

Issues with T50 and T90 as Match Criteria for Ethanol-Gasoline Blends

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ABSTRACT

Modification of gasoline blendstock composition in preparing ethanol-gasoline blends has a significant impact on vehicle exhaust emissions. In “splash” blending the blendstock is fixed, ethanol-gasoline blend compositions are clearly defined, and effects on emissions are relatively straightforward to interpret. In “match” blending the blendstock composition is modified for each ethanol-gasoline blend to match one or more fuel properties. The effects on emissions depend on which fuel properties are matched and what modifications are made, making trends difficult to interpret. The purpose of this paper is to illustrate that exclusive use of a match blending approach has fundamental flaws.

For typical gasolines without ethanol, the distillation profile is a smooth, roughly linear relationship of temperature vs. percent fuel distilled. Hence the use of three points on the curve (T10, T50, and T90, defined as the 10%v, 50%v, and 90%v evaporated temperatures) has been sufficient to define their volatility-related behavior in engines. These parameters are commonly “matched” in studies intended to evaluate fuel composition effects on emissions. For ethanol-gasoline blends, higher boiling-point hydrocarbons must be added to match T50 and T90 with fuels having less ethanol. The degradation of emissions which can result is primarily due to the added hydrocarbons, but has often been incorrectly attributed to the ethanol. Studies to evaluate the effects of ethanol should be conducted by adjusting the blendstock only as necessary to satisfy ASTM D4814 requirements. Blending ethanol at up to 30%v with an E10 blendstock should generally require only minimal changes in composition to meet ASTM D4814.

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INTRODUCTION

Ethanol is widely used in U.S. gasoline as a means to increase renewable fuel content with corresponding benefits in CO₂ emissions, support for the agricultural economy, and reduced dependence on oil imports. Ethanol is also a cost-effective high-octane fuel component, allowing fuel refiners to substitute lower-cost, lower-octane hydrocarbons in the blendstock while maintaining the octane ratings of the finished fuel [1,2]. A gasoline blendstock specifically formulated to be blended with ethanol is commonly identified as a “blendstock for oxygenate blending” or BOB. At the present time almost all gasoline sold in the U.S. contains 10%v ethanol, with 15%v approved for use in some vehicles, and greater ethanol content being discussed.

Many studies have examined the effect of ethanol content in gasoline on exhaust emissions. These studies can be broadly separated into two types: 1) studies in which ethanol is simply

added (“splash-blended”) to a fixed-composition hydrocarbon blendstock, or 2) studies in which, after adding ethanol, the fuel is “match-blended” for one or more properties by varying the BOB composition to maintain certain characteristics of the finished fuel, such as octane ratings, vapor pressure, or parameters of the distillation profile from ASTM International's test method D86.

For typical full-boiling-range gasolines, the distillation profile from an ASTM D86 test is a smooth, roughly linear relationship of temperature vs. percent fuel distilled. Hence the use of three discrete points on the distillation curve (T10, T50, and T90, defined as the 10%v, 50%v, and 90%v distilled temperatures) together with the Reid vapor pressure (RVP) and vapor-liquid ratio temperature have been sufficient to characterize the volatility-related behavior of gasoline in engines. These

parameters have also been commonly used as “match” criteria for blending fuels in studies intended to evaluate the effects of fuel composition on vehicle emissions.

A recent study of particular importance that incorporated match blending of T50 and T90 to evaluate the effect of fuel ethanol content on vehicle emissions is the EPA/V2/E-89 study [3] conducted by the U.S. EPA in partnership with the Department of Energy and the Coordinating Research Council (CRC). The program was conducted to provide the basis for generating updated fuel effects models of the on-road gasoline vehicle fleet, as required by the Energy Policy Act of 2005 (EPA). The purpose of this paper is to illustrate the substantial difference in the distillation characteristics of typical gasoline without ethanol compared to ethanol-gasoline blends, and to illustrate potential issues with match-blending practices for ethanol-gasoline blends used in testing of fuel effects on emissions, particularly the use of T50 and T90 as match-blend criteria.

