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DENSITY MEASUREMENTS OF LIQUID FUELS TO DETERMINE TEMPERATURE CONVERSION FACTORS FOR LEGAL METROLOGY

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Abstract: Worldwide there are great efforts to reduce the CO_2 emission into the atmosphere by using fuels made from biomass. These biofuels are normally blended with fossil fuels.

For legal metrology the thermal expansion coefficient, the so-called temperature conversion factor, is of great importance to guarantee correct measurements of the fuel volume. Thus, the density of fossil fuels blended with biofuels was measured at the Physikalisch-Technische Bundesanstalt (PTB). Investigations were performed on mixtures of fossil petrol with ethanol and of fossil Diesel with biodiesel.

The volume concentration of the biofuels component varied between 0 % and 100 % in order to have data available for all possible mixtures. The data were measured in a temperature range between -10 °C and +50 °C.

Keywords: biofuels, density, thermal expansion coefficient, temperature conversion factor

1. INTRODUCTION

Biofuels are considered to be one way to reduce the CO_2 emission into the atmosphere. Commonly, these fuels are plant-based and, thus, run under the name biofuels. The main groups of biofuels nowadays available on the market fall into two categories: ethanol, which can be blended with fossil petrol, and methyl esters of some oils, which can be blended with fossil Diesel, e. g. rape seed oil or soy bean oil or palm oil.

The European directive 2009/28/EC [1] demands: ‘Each Member State shall ensure that the share of energy from renewable sources in all forms of transport in 2020 is at least 10 % of the final consumption of energy in transport in that Member State.’ Thus, usually a mixture of fossil fuels with biofuels is offered in most European countries with the percentage of biofuel growing from year to year.

To ensure proper trade and an adequate adaption of engines to such mixtures their material data have to be known with sufficient uncertainty. As liquid fuels are usually measured not as mass but as volume the knowledge of their density including its temperature dependence is a crucial quantity. In legal metrology such data are used for a temperature conversion of the measured volumes to a standard volume at 15 °C. The conversion is performed using the so-called “temperature conversion factor”, a factor used for all fuels inside a class of nominally equal fuels.

Apart from the legal requirements the material data are important inputs for process control in automotive industries.

2. MEASUREMENT PROCEDURE

Density measurements were performed using a DMA 5000 by Anton Paar, modified to be able to measure down to -20 °C. The temperature dependence of the density was determined for each fuel blend in the temperature range between -10 °C and +50 °C. This was done by stepping the temperature in steps of 5 K from -10 °C to +50 °C for petrol and vice versa for Diesel. The direction of the temperature scan was different for petrol blends and for Diesel blends to minimize temperature effects on the material’s parameter.

A typical difficulty of these experiments comes from possible changes in the composition in the investigated materials caused by evaporation effects. This is in particular for petrol blends the main source of poorly reproducible results. For Diesel fuels the beginning solidification at low temperatures can influence the material’s parameters.

A considerable advantage of the device used in the present experiments is that its construction allows the almost complete avoidance of evaporation effects.

The uncertainty of these measurements is less than 0.02 kg/m³.

3. MEASUREMENT RESULTS

Within the project at PTB the range of mixtures was not restricted to a percentage of biofuel at the 10 % level as used nowadays but the full range from 0 % biofuel content (pure fossil fuel) up to 100 % biofuel content (pure biofuel) was investigated in order to have data available in the case that the fraction of biofuel given by law will increase further.

The investigation covered blends of petrol (octane number 95) with ethanol, blends of Diesel with rape seed methyl ester (RME), and with soy bean methyl ester (SME). These two types of biodiesels are commonly available on the European market. Both the blends with summer quality and winter quality of the fossil fuels common in Germany were investigated. Samples were mixed at PTB using pure fossil fuel and pure biofuel as origin material.

3.1. Variation of the density for blends of fossil petrol with ethanol

The density of the pure fossil petrol studied in the PTB experiments was 742.31 kg/m³ for summer quality, and 733.89 kg/m³ for winter quality. When blending with ethanol the density increases nearly linearly up to a value of 794.0 kg/m³, the value of pure ethanol. These data were measured at 15 °C and are shown for this temperature in fig. 1.

Looking more closely and comparing with a linear behaviour that uses only the pure petrol value and the pure ethanol value as anchor points, a small enhancement in density of about 1.5 kg/m³ is to be seen at low ethanol contents (volume concentrations up to 20 %). The density values in this range were poorly reproducible and so these density variations have to be investigated more carefully in the future.

