

API MPMS Chapter 11.3.3, Miscellaneous Hydrocarbon Product Properties – Denatured Ethanol Density and Volume Correction Factors

Proposed changes to the 2nd edition, this would become the 3rd edition:

Rationale for Ballot:

A new Annex E is proposed to be added to API MPMS Chapter 11.3.3. The addition of Annex E is needed to address the custody transfer of fuel ethanol at elevated pressures. The research work that went into development of 11.3.3 was limited to 50 psig pressures and the pressure effect on the density was not considered significant during the initial development of 11.3.3. Further discussions with users of the standard have indicated that there is an industry need for correction of fuel ethanol volumes at elevated pressures. The inclusion of Annex E allows volume of fuel ethanol at elevated pressures to be corrected in a manner that is consistent with other API MPMS standards.

Because of the addition of Annex E, it was necessary for clarification to add new wording to Sections 3, 4.1, 4.2. Also, a new Section 4.3 was added to explain the pressure correction for Fuel Ethanol and point to Annex E

Below are the proposed modifications to the body of API MPMS Chapter 11.3.3. The proposed new Annex E follows those proposed modifications.

The remainder of the document is NOT open for ballot. Please vote and comment only on the proposed changes below.

The following sections are proposed to be modified in MPMS 11.3.3

Section 3 Terms and Definitions

The following terms and definitions are proposed to be added and are part of this revision

3.16 Correction for the effect of Temperature on Liquid (CTL)

Compensates for the effect of temperature on a liquid.

3.17 Correction for the effect of Pressure on Liquid (CPL)

Compensates for the effect of pressure on a liquid.

3.18 Correction for Temperature and Pressure of a Liquid (CTPL)

Corrects a volume at an observed temperature and pressure to an equivalent volume at a reference temperature and pressure and is equal to $CTL \times CPL$. This combination of factors is also often referred to as a VCF.

Section 4.1 Denatured 99+% Fuel Ethanol

The following sentences are proposed to be added at the end of the first paragraph of Section 4.1

If the observed conditions are at elevated pressure, then a CPL for the liquid should be calculated according to the procedures outlined in Annex E and a combined CTPL should be applied to correct the observed density or volume to 60 °F and standard atmospheric pressure.

The first paragraph therefore becomes:

For volume or density correction from observed temperature to 60 °F, the implementation procedure given in API MPMS Ch. 11.1-2004 shall be used for denatured 99 % fuel ethanol. Denatured 99+ % fuel ethanol is considered to be a “special application” (formerly known as Table 6C or Table 54C) with an alpha coefficient of 0.000599 °F or 0.001078 °C (Annex A). If the observed conditions are at elevated pressure, then a CPL for the liquid should be calculated according to the procedures outlined in Annex E and a combined CTPL should be applied to correct the observed density or volume to 60 °F and standard atmospheric pressure

Section 4.2 Denatured 95 % to 99 % Fuel Ethanol

The following sentence are proposed to be added at the end of the first paragraph of Section 4.2

If the observed conditions are at elevated pressure, then a CPL for the liquid should be calculated according to the procedures outlined in Annex E and a combined CTPL should be applied to correct the observed density or volume to 60 °F and standard atmospheric pressure.

The first paragraph becomes:

For volume or density correction from observed temperature to 60 °F, the implementation procedure given in API MPMS Ch. 11.1-2004 shall be used for ethanol denatured with 1 % to 5 % by volume of either natural gasoline or gasoline (Annex B). Such denatured ethanol is considered to be a “special application” (formerly known as Table 6C or Table 54C) with an alpha coefficient of 0.000603 °F or 0.001085 °C (Annex C). For more information on denaturant choice, see Annex B. For more information on the applicability of these alpha coefficients to other denaturants, see Annex C and Annex D. If the observed conditions are at elevated pressure, then a CPL for the liquid should be calculated according to

the procedures outlined in Annex E and a combined CTPL should be applied to correct the observed density or volume to 60 °F and standard atmospheric pressure.

The following section is proposed as a new section to be added to MPMS 11.3.3

4.3 Pressure Correction of Fuel Ethanol

For volume correction of fuel ethanol being transferred at elevated pressures, the compressibility of the fuel ethanol should be considered. The experimental program for development of the temperature correction factors did not account for elevated pressures, so no independent data for fuel ethanol exist to demonstrate the differences between fuel ethanol and reagent grade at the denaturant concentrations considered by this standard. Annex E was developed based upon reagent grade ethanol and should be used for applications where pressure corrections are applied.

