen delignification and bleaching conditions.

Pulping Stage	Time, min	Temperature, °C	Alkali Split, %
Steaming	20	100	-
Impregnation	30	120	50
1st change + pulping	110	Variable	30
2nd change + pulping	125	Variable	20

I. Pulping conditions.

Bleached pulps were refined in a PFI mill in four levels: 0, 750, 1500, and 3000 revolutions. These pulps were evaluated through their physical properties on each level of refining according to ISO Standards (ISO 534:2011 "Paper and board — Determination of thickness, density and specific volume"; ISO 1924-3:2005 "Paper and board — Determination of tensile properties — Part 3: Constant rate of elongation method [100 mm/min]"; ISO 2758:2014 "Paper — Determination of bursting strength"; ISO 1974:2012 "Paper — Determination of tearing resistance — Elmendorf method"; ISO 8787:1986 "Paper and board — Determination of capillary rise — Klemm method"; ISO 23714:2014 "Pulps — Determination of water retention value [WRV]").

All physical-mechanical test results were analyzed using statistical software. A regression analysis was performed with all the data. **Figure 4** shows the response curves for each parameter.

RESULTS AND DISCUSSION

Table III shows the wood characterization, including basic density, chemical composition, and fiber dimensions.

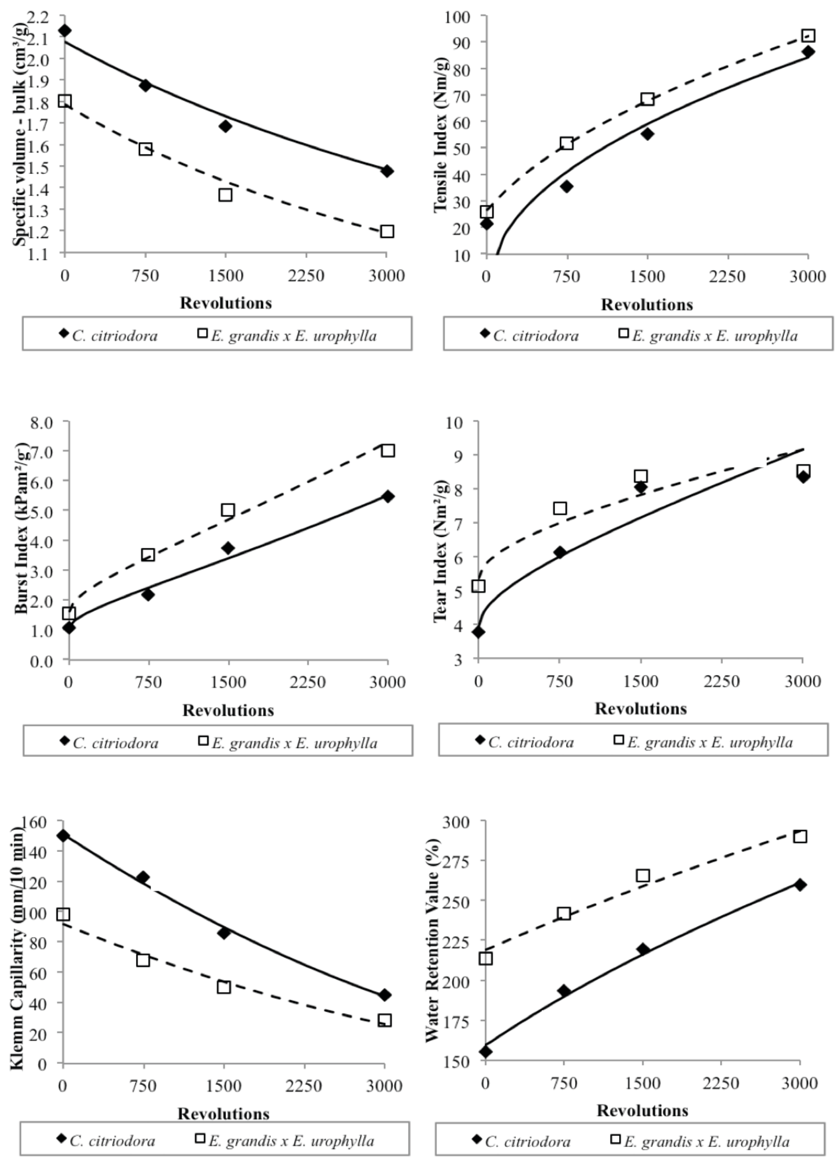
Basic density is an important characteristic for wood quality evaluation in the pulping process; it is correlated to genetic and environmental parameters. In this work, *C. citriodora* wood shows a basic density higher than *Eucalyptus*. A dense wood, as observed with *C. citriodora*, can hinder some important pulping production phases, such as wood chipping and cooking liquor impregnation [7]. On the other hand, a higher wood basic density can result in a reduction in specific wood consumption [16].

