

Predicting vapour composition and flammability in a fuel tank



Fuel blends consisting of a mixture of gasoline, diesel fuel and ethanol—referred to as dieseline—have shown promise for use in high-compression engines. Such mixtures could be flammable in the headspace above the liquid in a vehicle fuel tank at common ambient temperatures, and it is therefore important to understand the flammability characteristics of these fuel blends.

Authors

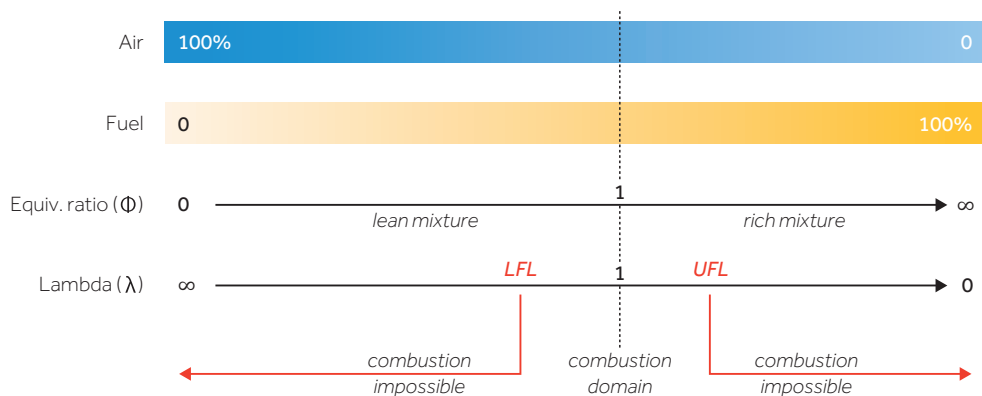
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Background

Current road fuel standards ensure that fuel can be stored in a tank onboard a vehicle in safe conditions. This means that, among other things, the fuel tank should remain free from any risk of fire or explosion. It is therefore desirable to avoid storing a flammable fuel/air mixture in the tank.

For any given fuel there exists a range of concentrations of its vapour in air in order for the mixture to be flammable. Beneath the lower end of that range, referred to as the lower flammability limit (LFL), the fuel/air mixture is too lean to support combustion. Similarly, there is an upper limit of concentration, referred to as the upper flammability limit (UFL), above which the fuel/air mixture is too rich to burn.

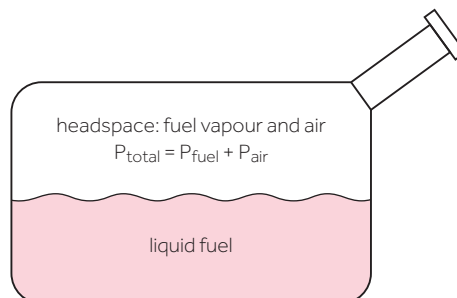
Figure 1: Lower and upper flammability limits



The range between the upper and lower flammability limits broadens slightly as temperature increases; nevertheless, over the range of ambient temperatures of interest for automobile fuel tanks, the two limits are essentially constant for any particular fuel vapour composition. The LFL and UFL values quoted in the literature for different compounds are typically those measured at room temperature.

In a fuel tank, the so-called 'headspace' above the liquid contains a quantity of air and fuel vapour as shown in Figure 2.

Figure 2: Schematic representation of a vehicle fuel tank

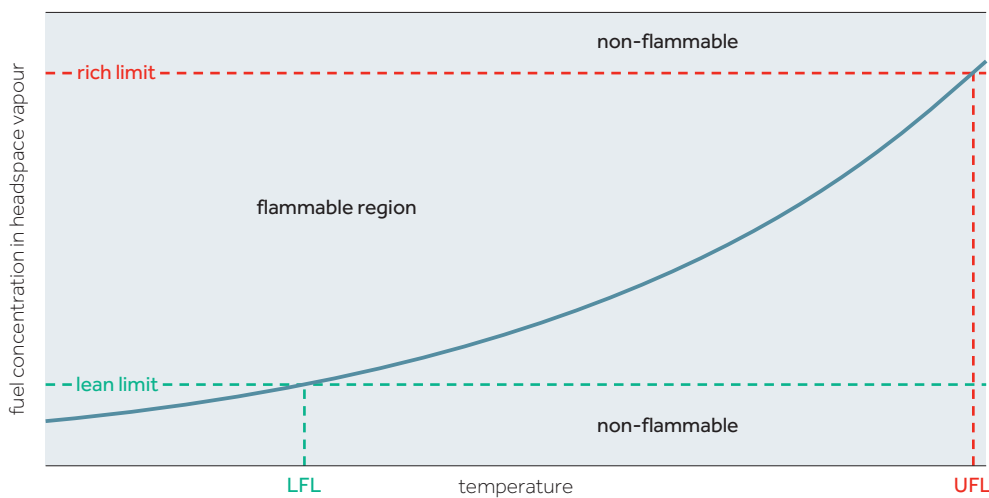




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The concentration of fuel vapour in the headspace at equilibrium depends only upon the temperature for any specific fuel. As the temperature rises, the vapour pressure of the fuel increases, thereby increasing the vapour concentration in the headspace (see Figure 3).

