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Stability, Lubricity, Viscosity, and Cold-Flow Properties of Alcohol–Diesel Blends

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Alcohols have an interesting potential as blending components for diesel fuels because of their capacity to reduce soot formation. Because they have increasing routes for their production from renewable sources, they could contribute toward increasing the renewable fraction of these fuels and, therefore, toward reducing the impact of diesel transportation on the global warming effect. To increase the knowledge about the implications of the use of short- and long-chain alcohols/diesel fuel blends in diesel engines, the stability, lubricity, viscosity, and cold filter plugging point (CFPP) have been tested. Blends of methanol, ethanol, propanol, butanol, and pentanol with diesel fuel have been analyzed at 1, 2.5, 7.7, 17, 50, 75, and 90% in volume [including 95% (v/v) in the case of CFPP]. Results have shown that short-chain alcohols depict poor blending stability and low viscosity (mainly for concentrations of ethanol and propanol in diesel fuel blends beyond 22 and 45%, respectively). A synergistic effect was observed in viscosity when moderate concentrations of butanol and pentanol were mixed with diesel fuel. The lubricity of the blends decreases with the alcohol content, but this effect is partially compensated by the alcohol volatility. The blends with the highest restriction of use are those containing pentanol, which should be limited to concentrations below 10% (v/v), because its volatility does not compensate for its lubricating capacity. The use of alcohol/winter diesel fuel blends provides a substantial benefit only when high alcohol concentrations are used. It can be concluded that alcohols can be blended with diesel fuel under low and high concentrations, although to improve the blending stability of short-chain alcohols in medium concentrations, the use of additives or fatty acid esters would be necessary.

1. Introduction

Bioalcohols are not only used to replace gasoline in spark-ignition engines but also to replace petroleum diesel fuel. This additional use enables the increase of the contribution of biofuels to reduce the greenhouse effect and the dependency upon foreign oil in non-producing countries, especially in the case of countries with high diesel share in the vehicle market. The hydroxyl group of the alcohol molecules contributes toward the reduction of soot formation and, consequently, particulate emissions, even more than other functional groups with the same oxygen content,^{1–3} especially at high engine loads.^{4,5} However, two main factors may become crucial for the future extension of the use of these alcohols as diesel fuel components to a large scale: first, the energy and environmental life-cycle assessments of the bioalcohols and, second, some key properties of the fuels, resulting from the blending of these alcohols with diesel fuel or previous biodiesel–diesel blends.

1.1. Life-cycle greenhouse emissions. The recently renewed commitments to further reduce greenhouse emissions from

transportation sources make this factor a crucial one. Ethanol has been proven to have a significant potential for reducing the life-cycle greenhouse emissions, as acknowledged by the recently approved European directive 28/2009/CE,⁶ where typical greenhouse savings range from 21% (in the case of using wheat as feedstock) to 75% (in the case of sugar cane ethanol) or even to 87% (in the case of wheat straw). Methanol is also gaining interest as a renewable fuel, because its production derived from gasification of waste biomass followed by catalytic synthesis at high pressure provides both high yield (45–55 wt %) and energy efficiency (70–75%).⁷ Biomass sources are even preferable for biomethanol production than for bioethanol because bioethanol is a high-cost and low-yield product.^{8,9} Butanol has also proven to have an interesting potential for saving the life-cycle greenhouse emissions if it is produced from aceto-butylicum fermentation, when the bioacetone obtained as a co-product is valued as such, including its own life-cycle emissions.¹⁰ Other alcohols could also become a sustainable alternative, because they could be produced in biorefineries. Biorefineries use renewable raw materials to produce energy together with a wide range of commodities, decreasing the

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dependency upon fossil fuel reserves. Although the compound that receives the most attention is ethanol, other commodities, such as methanol and higher alcohols, have also been examined.¹¹ Thus, higher alcohols as butanol and pentanol may be produced through this promising route for sustained growth while preserving the environment.^{12,13} The aim of a biorefinery for higher alcohol production is to integrate ethanol and methanol formation via fermentation and biomass gasification, respectively, with conversion of these simple alcohol intermediates into higher alcohols via the Guerbet reaction. All of these higher alcohols have more interesting market values than the simple alcohol intermediates.¹⁴ At present, research is underway to provide cost-effective methods, including fermentation, to produce biopentanol.

