MODELING OF THE THERMO-PHYSICAL PROPERTIES OF GRAPES JUICE II. BOILING POINT AND DENSITY♦

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Abstract: When optimizing the process of grape juice manufacture not just to obtain an excellent quality, but also to develop a data base is essential to know the evolution of physical properties, such as density or boiling point elevation. These properties are affected by pressure, temperature and solid content. The aim of this work was to establish a mathematical relation between these variables. In order to assess and select a suitable mathematical model the known data were fitted in different equations. Tests results have shown that at constant dry matter content the pressure and the boiling point are related by a "shifted power" equation while between temperature and density variation a logarithmic model seems to be the most appropriate.

Keywords: *grapes juice, thermo-physical properties, density, boiling point, mathematical modeling, food industry*

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INTRODUCTION

Fruits constitute a major part of the food crops. With 67.79 millions of tons produced in 2008 grape is one of the most world-wide appreciated fruit. An important part of this quantity is processed into different products such as juice, wine, jams, raisins etc [1]. Lately the grape juice has become very popular because it can be consumed directly either as a final product or as a raw material (i.e., winemaking). In both manufacturing processes, grape juice is undergone to different treatments [2].
Knowledge at any time of the thermo physical properties, such as boiling temperature and density variation, is important not only for process design but also for the prediction and control of various changes that occur in juice during processing [3].
A major part of the existing data is presented in graphical form and it cannot be used for further determination of different physical and thermo dynamical properties.
Using a methodology previously used in other liquid foods modeling [4 – 9], the paper presents simple and reliable mathematical relationships between the grape juice boiling temperature and density variation and pressure, temperature and dry mater content.

MATERIALS AND METHODS

Tabular data (Table 1 and Table 2) and graphic representation (Figure 1) concerning the variation of grapes juice boiling temperature and density with dry matter and pressure or temperature were used as primary data for the regression analysis. These data were selected due to their wide use in research, development and design of the grapes juice processing industry.

Table 1. *Variation of grapes juice boiling temperature [K] with presure (P) and dry matter content (X) [10]*

Pressure		Dry matter content [%]		
[mm Hg]	[Pa]	20	40	60
56	7460	315.8	317.9	319.4
156	20800	336.1	338.9	340.2
256	34100	347.6	349.9	352.0
356	47500	355.4	357.4	359.5
456	60700	361.4	363.7	366.1
556	74100	366.8	368.7	371.1
656	87500	370.9	372.9	374.8
756	100800	374.8	376.9	379.1

Different experimental extrapolated equations presented in various scientific papers concerning the grapes juice density variation were also used (Table 3).
Frequently thermo-physical properties of various products in food industry are presented in graphics forms. Therefore xyExtract Graph Digitizer.v2.3 software was used to extract numerical data from graphical representations.
The experimental data were plotted in *Temperature – Thermo-physical property, Dry matter content – Thermo-physical property* coordinates. Linear regression techniques, involving the method of least squares were used to reveal the best-fit equation. Microsoft

Excel™ 2007 spreadsheets and CurveExpert® software were used to establish the equations.

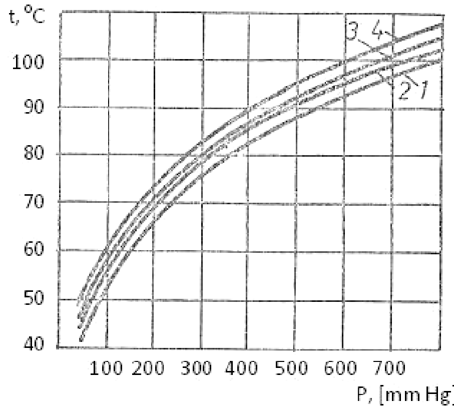

Figure 1. *Variation of grapes juice boiling temperature with presure (P) and dry matter (X) content: 1 – water, 2 – 20%, 3 – 40%, 4 – 60% [10]*

Table 2. *Variation of grapes juice density with temperature and dry matter content [11]*

