Rheological properties of Canadian maple syrup

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Ngadi, M.O. and Yu, L.J. 2004. **Rheological properties of Canadian maple syrup**. Canadian Biosystems Engineering/Le génie des biosystèmes au Canada **46**: 3.15 - 3.18. Rheological properties of five grades of Canadian maple syrup, namely Canada No. 1 - Very Clear; Canada No. 1 – Clear; Canada No. 1 – Medium; Canada No. 2 - Amber; and Canada No. 3 - Dark were studied. The effects of temperature varying from 5 to 55°C and soluble sugar concentration varying from 66 to 75°Brix on the rheological properties were investigated. Grade, temperature, and concentration influenced the apparent viscosity of maple syrup. The Dark grade had the highest viscosity whereas the Very Clear grade had the least viscosity. The other grades of maple syrup, namely Clear, Medium, and Amber had medium viscosity with no statistical difference ($p<5\%$) between them. Maple syrup was predominantly Newtonian as the flow behavior index was close to unity. Apparent viscosity of the maple syrup samples ranged from 0.035 to 0.651 Pa s for all the different grades within the range of temperatures studied. Increasing temperature decreased the apparent viscosity of maple syrup. The effect of temperature on the viscosity of maple syrup was modeled using the Arrhenius model. The activation energy for the temperature change varied from 43.97 to 44.86 kJ/mol. Increasing concentration of maple syrup increased the non-Newtonian behavior of the syrup. **Keywords**: rheology, maple syrup, viscosity, Newtonian, temperature effect.

Dans cette étude, nous avons mesuré et comparé les propriétés rhéologiques d'échantillons de sirop d'érable classés : Canada no.1 – *Extra Clair*, Canada no. 1 – *Clair*, Canada no.1 – *Médium*; Canada no.2 – *Ambré*; et Canada no.3 *Foncé*. Cette étude a permis d'établir les relations entre les propriétés rhéologiques du sirop d'érable, sa température (entre 5 et 55°C) et sa teneur en sucre (entre 66 et 75°Brix). Lors des essais, les valeurs mesurées de viscosité apparente ont variées de 0,035 à 0,651 Pa s. Avec un indice près de l'unité, le comportement fluidique du sirop d'érable a été de nature newtonien. Nous avons démontré que la classification, la température et la teneur en sucre affectaient la viscosité apparente du sirop. Les sirops classés *Foncé* ont eu des valeurs de viscosité les plus élevées tandis que les sirops classés *Extra Clair* ont eu les plus basses. Des valeurs intermédiaires de viscosité ont été enregistrées pour les sirops classés *Clair, Médium et Ambré* et les différences observées n'étaient pas significatives dans un intervalle de confiance de 0,05. L'augmentation de la température a eu pour effet de diminuer la viscosité apparente des échantillons. Un model Arrhenius a été utilisé pour relier les deux variables. Les valeurs d'énergie d'activation pour le changement de température ont varié entre 43.97 et 44.86 kJ/mol. L'augmentation de la teneur en sucre du sirop d'érable a eu pour effet d'accroître sa viscosité. **Mots-clés**: rhéologie, sirop d'érable, viscosité, newtonien, effet de la température.

INTRODUCTION

Maple syrup is one of the hallmark products of Canada. About 85% of the world's production of maple syrup is made in Canada and more than 90% of it originates from the province of Quebec (Agriculture and Agri-food Canada 2001). The syrup is rich in minerals including calcium, potassium, manganese, magnesium, phosphorus, and iron. It has the same calcium content as whole milk. Vitamins B2, B5, B6, niacin, biotin, and folic acid are also present in maple syrup. The caloric content of maple syrup at standard density is 11.36 J/mL, lower than corn syrup and honey. These make maple syrup an interesting product from a nutritional point of view.