1.2. Blending Stability. Alcohol and diesel blends may separate into different liquid phases under certain conditions. The stability of ethanol–diesel is prejudiced by humidification, improved by temperature and additivation,¹⁵ and also strongly improved when a certain biodiesel content is also added in the diesel fuel^{3,16} or even when ethanol is blended just with biodiesel.¹⁷ Better stabilities have been reported when blending butanol with diesel fuel, with this also being improved with the addition of biodiesel.¹⁸ In fact, butanol has also been used as a surfactant in ethanol–diesel^{5,19} and methanol–diesel^{20,21} blends.

1.3. Lubricity. Although the lubricity of alcohols is much worse than that required in diesel fuel specifications (EN 590),²² as it is commented by Hansen et al.²³, the lubricity of blends with short-chain alcohols is better than expected as a consequence of the alcohol evaporation from the lubricating layer. Speidel and Ahmed²⁴ reported enhanced lubricity for the blend containing 15% dry ethanol, 5% PEC additive, and 80% diesel, as compared to that of number 2 diesel fuel. This synergistic effect has been recently proven to be extended to a wide range of ethanol concentrations with no additives.²⁵ No information about lubricity of other blends with lower volatility alcohols has been found in the literature.

1.4. Viscosity. The viscosity has effects on the injection timing and pressure, atomization quality, size of fuel drop, and jet penetration, and therefore, it influences the timing and quality of combustion. In the case of alcohol blends, a precise knowledge of the viscosity of the blends is necessary

to provide the adequate corrections from the electronic control unit. The addition of ethanol to diesel fuel lowers fuel viscosity.²³ Wrage and Goering²⁶ found that blending 10% ethanol with different diesel fuels reduced their viscosity around 25% of the difference with respect to the ethanol viscosity.

1.5. Cold-Flow Properties. Blended alcohols may contribute to compensate for the drawback of diesel fuel to fulfill the cold filter plugging point (CFPP) specification during winter time, especially when containing biodiesel produced from saturated oils. In the case of ethanol–diesel blends, McCormick and Parish²⁷ showed that the blends flowed better through the filters than the diesel fuel, despite the appearance of liquid micelles causing an increase of the cloud point.

1.6. Cetane Number. Although diesel engines need to be fueled with high-cetane-number fuels (above 51 as stated by norm EN 590) to facilitate autoignition and provide short ignition delay, alcohols exhibit low cetane numbers.^{28,29} For this reason, the direct use of alcohols as fuels for unmodified diesel engines is not recommended, unless they are blended with diesel fuel. However, long-chain alcohols have a higher cetane number than short-chain alcohols,^{20,30} thus enhancing their interest for being used in diesel engines.

2. Tested Fuels and Blends

The main characteristics of pure alcohols and reference diesel fuel are shown in Table 1. Blends of these alcohols with diesel fuel were also analyzed at 1, 2.5, 7.7, 17, 50, 75, and 90% in volume [plus 95% (v/v) in the case of CFPP]. These concentrations were selected aiming to (a) cover the whole blending range, (b) provide specific information for very diluted blends (with special interest in the case of viscosity and lubricity), and (c) include some strategic blends for commercial reasons (7.7% ethanol blend) or for their proximity to the limit of stability at room temperature (17% ethanol blend).³ The diesel reference fuel is a biodiesel-free petroleum-derived fuel, similar to many diesel fuels supplied by petrol stations in Europe in winter (before the recent compulsory introduction of a certain renewable fraction), fulfils the European standard (EN 590:2009),²² and was provided by Repsol (Madrid, Spain). Anhydrous ethanol (99.7%) was provided by Abengoa Bioenergy (Seville, Spain) and was made by fermentation of wheat, barley, and corn, fulfilling the European norm EN 15376:2007.³¹ Other alcohols (methanol, 1-propanol, 1-butanol, and 1-pentanol) were purchased to Panreac Quimica SAU (Barcelona, Spain).

