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CONTRIBUTION TO DETERMINATION OF DENSITY AND ALCOHOLIC CONTENT IN MIXTURES ETHANOL-WATER IN BRAZIL

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Abstract: Ethanol is one of the most important Brazilian export goods and its international market is growing strong, mainly because of a number of measures taken by several countries in order to reduce environmental pollution, for example, adding amounts of ethanol into regular gasoline or even using pure ethanol-moved motors. Quality assurance of ethanol is becoming more and more important in order to make Brazil able to achieve larger shares of international market, every day more demanding and competitive. Chemical composition of ethanol-water blends can be determined from their density. In this paper is presented an analysis comparing the density of blends of ethanol with water at 20°C, obtained using Brazilian standard NBR 5992-80, and by using the model described in the International Recommendation OIML R22. The analysis has identified systematic differences between the results, suggesting that the Brazilian standard should be revised.

Keywords: ethanol, density, regulations, standardization

1. INTRODUCTION

Since the last decade, growing pressures have been observed for the reduction of the environmental pollution by emissions of CO_2, as a form of preventing the greenhouse effect. The Kyoto's Protocol has defined reductions up to 20% of the emissions of CO_2 until 2012. Several developing countries, such like United States, Japan, and Germany among others, started to consider the substitution of part of the fossil sources of energy by new renewable ones, with prominence for the combustible alcohol and the biodiesel.

In the study accomplished under the project OPTI [1], it was verified that the potential of the world market of ethyl alcohol is growing quickly, what makes possible the arising of great new suppliers, futures competitors of Brazil, that is today one of the largest producers of ethyl alcohol, and the largest exporter. In order to achieve larger shares of international market, every day more demanding and competitive, Brazilian producers of ethyl alcohol need to demonstrate the quality of their product. However, the sector demands standardized methods, reference materials widely recognized and up-to-date technical standards.

For example, the technical standard NBR 5992-80 [2] presents the reference method for the determination of the density and alcoholic content in mixtures ethanol-water using the hydrometer-method. It also allows to calculate the density of a mixture at 20°C and its alcoholic content, using the measured density of that mixture at an arbitrary temperature between 10°C and 40°C.

This is the only Brazilian technical standard that defines the behavior of the densities of mixtures ethanol-water, and that is why used as the reference in analysis and research, being also used as technical foundation for several legal and normative documents, such as the specifications of fuels [3] [4] and beverages [5].

Considering its importance and the long validity period without revisions, in this work, was evaluated the accuracy of density of mixtures at standard temperature of 20ºC, in comparison with the Recommendation R22 of the International Organization of Legal Metrology, that presents a international recognized model to densities of mixtures ethanol-water.

2. BEHAVIOR MODELS OF DENSITY OF MIXTURES ETHANOL-WATER

2.1. The Brazilian Model

The Brazilian standard, NBR 5992-80, based in governmental decree, is the only Brazilian model for the densities of mixtures ethanol-water in function of temperatures, it also allows to determinate of alcoholic contents, that can be expressed in ºINPM and ºGL.

This standard, presents a group of tables from where, using experimental densities in any temperature between 10°C and 40°C, can be obtained the specific gravity at 20°C and the alcoholic content.

The standard was established to obtain measurements of densities using the hydrometer–method, with accuracy of 0,0010 g/cm^3, in function of variabilities of thermometer and hydrometers. However it is necessary, to assure that the model presented in the tables does not have errors, because the accuracy have to defined from the very precise values.

Moreover, the model presented in this standard, can be used to convert density values, that can be obtained from the another measurements methods, and for determination of their alcoholic contents.

2.2. The OIML Model

The International Organization of Legal Metrology (OIML) uses a mathematical model that represents the density of mixtures ethanol-water in function of their alcoholic contents and temperatures, that is presented in Recommendation OIML R 12.

The original model was obtained by Wagenbreth and Blanke[6]. This model was based in IPTS-68, represented by Equation 1:

$$\rho = A_1 + \sum_{k=2}^{12} A_k \cdot p^{k-1} + \sum_{k=1}^{6} B_k \cdot (t-20)^k + \sum_{i=1}^{n} \sum_{k=1}^{m_i} C_{i,k} \cdot p^k \cdot (t-20)^i \quad (1)$$

In this equation, the density, ρ, is expressed in kg/m3, the temperature, t, in °C, and the alcoholic content, p, is an adimensional factor. The Table 1, presents the coefficients of this model.

