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Improving lubricity and electrical conductivity of ultra-low sulphur diesel using additives

Mejoramiento de la lubricidad y conductividad eléctrica del diésel de ultra bajo azufre mediante el uso de aditivos

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Abstract

The ultra-low sulphur diesel (ULSD) is currently used to meet environmental regulations regarding to the sulphur content below 15 wppm throughout the world. However, lubricity and electrical conductivity are commonly out of specifications; therefore, some additives are added to a diesel fuel before merchandising it to upgrade these properties. In this research, the effects of two different additives were studied: 1) commercial additive and 2) fatty acid methyl esters (FAME). Several properties of the diesel fuel such as sulphur content, kinematic viscosity, specific gravity, distillation curve, lubricity and electrical conductivity were determined according to standardized methods. Additives were used in different concentrations: 50, 100, 150, 200, and 250 wppm for the commercial additive and 1, 3, 6, 9, and 12 vol% for the FAME. It was found that all properties of the commercial additive/ULSD and FAME/ULSD blends were attained with both additives. In the case of the commercial additive, the lowest concentration needed was 50 wppm while it was 1 vol% for the FAME. Although the cost of the commercial additive is 5 times higher than that of the FAME, usage of the commercial additive is the most profitable option because of its low concentration in the commercial additive/ULSD blends.

Keywords: Electrical conductivity, lubricity, ultra-low sulphur diesel, commercial additive, biodiesel.

Resumen

El diésel de ultra bajo azufre (DUBA) se usa actualmente en varios países del mundo para cumplir con la normatividad ambiental referente al contenido de azufre (15 ppm máximo). Sin embargo, la lubricidad y la conductividad eléctrica del DUBA están frecuentemente fuera de especificación, por lo que se usan algunos aditivos para mejorar estas propiedades. En esta investigación, se estudió el efecto de dos aditivos en el DUBA: 1) aditivo comercial y 2) FAME (Ésteres metílicos de ácidos grasos). Se determinaron diferentes propiedades del combustible diésel, como el contenido de azufre, la viscosidad cinemática, la gravedad específica, la lubricidad, la conductividad eléctrica y la curva de destilación, con métodos estandarizados. Ambos aditivos se mezclaron con el DUBA en diferentes concentraciones: 50, 100, 150, 200 y 250 ppm en peso con el aditivo comercial y 1, 3, 6, 9 y 12%vol con el FAME. Los resultados mostraron una mejoría con ambos aditivos en todas las propiedades de las mezclas de aditivo comercial/DUBA y FAME/DUBA. En el caso del aditivo comercial, la concentración más baja para cumplir con las especificaciones de lubricidad y conductividad eléctrica fue de 50 ppm mientras que para el FAME fue de 1% vol. Aunque el costo del aditivo comercial es 5 veces mayor que el del FAME, el aditivo comercial es la opción más rentable debido a su baja concentración en sus mezclas con DUBA.

Palabras clave: Conductividad eléctrica, lubricidad, diésel de ultra-bajo azufre, aditivo comercial, biodiésel.

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1 Introduction

The environmental regulations worldwide are stringent and tend to reduce the sulphur content mainly in diesel fuel. To meet the sulphur specification, hydrotreating process is used in refineries to remove organic compounds of sulphur, nitrogen, and oxygen (Baloch *et al*., 2018). As ultra-low sulphur diesel (ULSD) production has gained huge interest worldwide, some studies to understand the key factors influencing on the deep hydrotreating of diesel fuel have been carried out. The removal of sterically hindered sulphur species from diesel feedstocks implies knowledge of inhibition effects, types of active sites, hydrogen partial pressure, and steric effect, particularly when dealing with refractory sulphur compounds such as 4,6-dimethyldibenzotiophene. Stanislaus *et al*., (2010) addressed a comprehensive review of these topics.