Annex E provides calculation methods for determining the pressure correction factor, CPL, for fuel ethanol. Sections 4.1 and 4.2 provide methods for determining the temperature correction factor, CTL, for fuel ethanol. Taken together the overall volume correction factor, VCF, or correction for temperature and pressure, CTPL is the product of CTL x CPL.

Proposed MPMS Chapter 11.3.3 Annex E

Abstract

The secant compressibility of ethanol has been correlated over the range of -40 to 60 °C (-40 to 140 °F) over the pressure range of 0 to 15 MPa (0 to 2200 psi) to a correlation form suitable for correction of pressurized liquid ethanol streams to saturation conditions.

Keywords: ethanol; compressibility

When ethanol is metered at elevated pressures, it is necessary to account for the difference between the density of ethanol at the elevated pressure and standard reference pressures. The isothermal compressibility of pure ethanol at elevated pressures has been determined by many experimentalists and several equations of state have been proposed. Sun and coworkers (Sun, Schouten, Kortbeek, & Biswas, 1990) found that a third-degree Davis-Gordon expansion fit experimental data best over a range of 0 to 280 MPa. An equation of state for thermodynamic properties of ethanol was developed by Dillon and Penocello (Dillon & Penocello, 2003) which agreed with the compressibilities found by Sun and coworkers.

Equations of State for Ethanol

Sun, et al. proposed two different equations of state for liquid ethanol to cover the ranges of 193 to 263 K (1991) and 273 to 333 K (1990) for pressure up to 280 MPa. However, these pressure explicit equations of state are not particularly useful for most fuel ethanol applications which were developed to follow the API MPMS Chapter 11.1 methodology (2004). The current methodology used in API MPMS Chapter 11.1 (2004) is based upon the pressure correction in the historical standard, API MPMS Chapter 11.2.1 (American Petroleum Institute, 1984) which expresses the pressure dependence of the density by the equation form:

$$CPL = \frac{\rho(t, P)}{\rho(t, P_0)} = \frac{1}{[1 - F(p - p_0)]}$$

Where

- CPL Correction for effect of Pressure on the Liquid
- $\rho(t, P)$ density at measured conditions (temperature and pressure)
- $\rho(t, P_0)$ saturation density at measured temperature
- P measured pressure
- P_0 saturation pressure at measured temperature
- F secant isothermal compressibility

This equation form and its relationship to CTL and CTPL are more thoroughly discussed in section 11.1.3.2 of API MPMS Chapter 11.1 (2004). The hydrocarbon correlation for F in API MPMS Chapter 11.1 (2004) is valid for temperatures between -30 to 90 °C (-20 to 200 °F) and 0 to 10.3 MPa gauge (0 to 1500 psig), so a similar range of application was selected for development of this standard.

Ethanol Correlation

The calculated density of ethanol using the equations of state developed by Sun (1991) (1990) was used to calculate the secant compressibility of pure ethanol from -40 to 60 °C and 0 to

15 MPa over-pressure. The secant compressibility of ethanol over this range is well represented by the correlation

$$F_s = a_0 + a_1 \times t + a_2 \times t^2$$

Where

F_s scaled compressibility factor, $F \times 10^6$ (SI) or $F \times 10^5$ (US Customary)

t temperature in °C (SI) or °F (US Customary)

Variable	SI Units	US Customary Units
F_p	$10^6/\text{MPa}$	$10^5/\text{psi}$
T	°C	°F
A_0	910.46	0.562134
A_1	5.6849	1.92283E-3
A_2	1.8703e-2	3.98002E-6

This correlation fit the reported density data within 0.05% and yielded a 1 σ relative uncertainty for F_s of 4.5%.

Example E-1 (US Customary Units)

The density of ethanol at 725 psig and 86 °F is required. The density of ethanol at 86 °F and saturation pressure is 6.5173 lb/gal. Since saturation pressure is below atmospheric pressure, zero gauge pressure will be used as the base pressure.