The omission of the last number, can create, rounding errors that can invalidate the utilization of the Equation 1, that can be verified with numerical examples.

Bettin and Spieweck [7], proposed a new model, based on the original model of Wagenbreth and Blanke, using the same experimental database properly corrected according to ITS-90. The model of Bettin and Spieweck, which coefficients with 8 significant numbers, is present by Equation 2:

$$\rho = A_1 + \sum_{k=2}^{12} A_k \cdot (p-0{,}5)^{k-1} + \sum_{k=1}^{6} B_k \cdot (t-20)^k + \sum_{i=1}^{n} \sum_{k=1}^{m_i} C_{i,k} \cdot (p-0{,}5)^k \cdot (t-20)^i \quad (2)$$

In Equation 2, the density, ρ, is expressed in kg/m3, the temperature, t, in °C, and the alcoholic content, p, is an adimensional factor, such as in the Wagenbreth and Blanke's model.

Table 1. Coefficients of Wagenbreth and Blanke's model.

k	A_k	Bk	$C_{1,k}$	$C_{2,k}$	$C_{3,k}$	$C_{4,k}$	$C_{5,k}$
1	$9,982012300 \cdot 10^{2}$	$-2,0618513 \cdot 10^{-1}$	$1,693443461530087 \cdot 10^{-1}$	$-1,193013005057010 \cdot 10^{-2}$	$-6,802995733503803 \cdot 10^{-4}$	$4,075376675622027 \cdot 10^{-6}$	$-2,788074354782409 \cdot 10^{-8}$
2	$-1,929769495 \cdot 10^{2}$	$-5,2682542 \cdot 10^{-3}$	$-1,046914743455169 \cdot 10^{1}$	$2,517399633803461 \cdot 10^{-1}$	$1,876837790289664 \cdot 10^{-2}$	$-8,763058573471110 \cdot 10^{-6}$	$1,345612883493354 \cdot 10^{-8}$
3	$3,891238958 \cdot 10^{2}$	$3,6130013 \cdot 10^{-5}$	$7,196353469546523 \cdot 10^{1}$	$-2,170575700536993 \cdot 10^{0}$	$-2,002561813734156 \cdot 10^{-1}$	$6,515031360099368 \cdot 10^{-6}$	
4	$-1,668103923 \cdot 10^{3}$	$-3,8957702 \cdot 10^{-7}$	$-7,047478054272792 \cdot 10^{2}$	$1,353034988843029 \cdot 10^{1}$	$1,022992966719220 \cdot 10^{0}$	$-1,515784836987210 \cdot 10^{-6}$	
5	$1,352215441 \cdot 10^{4}$	$7,1693540 \cdot 10^{-9}$	$3,924090430035045 \cdot 10^{3}$	$-5,029988758547014 \cdot 10^{1}$	$-2,895696483903638 \cdot 10^{0}$		
6	$-8,829278388 \cdot 10^{4}$	$-9,9739231 \cdot 10^{-11}$	$-1,210164659068747 \cdot 10^{4}$	$1,096355666577570 \cdot 10^{2}$	$4,810060584300675 \cdot 10^{0}$		
7	$3,062874042 \cdot 10^{5}$		$2,248646550400788 \cdot 10^{4}$	$-1,422753946421155 \cdot 10^{2}$	$-4,672147440794683 \cdot 10^{0}$		
8	$-6,138381234 \cdot 10^{5}$		$-2,605562982188164 \cdot 10^{4}$	$1,080435942856230 \cdot 10^{2}$	$2,458043105903461 \cdot 10^{0}$		
9	$7,470172998 \cdot 10^{5}$		$1,852373922069467 \cdot 10^{4}$	$-4,414153236817392 \cdot 10^{1}$	$-5,411227621436812 \cdot 10^{-1}$		
10	$-5,478461354 \cdot 10^{5}$		$-7,420201433430137 \cdot 10^{3}$	$7,442971530188783 \cdot 10^{0}$			
11	$2,234460334 \cdot 10^{5}$		$1,285617841998974 \cdot 10^{3}$				
12	$-3,903285426 \cdot 10^{4}$						

Another Parameters: n=5; m1=11; m2=10; m3=9; m4=4; m5=2

Using this model it is possible to calculate the density of any ethanol mixture with water, saturated with air, in temperatures from -20°C to 40ºC. The procedure allows the calculation of the alcoholic content of the mixtures in function of density readings in any temperature in the range of validity of the model.

