QuantityWare Working Paper

Temperature corrections for biofuel – mineral fuel/heating oil mixtures

Which temperature correction measurement standard can I apply for my biofuel mixtures?

Version History

Version	Date	Description
00	2011-11-01	Initial Version
01	2021-06-23	Modern QW document style applied

Contents

1. Introduction 4
2. Management Summary and Recommendations 5
3. Experimental Data Analysis – Details 7
4. ASTM D1250 Table C – Details 16
5. References 18

1. Introduction

During the last decade, the blending of classic petroleum automotive fuel products such as diesel and gasoline with so-called biofuels (ethanol, RME [Rape seed oil Methyl Ester], SME [Soy bean oil Methyl Ester] etc.) has been increasingly enforced by various national regulatory bodies. With respect to quantity conversion calculations and corrections for the effect of temperature on such products, the oil industry is thus facing a new, complex challenge.

Apparently, there is a lack of global standardization regarding the treatment of such mixed products, which is causing uncertainty within the oil industry.

In Germany, the PTB (Physikalisch-Technische Bundesanstalt) is investigating the temperature- density behavior of such mixtures in order to validate legally required temperature conversions. The first results of this high precision work were published to the public domain in 2010: Temperature conversion of biofuel-mineral fuel mixtures and biofuel-heating oil mixtures.

Similar measurement series have also been executed by the Energy Institute (EI) in the UK.

The redefinition of currently existing measurement standards allowing the consideration of biofuel mixtures with respect to temperature changes is still ongoing in various countries. In order to provide “ad hoc” guidance for QuantityWare customers and other interested parties, QuantityWare has prepared this working paper.

2. Management Summary and Recommendations

In this paper, we compare the PTB's experimental data with the theoretical results obtained via several different VCF (Volume Correction Factor)[1] calculation standard implementations.

Based on the detailed results of our comparison analysis, which we present in subsequent chapters of this working paper, we recommend, largely also in agreement with / support from the experts in the responsible German standardization group DIN-FAM, the following approach in order to choose the relevant volume correction calculation standard:

- Ask your national standardization organization which measurement standard should be used for such mixed products
- Confirm with your responsible governmental organization which measurement standard shall be applied
- If no guidance can be given from the above organizations, we recommend application of ASTM D1250 "Table B" procedures for **all biofuel(RME/SME) - heating oil/diesel mixtures**
- If no guidance can be given from the above organizations, we recommend application of ASTM D1250 "Table B" procedures for ethanol-gasoline mixtures with **an ethanol volume % content of 10% or less**
- If no guidance can be given from the above organizations, we recommend application of ASTM D1250 "Table C" procedures for ethanol-gasoline mixtures **with an ethanol volume % content of 80% or higher**
- Alternatively, if you have laboratory measurement data similar to the data provided by the PTB for your products, you may apply the ASTM D1250-04 calculation procedure ("Table C") to calculate your company specific thermal expansion coefficient α **for any product**. The pragmatic approach utilizing the ASTM D1250 "C Tables" has always been possible**, if buyer and seller agree**.

[1] In 2004, ASTM D1250 replaced VCF with the expression CTL: Correction for the effect of Temperature on the Liquid

- Example: For Gasohol, which the API defines as mixture of gasoline and 10 vol% ethanol, the API recommends (as defined in the MPMS Chapter 11.1 documentation, page 13 [2]) utilization of a special application table ("C Table") with a thermal expansion coefficient α at 60 °F of 714.34 10^{-6} $°F^{-1}$
- For ethanol-gasoline mixtures with ethanol content between 10% and 80%, no experimental data is publically available. Here, application of ASTM D1250 "Table C" is recommended as a "safe choice"

These recommendations consider the fact that ASTM D1250 calculation software is readily available and known within the oil industry and thus utilization for biofuel mixtures will lead to a minimum financial impact risk.