3. Blending Stability

The stability of alcohol–diesel blends depends upon the temperature, humidity, and fuel (both diesel fuel and alcohol) composition. It was obtained by means of optical equipment (Turbiscan), specifically designed for the characterization of liquid emulsion suspensions and solutions. The device has an infrared light source of 850 nm wavelength and two detectors operating simultaneously (transmission and backscattering). In this case, where the stable blends are transparent, only the data recorded by the transmission detector are used, this being located in the prolongation of the light beam.¹⁵ Tests were

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Table 1. Specifications of the Tested Fuels

properties	method	diesel	methanol	ethanol	propanol	butanol	pentanol
purity (% v/v)		100	99.8	99.7	99.5	99	98
density at 15 °C (kg/m ³)	EN ISO 12185	835	791.3	789.4	803.7	809.7	814.8
kinematic viscosity at 40 °C (cSt)	EN ISO 3104	2.72	0.58	1.13	1.74	2.22	2.89
gross heating value (MJ/kg)	UNE 51123	45.54	22.31	29.67	33.52	36.02	37.60
lower heating value (MJ/kg) ^a	UNE 51123	42.49	19.58	26.83	30.63	33.09	34.65
C (wt %)		86.13 ^b	37.48	52.14	59.96	64.82	68.13
H (wt %)		13.87 ^b	12.58	13.13	13.42	13.60	13.72
O (wt %)		0 ^b	49.93	34.73	26.62	21.59	18.15
water content (ppm wt)	EN ISO 12937	57	1382	2024	309	1146	2970
molecular weight (kg/kmol)		211.7 ^c	32.04	46.07	60.09	74.12	88.15
boiling point (°C)			64.7	78.3	97.1	117.5	137.9
stoichiometric fuel/air ratio ^d		1/14.67	1/6.47	1/9.01	1/10.35	1/11.19	1/11.77
CFPP (°C)	EN 116	−17	< −51	< −51	< −51	< −51	−40
lubricity (μm corrected wear scar)	EN ISO 12156	315	1100	1057	922	591	670.5
cetane number		52 ^e	5 ^f	8 ^g	12 ^h	17 ⁱ	18.2 ^j

^a Calculated from the composition and gross heating value. ^b Analyzed following norm ASTM D5291. ^c Calculated by AspenTech HYSYS software.

^d Calculated from elemental analysis and molecular weight. ^e Provided by the fuel manufacturer. ^f Obtained from refs 20 and 29. ^g Obtained from refs 29 and 32. ^h Obtained from ref 33. ⁱ Obtained from refs 5 and 33. ^j Obtained from ref 30.

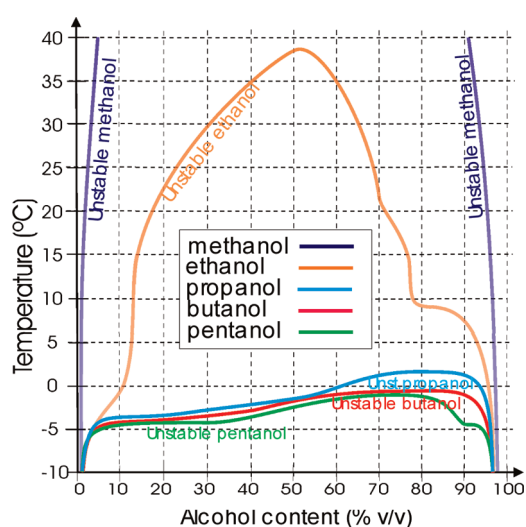


Figure 1. Blending stability of alcohols with diesel fuel.

made at different temperatures, while water contamination was avoided as far as possible during manipulation (see Table 1).