Figure 3: Flammability of the headspace vapour in a fuel tank



Eventually the vapour concentration reaches the lean limit, at which point the mixture in the headspace becomes flammable. The temperature at which this occurs at equilibrium is the LFL temperature. This is similar to the flashpoint temperature, but the apparatus, test procedures and pass/fail criteria are different for flashpoint and flammability limit tests. As a result, the flashpoints measured for liquid fuels are usually close to, but not necessarily exactly the same as, their LFL temperatures.

Above the LFL temperature the headspace contains a flammable mixture. However, if the tank temperature continues to rise, the concentration eventually reaches the UFL temperature, and the mixture in the headspace then becomes too rich to burn. For example, in the case of pure ethanol, the LFL temperature occurs at approximately -18°C and the UFL temperature is reached at about $+43^{\circ}\text{C}$. The headspace in an ethanol fuel tank would therefore be flammable at ambient temperatures from about -18° to $+43^{\circ}\text{C}$.^[1]

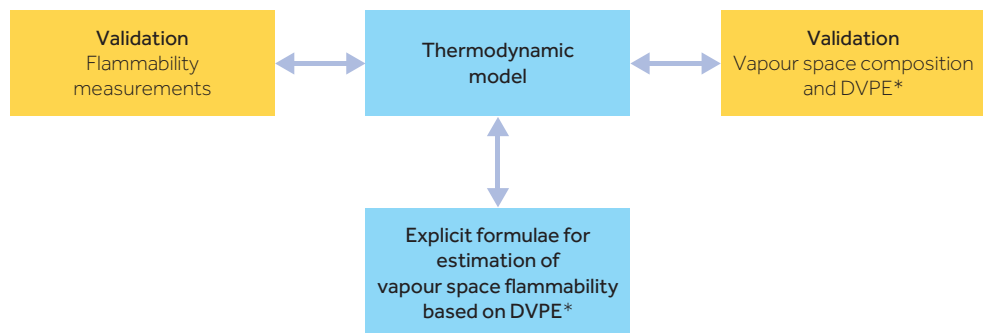
Generally speaking, gasoline volatility requirements have been driven by considerations of cold weather driveability to allow an ignitable mixture in the engine,^[2] with higher vapour pressures stipulated in winter than summer. Nevertheless, there has been a recognition, going back more than 80 years, that it is preferable from a safety perspective to use gasoline fuels which have a fuel/air mixture in the headspace of the tank that is too rich to be flammable.^[3] By contrast, diesel fuels have a low volatility (constrained to have a flashpoint greater than 55°C), which enables them to operate at temperatures below the LFL in the fuel tank.^[2] Mixtures of gasoline, diesel and ethanol, commonly known as 'dieseline mixtures', with an ignition quality which is intermediate between gasoline and diesel, may facilitate the uptake of advanced combustion concepts such as partially premixed combustion (PPC).^[4] The question is, how can these



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mixtures be stored under safe conditions, being that mixing low and high volatility compounds could lead to a flammable vapour in the fuel tank headspace at ambient temperature? This question is the subject of this article which summarises the work published jointly by Concawe and Nexum Research Corporation in four SAE papers.^[5,6,7,8] The elements of the study are outlined in Figure 4.

Figure 4: Elements of the study



* Dry vapour pressure equivalent

The basis of the mathematical model

An outline of the mathematical formulation is given below (for full details please see references 5–8):

1. Find the saturation vapour pressure for each volatile component.
2. Determine the liquid and vapour phase fraction of each component.
3. Determine the amount of air present in the headspace, from the difference between atmospheric pressure and the summed partial pressures of all components.

As part of the above three steps, there is a need to account for non-ideal mixing between ethanol and hydrocarbons using activity coefficients (γ_i):

$$P_i = \gamma_i X_i P_{i,sat} \quad (1)$$

where:

P_i = vapour pressure of component i in the fuel mixture at equilibrium

γ_i = activity coefficient of component i in the blend (estimated using a Margules two-suffix equation^[5])

X_i = mole fraction of component i in the liquid phase of the blend at equilibrium

$P_{i,sat}$ = equilibrium saturation pressure of component i alone

If no ethanol is present, the activity coefficient for the hydrocarbons is equal to 1.