The chemical composition of the wood chips also affects the pulping process. Considering the woods analyzed in this work, *C. citriodora* shows more favorable characteristics than *E. grandis x E. urophylla*, concerning lower extractives and lignin contents, and higher holocellulose content. The main pulping objective is to remove the lignin, thereby separating the fibers. Consequently, lignin content directly

Parameter	Oxygen Delignification	DA	Ep	D_1	P
Consistency, %	11	11	11	11	11
Temperature, °C	95 + 100	90	85	80	80
Time, min	10 + 50	90	60	60	90
H_2O_2, kg/a.d. ton	-	-	3.0	-	0.5-1.0
ClO_2, kg/a.d. ton	-	CF = 0.2*	-	5.5-6.5	-
NaOH, kg/a.d. ton	19	-	8	-	2
H_2SO_4, kg/a.d. ton	-	4.0	-	1.5	-
Pressure, bar	5.5	-	-	-	-

*CF = chlorine factor. ClO_2 charge (kg/a.d. ton) = (kappa number after oxygen delignification × CF × 10).

II. Oxygen delignification and bleaching conditions.



4. Physical and mechanical tests.

Parameter	*C. citriodora*	*E. grandis x E. urophylla*
Basic density, g/cm³	0.568	0.451
Total extractives, %	4.6	5.6
Total lignin, %	22.3	27.1
Ash, %	0.45	0.24
Holocellulose, %	73.1	67.3
Fibers length, mm	1.07	1.02
Fibers width, μm	16.1	19.8
Fibers wall width, μm	5.3	3.5
Fibers wall fraction, %	66	33

III. Wood characterization.

influences chemical pulping. The holocellulose ratio represents the carbohydrate portion of the wood, which affects pulp yields.

The wood chemical composition of *C. citriodora* found in this study is similar to that presented in the literature. Other authors also mention the low lignin content as a characteristic of this species [12,17]; extractives content is at the same level as was found in this work [17].

Compared with *E. grandis x E. urophylla*, *C. citriodora* has fibers with longer length, thinner width, thinner lumen width, higher wall thickness, and higher wall fraction. The differences in wall fraction reflect the basic density differences: a denser wood shows fibers with higher wall fraction. Morphology results are in agreement with results in other works. Other authors cite fibers of *C. citriodora* wood with 0.915 mm to 0.943 mm of length, 15.50 μm to 15.89 μm of

Parameter	*C. citriodora*	*E. grandis x E. urophylla*
Kappa number	18.0	18.5
Effective alkali, % as NaOH	19.0	20.0
Maximum temperature, ºC	153	155
Total yield, %	54.1	54.0
Screened yield, %	54.1	54.0
Hexenuronic acids, μmol/g	53.2	49.5
Viscosity, cm^3/g	1,273	1,341
Specific wood consumption, m^3/a.d. ton	2.93	3.70
Dry solids, tons/a.d. ton	1.08	1.10

IV. Pulping results.

Parameter	*C. citriodora*	*E. grandis x E. urophylla*
Kappa after oxygen delignification	7.6	11.0
Bleached brightness, % ISO	90.0	89.6
Bleached viscosity, cm^3/g	703	798
Brightness reversion, % ISO	2.1	2.0
Chlorine dioxide consumption, as active chlorine kg/a.d. ton	24.0	27.3
Hydrogen peroxide consumption, kg/a.d. ton	4.0	3.5

V. Oxygen delignification and bleaching results

width, lumen diameter with 4.41 μm to 4.75 μm, and 5.37 μm to 5.74 μm of wall width [12].

Table IV shows the pulping results.

