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Solvent effects in autocatalyzed alcohol–water pulping Comparative study between ethanol and methanol as delignifying agents

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Abstract

The autocatalyzed pulping (without additives) of *Eucalyptus globulus* with ethanol–water and methanol–water is studied in order to compare the effects of the two more frequently used solvents in Organosolv pulping. The study about the influence of the pulping alcohol on pulp properties (measured as Kappa number, yield and viscosity) is carried out by means of a 2^4 factorial design including the type of alcohol as a categorical variable. The effects for the variables (temperature, time, concentration and type of alcohol) and the interactions among them are determined. The statistical analysis for each response makes it possible to evaluate if the type of alcohol has a significant influence on the properties of the pulp obtained.

In the range of temperature, time and solvent concentration studied, methanol yields pulps with lower Kappa number, on average; whereas ethanol provides better delignification at high-intensity cooking conditions. Both alcohols show similar selectivity when pulp total yield is considered, but higher screened yield values can be obtained in ethanol pulping. The viscosity is better for ethanol pulps on average, however, in the 20–30 Kappa number range methanol pulps exhibit higher viscosity.

Keywords: Organosolv pulping; Ethanol; Methanol; *Eucalyptus globulus*; Delignification

1. Introduction

A wide variety of organic solvents including alcohols, ketones, glycols, esters and organic acids has been proposed for the delignification of lignocellulosic materials in Organosolv pulping processes [1]. The most used solvents are low molecular weight aliphatic alcohols, given the industrial interest on ethanol and methanol due to their relatively low cost. In fact, three of the four processes that have been operated at pilot plant or commercial scale use either ethanol or methanol as the delignifying agent. In the ALCELL process, where the pulping medium is a mixture of ethanol and water, pulps with Kraft equivalent quality are obtained [2]. In the Organocell and ASAM processes, the most relevant industrial applications of methanol pulping, the alcohol is used in an alkaline medium [3,4]. Ethanol has been mainly used in autocatalyzed pulping, i.e., without additives [1,2,5]. The focus of methanol use has been alkaline pulping [6], although it has been shown that pulps with low lignin content and acceptable viscosity can be obtained in an acidic medium by methanol autocatalyzed pulping [7].

The interest in ethanol and methanol is justified not only in terms of cost. The acceptable quality of the pulp produced and the ease of recovery of the solvent by rectification also make the use of ethanol and methanol attractive. Furthermore, some valuable by-products, such as lignin and carbohydrates, can be obtained during solvent recovery. Methanol has some interesting features such as easy recovery by distillation and lower material cost than ethanol. In addition to this, some methanol is generated in pulping reactions, which can compensate for losses during its recovery. In spite of this, ethanol has been studied more due to its lower toxicity, flammability and volatility.

One of the main drawbacks of ethanol and methanol Organosolv systems is the high pressure generated during the pulping stage. Besides, they are highly volatile and flammable. The investments required to reduce the risk associated with the use of alcohol would increase the production cost [5,8]. Another disadvantage is that autocatalyzed processes only provide pulp with acceptable quality and high yield from hardwoods [9]. Thus, it is not possible to obtain pulps with acceptable Kappa numbers from softwoods in autocatalyzed processes [5]. Rather, catalysis with

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alkali earth metal salts are used for pulping the all wood species [9].

In Organosolv pulping, alcohols promote the solvolysis reactions [10–12], but they also reduce the viscosity of the pulping liquor, which makes possible a better penetration and diffusion of chemicals into wood chips [13–15]. Besides, the higher solubility of lignin fragments in solvent-based liquors helps to increase lignin removal and to reduce lignin condensation [11,12].

This work deals with the comparative study of ethanol and methanol as delignifying agents in autocatalyzed Organosolv pulping of *Eucalyptus globulus*. The study complements previous papers [7,16] where the influence of several pulping variables was also analyzed for both alcohols.