Dry matter [%, w/w]	Soluble solids [%, w/w]	°Bx	Temperature [°C]						
			20	30	40	50	60	70	80
24.77	22.9	21.60	1097.3	1093.2	1089.2	1084.5	1078.5	1071.4	1065.0
26.94	25.5	23.21	1108.3	1102.9	1098.9	1094.0	1088.0	1082.7	1076.0
31.19	31.0	27.51	1130.0	1126.2	1121.8	1116.6	1111.2	1105.7	1095.7
36.05	34.0	32.86	1150.3	1144.4	1140.6	1135.5	1130.3	1123.9	1117.5
44.06	41.0	38.18	1190.6	1185.4	1180.5	1174.9	1169.8	1163.3	1155.8
47.84	45.0	41.71	1208.4	1203.4	1197.6	1192.5	1185.9	1180.2	1173.8
53.98	51.0	46.77	1240.0	1234.5	1228.3	1222.8	1216.8	1211.7	1203.7
58.14	53.4	48.49	1253.8	1248.1	1242.2	1236.6	1230.1	1226.2	1218.7
64.72	60.7	57.14	1297.2	1290.9	1284.7	1278.8	1271.8	1268.2	1261.8
68.49	67.0	60.62	1337.3	1328.8	1322.6	1315.7	1309.0	1302.7	1295.4
76.57	70.6	66.25	1358.4	1351.8	1346.3	1339.2	1332.5	1328.3	1321.8

Table 3. *Equations used in grapes juice density calculus as a function of temperature (T) and dry matter content (X) or degrees Brix (Bx)*

Eq. no.	Equation	Ref.
(1)*	$\rho = 1768 - 7\cdot(100 - X) - 0.928\cdot t + 0.0062\cdot(100 - X)\cdot t$	[10]
(2)	$\rho = 1.1391\cdot 10^3 - 5.7760\cdot 10^{-1}\cdot T + 5.3941\cdot 10^3\cdot Bx$	[11]
(3)	$\rho = 1.0462\cdot 10^3 + 1.9630\cdot 10^{-1}\cdot T + 3.8568\cdot Bx + 1.1973\cdot 10^{-3}\cdot T^2 + 1.6533\cdot 10^{-2}\cdot Bx^2$	[11]
(4)	$\rho = 2.0816\cdot 10^3 - 9.4737\cdot T + 3.9796\cdot Bx + 2.8793\cdot 10^{-2}\cdot T^2 + 1.3724\cdot 10^{-2}\cdot Bx^2 - 3.0934\cdot 10^{-5}\cdot T^3 + 2.0035\cdot 10^{-5}\cdot Bx^3$	[11]
(5)	$\rho = 0.83 + 0.35\cdot \exp(0.01X) - 5.64\cdot 10^{-4}\cdot T$	[12]

* Equation (1) applies for the following values of *X* and *t*: *X* = 15…60%; *t* = 0…70 °C

RESULTS AND DISCUSSIONS

Boiling point

Using CurveExpert® software, a ”shifted power” correlation between pressure (measured in Pa) and boiling point, at constant dry matter content has been established:

$$t_b = A \cdot (P - B)^C \qquad (5)$$

The *A*, *B* and *C* values are presented in Table 4. The regression coefficients are > 0.99, thus indicating a good correlation of variables.

Table 4. *Coefficients for equation (5)*

Dry matter [%]	*A*	*B*	*C*	R^2
20	162	-2.331	0.072677	0.9999
40	168	-1.708	0.070148	0.9999
60	167	-1.688	0.070776	0.9999

In order to correlate *A*, *B* and *C* coefficients with dry matter content, more models were used in CurveExpert® software (1st, 2nd and 3rd degree polynomial equations, “vapor pressure” model, “heat capacity” model etc.). The best mathematical model final form is represented by a logarithmic equation (Table 5):

$$Coefficient = a + b \cdot \ln(X) \qquad (6)$$

Table 5. *Coefficients for equation (6)*

Coefficient	*a*	*b*	R^2
A	5.3746	146.38	0.8462
B	618.51	-4131.3	0.8848
C	-0.002	0.0782	0.6676

After combining the equations (5) and (6) and replacing the coefficients with numeric values, in order to correlate the boiling point of grapes juice with pressure and dry matter, the final form of proposed model is:

$$t_b = [146.38 + 5.3746 \cdot \ln(X)] \cdot [P_{Pa} + 4134.3 - 618.51 \cdot \ln(X)]^{0.0782 - 0.002 \cdot \ln(X)} \qquad (7)$$

This mathematical model is valid when pressure is measured in Pa. If measurement unit is changed in mm Hg, after following the same steps, the mathematical model becomes:

$$t_b = [215.24 + 5.4137 \cdot \ln(X)] \cdot [P_{mmHg} + 31.006 - 4.64 \cdot \ln(X)]^{0.0782 - 0.002 \cdot \ln(X)} \qquad (8)$$