2.3. A revision of OIML Model

In 1990, the new fundamental scale of temperature, denominated International Temperature Scale ITS-90, was present. This scale incorporated corrections based in the more recent researches about standards points of temperature.

On the other hand, it is possible to observe, that the parameters, C_i, K of the OIML model, has 16 significant numbers. The computers languages of 1970, such as Fortran IV, allows to utilize many significant numbers.

The spreadsheet and many modern computer languages, allows to utilize numbers with only 15 significant numbers. The Table 2 presents the coefficients of this model.

According to Bettin and Spieweck, the largest difference among the densities calculated by their model and the original model of OIML is near 1,2 x $10^{-6}\rho$. By the way, for practical applications, it is possible to consider Bettin and Spieweck's model equivalent to the original recommend by OIML.

3. A SOFTWARE FOR THE COMPUTATION

The necessaries calculations to determinate density in functions of temperature and alcoholic contents by the original model of OIML, are not complexes, however this calculations, are relative arduous. It was developed in Metrology Reference Laboratory of Center of Metrology in Chemistry of IPT, a computer program that implements the model of Bettin and Spieweck, equivalent to the model adopted by OIML. The program was validated in according to a method statically robust, and it was considered better representative of Bettin and Spieweck's model.

Table 2. Coefficients of Bettin and Spieweck' s model.

k	A_k	B_k	$C_{1,k}$	$C_{2,k}$	$C_{3,k}$	$C_{4,k}$	$C_{5,k}$
1	$9,1376673 \cdot 10^{2}$	$-7,9437550 \cdot 10^{-1}$	$-3,9158709 \cdot 10^{-1}$	$-1,2083196 \cdot 10^{-4}$	$-3,8683211 \cdot 10^{-5}$	$-5,6024906 \cdot 10^{-7}$	$-1,4441741\ 10^{-8}$
2	$-2,2175948 \cdot 10^{2}$	$-1,2168407 \cdot 10^{-3}$	$1,1518337 \cdot 10^{0}$	$-5,7466248 \cdot 10^{-3}$	$-2,0911429 \cdot 10^{-4}$	$-1,2649169 \cdot 10^{-6}$	$1,3470542\ 10^{-8}$
3	$-5,9617860 \cdot 10^{1}$	$3,5017833 \cdot 10^{-6}$	$-5,0416999 \cdot 10^{0}$	$1,2030894 \cdot 10^{-1}$	$2,6713888 \cdot 10^{-3}$	$3,4863950 \cdot 10^{-6}$	
4	$1,4682019 \cdot 10^{2}$	$1,7709440 \cdot 10^{-7}$	$1,3381608 \cdot 10^{1}$	$-2,3519694 \cdot 10^{-1}$	$4,1042045 \cdot 10^{-3}$	$-1,5168726 \cdot 10^{-6}$	
5	$-5,6651750 \cdot 10^{2}$	$-3,4138828 \cdot 10^{-9}$	$- 4,5899913 \cdot 10^{0}$	$-1,0362738 \cdot 10^{0}$	$-4,9364385 \cdot 10^{-3}$		
6	$6,2118006 \cdot 10^{2}$	$-9,9880242 \cdot 10^{-11}$	$-1,1821000 \cdot 10^{2}$	$2,1804505 \cdot 10^{0}$	$-1,7952946 \cdot 10^{-2}$		
7	$3,7824439 \cdot 10^{3}$		$1,9054020 \cdot 10^{2}$	$4,2763108 \cdot 10^{0}$	$2,9012506 \cdot 10^{-1}$		
8	$-9,7453133 \cdot 10^{3}$		$3,3981954 \cdot 10^{2}$	$-6,8624848 \cdot 10^{0}$	$2,3001712 \cdot 10^{-2}$		
9	$-9,5734653 \cdot 10^{3}$		$-9,0032344 \cdot 10^{2}$	$-6,9384031 \cdot 10^{0}$	$-5,4150139 \cdot 10^{-1}$		
10	$3,2677808 \cdot 10^{4}$		$-3,4932012 \cdot 10^{2}$	$7,4460428 \cdot 10^{0}$			
11	$8,7637383 \cdot 10^{3}$						
12	$-3,9026437 \cdot 10^{4}$						

