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Stability of diesel–bioethanol blends for use in diesel engines

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Abstract

Bioethanol is an attractive fuel due to its renewable origin and its oxygen content, but it is unable to be used directly in diesel engines. Although biodiesel can be produced with bioethanol through ethanolisis, direct blending of ethanol and diesel fuel, called e-diesel, has at least the same potential to reduce particulate emissions, despite their much lower production cost. The main drawback is that ethanol is immiscible with diesel fuel over a wide range of temperatures, leading to phase separation. Consequently, in many cases the presence of a surfactant and cosolvent additive in the e-diesel blend becomes necessary. In this paper the conditions in which the e-diesel blends are stable have been studied. The stability of samples is affected by three factors mainly: temperature, water content and initial ethanol content. The results show that the presence of water in the blends, low temperatures and high ethanol contents favour the phase separation whereas the presence of the additive leads to the opposite effect. These effects have been quantified through level curve maps for stability and for separation time.

Keywords: Diesel engines; Biofuels; Ethanol

1. Introduction

An increase in the use of renewable fuels in diesel engines is becoming an essential target of European governments for several reasons: (a) the objective of 5.75% of the automotive fuels, in energy basis, must be fulfilled before 2010, as stated by the European directive 2003/30/CE [1], (b) the sharp increase of the demand of diesel cars in front of that of gasoline ones leads to gasoline surplus and diesel default in oil refineries, and (c) after the implementation of the CO_2 emissions rights market in several industrial sectors, diffuse automotive CO_2 emissions are next to be penaltized. In this context, bioethanol has various advantages in comparison with biodiesel as a component of diesel blends to be used in diesel engines: (a) its production is simpler and cheaper than biodiesel [2,3], (b) there are expectancies to produce it from lignocellulosic biomass in the future while no further materials but oleiforous ones are expected for biodiesel production [3], (c) it is 100% renewable – with life-cycle renewability efficiency near 50% [4], while biodiesel is just 89% renewable, as it is made from fossil methanol in most of the cases, and (d) its oxygen concentration is higher, and thus its potential for particulate emissions reduction is also higher [5–8]. However, the use of ethanol–diesel blends, usually named as e-diesel, has also some limitations: it has lower viscosity and lubricity [9], reduced ignitability and cetane number, higher volatility [10], which may lead to increased unburned hydrocarbons emissions [11], and lower miscibility, which may cause phase separations with catastrophic consequences [12]. In front of these difficulties, the use of cetane enhancers and cosolvent additives has recovered the potential of these blends as a promising fuel for automotive diesel engines [13].

Different studies have proved that water-free ethanol has good miscibility with diesel fuel at room temperature in warm countries. Separation begins to occur either when the mixture is doped with water or when temperature drops

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Nomenclature

C	concentration
n	number of tests with different initial ethanol concentrations
S	solubility
SR	separation ratio
t	time
T	temperature
V	volume

Subscripts

d	diesel
cell	cell
et	ethanol
max	maximum
sep	separated
0	initial
1	after stabilization

below 10 °C [10]. In fact, low room temperature, high humidity or water contamination in fuel delivery tanks or ducts are the most usual conditions which may cause phase separation. However the miscibility and the separation kinetics do not only depend on temperature and water content but also on the ethanol concentration in the mixture. Consequently, a precise knowledge of the effect of these parameters on miscibility is essential [7]. In this paper, a description of the miscibility behavior of e-diesel blends is presented for different ethanol concentrations, temperatures and water concentrations, as well as the effect of an additive on such miscibility behavior.

2. Experimental installation and procedure

The stability and the rate of separation of diesel–bioethanol blends were measured with an optical device named TurbiScan, specifically designed for the characterization of liquid emulsions suspensions and solutions. The device has an infrared light source of 850 nm wavelength, and two detectors operating simultaneously. The first one detects the light transmitted with no refraction and is located in the prolongation of the light beam (0°), while the second one detects the backscattered light in the direction 135° with respect to the incident light beam.