Many attempts to increase the ULSD production have been made from several fronts. For example, synthesis of $CoMo/\gamma Al_2O_3$ or $NiMo/\gamma Al_2O_3$ catalysts has focused on improving the catalytic activity and involved the usage of: 1) chelating agents such as ethylenediaminetetraacetic acid (EDTA), 1,2-cyclohexanediaminetetraacetic acid (CyDTA), citric acid, among others; 2) hybrid supports like zirconia, MgO, MCM-41, SAPO-11, etc., to reduce the surface acidity and improve the metal dispersion and textural properties; 3) other elements incorporated to the alumina support such as Li, P, Ce, Mn, F to increase the metal dispersion and length and stacking of slabs highly sulfided to promote the direct desulphurization pathway. Shafiq *et al*., (2022), reported a deep discussion of these topics. Different attempts to synthesize new materials have been reported to obtain highly dispersed active phases and to improve the activity during hydrodesulfurization. For example, a series of catalysts of CoMo supported on ZSM-5 and faujasite have been tested on the HDS of dibenzothiophene used as model compound. The use of dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammonium chloride (DMOTPAC) and cetyltrimethylammonium bromide-polyethylene glycol (CTAB-PEG) improved the formation of mesopores, which increased the activity towards the HDS of DBT (Yocupicio *et al*., 2017). The use of cetyltrimethylammonium bromide and sodium dodecyl sulfate as surfactants in the synthesis of $CoMo/Al_2O_3$ has also been reported. Higher catalytic activity was obtained using CTAB during the dibenzothiophene hydrodesulfurization (Munguía-Guillén *et al*., 2016).

Other strategies involve the revamping of hydrotreating units, usage of highly active catalysts or construction of new facilities in existing refineries. The catalyst stacking technology is a feasible approach to meet ULSD specifications. A synergistic effect of conventional and highly active catalysts is enhanced by studying the order and ratio among the catalysts in the combined bed; thus, mathematical modeling allows selecting the best choice (Leal *et al*., 2022).

Some properties of the ULSD such as lubricity and electrical conductivity are affected by the hydrotreating of diesel feedstocks, causing friction troubles in engines and poor electrical dissipation (Static electricity is accumulated dangerously during diesel transportation through pipelines or during discharging fuel from tankers). In addition, diesel fuel with low electrical conductivity may also damage electric circuits of cars. Anastopoulos *et al*., (2005) reported that the polyaromatic compounds as well as cyclic organic compounds containing atoms of nitrogen and oxygen, which are present in additives, tend to form a protective layer on metal surfaces.

When deep hydrotreating takes place, thermal stability and cetane number of the diesel fuel increase but lubricity, electrical conductivity, and oxidation stability decrease. For this reason, usage of additives is required to keep lubricity and electrical conductivity under ULSD specifications. Lubricity measured like scars on metal surfaces must be below 520 μm as claimed by the Mexican norm (NOM-016-CRE-2016, 2016) and the US standardized method (ASTM D975, 2021), and 460 μm as stated by the European norm (EN 590, 2013).

Hazrat *et al*., (2015) found that biodiesel, which is a type of unrefined biofuel, contained some amounts of monoglycerides and free fatty acids that enhanced the lubricity when they were added to the diesel fuel. Hu *et al*., (2005) measured the lubricity with the high-frequency reciprocating rig (HFRR) method, finding high values in the blends with the diesel fuel due to the presence of fatty acid methyl esters, monoglycerides, free fatty acids, and diglycerides; but triglycerides did not modify the lubricity when they were mixed with the diesel fuel.

Addition of biodiesel (up to 20 vol%) to blends with low-sulphur diesel and ULSD was studied by Dunn (2011). Based on the determination of properties such as cloud point, kinematic viscosity, specific gravity, and refractive index, Dunn found that the higher the biodiesel volume in blends the higher the cloud point and specific gravity; besides, the kinematic viscosity fitted to a polynomial correlation as the content of biodiesel increased.

Chen *et al*., (2013) reported the relation among biodiesel in ULSD with heat capacity, density, kinematic viscosity, cold filter plugging, and oxidation stability. Knothe and Steidley (2005) reported that 1-2 wt% of biodiesel in ULSD improved lubricity of the blend due to some oxygenated moieties in the biodiesel.

The wear rates of biodiesel were 2-4 times lower than those of vegetable oils, but 5-7 times higher than those of a fossil diesel. The wear rates decreased when using blends of biodiesel in dodecane; the results showed that increasing the chain length and unsaturation in additives reduced the wear rates of pure hydrocarbons (Tat *et al*., 2022).

Additives derived from Tung-oil have been obtained by reacting maleic acid with eleostearic acid methyl ester and further reacted with methanol or butanol. Those additives upgraded lubricity of the ULSD in concentrations of 500 to 1000 wppm. These concentrations were up to 40 times lower than those of blending ULSD with biodiesel in concentrations of 1-2 wt%. The usage of synthesized additives allowed to reduce wear scar and friction of the ULSD by 40% and 46-47%, respectively (Liu *et al*., 2019).

