

Thermodynamics of Biodiesel: Combustion Experiments in the Standard Conditions and Adjusting of Calorific Values for the Practically Relevant Range (273 to 373) K and (1 to 200) bar

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Poder calorífico de misturas de biodiesel dos ésteres metílicos de colza (RME) e soja (SME) foram determinados usando um calorímetro de combustão de alta precisão. A dependência dos valores calóricos com a temperatura e pressão no intervalo (273-373) K e (1 a 200) bar foram derivados para misturas de RME e SME de biodiesel B100. Foram propostas equações práticas para o cálculo da correção da temperatura para poder calorífico, considerando a composição, temperatura e pressão.

Calorific values of rapeseed methyl ester (RME) and soybean methyl ester (SME) biodiesel blends have been determined by using of the high-precision combustion calorimeter. Temperature and pressure dependences of the calorific values in the range (273 to 373) K and (1 to 200) bar have been derived for the RME and SME biodiesel blends B100. Practical equations for calculating of the thermal correction for calorific values taking into account the composition, temperature, and pressure have been proposed.

Keywords: rapeseed methyl ester, soybean methyl ester, energy of combustion, temperature and pressure dependence

Introduction

The foreseeable depletion of fossil fuel resources and the increasing environmental benefits of the renewable fuels have attracted a lot of interest to biodiesel in the recent time. Its crucial advantages are due to renewable sources as well as due to non-toxicity and biodegradability. Biodiesel is renewable, non-toxic, biodegradable, and it can be used directly in most engines without specific modification. Biofuels have different heating (calorific) values and these differences impact the engine performance. The calorific values are commonly obtained from the combustion calorimetry at the standard conditions and the reference temperature 298 K. However, the reality is that fuels are used at significantly different T and P conditions. In this work we have developed a thermodynamic procedure based on the combustion results for calculation of calorific values of biodiesel fuels at different the temperatures and pressures. This procedure has been implemented in the final

results of the European Union project “ENG09-Metrology for Biofuels”

Experimental

Chemicals

Samples of the RME (rapeseed methyl ester) and SME (soyabean methyl ester) biodiesel blends referred to the specification B100 (pure biofuel) were supplied by Shell Oil Deutschland GmbH. These samples were used as the reference materials in the frame of the EURAMET (European Association of National Metrology Institutes) Joint Research Project “ENG-09 Biofuels”. Molar compositions of RME and SME are given in Table S1 of the Supplementary Information (SI).

Combustion calorimetry

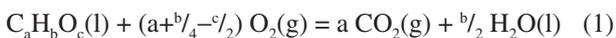
An isoperibol bomb calorimeter was used for the measurement of energy of combustion of RME and SME blends. Our preliminary experiments have shown an

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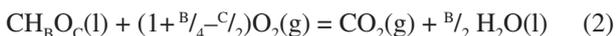
incomplete combustion when burned in open crucible. In order to achieve completeness of combustion we used commercially available polyethylene bulbs (Fa. NeoLab, Heidelberg, Germany) of 1 cm³ as sample containers. The sample was transferred from the stock bottle into the polyethylene bulb with a syringe and the sealed according to a procedure described previously.¹ The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none was detected. Six to seven successful experiments were performed for each blend (see Tables S2 to S4). The energy equivalent of the calorimeter ϵ_{calor} was determined with a standard reference sample of benzoic acid (sample SRM 39j, N.I.S.T.). Correction for nitric acid formation was based on the titration with 0.1 mol dm⁻³ NaOH (aq). The atomic weights used were those recommended by the IUPAC Commission.² The sample masses were reduced to vacuum, taking into consideration the known density of the samples. For converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states, the conventional procedure was applied.³ Values of the standard specific energies of combustion $\Delta_c u^\circ$, together with the necessary auxiliary quantities, are given in Tables S3 and S4.