Equation 1 then represents Raoult's Law for ideal mixtures.



Gasoline can contain several hundred hydrocarbon components. The method puts each hydrocarbon into one of 14 buckets of C₃ to C₈ compounds chosen to represent the volatile hydrocarbon fraction of the gasoline. The hydrocarbons range from propane for the lightest fraction to xylene representing the heaviest.

All heavier hydrocarbon species (e.g. diesel) were considered to have a negligible direct impact on the vapour phase composition and pressure, acting only as inert diluents in the liquid phase.

The rich limit of the mixture is estimated from the literature flammability limits for the 14 hydrocarbon pseudo-components plus ethanol, along with the Le Chatelier mixing rule:

$$X_L = 1 / \sum_{i=1}^N X_i / X_{Li} \quad (2)$$

where:

X_L = mole fraction of the gasoline vapour in the gasoline/air mixture at the lean or rich flammability limit

X_i = mole fraction of component i in the gasoline vapour

X_{Li} = mole fraction of component i in air at the rich limit if it were present on its own

Experimental measurements to validate the model

There are two aspects to be validated: the ability of the model to predict the properties of the vapour phase; and the determination of flammability based on the vapour phase composition determined by the model.

Various mixtures were created based on the components in Table 1.

Table 1: Components used in the test fuel blends

Base fuel	Mixture
Diesel	European ULSD ^a , 5% FAME (cloud point = -4°C)
Gasoline G1	45 kPa DVPE gasoline, summer blend (E0)
Gasoline G2	60 kPa DVPE gasoline, mid-season blend (E0)
Gasoline G3	90 kPa DVPE gasoline, winter blend (E0)
Gasoline G4	54 kPa DVPE gasoline, containing ETBE ^b (E0)
Ethanol	Neat ethanol containing no denaturant

^a Ultra-low-sulphur diesel ^b Ethyl tertiary butyl ether



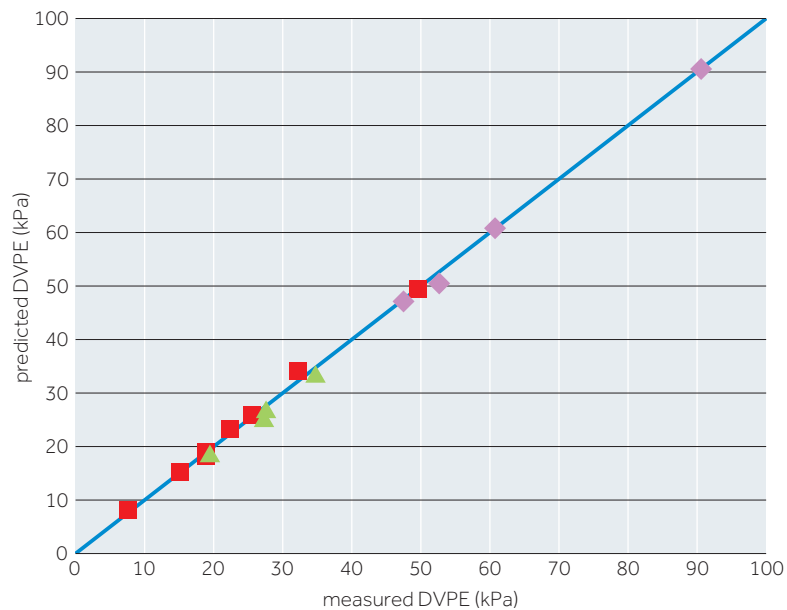
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The measure of 'dry vapour pressure equivalent' (DVPE)^[2] is a standard vapour pressure measurement for gasoline, corresponding to equilibrium at 37.8°C (100°F) in a container that is 20% full of liquid fuel. By specifying these conditions in the model, the total vapour pressure computed by the model is then the estimated DVPE for any particular sample composition. DVPE is used here as the primary indicator of the accuracy of the model in predicting the state of the mixture in the headspace, although it is possible that different combinations of components could lead to the same overall vapour pressure.

Figure 5 compares the predicted values of DVPE with those measured. A perfect correlation between measured and predicted values would lie exactly along the diagonal line on the figure.