Another Parameters: n=5; m1=11; m2=10; m3=9; m4=4; m5=2

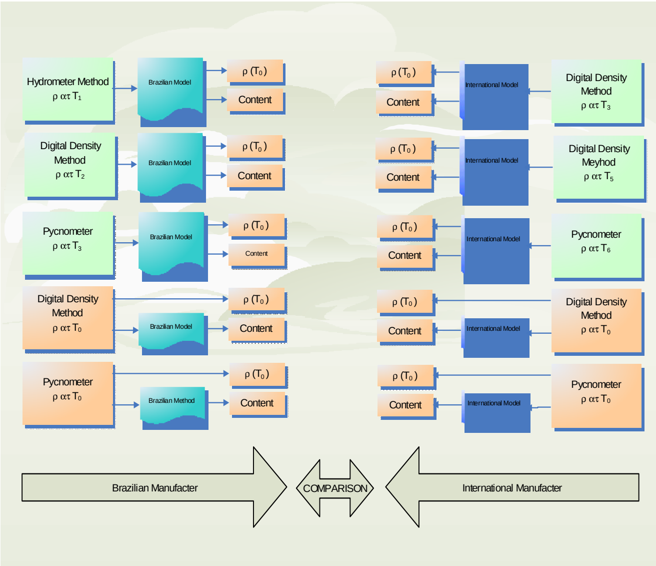

Figure 1. Uses of the behavior models in the Foreign Commerce.

4. COMPARISON BETWEEN NBR RESULTS AND OIML RESULTS

The Figure 1, presents an illustration of these behavior methods, that can be use in comparisons among the results obtained by customer.

A comparison of differences among the densities to 20ºC obtained by NBR 5992-80 and densities obtained by OIML model, was done, for a set 296 compositions where the alcoholic concentrations were between 63% and 100% at temperatures of: 10ºC, 25ºC, 30ºC, and 40ºC, using the computer program developed for this work.

The Table 3, presents some examples, selected between the 296 studied cases, only for general observations and the corrections realized by calculations of OIML and the application of the tables of Brazilian standard.

Table 3. Examples of corrected values by NBR e OIML

Temperature of mensurement (℃)	Observed Density (g/cm ^{3})	Corrected Density values at 20ºC by NBR 5892-80 (g/cm^3)	Corrected Density values at 20ºC by OIML (g/cm^3)	Difference (NBR-OIML) (g/cm^3)
10	0,8045	0,7962	0,7959	0,0003
25	0,7920	0,7963	0,7963	0,0000
25	0,8645	0,8686	0,8688	-0,0002
30	0,7945	0,8029	0,8032	-0,0003
30	0,8645	0,8729	0,8731	-0,0001
40	0,7820	0,7990	0,7994	-0,0004
40	0,8070	0,8243	0,8248	-0,0005

In Figure 2, it is presents the histogram of the differences among the corrected values by NBR and corrected values by OIML model, considering all cases in study. It is possible to observe that the histogram is bi-modal, with a group to the left with a larger numbers of results where there are negative differences, in the other words, representing results where the values obtained by NBR were smaller than the values obtained by OIML . In the second group, with less cases we have the opposite behavior, in the other words, values of OIML smaller than NBR values.

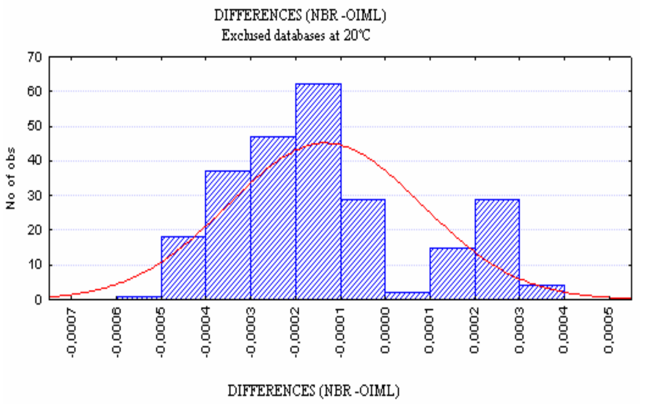

Figure 2. Differences between the corrects values by NBR and OIML.

Figure 3 presents the distributions of differences among the corrected values, grouped by temperature of the mixture.

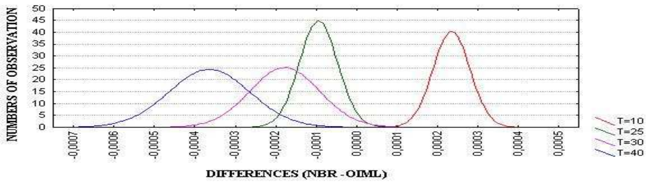

Figure 3. Distributions of corrections performed using NBR and OIML grouped by the temperature of the sample.