Maple syrup is sold in different grades or classes. The classification is controlled by government regulations according to amount of soluble solid contents as determined by refractometer or hydrometer at 20°C. The different grades of Canadian maple syrup, grouped by color, are: grade AA (Canada No. 1 - Very Clear); grade A (Canada No. 1 - Clear); grade B (Canada No. 1 - Medium); grade C (Canada No. 2 - Amber); and grade D (Canada No. 3 - Dark) (Koelling and Heiligmann 1996). Canada No. 1 and Canada No. 2 maple syrups are required by regulation to be free from fermentation and any cloudiness or turbidity. Canada No. 3 syrup is only required to have a characteristic maple flavour and be free from any objectionable odour. Production of maple syrup is essentially by evaporative concentration of the maple sap to a predetermined concentration. Favreau (1996) investigated the application of microwave heating to produce maple syrup. Rheological characteristics of the syrup are required for pumping and handling of the product from one unit operation to the other. Knowledge of the rheological properties of maple syrup is therefore necessary in quality control, storage stability, and in understanding and designing texture of downstream maple syrup products such as maple sugar, maple candies, maple cream, and maple spread. However, there is currently little research on rheological properties of maple syrup.

Rheological properties of similar products such as honeys, juices, and sugar solution have been studied (Abu-Jdayil et al. 2002; Bhandari et al. 1999; Giner and Ibarz 1996; Schmidt et al. 1998). Light and dark types of honey have been reported to exhibit Newtonian flow behavior regardless of the conditions of heating (Abu-Jdayil et al. 2002). Bhandari et al. (1999) investigated seven varieties of Australian honeys over the temperature range of 4 to 30°C. The authors reported that all these honey varieties were Newtonian. Clarified cherry juices were reported as Newtonian fluids over a wide temperature range from 5 to 70°C and the effect of temperature on the products' viscosities was described by an Arrhenius-type equation (Giner and Ibarz 1996). Rheological studies of pure sucrose solutions within selected temperatures (5 to 70°C) and concentrations (60 to 75%) showed deviations from the Newtonian behavior (Schmidt et al. 1998). This was attributed to structural changes occurring in the sucrose solutions.

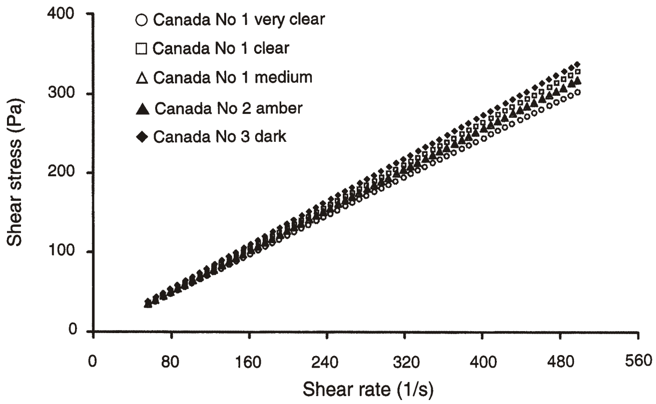

Fig. 1. Flow curves for different grades of maple syrup at 5°C.

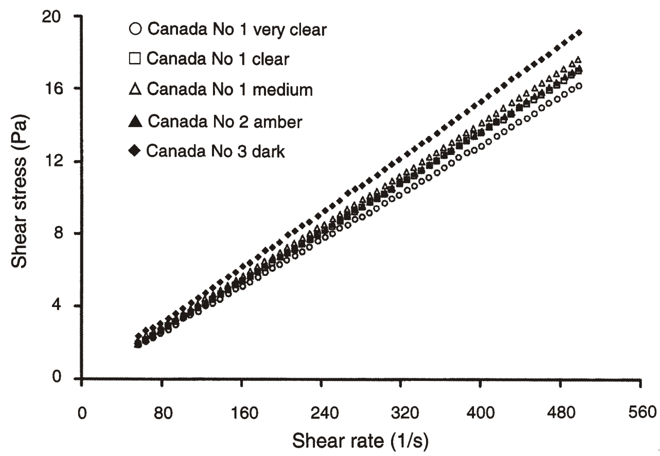

Fig. 2. Flow curves for different grades of maple syrup at 55°C.