Another additive for enhancing lubricity in ULSD is 1-amino glycerol, which gave less wear scars compared to glycerol compounds (Agarwal *et al*., 2013). The usage of butanol as additive increased lubricity (Molina *et al*., 2019). Blends of methyl esters up to 20% in ULSD promoted acceptable physicochemical properties in diesel engines as reported elsewhere (Shah *et al*., 2013). Different additives have been tested for improving some ULSD properties such as addition of methanol (10 and 20%) to biodiesel (Huang *et al*., 2020) and blends of methanol (5%), biodiesel (20%) and diesel (75%), and biodiesel (20%) with diesel (80%) (Yasin *et al*., 2015).

It is noteworthy to mention that vegetable oils own good properties such as lubricity, biodegradability, viscosity, and low volatility; however, their use as lubricants or additives is restricted due to their poor cold flow and low thermo-oxidative stability behavior. For this reason, additives like zinc diamyl dithiocarbamate and antimony dialkylditiocarbamate were added to polyalphaolefin (Erhan *et al*., 2006). Shahabuddin *et al*., (2013) tested blends of Jatropha oil and lubricant SAE 40 finding an enhanced performance against wear, coefficient of friction, flash temperature parameter, and viscosity. The high content of ricinoleic acid (12-hydroxyoleic acid) in castor oil turned it into a good candidate to be used as additive. It was reported elsewhere that the higher the number of double bounds in the hydrocarbon chains the lower the wear scars (Tumanyan *et al*., 2020).

Reports disclosing electrical properties of low-sulphur diesel and its blends with biodiesel are scarce, only few articles have been published. Nicolau *et al*., (2014) studied relation between lubricity and electrical impedance on blends of biodiesel/diesel, finding that biodiesel content impacted on the wear scar diameter and resistivity of the ULSD. These results correlated well to an exponential function; also, a linear correlation between electrical resistivity and reciprocal of wear scar diameter (1/WSD) was obtained.

The aim of this research was to study some properties of the ULSD such as sulphur content, kinematic viscosity, specific gravity, lubricity, electrical conductivity, cetane number, and distillation curves using a commercial additive and FAME obtained by transesterification of palm oil.

2 Materials and methods

2.1 Materials

ULSD was obtained from a pilot plant test at temperatures ranging from 345 to 365°C, isothermal mode, hydrogen partial pressure of 54 bar, LHSV of 1.5-2 h^{-1}, using a combined bed of $NiMo/\gamma Al_2O_3$ and $CoMo/\gamma Al_2O_3$ catalysts. The catalyst loading, activation, and soaking steps have been reported previously (Marroquín-Sánchez and Ancheyta-Juárez, 2001). A commercial additive, which will be named as additive in advance, was purchased and used to improve electrical conductivity and lubricity in ULSD. The FAME, which will be named as biodiesel in advance, was obtained from transesterification of palm oil using methanol and NaOH as reactants.

2.2 Characterization of biodiesel, ULSD, and additive

Sulphur content was determined by using the ASTM D7039 (2020) method, in which a sample is placed in a sample holder and analyzed by monochromatic wavelength dispersive X-ray fluorescence spectrometer. Lubricity was analyzed with the ASTM D7688 (2018) method, where a sample is placed in a sample holder to cover a test disc; afterwards, the sample is heated up to 60°C while a metallic ball is in contact with the disc during 75 min at 50 Hz; finally, the scar diameter is measured. Electrical conductivity was determined by using the ASTM D4308 (2021) method, in which a sample is placed into a conductivity cell and connected in series to a voltage source; then, the Ohm's law is applied through current, voltage and cell constant to obtain the conductivity result automatically. Viscosity was determined by applying the ASTM D7042 (2021) method using an automated viscometer consisting of a rotating coaxial cylinder; first, a bubble-free sample is manually injected to a measurement cell by using a syringe; next, the sample is heated up to the analysis temperature to determine kinematic viscosity. This apparatus not only performs kinematic viscosity, but also specific gravity tests based on the U-shaped oscillating sample tube.

To determine the pour point (ASTM D97, 2017), a sample is placed into a test jar and cooled at a specified rate and intervals of 3°C; thus, the lowest temperature at which movement of the sample is stopped is recorded as pour point. Flash point (ASTM D93, 202) is based on the Pensky-Martens closed cup tester in the temperature range from 40 to 370°C; initially, a sample is stirred at 90 to 120 rpm while temperature goes up at 5 to 6°C/min; an ignition source is applied at each temperature increment of 1°C and readings are taken.