Figure 5: Predicted and measured DVPE

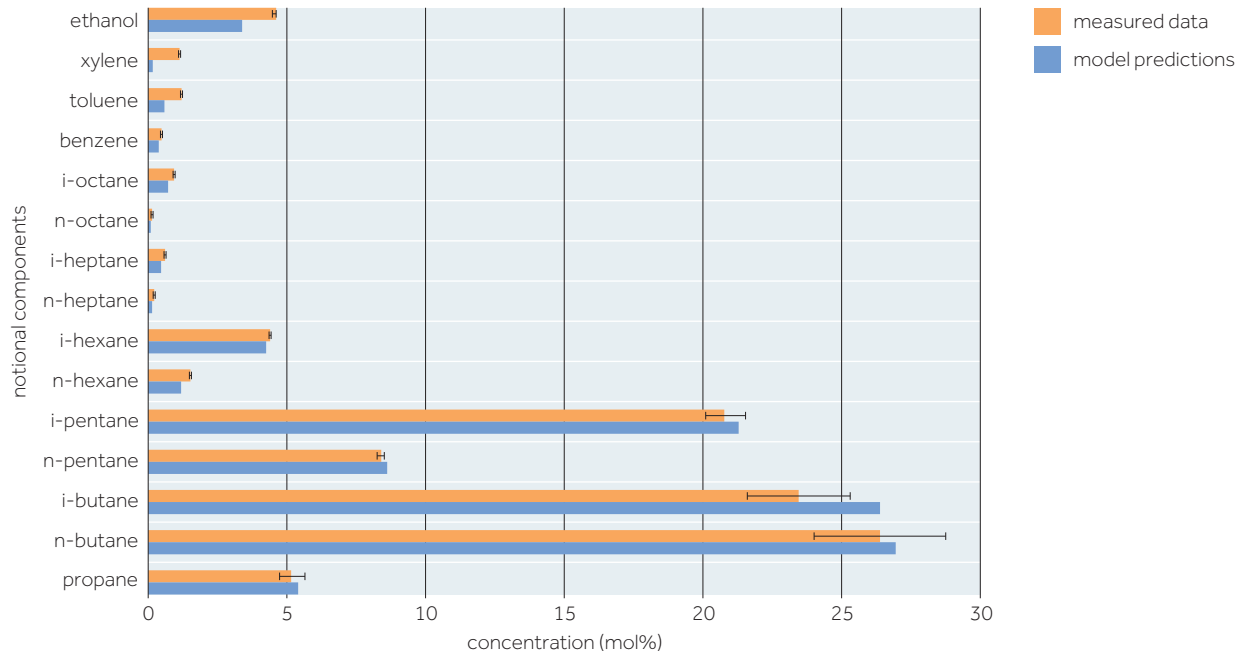
- ◆ base gasolines
- blends without additional alcohol
- ▲ blends with additional alcohol
- perfect match between measured and predicted values



Samples of headspace vapours were collected from 20 ml vials, each 75% full of liquid, which were stored at a constant temperature overnight to achieve equilibrium. The vapour composition (measured by gas chromatography (GC) and then placed into the 15 pseudo-component buckets) was compared against model predictions. An example of the vapour space composition validation is given in Figure 6 on page 49.

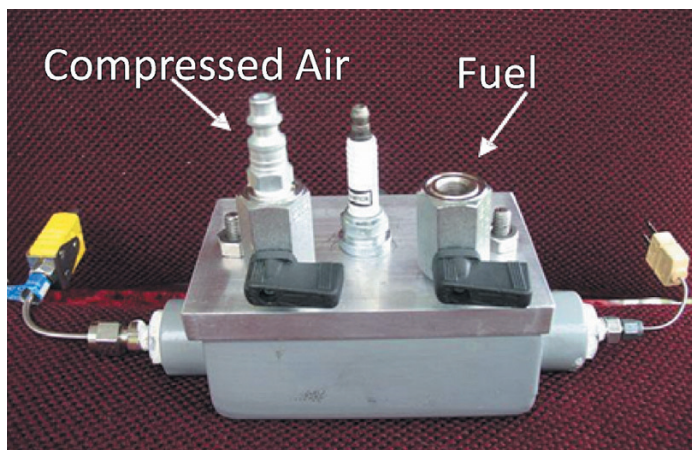


Figure 6: Representative prediction of vapour space composition of one of the blends



Actual investigations of the UFLs were conducted in a constant volume vessel (Figure 7).^[5] The tank had a 5% fill level representing a realistic worst-case scenario, as an emptier tank results in a leaner headspace that is more likely to be below the UFL. Mixtures were deemed flammable when pressure exceeded a threshold value following ignition. Four replicate tests were conducted at a given temperature.

Figure 7: Upper flammability limit test chamber (Vol = 296 ml)





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The model was found to consistently overpredict the UFL temperature measured in the constant volume chamber by 5–10°C (Figures 8 and 9). For blends without ethanol, the UFL temperature can be predicted from the DVPE — the more volatile the fuel the lower the UFL temperature. Ethanol-containing fuels still trend with DVPE, but the trend is slightly different.