The objectives of this work were to determine the rheological properties of different grades of Canadian maple syrup and to determine the influence of temperature and concentration on the rheological properties of maple syrup.

MATERIALS and METHODS

Five grades of Canadian maple syrup were selected for the study. These were Canada No. 1 - Very Clear; Canada No. 1 – Clear; Canada No. 1 – Medium; Canada No. 2 - Amber and Canada No. 3 - Dark. The samples were obtained from the Citadelle Maple Syrup Producers' Cooperative (Plessisville, QC). Total soluble solids of maple syrup samples (°Brix) were measured at 20°C using a refractometer (ATC, 0-90%, Fischer Scientific, Nepean, ON). The Brix scale is particularly well suited for measuring the density of maple syrup since 98% of the dissolved solids are sugar (Koelling and Heiligmann 1996). Maple syrup samples with higher concentrations were obtained by evaporating regular samples using a hot plate (Corning Stirrer/hotplate, PC-520, Corning Inc., Corning, NY). The samples were stirred continuously while heating until the desired concentrations were attained.

Rheological measurement was by using a rheometer (AR2000, TA Instruments, New Castle, DE). The peltier controlled concentric cylinder system with DIN geometry was used. The rotor and stator radius of the concentric cylinder were 14 and 15 mm, respectively. The immersed height was 42 mm; the gap was 5920 µm; and the approximate sample volume was 19.6 mL. Rheological measurements were conducted at the constant temperatures of 5, 15, 25, 35, 45, and 55°C. Sample temperature during test was controlled automatically by the peltier system of the concentric cylinder system. The flow procedure used was a continuous ramp, shear rate varying from 50 to 500 s^{-1} (50 to 500 s^{-1} and 500 to 50 s^{-1} for thixotropy test). Two replicates were conducted for all of the rheological measurements. Statistical analysis of data was by using the SAS software (SAS Version 8, SAS Institute Inc., Cary, NC). Statistical significance was determined at $p < 0.05$. The best-fit rheological model for the stress - shear data was determined from three different models, namely, the Newtonian, Power law, and Bingham equations. The model with the least standard error was selected as the best fit model.

RESULTS and DISCUSSION

The five grades of maple syrup samples used in this study measured the same value for total soluble solids at 66°Brix before they were further concentrated. This implies that all the grades of maple syrup samples have the same standard density and have the same total sugar content in accordance with regulatory specifications (Favreau 1996). Typical shear stress versus shear rate responses of the various grades are shown in Figs. 1 and 2 for the constant temperatures of 5 and 55°C, respectively. As expected, shear stress increased with increasing shear rate in a fairly linear fashion.

The three rheological models, namely Newtonian, Power law, and Bingham were fitted to the experimental data. The Power law and Bingham models have one parameter more than the Newtonian model. The standard errors obtained using the various models were compared. The results indicate that between the tested models, the Power law model had the least standard error. The Power law model more closely described the flow behavior of the maple syrup samples regardless of their grades and temperatures. Values of the parameters for the Power law models at the different temperatures are presented in Table 1. The flow behavior indexes varied between 0.980 and 1.015 for all the samples. Within the narrow temperature range of 25 to 45°C, the flow behavior indexes were closer to unity varying between 0.990 and 1.007. Herh et al. (2000) measured the flow characteristics of light and regular maple syrup (grades not identified) at 37°C. The authors reported that the regular maple syrup was predominately Newtonian whereas the light syrup showed some non-Newtonian flow behavior. The results obtained in this study over the wider temperature range corroborated the results of Herh et al. (2000). Maple syrup is predominantly Newtonian especially within the temperature range of 25 to 45°C. However, depending on the grade of the syrup, it showed very slight deviation from Newtonian at temperatures outside the temperature range.