As shown in Figure 1, the blends become unstable at a certain temperature when the alcohol concentration remains between a lower and an upper limit. As the temperature decreases, the region of unstable blends (between these limits) becomes wider. Inside of the unstable region, different regimes could be distinguished (with liquid-phase separation and/or with cloud or gel formation), although no details of these regimes are given here.

Alcohols of three or more carbons (propanol and higher) depict better blending stability than short-chain alcohols as a consequence of their lower polarity. Moreover, the stability of propanol, butanol, and pentanol is very similar, and their unstable blends are caused by the appearance of a gel phase, whereas the stability of ethanol and methanol is much more sensitive to the temperature, and their unstable blends are mainly the consequence of liquid-phase separation. The main differences of stability between propanol, butanol, and pentanol appear at high concentrations.

The low stability of methanol blends prevented from measuring most of their properties, especially those whose tests are made at low temperature. In the case of ethanol blends only CFPP could not be measured in the intermediate concentration range.

4. Viscosity

The kinematic viscosity of the blends was measured at 40 °C, following norm EN ISO 3104. Every experiment was replicated twice, and the relative standard deviation was ± 0.016 cSt. As shown in the right panel of Figure 2, the viscosity is sharply reduced with a small alcohol concentration regardless of the alcohol blended. This reduction is highest for ethanol and propanol blends at very low concentrations and becomes inversely proportional to the alcohol carbon chain for higher concentrations (although only a few methanol blends could be measured because of their unstability), coherently with the viscosity of pure alcohols (see Table 1). The measured results show that the viscosity does not change linearly with either the alcohol volume content, mass content, or molar content.

With regard to the diesel quality norm EN 590, which requires viscosities above 2 cSt, only blends with more than 22% (v/v) ethanol or more than 45% (v/v) propanol would not fulfill this requirement (apart from methanol blends, for which unstability is more restrictive than viscosity). Other more viscous diesel fuels, such as those available in petrol stations during summer time, would probably enable higher alcohol concentration blends.

In the cases that the viscosity is close to that of diesel fuel (butanol and especially pentanol), the interaction between both components leads to synergistic effects when blending; intermediate concentration blends have viscosities lower than those of their pure components. This effect could be used to optimize the injection characteristics of diesel engines when fueled with these blends.

The absolute viscosity of the blend, μ , has been observed to follow the Grunberg–Nissan equation³⁴ for binary blends. In this equation, the content of each component is quantified by its molar fraction (x_d for diesel fuel and x_i for alcohols, with $i = 1, 2, 3, 4$, and 5).

$$\ln \mu = x_d \ln \mu_d + x_i \ln \mu_i + x_d x_i G_{di} \quad (1)$$

Because the density of the blend, ρ , has been proven to vary linearly with the volume fraction (z_i), the kinematic