Table 1. Properties of ultra-low sulphur diesel (ULSD), biodiesel, and additive.

Property	ULSD	Biodiesel	Additive
Sulphur content, wppm	5	3	-
Lubricity, μm	455	192	-
Electrical conductivity, pS/m	0.5	>2000	-
Specific gravity 20/4°C	0.82	0.9	0.946
Kinematic viscosity at 40°C, mm^2/s	2.77	24.55	129
Flash point, °C	-	-	30
Pour point, °C	-	-	<0

2.3 Preparation and characterization of biodiesel/ULSD and additive/ULSD blends

Five blends of biodiesel/ULSD were prepared by varying the biodiesel content from 1 to 12 vol%; the volume of each blend was 300 mL. In the case of the additive/ULSD blends, five blends varying the concentration of additive from 50 to 250 wppm were prepared; the mass of each blend was 300 g. The characterization of those blends including sulphur content, lubricity, electrical conductivity, specific gravity, and kinematic viscosity was done by using the aforementioned methods. In addition, distillation was carried out according to the method ASTM D86 (2020), in which a sample is placed into a flask while heating; temperature readings are made at the initial boiling point, T10 (Temperature at 10 vol%), T50 (Temperature at 50 vol%), T90 (Temperature at 90 vol%), and final boiling point. Also, cetane number was calculated for all the biodiesel/ULSD and additive/ULSD blends.

3 Results and discussion

3.1 Characterization of materials

Table 1 summarizes the characterization results for the ULSD, biodiesel, and additive. For the ULSD, sulphur content was below 15 wppm and lubricity measured as the wear scar diameter (WSD) by the high-frequency reciprocating rig test was less than 520 microns, while kinematic viscosity ranged from 1.9 to 4.1 mm^2/s at 40°C. However, electrical conductivity of the ULSD was very low (0.5 pS/m); this property is relevant because of its relation to the ignition of diesel fuel by poor dissipation of static electricity during transportation through either pipelines or combustion in engines, which further may damage electric and electronic circuits of vehicles.

Table 1 also shows results of the biodiesel analysis. Specifications of sulphur content, specific gravity, and lubricity were fulfilled. But high values of electrical conductivity and kinematic viscosity at 40°C were observed, which impedes to use biodiesel directly in engines. However, adding biodiesel to the ULSD may improve its electrical conductivity.

Additives composed by aromatic and compatible compounds enhance electric conductivity of the ULSD if they are added to this fuel. Composition of the additive is divided into two main groups: aromatics and a compatible compound. Aromatics account for monoaromatics (20 wt%), diaromatics (1 wt%), and polyaromatics (30 wt%), while the compatible compound accounts for 49 wt%. Thus, high values of specific gravity and kinematic viscosity at 40°C (Table 1) are consistent with composition of the additive.

3.2 Sulphur content

Sulphur content was below 15 wppm for all blends as specified. When the additive was mixed with ULSD, a slight increment in sulphur content was attained since paraffinic derivatives containing sulphur were present in the additive. This small increment was also found in the first three biodiesel/ULSD blends as observed in Figure 1, but as the biodiesel content increased in the blend, dilution of sulphur species occurred, and the sulphur content was lower than that of the ULSD.

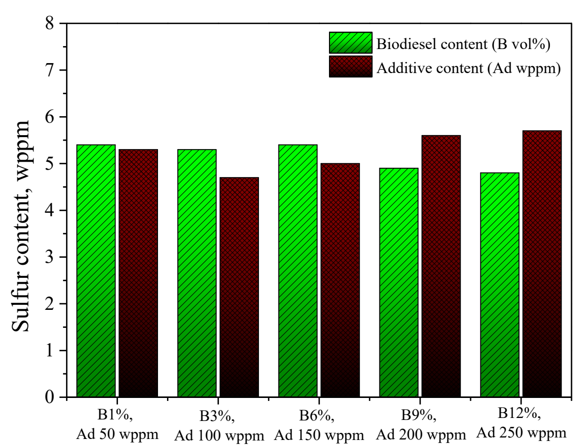

Figure 1. Sulphur content for biodiesel/ULSD and additive/ULSD blends.