For a better fit to experimental data, for both proposed equations, the coefficient *C* could be replaced by a linear equation: $C = 0.0731 + 5 \cdot 10^{-5} \cdot X$, equations (7) and (8) become respectively:

$$t_b = [146.38 + 5.3746 \cdot \ln(X)] \cdot [P_{Pa} + 4134.3 - 618.51 \cdot \ln(X)]^{0.0731 + 5 \cdot 10^{-5}(X)} \qquad (9)$$

$$t_b = [215.24 + 5.4137 \cdot \ln(X)] \cdot [P_{mmHg} + 31.006 - 4.64 \cdot \ln(X)]^{0.0731 + 5 \cdot 10^{-5}(X)} \qquad (10)$$

Using the equations (7), (8), (9) and (10) in grape juice boiling point calculus, the results were compared with experimental values (Table 6).

Table 6. *Comparison between measured and calculated values of grapes juice boiling point*

Pressure, [Pa, (mm Hg)]	Dry matter, [%]	Boiling point, t_B [°C]								
		Experimental [1]	Calculated with equation:							
			7		8		9		10	
			t_B	ε, [%]	t_B	ε, [%]	t_B	ε, [%]	t_B	ε, [%]
7460 (76)	20	315.8	315.5	-0.08	315.3	-0.14	315.4	-0.13	315.0	-0.24
	40	317.9	317.7	-0.05	317.4	-0.13	318.1	0.07	318.3	0.13
	60	319.4	319.0	-0.13	318.6	-0.23	319.1	-0.09	318.9	-0.15
20800 (156)	20	336.1	335.8	-0.09	335.6	-0.14	335.6	-0.14	335.2	-0.25
	40	338.9	338.3	-0.15	338.1	-0.23	338.8	-0.01	339.0	0.05
	60	340.2	339.8	-0.10	339.5	-0.20	340.0	-0.06	339.8	-0.11
34100 (256)	20	347.6	347.0	-0.16	346.8	-0.22	346.8	-0.22	346.4	-0.33
	40	349.9	349.6	-0.07	349.3	-0.15	350.2	0.09	350.3	0.14
	60	352.0	351.1	-0.24	350.7	-0.35	351.3	-0.19	351.1	-0.25
47500 (356)	20	355.4	354.9	-0.12	354.7	-0.17	354.7	-0.19	354.3	-0.29
	40	357.4	357.5	0.04	357.3	-0.03	358.1	0.21	358.3	0.27
	60	359.5	359.0	-0.13	358.7	-0.22	359.2	-0.08	359.0	-0.13
60700 (456)	20	361.4	361.1	-0.08	360.8	-0.15	360.8	-0.15	360.4	-0.27
	40	363.7	363.6	-0.01	363.3	-0.10	364.2	0.16	364.4	0.21
	60	366.1	365.1	-0.27	364.7	-0.38	365.3	-0.21	365.0	-0.28
74100 (556)	20	366.8	366.1	-0.18	365.9	-0.24	365.8	-0.25	365.4	-0.36
	40	368.7	368.6	-0.01	368.3	-0.09	369.3	0.17	369.5	0.23
	60	371.1	370.1	-0.27	369.7	-0.37	370.3	-0.21	370.1	-0.27
87500 (656)	20	370.9	370.4	-0.13	370.2	-0.18	370.1	-0.20	369.7	-0.31
	40	372.9	372.9	0.00	372.6	-0.07	373.5	0.18	373.8	0.25
	60	374.8	374.3	-0.12	373.9	-0.22	374.5	-0.07	374.3	-0.12
100800 (756)	20	374.8	374.1	-0.18	373.9	-0.23	373.8	-0.25	373.4	-0.36
	40	376.9	376.6	-0.08	376.3	-0.15	377.3	0.10	377.5	0.17
	60	379.1	378.0	-0.29	377.6	-0.39	378.2	-0.23	378.0	-0.28

To quantify the deviation from experimental data, between measured and calculated boiling point, the relative error was used:

$$\varepsilon = \left(\frac{t_{b\,measured} - t_{b\,calculated}}{t_{b\,measured}} \right) \cdot 100 \quad [\%] \qquad (11)$$

By analyzing the obtained values it can be observed that the induced relative error for proposed equation model is only -0.12% in average for equation (7), -0.19% for equation (8), -0.07% for equation (9) and -0.10% in average for equation (10).