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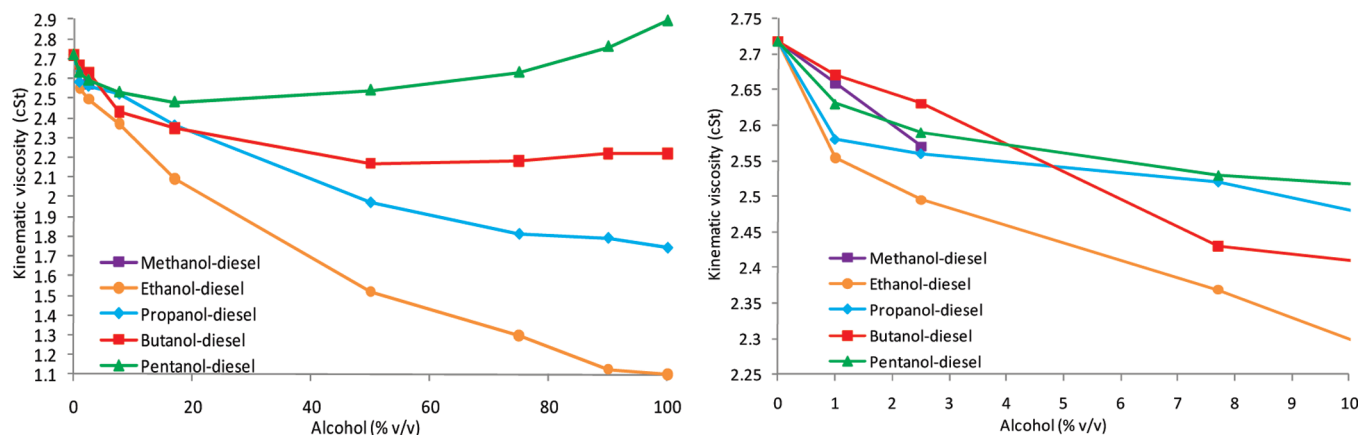


Figure 2. Measured viscosity of alcohol blends on (left) full scale and (right) reduced scale for low alcohol concentrations.

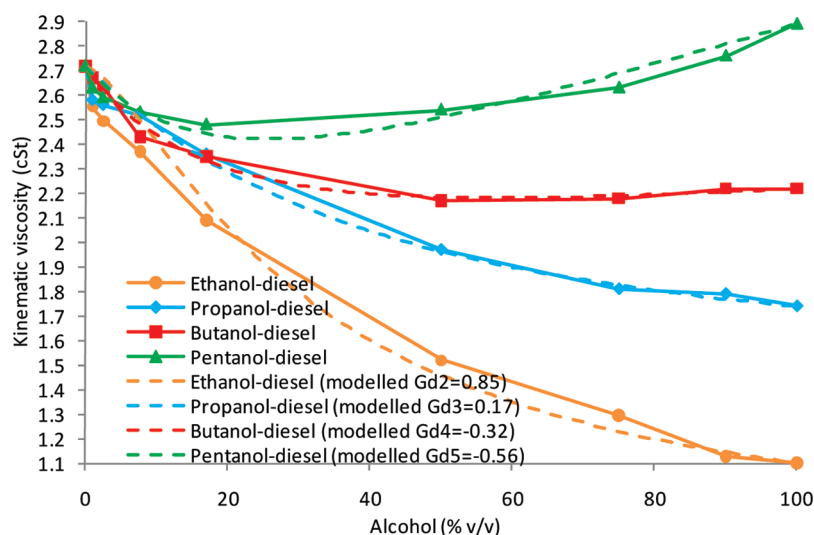


Figure 3. Comparison between the measured viscosity of alcohol blends (solid lines) and modeled values obtained with the Grunberg–Nissan correlation with adjusted interaction coefficients (dotted lines).

viscosity, v , responds to

$$v = \frac{\exp(x_d \ln \rho_d v_d + x_i \ln \rho_i v_i + x_d x_i G_{di})}{z_d \rho_d + z_i \rho_i} \quad (2)$$

The interaction coefficients providing an optimal fitting (see Figure 3) are $G_{d2} = 0.85$ for ethanol blends, $G_{d3} = 0.17$ for propanol blends, $G_{d4} = -0.32$ for butanol blends, and $G_{d5} = -0.56$ for pentanol blends. These interaction coefficients have been adjusted to the following equation (with n_i being the number of carbon atoms of the alcohol molecule):

$$G_{di} = 0.11n_i^2 - 1.242n_i + 2.897 \quad (3)$$

The interaction coefficient between propanol and diesel fuel is significantly lower than but with the same sign as that obtained by Jiménez et al.³⁵ for propanol and *n*-heptane. Only blends with very low propanol content (less than 5%, v/v), low ethanol content (less than 20%, v/v), and high pentanol content (more than half) would need models with more than one adjusting parameter to improve the fitting. The McAllister correlation (on the basis of the absolute reaction rate

theory)³⁶ was also tested, but no substantial improvement was found, despite including two adjusting parameters. Methanol was not included in this adjustment because the data available were not considered enough.