Many examples in this paper are from a fuels study conducted by the American Petroleum Institute (API) [4] which includes an extensive set of volatility property data for ethanol blends with market gasolines and BOBs of widely varying volatility.

VOLATILITY PROPERTIES

The volatility properties (RVP, vapor-liquid ratio temperature, and distillation profile) of ethanol-gasoline blends are greatly affected by non-ideal mixture behavior. This behavior is a consequence of molecular interactions between the gasoline components and ethanol. In ethanol-gasoline blends, the nonpolar hydrocarbon molecules in gasoline interfere with the intermolecular hydrogen bonding between the polar ethanol molecules, and the ethanol interferes with molecular interactions between the gasoline hydrocarbons. (Nonpolar molecules have an even distribution of electron charge, while polar molecules have an uneven distribution creating positive and negative poles.) These interferences with intermolecular bonding allow both types of molecules to more readily escape the liquid as vapor, which is manifested as increased vapor pressure and reduced distillation temperatures [1,4, 5, 6, 7, 8].

The polar nature of ethanol also leads to a heat of vaporization (HoV) of ethanol that is ~2.6 times greater than typical gasoline on a mass basis and ~4.2 times greater on a stoichiometric air-fuel mixture basis [1]. This difference is considerably less for low- and mid-level ethanol blends, however. For example, the HoV of a stoichiometric air-fuel mixture for E20 is approximately 20% greater than for E10.

Vapor Pressure

When ethanol is added to gasoline at low concentrations, the blend (a non-ideal mixture) exhibits a vapor pressure that is higher than that of both the original gasoline and pure ethanol.

The maximum Reid vapor pressure (RVP) is usually observed when 10%v ethanol or less is added, and further increasing ethanol content typically reduces the RVP [4, 5, 6, 7, 8].

An extensive set of vapor pressure data for ethanol blends with market gasolines and BOBs of varying volatility (ASTM D4814 Class AA to Class E) [9] was reported in the study by API [4]. RVPs for blends of ethanol in three representative gasoline blendstocks spanning a wide range of volatility classes are shown in Figure 1.

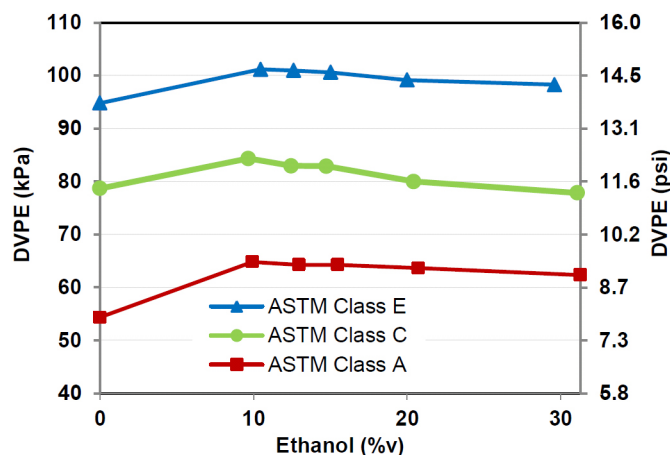


Figure 1. Reid vapor pressures (Dry Vapor Pressure Equivalent) for ethanol-gasoline blends of varying volatility [4]. The ASTM volatility classes shown are for the gasoline blendstock without ethanol (E0).

As shown in Figure 1, the RVP increase with ethanol addition to gasoline is dependent on the RVP (and thus composition) of the gasoline, with greater RVP increase observed for gasoline with lower RVP. Of the 68 E0 gasolines and BOBs included in the API study, the RVP of the resulting E10 blends were nearly always greater than or equal to the RVPs of the E12.5, E15, E20, and E30 blends from the same blendstock.