The definition of the thermal expansion coefficient α is given in chapter "ASTM D1250 Table C – Details"

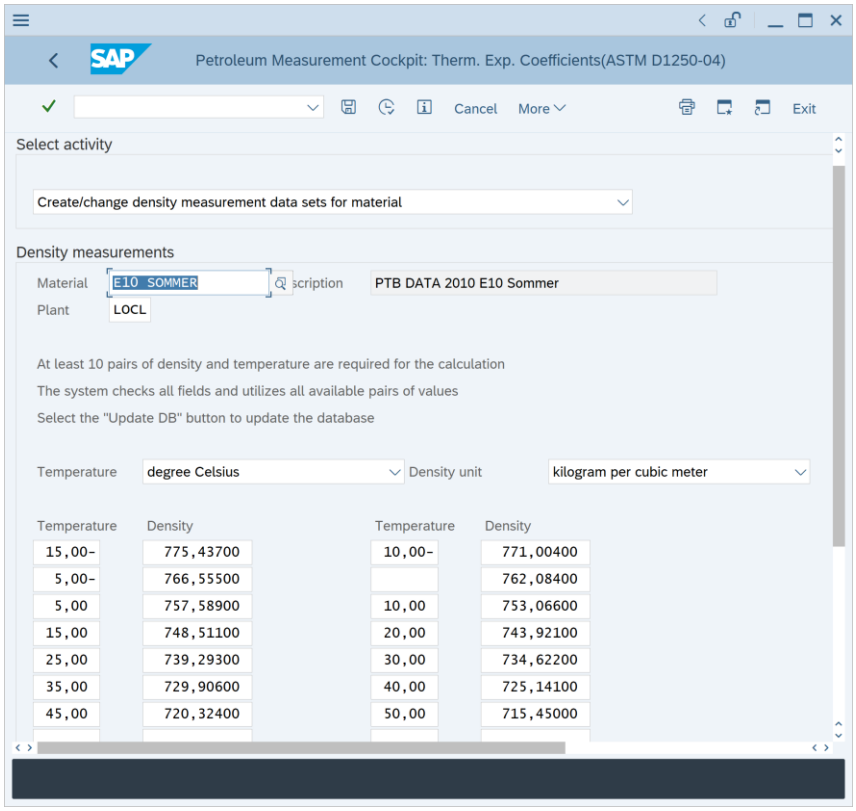
The determination of a thermal expansion coefficient α requires data samples of at least 10 data points as provided by the PTB in reference [1]. Once such data is available, the determination of $\boldsymbol{\alpha}$ is a straightforward ASTM D1250-04 calculation method, which is also included into QuantityWare BCP 10B. However, the industry will most likely require detailed guidance on the numerical values of thermal expansion coefficients $\boldsymbol{\alpha}$ for common product groups. Such guidance has been given by the API for gasohol (see example above). Although QuantityWare presents results for thermal expansion coefficients $\boldsymbol{\alpha}$ based on the experimental PTB data in this paper, **no guidance can be given in this paper concerning the exact values to be utilized for defined product groups**. Such guidance requires additional data analysis and standardization work of national or international standardization working groups, which is published in updates of existing or new standard documents. It is anticipated that such values will be included into volume counter calibrations and updates of currently existing density/metering standards, as they become available. Finally, it shall be noted that new constants are not only needed for updating the calibration of volume counters. They must also be in line with corresponding offline measurement procedures in the laboratory.