5. Lubricity

The lubricity tests were carried out in a high-frequency reciprocating rig (HFRR) by PCS Instruments. These tests provide the wear scar in micrometers of a fuel, following either the European or American norms (EN ISO 12156-1:2006 or ASTM D6079). Although the European standard establishes 60 °C as the fuel temperature (this specification is just required for diesel fuels), the ASTM standard also accepts testing at 25 °C and indicates that this temperature is preferred when there may be concerns about the loss of fuel because of its volatility or degradation. In this case, the high volatility of alcohols motivates comparing tests at both temperatures. Although the temperature of the engine metallic surfaces will certainly be closer to 60 °C, the comparison between both temperature tests permits the separation of the effect of the loss of alcohol by evaporation. Prior to each test, all of the components of the HFRR having contacted the tested fuels were subjected to a cleaning procedure composed of three 10 min immersions in an ultrasonic bath with toluene (the first and

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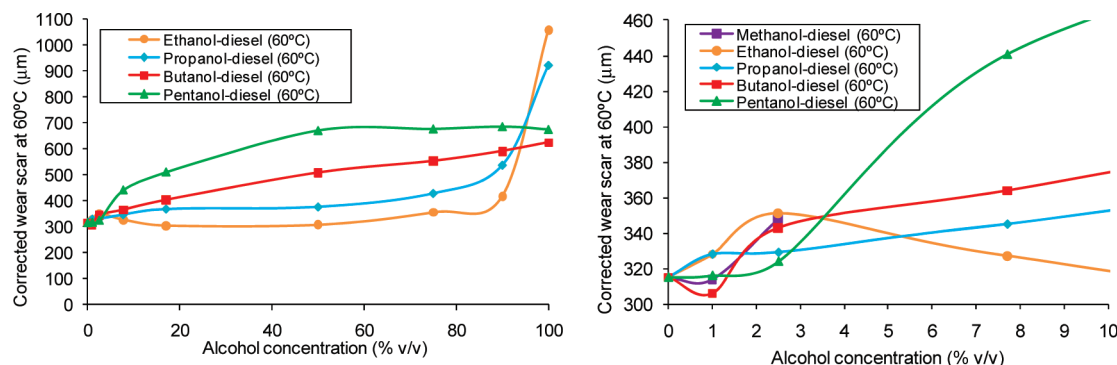


Figure 4. Wear scar of alcohol blends at 60 °C on (left) full scale and (right) reduced scale for low alcohol concentrations.

second) and acetone (the third). All tests were replicated twice, and if differences in the wear scar were higher than 20 μm , then they were repeated once more. During the tests, the samples were shaken at a frequency of 50 Hz and remained open to the atmosphere, which favored evaporation. Afterward, the size of the wear scar was measured in an electronic microscope Leica DM IRM equipped with a 100 \times magnification lens. The mean diameter of the scar observed in the HFRR ball (MWSD) was obtained by averaging the maximum and minimum diameters, as prescribed in the norms. When the tests were made at 60 °C, as required by the EN ISO 12156-1 norm, the resulting scar size was corrected to normalize the vapor pressure to 1.4 kPa (WS 1.4).