The sample to be analysed is contained in a cylindrical glass measurement cell and is examined throughout all its length in about 20 s, obtaining data on the percentage of transmission and backscattering per 40 μm of height of sample. Whenever the sample is examined, a profile of transmission light flux (in %, relative to external standards) and another one of backscattering are obtained as a function of the sample height (mm). These profiles constitute the macroscopic fingerprint of the sample at a given time. Figs. 1 and 2 show examples of these profiles for stable and unstable blends respectively, with differently coloured curves indicating different times.

One of the two mentioned profiles must be chosen to interpret the results obtained. In emulsions studies the backscattering profile is normally used because the transmission signal is hardly detected. In tests with e-diesel, the transmission profile was chosen, as it is more intense in light and can be better distinguished.

When superposed profiles are obtained, the phases have not separated, that is to say, the mixture remains stable. When the profiles obtained at different times are not

Fig. 1. Transmission (above) and backscattering (below) profiles for a stable sample.

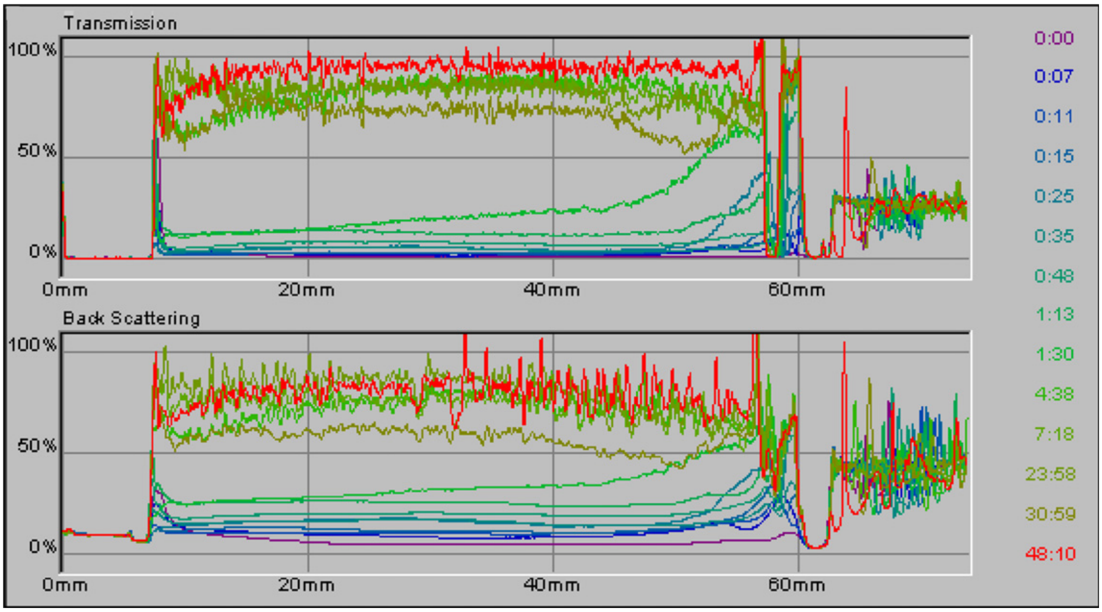

Fig. 2. Transmission (above) and backscattering (below) profiles for an unstable sample.

superposed, separation has taken place between bioethanol and diesel. The phase separation of an unstable mixture consists of the following stages:

(1) *Initial turbidity*. The sample turns quickly into a turbid phase, with no distinction between the two phases. This turbidity is the first symptom of an instable sample, previous to the phase separation, but there are humidity and temperature conditions (in the limit of stability) in which the initial turbidity remains unchanged.
(2) *Interface appearance*. A more transparent phase in the superior part of the mixture is distinguished, corresponding to the less dense phase (bioethanol). The phase below the interface continues maintaining the turbidity.
(3) *Displacement of the interface until equilibrium*. The width of the bioethanol phase increases, moving the interface towards the inferior part until an equilibrium position, whereas diesel phase becomes transparent.

In some cases, the phase separation has not taken place (the blend remains stable) even if the profiles are not superposed. This occurs because the initial turbidity disappears with time. This effect is typically observed when the conditions are in the limit of the stability.