In contrast, for larger ethanol contents the mixtures show a small decrease in density of about 0.5 kg/m³ maximum when compared to the linear approximation.

A more pronounced anomaly is found in the thermal expansion coefficient. This coefficient increases at low ethanol contents, showing a maximum for an ethanol content near 10 %, and decreases for larger ethanol contents to match finally the value of pure ethanol. We presume that for low ethanol contents there is a masking effect of the polar ethanol molecules by nonpolar hydrocarbon molecules causing this behaviour.

Irrespective of these findings the thermal expansion coefficient of the blends changes only by 2 % if the ethanol content is less than 20 %. This has to be set in relation to the difference in the thermal expansion coefficient between summer and winter quality of the fuels, which is 2 %, too.

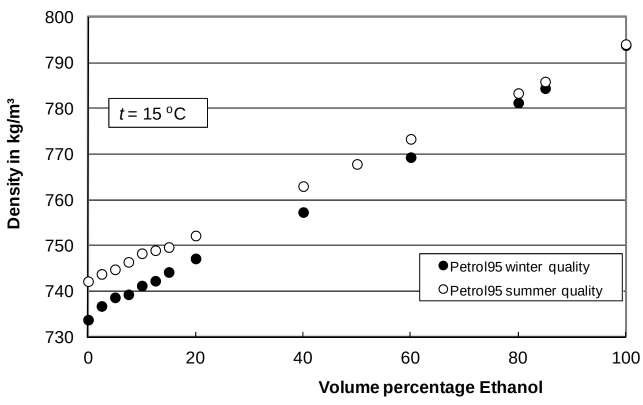

Fig. 1. Density of petrol-ethanol blends at *t* = 15 °C.

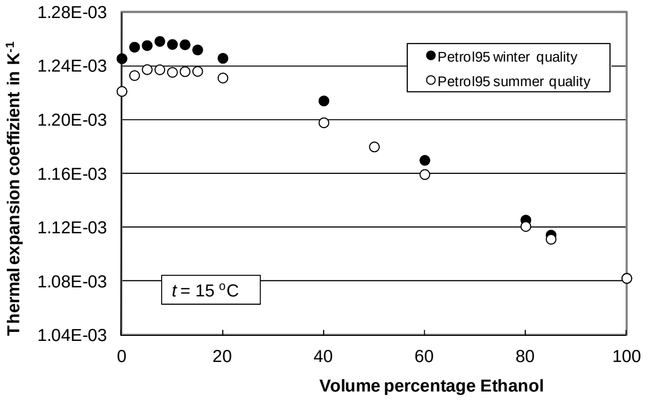

Fig. 2. Thermal expansion coefficient of the petrol-ethanol blends shown in fig. 1 at *t* = 15 °C.

3.2. Variation of the density for blends of fossil Diesel with RME

The situation with Diesel-biodiesel blends is much easier to handle than the one related to petrol. The density of the blends increases at first order linearly with the biodiesel content. There is a small deviation from this linear behaviour resulting in a density decrease of maximum 0.5 kg/m³ for a biofuel percentage of 50 %.

The thermal expansion coefficient of the summer quality is nearly unchanged when blending with RME, the deviations are in the order of 0.2 %. This result has again to be compared with the difference in the thermal expansion coefficients between summer and winter quality of the pure fossil Diesel which is 4 %.

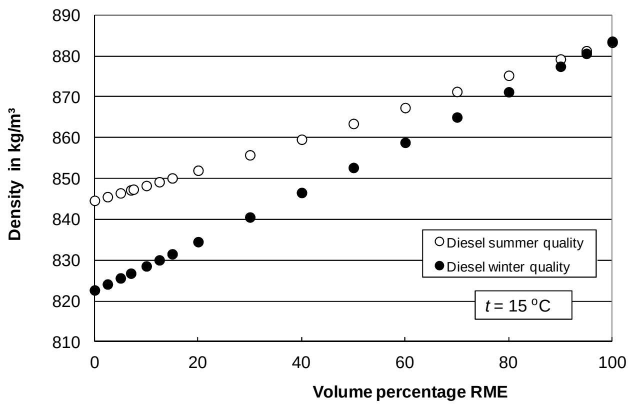

Fig. 3. Density of Diesel-biodiesel (RME) blends at *t* = 15 °C.