3. Experimental Data Analysis – Details

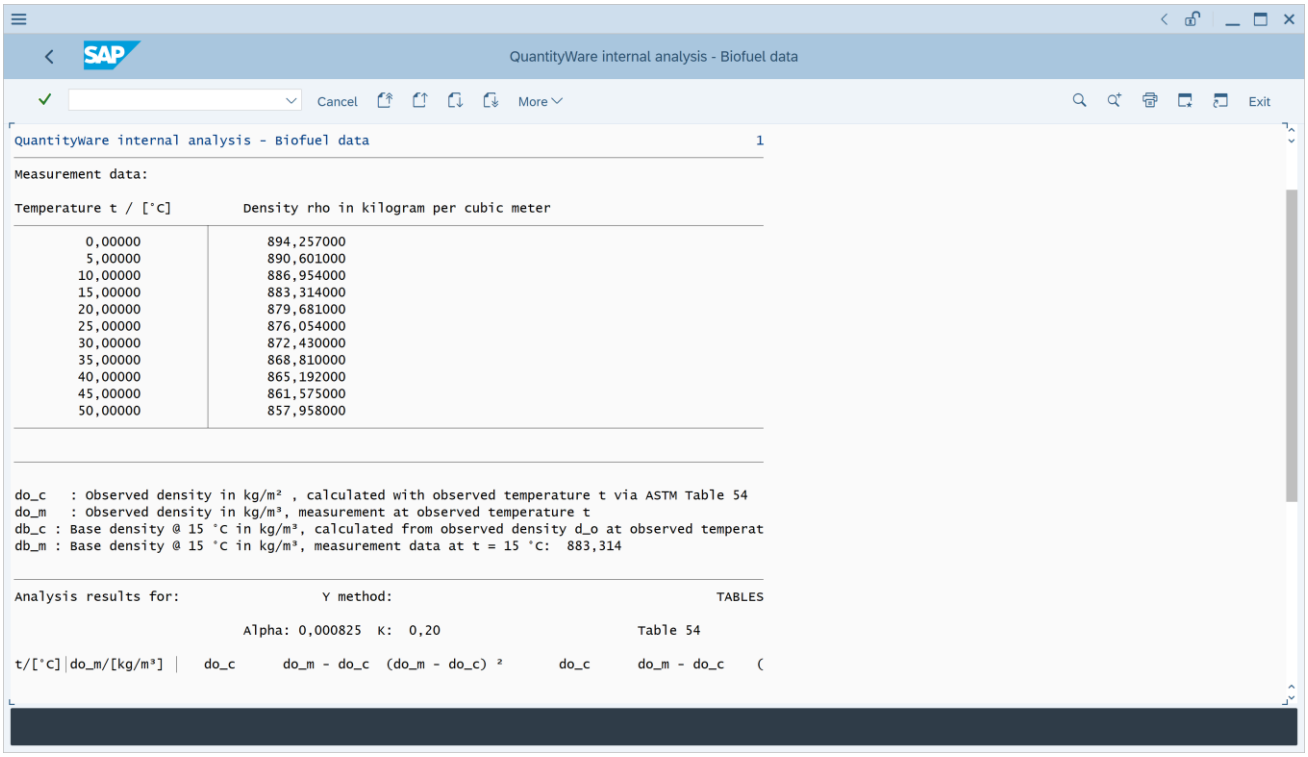
The data presented in reference [1] provides experimentally obtained density values for temperature data in the range of 0 °C to 50 °C (diesel mixtures) and -15 °C to 50 °C (gasoline mixtures), in 5 °C increments for different gasoline and diesel/heating oil mixtures with biofuels. Using a QuantityWare analysis tool, we calculate the theoretical densities for the given temperature points, normalized to the experimentally determined base density at 15 °C, using five different measurement standard models:

- ASTM D1250-04, Table 54B
- DIN 51757-11, Table 54B (essentially ASTM D1250-80 with “German Rounding” and wider ranges)
- ASTM D1250-04, Table 54C
- DIN 51757-11, Table 54Y (essentially representing the ASTM D1250 exponential model with **two** free parameters)
- EN 14214 (biofuel-diesel/heating oil mixtures only) – linear model

The analysis tool is built on the proven QuantityWare BCP implementation and conversion group configuration – in global productive use within the industry.



The difference between the experimental density value and the theoretical value is calculated for each data point, then squared and the sum of these squared residuals (SSR) for all data points of one product mix is calculated as a measurement of the agreement quality between experimental data and theory. The data samples consist of either 11 (diesel mixtures) or 14 (gasoline mixtures) data points [1].



For the ASTM D1250-04, Table 54C calculations, we utilize the standard QuantityWare BCP implementation to calculate the thermal expansion coefficient α at 60 °F. For DIN 51757- 11, Table 54Y calculations, we utilize the standard QuantityWare BCP implementation to calculate the thermal expansion coefficient α at 15 °C and the model constant K.

The collected overall results are presented in the following tables. In these tables we present the relevant calculation parameters as well as the SSR values for all product mixtures.