Values of apparent viscosities of maple syrup were from 0.035 to 0.651 Pa s for the different grades of maple syrups and temperatures. Scarce information is available in the literature. The viscosity of maple syrup at 25°C has been reported as 0.1635 Pa s (Johnson 1997). The reported viscosity is within the range obtained in this study. Statistical analysis of the data obtained for the regular maple syrup concentration (66°Brix) showed that type of syrup and temperature significantly

Table 1. Parameters of the Power Law model for maple syrup at different temperatures.

Grade of syrup	Temperature (°C)	K (Pa s)	n	Standard error
Canada No. 1 Very Clear	5	0.610	1.000	0.982
	15	0.283	0.995	0.475
	25	0.138	1.000	0.378
	35	0.074	0.997	0.863
	45	0.045	1.007	2.055
	55	0.029	1.015	3.262
Canada No. 1 Clear	5	0.634	1.006	0.681
	15	0.335	0.980	0.846
	25	0.157	0.990	0.568
	35	0.083	0.997	1.359
	45	0.048	1.006	2.122
	55	0.032	1.012	2.099
Canada No. 1 Medium	5	0.645	0.998	0.996
	15	0.299	0.993	0.441
	25	0.149	0.996	0.468
	35	0.081	1.000	1.157
	45	0.051	0.994	1.815
	55	0.035	1.000	2.603
Canada No. 2 Amber	5	0.689	0.989	1.022
	15	0.313	0.987	0.529
	25	0.154	0.991	0.470
	35	0.083	0.996	0.869
	45	0.049	1.000	1.497
	55	0.032	1.012	2.219
Canada No. 3 Dark	5	0.719	0.991	1.191
	15	0.319	0.991	0.487
	25	0.160	0.992	0.442
	35	0.086	1.000	0.444
	45	0.053	1.000	1.974
	55	0.041	1.001	2.019

Model: $\tau = K\dot{\gamma}^n$, where: τ = shear stress (Pa), $\dot{\gamma}$ = shear rate (s^{-1}), n = power law index, and K = consistency (Pa s^n).

(p<0.05) influenced viscosity of the products. Further analysis by Duncan mean separation showed that apparent viscosity decreased consistently with increasing temperature. The mean value of apparent viscosity at each temperature level was significantly different from the mean value at the other temperature. Duncan mean separation analysis also showed that the apparent viscosity of the Canada No. 1 - Very Clear and the Canada No. 3 - Dark were significantly ($p < 0.0001$) different. There was no significant difference between the mean apparent viscosities of Canada No. 1 - Clear, Canada No. 1 - Medium, and Canada No. 2 - Amber. However, these Clear, Medium, and Amber types were significantly different from both the Very Clear and the Dark types. These differences may be attributed to the biochemical reactions during processing of the different types of maple syrup. The Dark grade may contain fermentation products whereas the other grades may not. Figure 3 shows variation of apparent viscosities of the different types of maple syrup with temperature. The effect of temperature on apparent viscosity was adequately modeled using the Arrhenius equation ($R^2 > 0.99$) as given in Eqs. 1, 2, and 3.

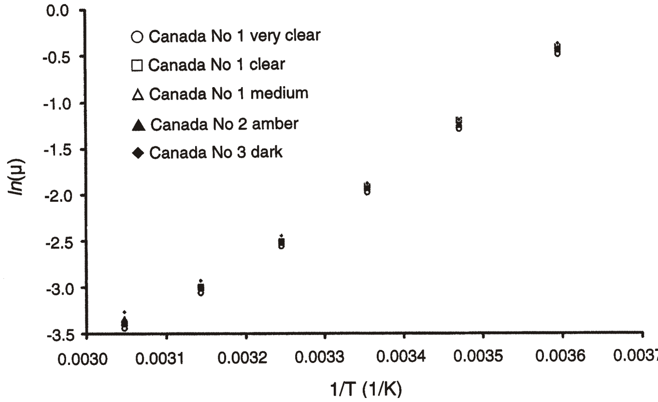

Fig. 3. Effect of temperature on apparent viscosity of maple syrup.