For the same delignification level, *C. citriodora* wood demanded lower alkali charge and lower temperature than *E. grandis x E. urophylla*. This reflects the two wood species chemical compositions. *C. citriodora* has higher ratio of holocellulose and lower lignin amount than *E. grandis x E. urophylla*. Despite this, the yields of both species for a kappa 18 were similar, although the *C. citriodora* pulping process results in pulp with lower viscosity. These results could be related to the chemical composition differences between these two species, indicating that *C. citriodora* shows higher hemicellulose content.

Hexenuronic acids are formed during alkaline pulping by the 4-O methyl glucuronic acids in xylans that are influenced by cooking conditions, mainly the active alkali, sulfidity, and temperature [18]. *C. citriodora* pulping formed a slightly higher amount of hexenuronic acids than did *Eucalyptus* pulping. Specific wood consumption is based on pulping yields and wood basic density. This is an important parameter for pulp mills and reflects the wood volume needed to achieve a certain production rate of pulp. *C. citriodora* is a denser wood and provides similar pulp yields as *E. grandis x E. urophylla*. In this way, *C. citriodora* has lower specific wood consumption. That means that for the same pulp production rate, the mill requires a lower volume of *C. citriodora* wood than *E. grandis x E. urophylla* wood. Because the wood is procured by volume basis and the pulp is sold by a mass basis, *C. citriodora* use is more economical to the papermaking industry in terms of wood costs.

Dry solids, which represent the amount of solids available for burning in the recovery boiler, were very similar for both wood species, reflecting the similar alkali charges and yields of the pulping processes for each species.

Brownstock pulps were oxygen delignified and bleached on an ECF sequence. **Table V** shows the oxygen delignification and bleaching results. Oxygen delignified pulp of *C. citriodora* showed lower kappa numbers than did *E. grandis x E. urophylla* pulp. Consequently, the oxygen delignification was more efficient for this species (57.7% vs. 38.9% for *Eucalyptus*). The better efficiency of *C. citriodora* delignification likely related to lignin differences of these two wood species, or can be explained by some modifications of this species' lignin during cooking [19].

E. grandis x E. urophylla bleached pulp showed higher viscosity than did *C. citriodora* bleached pulp, but brightness reversions of both pulps were maintained in the same level. To achieve a minimum brightness of 89.5% ISO, *C. citriodora* pulp used lower amounts of chemical reagents – chlorine dioxide and hydrogen peroxide. The lower demand of bleaching chemicals of this species is directly related to its better delignification efficiency.

Figure 4 shows the bleached pulps physical and mechanical characteristics.

Despite showing bleached pulp with lower physical strength than *E. grandis x E. urophylla* pulps (lower tensile, burst, and tear indexes), *C. citriodora* pulp has some particular characteristics that suggest it could be suitable for tissue paper production. The first one is high specific volume, also known as bulk, which is a parameter appreciated by tissue manufacturers. Another is the high capillarity of this pulp, reflecting the high capacity of this pulp to absorb liquids. The low water retention value indicates that this pulp is easier to dry, representing an advantage in this pulp manufacturing stage.

CONCLUSIONS

This work compares a high density wood (*C. citriodora*) to a reference wood (*E. grandis x E. urophylla*). We showed that *C. citriodora* wood chemical composition is more responsive to kraft pulping than is the reference material.

C. citriodora kraft pulping requires a lower active alkali charge, reflected in similar yields and lower specific wood consumption than *E. grandis x E. urophylla*. Oxygen delignification was more effective to *C. citriodora* demands, while this pulp consumed less chlorine dioxide and more hydrogen peroxide than *E. grandis x E. urophylla* to bleach.

C. citriodora shows very particular pulp characteristics: compared to *E. grandis x E. urophylla*, the species pulp had lower resistance and water retention values, and higher specific volume and capillarity.

These findings indicate the *C. citriodora* potential for kraft pulping. The main advantages of this wood specie are its high basic density and its favorable wood chemical composition; these factors result in lower wood consumption, which makes kraft pulp production with *C. citriodora* more economical. Moreover, the *C. citriodora* pulp physical-mechanical characteristic indicates it is suitable to tissue paper production, mainly due to its high capillarity and specific volume. **TJ**

ACKNOWLEDGEMENTS

The authors thank the Chemistry, Pulp, and Energy Laboratory team for support in the research.