PTB Product ID	DIN 51757-11 54Y			ASTM D1250-04 54C		DIN 51757 54B	ASTM D1250-04 54B
	α (15 °C)	K	SSR	α (60 °F)	SSR	SSR	SSR
Product:							
Table 1:							
Summer Gasoline (Super)	0.001271	0.91	0.01	0.001218	0.09	0.09	0.11
Ethanol(E100)	0.001078	1.04	0.09	0.001080	0.09	70.01	68.34
E5	0.001231	1.11	0.03	0.001234	0.46	1.78	1.70
E10	0.001228	1.13	0.03	0.001231	0.62	2.79	2.84
E80	0.001115	1.07	0.05	0.001118	0.28	47.86	43.78
E85	0.001106	1.01	0.04	0.001109	0.21	59.88	63.25
Table 2:							
Winter Gasoline (Super)	0.00124	0.93	0.02	0.001242	0.13	0.15	0.13
Ethanol(E100)	0.001079	0.88	0.04	0.001080	0.84	68.92	67.96
E5	0.001248	1.17	0.05	0.001251	0.52	2.41	2.06
E10	0.001248	1.12	0.04	0.001252	0.70	3.56	3.43
E80	0.001120	1.04	0.03	0.001123	0.28	34.13	30.00
E85	0.001111	0.95	0.07	0.001112	0.23	50.95	48.12

- **SSR: Sum of Squared Residuals in $(kg/m^3)^2$**
- **α (15 °C) and (60 °F) in 1 / °C are the thermal expansion coefficients calculated via the respective model function from the data samples**
- **K is a dimensionless model constant**

The “best fit” SSR value is highlighted with green background color in the result table, the “second best fit” SSR value is highlighted with light green background color.

PTB Product ID	DIN 51757-11 54Y			ASTM D1250-04 54C		DIN 51757 54B	ASTM D1250-04 54B	BS EN 14214
	α (15 °C)	K	SSR	α (60 °F)	SSR	SSR	SSR	SSR
Table 3:								
Winter diesel	0.000853	0.68	0.01	0.000851	0.02	2.22	2.23	1.39
B100(RME)	0.000823	0.46	0.02	0.000818	0.05	2.19	2.19	0.06
B5(RME)	0.000854	0.40	0.01	0.000850	0.02	1.58	1.60	1.43
B7(RME)	0.000852	0.57	0.01	0.000849	0.02	1.32	1.38	1.22
B100(SME)	0.000826	0.37	0.02	0.000819	0.05	2.91	2.88	0.17
B5(SME)	0.000853	0.51	0.00	0.000850	0.02	1.55	1.58	1.40
B7(SME)	0.000853	0.45	0.01	0.000849	0.02	1.48	1.34	1.37
Table 4:								
Summer diesel	0.000822	0.47	0.01	0.000819	0.03	1.27	1.17	3.22
B100(RME)	0.000825	0.20	0.01	0.000818	0.05	2.12	2.16	0.05
B5(RME)	0.000823	0.36	0.01	0.000819	0.03	1.14	0.91	3.04
B7(RME)	0.000821	0.61	0.01	0.000819	0.03	0.79	0.82	2.49
Table 5:								
Heating oil	0.000834	0.60	0.01	0.000831	0.02	1.20	1.50	2.39
B10(RME)	0.000834	0.49	0.01	0.000830	0.02	0.64	0.68	1.98
B20(RME)	0.000833	0.49	0.01	0.000829	0.03	0.33	0.32	1.51
B50(RME)	0.000828	0.48	0.01	0.000825	0.04	0.11	0.10	0.51

- **SSR: Sum of Squared Residuals in $(kg/m^3)^2$**
- **α (15 °C) and (60 °F) in 1 / °C are the thermal expansion coefficients calculated via the respective model function from the data samples**
- **K is a second dimensionless model constant**

In order to be able to interpret the SSR values, QuantityWare has analyzed the individual theoretical and experimental value deviations carefully. The following tables provide a classification of the SSR values listed above.