Canada No. 1 - Very Clear

$$\mu = 2.05 \times 10^{-9} \exp\left(\frac{44.86}{RT}\right) \quad (1)$$

Canada No. 1 - Clear
Canada No. 1 - Medium
Canada No. 2 - Amber

$$\mu = 2.18 \times 10^{-9} \exp\left(\frac{44.86}{RT}\right) \quad (2)$$

Canada No. 3 - Dark

$$\mu = 3.32 \times 10^{-9} \exp\left(\frac{43.97}{RT}\right) \quad (3)$$

where:
μ = viscosity (Pa s),
R = gas constant (8.314 x 10^{-3} kJ/mol K), and
T = temperature (K).

Activation energies obtained were 44.86 kJ/mol for the Very Clear type, 44.86 kJ/mol for the Clear, Medium and Amber types, and 43.97 kJ/mol for the Dark type. The activation energy values for all types of maple syrup were very similar. Activation energy indicates sensitivity to temperature changes. The sensitivity of the different types of maple syrups to temperature changes may be close considering their activation energy values. The Dark maple syrup type had higher frequency factor compared to the other types. Considering the activation energy and frequency factor values of the different types of maple syrup, differences in response to temperature changes become more apparent at lower temperatures.

The effect of concentration on the rheological behavior of maple syrup was studied using the concentrations of proximately 70 and 75°Brix at a temperature of 35°C. Statistical analysis showed that concentration effect was significant ($p < 0.0001$). The Power law model can also well describe the flow behavior of the concentrated samples. Parameters of the Power law model are shown in Table 2. The flow behavior index was between 0.969 and 0.992 indicating increased departure from Newtonian behavior compared to the non-concentrated samples at 66°Brix. This result is similar to several works on pure sucrose solutions that report larger departure from Newtonian

Table 2. Parameters of the Power Law model for concentrated maple syrup at 35°C.

Grade of syrup	°Brix	K (Pa s)	n	Standard error
Canada No. 1 Very Clear	66	0.074	0.997	0.863
	70	0.208	0.991	1.265
	75	0.595	0.989	0.817
Canada No. 1 Clear	66	0.0826	0.997	1.359
	70	0.1364	0.992	0.945
	75	0.5125	0.978	0.829
Canada No. 1 Medium	66	0.081	1.000	1.157
	70	0.181	0.988	0.575
	75	0.815	0.971	1.424
Canada No. 2 Amber	66	0.083	0.996	0.869
	70	0.273	0.976	1.116
	75	0.966	0.988	1.396
Canada No. 3 Dark	66	0.086	1.000	0.444
	70	0.168	0.991	0.911
	75	1.066	0.969	1.202

Model: $\tau = K\dot{\gamma}^n$, where: τ = shear stress (Pa), $\dot{\gamma}$ = shear rate (s^{-1}), n = power law index, and K = consistency (Pa s^n).

behavior when solutions were concentrated. This is due to structure changes in the solution (Schmidt et al. 1998). Further and detailed studies should be designed to investigate rheological and structural changes in maple syrup resulting from concentration and their influence on maple syrup products.

CONCLUSION

Grade, temperature, and concentration of maple syrup influenced its flow properties. The Canada No. 3 – Dark was more viscous than the other grades. The Canada No. 1 - Very Clear had the least viscosity. Other grades such as Canada No. 1 - Clear, Canada No. 1 - Medium, and Canada No. 2 - Amber had medium viscosity. The power law equation provided the best model for the experimental data obtained for the maple syrup samples. However, the flow behavior indexes were close to unity indicating that maple syrup was largely Newtonian especially between the temperatures of 25 to 45°C. The effect of temperature on viscosity was modeled using the Arrhenius equation.

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