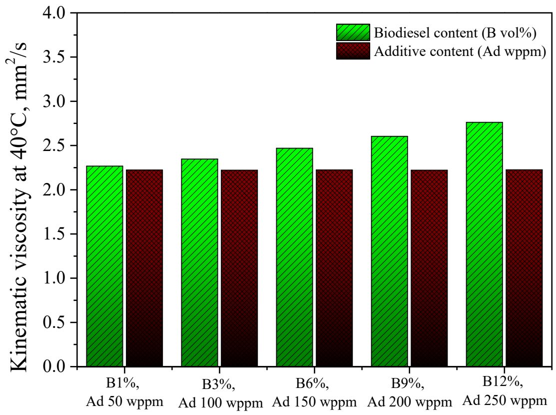

Figure 2. Kinematic viscosity for biodiesel/ULSD and additive/ULSD blends.

3.3 Kinematic viscosity

Kinematic viscosity at 40°C was in the specified range (1.9 - 4.1 mm^2/s) for all blends and showed a slight variation using both additive and biodiesel (Figure 2). This property increased when biodiesel was added to the blends, but it was always lower than that of the ULSD, even when using the highest concentration of biodiesel (12 vol%) as observed in Figure 2. Kinematic viscosity was almost constant, having an average value of 2.22 mm^2/s at different concentrations of the additive.

3.4 Specific gravity

Specific gravity 20/4°C of biodiesel/ULSD blends increased as biodiesel content was larger in the blend, ranging from 0.822 to 0.832 compared to the value for ULSD (0.820). Figure 3 shows that the higher the volume of biodiesel in the blend the higher the specific gravity of the blend. Moreover, specific gravity of additive/ULSD blends increased slightly with the addition of additive, remaining almost constant at each concentration of additive (Figure 3). Based on Figure 3, it is possible to establish correlations among specific gravity and concentrations of biodiesel and additive in their blends with ULSD. When using biodiesel, a linear correlation was obtained as shown in Equation (1), while a polynomial adjustment describes the usage of additive (Equation (2)); determination coefficients (R^2) are shown.

$$\text{Specific gravity} = 0.0025(\text{Biodiesel vol\%}) + 0.8196; \quad R^2 = 0.998 \tag{1}$$

$$\text{Specific gravity} = 8\times10^{-5}(\text{Additive wppm})^2 - 0.0006(\text{Additive wppm}) + 0.8232; \quad R^2 = 0.973 \tag{2}$$

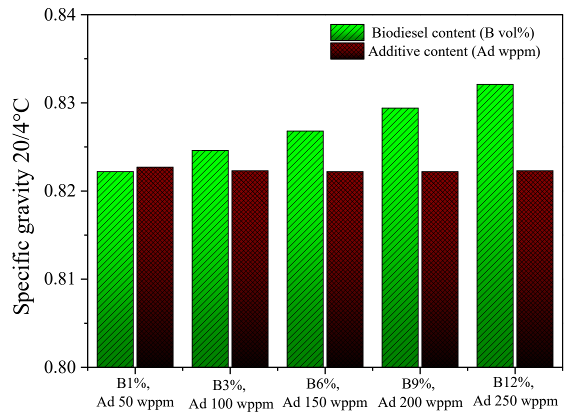

Figure 3. Specific gravity for biodiesel/ULSD and additive/ULSD blends.

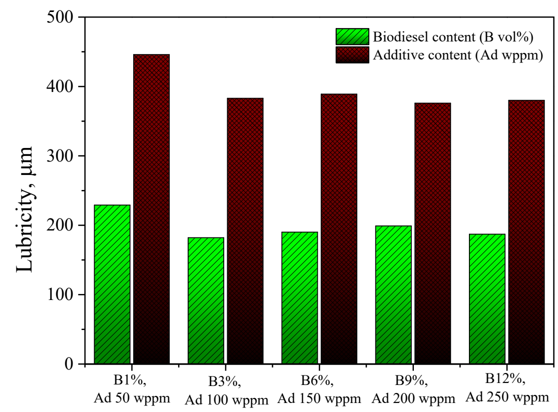

Figure 4. Lubricity for biodiesel/ULSD and additive/ULSD blends.

3.5 Lubricity

Lubricity of all additive/ULSD and biodiesel/ULSD blends was lower than the Mexican standard. According to Figure 4, lubricity of the ULSD decreased just by adding biodiesel or additive. Lubricity of the additive/ULSD blends was such that of the ULSD at the lowest concentration of additive and kept almost constant from 100 to 250 wppm. Addition of 1 vol% of biodiesel to the ULSD diminished wear scar diameter by almost 50% (Figure 4), remaining with small variations after that content.