The results for ethanol–diesel blends, which were already published in ref 25, are compared here to those for other alcohol blends (Figure 4). As observed in the left panel of Figure 4 and Table 1, the lubricity of pure alcohols (measured at 60 °C) increases (the wear scar decreases), in general, with the alcohol molecular weight, although the lubricity of pure pentanol was not better than that of butanol. Similarly, when the alcohol concentration is very low (right panel of Figure 4), the lubricity of the blends also increases with the alcohol molecular weight. On the contrary, a wide range of intermediate alcohol contents can be found where this trend is reversed, with the lubricity decreasing as the molecular weight increases. Moreover, in the case of volatile alcohols (see boiling points in Table 1), some of the intermediate content blends show even better lubricities (ethanol blends from 10 to 60%, v/v) or at least not significantly worse lubricities (propanol blends) than diesel fuel. This effect is due to the evaporation losses occurring during the HFRR tests, and therefore, it is less noticeable (in fact, it is extended to a narrower concentration range) as the carbon chain alcohol is increased and as the temperature of the test is decreased, as observed in Figure 5. In the case of pentanol blends, the lubricity is worst because evaporation losses are most unlikely.

With regard to the European norm EN 590, which requires a corrected wear scar at 60 °C below 460 μm , only blends with more than 92% (v/v) ethanol, more than 80% (v/v) propanol, more than 35% butanol, or more than 10% pentanol would not fulfill this requirement.

6. Cold-Flow Properties

The CFPP of the blends was measured following norm EN 116. The benefit of blending alcohols with low freezing temperature is limited because the reference diesel fuel was formulated for winter time or even for arctic weather.

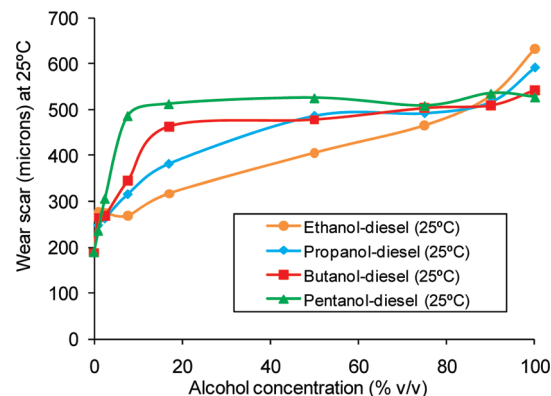


Figure 5. Wear scar of alcohol blends at 25 °C.

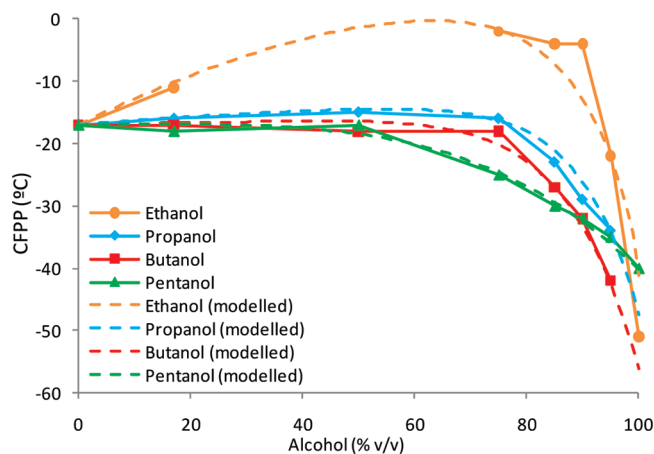


Figure 6. Measured CFPP of alcohol blends (solid lines) and modeled values obtained with adjusted coefficients (dotted lines).

The measured results show (solid lines in Figure 6) that there are two groups of alcohols: short-chain alcohols, such as ethanol, whose blending instability leads to an anti-synergistic effect in the mid-concentration region, and the higher chain alcohols (propanol, butanol, and pentanol), not presenting any anti-synergistic effect (or very slightly in the case of propanol). Only some ethanol blends could present filter plugging problems when used in cold-weather countries. In any case, the alcohol content does not reduce the CFPP until it reaches more than half volume. It was impossible to measure the CFPP of short-chain, pure alcohols because their plugging temperature was below the operation limit of the equipment. As observed in the figure, the effect of alcohol blending on the