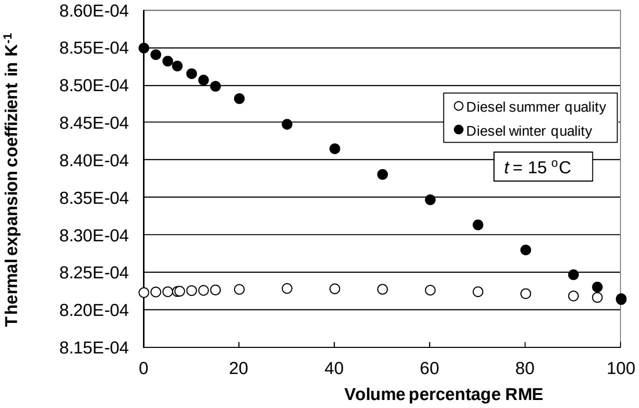

Fig. 4. Thermal expansion coefficient of the Diesel-biodiesel blends shown in fig. 3 at t = 15 °C.

This means, a change of the temperature conversion coefficient is not necessary when switching from fossil Diesel to blends with RME. Quite the contrary the situation becomes more convenient, as the real thermal expansion coefficients of summer and winter qualities converge when using blends.

3.3. Biodiesel other than RME

In addition of RME the studies at PTB covered also SME. The densities of RME and SME differ only by 2 kg/m³. The measurements results obtained with SME blends are very similar to those obtained with RME and therefore are not discussed separately.

3.4. Spread of data when measuring nominally equal fuels coming from different sources

As mentioned in section 3.2., in the Diesel-biodiesel system the variation of the thermal expansion coefficient data when mixing with biofuels is comparable to the difference between summer and winter quality of fossil Diesel.

To get a broader base of data, the spread of data was determined by measuring nominally equal fuels coming from different sources. This offers the possibility to derive a threshold indicating that a variation is relevant for metrological purposes. Nominally equal samples as sold at petrol stations were collected from 17 different refineries in Germany (summer and winter quality) and were measured using the same procedure as the self-mixed samples. Because of the low content of biocomponents the variation of the data can be referred mainly to the fossil components of the fuels, thus, reflecting the situation before the ‘biofuel era’.

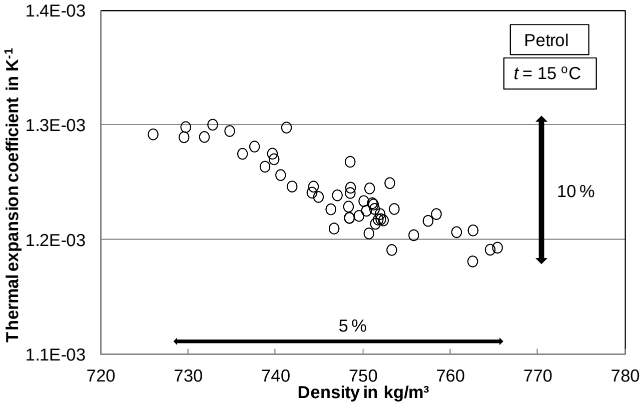

Fig. 5. Parameter spread of different samples of petrol E5 ‘as sold at petrol stations’

The variation of these data is considered to describe the natural diversity of fuels in Germany and should be transferable also to other countries.

The results of these measurements are summarized in fig. 5 for petrol-ethanol blends (at that time E5 in Germany) and fig. 6 for Diesel-biodiesel blends (at that time B7 in Germany).

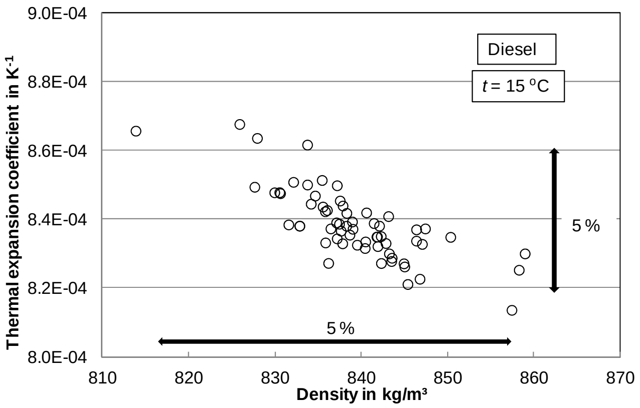

Fig. 6. Parameter spread of different samples of Diesel B7 ‘as sold at petrol stations’

In both cases the thermal expansion coefficient at 15 °C is shown versus the density of the samples at 15 °C to keep the spread of data within one figure. The non-uniform distribution of the data reflects the fact that the thermal expansion coefficient itself depends on the density of the fuel.