Gasoline data:

SSR/ $(kg/m^3)^2$	Agreement: measurement - calculation
0.0 - 0.1	excellent
>0.1 - 0.5	very good
>0.5 - 2.0	good
>2.0 - 3.5	acceptable for temperatures at or below 40 °C
>3.5 - 5	acceptable for temperatures at or below 35 °C
> 5	not acceptable

Diesel data:

SSR/ $(kg/m^3)^2$	Agreement: measurement - calculation
0.0 - 0.1	excellent
>0.1 - 0.3	very good
>0.3 - 1.0	good
>1.0 - 2.5	acceptable for temperatures at or below 40 °C
>2.5 - 4	acceptable for temperatures at or below 35 °C
> 4	not acceptable

These two classification matrices have been derived via a careful inspection of all 30 single product data samples from reference [1], considering the following measurement accuracy statements:

1. Assuming a statistically even distribution of deviations between measurement data values and theoretical values, an SSR of e.g. 3.5 $(kg/m^3)^2$ equals an average residual for a single data point (11 / 14 data points) of ±0.56 kg/m^3 / ±0.5 kg/m^3.

However, all 30 data samples show that for temperatures above 30 °C, deviations increase exponentially, such that the deviation below 35 °C is typically ±0.4 kg/m³ or less for SSR values below 3.5 $(kg/m^3)^2$.

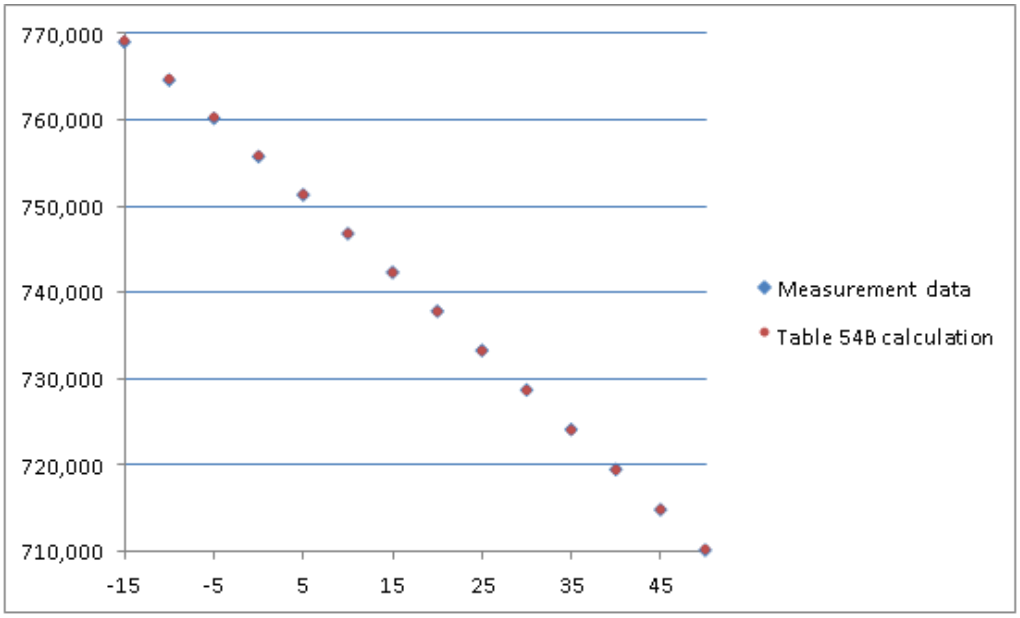
2. The typical measurement accuracy (repeatability / reproducibility) of density data **in the field** may spread globally - depending on the apparatus and method chosen – between 0.1 kg/m³ and 1 kg/m³.
3. The precision statement (95% confidence level) for VCF/CTL calculation values of ASTM D1250 [2] at 100 °F (approx. 38 °C) is ±0.05% , and at 150 °F (approx. 66 °C) ±0.15%, which corresponds to absolute density calculation precisions - assuming a base density of 800 kg/m³ - of approx. ±0.4 kg/m³ (38 °C) to ±1.2 kg/m³ (66 °C).

The following four examples provide a graphical representation of the experimental and theoretical density values for selected data samples. Note that at 15 °C, the theoretical and experimental values coincide, since the measured base density at 15°C has been taken as a normalization reference point for the theoretical calculations. Each calculation requires the input of a base density and an observed temperature, for which a volume correction factor (VCF/CTL) is calculated. This volume correction factor is then used to calculate the density at observed temperature. All four examples are ASTM D1250-04 Table 54B calculations.