Vapor-Liquid Ratio

The temperature at which a gasoline exists at an equilibrium vapor-liquid volume ratio of 20:1 at atmospheric pressure ($T_{V/L=20}$) has been shown to correlate with vehicle vapor lock and other hot fuel handling problems. $T_{V/L=20}$ of retail gasoline is controlled depending on the season, with specified minimum values ranging from 35°C to 60°C (95°F to 140°F). Higher volatility corresponds to a lower $T_{V/L=20}$ temperature, and hence fuels with higher $T_{V/L=20}$ values provide greater protection against vapor lock and hot fuel handling problems. This correlation was initially developed for vehicles with suction-type fuel pumps and carburetors. Tests in modern vehicles with pressurized port fuel injection systems have shown good correlation for hydrocarbon-only gasoline [10]. The addition of ethanol to gasoline at a concentration of 10%v significantly decreases the $T_{V/L=20}$ due to non-ideal mixture behavior [4]. The magnitude of the change is dependent on the $T_{V/L=20}$ of the gasoline blendstock, as shown in Figure 2. Additions of higher

levels of ethanol generally result in either no change or a slight increase in $T_{V/L=20}$. As can be seen from the similarities with RVP trends in Figure 1, $T_{V/L=20}$ tends to be correlated with RVP.

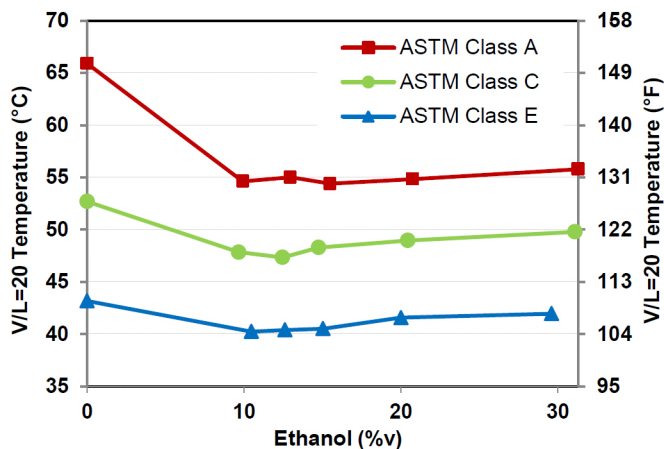


Figure 2. $T_{V/L=20}$ for fuels of varying volatility [4]. The ASTM volatility classes shown are for the gasoline blendstock without ethanol (E0).

Distillation Curve

The non-ideal mixture behavior of ethanol blends with gasoline greatly changes the shape of the distillation curve in the mid-distillation region [4,8]. Figure 3 shows examples of representative distillation profiles from the aforementioned API study [4] for ethanol-gasoline blends made from retail gasoline blendstocks of varying volatility with high, medium, and low T50 values.

As shown in Figure 3, the distillation profiles of the E0 gasolines behave in a smooth and steadily increasing fashion. The non-ideal mixture behavior of the ethanol-gasoline blends is visible as a more slowly rising curve than the gasoline blendstock (i.e., lower temperature for a given volume distilled, or greater volume distilled at a given temperature). This slowly rising curve, or plateau, has been attributed to “near-azeotropic” behavior [8]. For a true azeotrope, the relative concentrations of the components in the vapor are the same as those in the liquid mixture, which leads to a perfectly flat distillation curve. While ethanol-gasoline blends are not true azeotropes, the distillation curve exhibits near-azeotropic behavior. As shown in Figure 3, the use of T10, T50, and T90 is adequate to characterize the distillation profile of the E0 gasolines, but is insufficient to describe the profiles of the ethanol blends as it fails to capture the lower distillation temperatures in the potentially broad near-azeotropic region.

As also shown in Figure 3, increasing ethanol content expands the near-azeotropic region to cover a larger portion of the distillation curve and increases the fraction of fuel evaporated at a given mid-range temperature (e.g., 100 °C, 212 °F). Increasing ethanol content also causes T90 to decrease slightly due to dilution (Figure 4).