In fig. 7 the data for petrol of fig. 1 and 2 are given in the same way as in fig. 5 and are directly compared to those data. The same procedure was applied to the data for Diesel (fig. 3, 4, and 6) shown in fig.8.

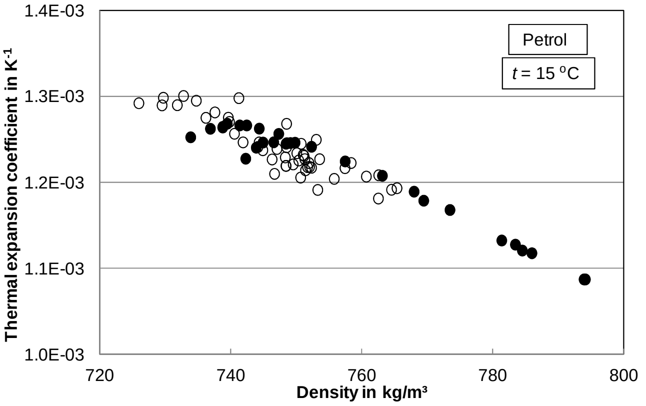

Fig. 7. Parameter spread of different samples of petrol E5 'as sold at petrol stations' (open circles) compared to the variation of data when mixing fossil petrol with ethanol (closed circles).

Compared to the natural spread of E5, the petrol-ethanol blend system shows a larger variation of the thermal expansion coefficient, when looking to the ethanol-rich side. For legal purposes it is here necessary to work with a new temperature conversion factor. But for the ethanol-poor side (below 40 % ethanol content) the variation of the thermal expansion coefficient is inside the span given by the natural spread of thermal expansion coefficients. Therefore, no new temperature conversion factors are needed in this range.

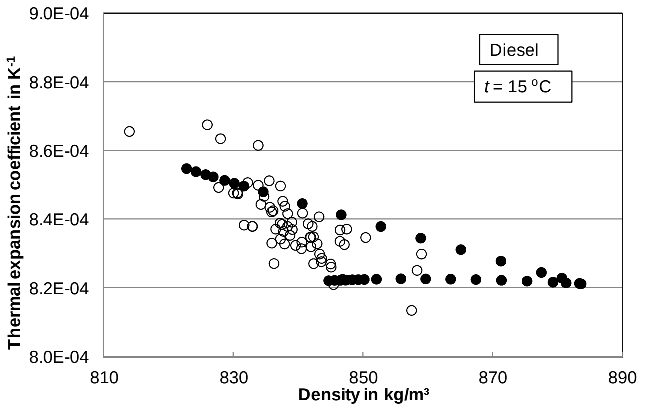

Fig. 8. Parameter spread of different samples of Diesel B7 'as sold at petrol stations' (open circles) compared to the variation of data when mixing fossil Diesel with biodiesel (closed circles).

For Diesel-biodiesel the variation of the thermal expansion coefficient when blending fossil fuel with biofuel is well inside the natural spreading band for all blends. Thus, from the point of view of legal metrology this system can be treated like pure fossil Diesel.

4. DISCUSSION

4.1 Reliability of the data pool

The measurements described in section 3.4 show that there is a spread of the density and thermal expansion coefficient data when looking at nominally equal materials but from different origin.

As the spread in density and thermal expansion coefficient is derived for commercially available fuels with minor biofuel content, it reflects mainly the variations in the data of the fossil components.

We had only two RME biodiesel samples of different origin at our disposal. They had a difference in density of less than 0.5 kg/m³. For the two corresponding SME samples of different origin a difference in density of less than 1 kg/m³ was obtained. Thus, we assume that the spread of data concerning pure biodiesel is not larger compared to that of fossil fuels. For bioethanol we had no additional material, but the same argumentation seems to be reasonable.

All mixtures of a series of blends of fossil fuels and biofuels were made using just **one** batch of the fossil fuel and **one** batch of the biofuel. Thus, these measurements can be considered as one representative measurement set out of a number of similar sets. Other measurements would yield comparable but in detail different results when using raw material from other sources.

However, in extreme situations the results might lead to wrong conclusions. As an example, the use of raw petrol with a density larger than 760 kg/m³ (the most right ones in fig. 5), might result in the conclusion that no extra temperature conversion coefficient is needed for ethanol-rich blends as the thermal expansion coefficient is not very much changed. To avoid such misinterpretation, the difference in density between the fossil component and the biofuel component should be as large as possible. This means that the material has to be selected accordingly.