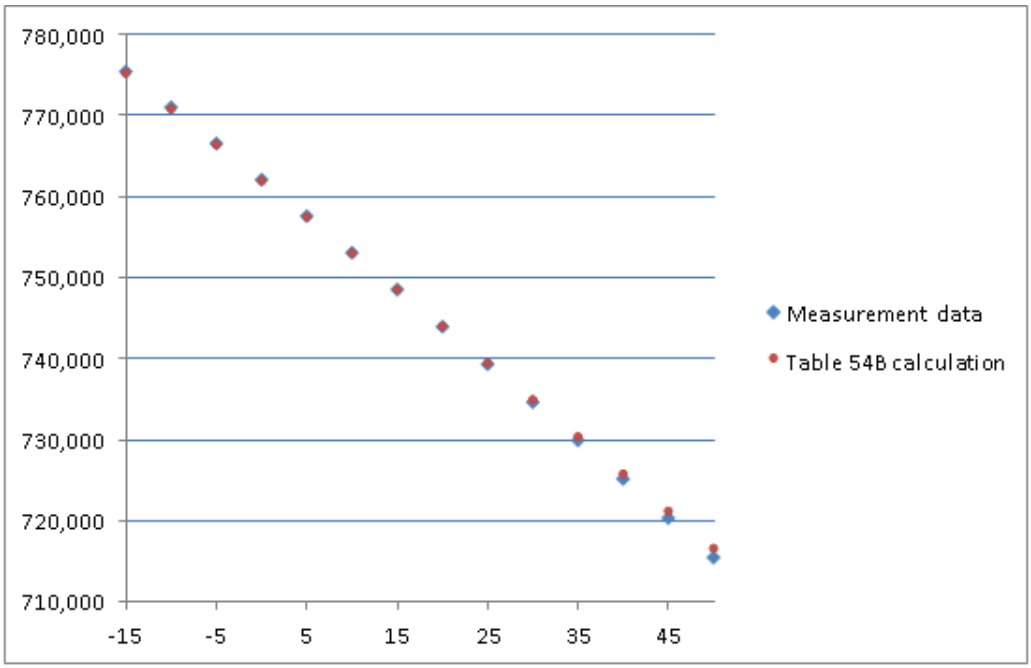
With ASTM D1250-04, the table nomenclature (e.g. Table 54A, Table 6B, Table 54C ...) has been replaced with implementation procedure names. Since many industry experts are not aware of this and adhere to the “legacy” table nomenclature, QuantityWare has decided to follow the “legacy” nomenclature in this paper too.

In all four graphics on the next two pages, the y-axis shows the density values in kg/m³, the x-axis the temperature values in °C.

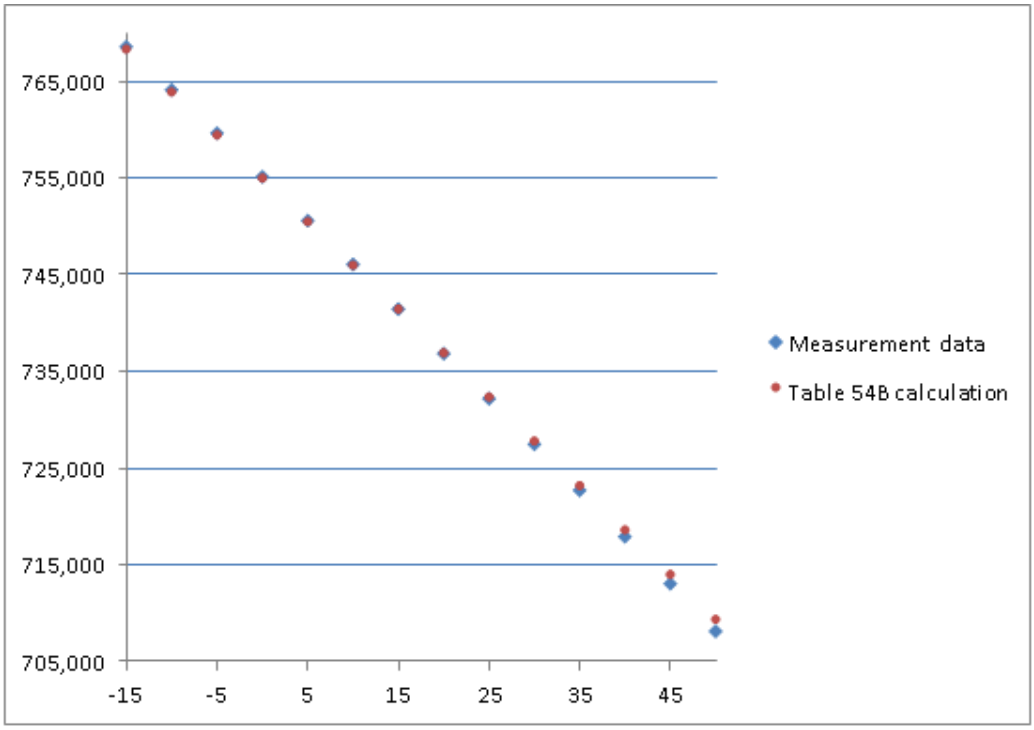
Example 1: SSR 0.11 (kg/m³)² - Gasoline (Summer, Super)



