Thermophysical Properties of Industrial Sugar Cane Juices for the Production of Bioethanol

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To design equipment for biofuel production and an optimizing process for heating, settling, and filtration of industrial sugar cane juices, the thermophysical properties must be known. Since the thermophysical properties of biological materials are strongly dependent upon chemical composition and temperature, composition- and temperature-based models provide a means of estimating these properties. In this work, the thermophysical properties of untreated sugar cane juice (USCJ), mixed sugar cane juice (MSCJ), and clarified sugar cane juice (CSCJ) were determined at a temperature range of (277.4 to 373.4) K. Simple polynomial models as a function of temperature were fitted to the experimental data, showing good agreement. Thermal conductivity and heat capacity varied from (0.475 to 0.493) $W \cdot m^{-1} \cdot K^{-1}$ and (3601.8 to 3802.9) $J \cdot kg^{-1} \cdot K^{-1}$, respectively. Density varied from (1044.5 to 1189.5) $kg \cdot m^{-3}$.

Introduction

The relative success of sugar cane bioethanol stems from the prolific growth rate of the crop in tropical Brazil and from a closed cycle production process, where the energy for refining and distilling comes from burning sugar cane residue. Hence, no fossil fuels are needed. Refining and distillation are very energy-intensive, especially for bioethanol. On average, sugar cane ethanol is estimated to have an energy balance of a staggering 8.3 but could reach to 10.2 in the best case, outperforming the energy balance of any other biofuel, especially those produced in temperate regions.[1]

The global production of bioethanol increased from 17.25 billion liters in 2000 to over 46 billion liters in 2007, which represents about 4 % of the 1300 billion liters of gasoline consumed globally.[2] Brazil, the United States, and some European Union (EU) members have the major programs to promote biofuel production. Considering the new programs of the American, Asian, and European governments, total global bioethanol demand could grow to exceed 125 billion liters by 2020.[3]

The bioethanol industry makes use of a number of unit operations such as pumping, heating, cooling, and sedimentation, which must be appropriately designed and controlled. Figure 1 shows a schematic of the main unit operations before fermentation and distillation. To allow an adequate process design, operation, and control, the thermophysical property behavior of industrial sugar cane juices such as untreated sugar cane juice (USCJ), mixed sugar cane juice (MSCJ), and clarified sugar cane juice (CSCJ) as affected by temperature is of primary importance.

The thermophysical properties of industrial sugar cane are of interest to engineers in modeling unit operations and in designing equipment. Simulation is no longer the problem, as with the advent of modern computers and numerical methods, nonlinear heat conduction equations can be accurately solved.[4] The reliability of these predictions, however, is directly related to the accuracy with which the researcher is able to predict thermophysical property values of the system in the temperature range. Thermophysical properties required for these predictions include density ρ, heat capacity C_p, and thermal conductivity k.

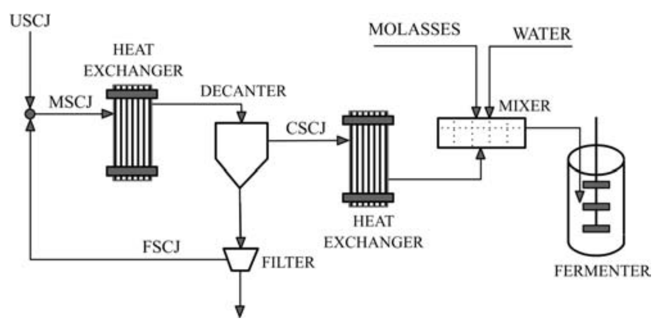

Figure 1. Schematic of the sugar cane juice clarification section for bioethanol production (FSCJ stands for filtered sugar cane juice).

An extensive review of existing methods for measurement of thermophysical properties of biological materials has been done by Reidy and Rippen,[5] Mohsenin,[6] and Singh.[7] Adiabatic calorimeters are often used for measurements of C_p.[8,9] It is a simple technique, though requiring a careful calibration. The differential scanning calorimeter is fast and allows systematic data acquisition and processing but has the disadvantage of being expensive.[10−12] A simple method can be used to determine k, according to Bellet et al.[13] The great advantage of this technique is that it is also possible to determine C_P employing the same device and modeling the unsteady state heat transfer in the system.