To define the significance of the results included in Figures 1 to 4, analysis of variance in an Excel® spreadsheet was done using F-tests to statistically evaluate equality of means between groups, in this case, additive/ULSD and biodiesel/ULSD blends. Results for lubricity, specific gravity, viscosity, and sulphur content were obtained separately and because of the amount of analysis for each blend, the F critical value was 5.32 for a significance level of 0.05. Then, the F-test values for lubricity, specific gravity,

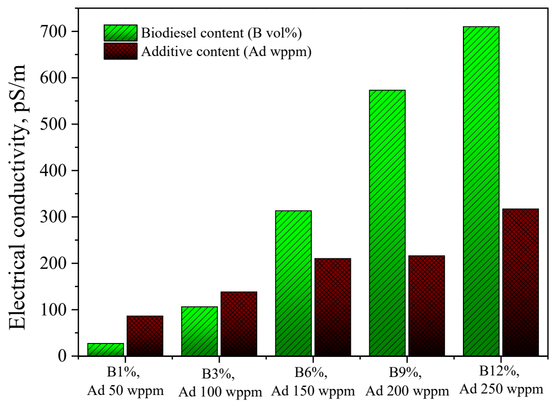

Figure 5. Electrical conductivity for biodiesel/ULSD and additive/ULSD blends.

and viscosity were 163.5 (p-value of 0), 7.21 (p-value of 0.03), and 9.02 (p-value of 0.02), respectively. In these cases, since F-test values were higher than the F critical value and the p-values were lower than the significance level, the null hypothesis is rejected. On the contrary, sulphur content had a F-test value of 0.19 (p-value of 0.67) and in consequence, there is not significant effect on this property when mixing ULSD with additive or biodiesel.

3.6 *Electrical conductivity*

The minimum value for electrical conductivity must be 25 pS/m according to the ULSD specification; however, this value was only 0.5 pS/m for the ULSD. When using 50 wppm of additive, electrical conductivity of this additive/ULSD blend increased up to 86 pS/m and so did other blends, increasing up to 317 pS/m for 250 wppm as depicted in Figure 5. In the case of biodiesel, an addition of 1 vol% to the ULSD increased electrical conductivity up to 27 pS/m (Figure 5); besides, results show that the higher biodiesel addition the higher electrical conductivity. An equation relating biodiesel content with electrical conductivity as well as the determination coefficient (R^2) are shown as follows:

$$\text{Electrical conductivity} = 183.3(\text{Biodiesel vol\%}) - 204.1; \quad R^2 = 0.975 \tag{3}$$

3.7 *Cetane number*

Cetane number for ULSD was 54.6 by which the Mexican regulation (45 minimum) was accomplished. When 50 wppm of additive were added to the ULSD, cetane number increased up to 55.7, improving the initial value by 1.1. For biodiesel/ULSD blends, since this type of biofuel is composed mainly of oxygenated and linear alkyl chains, an addition of 1 vol% of biodiesel to the ULSD increased cetane number up to 55.1. Thus, usage of both additives enlarged slightly the cetane number.

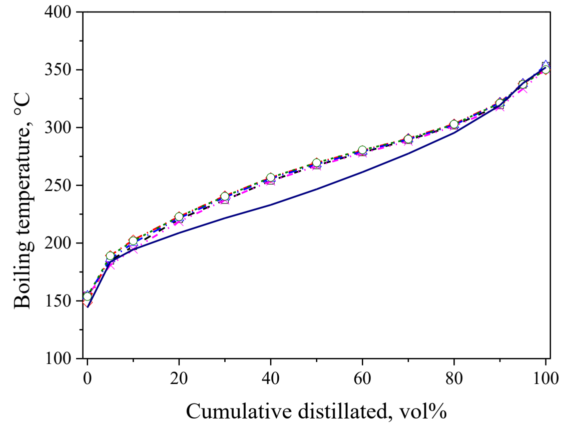

Figure 6. Distillation curve for ULSD (solid line) and additive/ULSD blends at: (□) 50 wppm, (◊) 100 wppm, (Δ) 150 wppm, (×) 200 wppm, (o) 250 wppm.

3.8 *Distillation curves*

Figure 6 depicts distillation curves based on the ASTM D86 method. All the curves were overlapped since concentration of additive was quite small to impact significantly on the behavior of the blends. However, ULSD must accomplish specifications for distillation: 275°C maximum at 10 vol% and 345°C maximum at 90 vol%. Figure 6 shows that all additive/ULSD blends met distillation specification. Considering ULSD as reference, additive increased the distillation temperature at 10 vol% from 197.3 to 201.9°C, while at 90 vol%, the distillation temperature ranged from 319.2 to 321.1°C. That is, the additive had a higher effect on the light fraction than on the heavy fraction of the additive/ULSD blends because the increment in the distillation temperature at 10 vol% (4.6°C) was higher than that at 90 vol% (1.9°C).