Table 2. Blending Recommendations Considering All Tested Alcohol and Fuel Properties

properties	alcohol–diesel fuel blends				
	methanol	ethanol	propanol	butanol	pentanol
blending stability	mostly unstable; only very low concentrations at high temperature are accepted	all blends are stable above 40 °C; < 12 and > 78% are recommended for temperatures > 10 °C	all blends are stable above approximately 2.5 °C	all blends are stable above 0 °C	all blends are stable above 0 °C
viscosity		> 22% (v/v)	> 45% (v/v)	all blends	all blends
lubricity		< 90%	< 80%	< 35%	< 10%
cold-flow properties		< 17 and > 90%	all blends ^a	all blends ^a	all blends ^a

^a Although the best results are achieved with very high alcohol concentrations, this is only interesting for HCCI, where the low cetane number of alcohols is not as important as in diesel engines.

mentioned CFPP reduction begins at higher concentrations as the length of the alcohol carbon chain increases. The observed results have been adjusted to the following equation:

$$\text{CFPP} = \text{CFPP}_d + \frac{z_i z_d^{0.5}}{n_i^{4.5}} - A_i z_i^{B_i} \quad (4)$$

The second term of this equation simulates the mentioned anti-synergistic effect, and the third term describes the final reduction caused by the alcohol content. Coefficients A_i and exponents B_i , with the latter coefficient describing how sharp the reduction is when it takes place, have been fitted to the following equations:

$$A_i = \exp(18.65 + 0.00599n_i^{4.5}) \quad (5)$$

$$B_i = 10 - 0.002n_i^5 \quad (6)$$

As observed in Figure 6, only for very high alcohol concentrations, the benefit obtained in CFPP would allow for the extension of the use of diesel blends to cold climates. Although such high concentrations are not feasible in current diesel engines because of the low cetane number of alcohols, they might be interesting in homogeneous charge compression ignition (HCCI) engines, where the cetane number is not considered as a relevant fuel-quality indicator.³⁷ In any case, further work must be performed to explore the potential benefits of alcohol blends in previous diesel/biodiesel blends, where the filter plugging or blocking is often a limit for use.

7. Conclusion

Four properties among those considered as crucial for diesel operation have been studied for different alcohols in blending proportions with a winter diesel fuel. The poor blending stability of short-chain alcohols is the main factor to discard methanol in a wide concentration range and to limit

the application of ethanol to extreme concentrations [outside the range between 12 and 78% (v/v) if the temperature remains above 10 °C and no stabilizing additives are added]. The loss of viscosity observed when diesel fuel is blended with alcohols would only limit the use of ethanol to blends with more than 22% (v/v) and the use of propanol to blends with more than 45% (v/v). On the contrary, butanol and pentanol could be used in any concentration and even some synergistic effects can be observed for intermediate concentrations.

The lubricity of the alcohol blends is not substantially reduced in any case until high (butanol) or very high (ethanol and propanol) concentrations are reached because the alcohols with poorest lubricities are also the most volatile ones, thus reducing their concentration in the lubricating layer. Only the use of pentanol would be limited to around 10% (v/v), because the volatility of this alcohol is not enough to compensate for its lubricating capacity. Finally, blending alcohols with a winter diesel fuel does not have any substantial benefit in cold properties until very high alcohol concentrations are reached [from 50 to 75% (v/v) depending upon the alcohol], despite their low freezing point. Only in the case of unstable blends or nearly stable blends (ethanol) is the CFPP increased. All of the mentioned limits and blending recommendations are summarized in Table 2.

The study presented proves that alcohols can be used as blending components of diesel fuel, in not only low concentrations but also high concentrations, although the blending stability is, together with the low cetane numbers, the major limitation for the use of short-chain alcohols in intermediate concentrations. This limitation could probably be minimized with the use of additives or the presence of fatty acid esters in the blend.

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