# Rheology of *Eucalyptus Globulus* Kraft Black Liquor

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**Abstract:**
Black liquor is the major by-product and biomass fuel of pulp mills, and the understanding of its thermophysical properties is essential for the improvement of the design and the operation of chemical recovery processes. In this work, the rheological behaviour of industrial samples of *Eucalyptus globulus* black liquor was investigated to study the influence of solids content ranging from 13 % for the white liquor sample, and from 30 to 65 % of dissolved solids for the black liquors, and of temperature from 298.15 to 338.15 K, covering shear rates from 0 to 1200 $s^{-1}$. The black liquor showed a complex non-Newtonian behaviour, presenting at low shear rates a pseudoplastic behaviour, followed by a viscosity Newtonian plateau. The modified Quemada model gives an expression applicable to all the shear rate range, which was used to describe the flow curves for the viscosity of *E. globulus* black liquors samples. Moreover, a correlation based on a VTF model with parameters dependent on solids content was successfully developed for the viscosity data of the Newtonian plateau.

**Zusammenfassung:**
Schwarzlauge ist das wichtigste Nebenprodukt und biobasierte Öl von Zellstofffabriken. Das Verständnis der thermophysikalischen Eigenschaften ist für die Verbesserung des Verfahrens und die Durchführung der chemischen Gewinnungsprozesse essentiell. In dieser Arbeit wurde das rheologische Verhalten der industriellen Proben von Eukalyptus-Schwarzlauge erforscht, um den Einfluss des Feststoffgehaltes in der Größenordnung von 13 % für die Weißlauge-Probe und von 30 bis 65 % für die aufgelösten Feststoffanteile für die Schwarzlauge-Proben bei Temperaturen zwischen 298.15 und 338.15 K im Schergeschwindigkeitsbereich von 0 bis 1200 $s^{-1}$ zu untersuchen. Die Schwarzlauge wies ein komplexes nicht-Newtonsches Verhalten auf mit einem pseudoplastischen Verhalten bei niedrigen Schergeschwindigkeiten und einem Newtonschen Plateau. Das modifizierte Quemada-Modell führt zu einem Ausdruck, der für alle Schergeschwindigkeiten angewandt werden kann, und wurde für die Beschreibung der Fließkurven der Eukalyptus-Schwarzlaugen-Proben herangezogen. Darüber hinaus wurde eine Korrelation, basierend auf dem VTF-Modell mit den Feststoffgehalt-Parametern, für die Viskositätsdaten im Newtonschen Bereich aufgestellt.

**Résumé:**
La liqueur noire est le principal sous produit et combustible de biomasse des moulins à pulpe, et la compréhension de ses propriétés thermophysiques est essentielle afin d'améliorer le design et l'opération des procédés de récupération chimique. Dans ce travail, le comportement rhéologique d'échantillons industriels de liqueur noire d'Eucalyptus globulus a été testé afin d'étudier l'influence de la fraction solide dans la gamme de 13 % pour l'échantillon de liqueur blanche, et de 30 à 65 % de solides dissous pour les liqueurs noires, et pour des températures de 298.15 à 338.15 K, en couvrant des vitesses de cisaillement de 0 à 1200 $s^{-1}$. La liqueur noire présente un comportement complexe non Newtonien, avec un comportement pseudo plastique à basses vitesses de cisaillement, suivi par un plateau de viscosité Newtonienne. Le modèle de Quemada modifié donne une expression applicable à toute la gamme de vitesses de cisaillement, qui a été utilisée pour décrire les courbes d'écoulement pour la viscosité des échantillons de liqueur noire d'E. globulus. De plus, une corrélation basée sur un modèle VTF avec des paramètres qui dépendent des fractions solides, a été développée avec succès pour les données de viscosité du plateau Newtonien.

**Key words:** viscosity, black liquor, *Eucalyptus globulus*, rheological model, shear thinning



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with the above referred values. It can be performed another comparison with the values published in a paper by Cardoso et al. [22] about *E. grandis* Brazilian black liquor. At 310.35 K and 51.5% solids content their black liquor has a viscosity of 196 mPa·s while using Equation 5 a value of 148 mPa·s is calculated. Samples by Cardoso et al. [22] were collected in a mill using a different Eucalyptus wood cooked at a $\kappa$ number of 17, while in the Portuguese mill where our samples were collected this number is 14. Moreover, the liquor organics/inorganics ratio for their samples is 1.98 while ours is 1.5. These data point out to a Brazillian liquor with larger dissolved organics content, which rise the viscosity and less degraded lignin possibly with a higher molecular weight. So these assessments confirm the good applicability of the developed correlation (Equation 5), especially for Eucalyptus wood and even for other hardwood liquors in all the several parts of the recovery process.