2. Experimental

2.1. Materials and procedure

Selected industrial size chips of *E. globulus* were cooked in a 4 l pressure vessel (Autoclave Engineers, Erie, PA/USA) provided with an external heating system, control of pressure and temperature, and a forced liquor circulation system. The chips and the liquor were placed in the vessel, which was purged with nitrogen, pressurized (a slight overpressure was maintained throughout the run to avoid flashing and boiling of the liquor) and heated to the cooking temperature. There was a difference of 6 min in heat-up time between the runs at minimum and maximum temperature, which amounted for less than 5% of the average overall cooking time. At the end of the cooking time, the vessel was cooled to room temperature in about 20 min using a heat exchanger included in the liquor circulation system. Then, the black liquor was drawn off and the pulp was washed with alkaline solution and excess of water. The alkali enabled the dissolution of the lignin condensed onto the fibers during the cooling cycle. Finally, the pulp was left to air-dry and screened with a Sommerville device. More details about the experimental and procedure setup can be found in a previous work [16].

The wood used in the pulping experiments was characterized and the following composition was obtained (% of the dry wood weight): 21.9% lignin (TAPPI test method T222), 47.2% cellulose (TAPPI T203), 27.8% pentosans (TAPPI T223), 2.5% extractives (TAPPI T204), and 0.3% ash (TAPPI T211). Chips moisture content was determined as 16.2% of the dry wood weight (TAPPI test method 264). The ethanol and methanol employed were of commercial grade (96.0 and 99.5% purity, respectively).

To study the effects of the more relevant factors affecting the quality of the pulp obtained and to compare the effect of the two alcohols, a 2^4 factorial design was used (22 runs: $2^4 + 6$ central points). In Table 1, the detailed conditions for the runs are shown. The pulping variables analyzed were reaction time (*t*: 56–104 min), temperature (*T*: 176–194 °C) and alcohol concentration (*C*: 38–62%, w/w) as quantitative factors, and the type of alcohol (S: ethanol or methanol) as a categorical or qualitative factor. Constant operating conditions were liquor-to-wood ratio (7 l of liquor per kg of wood), heating rate (3 °C/min), and digester overpressure (2 kg/cm^2). The cooking time was measured from the moment that the system reached the desired cooking temperature. The results obtained were reported using the following pulp properties: Kappa number, viscosity, total yield and screened yield. A Statgraphics® plus 4.0 software package was used in the statistical analysis of the results obtained.

Pareto charts were employed to determine the significance of the statistically determined effects. In this plot, each of the estimated effects appears as bars in decreasing order of magnitude. The length of each bar is proportional to the standardized effect calculated with the estimated effect divided by its standard error.

Interaction plots for the responses were employed to interpret the results. In each plot, the first factor of the interaction varies from its lowest level to its highest level. The second factor is held at its low level on one line and at its high level on the other line.

Table 1
Pulping conditions and experimental results

T (°C)	*t* (min)	[Alcohol] (%, w/w)	Screened yield (%)		Total yield (%)		Kappa number		Viscosity (ml/g)		pH (black liquor)	
			Methanol	Ethanol	Methanol	Ethanol	Methanol	Ethanol	Methanol	Ethanol	Methanol	Ethanol
176	56	38	49.7	50.9	60.5	62.4	53.4	56.7	933	986	3.93	3.92
194	56	38	51.6	51.8	51.7	51.9	17.7	16.0	847	821	3.84	3.68
176	104	38	55.1	55.4	55.5	55.8	31.9	31.8	1110	991	3.78	3.78
194	104	38	51.0	50.5	51.1	50.6	12.6	9.2	590	452	3.66	3.55
176	56	62	45.1	47.7	74	77.4	85.4	91.6	435	548	4.51	4.51
194	56	62	56.0	54.5	59.5	58.5	40.7	42.2	993	957	4.43	4.45
176	104	62	52.9	51.0	64.3	65.4	59.4	64.9	816	844	4.30	4.34
194	104	62	55.8	55.1	55.9	55.3	23.7	23.0	1052	1010	4.40	4.50
185	80	50	55.3	55.9	55.9	56.5	29.2	32.3	1069	1026	4.03	4.06
185	80	50	55.1	56.3	55.2	57.2	25.9	34.2	1080	949	4.08	4.16
185	80	50	55.6	56.7	55.7	57.0	26.4	30.6	1097	972	4.03	4.01

2.2. Analysis

Pulp yield was calculated before (total yield) and after screening (screened yield) using a Somerville device (Büchel van der Korput B.V., Vendelier, the Netherlands). The Kappa number and viscosity of screened pulp were determined according to TAPPI 236 and SCANC15:62 test methods, respectively. Prior to viscosity analysis, the pulps were chlorite-bleached according to TAPPI 230 method.