Table 1. Composition Parameters and Associated Uncertainties of USCJ, MSCJ, and CSCJ

	100 Brix	100 Pol	100 Purity	100 total solids	pH
USCJ	17.9 ± 0.3	14.7 ± 0.3	82.1	19.1 ± 0.2	7.2 ± 0.1
MSCJ	18.0 ± 0.2	14.9 ± 0.3	82.8	18.8 ± 0.3	6.8 ± 0.1
CSCJ	18.2 ± 0.1	16.1 ± 0.6	88.5	18.2 ± 0.3	6.1 ± 0.1

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10.1021/je900590t
Published on Web 12/09/2009

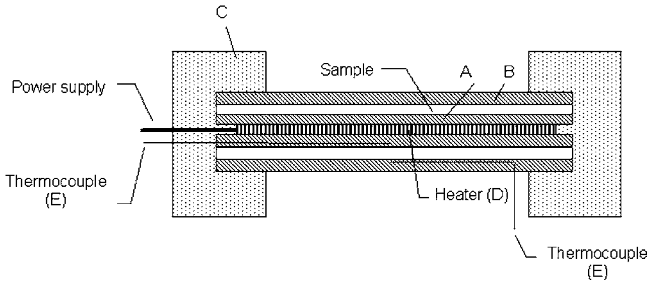

Figure 2. Cross section of the cell used for thermal conductivity and heat capacity measurements.

Table 2. Heat Capacity, C_p, at Different Temperatures of USCJ, MSCJ, and CSCJ

	USCJ	MSCJ	CSCJ
T/K	C_p/J·kg^{-1}·K^{-1}	C_p/J·kg^{-1}·K^{-1}	C_p/J·kg^{-1}·K^{-1}
277.4	3611.8	3609.1	3603.3
286.5	3628.2	3625.6	3620.7
296.4	3648.9	3646.2	3640.8
307.0	3669.8	3667.1	3662.2
317.4	3690.0	3687.3	3682.7
328.2	3712.1	3709.5	3703.7
340.4	3736.3	3733.7	3727.5
352.0	3758.7	3756.1	3751.5
364.1	3783.9	3781.2	3775.5
373.4	3801.7	3799.0	3793.5

Table 3. Thermal Conductivity, k, at Different Temperatures of USCJ, MSCJ, and CSCJ

	USCJ	MSCJ	CSCJ
T/K	k/W·m^{-1}·K^{-1}	k/W·m^{-1}·K^{-1}	k/W·m^{-1}·K^{-1}
277.4	0.478	0.477	0.475
286.5	0.480	0.478	0.476
296.4	0.481	0.480	0.478
307.0	0.483	0.481	0.479
317.4	0.484	0.483	0.480
328.2	0.486	0.484	0.482
340.4	0.488	0.486	0.484
352.0	0.489	0.488	0.485
364.1	0.491	0.490	0.488
373.4	0.492	0.491	0.489

Table 4. Density, ρ, at Different Temperatures of USCJ, MSCJ, and CSCJ

	USCJ	MSCJ	CSCJ
T/K	ρ/kg·m^{-3}	ρ/kg·m^{-3}	ρ/kg·m^{-3}
277.4	1188.3	1081.8	1082.9
286.5	1182.9	1077.5	1078.1
296.4	1185.6	1073.8	1074.9
307.0	1178.2	1074.3	1070.5
317.4	1173.5	1066.0	1066.4
328.2	1171.9	1063.2	1062.3
340.4	1166.0	1060.6	1058.3
352.0	1156.2	1057.6	1056.0
364.1	1154.9	1050.5	1051.0
373.4	1153.0	1047.5	1048.2

Thermophysical properties of industrial sugar cane juices are scarce in literature, and an extensive study on the dependence of such properties on temperature has not yet been published. Thus, the objective of this work was to measure the thermophysical properties (k, C_p, and ρ) of USCJ, MSCJ, and CSCJ as a function of temperature T and to develop correlations for predicting these properties.

Experimental Section

Materials. Samples were obtained from a single batch of about 100 L of sugar cane juice collected in a local sugar cane factory. The soluble solids (°Brix/%), which include sugars and organic acids, measured using a digital refractometer with automatic temperature compensation (Pal 3, Atago, Tokyo, Japan), the polarizable sugars (Pol/%), that indicate the sucrose mass content in the solution, measured using a digital polarimeter (Series P3000, A. Krüss Optronic, Germany), and Purity, given as (Pol)/(°Brix), are the parameters usually employed in industrial practice to characterize the quality of sugar cane juice, and all of the industrial calculations are carried out on the basis of these values. The quality parameters of the juice batch were measured in triplicate and are shown in Table 1 with the associated uncertainties. The thermophysical properties were measured in triplicate for each value of T, taking different samples from the same batch of sugar cane juice to carry out each measurement. The average uncertainties were estimated from the propagation law errors. All statistical analyses were performed using the GLM (general linear model) procedure, while fitted functions were obtained by using the REG (regression) procedure from the SAS statistical package.[14] The suitability of the fitted functions was evaluated by the level of significance (p), the coefficient of determination (R^2), and residual analysis.