## 4 CONCLUSIONS

In this work, experimental data on *E. globulus* white and industrial black liquors viscosity over shear rate range of 0 to 1200 $s^{-1}$, solids content range of 13% for white liquor and 30 to 59.5% for black liquors, and temperature range of 298.15 to 338.15 K is presented and discussed. We found that black liquor showed a complex shear dependent non-Newtonian rheological behaviour presenting different types of flows as a function of shear rate, solids content, and temperature. Moreover, all the samples analysed showed time-dependent effects clearly stated in the hysteresis flow curves reported. Black liquors viscosity increases when the solids content is raised and/or the temperature is decreased, results that are in close agreement with those found by other authors. The modified Quemada model was used to express the viscosity in all the shear rate range. The model was fitted with (most) satisfactory results to the data. Starting from the VTF model a correlation was found, which incorporates solids content dependent parameters. This equation was successfully fitted to the viscosity value of the Newtonian plateau. The utility of this correlation to predict hardwood black liquor viscosity, in ordinary industrial conditions, was tested by performing several successful comparisons with data available in the literature. It is observed that at fixed solids content the viscosity decreases exponentially with an increase in temperature. At a fixed temperature, higher values of viscosity correspond to the highest values of solids content.

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## REFERENCES

[1] Tran H, Vakkilainnen EK: Advances in the Kraft chemical recovery process, 3rd ICEP – International Colloquium on Eucalyptus Pulp, Belo Horizonte, Brasil (2007). http://www.celuloseonline.com.br/imagembank/Docs/DocBank/Eventos/430/2TranOral.pdf.

[2] Louhelainen J, Alén R, Zielinski J, Sågfors P-E: Effects of oxidative and non-oxidative thermal treatments on the viscosity and chemical composition of softwood Kraft black liquor, J. Pulp Pap. Sci. 28 (2002) 285–291.

[3] Grace TM: Black liquor evaporation, in Grace TM., Malcolm EW., Kocurek MJ (Eds.) Alkaline Pulping, Pulp and Paper Manufacture Series Vol.5. TAPPI CPPA, Atlanta (1989) 477–530.

[4] Zaman AA, Fricke AL: Effect of pulping conditions and black liquor composition on newtonian viscosity of high solids Kraft black liquors, Ind. Eng. Chem. Res. 35 (1996) 590–597.

[5] Louhelainen J, Alén R, Feng Z: Combustion properties of black liquors from alkaline pulping of wheat straw and reed canary grass, Tappi J., Online Exclusive 2 (2003) 1–16.

[6] Söderhjelm L, Sågfors P-E, Janson J: Black liquor viscosity - Influence of polysaccharides, Paperi ja Puu – Paper and Timber 74 (1992) 56–58.

[7] Söderhjelm L, Hausalo T: Extensive analysis of strong black liquor, Appita 49 (1996) 263–268.

[8] Frederick WJ, Adams TN: Black liquor thermal and transport properties, TAPPI Kraft Recovery Short Course, Orlando, TAPPI Press, Atlanta (1995) 3.1.1–3.1.31.