3. Results and discussion

The characteristics of the pulps obtained in the 22 pulping runs are summarized in Table 1. Data processing enabled estimation of the main effects and the interactions of the factors for the responses considered. The effect of a factor is the change in the response when it is changed from the low (-1) to the high level ($+1$). The main effect of each factor estimates its average effect over all possible conditions of the other variables. Each of the responses analyzed can be affected only by the main effects or by interactions among them. The main effect of a variable should be individually interpreted only if there is no evidence that the variable interacts with other variables. When there is evidence of one or more such interactions, the interacting variables should be considered jointly.

The experimental design applied includes four main effects, six two-factor interactions, four three-factor interactions and one four-factor interactions. Therefore, a 2^4 design would contain 15 effects. All of these effects can be estimated, but usually not all of them are statistically significant. There is a certain hierarchy in the effects. In terms of absolute magnitude, main effects tend to be larger than two-factor interactions, which in turn tend to be larger than three-factor interactions, and so on. In this work, only the two-factor interactions have been considered.

The vertical line in Pareto chart (Fig. 1a) indicates the effects that are statistically significant, i.e. those with a significance level higher than 95%. It can be seen that all main effects are statistically significant for Kappa number. The values of the effects show that lower Kappa number pulps can be obtained for high cooking temperature and long cooking time, as expected from the higher degree of severity of the cooking conditions. A low alcohol concentration leads to a decrease in Kappa number. In these conditions, the black liquor has a higher water content and the dissociation of the acetic acid released by wood is enhanced [7]. Therefore, a higher hydrogen ion concentration is reached, which results in a more extensive delignification.

The effect of the type of alcohol on Kappa number is lower than those of temperature, time and alcohol concentration. The main effect for the type of alcohol has a value of 2.4 ± 0.76 units and it is significant at a 96.5% confidence level. Therefore, within the range studied methanol pulps have, on average, a lower lignin content than ethanol pulps.

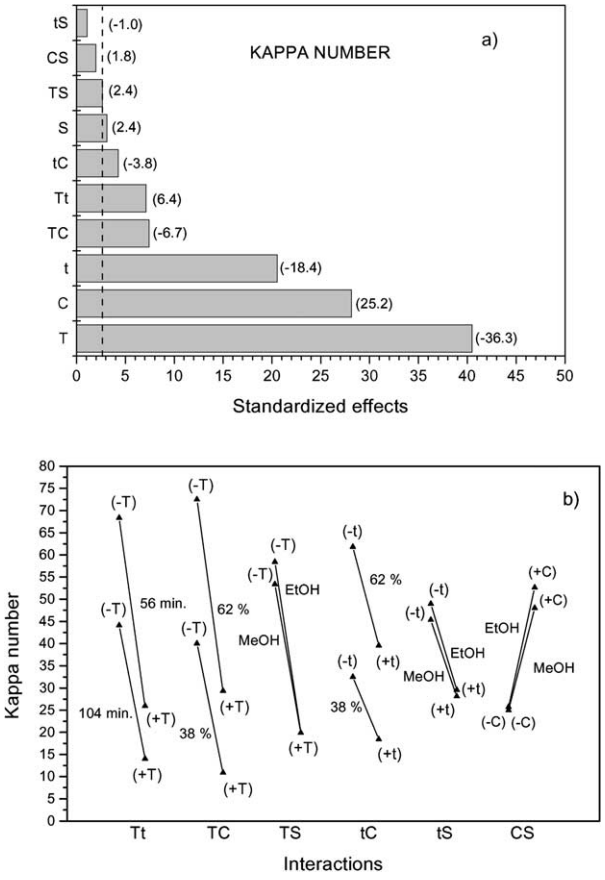

Fig. 1. (a) Pareto chart for Kappa number (the values in brackets are the estimated effects). (b) Interactions plot for Kappa number.