Density

Using Microsoft Excel™ 2007 spreadsheets and CurveExpert® software, a logarithmic correlation between temperature and density, at constant dry matter content has been established:

$$\rho = V \cdot W \cdot \ln(T) \quad (12)$$

The *V* and *W* values are presented in Table 7. The regression coefficients are > 0.98, thus indicating a good correlation of variables.

Table 7. *Coefficients for equation (12)*

Dry matter, [%]	*V*	*W*	R^2
24.77	2084.1	-173.4	0.98
26.94	2075.9	-170.2	0.99
31.19	2137.9	-177.0	0.96
36.05	2127.5	-171.9	0.99
44.06	2230.7	-182.9	0.99
47.84	2266.2	-186.0	0.99
53.98	2324.5	-190.8	0.99
58.14	2307.3	-185.4	0.99
64.72	2372.9	-189.4	0.99
68.49	2588.7	-220.4	0.99
76.57	2473.8	-196.4	0.99

In order to correlate *V* and *W* coefficients with dry matter content, more models were used in CurveExpert® software (1st, 2nd and 3rd degree polynomial equations, "vapor pressure" model, "heat capacity" model etc.). The best mathematical model final form is represented by a linear equation (Table 8):

$$Coefficient = v + w(X) \quad (13)$$

Table 8. *Coefficients for equation (13)*

Coefficient	*v*	*w*	R^2
V	1842.7	8.8595	0.8957
W	-153.69	-0.6631	0.6683

The equation (14) presents the final form of mathematical model obtained after combining the equations (12) and (13) and replacing the coefficients with numeric values in order to correlate the density of grapes juice with temperature and dry matter.

$$\rho = (1842.7 + 8.8595 \cdot X) + (-153.69 - 0.6631 \cdot X) \cdot \ln(T) \quad (14)$$

Using the above equation in grape juice density calculus, the results were compared with experimental values (Table 9).

The analysis of the induced relative error values for proposed equation model shows an average of -0.005% for equation (14), 0.98% for equation (1), approximately -0.01% for equations (2), (3), (4) and 1.95% for equation (5).

The calculated values graphic representations were presented in Figures 1 – 11.

Table 9. *Comparison between measured and calculated density of grapes juice*

Temperature [°C]	Dry matter [%]	Density, ρ [kg/m^3] Experimental [2]	Calculated with equation (14) ρ	Calculated with equation (14) ε [%]	Temperature [°C]	Dry matter [%]	Density, ρ [kg/m^3] Experimental [2]	Calculated with equation (14) ρ	Calculated with equation (14) ε [%]
20	24.77	1097.3	1095.8	-0.13	50	47.84	1192.5	1195.3	0.23
	26.94	1108.3	1106.9	-0.12		53.98	1222.8	1226.2	0.27
	31.19	1130.0	1128.5	-0.13		58.14	1236.6	1247.1	0.84
	36.05	1150.3	1153.3	0.26		64.72	1278.8	1280.2	0.11
	44.06	1190.6	1194.1	0.29		68.49	1315.7	1299.1	-1.28
	47.84	1208.4	1213.3	0.41		76.57	1339.2	1339.8	0.04
	53.98	1240.0	1244.6	0.37	60	24.77	1078.5	1074.1	-0.41
	58.14	1253.8	1265.8	0.95		26.94	1088.0	1085.0	-0.28
	64.72	1297.2	1299.3	0.16		31.19	1111.2	1106.2	-0.45
	68.49	1337.3	1318.5	-1.42		36.05	1130.3	1130.6	0.03
	76.57	1358.4	1359.6	0.09		44.06	1169.8	1170.7	0.08
30	24.77	1097.3	1090.2	-0.28		47.84	1185.9	1189.6	0.31
	26.94	1108.3	1101.2	-0.16		53.98	1216.8	1220.4	0.29
	31.19	1130.0	1122.7	-0.31		58.14	1230.1	1241.2	0.90
	36.05	1150.3	1147.4	0.26		64.72	1271.8	1274.2	0.19
	44.06	1190.6	1188.0	0.22		68.49	1309.0	1293.1	-1.23
	47.84	1208.4	1207.1	0.31		76.57	1332.5	1333.5	0.08
	53.98	1240.0	1238.3	0.30	70	24.77	1071.4	1069.1	-0.22
	58.14	1253.8	1259.4	0.89		26.94	1082.7	1079.9	-0.26
	64.72	1297.2	1292.7	0.14		31.19	1105.7	1101.1	-0.42
	68.49	1337.3	1311.9	-1.29		36.05	1123.9	1125.3	0.13
	76.57	1358.4	1352.8	0.08		44.06	1163.3	1165.3	0.17
40	24.77	1089.2	1084.6	-0.42		47.84	1180.2	1184.1	0.33
	26.94	1098.9	1095.6	-0.30		53.98	1211.7	1214.8	0.25
	31.19	1121.8	1117.1	-0.43		58.14	1226.2	1235.5	0.76
	36.05	1140.6	1141.6	0.09		64.72	1268.2	1268.4	0.01
	44.06	1180.5	1182.0	0.13		68.49	1302.7	1287.2	-1.21
	47.84	1197.6	1201.1	0.29		76.57	1328.3	1327.5	-0.06
	53.98	1228.3	1232.1	0.31	80	24.77	1065.0	1064.2	-0.08
	58.14	1242.2	1253.1	0.87		26.94	1076.0	1075.0	-0.10
	64.72	1284.7	1286.3	0.13		31.19	1095.7	1096.1	0.03
	68.49	1322.6	1305.4	-1.32		36.05	1117.5	1120.2	0.24
	76.57	1346.3	1346.2	-0.01		44.06	1155.8	1160.0	0.37
50	24.77	1084.5	1079.3	-0.48		47.84	1173.8	1178.8	0.43
	26.94	1094.0	1090.2	-0.35		53.98	1203.7	1209.3	0.47
	31.19	1116.6	1111.6	-0.45		58.14	1218.7	1230.0	0.92
	36.05	1135.5	1136.0	0.04		64.72	1261.8	1262.7	0.07
	44.06	1174.9	1176.3	0.12		68.49	1295.4	1281.4	-1.09