3. Preliminary experiments

A chromatographic analysis has been carried out to verify that the less dense phase after separation is composed solely by ethanol (the integration of the low peaks contributes less than 5% of the area above the base line). The used equipment is a chromatograph Shimadzu GC-14 with detector FID and one non-polar column with phase of methyl silicone (Supelco, SPB-1 30 m ∗ 0.25 mm ∗ 0.25 μm). The temperature profile programme for the column was: 40 °C during 5 min, increase of 10 °C/min until 280 °C. The detector and injector temperatures were fixed in 320 °C and 220 °C respectively, and 0.01 μl of sample was injected. As shown in Fig. 3, a single tip appears few minutes after the test beginning, which corresponds to ethanol. From this experiment, it is possible to conclude that the light phase is composed only by ethanol. The test condition of the sample was: −5 °C and 2.5% water in ethanol (w/w).

The effect of the diameter of the vessel on the separation process was also studied in order to extrapolate the conclusions to the storage conclusions either in the vehicle tank or in the injection ducts. An E-20 blend was introduced into three vessels with different diameters (28.2 mm, 47.6 mm and 87 mm). As shown in Fig. 4, the height corresponding to the separated ethanol was very similar in the three cases.

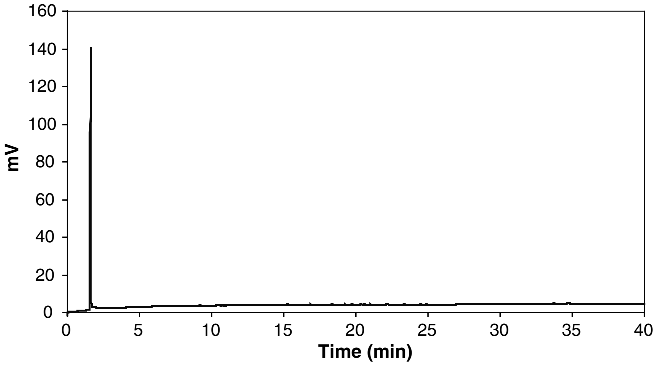

Fig. 3. Chromatographic analysis of the upper phase.

Fig. 4. Comparison of heights of the separated ethanol phase with different vessels.

Consequently, the effect of the wall proximity on the separation process can be neglected.

4. Data processing

The time evolution of the transmission profiles of unstable mixtures provides a quantitative description of the separation process. The thickness of the phase located at the top (composed of separated ethanol) increases with time. A non-dimensional separation ratio, SR, was defined indicating the instantaneous proportion of ethanol separated with respect to the initial ethanol content in the blend, $C_{\mathrm{et},0}$. This parameter is expressed as the ratio between the instantaneous volume occupied by the upper phase, $V_{\mathrm{et,sep}}$ and the initial ethanol volume in the blend, $V_{\mathrm{et},0}$, or as a function of the initial ethanol content:

$$\mathrm{SR}(t) = \frac{V_{\mathrm{et,sep}}(t)}{V_{\mathrm{et},0}} = \frac{\frac{V_{\mathrm{et,sep}}(t)}{V_{\mathrm{cell}}}}{C_{\mathrm{et},0}} \tag{1}$$

As the volume fraction of ethanol is conservative in the measurement cell, the initial ethanol concentration can be expressed as a function of the instantaneous concentration of ethanol in the non-separated phase, $C_{\mathrm{et}}(t)$:

$$C_{\mathrm{et},0} = \frac{V_{\mathrm{et,sep}}(t) + (V_{\mathrm{cell}} - V_{\mathrm{et,sep}}(t))C_{\mathrm{et}}(t)}{V_{\mathrm{cell}}} \tag{2}$$

After the equilibrium has been reached, the initial ethanol concentration can be expressed as a function of the maximum separation ratio, $\mathrm{SR}_{\max}$, and the ethanol concentration remaining in the blend at this moment, identified with subscript 1:

$$C_{\mathrm{et},0} = \mathrm{SR}_{\max} C_{\mathrm{et},0} + (1 - \mathrm{SR}_{\max} C_{\mathrm{et},0}) C_{\mathrm{et},1} \tag{3}$$