From the Kappa number interactions plot (Fig. 1b), it can be deduced that the better delignification obtained with methanol is restricted to mild cooking conditions. The interaction between temperature and type of alcohol (*T*S, 94.5% significance) shows that methanol treatment produces pulps with lower Kappa number when cooking temperature is at the low level (176 °C). However, at 194 °C no difference can be appreciated between ethanol and methanol. If the cooking temperature is high enough, the behavior is observed to reverse. Thus, it was reported that in pulping runs carried out at 200 °C the lignin content for ethanol pulps is 37% lower than for methanol pulps [7,16].

The better delignification attained with ethanol at high-intensity cooking conditions can be explained in terms of both delignification kinetics and black liquor pH. In ethanol delignification, the transition from bulk to residual delignification takes place for a lignin conversions of 84%, whereas a value of 79% was found for methanol [17,18]. Therefore, for high-intensity cooking conditions, where very low Kappa number pulps are obtained and residual delignification plays an important role, the later transition to residual delignification in ethanol pulping makes it possible to obtain more delignified pulps. On the other hand, the pH of the black liquors is low for ethanol pulping when the

alcohol concentration is at the low level (38%, w/w), as it can be seen in Table 1. It has been reported that in ethanol pulping, a higher amount of acetic acid is released [19]. In high alcohol content liquors no differences in pH are observed. However, in high water content liquors, the better dissociation of acetic acid results in lower pH for ethanol pulping, which also explains the lower pulp lignin content.

Pareto chart for total yield (Fig. 2a) indicates that all main effects are significant. Parallelism can be noticed between this response and the pulp Kappa number analyzed previously. The rise in the severity of pulping conditions results in a greater loss of total yield due to the important dissolution of wood components [20].

The runs carried out with ethanol provide a higher total yield than those performed with methanol, 0.79 ± 0.15 percentage units on average. The difference is significant at a 99.3% confidence level. This fact can be explained by the higher lignin content of ethanol pulps, which means lower dissolution of wood components and higher yield.

From the total yield plot (Fig. 2b), it can be deduced that the most important effect is that corresponding to the interaction between cooking temperature and the type of alcohol (*T*S, 99.6% significance). Thus, it can be seen that, at high temperature, ethanol and methanol pulps exhibit a similar total yield, which is consistent with that observed for

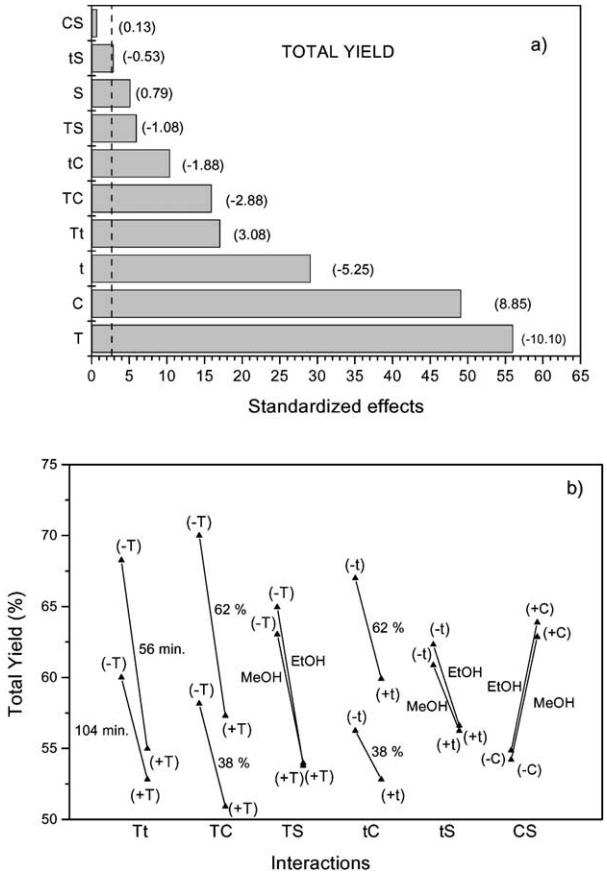

Fig. 2. (a) Pareto chart for total yield (the values in brackets are the estimated effects). (b) Interactions plot for total yield.