Apparatus and Methods. a. Thermal Conductivity (k). Thermal conductivity at various T for USCJ, MSCJ, and CSCJ was measured using the method described by Bellet et al.,[13] based on a cylindrical cell, where the liquid whose properties are being determined fills the annular space between two concentric cylinders. The equipment is schematically shown in Figure 2 and presented the following physical characteristics: two coaxial copper cylinders (A and B), 180 mm length, separated by a 2 mm annular space, which was filled with the sample; 50 mm thick covers (C) made of a low thermal conductivity material (0.225 W·m^{-1}·K^{-1}) to prevent axial heat transfer; an inner cylinder (A) containing a heater (D) made with a constantan wire (resistance 15 Ω), electrically insulated by a varnish and coiled around a copper stick; and two thermocouples type T (E) to measure temperature differences between the two cylinders, located at half-length of the cell. The wires were placed inside 0.5 mm gaps, parallel to the cell axis. During measurements, the cell was immersed in a water bath (MK70, MLW, Dresden, Germany), to maintain constant external temperature to within ± 0.05 °C. The power input to

Table 5. Coefficients of Equation 1 and Associated Standard Errors, for USCJ, MSCJ, and CSCJ

property	sugar cane juice	β_0	β_1	β_2
ρ/kg·m^{-3}	USCJ	1234.71515 ± 3.8		$-0.0005999 \pm 3.5\cdot10^{-5}$
	MSCJ	1121.80482 ± 2.8		$-0.00053244 \pm 2.6\cdot10^{-5}$
	CSCJ	1263.64413 ± 36.3	−0.87491 ± 0.2	0.00080006 ± 0.0003
k/W·m^{-1}·K^{-1}	USCJ	0.43781 ± 0.001	$0.00014656 \pm 3.1\cdot10^{-6}$	
	MSCJ	0.43543 ± 0.001	$0.00014989 \pm 2.9\cdot10^{-6}$	
	CSCJ	0.43479 ± 0.001	$0.00014416 \pm 2.5\cdot10^{-6}$	
C_p/J·kg^{-1}·K^{-1}	USCJ	3059.62318 ± 2.3	1.9875 ± 0.007	
	MSCJ	3056.97042 ± 2.1	1.98751 ± 0.006	
	CSCJ	3052.37418 ± 1.9	1.98521 ± 0.006	

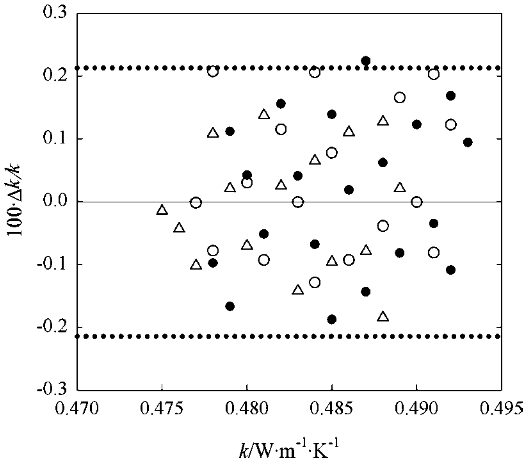

Figure 3. Fractional deviations $\Delta k = (k_{obs} - k_{pred})$ of the observed thermal conductivity k_{obs} of sugar cane juice as a function of k_{obs}. Standard deviation of the fit using eq 1 ($\pm 2\sigma$): ●, USCJ; ○, MSCJ; △, CSJC.