Results and Discussion

The calorific value is commonly related to the change of the internal energy due to the combustion process according to the following chemical reaction:



Because of composition of biodiesel blends is usually ill defined composition, the general formula $\text{C}_a\text{H}_b\text{O}_c$ becomes impractical for an anchoring of thermodynamic procedures to the chemical compositions. It seems to be more practical when the chemical formula was normalized by the carbon index "a" (see equation 1). For example, the biodiesel mixture of the general formula $\text{C}_a\text{H}_b\text{O}_c$ divided by "a" provided the normalized formula $\text{CH}_{b/a}\text{O}_{c/a}$. For the sake of brevity we introduced the simplified spelling of ratios as follows: $b/a = B$ and $c/a = C$. With this abbreviation the combustion reaction (see equation 1) was re-written as follows:



Using of equation 2 instead of the equation 1 makes thermodynamic modeling procedure for biodiesel blends principally possible and in addition even easier due to

reducing of a number of parameters required for the calculations of calorific values.

The temperature and pressure dependence of the calorific value (internal energy of combustion $\Delta_c u^\circ$) is determined according to the fundamental dependences of thermodynamic functions as an exact differential:⁴

$$d\Delta_c u = \left(\frac{d\Delta_c u^\circ}{dT} \right)_p dT + \left(\frac{d\Delta_c u}{dP} \right)_T dP \quad (3)$$

This equation consists of two contributions: the temperature dependence of the calorific value with the thermal correction $\Delta\Delta_c u^\circ(T)$ and the pressure dependence of the calorific value with the contribution $\Delta\Delta_c u(P)$. We shall describe development of these two contributions separately.

The first contribution in the right side of equation 3 is the temperature dependence of internal energy which is also defined as the isochoric heat capacity ($\Delta_c C_v^\circ$):⁴

$$\left(\frac{d\Delta_c u^\circ}{dT} \right) = \Delta_c C_v^\circ \quad (4)$$

Values of $\Delta_c C_v^\circ$ for gases O₂ and CO₂,⁵ and the liquid water,⁶ which are participants of the reaction (2) are available from the literature. Unfortunately the experimental data on the isochoric heat capacity of the complex biodiesel mixtures are absent in the open literature. Surprisingly, the data on methyl oleate and the methyl linoleate (main components of biodiesel) which could help as the model compounds to derive the missing isochoric heat capacity values for biodiesel are also absent in the literature. In order to get any reasonable estimate relevant to biodiesel blends we used the experimental $\Delta_c C_v^\circ$ -data for the methyl stearate as the compound most structurally close to the biodiesel blends. The heat capacity at constant pressure for methyl stearate was reliably measured by van Bommel *et al.*⁷ by using the adiabatic calorimetry. Obviously, the methyl stearate represents only the saturated esters present in biodiesel. Thus for the unsaturated esters we need to apply an additional contribution to the heat capacity in order to take into account the double bond in the alkyl chain. Quantitatively this contribution can be easily assessed from comparison of heat capacities of pairs of similarly shaped saturated and unsaturated liquid hydrocarbons: *n*-hexadecane,⁸ 1-hexadecene,⁹ *n*-dodecane,⁸ and 1-dodecene.¹⁰ The difference in heat capacities should represent the contribution due to introduction of the double bond into the alkyl chain of esters. We have found that the specific isobaric heat capacities of saturated hydrocarbons were of (2 to 4) % higher than those for

unsaturated. This observation was also assigned for the esters containing double bonds. Provided that methyl oleate can be considered as the main representative of unsaturated esters in biodiesel blends we suggested the methyl oleate as the model compound for estimation of heat capacities of biodiesel relevant compounds.

The available in the temperature range (320 to 350) K experimental data for heat capacities of the liquid saturated ester methyl stearate (model compound) were fitted with the linear equation:

$$C_p^o(T, \text{J K}^{-1} \text{g}^{-1}) = (1.329 \pm 0.045) + (2.51 \pm 0.14) \times 10^{-3} T \quad (5)$$

Equation 5 we used to estimate heat capacities in the temperature range (273.15 to 373.15) K for the saturated esters present in the biodiesel blends. For practical purposes we converted the available in the literature⁷ molar heat capacities C_{pm}^o ($\text{J K}^{-1} \text{mol}^{-1}$) of the liquid methyl stearate to the specific heat capacity in $\text{J K}^{-1} \text{g}^{-1}$ (Table 1, column 2). In order to derive specific heat capacities for methyl oleate (as a model for unsaturated esters) we scaled with the factor of 0.97 the C_{pm}^o values of methyl stearate (Table 1, column 3). As a matter of fact the specifications for RME and SME blends revealed that methyl oleate predominates in the B100 compositions. Thus we assumed that the heat capacity of methyl oleate (Table 1, column 3) in a good approximation could be ascribed to the biodiesel samples B100.