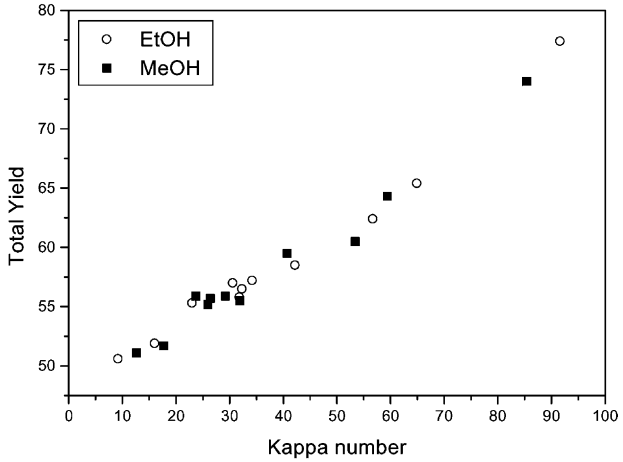

Fig. 3. Total yield vs Kappa number.

Kappa number and selectivity. The interaction between the type of alcohol and cooking time (*t*S, 95.6% significance) indicates that the difference in behavior is higher for short cooking times.

With regard to selectivity towards delignification, the lower lignin content of methanol pulps is compensated by the lower total yield obtained and both alcohols have a nearly identical selectivity, as can be seen in Fig. 3.

In the Pareto chart for screened yield (Fig. 4a), it can be shown that only the main effects for time and temperature have a significant effect. At high temperature and long cooking time, the dissolution of lignin is high, which leads to better fiber liberation and lower screenings content. However, extreme conditions are not desirable since other wood components such as cellulose and the hemicelluloses dissolve as well. At high alcohol concentration conditions, i.e. high pH, delignification is poor and the pulp screenings content is very high, which results in low screened yield values. For low alcohol concentration conditions, i.e. low pH, delignification is good and the pulp screenings is negligible, but polysaccharide dissolution is important and the screened yield is low. Therefore, similar screened yield values are obtained for the alcohol concentration extreme conditions (-1 and $+1$) and the main effect is not significant. This is the reason for the low significance of alcohol concentration as a single-effect variable.

The main effect for the type of alcohol is non-significant (0.24% units, 82.7% significance); however, the interactions with time and temperature are significant. Fig. 4b shows that in both cases methanol enables a slightly higher screened yield for low-intensity cooking conditions, i.e. short time and low temperature. This may be due to the higher removal of lignin at these conditions when compared with ethanol, which permits better fiber liberation.

The screened yield values are plotted vs Kappa number in Fig. 5. It can be seen that screened yield peaks for Kappa numbers around 30. Besides, screened yield values are over 55% in the 20–35 Kappa number range. The highest