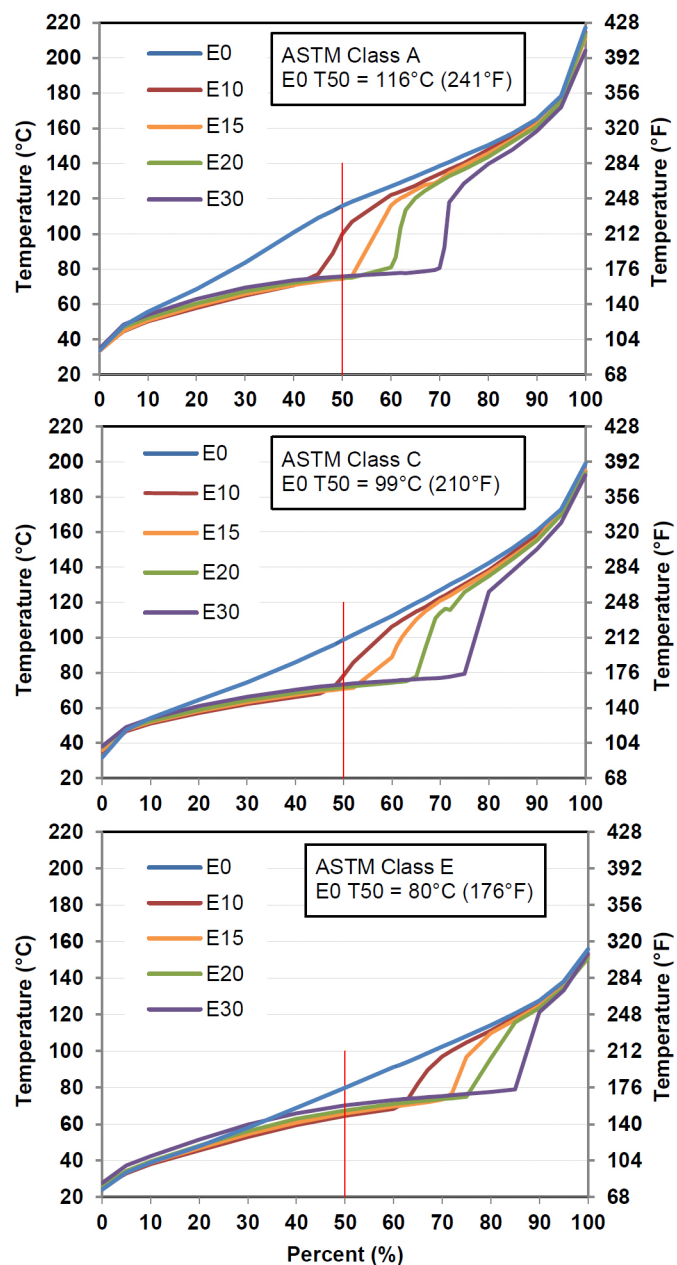


Figure 3. Effect of ethanol addition on D86 distillation profiles for retail gasoline blendstocks with high, mid, and low T50 [4]. The ASTM volatility classes shown are for the gasoline blendstock without ethanol (E0).

The volatility of the gasoline blendstock also influences the magnitude of the T50 response to ethanol. As shown in Figure 4, for a gasoline blendstock with higher T50 (lower mid-range volatility), there is a greater reduction in T50 down to the near-azeotropic region. These trends have implications for whether and how T50 can be matched.

Matching the T50 of an ethanol-containing fuel with the T50 of a fuel with lesser or no ethanol content requires a lower volatility blendstock. This can be accomplished by including a greater fraction of higher boiling point hydrocarbons in the blendstock. For example, in Figure 4 the T50 of the high volatility Class E E0 fuel effectively matches the T50 of the E10

splash blend in the mid-volatility Class C blendstock. Likewise, the T50 of the Class C E0 fuel matches the T50 of the E10 splash blend with the low-volatility Class A blendstock. However, there are limits to how high T50 can be raised for ethanol blends above E10. As can be seen in Figure 4 and from the extensive fuel testing in [4], it becomes essentially infeasible to produce T50 values above 74°C (165°F) even using extremely low volatility blendstocks.