The volumetric concentration of ethanol remaining in the blend after the separation, $C_{\mathrm{et},1}$, can be solved as

$$C_{\mathrm{et},1} = C_{\mathrm{et},0} \cdot \frac{1 - \mathrm{SR}_{\max}}{1 - \mathrm{SR}_{\max} \cdot C_{\mathrm{et},0}} \tag{4}$$

As shown in the results presented below, the concentration of ethanol remaining in the blend after the separation is not only function of the temperature, but it also depends on the initial ethanol concentration. This dependency confirms that the extraction process is affected by the initial solute concentration, showing a certain memory effect [14]. Therefore, the mean solubility [15] was calculated as the average of the ethanol concentrations remaining in the blend after the phase separation, obtained from a number (n) of different initial ethanol concentrations:

$$S = \frac{\sum^{n} C_{\mathrm{et},1}}{n} \tag{5}$$

5. Materials and experimental matrix

The stability of the e-diesel blends depends on two factors mainly: temperature and water content. Other parameters that affect the stability of these blends are the properties of diesel fuel [16] and the use of additives. A reference fuel provided and analysed by Repsol-YPF was

Table 1
Reference fuel characteristics

Density (kg/m^3) at 15 °C	833.5	EN 12185
Kinematic viscosity (cSt) at 40 °C	2.7878	EN 3104
Gross heating value (MJ/kg)	45.894	ASTM D 240
Lower heating value (MJ/kg)	42.837	1
Sulfur (ppm w)	267	EN 20846
Water (ppm w)	40	EN 12937
Paraffins (%w)	37.24	2
Aromatic content (%w)		
Mono-aromatics	22.42	EN 12916
Di-aromatics	4.09	
Poly-aromatics	0.56	
Total	27.07	
Distillation (°C)		
IBP	182	EN 3405
T10	204	
T50	268	
T90	348	
FBP	361.4	
Flash point (°C)	64	EN 2719
CFPP (°C)	−7	EN 116

Note 1 – Calculated from Gross heating value and CHNS composition.
Note 2 – Measured with gas chromatograpy/mass spectrometry.

used. The characteristics of reference fuel are shown in Table 1. A surfactant and cosolvent additive with lubricity, corrosion, cold flow a cetane number improvers, with renewable origin, provided by O_2Diesel™ was also occasionally used. Finally, the bioethanol, with 99.94% purity, was provided by Abengoa Bioenergy.

Different tests were carried out to determine under which conditions of ethanol concentration, temperature, water content (% water/ethanol w/w) and additive content (% additive/ethanol v/v) the blends remain stable, and if not, how fast do they separate and to which extent. Table 2 shows the test schedule for studying the temperature, water and additive influence. The amount of added water is in all cases much higher than those corresponding to the European standards for both ethanol for blending (0.3% w/w, prEN-15376) and diesel fuel standards (0.02% w/w, EN-590), in order to reproduce the conditions of phase separation due to water contamination.

6. Experimental results

The effect of temperature was studied by means of a level curve map, where each level curve corresponds to a different maximum separation ratio (SR_{max}).

Fig. 5 shows that as the initial ethanol content increases and as the temperature decreases, the maximum separation ratio of the alcohol phase increases. A blend is considered unstable when the maximum separation ratio is at least 0.1. Therefore, the region located at the left side of curve 0.1 corresponds to the stability zone of the blends. The kinetics of the separation process has been studied too. Fig. 6 shows the level curves corresponding to the time until the