The calculated value of

$$F_s = 0.562134 + 86 \times (1.92283 \times 10^{-3} + 86 \times 3.98002 \times 10^{-6}) = 0.7659$$

$$F = F_s \times 10^{-5} = 0.7659 \times 10^{-5} \text{ psi}^{-1}$$

$$\begin{aligned}
CPL &= \frac{1}{[1 - F(p - p_0)]} \\
&= \frac{1}{[1 - 0.7569 \times 10^{-5}(725 - 0)]} \\
&= \frac{1}{[0.994512]} = 1.005518 \\
\rho &= \rho_0 \times CPL \\
&= 6.5173 \times 1.005518 \\
&= 6.5533 \text{ lb/gal}
\end{aligned}$$

Example E-1 (SI Units)

The density of ethanol at 5 MPa gauge and 30 °C is required. The density of ethanol at 30 °C and saturation pressure is 780.945 kg/m³. Since saturation pressure is below atmospheric pressure, zero gauge pressure will be used as the base pressure.

The calculated value of

$$F_p = 910.46 + 30 \times (5.6849 + 30 \times 1.8703 \times 10^{-3}) = 1097.84$$

$$F = F_p \times 10^{-6} = 1.09784 \times 10^{-3} \text{ MPa}^{-1}$$

$$\begin{aligned}
CPL &= \frac{1}{[1 - F(p - p_0)]} \\
&= \frac{1}{[1 - 1.09784 \times 10^{-3}(5 - 0)]} \\
&= \frac{1}{[0.994511]} = 1.005519 \frac{\text{kg}}{\text{m}^3} \\
\rho &= \rho_0 \times CPL \\
&= 780.945 \times 1.005519 \\
&= 785.255 \text{ kg/m}^3
\end{aligned}$$

Example E-2 (US Customary Units)

A container has a gross observed volume of 10,000 gallons of fuel ethanol at 1500 psig and 85 °F. What is the volume at 60 °F?

Note, that since the saturation pressure is below atmospheric pressure, zero gauge pressure will be used as the base pressure and that since this is fuel ethanol, the density at 60 °F is not required to perform the calculation.

For this calculation, both the CTL and CPL are required.

API MPMS Ch. 11.1-2004, Section 11.1.6.1, returns a VCF of 0.98496 for inputs of 85°F and an alpha of 0.000599/°F. The calculated value of

$$F_s = 0.562134 + 85 \times (1.92283 \times 10^{-3} + 85 \times 3.98002 \times 10^{-6}) = 0.75433$$

$$F = F_s \times 10^{-5} = 0.75433 \times 10^{-5} \text{ psi}^{-1}$$

$$\begin{aligned} CPL &= \frac{1}{[1 - F(p - p_0)]} \\ &= \frac{1}{[1 - 0.75433 \times 10^{-5}(1500 - 0)]} \\ &= 1.011444 \\ GSV &= GOV \times CPL \times CTL \\ &= 100000 \times 1.011444 \times 0.984960 \\ &= 9962.32 \text{ gal} \end{aligned}$$

Example E-2 (SI Units)

A container has a gross observed volume of 40.00 m³ at 10 MPa gauge and 30 °C is required. The density of ethanol at 30 °C and saturation pressure is 780.945 kg/m³. Since saturation pressure is below atmospheric pressure, zero gauge pressure will be used as the base pressure.

Note, that since the saturation pressure is below atmospheric pressure, zero gauge pressure will be used as the base pressure and that since this is fuel ethanol, the density at 60 °F is not required to perform the calculation.

API MPMS Ch. 11.1-2004, Section 11.1.7.1, returns a VCF of 0.98377 for inputs of 30 °C and an alpha of 0.001078/°C. The calculated value of

$$F_p = 910.46 + 30 \times (5.6849 + 30 \times 1.8703 \times 10^{-3}) = 1097.84$$

$$F = F_p \times 10^{-6} = 1.09784 \times 10^{-3} \text{ MPa}^{-1}$$

$$\begin{aligned} CPL &= \frac{1}{[1 - F(p - p_0)]} \\ &= \frac{1}{[1 - 1.09784 \times 10^{-3}(10 - 0)]} \\ &= 1.01110 \\ GSV &= GOV \times CPL \times CTL \\ &= 40.00 \times 1.01110 \times 0.98377 \\ &= 39.7876 \text{ m}^3 \end{aligned}$$

References

(These references will be added to API MPMS Chapter 11.3.3 Bibliography)

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