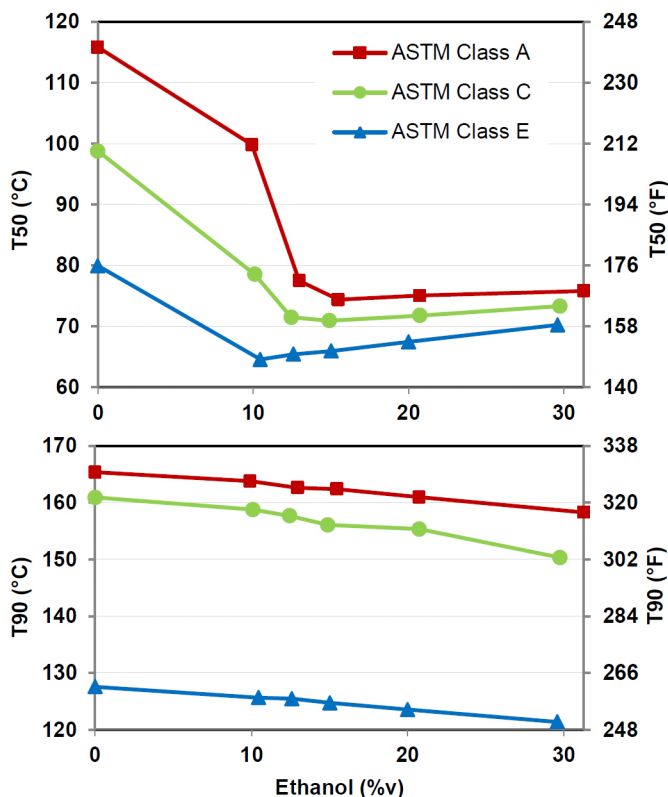


Figure 4. Effect of ethanol addition on T50 and T90 for fuels of Figure 3.

REQUIREMENTS OF ASTM D4814

ASTM D4814, the Standard Specification for Automotive Spark-Ignition Engine Fuel, specifies limits that depend on the volatility class of the fuel [9], as summarized in Tables A-1 and A-2 in Appendix 1 of this paper. Volatility classes are used to ensure that fuel with appropriate volatility is provided for the various geographical and seasonal temperature conditions in the U.S. ASTM D4814 specifies maximum limits on RVP, T10, T50, and T90, and minimum $T_{V/L=20}$ values for six vapor lock protection classes.

ASTM D4814 has been developed and is periodically updated for gasoline in the U.S. market, which until recently contained up to 10%v ethanol and now may contain up to 15%v ethanol. Fuel containing 51-83%v ethanol (only for use in flexible-fuel vehicles, FFVs) is controlled under ASTM specification D5798. At present, mid-level ethanol-gasoline blends containing up to 50%v ethanol are governed by ASTM blend practice D7794 which presumes that blends of gasoline complying with D4814 and fuel complying with either D5798

or D4806, with qualifications, are appropriate for use in FFVs. Certain fuel parameter specifications in D4814 have limits that depend on ethanol content (as discussed below), thus the availability of gasoline with higher ethanol content (e.g., E15) requires that these specifications be verified and possibly updated for those concentrations.

The limits on RVP, $T_{V/L=20}$, and T10 are intended to ensure an acceptable trade-off between vehicle cold starting behavior and vapor lock, but these parameters also influence cold start exhaust emissions and evaporative emissions. The maximum limits on T50 are intended to provide adequate fuel vaporization for good vehicle driveability during the vehicle's transition from cold start to a warmed-up state. A minimum limit on T50 is also specified and is intended to avoid hot fuel handling driveability issues. Limits on maximum T90 are specified to avoid excessive oil dilution and combustion chamber deposits [9,10].