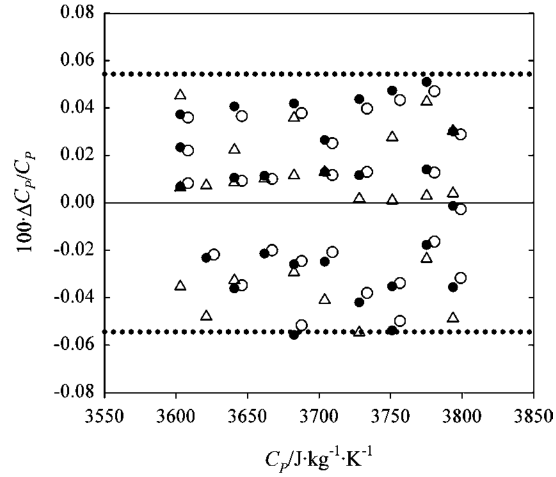

Figure 4. Fractional deviations $\Delta C_p = (C_{p,obs} - C_{p,pred})$ of the observed heat capacity $C_{p,obs}$ of sugar cane juice as a function of $C_{p,obs}$. Standard deviation of the fit using eq 1 ($\pm 2\sigma$): ●, USCJ; ○, MSCJ; △, CSJC.

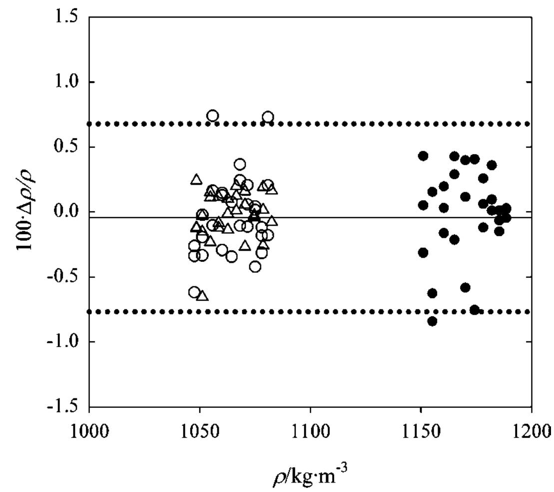

Figure 5. Fractional deviations $\Delta\rho = (\rho_{obs} - \rho_{pred})$ of the observed densities ρ_{obs} of sugar cane juice as a function of ρ_{obs}. Standard deviation of the fit using eq 1 ($\pm 2\sigma$): ●, USCJ; ○, MSCJ; △, CSJC.

the heater resistance was made by means of a microprocessed, stabilized source (ETB-252, Entelbra, São Paulo, Brazil), which permitted the adjustment of the current with a stability of 0.05 %. The temperatures inside the cell were recorded by means of a data logger (HP 75000-B, U.S.) with a standard uncertainty of ± 0.1 K, calculated from the standard deviations of repeated experimental measurements.

b. Heat Capacity (C_p). Heat capacity was measured using the same apparatus employed to measure thermal conductivity. Considering unsteady state heat conduction through an isotropic, homogeneous medium, the equation of energy conservation was written for the system. The solution of the differential equation with the proper boundary conditions is presented in detail by Bellet et al.[13]

c. Density (ρ). Gravimetric determination of sugar cane density at different temperatures was carried out using an analytical balance with a given uncertainty of ± 0.0001 g and a standard volumetric glass density bottle of 25 mL with a coupled thermometer.[10] The density bottle was previously calibrated with distilled water, at each temperature.

Results and Discussion

The thermal conductivity, heat capacity, and density of USCJ, MSCJ, and CSCJ were determined in triplicate at (277.4, 286.5, 296.4, 307.4, 317.4, 328.2, 340.4, 352.0, 364.1, and 373.4) K (Tables 2 to 4). The average uncertainty of k, C_p, and ρ is estimated to be $\pm$ 0.004 $W\cdot m^{-1}\cdot K^{-1}$, $\pm$ 15.4 $J\cdot kg^{-1}\cdot °C^{-1}$, and $\pm$ 12.8 $kg\cdot m^{-3}$.

Polynomial models for the thermophysical properties as a function of T were fitted to the experimental data. It is important to obtain simple models as they can be used for online simulation and control. Minim et al.[16] obtained simple models for the prediction of the thermophysical properties of lemon juice. In this work, the quadratic model was first analyzed, and the non-significant parameters were taken off from the model based on the t (student) test and $p > 0.05$. The final models are presented by a polynomial like eq 1. Table 5 shows the coefficients of eq 1 for k, C_p, and ρ.

$$y = \beta_0 + \beta_1(T/K) + \beta_2(T^2/K^2) \qquad (1)$$

where y represents the thermophysical property.

The agreement between experimental and calculated values for the thermophysical properties was very good. Figures 3 to 5 show the fractional deviations between observed and predicted values of k, C_p, and ρ. In all cases, despite its simplicity, eq 1 with the associated parameters in Table 5 was found to represent accurately the physical properties of USCJ, MSCJ, and CSCJ in the studied range of T, with the determination coefficient (R^2) superior to 0.98.