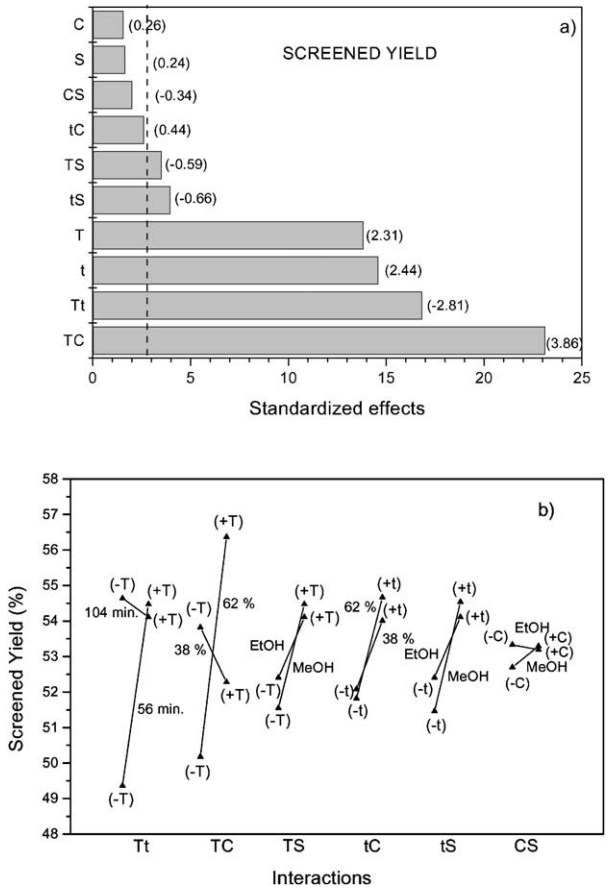

Fig. 4. (a) Pareto chart for screened yield (the values in brackets are the estimated effects). (b) Interactions plot for screened yield.

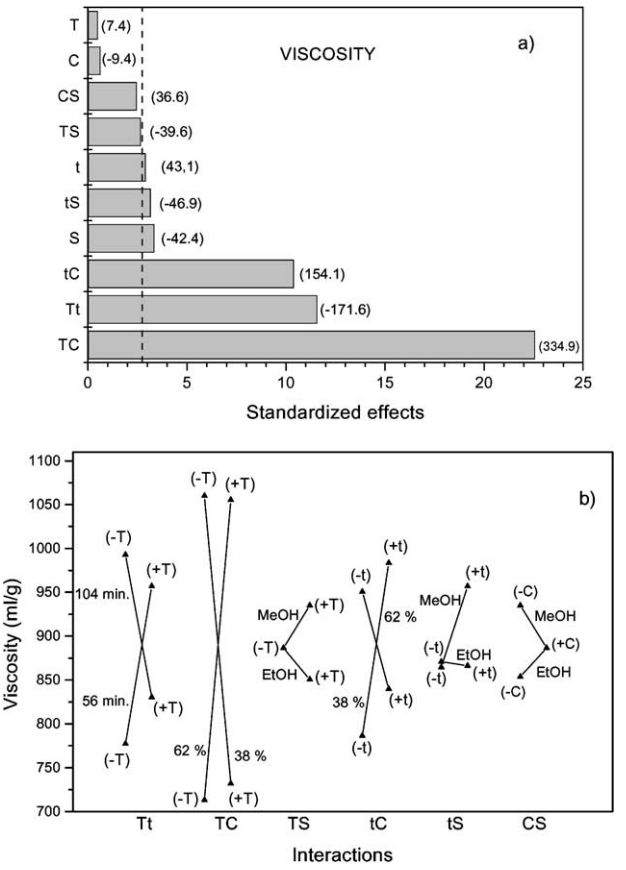

Fig. 6. (a) Pareto chart for viscosity (the values in brackets are the estimated effects). (b) Interactions plot for viscosity.

screened yields are obtained for ethanol pulps with Kappa numbers of 30. Selectivity is similar in this region for both alcohols if wood components dissolution is taken into account, but pulp yield is higher for ethanol pulping when screened pulp is considered.

The Pareto chart for the last response analyzed, pulp viscosity, is shown in Fig. 6a. The main effects for cooking temperature and alcohol concentration are not significant. The viscosity values are low when the severity of the cooking conditions is low. The pulps obtained in these conditions contain important amounts of the hemicelluloses. Therefore, both the average molecular weight of the cellulose obtained and the viscosity values decrease. At high-intensity cooking conditions most of the hemicelluloses dissolve, but serious cellulose depolymerization takes place and the viscosity drops. Thus, the best conditions correspond to mild cooking conditions, where the hemicelluloses dissolution is of importance but cellulose depolymerization is moderate. This phenomenon can be seen in the viscosity vs Kappa number plot (Fig. 7), where pulp viscosity peaks for Kappa numbers around 30. These Kappa numbers correspond to mild condition cooks.