Figure 8: Measured and predicted rich temperature limits for diesel blends with no additional ethanol

- ◆ model—blends with no extra EtOH
- measured—blends with no extra EtOH

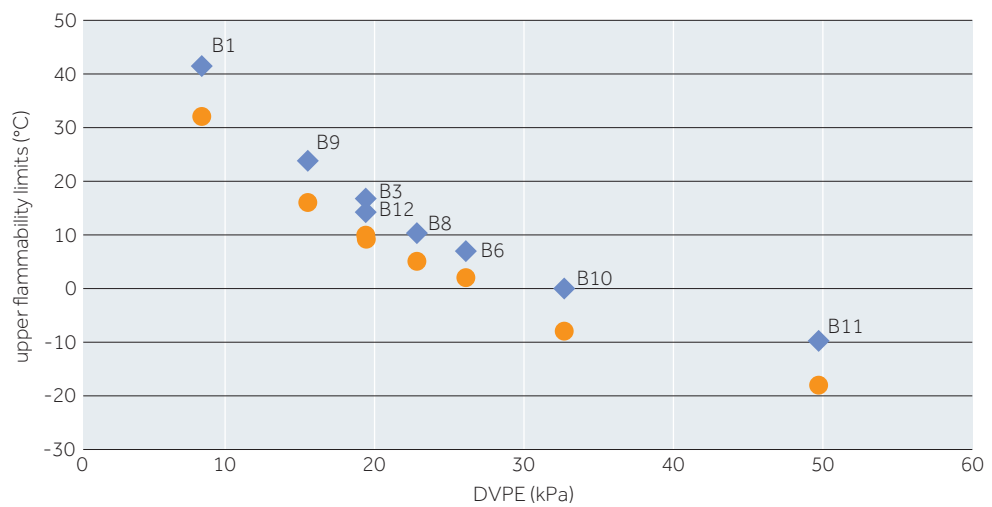
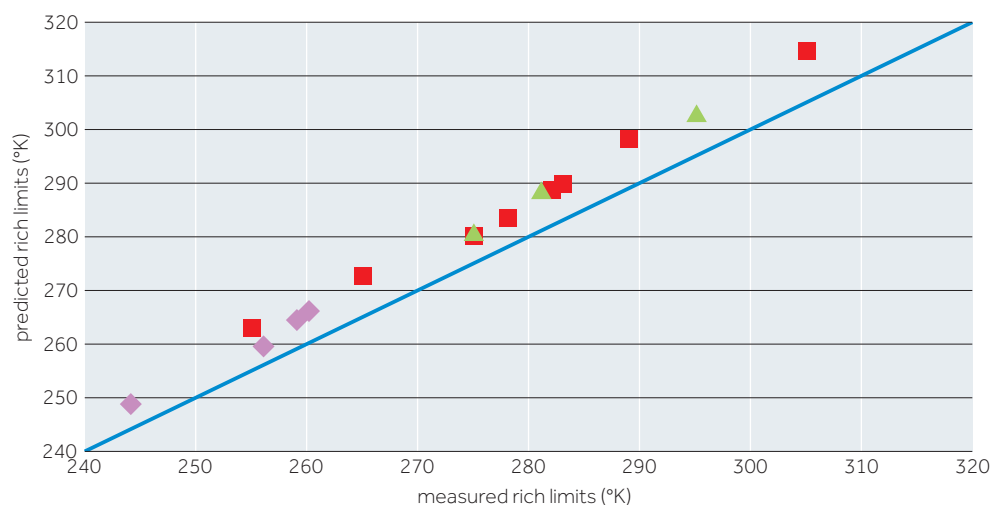


Figure 9: Comparison of measured and predicted upper flammability limits

- ◆ base gasolines
- blends without extra EtOH
- ▲ blends with extra EtOH
- perfect match between measured and predicted values