Table 2
Test conditions of e-diesel blends

%Vol. ethanol	T (°C)	% water/ethanol (w/w)						% additive/ethanol (v/v)					
		0	0.5	1	1.5	2	2.5	0	1	2	3	4	5
5	−5	X	X				X	X					
	0	X	X				X	X					
	2.5	X						X					
	5	X						X					
	10	X	X	X	X	X	X	X					
	15	X	X					X					
10	−5	X	X				X	X					
	0	X	X				X	X					
	2.5	X						X					
	5	X						X					
	10	X	X	X	X	X	X	X					
	15	X	X					X					
12.5	−5	X	X				X	X					
	0	X	X				X	X					
	2.5	X						X					
	5	X						X					
	10	X	X				X	X					
	15	X	X					X					
15	−5	X	X				X	X				X	X
	0	X	X				X	X			X	X	X
	2.5	X						X					
	5	X						X	X	X	X	X	X
	10	X	X	X	X	X	X	X	X	X	X	X	X
	15	X	X					X					
17.5	−5	X	X				X	X					
	0	X	X				X	X					
	2.5	X						X					
	5	X						X					
	10	X	X				X	X					
	15	X	X					X					
20	−5	X	X				X	X					
	0	X	X				X	X					
	2.5	X						X					
	5	X						X					
	10	X	X				X	X					
	15	X	X					X					

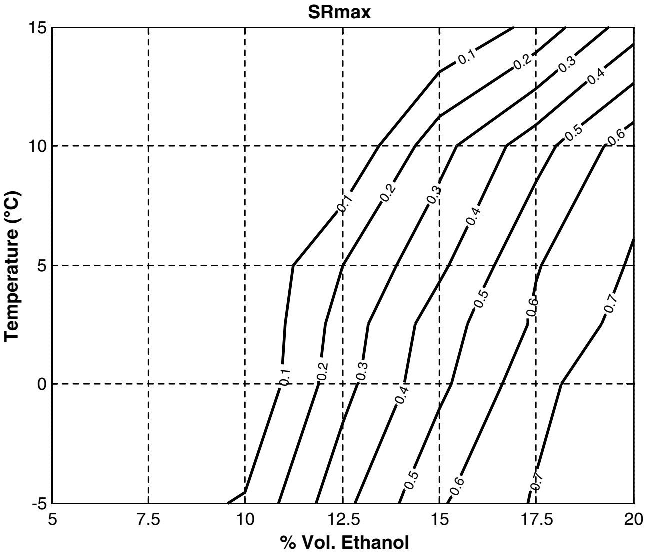

Fig. 5. Level curves for SR_{max} in the map temperature/ethanol content.

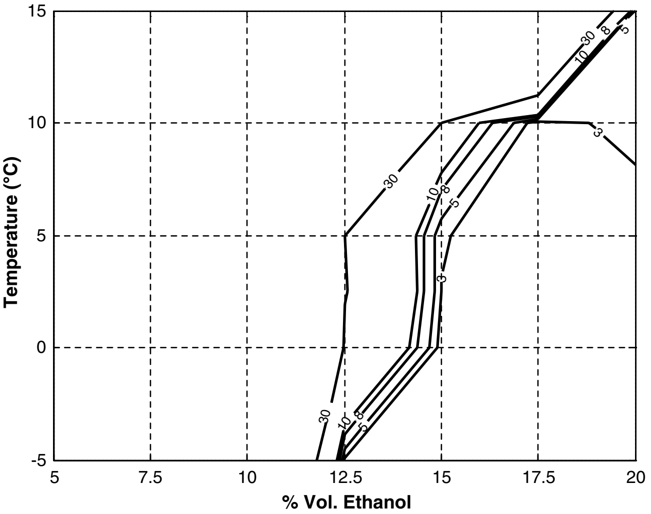

Fig. 6. Level curves for separation time (min) in the map temperature/ethanol content.

separation ratio reaches a value of 0.1. The region in the temperature-ethanol content map at the right of the stability limit in Fig. 5 and at the left of the 30 min curve in Fig. 6 corresponds to unstable blends which take very long for separation. As the temperature decreases and the ethanol content increases, the time necessary for blends to separate decreases.

Fig. 7 shows the stability zone limits obtained for different water and additive contents. As water content increases in the blends, the separation occurs for lower initial ethanol contents. The region located at the right side of each curve, again corresponds to the conditions in which the blends are unstable. As temperature decreases, lower ethanol concentration is necessary for separation. The additive generates the opposite effect. As the additive content is increased, the stability region becomes wider.