Table 1. Heat capacities of the model compounds methyl stearate and methyl oleate at different temperatures.

T / K	$C_p^o /$ $\text{J K}^{-1} \text{g}^{-1}$	$C_p^o /$ $\text{J K}^{-1} \text{g}^{-1}$	$C_p^o - C_v^o /$ $\text{J K}^{-1} \text{g}^{-1}$	$C_v^o /$ $\text{J K}^{-1} \text{g}^{-1}$ ^a
	Methyl stearate (eq. 5)	Methyl oleate	(eq. 6)	
273.15	2.015	1.955	0.3291	1.6255
280	2.032	1.971	0.3308	1.6404
290	2.057	1.996	0.3328	1.6628
298.15	2.078	2.015	0.3339	1.6816
300	2.082	2.020	0.3341	1.6859
310	2.110	2.046	0.3347	1.7117
320	2.132	2.068	0.3344	1.7332
330	2.156	2.091	0.3335	1.7576
340	2.182	2.117	0.3320	1.7847
350	2.210	2.144	0.3297	1.8139
360	2.233	2.166	0.3266	1.8395
370	2.258	2.190	0.3229	1.8676
373	2.266	2.198	0.3216	1.8761

^acalculated as the difference $C_p^o - (C_p^o - C_v^o)$.

The isobaric heat capacities C_p^o derived in Table 1, column 3 have to be re-calculated into the isochoric heat capacity, $\Delta_c C_v^o$, in order to apply them in equations 3 and 4. Relation between isochoric and isobaric heat capacity is well established in the thermodynamics by the following equation:^{4,11}

$$C_p^o - C_v^o = \frac{\alpha_p^2 T}{\kappa_T \rho} \quad (6)$$

where α_p , is the isobaric thermal expansion, K^{-1} ; κ_T , is isothermal compressibility, Pa^{-1} ; ρ , is the density, g m^{-3} ; T , is the temperature, K. In equation 6 the difference ($C_p^o - C_v^o$) is given in $\text{J K}^{-1} \text{g}^{-1}$.

Equation 6 can be easily applied for calculations of isochoric heat capacities of esters and blends relevant to biodiesel provided that sufficient amount of experimental data on temperature dependences of the transport properties – α_p , κ_T , and ρ are available. Unfortunately amount of the precise experimental data for pure esters and biodiesel blends are restricted. In order to encompass transport properties for the broad variation of the biodiesel mixtures some generalization was required. For example, it has turned out, that the experimental densities for long-chained pure esters and different biodiesel blends are similar within 2% regardless on plants used for biodiesel production.^{12,13} Fluctuations of the thermal expansion coefficients, α_p , have been also observed at the same level of 2%. These findings have simplified application of equation 6 for biodiesel blends. We fitted the available temperature dependences of volumetric properties^{12,13} for blends by equations 7 and 8 and assumed that these equation are valid for the B100 biodiesel blends within the assessed uncertainty of ($\pm 2\%$):

$$\rho(\text{kg m}^{-3}) = (1096.2 \pm 1.9) - (0.7356 \pm 0.0058) T(\text{K}) \quad (7)$$

$$\alpha_p(\text{K}^{-1}) = (6.159 \pm 0.014) + (7.232 \pm 0.043) \times 10^{-7} T(\text{K}) \quad (8)$$

In contrast to the density and the thermal expansion coefficient, which are easily available from experiment, the determination of the isothermal compressibility, κ_T , is thwarted with complications. This property is usually derived directly from the pressure dependence of density at high pressures. But an alternative way to obtain the isothermal compressibility is to measure the speed of sound and to calculate κ_T -values according to equation:^{4,11}

$$\kappa_T = \frac{1}{\rho} \left(\frac{1}{w^2} + \frac{\alpha_p^2 T}{C_p^o} \right) \quad (9)$$

where w , is the speed of sound in the investigated sample, m s^{-1} ; C_p^o , is the isobaric heat capacity (in our

case in $\text{J K}^{-1} \text{kg}^{-1}$). The experimental data on speed of sound measurements for biodiesel blends available in the literature¹⁴ have revealed that the speed of sound in methyl ester biodiesel blends insignificantly depends on the composition of biofuels. Fluctuations of the speed of sound measured in different blends were not larger than 1 % and the corresponding k_T -values derived according to equation 9 were reproducible within 2 %. In order to simplify data treatment with equation 9 we fitted the literature data¹⁴ for the temperature dependences of speed of sound for different blends with the following linear equation:

$$w(\text{m s}^{-1}) = (2424 \pm 12) - (3.461 \pm 0.038) T(\text{K}) \quad (10)$$

