Eucalyptus globulus chemical composition and its effect on Kraft pulping parameters

Luis M. Reina, Professor, Universidad de la República, Uruguay, luismreina@gmail.com
Fernando Resquin, Researcher, INIA, Uruguay, nando@inia.org.uy

Abstract

Eucalyptus globulus is one of the main species planted in Uruguay. In the way of improve its use for pulp production it is necessary to determine the effect of its chemical composition on pulping process. With that evaluation is possible to improve the wood produced by a forest and the selection of trees to forest.

In the research were analyzed twenty-one samples from seven origins, three samples per origin. Samples came from trials of 9 years, they were located near Minas city, Lavalleja department, Uruguay.

For each sample were determined, pulp yield and the content of, glucans, xylans, mannans, cellulose uronic acids, acid soluble lignin, acid insoluble lignin, total lignin, ethanol-toluene extractives, total extractives. Those components were correlated with alkali charge and pulp yield.

There was a positive correlation coefficient between yield and mannans and mannans / total lignin ratio. Seed origins evaluated, present significant difference in acid soluble lignin content. Correlations between alkali charge and chemical components were not significant.

Introduction

The first eucalypts were planted in Uruguay in 1853 by Tomás Tomkinson(1), and the cover area by *Eucalytus globulus* forest reached 257516ha in 2008(2). Almost all wood production of *E. globulus* is used as pulp wood. Considering that pulpwood is the highest cost in kraft pulp production (3), it is possible to reduce the costs improving the pulp yield. That improvement permit to diminish the amount of wood use, hence decrease the cost of it and the costs of harvest, transportation and handling. One of the option to improve pulp yield is use wood which produce more pulp. For that it is necessary to determinate the wood features which are related to pulping process in the way of include it in a breeding program.

To determinate the chemical components of wood and pulp yield, there are different methods some of there are: wet methods, NIR (Near infrared reflectance), phenotypical correlations and genetycal correlations among wood characteristics. NIR is a fast and reliable method (4) useful to analyze many samples. But it is necessary enough calibration samples to cover all range of the composition of the samples to be analyzed and the calibration curves are site specific (4). Phenotyìcal characteristics like DBH (Diameter at breast height) has medium correlation with cellulose content (5) and there was found correlations among genetic characteristics and pulp yield or chemical components, but those correlations are medium to low (6,7). Wet methods in spite of being costly (8) and time consuming there could be used to different number of samples without calibration standards, and permit to determinate directly pulp yield and wood chemical components to be used as selection criteria.

The objective of the present work is to determinate the chemical components which are related to pulping yield and alkali used.

Experimental

Twenty-one samples from the same origin were collected near Minas city, Lavalleja department, Uruguay. Those samples came from seven seeds origin, six of them from Victoria state, Australia and other local. The tree 9 years were selected from tree diameter classes: 3

from low diameter, 5 from intermediate diameter and 3 threes from high diameter. For each tree discs were cut at 0, 25, 50, 75, 100 % of commercial height (8cm with bark). Discs were manually chipped and mixed to obtain one sample per each diameter class per each origin. Two hundred fifty grams of each sample were cooked using the following conditions, Sulfidity = 25%, liquor / wood ratio = 3.5, maximum temperature = 170 ºC, time to reach maximum temperature = 90min, time at maximum temperature = 50min, alkali charge were selected for each sample to obtain a final Kappa number of 18±1.

For chemical analysis a sample of chips were milled to 40-60 mesh. Extractives were determined by weight difference, in the case of ethanol- toluene extractives, samples of 0.5g were extracted in a soxhlet, 8 hours with a mixture of ethanol toluene 1:2. Samples for extractives free wood and total extractives determination were extracted 8 hours ethanol-toluene 1:2, 8 hours ethanol 95%, and 4 extractions with distilled water.

Two samples of 1 gram of extractives free wood were trated with 10ml of sulfuric acid 72% per 1hour at 30ºC and next diluted to 4% an placed at 120ºC per 1hour. The hydrolyzate were filtered using a glass filtering crucible of fine porosity the solid retained is acid insoluble lignin. From the hydrolyzate were determined acid soluble lignin glucans, xylans, mannans and uronic acids. The former with UV-vis spectrophotometry using an absorptivity of 110 l/g-cm at 205nm, glucans xylans and mannans with Scott method (9) as well as uronic acids (10).Cellulose were determined as the difference between glucans and mannans (11).