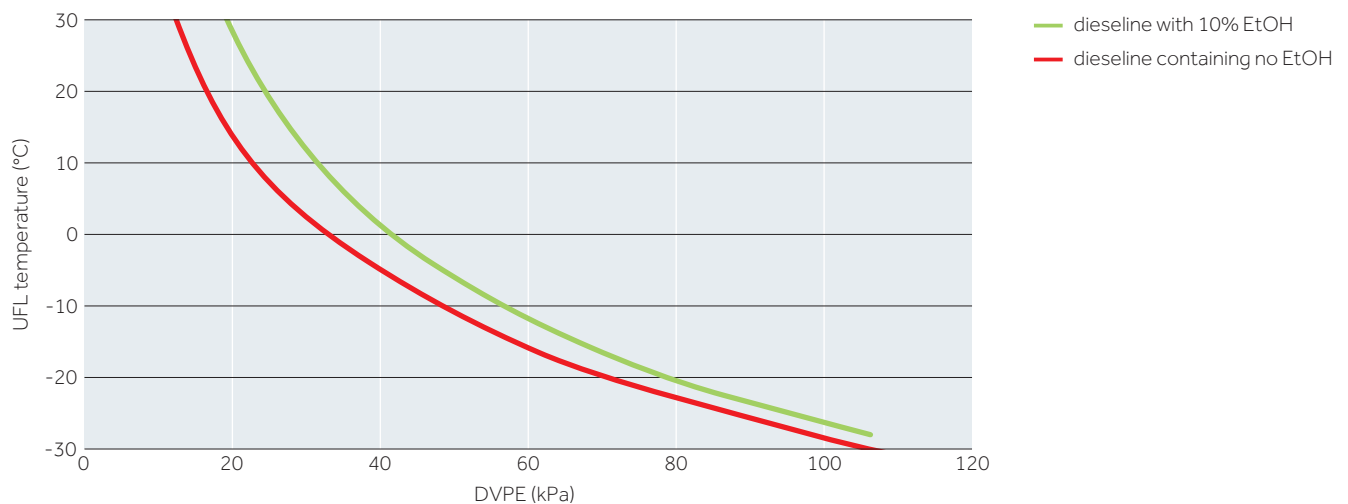
The discrepancy between measured and predicted rich flammability limit temperatures in this study were attributed to the impact of downward flame propagation in the apparatus employed in these tests, compared with upward propagation in the apparatus normally used to determine published flammability data. The model is therefore somewhat conservative.



Development of explicit formulae for the prediction of vapour space flammability

To make the model easier to use in practice, a set of explicit equations have been developed that are simple to use and allow changes in headspace flammability to be quickly assessed quantitatively as diesel/ethanol formulation is varied over any desired range. For the model, a single curve correlates the UFL temperature with DVPE for any hydrocarbon-only diesel/ethanol blend, regardless of its specific composition. All diesel/ethanol blends containing ethanol are also correlated by blend DVPE, but that correlation can differ considerably from the curve for HC-only blends (Figure 10).

Figure 10: Variation in UFL temperature with DVPE for diesel/ethanol blends with and without ethanol



The approach adopted for developing the explicit formulae is to determine the correlation between UFL and DVPE for an ethanol-free diesel/ethanol blend and then make a correction for the ethanol content:

$$T_{UFL} = f_1(DVPE_{HC}) + f_2(\%EtOH) \cdot f_3(DVPE_{HC}) \quad (3)$$

where:

T_{UFL} = UFL temperature for the blend [°C]

$f_1(DVPE_{HC})$ is the correlating function for the curve of hydrocarbon-only blends

$f_2(\%EtOH)$ is the correction factor to account for the volume % ethanol in the blend

$f_3(DVPE_{HC})$ is a factor to adjust f_2 to account for the effect of $DVPE_{HC}$

Each of the above terms is determined from a 6th order polynomial:

$$f = C_0 + C_1 \cdot arg + C_2 \cdot arg^2 + C_3 \cdot arg^3 + C_4 \cdot arg^4 + C_5 \cdot arg^5 + C_6 \cdot arg^6 \quad (4)$$



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Table 2: Coefficients in the correlation equation

	C_0	C_1	C_2	C_3	C_4	C_5	C_6
f_1	8.95413E+01	-7.44858E+00	2.78985E-01	-6.07073E-03	7.33348E-05	-4.57018E-07	1.14437E-09
f_2 if %EtOH = 0	0	0	0	0	0	0	0
f_2 if $DVPE_{HC} \leq 20$ and $0 < \%EtOH \leq 10$	0	-4.40806E+00	7.98908E-01	-7.00812E-02	2.39390E-03	0	0
f_2 if $DVPE_{HC} \leq 20$ and $\%EtOH > 10$	-9.89867E+00	-5.14490E-02	1.79400E-03	0	0	0	0
f_2 if $DVPE_{HC} > 20$ and $\%EtOH > 0$	1.04207E-01	2.90263E-01	-1.31394E-02	2.27509E-04	-1.34341E-06	0	0
f_3 if $DVPE_{HC} \leq 20$	2	-0.1	0	0	0	0	0
f_3 if $20 < DVPE_{HC} < 40$	-1.67230E+00	9.36900E-02	-6.25320E-04	0	0	0	0
f_3 if $DVPE_{HC} \geq 40$	1	0	0	0	0	0	0