Volumetric properties of biodiesel blends derived with Eqs. 7-9 were now used in equation 6 to obtain the temperature dependence of $(C_p^\circ - C_v^\circ)$ difference (see Table 1, column 4). The final values of the isochoric specific heat capacity estimated from combination of equation 6 and equation 5 are listed in Table 1, column 5. These values we used in equation 4 in order to derive the temperature dependence of calorific values for biodiesel.

As a matter of fact, calculations with equation 4 are commonly used for individual compounds, but they could provide ambiguous results for blends, because according to the combustion reaction for biodiesel (equation 2) the temperature correction of the calorific value $\Delta\Delta_c u^\circ(T)$ is dependent on the elemental composition of the mixture. Following, the temperature dependence have to be unique for each type of biodiesel blend. In order to develop equation 4 suitable for different types of B100 biodiesel blends we have suggested to specify the range of typical compositions with parameters $B(\text{H}) = (1.75 \text{ to } 2.00)$ and $C(\text{O}) = (0 \text{ to } 0.12)$ according to equation 2. We also restricted the temperature range of $T = (273.15 \text{ to } 373.15) \text{ K}$ where the difference of isochoric heat capacities $\Delta_c C_v^\circ$ of combustion reaction 2 participants has a practical meaning. With these limitations we evaluated and fitted the $\Delta_c C_v^\circ$ values by the following:

$$\Delta_c C_v^\circ = (0.486 \pm 0.052) - (5.70 \pm 0.07) 10^{-3} T + (1.92 \pm 0.03) n_{\text{H}} - (1.565 \pm 0.063) n_{\text{O}} \quad (11)$$

where n_{H} , is the number of H atoms in the formula of biodiesel (B in equation 2); n_{O} , is the number of O atoms in the formula of biodiesel (C in equation 2); T , is the temperature in K; $\Delta_c C_v^\circ$, is the isochoric heat capacity difference for the combustion process, $\text{J K}^{-1} \text{g}^{-1}$. Integration of equation 4 with the heat capacity difference derived according equation 11 provided the thermal correction $\Delta\Delta_c u^\circ(T)$

$$\Delta\Delta_c u^\circ(T) = (0.486 + 1.92n_{\text{H}} - 1.565n_{\text{O}})(T - 298.15) - 2.85 \times 10^{-3} (T^2 - 298.15^2) \quad (12)$$

Equation 12 was considered to be the final expression for the first contribution to the general equation 3 responsible for the temperature dependence of the calorific value. For validation of equation 12 we used the results of our combustion experiments (see Table S1 to S3) with the biodiesel blends RME and SME B100 with the certified composition (see Table 2 and Figure 1). It was apparent from these tables that the maximal deviation between smoothed values and direct calculations was not larger than 1.5 J g^{-1} .

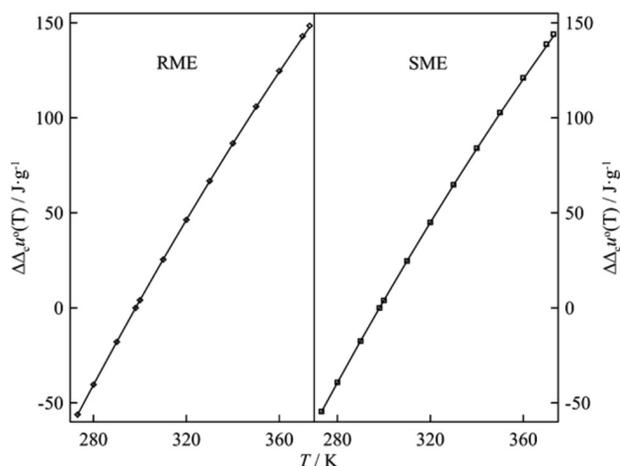


Figure 1. The values of temperature dependence corrections $\Delta\Delta_c u^\circ(T)$ of the calorific values for RME and SME B100 biodiesel blends: rhombs, are RME B100; squares, are SME B100 blends; solid lines, are calculated with equation 12.