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[9] Llamas P, Dominguéz T, Vargas JM, Llamas J, Franco JM and Llamas A: A novel viscosity reducer for Kraft process black liquors with a high dry solids content, Chem. Eng. Processing 46 (2007) 193–197.
[10] Moosavifar A, Sedin P, Theliander H: Viscosity and boiling point elevation of black liquor: Consequences when lignin is extracted from the black liquor, Nordic Pulp & Paper Res. J. 21 (2006) 180–187.
[11] Frederick WJ: Black liquor properties, TAPPI Kraft Recovery Operations Seminar, Orlando, USA (1987) 97–107.
[12] Laurola H, Wallendahl U: Properties of spent pulping liquors, Proceedings of TAPPI Pulping Conference, Denver, USA (1981) 97–102.
[13] Milanova E, Dorris GM: Effects of residual alkali content on the viscosity of Kraft black liquors, J. Pulp Pap. Sci. 16 (1990) J94–J101.
[14] Shen Q, Rosenholm JB: Kraft black liquor properties in relation to delignification, Nordic Pulp & Paper Res. J. 13 (1998) 206–210.
[15] Tiu C, Nguyen KL, Guzman M: Non-newtonian behaviour of Kraft black liquors, Appita 46 (1993) 203–206.
[16] Zaman AA, Fricke AL: Viscosity of softwood Kraft black liquors at low solids concentrations: Effects of solids content, degree of delignification and liquor composition, J. Pulp Pap. Sci. 21 (1995a) J119–J126.
[17] Zaman AA, Fricke AL: Effect of pulping conditions and black liquor composition on viscosity of softwood Kraft black liquors: predictive models, Tappi J. 78 (1995) 107–119.
[18] Zaman AA, Fricke AL: Steady shear flow properties of high solids softwood Kraft black liquors: Effects of temperature, solids concentration, lignin molecular weight and shear rate, Chem. Eng. Commun. 139 (1995) 201–221.
[19] Ferreira AGM, Ribeiro ISA, Lobo LQ: The surface tension of Kraft black liquor from eucalyptus, Silva Lusitana 13 (2005) 113–119.
[20] Gonçalves IMR, Lobo LQ: Estudo preliminar da reologia do licor negro de eucalipto, Silva Lusitana 1 (1983) 131–140.
[21] Gouveia SP, Farinha AI, Egas AP, Ferreira AGM: Influence of lignin content on the viscosity and surface tension of hardwood Kraft black liquor, Book of Abstracts of CHEMPOR 2005 – 9th International Chemical Engineering Conference, Coimbra, Portugal (2005) 178–179.
[22] Cardoso M, de Oliveira ED, Passos ML: Chemical composition and physical properties of black liquors and their effects on liquor recovery operation in Brazilian pulp mills, Fuel 88 (2009) 756–763.
[23] Gonçalves CRS, Cardoso M, Oliveira ED, Passos MLA: Analysis of composition and characteristics of "Kraft" black liquor from Brazilian pulp and paper industries, Proceedings of 2004 International Chemical Recovery Conference, Charleston, USA (2004) 01–10.
[24] Passos ML, Trindade ALG, d´Angelo JVH, Cardoso M: Drying of black liquor in spouted bed of inert particles, Drying Tech. 22 (2004) 1041–1067.
[25] Da Silva MA, Rocha NO, Carvalho CH, Sabadini E: New experimental technique to measure the efficiency of drag reducer additives for oil samples, Energy Fuels 23 (2009) 4529–4532.
[26] Lim TT, Tan KS: A note on power-law scaling in a Taylor-Couette flow, Phys. Fluids 16 (2004) 140–144.
[27] White JL: Principles of polymer engineering rheology, John Wiley & Sons, New York (1990).
[28] Edwards BJ, Keffer DJ, Reneau CW: An examination of the shear-thickening behaviour of high molecular weight polymers dissolved in low-viscosity newtonian solvents, J. Appl. Polym. Sci. 85 (2002) 1714–1735.
[29] Podolsak AK, Tiu C, Fang TN: Flow of non-Newtonian fluids through tubes with abrupt expansions and contractions (square wave tubes), J. Non-Newtonian Fluid Mech. 71 (1997) 25–39.
[30] Zupancic A, Lapasin R, Zumer M: Rheological characterisation of shear thickening $TiO_2$ suspensions in low molecular polymer solution, Prog. Org. Coat. 30 (1997) 67–78.
[31] Miller AA: Free volume and viscosity of liquids: Effects of temperature, J. Phys. Chem. 67 (1963) 1031–1035.
[32] Zaman AA, Fricke AL: Newtonian viscosity of high solids Kraft black liquors: Effects of temperature and solids concentrations, Ind. Eng. Chem. Res. 33 (1994) 428–435.
[33] Söderhjelm L: Viscosity of strong black liquor, Paperi ja Puu – Paper and Timber 9 (1986) 642–652.
[34] Veeramani H, Baba MA, Chowdhary LN, Saksena UL: Effect of alkali pre-treatment on eucalypt chips on Kraft black liquor viscosity and pulp strength, J. Wood Chem. Technol. 3 (1983) 17–34.

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