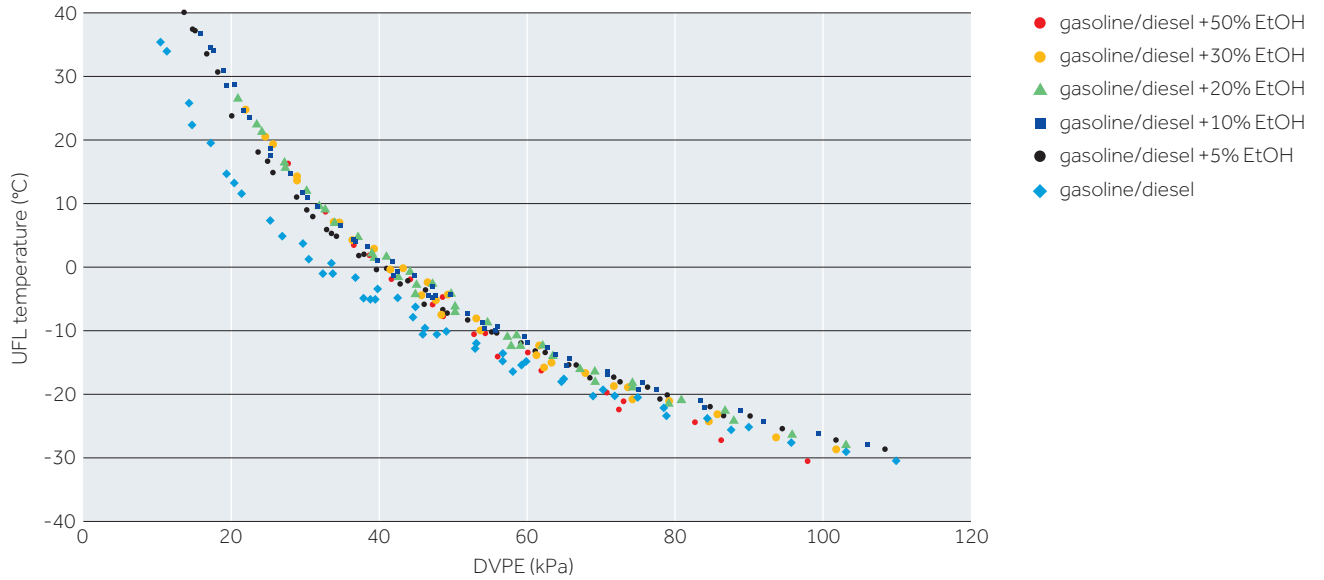
Each of the coefficients for equation 4 are given in Table 2, enabling f_1 , f_2 and f_3 to be calculated for any situation, and the UFL temperature determined. Specific examples of the calculation in different circumstances are given in Pellegrini, L. *et al.* (2020).^[8]

Selected results

Figure 11 on page 53 shows the relationship between DVPE and UFL temperature for diesel blends containing differing amounts of ethanol. For DVPEs up to 60 kPa, the curve for blends containing ethanol have a higher UFL temperature for a given DVPE than is the case of the pure hydrocarbon blends. For DVPEs above 60 kPa, blends with a high ethanol content can have a lower UFL temperature than the pure hydrocarbon. The reason for this is that while ethanol has an intrinsically higher UFL temperature than hydrocarbons it tends to raise the mixture vapour pressure because of deviations from Raoult's law, and the effect is more significant if the HC fraction has a low vapour pressure.

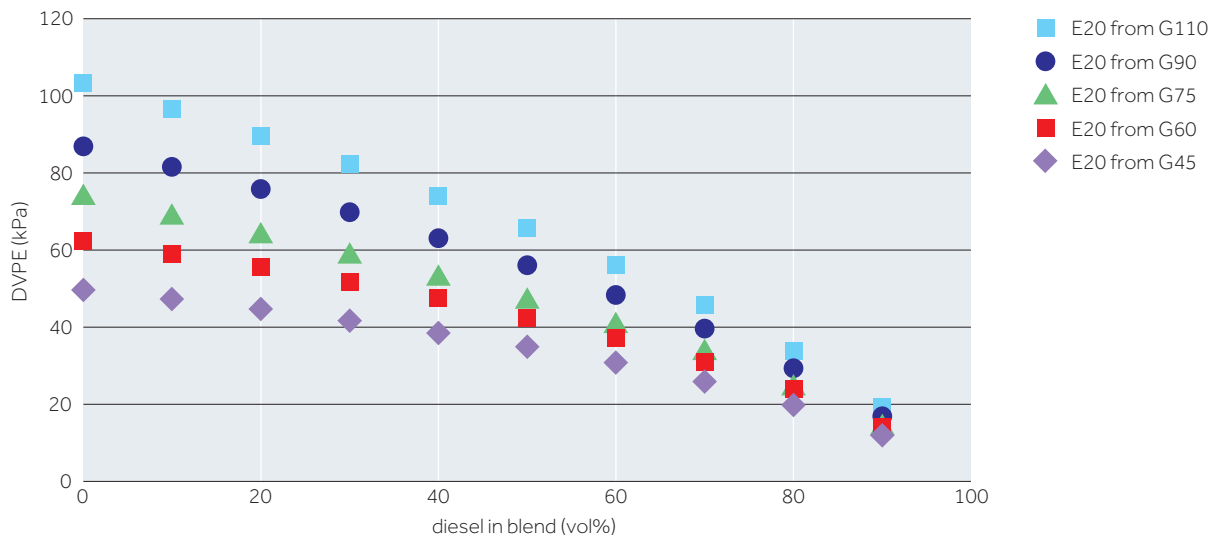


Figure 11: The impact of DVPE on the UFL temperature of dieseline comprising various ethanol levels