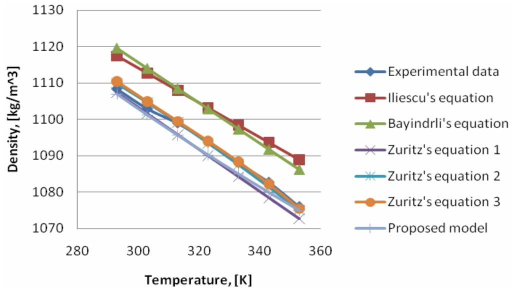

Figure 1. *Density of grapes juice with 24.77% dry matter content*

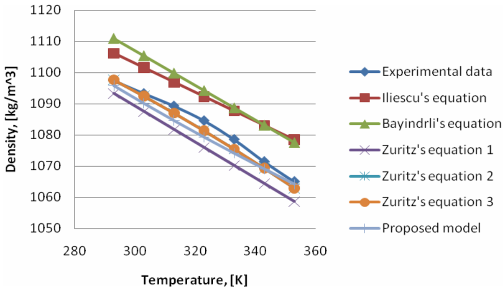

Figure 2. *Density of grapes juice with 26.94% dry matter content*

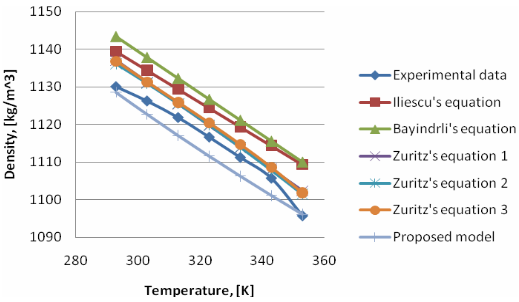

Figure 3. *Density of grapes juice with 31.19% dry matter content*

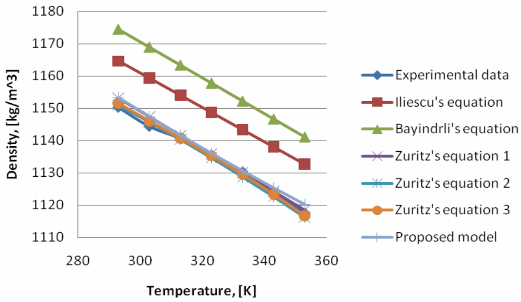

Figure 4. *Density of grapes juice with 36.05% dry matter content*

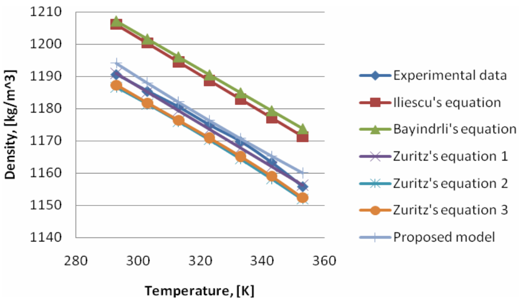

Figure 5. *Density of grapes juice with 44.06% dry matter content*

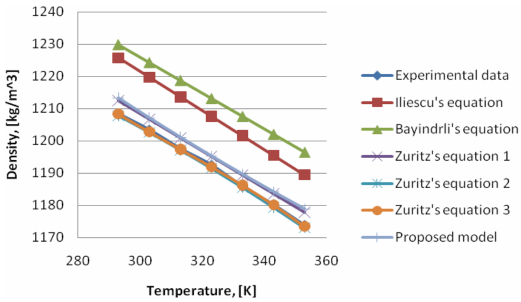

Figure 6. *Density of grapes juice with 47.84% dry matter content*

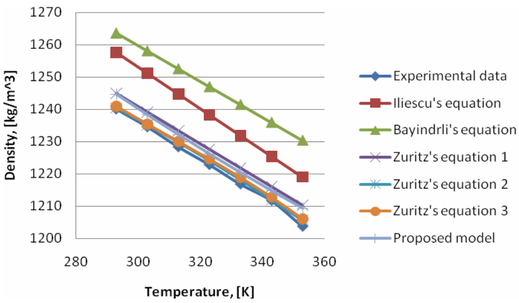

Figure 7. *Density of grapes juice with 53.98% dry matter content*

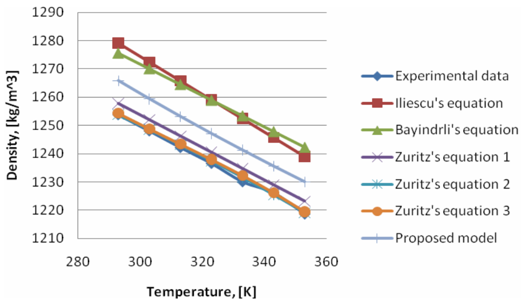

Figure 8. *Density of grapes juice with 58.14% dry matter content*

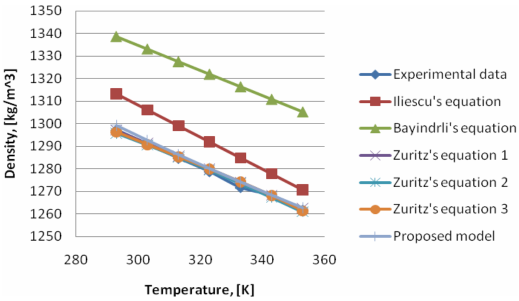

Figure 9. *Density of grapes juice with 64.72% dry matter content*

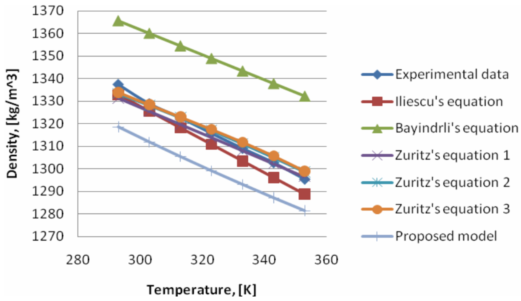