It is possible to observe that the corrections by NBR from temperatures higher than 20°C are systematically smaller than the OIML ones. In temperatures lower than 20°C happens an opposite behavior. This behavior explains why there were more negative than positive results in the Figure 1, once there were more cases of corrections from temperatures higher than 20°C.

In the Figure 4, the differences obtained are presented as contours, prepared using distance weighted minimum square technique (DWLSF), according to the algorithm from McLain(10), making possible the analysis of their magnitudes in function of the reading of temperatures and specific gravities. It is possible to observe that at 20°C it is located the zero error curve, as it should be waited for the situation.

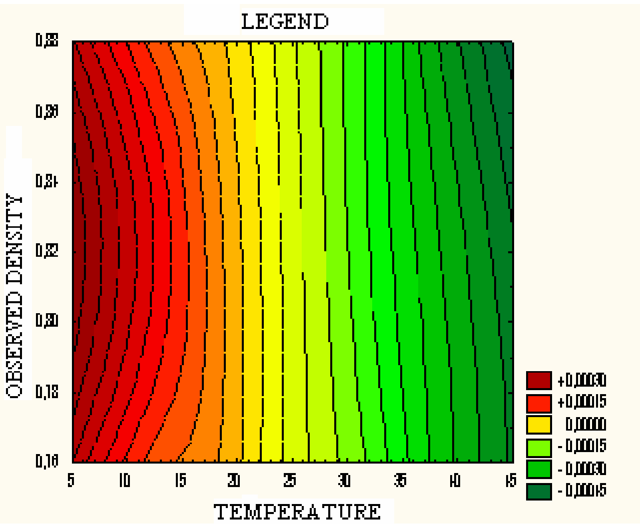

Figure 4 – Differences among densities at 20ºC obtained by NBR and OIML

5. CONCLUSIONS

The analysis of comparative data allows affirming that the results of corrections obtained by Brazilian standard present significant systematic differences in relation of the OIML model. The magnitude of these errors is proportional to difference among observed temperature and standard temperature at 20ºC, and the alcoholic contents of the mixtures. This way, at observed temperatures smaller than 20ºC, the standard produces results systematically larger than the results obtained by OIML model.

At temperatures higher than 20ºC, the Brazilian standard produces results smaller than the OIML model. The largest errors obtained in this work was + 0,0004 and – 0,0006 g/cm^3, at temperatures 10ºC and 40ºC, respectively. Errors of this magnitude can affect results obtained by other methods, such pycnometer method and digital density method, nowadays widely employed in laboratories of analysis.

Considering the necessity of utilization of consistent, comparables and right values, the authors suggest that be made a revision of the Brazilian standard NBR 5992-80, with the aim of incorporate more recent models to describe the behavior of density in mixtures ethanol-water, as well as the model of Bettin and Spieweck, used by OIML.

6. REFERENCES

[1] Estudo Prospectivo da Aplicação de Barreiras Não Tarifárias (BNT) no Setor Sucroalcooleiro do Estado de São Paulo; Observatório Paulista de Tecnologia e Inovação (OPTI); IPT, DEES; São Paulo; 2004.

[2] NBR 5992-80; Determinação da massa Específica e do Teor Alcoólico do Álcool Etílico e suas Misturas com Água

[3] ANP - Agência Nacional do Petróleo, Portaria nº2, de 16/01/2002

[4] ANP – Agência Nacional do Petróleo, Regulamento Técnico ANP nº 1/2002

[5] Portaria do Ministério da Agricultura para Bebidas alcoólicas

[6] International Organisation of Legal Metrology, International Recommendation nº22 - OIML R22; 1973.

[7] WAGENBRETH, H. BLANKE, W. Analytische Darstellung der Dichte von Äthanol-Wasser-Mischungen zur Berechnung der Interlationalen Alkoholtafeln der OIML, PTB Mitteilungen 2/73, p.90-96, 1973.

[8] BETTIN, H. SPIEWECK, F. A Revised Formula for the Calculation of Alcoholometric Tables, PTB Mitteilungen 6/90, p.457, 1990.

[9] ZUCCHINI, R.R. Método para Validação de Similaridade de Software para Simulação, Dissertação de Mestrado, IPT, EPUSP, São Paulo, 108p., 2002.

[10] McLAIN, D. H. Drawing contours from arbitrary data points. The Computer Journal, 17, 318-324. (1974).