Another important perspective of the study is to understand exactly how the relative gasoline/diesel content affects the DVPE, and hence the UFL temperature. Figure 12 shows the impact of the addition of diesel to various E20 gasolines with different volatilities. The blend DVPE is principally determined by the DVPE of the gasoline. If an E20 gasoline with a DVPE of 75 kPa is mixed with 50% diesel, the dieseline can be seen to have a DVPE of about 45 kPa.

Figure 12: DVPE of E20/diesel blends using gasolines of different volatility (G110 refers a gasoline BOB with a DVPE of 110 kPa)

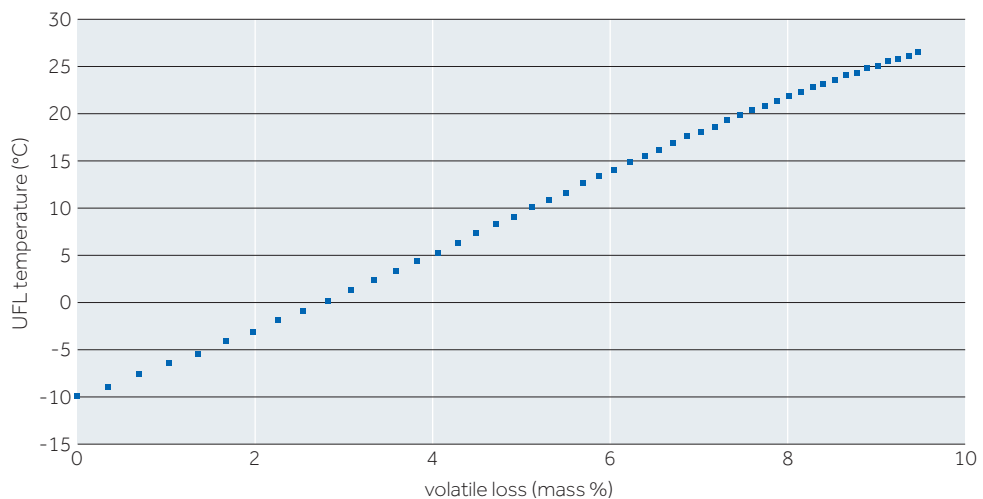




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Loss of volatile material in the tank (e.g. from evaporative emissions) can increase the likelihood of having a flammable mixture: this is something that the model can be used to assess. Figure 13 shows an example scenario — the temperature needs to be lower than -10°C for a flammable mixture to exist, but if 5% of the fuel evaporates and is able to escape the tank, the temperature only needs to be lower than $+10^{\circ}\text{C}$ for a flammable mixture to exist.

Figure 13: The effect of volatile loss on headspace flammability for a blend of 60% diesel, 30% G110 and 10% EtOH



Conclusions

A mathematical model has been developed that predicts the flammability of the headspace vapours in a tank that contains mixtures of diesel fuel and gasoline containing various amounts of ethanol. The non-ideality of the blends of hydrocarbons and ethanol is accounted for using activity coefficients.

It was found that the UFL temperature is correlated with the DVPE of the mixture, with the exact correlation being sensitive to the amount of ethanol in the blend.

The model has been validated against vapour space compositions measured by gas chromatography, and against ignition in a constant volume chamber. The UFLs predicted by the model were consistently $5\text{--}10^{\circ}\text{C}$ higher than measured in this apparatus. The discrepancy was attributed mainly to the impact of downward flame propagation in the apparatus, compared to upward propagation used in flammability data found in the literature and used in the model.

Explicit correlation equations have been derived from the full mathematical model that enable the UFL temperature to be estimated for dieseline blends with or without ethanol. The equations can be readily incorporated into spreadsheets or programs to assess the UFL temperatures of a wide variety of dieseline formulations, and for evaluating practical issues arising in-service.



The minimum value for the DVPE required to ensure a non-flammable headspace mixture depends on the ambient conditions. The DVPE of a dieseline mixture is largely influenced by the DVPE of the gasoline, and winter-grade gasolines have higher DVPEs. Provided that the dieseline mixture contains at least 40% gasoline, it would be unlikely that the headspace of a dieseline mixture would be in the flammable region.

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