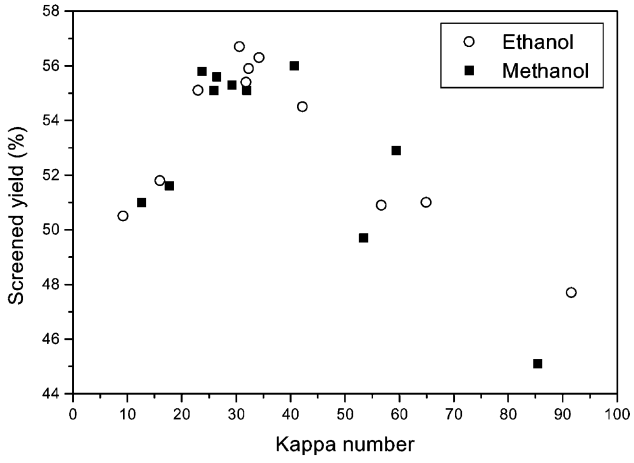

Fig. 5. Screened yield vs Kappa number.

The main effect for the type of alcohol has a significance of 97.1%. The pulps obtained in methanol pulping have, on average, 42 ± 13 viscosity units less than ethanol pulps. The effect produced by the change in alcohol type is comparable, in absolute value, to that produced by the time. The interactions of the type of alcohol with time (*t*S), temperature (*T*S) and concentration (*C*S) have a significance of 96.6, 94.4 and 93.1%, respectively. The plot for these interactions (Fig. 6b) indicates that ethanol pulping provides higher

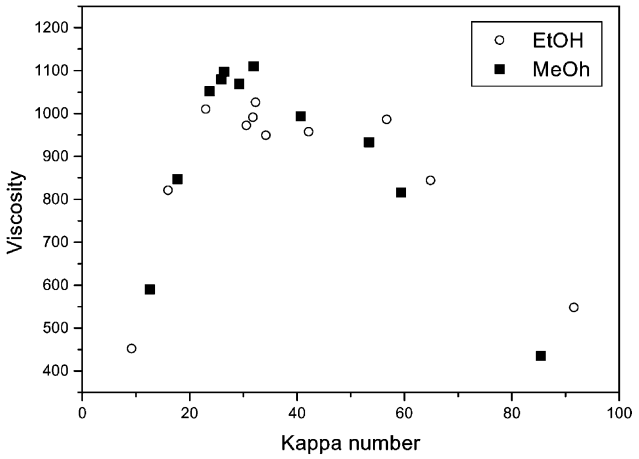

Fig. 7. Pulp viscosity vs Kappa number.

viscosity at high-intensity cooking conditions, i.e. high temperature, long time and low alcohol concentration. However, methanol shows higher viscosity values in the 20–30 Kappa number range (Fig. 7). It can be deduced that although the selectivity towards delignification is similar for both alcohols when wood components dissolution is considered, the reduction of cellulose polymerization degree is lower for methanol pulping in the range 20–30 Kappa number. This range is of special interest since the pulp obtained would have the best properties for papermaking: the screened yield and viscosity have maximum values and the pulp Kappa number enables bleaching.

4. Conclusions

The behavior of ethanol and methanol as delignifying agents in autocatalyzed Organosolv pulping of *E. globulus* has been compared. Methanol shows better lignin dissolution on average (−2.4 Kappa number units); however, ethanol pulping produces pulps with less lignin at high-intensity cooking conditions, where Kappa numbers lower than 10 can be obtained. The selectivity towards lignin dissolution is similar for ethanol and methanol, as it can be deduced from the selectivity plots of total yield vs Kappa number. In the case of screened yield, higher values can be observed for ethanol pulping in the 20–30 Kappa number range.

The most important differences are those observed for pulp viscosity. Although ethanol pulps have a higher viscosity on average, the best results correspond to methanol pulping. Thus, viscosity values well over 1000 ml/g are obtained for pulps with Kappa number between 20 and 30 in the methanol system. These pulps, which are obtained at mild cooking conditions, are of special interest since they can be bleached and are obtained at good screened yield (55%).

From these results, if Organosolv pulp is used instead of Kraft pulp, methanol pulping is recommended, since high viscosity pulp can be attained at high screened yield. Ethanol provides lower viscosity pulp but at slightly higher screened yield. In both cases, acceptable pulp Kappa numbers can be reached.

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