Table 1 of ASTM D4814 also includes maximum limits on the driveability index (DI), which is a function of T10, T50, and T90, and %v ethanol. The DI is defined by equation (1), calculated using temperatures in either °C or °F with appropriately scaled DI limits for each approach:

$$\text{Driveability Index} = 1.5 T_{10} + 3.0 T_{50} + 1.0 T_{90} + 1.33^{\circ}\text{C} (2.4^{\circ}\text{F}) \times \%v \text{ ethanol} \quad (1)$$

Lower values of this index correspond to improved cold start and warm-up driveability due to greater fuel volatility, resulting in improved fuel vaporization and air-fuel mixing. The multiplier of 3 on T50 is indicative of the importance of lower T50 in providing acceptable driveability. In effect, the DI places a weighted combined maximum limit on T10, T50, and T90 in addition to the individual limits on these parameters in ASTM D4814. This index was developed for ethanol blends up to 10%v [11] and was determined in a recent CRC study to be inadequate for 15%v and 20%v ethanol blends [12]. The new equation that has been proposed for ethanol blends from E0 to E20 includes a factor of $9.49 \times \%v \text{ ethanol}$ in place of $2.4 \times \%v \text{ ethanol}$ (°F basis).

According to the API study on property ranges of mid-level ethanol blends [4], blending ethanol with an E10 gasoline BOB at concentrations up to 30% by volume should not pose a problem for meeting ASTM D4814 $T_{V/L=20}$ specifications. Similarly, RVP generally reaches a maximum at an ethanol content of 10%v and is constant or declines with higher ethanol content. (In certain regions of the U.S. during summer months, E10 blends are allowed an RVP that is 1 psi (7 kPa) higher than otherwise required, generally offsetting the RVP increase associated with the ethanol addition.) Hence, BOB modifications should generally not be needed to control these parameters in studies evaluating the effects of ethanol content on emissions if starting with an E10 fuel or using an E10-intended BOB.

There is no minimum limit for T90 and the addition of ethanol (up to and above E10 levels) typically does not cause T50 to decrease below the existing minimum limit of 66 °C (150 °F) applicable for E1 to E10 fuels [4]. It seems reasonable to assume that this limit for E10 could be carried over for E15 and E20-E30 (subject to validation testing) in the future [4]. If so, these fuels should satisfy ASTM D4814 requirements for T50 and T90 and high-boiling-point hydrocarbons would not need to be added to gasoline BOBs to compensate for the ethanol addition.

ANALYSIS AND DISCUSSION

Numerous studies in which ethanol was splash-blended with a fixed gasoline blendstock have demonstrated reductions of vehicle exhaust emissions, particularly particulate matter (PM), non-methane hydrocarbons (NMHC), and the air toxics 1,3-butadiene and benzene. A detailed discussion can be found in [1]. Particularly noteworthy is the reduction of PM emissions with the addition of ethanol, which has been demonstrated in many studies [13, 14, 15, 16, 17, 18, 19] and is supported by fundamental combustion chemistry considerations [15,20,21,22]. As discussed in several papers [1,15,21,22], high-boiling-point gasoline hydrocarbons with low vapor pressure and high double-bond equivalent (DBE) value, primarily aromatic hydrocarbons, have been identified as the predominant contributors to PM emissions. Because the occurrence of decreased PM emissions with splash blending of ethanol is particularly well documented, it serves as a good example to illustrate the potential issues with ethanol-gasoline blend studies that use match blending to maintain T50 and T90 (and appear to obtain the opposite result).

Vehicle emissions studies that employ match blending for T50 and T90 with ethanol-gasoline blended fuels encounter the following four potential issues:

1. T60-T80 can be unmatched despite matched T50 and T90.
2. Effects related to hydrocarbons added with ethanol can confound the observed emissions.
3. Emissions models derived from match-blend emissions studies have the potential for misuse or misinterpretation.
4. Results from these models may not adequately reproduce the actual vehicle emissions data on which the models were based.