The maximal value of the thermal correction $\Delta\Delta_c u^\circ(T)$ was at the level of 150 J g^{-1} or about 1%. Such deviations were considered as acceptable taking into account that the experimental uncertainties of calorific values measured according to DIN 51900 in the certified laboratories were at the level of $(\pm 140 \text{ J g}^{-1})$. Following we suggest equation 12 for estimation of the thermal correction (the first term in the equation 3) for the calorific values of the B100 biodiesel blends.

The pressure dependence $\Delta\Delta_c u(P)$ of calorific values is described by the second term in the right side of equation 3. We used the Maxwell equations and basic thermodynamic rules to convert this term into the following form:

$$\left(\frac{d\Delta_c u}{dP}\right)_T = T \left(\frac{d\Delta_c S}{dP}\right)_T - P \left(\frac{d\Delta_c V}{dP}\right)_T; \left(\frac{dS}{dP}\right)_T = -\left(\frac{dV}{dP}\right)_T \quad (13)$$

$$\left(\frac{d\Delta_c u}{dP}\right)_T = -T \left(\frac{d\Delta_c V}{dT}\right)_P - P \left(\frac{d\Delta_c V}{dP}\right)_T \quad (14)$$

Table 2. Comparison of the temperature dependence corrections $\Delta\Delta_c u^o(T)$ of the calorific values for RME and SME B100 biodiesel blends obtained from experimental data for the combustion reaction 2 with those estimated with equation 12.

T / K	RME B100		SME B100	
	$\Delta\Delta_c u^o(T) / \text{J g}^{-1}$	$\Delta\Delta_c u^o(T) / \text{J g}^{-1}$ (eq. 12)	$\Delta\Delta_c u^o(T) / \text{J g}^{-1}$	$\Delta\Delta_c u^o(T) / \text{J g}^{-1}$ (eq. 12)
273.15	-56.1	-56.3	-54.5	-54.7
280	-40.4	-40.5	-39.2	-39.4
290	-17.9	-18.0	-17.4	-17.4
298.15	0.0	0.0	0.0	0.0
300	4.0	4.0	3.9	3.9
310	25.4	25.5	24.7	24.7
320	46.3	46.3	45.0	44.9
330	66.7	66.6	64.8	64.6
340	86.6	86.4	84.1	83.7
350	105.9	105.6	102.8	102.3
360	124.7	124.2	121.1	120.3
370	143.0	142.3	138.8	137.7
373	148.4	147.6	144.0	142.9

In this way the pressure dependence of the calorific values was completely described by using the values of the thermal expansion and isothermal compressibility of the participants of combustion reaction (2). For practical use we modified equation 14 by introducing terms available from the experiment:

$$\Delta\Delta_c u(P) = \int_{1 \text{ bar}}^P \Delta_c(V\kappa_T)PdP - \Delta_c(V\alpha_p)TdP \quad (15)$$

Assuming the ideal behavior of the gaseous participants (CO_2 and O_2) of the combustion reaction 2 at the standard conditions and moderate temperatures, the pressure derivative of internal energies of gaseous species was equal to zero. Such assumption was tested to be sufficient within the experimental uncertainties of calorific values. Moreover, the pressure dependence of calorific values is mainly stipulated by the properties of the liquid species in the combustion reaction 2: the biodiesel blend and the liquid water. Values of thermal expansion and isothermal compressibility required for equation 15 can be estimated with equations 7-10. Similar to the procedure developed for equation 6 we restricted the variation of biodiesel blends composition to typical parameters $B(\text{H}) = (1.75 \text{ to } 2.00)$ and $C(\text{O}) = (0 \text{ to } 0.12)$ according to equation 2. We also used the temperature range of $T = (273.15 \text{ to } 373.15) \text{ K}$ and pressure range (1 to 200) bar. The evaluated values of $\Delta_c(k_T V)$ and $T\Delta_c(\alpha_p V)$ were fitted by following equations:

$$\Delta_c(\kappa_T V) / (\text{J g}^{-1} \text{ bar}^{-2}) = (1.09 \pm 0.11) \times 10^{-5} - (6.70 \pm 0.68) \times 10^{-8} T + (3.26 \pm 0.11) \times 10^{-6} n_{\text{H}} + (5.38 \pm 0.27) \times 10^{-6} n_{\text{O}} \quad (16)$$