LITERATURE CITED

1. Rozefelds, A.C., *Tasforests* 8(1): 15(1996).
2. Hill, K.D. and Johnson, L.A.S., *Telopea* 6(2,3): 185(1995).
3. Dezsi, S., Bădărău, A.S., Bischin, C., et al., *Molecules* 20(1): 4720(2015).
4. Shepherd, M., Baker, N., Kasem, S., et al., "Comparative mapping of *Eucalyptus* and *Corymbia*," *13th Australasian Plant Breeding Conf., Proc.,* New Zealand Grassland Association, Dunedin, New Zealand, 2006.
5. Reis, C.A.F., Assis, T.F., Santos, A.M., et al., "*Corymbia citriodora*: estado da arte de pesquisas no Brasil," Documentos 255, Embrapa Florestas, Colombo, Brazil, 2013.
6. Forestry Compendium, "Corymbia citriodora (lemon-scented gum)," *Invasive Species Compendium.* Available [Online] http://www.cabi.org/isc/datasheet/22602 <17Mar2016>.
7. Foelkel, C.E.B., Mora, E., and Menochelli, S., *O Papel* 53(5): 35(1992).
8. Queiroz, S.C.S., Gomide, J.L., Colodette, J.L., et al., *Árvore* 28(6): 901(2004).
9. Santos, S.R. dos and Sansígolo, C.A., *Ciência Florestal* 17(1): 53(2007).
10. Mezzomo, L.X., "Potencialidade de *Eucalyptus cloeziana* S. Muell, *E. citriodora* Hook, *E. urophylla* St Blake e *E. urophylla x E. grandis*, cultivados na Bahia, para a produção de celulose solúvel," Master in Forestry thesis, Federal University of Santa Maria, Santa Maria, Brazil, 1996.
11. Barrichelo, L.E.G. and Brito, J.O., *IPEF* 3(1): 9(1976).
12. Foelkel, C.E.B., Barrichelo, L.E.G., and Milanez, A.F., *Revista IPEF* (*Atual Scientia Forestalis*) 10(1): 17(1975).
13. Gardner, R.A.W., Little, K.M, and Arbuthnot, A., *Aust. For.* 70(1): 37(2007).
14. Foelkel, C.E.B., Brasil, M.A.M., and Barrichelo, L.E.G., *O Papel* 33(8): 57(1972).
15. International Association of Wood Anatomists (IAWA) Committee, *IAWA J.* 25(1): 1(2004).
16. Segura, T.E.S. and da Silva Jr., F.G., "Influência do Fator H e da carga alcalina na polpação kraft de *Corymbia citriodora,*" *6th Grad. Symp. For. Sci.* and *2nd Symp. Wood Technol. Rio de Janeiro*, Federal Rural University of Rio de Janeiro (UFRRJ), Seropédica, Rio de Janeiro, Brazil, 1(1): 2010 (on CD).
17. Costa, M.M., Colodette, J.L., Gomide, J.L., et al., *Árvore* 21(1): 385(2007).
18. Costa, M.M., Mounteer, A.H., and Colodette, J.L., *O Papel* 62(5): 75(2001).
19. Prinsen, P., Rencoret, J., Gutiérrez, A., et al., *Ind. Eng. Chem. Res.* 52(1): 15702(2013).

ABOUT THE AUTHORS

We chose this topic based on results of previous studies that showed high potential of this wood species for pulp production. Moreover, some studies indicate that the use of dense wood for pulp production is not recommended, transforming this topic into a big challenge for us.

Segura

The main difference between this research and previous studies is the alternative wood species that we used. Even though *C. citriodora* is not a new species, research on this wood for pulp production dates back more than 25 years. Consequently, new pulping methods, such as modified cooking processes (that we considered in our study), were not tested for this species in previous studies.

da Silva

The most difficult aspect of this research was to find the best way to avoid high reject content formation during *C. citriodora*'s pulping. A good steaming/impregnation was sufficient for that.

Our discoveries showed that it is possible to achieve interesting and positive results even though other research presented different conclusions. The most surprising result in this study is the good yield that we were able to find for this wood species.

The use of dense wood with low lignin content and good forest productivity for pulp production can reduce production costs of pulp mills, as wood consumption can be reduced.

The next step in this study is to consider new species and hybrids with high basic density and to test these materials.

Segura is project specialist, Eldorado Brasil Celulose, São Paulo, Brazil, and da Silva is professor, Department of Forest Science, University of São Paulo, São Paulo, Brazil. Email Segura at tiago.segura@eldoradobrasil.com.br.