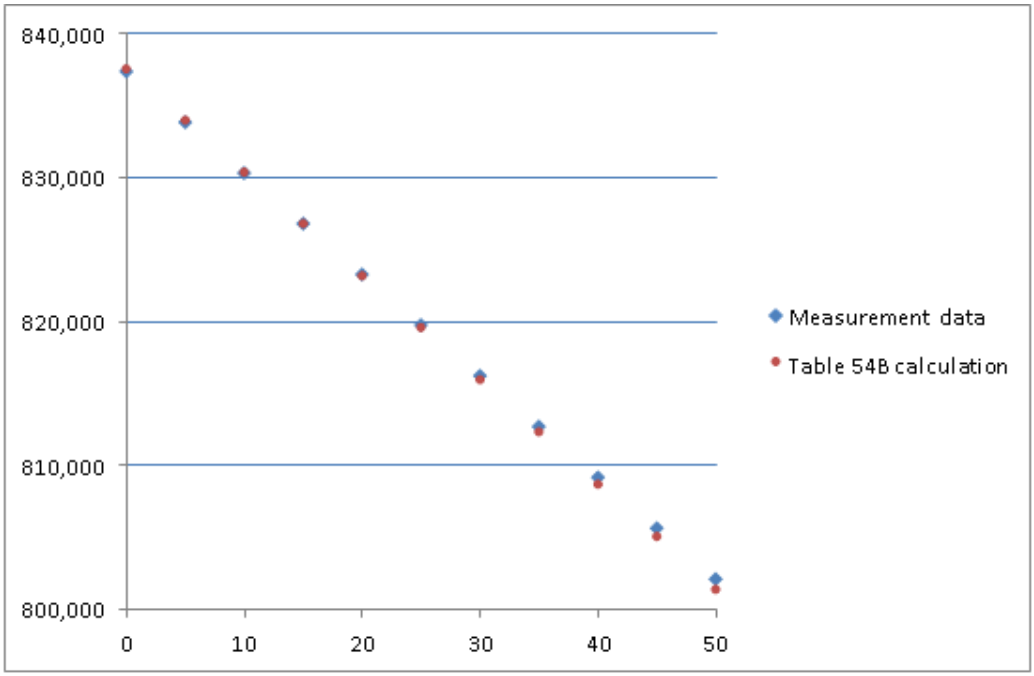
Example 2: SSR 2.84 (kg/m³)² - E10 (Summer, Super)



Example 3: SSR 3.43 (kg/m³)² - E10 (Winter, Super)



Example 4: SSR 1.38 (kg/m³)² - B7 RME Winter Diesel



ASTM D1250 Table C calculations always provide a very good to excellent agreement between measurement and calculation data. However, the determination of a product specific thermal expansion coefficient α requires more effort (laboratory analysis of sample data) compared to density measurements, thus application of Table C calculations is not as wide-spread within the industry.

Since DIN 51757-11 Table 54Y calculations are based on a theoretical model with two free

parameters, these results always provide an excellent agreement between measurement and calculation data.