$$T\Delta_c(\alpha_p V) / (\text{J g}^{-1} \text{ bar}^{-1}) = -(1.25 \pm 0.60) \times 10^{-2} + (4.93 \pm 0.37) \times 10^{-4} T - (1.05 \pm 0.06) \times 10^{-2} n_{\text{H}} - (1.81 \pm 0.15) \times 10^{-2} n_{\text{O}} \quad (17)$$

where n_{H} , is the number of H atoms in the formula of biodiesel (B in equation 2); n_{O} , is the number of O atoms in the formula of biodiesel (C in equation 2); T , is the temperature in K. With these equations, the final correction for the pressure dependence of calorific value was:

$$\Delta\Delta_c u(P) = \frac{\Delta_c(V\kappa_T)}{2} (P^2 - 1) - T\Delta_c(V\alpha_p)(P - 1) \quad (18)$$

where P , is the pressure in bars (1 bar is used as standard pressure).

For validation of equation 18 we used the experimental data (see Table S5 ESI and Figure 2) for B100 biodiesel blends with the certified composition. The estimated with equation 18 values were in acceptable agreement with the experiment within 0.2 J g^{-1} . It was apparent from the analysis of data collected in Table S5 ESI that for the pressure correction the compressibility term is insignificant at pressures lower than few kbar. At pressure of 200 bar the maximal value of compressibility term doesn't exceed 0.2 J g^{-1} . This value is of four orders lower than uncertainties of calorific values measured with the

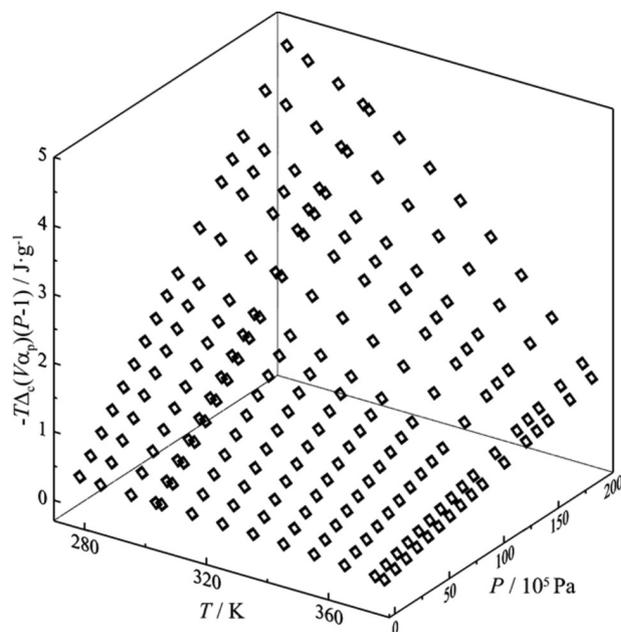


Figure 2. The value of thermal expansion contribution in the pressure adjustment of calorific values for SME.

combustion calorimetry. This fact has tempted to simplify equation 18 by removing of the first term in equation 18 and in the reduced form we obtained:

$$\Delta\Delta_c u(P) = -T\Delta_c(V\alpha_p)(P - 1) \quad (19)$$

The simple equation 19 was tested to be precise enough for calculation of the pressure dependence of the calorific values for B100 biodiesel blends.

Combination of equations 12 and 19 has allowed to take into account both the temperature dependence $\Delta\Delta_c u^o(T)$ and the pressure dependence $\Delta\Delta_c u(P)$ of the calorific value in the conditions (273 to 373) K and (1 to 200) bar important for the practical application of the biodiesel blends.

Conclusion

In this work we have developed the temperature and pressure correction for the calorific values based on the experimental thermodynamic property – the internal energy of combustion $\Delta_c u^o$, which had the negative sign. However, traditionally the calorific values are discussed with the positive sign (having the same absolute value). For conventional application of equations 12 and 19 for estimation of the calorific values of biodiesel blends, corrections $\Delta\Delta_c u^o(T)$ and $\Delta\Delta_c u(P)$ have to be used with the opposite sign.

Supplementary Information

Supplementary data is available free of charge at <http://jbcs.s bq.org.br> as PDF file.

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