Results and Discussion

Table 1 shows the values of, mean for samples and variance, standard deviation, coefficient of variation for samples and replicates. The values of glucans, xylans, mannans and uronic acids are expressed as anhydro sugars, and uronic acids as 4-O-methyl glucuronic acid.

Table 1: Statistics for chemical composition of *E. globulus*.

	Gluc.	Xyl.	Man.	Ur.Ac	Cel.	Insol. Lign.	Sol. Lign.	Total Lign.	E-T Extr.	Extr.	Alkali (Na_2O)	Yield
Mean	46,99	10,57	3,23	3,63	43,76	22,41	4,72	27,14	1.81	3.33	13,86	52,44
Var.s	19,6	2,98	2,88	0,084	24,54	1,2	0,11	1,01	0.70	1.96		
Std.s	4,43	1,73	1,7	0,29	4,95	1,09	0,34	1,01	0.835	1.40		
C.V.s%	9,42	16,37	52,6	8,0	11,32	4,88	7,09	3,71	46.15	42.12		
Var.r	57,48	72,96	7,4	0,14	59,98	0,19	0,05	0,28				
Std.r	7,58	8,54	2,72	0,37	7,74	0,44	0,22	0,52				
C.V.r %	16,13	80,8	84,2	10,31	17,69	1,96	4,72	1,93				
n	17	17	17	21	17	21	21	21	19	21	21	21

Gluc.= Glucans, Xyl.=Xylans, Man=Mannans, Ur. Ac.= Uronic Acids, Cel.=cellulose, Insol. Lig.= Insoluble Lignin, Sol. Lig.= Soluble Lignin, Total Lig. = Total Lignin, E-T Extr. = Ethanol-Toluene Extractives, Extr.=Total extractives , Alkali=Alkali charge, Var.= variance, Std.= standard deviation, C.V.= coefficient of variation, s= sample, r= replicates, n=number of samples.

The mean values of glucans, cellulose, total lignin, insoluble lignin, soluble lignin and total extractives are in the range of bibliography as shows table 2. In the case of xylans and mannans the mean values are outside the range for *E. globulus* but in the range of 10.3%-16.8% for eucalypt in xylans (13,11).

Table 2: Bibliography range for *E. globulus* chemical composition.

	Gluc.	Xyl.	Man.	Cel.	Insol.Lign	Sol.Lign.	Total Lign.	Extr.
Max.	53.4	16.8	2.59	51.3	23.2	6.12	28.48	6.0
Min.	41.7	11.7	0.7	40.6	18.2	3.5	21.9	1.3
Ref.	(14,15)	(11)	(15,11)	(16,11)	(11)	(17,11)	(17,11)	(17,16)

Gluc.= Glucans, Xyl.=Xylans, Man=Mannans, Insol. Lig.= Insoluble Lignin, Sol. Lig.= Soluble Lignin, Total Lig. = Total Lignin, Extr.= Extractives, Max.=maximum value, Min.=minimum value, Ref.= reference.

There were correlated the chemical components with yield and alkali charge. The correlation coefficient was significantly different from zero for correlation between yield and mannans as well as yield and mannans / total lignin ratio (table 3, Figure 1). The retention of glucomannan in pulp increase when increasing the alkali charge (18,19) that tendency was observed for mannans in eucalyptus pulp (20). Considering that pulp yield diminish when alkali charge increasing (r = -0.68 among yield and alkali in our case) and the relation mannans – alkali charge, it is possible to consider a counterbalance effect of mannans in pulping yield. The sum of more mannans in wood and more retention when alkali increasing have the opposite effect of more alkali more carbohydrates dissolve in relation to pulp yield. That is the situation when is comparing the comportment of softwoods and hardwoods in relation to the effect of alkali charge increment. Softwoods diminish less the pulping yield when increase the alkali because softwoods have more glucomannnan and less xylan than hardwoods (18,19)

Table3: Correlation among chemical component and yield, alkali charge.