From an industry point of view, a recommendation concerning the usage of a measurement standard for biofuel mixtures has to consider any additional effort that such a recommendation may require. Thus, the guiding principles for our recommendation are:

- "Keep it simple". ASTM D1250 methods are already available, known and accepted within the industry
- If possible, utilize an ASTM D1250 Table B procedure – all required data (density and temperature) is already known
- If Table B procedures cannot be used, use ASTM D1250 Table C procedure, which require knowledge of the thermal expansion coefficient α – this introduces a minor effort to existing software landscapes, since validated ASTM D1250 implementations already contain Table C calculation methods

The recommendations in the "Management Summary and Recommendations" chapter of this working paper have been derived based on the guiding principles and detailed data presented in this chapter.

4. ASTM D1250 Table C – Details

In this chapter we provide a brief overview of the basic equation for temperature corrections of crude oil and products, with a focus on the "C table" implementations for interested experts.

The fundamental equation for ASTM D1250 calculations has the following mathematical expression:

$$CTL = \rho(t)/\rho(60\ °F) = e^{[-\alpha\Delta t(1+0.8\ \alpha\Delta t)]}$$

where CTL (formerly known as VCF (volume correction factor)) is the correction factor for the temperature of the liquid, t is the alternate temperature in °F, α is the thermal expansion coefficient α at the base temperature of 60 °F in 1/°F and Δt is the difference between the alternate temperature and base temperature. ρ (t) is the product density at temperature t, ρ(60 °F)is the density of the product at 60 °F.

Once the thermal expansion coefficient α at 60 °F is known for a product, the volume correction factors can be calculated.

Since it is easier to measure a product density (either at base or any observed temperature), additional equations have been defined - based on experimental data - to include product specific calculation models to calculate the thermal expansion coefficient α using the base density of a product. If the density is not known at base temperature, the solution for this equation is then found via mathematical iteration (ASTM D1250-04 utilizes a modern Newtonian iteration scheme).

Thus, if oil companies utilize ASTM D1250 Table A, B or D calculations, software implementations calculate the thermal expansion coefficient α at the base temperature of 60 °F based on "hard coded" product specific constants and additional equations and apply the above noted fundamental equation. These constants have been derived from experimental data collected and analyzed roughly between 1970 and 1980. The original developers of the ASTM D1250 exponential model foresaw that future crude oil and products may show slightly different thermal expansion behavior and included the Table C calculations into ASTM D1250, so that companies would have the option to rely on ASTM D1250 Table C calculations for all products, if they are willing to work with thermal expansion coefficients for well-defined product groups in addition to (base) density values and temperatures.

What should also be noted is that the exponential ASTM D1250 model described in this chapter can be rewritten as a linear equation (Taylor expansion of exponential function: $e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots, -\infty < x < \infty$, considering only the first term, neglecting also the quadratic term of Δt):

$$\rho(t) = \rho(60\ °F)\ (\ 1 - \alpha\ \Delta t)$$

This approximation is valid for temperature deviations Δt such that $\alpha\ \Delta t << 1$. This fact explains why linear models may also be utilized to describe the thermal behavior of crude oil and products, such as EN 14214. The producers of biofuel products have started to apply such apparently simpler models in their calculations, which has unfortunately lead to uncertainty within the industry. It is not the aim of this paper to favor either model, both approaches can be justified; however, considering the fact that the oil industry has invested massive resource into existing solutions, and that with the ASTM D1250 Table C approach, a universal and future proof concept is already available and in use within the industry, the recommendations of this paper are justifiable from both scientific and business standpoint.

If one replaces the constant factor of 0.8 in the fundamental equation above and introduces a second model constant K, the DIN 51757-11 Table 54Y model is defined, at base temperature of 15 °C

The overview above is also valid for base temperatures of 15 °C and 20 °C. While ASTM D1250-80 introduced additional “hard coded” product specific constants for these temperatures, ASTM D1250-04 internally always performs calculations at 60 °F and converts results via soft conversions to other base temperatures. Thus, ASTM D1250-04 Table C calculations always require a thermal expansion coefficient α at 60 °F (either in 1/°C or 1/°F)

5. References

[1]: Temperature conversion of biofuel-mineral fuel mixtures and biofuel-heating oil mixtures.

[2]: API MPMS Chapter 11.1, adjunct to ASTM D1250-04

Legal Notices