On the other hand, when biodiesel was added to the ULSD, the distillation temperature at 10 vol% increased from 200.8 to 204.4°C (Increment of 3.6°C), whereas at 90 vol% the distillation temperature increased from 321.7 to 340.9°C (Increment of 19.2°C) as observed from Figure 7. Despite increments of the distillation temperature at 90 vol%, the biodiesel/ULSD blends kept below 345°C. Addition of biodiesel to the ULSD influences on the heavy fraction of the biodiesel/ULSD blends due to fatty acid methyl esters commonly have high boiling points. For example, boiling point for methyl oleate is 351°C at 760 mmHg. Then, increasing amount of biodiesel in biodiesel/ULSD blends will increase boiling point as well.

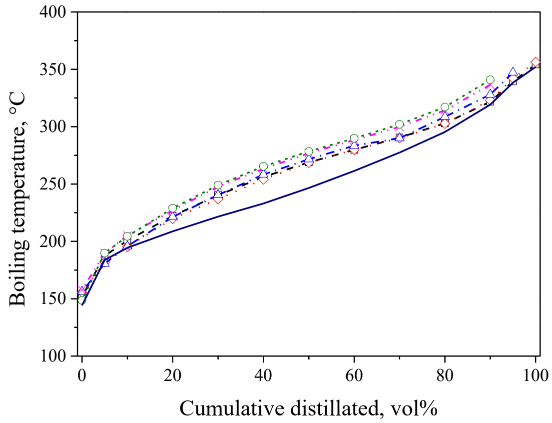

Figure 7. Distillation curve for ULSD (solid line) and biodiesel/ULSD blends at: (□) 1 vol%, (◊) 3 vol%, (Δ) 6 vol%, (×) 9 vol%, (o) 12 vol%.

Summarizing, additive influences more on the light fraction of the additive/ULSD blends while biodiesel does on the heavy fraction of the biodiesel/ULSD blends as observed in the initial and final boiling points, respectively.

Lubricity was highly enhanced when using the additive. Despite composition is proprietary and unknown for the authors, it may be assumed that some oxygenated compounds are present as well as kerosene-derivatives. It has been reported that in different oxygenated C10 compounds, lubricity measured by the HFRR test is enhanced by the following functional groups: COOH>CHO>OH>$COOCH_3$>C=O>C-O-C. Moreover, other functional groups such as OH, NH_2, and SH in C_3 compounds were also evaluated and lubricity increased with oxygenated compounds in a higher level than with nitrogen and sulphur containing compounds (Knothe and Steidley, 2005).

Fatty acid methyl esters from rape-seed oil have been also confirmed to improve lubricity of biodiesel/fuel oil blends by forming a stable lubricant film in sliding surfaces (Sulek *et al*., 2010). Lubricity improved with addition of biodiesel to the ULSD by the presence of an ester group. However, enhancement of this property was marginal when adding more than 1 vol% of biodiesel to the ULSD.

The impact of functional groups present in additives in the lubricity of ULSD has been discussed elsewhere (Anastopoulos *et al*., 2005). For example, addition of biodiesel obtained from sunflower, corn, olive, and spent cooking oil at concentrations from 0.15 to 0.5 vol% showed a significant decrease of wear scar diameter. Aliphatic amines at 3 vol%, amides at 0.5 vol%, monocarboxylic esters at 500 wppm, dicarboxylic esters at 500-750 wppm, and acetoacetic esters at 750 wppm have been reported to improve lubricity of diesel fuel.

Polar molecules even at trace levels and organic compounds containing oxygen and nitrogen form a layer on metal surfaces, improving lubricity because of additives

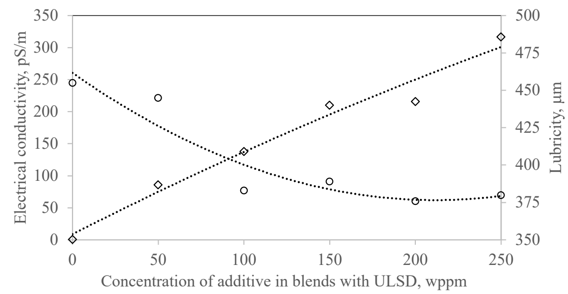

Figure 8. Electrical conductivity and lubricity for additive/ULSD blends. (o) Lubricity, and (◊) Electrical conductivity.