Figure 10. *Density of grapes juice with 68.49% dry matter content*

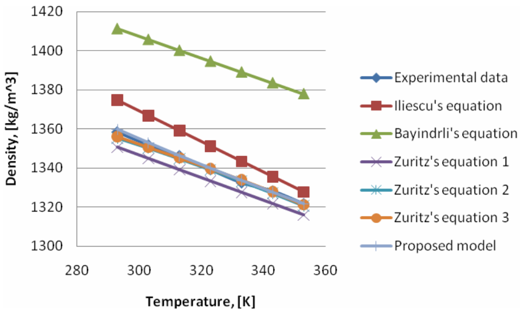

Figure 11. *Density of grapes juice with 76.57% dry matter content*

CONCLUSIONS

Since computer based programs or spreadsheets require correlation equations of the thermal properties of materials with state parameters (pressure, temperature and concentration) some regression equations that correlate grapes juice boiling points and density with pressure or temperature and dry matter content were established.

The models presented have a high degree of accuracy for a wide range of parameters: dry matter between 20 and 70%, pressure for boiling point calculus between 7.4 and 100 kPa, and temperatures for density calculus between 20 and 80 °C, which recommend them for use in industrial processing of fruit juices and sizing calculation of different technological equipments.

The proposed equations present a higher precision that other equations existing in the literature.

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