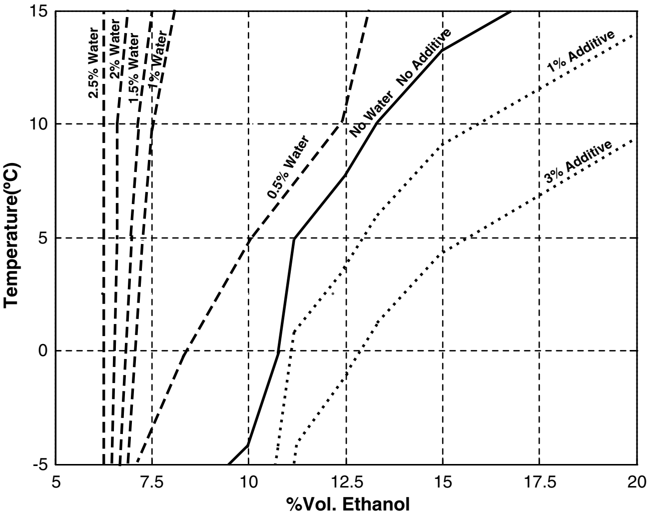

Fig. 7. Stability curves for different water and additive contents.

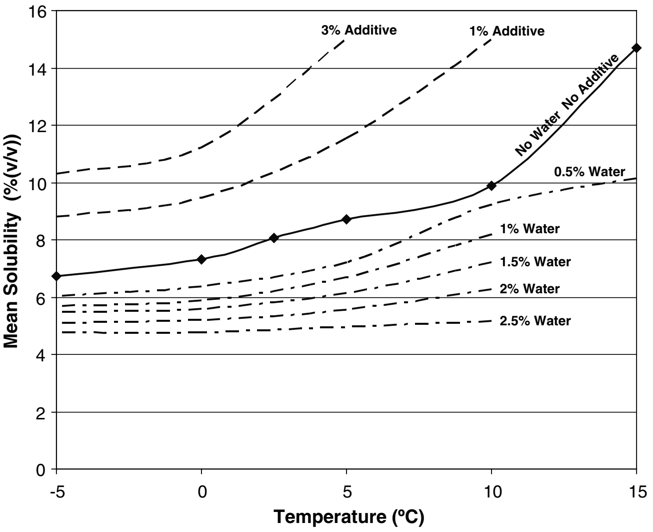

Fig. 8. Effect of water and additive on the mean solubility at different temperatures.

The presence of water and additive also affects the solubility of alcohol in diesel. This effect is shown in Fig. 8. As temperature increases, the mean solubility increases. The presence of water reduces the solubility of ethanol in diesel. This effect is more important as temperature increases. However, the opposite effect was observed when additive was added.

7. Conclusions

The stability of blends bioethanol–diesel has been studied, aiming to provide essential information previous to their use in diesel engines. Tests have been carried out at different temperatures and with different water and additive contents, in order to study their effect on the stability and solubility of the blends. Level maps have been used to show the stability zone of the blends, as well as their separation kinetics. The main conclusions are the following:

(1) The presence of water in the blends favours the separation of the ethanol phase. As the water content increases, the separation occurs with lower initial ethanol content. Consequently, the stability zone becomes narrower. On the contrary, as the additive is added into the blends, the stability zone becomes wider. This behavior can also be observed through the mean solubility: as the water content increases the solubility decreases whereas the presence of additive generates the opposite effect.
(2) When the temperature of the blend increases it becomes more stable and the solubility of ethanol in the diesel fuel increases. This effect is also observed for different water and ethanol contents.
(3) The sensitivity of the effect of water content, as well as that of the effect of additive content, become higher as the temperature of the blend increases.
(4) Blends with bioethanol contents up to 10% v/v can be used in diesel engines in countries where winter temperatures rarely fall to −5 °C, such as Spain, if care is taken about water contamination. Blends with 7% bioethanol, such as those commercially used, can be used in even colder countries, although further experimentation at lower temperatures is needed for confirmation.
(5) The use of stability additives may increase either the range of ethanol content in the blends, or the geographic extent of application comprising colder countries, or the security margins to avoid phase separation.

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