In the present case the density of ethanol is larger than that of petrol. Therefore, a petrol batch used for the studies should have a density which is at least smaller than the mean of the data cloud shown in fig. 5. The same argumentation holds for Diesel-biodiesel blends.

4.2. Approximation of the temperature dependence of the density

The natural spread of the real thermal expansion coefficients in a class of fuels, e.g. the Diesel class, makes it impossible to describe the thermal expansion very exactly by one temperature conversion coefficient. Thus, in legal metrology usually a mean coefficient is used describing the thermal expansion within a given uncertainty, the maximum permissible error for the temperature conversion.

To find an optimum approximation for the temperature dependence of measured data, the exponential description mostly used up to now in legal metrology (1) for the temperature conversion of volumes [2] was compared to a polynomial approximation of first, second, and third order.

$$\rho_t = \rho_0 e^{-\alpha \Delta t (1+0,8\, \alpha\, \Delta t)} \quad (1)$$

$$\Delta t = t - 15\ ^\circ\mathrm{C}, \quad \alpha = \frac{K_0}{\rho_0^2} + \frac{K_1}{\rho_0}, \quad K_0, K_1 = \mathrm{const}$$

These comparisons showed an excellent description of the temperature dependence of the density by a polynomial of third order with relative deviations between measured data and approximation at the 10^{-6} level. But even the linear approximation shows very good matching between measured data and approximation with relative deviations less than 10^{-5} for Diesel blends and less than 10^{-3} for petrol blends. This is comparable to the deviations if the exponential equation is used.

Thus, the natural spread of the thermal expansion coefficients has a much larger effect on the correct temperature conversion than the simplification by using a linear approximation.

Based on these results it has been recommended in the meantime, that in Germany the linear temperature conversion can be used for legal purposes.

4.3 Implementation of new biocomponents

In the study it was shown that a measurement series using only blends made from one fossil fuel and one biofuel can just be used as one representative result and cannot be transferred with high precision to all batches of the nominally equal fuels on the market.

This implies a strategy for the line of action when the effect of blending fossil fuel with new biocomponents on the temperature conversion factor has to be investigated.

The fossil material acting as the base component should have a density at that side of the density spread of fossil fuels which is opposite to that of the biocomponent (which might be smaller than now for future generation biofuels).

Measurements of the density and its temperature dependence have to be performed just for the pure fossil fuel and the pure biofuel, a linear interpolation between these data is sufficient. An additional measurement for a 20 % blend ensures that there are no anomalous effects which would be indicated by a larger deviation from the linear interpolation result. Only if there are indications for anomalies, additional measurements have to be performed.

If the behaviour is conventional, the data can be treated as one representative, but for providing a temperature conversion factor for the entire ensemble, the mean of the density-thermal expansion coefficient spread should be used as anchor point instead of the data of the actual material.

Having ensured that there are no anomalies just the measurement of the new biofuels density and thermal expansion coefficient together with the already known mean density and mean thermal expansion coefficient of the fossil fuel yield enough information to calculate the data of the new blends with sufficient small uncertainty.

5. CONCLUSIONS

From the studies of the density of fossil fuels and their blends with biofuels and their temperature dependence emerges that there is no urgent need to introduce new legal regulations for the temperature conversion of measured volumes of these fuels to a standard volume.

The changes in the conversion factors of Diesel-biodiesel blends are sufficiently small that it is possible to stay within small maximum permissible errors (0.2 %) without using new conversion factors.

Petrol-ethanol blends with low ethanol percentage below 40 % do also not require a new conversion factor. The only exception is when using ethanol rich blends such as E85. In this case a new conversion factor has to be used.

Because of the natural spread of thermal expansion coefficients it is sufficient to calculate the temperature conversion factor using a linear approximation for the temperature dependence of the volume to get a standard volume. For the same reason it is appropriate to calculate the behaviour of blends by linear interpolation between the data of the pure components if there are no anomalies caused by polar components.

This proposes a strategy for the determination of density and temperature conversion factors for future fossil fuel-biofuel blends using only a very limited number of measurements.

REFERENCES

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[2] D. Mencke: "Setting values for temperature conversion devices of liquid meters", PTB-Mitteilungen, Vol. 109, Issue 5, 1999, pp 385-388