Issue 1: Unmatched T60-T80

One potential issue with match blend studies is the behavior of the distillation profile between T50 and T90. Because the distillation curve for ethanol-gasoline blends is not smooth and steadily increasing as it is for gasoline without ethanol (Figure 3), matching T50 and T90 for ethanol-gasoline blends does not ensure that the region in between will also be matched. The addition of higher-boiling-point hydrocarbons to increase T50 also has an impact on the T60 through T80

region. Examples are shown in Figure 5 using data from the EPA/V2/E-89 study [3] and from a recent CRC driveability study (Report No. 666) [12].

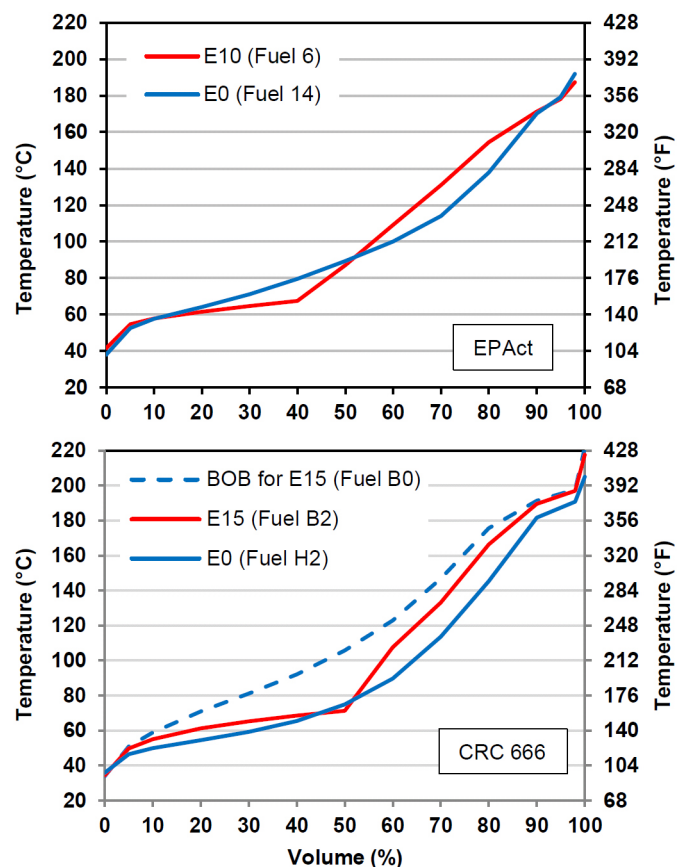


Figure 5. Distillation curves for fuels having matched T50 and T90 in the EPA/V2/E-89 study [3] (top panel) and matched DI (similar T10, T50, and T90, excluding ethanol factor) in the CRC driveability study, CRC Report No. 666 [12] (bottom panel).

In both studies, a variety of fuels were match blended to certain predefined values for T50, T90, or other properties. The E0 and E10 fuels from the EPA/V2/E-89 study shown in Figure 5 (top panel) were formulated to yield matching T50 and T90, as well as matching %v aromatics content and RVP. Similarly, the E0 and E15 fuels from the CRC study (bottom panel) were formulated to have matched DI (excluding the ethanol factor) by having similar T10, T50, and T90 values. However, in both cases, the T60, T70, and T80 values were considerably higher for the ethanol blends than for the corresponding “matched” E0 fuels despite having similar T50 and T90 values. The differences, up to 17 °C (30 °F) for the EPA/V2/E-89 study fuels and up to 21 °C (38 °F) for the CRC study fuels, were similar in magnitude to the increments in T50 and T90 used in the EPA/V2/E-89 study.

These comparisons illustrate a potential issue with using single points on the distillation curve as match blending criteria. Higher T60, T70, and T80 values will likely have an adverse impact on tailpipe emissions (similar in magnitude as the T50 and T90 impacts), even though T50 and T90 are the same.