	Yield		**Alkali charge**	
	r	P	r	P
Glucans	-0.038	0.88	-0.11	0.67
Xylans	-0.13	0.6	0.26	0.30
Mannans	**0.61**	**0.01**	0.66	0.80
Cellulose	-0.24	0.35	-0.76	0.77
Uronic acids	0.096	0.68	0.14	0.54
Soluble lignin	0.26	0.25	-0.22	0.33
Insoluble lignin	-0.24	0.28	-0.31	0.89
Total lignin	-0.18	0.43	-0.11	0.64
E-T Extr.	0.065	0.79	-0.10	0.69
Extractives	-0.18	0.42	-0.036	0.88
Gluc./ Total Lig.	0.052	0.83		
Xyl./ Total Lig.	-0.084	0.75		
Man./ Total Lig.	**0.59**	**0.01**		
Cel./ Total Lig.	-0.17	0.52		
Ur.Ac./ Total Lig.	0.14	0.54		

P= significance of the correlation coefficient, r= Pearson correlation coefficient, Gluc.= Glucans, Xyl.=Xylans, Man=Mannans, Ur. Ac.= Uronic Acids, Cel.=cellulose, Total Lig. = Total Lignin, E-T Extr. = Ethanol-Toluene Extractives, Extr.=Total extractives.

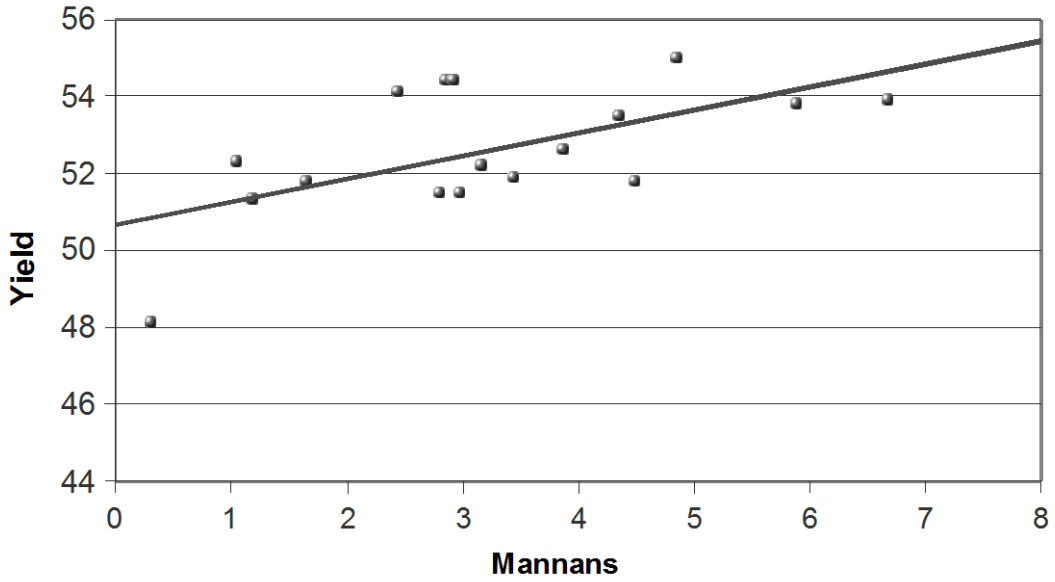

Figure 1 : Pulp yield vs. mannans

The correlated values among alkali charge and wood chemical components were not significant (table 3). Multiple factors are related to alkali charge used in pulping, one of the most important is lignin structure. That is analyzed using sytingyl (S) / guaiacyl (G) ratio, more S/G in lignin result in an easier to react lignin in pulping (21), hence it is necessary less alkali. Another factor is alkali consumed by the components of wood dissolved in pulping process. That depends on the quantity of components in wood in the case of lignin and acetyl groups because lignin is dissolved until the same level (Kappa 18) and all acetyl groups are dissolved during pulping (22). For carbohydrates most of the alkali consumed in pulping is caused by their reaction (18) and the quantity dissolved depends on the alkali charge (23).

Using diametric classes as replicates in an ANOVA , there was found a significative difference among seed origins for soluble lignin. Hence, it is possible to select seeds in base of that factor.

References

1. Berro, M.B. La agricultura colonial. Colección de clásicos uruguayos. Ministerio de Educación y Cultura. Uruguay. Vol. 148, (1974).

2. Uruguay. Dirección General Forestal 2011. Superficie forestada bajo proyecto, periodo 1975-2008, genero: *Eucalyptus globulus ssp. globulus*. In: http://www.mgap.gub.uy/Forestal/egloglo.xls

3. Bränvall, E. Wood handling. In: Pulp and paper chemistry and technology, Vol. 2, Pulping chemistry and technology.(Ed: M. Ek, G. Gellerstedt, G. Henriksson), Walter de Gruyter, Berlin, Germany (2009).