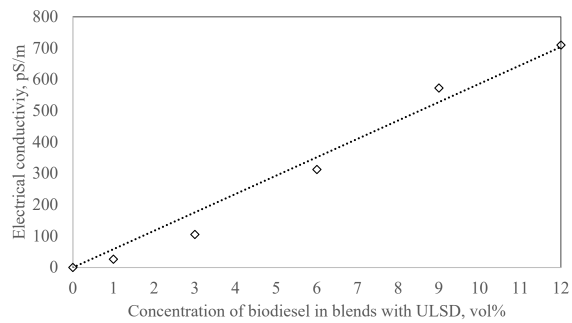

Figure 9. Electrical conductivity (◊) for biodiesel/ULSD blends.

have a polar group attached to a long hydrocarbon tail. Polar groups can be adsorbed on the metal surface vertically while hydrocarbon chains may be aligned parallel to each other forming films. Thus, wear and friction effects are reduced between sliding films (Shaigan *et al*., 2020). Polar groups dissipate static electricity in the ULSD, avoiding bursts.

Specific gravity and viscosity values showed slight increases in the biodiesel/ULSD blends and did not vary significantly in the additive/ULSD ones. Figure 8 depicts variations of electrical conductivity and lubricity in the additive/ULSD blends; here, data was fitted to a polynomial function. As well, only variation of electrical conductivity was plotted in Figure 9 for the biodiesel/ULSD blends because lubricity did not fit to any trend line.

ULSD specifications were fully accomplished by using both biodiesel and additive. It is noticeable how the specified electrical conductivity was achieved when adding 50 wppm of additive and 1 vol% of biodiesel. For this reason, using the minimum concentration of additive or biodiesel may be recommended. However, environmental, and toxicological issues arising from using both additives mainly in gas exhausts should be also considered to select the proper additive. Type of oil or fat used as feedstock to obtain biodiesel determine its composition, which in turn changes also the combustion exhaust and causes health impacts (Landwehr *et al*., 2021). It is known that biodiesel combustion generates high amounts of NO_x and particulate matter (Fontaras *et al*., 2009). In addition, experimental tests carried out with tallow and canola biodiesel to analyze their toxicity in human airway epithelial cells proved that tallow biodiesel resulted to be more toxic than that coming from canola (Landwehr *et al*., 2022). As reported by other authors, synthetic additives used to improve quality of mineral diesel had a greater propensity to partition in water with lower tendency to bioaccumulate (Arellano-Treviño *et al*., 2022).

On the other hand, it must be considered cost of the biodiesel production including type of oil, alcohols, and possible contamination to water through the process. The same concern is applied to the synthesis of additives, reagents and their toxicity, reaction conditions and by-products. Thus, the right choice of an additive also depends on tribological tests besides the enhancement of quality of the ULSD, overall economy of the processes involving the synthesis of additives and possible contamination to water or air.

Regarding to the tribological tests and in the case of biodiesel, not only the ester groups upgrade anti-wear property of the ULSD, but also traces of free glycerin, antioxidants, etc. In the case of additives, additives containing oxygenated compounds also improve lubricity because of ionic interactions among molecules and metal substrate through a hydrogen bonding (Agarwal *et al*., 2013). Then, fully characterization of additives will allow to understand any interactions among functional groups and metal surfaces.

Conclusions

Biodiesel and a commercial additive were added to ultra-low sulphur diesel to upgrade its lubricity and electrical conductivity. Lubricity improved as the concentrations of biodiesel and additive increased in the ULSD due to the wear scar diameter decreased. Similarly, electrical conductivity improved as the concentrations of biodiesel and additive increased in the ULSD, sharply with biodiesel and moderately with the additive. Thus, the specified minimum value for electrical conductivity (25 pS/m) was achieved with the additive at 50 wppm and with biodiesel at 1 vol%. These upgradings of lubricity and electrical conductivity are attributed to ester groups that form a protective layer on metal surfaces and dissipate electrical charge in a better way.

As expected, sulphur content of the ULSD was below 15 wppm in all additive/ULSD and biodiesel/ULSD blends. Besides, some improvements in specific gravity and kinematic viscosity were observed when adding biodiesel to ULSD whereas these properties varied slightly in the additive/ULSD blends.

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