The properties studied here varied from (0.475 to 0.493) $W\cdot m^{-1}\cdot K^{-1}$ for thermal conductivity, (3601.8 to 3802.9) $J\cdot kg^{-1}\cdot K^{-1}$ for heat capacity, and (1044.5 to 1189.5) $kg\cdot m^{-3}$ for density. In accordance with what was observed in the literature,[16,17] the variables k and C_p increased linearly with T, and ρ decreased with T in a quadratic way.

Conclusions

In this paper, the effect of T on the thermophysical properties (k, C_p, and ρ) of industrial sugar cane (USCJ, MSCJ, and CSCJ) were studied. Simple polynomial models were successfully fitted to the experimental data, considering the range of temperature explored. As expected, k and C_p increased with increasing temperature, while density decreased with increasing temperature.

Literature Cited

(1) Coelho, S. T.; Goldemberg, J.; Lucon, O.; Guardabassi, P. Brazilian Sugarcane Ethanol: Lessons Learned. *Energy Sustainable Dev.* **2006**, *10*, 26–39.

(2) Renewable Energy Network for the 21st Century (REN21). Renewable 2007 Global Status Report. REN21 Secretariat, Paris; Worldwatch Institute: Washington, DC, 2008.

(3) Demirbas, A. Producing and Using Bioethanol as an Automotive Fuel. *Energy Sources B* **2007**, *2*, 391–401.

(4) Wang, D. Q.; Kolbe, E. Thermal Conductivity of Surimi-Measurement and Modeling. *J. Food Sci.* **1990**, *55*, 1217–1221.

(5) Reidy, G. A.; Rippen, A. L. Methods for Determining Thermal Conductivity in Foods. *Trans. ASAE* **1971**, *14*, 248–254.

(6) Mohsenin, N. N. *Thermal Properties of Foods and Agricultural Materials*; Gordon and Breach: New York, 1980.

(7) Singh, R. P. Thermal Diffusivity in Food Processing. *Food Technol.* **1982**, *36*, 87–91.

(8) Riedel, L. The Refrigerating Effect Required to Freeze Fruits and Vegetables. *Refrig. Eng.* **1951**, *59*, 670–673.

(9) Hwang, M. P.; Hayakawa, K. I. A Specific Heat Calorimeter for Foods. *J. Food Sci.* **1979**, *44*, 435–438.

(10) Constenla, D. T.; Lozano, J. E.; Crapiste, G. H. Thermophysical Properties of Clarified Apple Juice as a Function of Concentration and Temperature. *J. Food Sci.* **1989**, *54*, 663–668.

(11) Sweat, V. E.; Haugh, C. G. A Thermal Conductivity Probe for Small Food Samples. *Trans. ASAE* **1974**, *17*, 56–58.

(12) Shamsudin, R.; Mohamed, I. O.; Yaman, N. K. M. Thermophysical Properties of Thai Seedless Guava Juice as Affected by Temperature and Concentration. *J. Food Eng.* **2005**, *66*, 395–399.

(13) Bellet, D.; Sengelin, M.; Thirriot, C. Determination des Proprietes Thermophysiques de Liquides Non-Newtoniens a L'áide d'une Cellule a Cylindres Coaxiaux. *Int. J. Heat Mass Transfer* **1975**, *18*, 1177–1187.

(14) *SAS User's Guide: Statistics*, 9th ed.; SAS Institute Inc.: Cary, North Carolina, 2008.

(15) Burjaili, M. M. *Desenvolvimento de um Secador Rotatório com Recheio de Inertes*. PhD Thesis, School of Food Engineering, State University of Campinas, Campinas, Brazil, 1996.

(16) Minim, L. A.; Telis, V. R. N.; Minim, V. P. R.; Lizzy, A. P.; Telis-Romero, J. Thermophysical Properties of Lemon Juice as Affected by Temperature and Water Content. *J. Chem. Eng. Data* **2009**, *54*, 2269–2272.

(17) Telis-Romero, J.; Telis, V. R. N.; Gabas, A. L.; Yamashita, F. Thermophysical Properties of Brazilian Orange Juice as Affected by Temperature and Water Content. *J. Food Eng.* **1998**, *38*, 27–40.

Received for review July 13, 2009. Accepted November 25, 2009. The authors wish to thank FAPESP-SP and FAPEMIG-MG for the financial support.

JE900590T