4. Schimleck, L.R. Near - infrared spectroscopy a rapid non-destructive method for measuring wood properties, and its application to tree breeding. N.Z.J. Forestry Sci. 38(1), pp. 14-35, (2008).

5. Quang, T.H., Hien, N.D., von Arnold, S., Jansson, G., Thinh, H.H., Clapham, D. Relationship of wood composition to growth traits of selected open-pollinated families of *Eucalyptus urophylla* from a progeny trial in Vietnam. New Forestry 39, pp. 301-312, (2010).

6. Rocha, R.B., Barros, E.G., Cruz,C.D., Rosado, A.M., Araujo, E.F. Mapping of QTLs related with wood quality and developmental characteristics in hybrids (*Eucalyptus grandis* X *Eucalyptus urophylla*). R. Árvore 31(1), pp. 13-24, (2007).

7. Freeman, J.S., Whittock, S.P., Potts, B.M., Vaillancourt, R.E. QTL influencing growth and wood properties in *Eucalyptus globulus*. Tree Genet. Genom. 5, pp. 713-722, (2009).

8. Poke, F.S., Wright,J.K., Raymond, C.A. Predicting extractives and lignin contents in *Eucalyptus globulus* using near infrared reflectance analysis. J. Wood Chem. Technol. 25(1), pp. 55-60, (2004).

9. Scott, R.W. Combined determinations of glucose, mannose, and xylose by spectrophotometry. Anal. Chem. 48, pp.1919-1922, (1976).

10. Scott,R.W. Colorimetric determination of hexenuronic acids in plant materials. Anal. Chem. 51, pp. 936-941, (1979).

11. Wallis, A.F.A.; Wearne, R.H.; Wright, P.J. Analytical characteristics of plantation eucalypt woods relating to Kraft pulp yields. Appita J. 49(6), pp. 427-432, (1996).

12. Fardim, P.; Durán, N. Retention of cellulose, xilan and lignin in Kraft pulping of *Eucalyptus* studies by multivariate data analysis: influences on physicochemical and mechanical properties of pulp. J. Braz. Chem. Soc. 15, pp. 514-522, (2004).

13. Gomide, J.L., Fantuzzi, H., Aspecto Fundamentais da polpação kraft de madeira de Eucalyptus. O papel 61, pp. 62-68, (2000).

14. Miranda, I.; Pereira,H. Variation of pulpwood quality with provenance and site in *Eucalyptus globulus*. Ann. For. Sci. 59, pp. 283-291, (2002).

15. Çentinkol, Ö.P., Dibble, D.C., Cheng, G., Kent, M.S.,Knierim, B., et al. Understanding the impact of ionic liquid pretreatment on eucalyptus. Biofuels 1(1), pp. 33-46, (2010).

16. Sjöström, E. Wood chemistry fundamentals and applications. Academic Press, New York, USA (1981).

17. Poke, F.S.; Potts, B.M.; Vaillancourt, R.E.; Raymond, C.A. Genetic parameters for lignin, extractives and decay in *Eucalyptus globulus*. Ann. For. Sci 63, pp. 813-821, (2006).

18. Sixta, H., Potthast, A., Krotschek, A.W. Chemical pulping process. In: Handbook of pulp. (Ed: H. Sixta) Wiley-VCH, Weinheim, Germany (2006).

19. Kleppe, P.J. Kraft pulping. Tappi J. 53(1), pp. 35-47,(1970).

20. Colodette, J.L., Gomiode, J.L., Girard, R., Jääskeläinen, A.-S., Argyropoulos, D.S. Influence of pulping conditions on eucalyptus kraft pulp yield, quality, and bleachability. TAPPI J. 1(3), pp. 14-20, (2002).
21. del Río , J.C., Gutiérrez, A., Hernando, M., Landim, P., Romero, J. Martínez, A.T. Determining the influence of eucalypt lignin composition in paper pulp yield using Py-GC / MS. J. Anal. Appl. Pyrolysis 74, pp. 110-115, (2005).

22. Gustafson, R.R., Sleicher, C.A., McKean, W.T., Finlayson, B.A. Theoretical model of the kraft pulping process. Ind. Eng. Chem. Process Des. Dev. 22, pp. 87-96, (1983).

23. Gellerstedt, G. Chemistry of chemical pulping. In: Pulp and paper chemistry and technology, Vol. 2, Pulping chemistry and technology.(Ed: M. Ek, G. Gellerstedt, G. Henriksson), Walter de Gruyter, Berlin, Germany (2009).